

Capillary-discharge ignition of dispersed-phase Al@CuO core-shell thermite particles in a liquid filled
microchannel

by

Alex Baranovsky

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Mechanical and Mechatronics Engineering

Waterloo, Ontario, Canada, 2022

© Alex Baranovsky 2022

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Aluminum based thermites are a broad class of highly tunable solid energetic materials that can be formulated to perform as pyrotechnics, propellants, or explosives. Their functional versatility, energy density, reactivity in inert environments, and compatibility with silicon-based fabrication techniques has garnered lots of interest from researchers in the past 20 years for microelectromechanical systems (MEMS) with industrial, aerospace, and life-science applications. Thermites have traditionally come in the form of physically mixed powders of discrete metallic fuel and metal-oxide oxidizer particles which require intimate contact to ignite, but new fabrication techniques can produce monolithic composites of fuel and oxidizer phases; examples of these include laminate and core-shell structures. Since the fuel and oxidizer phases in a core-shell thermite exist within a single particle, individual particles can theoretically combust. Thus, a core-shell dispersion can theoretically remain reactive even in an inert fluid. As a result, there is growing interest in the use of core-shell thermites as energy carriers in liquids or gasses so they can be easily transported and ignited on-demand.

This thesis focusses on the design, characterization, and evaluation of a microfluidic system which uses electrokinetic techniques to transport dispersed core-shell thermite particles and ignite them in an inert, aqueous environment. The system consists of a single microchannel with a converging-diverging geometry and $30\mu\text{m} \times 30\mu\text{m}$ throat for the collection of dispersed $1\mu\text{m}$ Al@CuO particles dispersed in 1[M] NaCl solution. Using electrodes at the inlet and outlet, a simple non-intrusive ignition system is incorporated by means of electrical discharge produced by capillary breakdown of the liquid at the throat.

The microchannel geometry is numerically modelled to determine the effects of applied voltage and solution conductivity on the electrical field, velocity, and temperature within the channel. The electric field is maximized at the transitions of the converging and diverging sections with the throat, producing magnitudes (6.4kV/cm for 500V across channel) which predict electrical breakdown for solutions with NaCl concentration exceeding 0.2 [mM] . Since phase change is not included in the model, temperature results can exceed the boiling point of water. It is also observed that the

electroosmotic velocity prediction begins to fail once temperatures reach 100°C; this is deemed a limitation of the practical usefulness of the model.

A single particle suspended in the electrolytic solution is also modelled. The presence of a particle in the liquid increases the maximum electric field by 3 to 10 times. Because a large spread of conductivity was considered, several heating modes are predicted by the model: heating at the liquid-shell interface for solutions less conductive than CuO, heating within the shell for solutions more conductive than CuO, and heating in the liquid and the shell when the solution is significantly more conductive than CuO. These results suggest that a higher solution concentration results in increased heating in both the electrolyte and particle phases, so experimentally, a high conductivity 1 [M] NaCl solution was used.

The microchannel was experimentally characterized using IR imaging and high-speed microscopy techniques. When operated in slow-heating mode (2.5mA through channel), the liquid in the channel undergoes a long Joule heating stage and eventually results in the formation of a bubble at the throat. Once the bubble fills the cross-section of the channel current flow is halted due to the formation of an open circuit and the bubble cools and shrinks. If the bubble shrinks enough, a conductive path may be re-established around the bubble and Joule heating may begin again. Maximum measured temperature does not exceed 75°C when only the solution is considered. When 1µm Al@CuO particles are added to the channel in slow-heating mode, the Joule heating period is substantially shortened. Additionally, thermal hot spots are observed exceeding 140°C in the IR video and bubbles grow more rapidly when energetic particles are added.

In fast-heating mode (500V across channel), a Joule heating stage is not observed. Instead, capillary discharge occurs, where bubble formation is nearly instantaneous and closely followed by visible electrical discharge once power is applied. When 1µm Al@CuO particles are added to the channel in high-power/fast-heating mode, the difference is difficult to observe because the presence of particle combustion is masked by the bright electrical discharge.

A narrow-band 488nm filter is placed inline with the high-speed camera to distinguish between electrical and combustion emission sources. When the microchannel is operated without particles, no emission is visible in the filtered video, but when particles are introduced, bright spots are visible

in the filtered video which correlate to hotspots observed in the IR video. This suggests that increased temperatures in particle tests are a result of thermite combustion. Morphological and chemical analysis is performed using SEM and EDS and both unreacted and reacted particles are observed in the channel post-test, further confirming presence of thermite combustion.

Finally, attempts to modulate the combustion size are made by purposeful collection of large particle aggregations at the channel throat. The capillary ignition technique used is found to be generally incompatible with this method because the bubbles formed by Joule heating destroy the particle clusters. A large-scale combustion event is observed when particles were clustered at the throat generating a flame which fills the entire channel and propagates at 1.9m/s, demonstrating that flame-size is indeed tunable with dispersed core-shell particles, but the event could not be reproduced due to limitations with the ignition system.

Acknowledgements

I would like to thank my co-supervising professors, Prof. John Wen and Prof. Jean-Pierre Hickey, for allowing me the opportunity to get involved in the exciting field of nanoenergetics. The insights and expertise they have provided from their respective fields has been extremely valuable to me over the course of my undergraduate and graduate degrees. I hope that opportunities to work together in the future will arise.

I would like to thank Prof. Carolyn Ren for supporting this work directly through the use of invaluable resources at the Waterloo Microfluidics Laboratory. I must thank Dr. Pei Zhao for her support with running experiments in the Microfluidics lab, as well as her expertise on experimental microfluidics. I would also like to thank Matt Courtney and Dr. Ning Qin for their contributions to discussions and feedback on the project scope and troubleshooting, as well as Weijia Cui for his support in fabricating microchannels for me.

Lots of support came from my colleagues at the Lab for Emerging Energy Research, and I must thank the great Dr. Anqi Wang for all his continued support and presence in the lab, Shina Maini for her help with fabricating and characterizing core-shell particles, as well as promising future researcher Michiyo Kagaya for helping me run experiments. I would also like to acknowledge the discussions, advice, and technical support from Ben Cha, as well as Dr. Florin Saceleanu for his support and inspiration early in my graduate degree.

Last but not least, I would like to thank my loving family. My parents have supported me throughout my academic career, and for that I am forever grateful. Finally, I would like to thank my sister not only for her support, but also for pushing and motivating me.

Dedication

Dedicated to Daniel.

Table of Contents

Author's Declaration	ii
Abstract	iii
Acknowledgements	vi
Dedication	vii
List of Figures.....	xi
List of Tables	xvi
Chapter 1 Background.....	1
1.1 Historical Context	2
1.2 Thermite definition and compositions	3
1.3 Modern progress in thermites	5
1.4 Thermite Microstructures	7
1.5 Reaction scale and inert surroundings	9
1.6 The Core Shell Structure.....	10
1.7 Energetics and MEMS.....	12
1.8 Dispersions and nanofluids	15
1.9 True Microscale EMEMS.....	17
Chapter 2 Microfluidics, Joule Heating, and Electrical Breakdown Physics	20
2.1 Microfluidic fundamentals	20
2.2 Mass transport and electrokinetic flows	21
2.3 Joule heating in liquids	23
2.4 Electrical breakdown of liquids	25
Chapter 3 Research Gap, Objective, and Scope	28

3.1 Research gap	28
3.2 Objective and scope	28
3.3 Research Methodology	30
Chapter 4 Numerical Modelling	32
4.1 Setup and methodology	32
4.2 Electric field, Joule heating, and their effects on temperature and velocity distribution	33
4.3 The role of Joule heating on velocity profile distortion	39
4.4 Input power and prediction of breakdown strength	41
4.5 Stokes number analysis and single particle model	43
Chapter 5 Experimental Methodology	51
Chapter 6 Experimental Results and Discussion	54
6.1 Characteristic results of particle-free operation of the microchannel in slow-heating mode...	54
6.2 Characteristic results of Al@ CuO particle-laden operation of the microchannel in slow-heating mode.....	59
6.3 Comparison between particle-free and particle-laden operation of the microchannel in slow heating mode	63
6.4 Operation of the microchannel in fast-heating mode and comparison with slow-heating results	64
6.5 Confirmation of optical and thermal emission sources by combined IR and narrow-band visible imaging	68
6.6 Post-test analysis of PDMS microchannel walls using SEM imaging and EDS elemental mapping	71
6.7 Evaluation of thermite reaction plausibility	75
6.8 Particle cluster collection techniques and large-scale ignition attempts	76

Chapter 7 Conclusion and Recommendations	82
7.1 Summary.....	82
7.2 Conclusion	83
7.3 Recommendations.....	84
Letters of Copyright Permission	87
References.....	149
Appendices	168
Appendix A Details of bubble growth rate analysis	169
Appendix B Details of COMSOL Models	172

List of Figures

Figure 1: Thermite coated wire used as a pyrotechnic ignitor ($t = 166.62$) to ignite main compressed nanothermite pellet charge in rocket motor (A), and nozzle exhaust of nanothermite propellant based microthruster (B).	2
Figure 2: Schematic diagrams of unstructured physically mixed thermite (A), structured thermite laminates (B), and core-shell particles (C), and respective SEM images showing microstructure and morphology (D, E, F) as obtained from Saceleanu et al. [36], Lesergent [37], and Zhang et al. [38], respectively.	8
Figure 3: Schematic diagram demonstrating consolidated, dispersed agglomerates, and fully dispersed physically mixed fuel-oxidizer particles and their ability to react.	10
Figure 4: Previously published energetic MEMS devices ranging from scientific and medical applications (A), commercial and industrial (B), micropropulsion devices (C), and defense-oriented applications (D). The images used are reproduced from Ardila Rodríguez et al. [62] (A), Nicollet et al. [63] (B), Ramachandran et al. [64] (C), and Pouchairet and Rossi [57] (D).	13
Figure 5: Previously published microchannel-based thermite MEMS including: multipoint ignitors (A) as published by Sullivan et al. [122], patterned Si/NaClO ₄ energetic charge published by Piekiet et al. [39], and shape-memory alloy-based actuator using thermite heat source as published by Ervin et al. [127].	18
Figure 6: Electrical breakdown of aqueous KCl with a solid electrode, showing transition from direct liquid breakdown into gas-phase breakdown as solution conductivity increases. Reproduced from Bruggeman et al. [160].	26
Figure 7: Schematic diagram of microchannel assembly (A), as-fabricated microchannel chip showing 5 channels per chip and attached reservoirs and copper electrodes (B), CAD used for microchannel throat geometry (C), and as fabricated microchannel geometry imaged using dark-field microscopy (D).	31

Figure 8: Schematic diagram of modelled domains showing domain geometry, material selections, boundary conditions, and thermal and electrical initial conditions.....	32
Figure 9: Numerical results for a 500V, 1E-03 [M] case taken at midplane of channel (equidistant between top and bottom walls) showing A) electrical field distribution with detailed view of throat section, and B) corresponding Joule heating source term magnitude.	34
Figure 10: Numerical results showing temperature distribution for 1[M] solution at A) and B): 100V, C) and D): 200V, and E) and F): 500V applied voltage cases, alongside G) contour plot of maximum temperatures obtained from simulated results with highlighted 100°C isotherm to denote electrolyte boiling threshold.	36
Figure 11: Numerical results showing velocity distribution for 1[M] solution at A) and B): 100V, C) and D): 200V, and E) and F): 500V applied voltage cases, alongside G) contour plot of maximum velocity obtained from simulated results with highlighted 100°C isotherm to denote electrolyte boiling threshold.....	38
Figure 12: Numerical results 500V applied channel voltage showing A) and B): velocity profile for 1[M] NaCl solution without Joule heating term, C) and D): velocity profile for 10[mM] NaCl solution with Joule heating term, and E) and F) temperature profile for 10[mM] NaCl solution with Joule heating term.	40
Figure 13: Numerically predicted log-scale input power contour plot for range of voltage and concentration combinations considered, showing estimated breakdown contour at 1.73 E-04 W (dotted red line).	42
Figure 14: Numerically predicted Stokes number (Stk) contour plot for range of voltage and concentration combinations considered.....	45
Figure 15: Schematic diagram of modelled domains showing domain geometry, material selections, and boundary conditions for single-particle model.	47

Figure 16: Electric field (A-D), current density (E-H), and Joule heating power (I-L) surface plots for solutions conductivities varying from 11 μ S/cm to 44000 μ S/cm showing transition from liquid heating to oxide-layer heating to combined heating modes. Results shown are for an applied voltage gradient of 4.75kV/cm (corresponding to 500V results from full channel model).	48
Figure 17: Schematic diagram of simultaneous high-speed + IR imaging system used to collect experimental results.....	53
Figure 18: Maximum, mean, and standard deviation of irradiance flux profiles, and voltage-current profiles for 1 [M] electrolyte-only microchannel test run in slow-heating mode (2.5mA input current), showing full test timescale (left-column plots), bubble formation timescale (right-column), and IR image snapshots (top, A-E).....	55
Figure 19: Maximum, mean, and standard deviation of irradiant flux profiles, and voltage-current profiles for a particle-laden flow (0.5g/L particle conc., 1 [M] electrolyte conc.) microchannel test run in slow-heating operating mode (2.5mA), showing full test timescale (left plots), bubble formation timescale (right), and IR image snapshots (top, A-E).	60
Figure 20: Microchannel operating in slow-heating mode (2.5mA) showing displacement of particle agglomerations and their collection at the liquid-gas interface. Red arrows indicate direction of particle motion as a result of the bubble expansion process. Particles used are 1 μ m Al@CuO at 0.5g/L concentration in 1 [M] NaCl.	61
Figure 21: Slow-nucleation bubble formation process followed by electrical discharge in a 1 [M] NaCl solution in a slow-heating operating mode microchannel.....	63
Figure 22: Bubble formation process in 1 [M] NaCl solution for two heating modes: slow heating mode (2.5mA, 120V, left column) showing damage of PDMS layer, and fast-heating mode (500V, right column) showing clear presence of electrical discharge.	65
Figure 23: Bubble formation process in energetic particle-laden flow showing optical emission for two heating modes: s heating mode (2.5mA, 120V, left column) showing damage of PDMS layer, and	

fast-heating mode (500V, right column) showing clear presence of electrical discharge. Particles are $1\mu\text{m}$ Al@CuO core-shell at 0.5g/L concentration dispersed in 1[M] NaCl solution..... 67

Figure 24: Emission spectrum of Al particles showing AlO characteristic peaks as obtained from Peuker et al. [169] with overlaid transmission band of Thorlabs FL488-10 laser line filter (top) and characteristic spectrum of electrical breakdown of aqueous NaCl solution as obtained from Bruggeman et al. [170] (bottom)..... 69

Figure 25: Simultaneous IR and 488nm filtered VIS imaging showing maximum irradiant heat flux trace and spatial and temporal correlation between hot-spots and AlO signal bright-spots for a 2.5mA heating current, 0.5g/L concentration of $1\mu\text{m}$ Al@CuO particles dispersed in 1 [M] NaCl solution..... 70

Figure 26: SEM images showing: A) overview of microchannel post-test, B) region of interest where optical emission was observed post 2.5mA applied current particle test, C) reacted or partially-reacted particles, D) unreacted particles, and EDS mapping showing: E) Al distribution in image C, F) Cu distribution in image C, G) Al distribution in image D, H) Cu distribution in image D. 73

Figure 27: Schematic diagram detailing the incompatibility of particle agglomeration and ignition method. 77

Figure 28: Attempts to ignite particle accumulation at throat produced by low EOF cycling using slow-heating mode (2.5mA, left) and fast-heating mode (500V, right), both resulting in characteristic behavior without large-scale particle ignition. Particles are $1\mu\text{m}$ Al@CuO at 0.5g/L concentration in 1 [M] NaCl solution, $t = 0$ corresponds to frame before first bubble is observed. 78

Figure 29: Successful ignition of large particle accumulation at throat produced by low EOF cycling, ignition occurring during 10V microchannel circuit continuity check. Particles are $1\mu\text{m}$ Al@CuO at 0.5g/L concentration in 1 [M] NaCl solution, $t = 0$ corresponds to frame before first ignition is observed..... 80

Figure 30: Proposed geometry change for future microchannels, red arrows indicating corners that trap bubbles during filling process.	85
Figure 31: Block diagram of bubble growth rate analysis image process.	171
Figure 32: Snapshots from bubble analysis process, showing as-recorded IR video, converted greyscale, and binary masked images taken before bubble formation ($t = 7.60\text{ms}$, top row) and after bubble formation ($t = 8.65\text{ms}$, middle row), as well as calculated bubble area plotted against time (bottom row).	171
Figure 33: Schematic diagram of modelled domains showing domain geometry, material selections, boundary conditions, and thermal and electrical initial conditions for full-channel model.....	172
Figure 34: Diagram of microchannel domain showing the location and type of applied grid node distribution control functions (A), and resultant grid for $n = 4$ (B, blue domain is liquid, grey domain is PDMS, glass domain not shown).....	174
Figure 35: Numerically predicted Stokes number (Stk) contour plot for range of voltage and concentration combinations considered.....	176
Figure 36: Schematic diagram of modelled domains showing domain geometry, material selections, and boundary conditions for single-particle model.	177
Figure 37: Diagram of single-particle model domains showing the location and type of applied grid node distribution control functions (A), and resultant grid for $n = 2$ (B, grey domain is Al, red domain is CuO, blue domain is water).....	178

List of Tables

Table 1: Available energy of oxidation of some common metals and metalloids, collected from Comet et al. [2].....	4
Table 2: Collection of common aluminum-based thermite reactions, their adiabatic flame temperature, theoretical heat of reaction, and gas production by mass as published by Fischer and Grubelich [16].....	5
Table 3: Conductivity used for liquid phase in numerical model for various NaCl solution concentration cases.....	33
Table 4: Summary of characteristic results for particle-free and particle-laden solutions in microchannel operating in slow-heating mode (2.5mA)	64
Table 5: Conductivity used for liquid phase in numerical model for various NaCl solution concentration cases.....	173
Table 6: Microchannel model predicted maximum temperature, velocity, and electric field results for the 500V, 1[M] NaCl case at increasing mesh density.	175
Table 7: Single particle model predicted maximum electric field, current density, and Joule heating power results for the 500V, 1[M] NaCl case at increasing mesh density.	178

Chapter 1

Background

Energetics are a broad class of materials with a large amount of stored chemical energy that can be extracted in the form of heat or pressure. The reactions that energetic materials undergo are self-sustaining, meaning that, once initiated, they produce enough heat to self-propagate. Often, the stored chemical energy is released by inciting a reduction-oxidation reaction between fuel and oxidizer components. The fuel and oxidizer are typically separate components, molecules, or phases, but some energetic materials contain both fuel and oxidizer on the same molecule. Energetic materials can be categorized into explosives, propellants, and pyrotechnics. A material is considered an explosive if it detonates upon ignition and performance is characterised by the material's detonation speed and the heat and pressure generated by the reaction. Like explosives, propellants are materials which can produce a large amount of heat and pressure upon combustion, which is converted to mechanical work by manipulating the flow of the combustion products. Compared to explosives, propellants have substantially lower burning rates; typically, detonation is undesirable for propellants since it may damage the confinement chamber, or the projectile being propelled. Like propellants, pyrotechnics are materials which do not detonate, but the purpose of a pyrotechnic device is to produce light, smoke, heat, and/or sound in a way that is not intended to be converted into mechanical work [1]. Since these classifications are based on the material's applications, rather than some intrinsic chemical property, sometimes a material may fall into more than one of these categories. Thermites are an example of such a material [2], as demonstrated in Figure 1 where a thermite is used as pyrotechnic to ignite an insensitive charge (A) as well as a propellant in a small rocket motor (B).

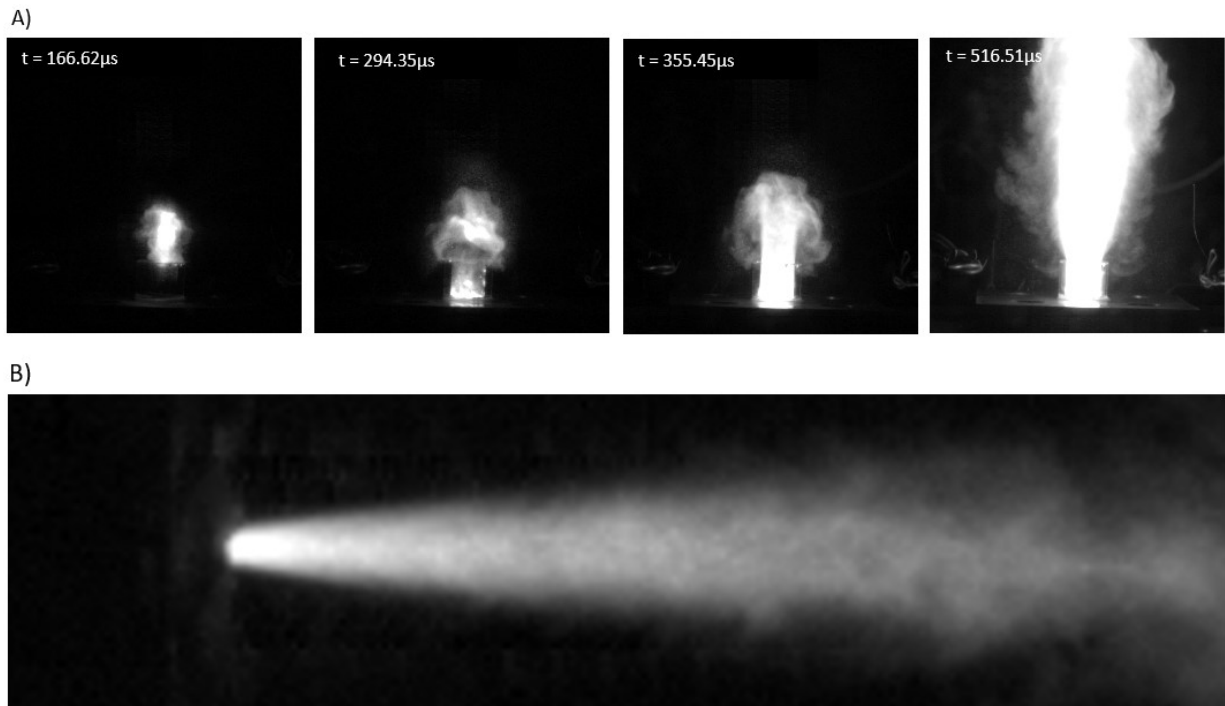


Figure 1: Thermite coated wire used as a pyrotechnic ignitor ($t=166.62$) to ignite main compressed nanothermite pellet charge in rocket motor (A), and nozzle exhaust of nanothermite propellant based microthruster (B).

1.1 Historical Context

Within the field of energetics, thermites are a highly useful and promising family of materials. First discovered by Dr. Hans Goldschmidt in 1893, thermites were used in a variety of welding processes, most notably in the joining of tram rails during the industrialization of Europe [3], [4]. Goldschmidt's composition can be categorized as a pyrotechnic and is one of the most classically known thermite mixtures: aluminum (Al) powder acting as a fuel and iron oxide (Fe_2O_3) acting as an oxidizer. The reaction produces aluminum oxide (alumina, Al_2O_3) and iron as a result. This process could be used to produce a tremendous amount of heat, especially when reactant mass was on the kilogram scale. This thermal reaction was one of the earliest modern welding techniques and revolutionized the rail industry, eliminating the maintenance and discomfort associated with bolted track connections.

Since then, thermites have been used as a source for heat for a multitude of applications. Examples include gas-free cutting torches, additives to explosives and propellants, airbag gas-generators, among others [5]. Since thermite mixtures contain both fuel and oxidizer, thermite mixtures are reactively self-contained and so can be ignited in inert, oxygen-free environments. As such, they have been proposed as candidates for underwater welding, cutting, blasting, and propulsion purposes [6]–[12].

1.2 Thermite definition and compositions

As the field of study has grown it has also become more generalized. A thermite, also known as a metastable intermolecular composite (MIC), is now generally defined as a solid-state energetic mixture of metallic fuel and metal-oxide oxidizer [13]. Traditionally, these have taken the form of powdered mixtures that are mixed to create an ignitable composite. Particles can be either micro- or nano-metric in size, with the latter being the primary focus of research in the 21st century. If either component of the thermite mixture is nanometric in scale, it is considered a nanothermite.

As the field of study has grown it has also become more generalized. A thermite, also known as a metastable intermolecular composite (MIC), is now generally defined as a solid-state energetic mixture of metallic fuel and metal-oxide oxidizer [13]. Traditionally, these have taken the form of powdered mixtures that are mixed to create an ignitable composite. Particles can be either micro- or nano-metric in size, with the latter being the primary focus of research in the 21st century. If either component of the thermite mixture is nanometric in scale, it is considered a nanothermite.

A variety of metals and metalloids are used as fuels in thermite compositions, including Al, B, Be, Ti, and Si as listed in Table 1. Of these, aluminum is the most used fuel due to elemental abundance, particle availability, price, environmental stability, and relative safety with respect to handling and toxicity [2]. This is coupled with high energy content compared to other metal fuels. Classical thermite compositions use metal oxides as the oxidizer. These include oxides of iron, nickel, copper, bismuth, molybdenum, among others [2], [14], [15].

Table 1: Available energy of oxidation of some common metals and metalloids, collected from Comet et al. [2]

Fuel	Oxide	Specific Energy [kJ/g]	Comment
Al	Al ₂ O ₃	31.1	Inexpensive, abundant
B	B ₂ O ₃	59.0	Reactive only at high temperature
Be	BeO	67.6	Highly toxic
Mg	MgO	24.8	Unstable
Si	SiO ₂	32.4	Reactive only at high temperature
Ti	TiO ₂	19.7	Low temperature ignition, costly
Zn	ZnO	5.4	Unstable

There are a large variety of compositions within the classification of ‘conventional’ thermites, each with their own unique reaction; some common Al-based thermite compositions are listed in Table 2. As a result, thermites are very versatile and have a broad range of applications with certain compositions gaining favor over others. In example, Al-Fe₂O₃ thermites react to output heat with little gas content [16]; this mixture can be classified as pyrotechnic. In contrast, Al-Bi₂O₃ thermites combust to produce 89% gas products by mass [16]. As a gas-generating pyrotechnic or propellant, the Al-Bi₂O₃ is more useful than Al-Fe₂O₃, but a welding application would prefer the low-gas nature of Al-Fe₂O₃ thermite. Elemental composition plays a large role in the nature of the thermite reaction, dictating ignition and flame temperature, but many other aspects such as particle size, fuel-oxidizer mixing ratio, active content, and environmental conditions play a role in the behaviour of combustion.

Table 2: Collection of common aluminum-based thermite reactions, their adiabatic flame temperature, theoretical heat of reaction, and gas production by mass as published by Fischer and Grubelich [16]

Reactants	Adiabatic flame temperature [K]	Heat of reaction [J/g]	Gas production [g _{gas} /g _{reactant}]
2Al + Bi ₂ O ₃	3253	2118	0.89
2Al + 3CuO	2843	4076	0.34
2Al + 3Cu ₂ O	2843	2408	0.08
2Al + Fe ₂ O ₃	3135	3954	0.08
10Al + 3I ₂ O ₅	>3253	6217	1.00
2Al + MoO ₃	3253	4703	0.25
2Al + 3NiO	3187	3441	0.01
2Al + WO ₃	3253	2914	0.15

1.3 Modern progress in thermites

In the past 20 years, academic work has focused on improving the performance and increasing the application potential of thermite mixtures. The transition from micrometer to nanometer scales in the late 20th century has been the greatest leap in thermite technology, resulting in lower ignition delay, higher flame speeds, and increased energy output [2], [14], [17]–[19]. This is a result of the increased specific surface area associated with reduction of particle size. Increased area results in more reacting area, and smaller size means more spatially homogeneous mixtures and improved fuel-oxidizer contact. However, because of reduced size and increased area, particle clustering is more challenging to overcome for nanoparticles than microparticles [17].

Aside from particle clustering, decreasing particle size also results in decreased active content in the metal fuel particles. This is because the thickness of the naturally occurring oxide shell that

forms on the metal particle surface is independent of particle size; typically for aluminum this is a 2-5nm layer [17], [18]. As particle diameter decreases, this inert surface layer becomes a greater proportion of the particle volume. Considering aluminum again with a 5nm oxide layer, a 1 μ m particle will have 97% active aluminum content by volume, but a 100nm particle will have 73% active content. This can be accommodated by using a higher equivalence ratio; equivalence ratio is a measure of how fuel-rich an energetic mixture is, with an equivalence ratio of one being equal to stoichiometric ratio.

More recently, the chemical definition of thermites has been challenged by novel compositions which do not fit in with the traditional 'thermite' classification. Oxidizers have shifted from metal oxides to oxygenated salts, such as KClO₄, which have higher density of electronegative species. Subsequently, the aluminum-salt reaction is more reactive and can be more exothermic than that of a metal-oxide, and so thermal performance is improved [20]. Likewise, fluoropolymers, such as polytetrafluoroethylene (PTFE), containing highly electronegative fluorine atoms can be used to substitute metal oxides to increase thermal performance [21]–[24].

The research boom of carbon nanomaterials has also fed into the field of thermites, with many acting as performance modifying additives [11], [25]–[28]. By adding carbon nanotubes to physically mixed thermites, the ignition temperature and ignition delay are reduced [11], [25], [26]. The carbon nanotubes improve the heat transfer to the reactive particles [11], [26], but may also have a liberating effect on the oxygen bond within the oxidizer, as is the case for I₂O₅ [25]. Carbon nanomaterials play a significant role by acting as a substrate for energetic particle to collect upon, enabling improved thermal conductivity and subsequent reaction propagation between the thermite components [11], [26]. The geometries of the carbon phase can be leveraged to create structures at the micro and nanometer scales, either by using hub-and-spoke carbon nanotube geometries [11], or graphene-based sheets [26], [27]. Carbon nanomaterials can also be used to create energetic superstructures: Wang et al. have developed a reduced-graphene oxide aerogel which can be impregnated with thermites and produce large flame speeds. This is attributed to the high porosity of the aerogel where convection heat transfer modes dominate, similar to loosely packed physically mixed powders but with the added mechanical stability provided by the graphene aerogel skeleton [28].

The reduced graphene oxide used by Wang et al. acts as a structure to hold particles together, like a binder [28]. Simple binders have been used in thermites for a long time, but often work against the thermite reaction because they contain less energy [1], [29]. Using a reactive (or energetic) binder, however, mitigates this effect by adding energy in the place of otherwise dead weight. This has resulted in mixed success when polymer binders are used, with environmental and mechanical stability improvements often coming at the cost of some combustion performance [30]–[33]. Addition of nitrocellulose has been shown to increase the mechanical resilience as well as specific impulse of thermites for propulsion applications, but at the cost of increasing ignition delay [20], [34].

Binders can improve environmental resistance of thermites by preventing the natural reaction of metallic fuels by air. Similarly, hydrophobic binders and coatings have enabled the ignition of particle-based thermites in underwater environments [6], [8], [11], [12], [35]. Early work in this field used PTFE as a hydrophobic coating for thermite composites [8] and as the oxidizer itself [12]; both these mixtures needed to be mechanically pressed to prevent the energetic from dispersing once submerged. Further work continued the use of fluorocarbon coatings on compressed thermite pellets and found that aging is slowed rather than prevented underwater and that, after submersion for 10 days, the energy output of the thermite was reduced by a factor of 10 [35]. More recently, fluoroalkylsilane (FAS) has been used as a hydrophobic coating for Al-nanorod based thermites, resulting in further improved underwater combustion performance [6], [9].

1.4 Thermite Microstructures

By far the most dominant form factor for thermite mixtures, historically, has been the mixed-powder composite, commonly referred to as ‘physically mixed’. More recently, research has explored a variety of form factors for thermite composites; for the purposes of this work, these can be broken down into unstructured and structured thermites.

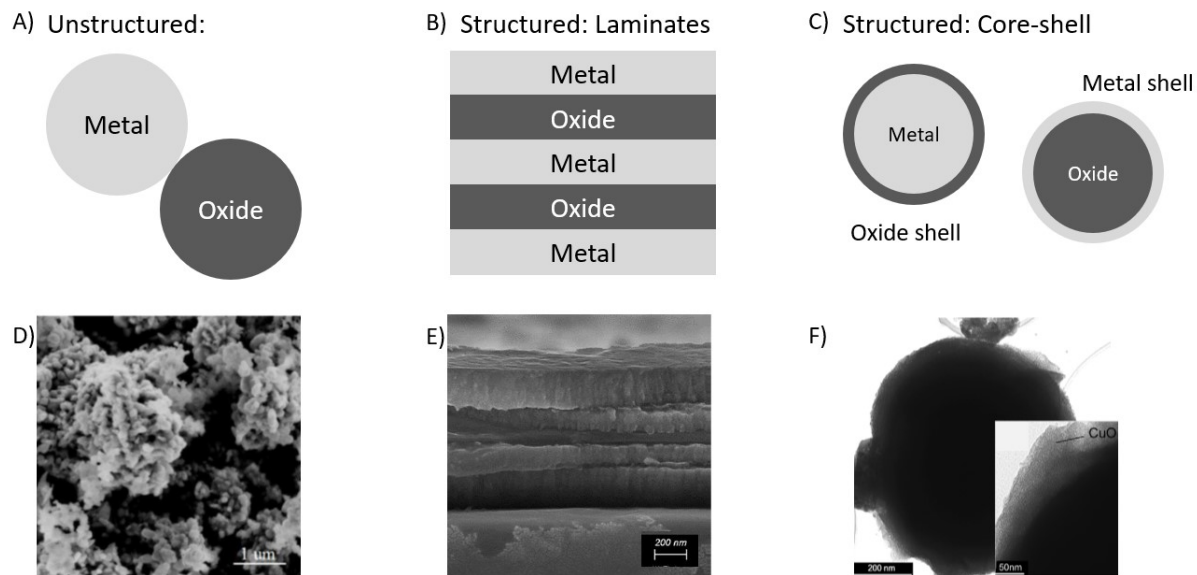


Figure 2: Schematic diagrams of unstructured physically mixed thermite (A), structured thermite laminates (B), and core-shell particles (C), and respective SEM images showing microstructure and morphology (D, E, F) as obtained from Saceleanu et al. [36], Lesergent [37], and Zhang et al. [38], respectively.

Unstructured form factors are those where powders of spheres, sheets, rods, and other geometric particles are physically mixed such that there is no order in the arrangement of fuel and oxidizer. An unstructured physically mixed nanothermite is shown in Figure 2B. Conversely, structured form factors are those where the fuel and oxidizer components are arranged in an ordered structure. This includes structures where microporous oxide substrates are filled with fuel particles [39], as well as laminate composites which are composed of distinct, continuous fuel and oxidizer phases in the microstructure. A nanolaminate thermite structure is shown in Figure 2E.

These laminate structures can be manufactured by deposition techniques such as magnetron sputtering, atomic layer deposition, and vacuum filtration with nano or micro scale layer thicknesses [37], [40]. Laminates are of interest because they isolate the reaction surface to the interface between the fuel and the oxidizer. In addition, they have remarkably close intimacy between the reactants; these attributes make laminates good candidates for studying the reaction mechanisms of thermites. Laminates are primarily used in academic studies but see occasional use in practical/device level applications. This is often because laminates do not always outperform

unstructured thermite mixtures, such as mixed powders, but require more effort to fabricate. As a result of the relative complexity of these manufacturing techniques, the practicality of laminate thermite structures is limited, especially at scale [41].

A significant advantage of laminated structures is the consolidation of fuel and oxidizer into a mechanically joined system. Consolidation is required for thermite reaction in flowing fluid environments, either gaseous or liquid, since convective forces will otherwise erode or sweep away the energetic charge [8], [12], [35]. While it is possible to consolidate particle mixtures in a binder matrix or to mechanically press powders into pellets, nanolaminates have the advantages of reactant intimacy and fine control over layer thickness. Layer thickness in laminates determines the equivalence ratio and energetic mass, both of which can be difficult to control for unstructured thermites locally at micro- and nanometer scales.

Physically mixed thermites are commonly prepared by dispersing the fuel and oxidizer powders in a solvent (ethanol, acetone, hexane, among others), and often mixed by ultrasonic agitation [2], [14], [15], [17], [18], [36], [41]. Dry mixing of thermites may produce localized heat through friction leading to potential reaction between phases if they are in powdered form, though some compositions can be mixed this way [2], [18]. Using a solvent enables mixing of the reactants without this risk since the dispersed particles are not in direct contact with each other. Other methods of preparing mixed thermites include resonant acoustic mixing (RAM), arrested reaction milling (ARM), electro-spraying and electrospinning, among others [2], [17], [18], [41], [42].

1.5 Reaction scale and inert surroundings

A major consideration for dispersed energetic materials is the size of the reactive system. The ‘neutralizing’ effect of the particle dispersion highlights a limitation to the useful scale of thermites: the thermite reaction needs direct contact between the fuel and oxidizer components to react. This acts as a major limitation of the usefulness of discrete fuel-oxidizer composite thermites in dispersed phases. This can be mitigated by ensuring agglomerations of particles exist, either by using binders, by mechanically pressing the powder into small pellets beforehand, or by controlling the flow of the dispersion to concentrate particles together. For structured thermites like laminates, fuel-oxidizer separation is mitigated by the strong mechanical bond between the two phases,

typically at nanometric scales. Structured thermites are therefore more applicable in dispersed-phase applications.

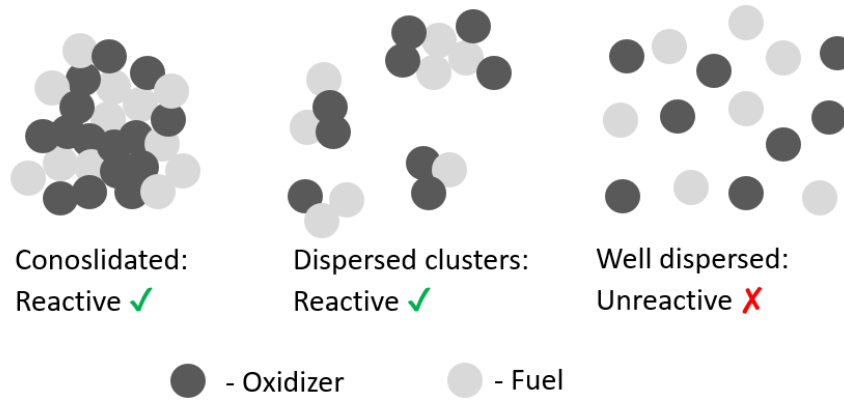


Figure 3: Schematic diagram demonstrating consolidated, dispersed agglomerates, and fully dispersed physically mixed fuel-oxidizer particles and their ability to react.

Reaction of thermites in submerged environments has long been seen as an opportunity for innovation in wet welding. Thermites can also be used for propulsion and flow/pressure generation underwater. However, these thermite mixtures require some form of reactant consolidation since they are typically composed from discrete particle mixtures. Use of binders or mechanical pression is one option, but novel techniques taking advantage of bubble geometries have enabled the deposition of loose, additive-free thermite particle films along a bubble surface using magnetic fields. When ignited via microwave radiation, the bubble-marble structure was successfully ignited [7]. This is an important innovation for the use of thermites in liquid phases but may prove to be difficult to replicate at submillimeter scales.

1.6 The Core Shell Structure

Sitting somewhere between laminated structures and particle mixtures is the core-shell particle structure. Developed within the last decade, core-shell thermite structures consist of a particle (core) coated with a secondary phase (shell) [2], [18], [23], [24], [38], [43]–[51]. In doing so, a quasi-laminated structure is formed with the benefit of mixing intimacy as observed in laminated structures in the form factor of a powder, as shown in Figure 2C and F. Unlike in monolithic

laminated structures, the loose-particle nature of core-shell particles preserves reaction propagation via hot gas convection and therefore maintains combustion performance. Additionally, these particles remove the limitations of dispersed phase thermites since an individual particle can theoretically react without contact with another particle.

Core shell thermites can have either the fuel [38] or the oxidizer at the core, with the converse phase acting at the shell. In example, it is possible to form aluminum core, copper oxide shell particles [38] as well as copper oxide core, aluminum shell particles [44]. The 'core@shell' nomenclature is often used to clarify the structure, and both fuel@oxidizer and oxidizer@fuel compositions exist. For uniform, well coated core-shell particles, this acts as a tuning parameter for dispersed phase flows since the surface forces on at the shell-fluid interface may affect flow properties. Another major consideration is the ability to deposit an appropriately thick shell layer. This is a current limitation for core-shell particles, as it is noted that core-shell particles are more energetic with equivalence ratios exceeding unity for most Al-based thermite particles [38], [43], [44], [48], [49], [51], [52]. This is yet another factor which may impact which phase is selected for the core and the shell.

Core-shell particles exist in micro and nanoparticle forms. In both cases, the mixing intimacy of fuel and oxidizer components typically yields lower reaction onset temperatures, and reduced ignition delay compared to physically mixed particles [23], [24], [38], [43], [49], [51]. Experimental works have shown that specific energy release for core-shell particles can be higher than for physically mixed particles of the same type [44], [51], but can also be lower [38]. As with physically mixed particles, micro particles burn slower than nano particles and generally have less specific energy [38].

Though core shell thermites are novel, researchers have already produced many interesting compositions. One of the earliest published works on core-shell thermites used atomic layer deposition to produce Al@ WO_3 [43]. As previously mentioned, both Al@CuO and CuO@Al thermite compositions exist, with both forms having similar combustion properties [38], [44], [51]. Al-core coated with Fe_2O_3 has also been developed in a core shell structure for micron scale particles, with enhanced interfacial processes between the core and shell phases to improve performance [49]. Core-shell structures are not limited to spherical particles; NiCo_2O_4 @Al, CoFe_2O_4 @Al nanowires have

also been developed as self-contained reactive structures [52], [53]. More contemporary thermite mixtures have also been synthesized in core-shell form. An Al@PVDF fluoropolymer coated particle structure has successfully been fabricated at the nanoparticle scale and it was shown that the PVDF improved the environmental stability compared to raw Al particles [23]. Similarly, Mg@PTFE coated nanowire films have been fabricated with excellent submersion resistance [54]. Core-shell Al@PTFE nanofibers have also been fabricated by electrospinning [55]. Core-shell MnO_2 @Al and Co_3O_4 @Al nanowire structures have also been coated with hydrophobic fluoropolymers PTFE and FAS, respectively, and shown good aging resistance [6], [56]. The coated Co_3O_4 @Al superhydrophobic film was also shown to be ignitable in underwater combustion tests.

1.7 Energetics and MEMS

One field where functional energetic materials, especially thermites, are particularly useful is within Micro-Electro-Mechanical systems (MEMS) [57]–[59]. Pioneered in the late 20th century following advances in silicon fabrication technology, MEMS have enabled huge technological progress via miniaturization. Many of the sensors used daily in electronics such as smartphones and wearables are MEMS devices, including accelerometers, microphones, barometers, and thermometers. Advances in MEMS have not influenced just the field of consumer electronics though, as MEMS pressure sensors have applications in a multitude of automotive and industrial applications [60], as well as biomedical applications like non-intrusive blood pressure and heart rate monitoring [61]. Research in the field of energetics over the last two decades has integrated thermite technologies as miniature energy sources in a multitude of energetic MEMS (EMEMS) devices.

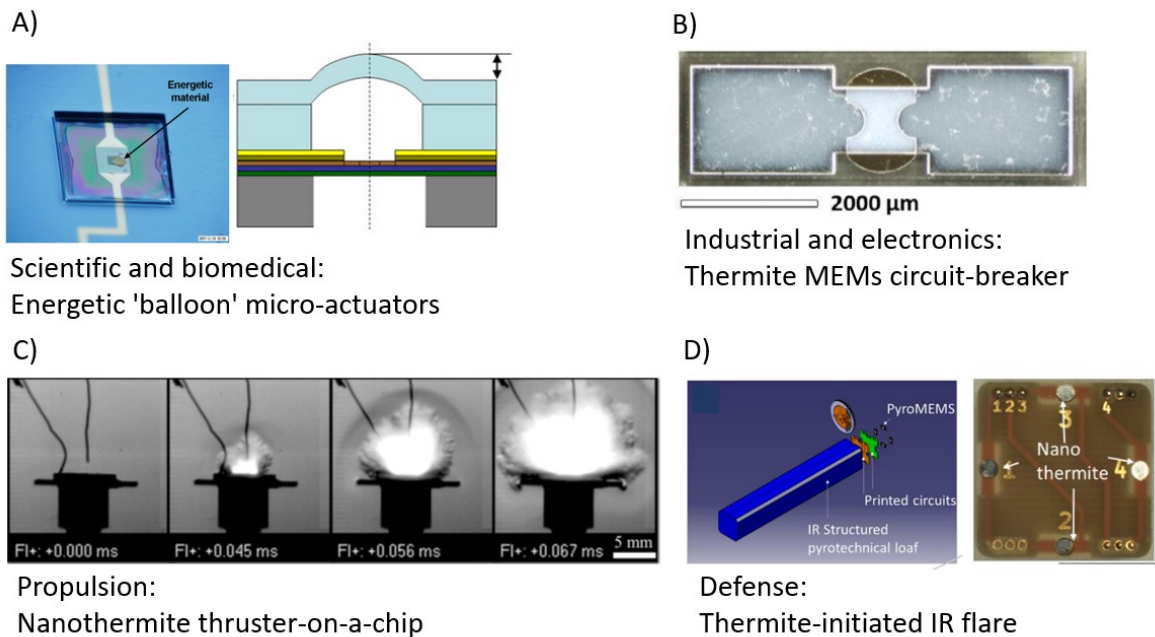


Figure 4: Previously published energetic MEMS devices ranging from scientific and medical applications (A), commercial and industrial (B), micropropulsion devices (C), and defense-oriented applications (D). The images used are reproduced from Ardila Rodríguez et al. [62] (A), Nicollet et al. [63] (B), Ramachandran et al. [64] (C), and Pouchairet and Rossi [57] (D).

Pyrotechnic microvalves and actuators are one such example of energetic applications for biomedical science. Although not using a thermite energetic, Ardila Rodríguez et al. has demonstrated an energetic pumping actuator with low heat transfer into the pumped fluid [62]. Using a concept first proposed by Rossi et al. [65], the energetic is used to create a rapid pressurization of a flexible membrane which allows for the transfer of that pressure force without direct contact with the energetic process. Life-science applications of this concept include devices to aid in administering drugs through skin [57], [66] and cell membranes [67].

EMEMS also have significant application in industrial and commercial electronics. Thermite-based electrical micro-fuses have been demonstrated in literature, where a thermite charge is deposited on or near an electrical trace [63], [68], [69]. When an overcurrent is applied, the trace heats up and triggers the thermite reaction, which destroys the conductive path and stops current flow. This

system has a faster response time than a mechanical breaker or a tradition wire-fuse, along with the advantage of being easily integrated into the circuit design and fabrication process [67].

Another active area of research for EMEMS, as with many other energetics, is the generation of thrust for propulsion. Since the late 20th century there has been incentive to minimize propulsion systems alongside the minimization of satellite hardware [70]–[72]. This stems from the prohibitive cost of launches into orbit, and so consolidating satellite hardware into a compact and lightweight package increases the accessibility of space projects since many missions can be launched simultaneously and individual mission costs reduced. In these applications, the thrust forces required are orders of magnitude less than those of traditional satellites, so compact integrated EMEMS based on solid fuels are a viable option for small-satellite propulsion [71]. Since EMEMS devices are single-use, it is proposed that they integrated into the form of a microthruster array with many small engines that are individually activated by an electronic ignition system [71]–[80]. Thermite based thrusters have been demonstrated using simple compositions such as Al/CuO [76], [81] and Al/Bi₂O₃[34], [64], [82], as well as more complex mixtures based on Al/KClO₄ [20] and Al/Cu(IO₃)₂ [83]. Ru et al. and Dai et al. demonstrated the integration of multiple thrusters into an array, highlighting the compatibility of thermites in the fabrication of a MEMS microthruster [76], [84]. The major limitation of these systems is their lack of versatility since the solid fuel acts in a burst with little ability for modulation, and once a charge is spent, it cannot be easily replenished.

A plethora of military applications also exist for EMEMS, often as compact ignition sources for difficult to ignite energetics [85]–[90]. Glavier et al. has demonstrated that thermite-based ignitors can be used to ignite high explosives such as RDX and used the explosive to launch a projectile [91]. Recently thermite igniters have been integrated into the design of a compact infrared flare. Because of the small size of the EMEMS, the researchers demonstrated new controllability by distributing several micro-igniters along a single chip that can independently ignite the flare pyrotechnic charge in different spots [57].

Microfluidic MEMS devices are often used for lab-scale production processes, including for fabrication of energetics. Microfluidic devices can produce finely controlled laminar flows, enabling precise size control for droplets. One paper describes the production of the high-explosive HMX in a microfluidic chip [92]. The chip uses a crossflow to pinch oil-suspended HMX into small droplets,

which are then transported in a water flow. Varying the parameters of the crossflow allows the droplet size and morphology to be controlled.

1.8 Dispersions and nanofluids

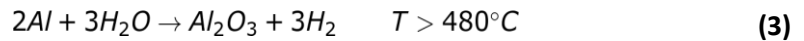
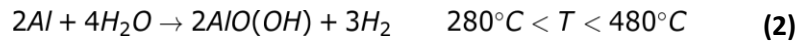
The aforementioned examples all use consolidated thermite, whether done so by mechanical compaction, electro-spraying, use of a binder, or other methods. This limits the usefulness of thermites since the devices have limited application flexibility. Unlike a distributable energy source, such as compressed gas or liquid fuel, the amount and location of the thermite cannot be changed in operation; liquid and gas-based energy sources can be modulated via valves, and if the storage tank is not empty, energy can be delivered as needed. These are problems faced by many solid-fuel based rocket motors due to the inherent simplicity of the solid-rocket design. Since thermite reactions cannot be stopped and restarted on command, the reusability of thrusters remains a problem which necessitates either a fluid energy source or a mechanical method of reloading the thruster. However, if the solid fuel could be dispersed in a fluid while keeping its reactivity, it may be possible to better control the location and amount of energy released by combustion, therefore overcoming some of the limitations of consolidated thermite thrusters. Moreover, this would enable multiple systems on the same device to operate on the same fuel source by distributing the energetic liquid.

The mixtures of micro and nanoparticles within a carrier liquid are called micro and nanofluids, respectively. Typically, these dispersions are created to modify the property of the fluid, such as the addition of CuO into water to improve thermal conductivity [93]. Similarly, energetic nanofluids are an active area of research, though few studies on thermite dispersions have been published. The energetic nature of aluminum particles is recognized in energetic nanofluids, though. Most often, metal nanoparticles are added to hydrocarbon fuels for increased energy density [94]–[99]. It has been shown that addition of aluminum nanoparticles to the hydrocarbon propellant JP-10 increases its energy and improves specific impulse and combustion efficiency when used in a rocket engine [94], [95]. When added to diesel, the Al particles reduce emissions [96], improve ignitability [98], and increase efficiency [99] when used in a compression ignition engine.

Aluminum-water nanofluid research is limited to only a handful of papers studying its use as heat transfer improving coolants [100], [101]; this field focusses instead on alumina-based nanofluids. The Al-H₂O nanofluid is chemically metastable and will undergo reaction at temperatures as low as 25°C [102].



This process is typically studied for hydrogen production, though the aluminum water reaction is exothermic, producing 5251 J/g, and is easily initiated if there is no oxide layer on the aluminum. In practice, the alumina layer slows the reaction at low temperatures, so the aluminum usually needs to be processed by mechanical or chemical methods to expose the aluminum core; addition of NaCl into the solution promotes the reaction by corroding the oxide layer. Heat output from reactions of unprocessed microparticles in liquid water at low temperature occurs at comparatively slow rates [103]. At higher temperatures, the dominant aluminum-water reactions are as follows:



The reactions are exothermic, producing 6557J/g and 7430J/g for equations (2) and (3) respectively [104]. The Al-H₂O reaction at high temperatures occurs much more rapidly [103], has flame temperatures around 2200°C [105] and has been proposed as an energy source for power generation as well as propulsion [105]–[109]. For these applications, it is more common to mix the Al and H₂O at values near the stoichiometric ratio resulting in a slurry rather than a liquid dispersion. This slurry can even be frozen to create a solid form of the energetic mixture (ALICE) [109]–[113].

The ignition of thermite particles within a carrier fluid is not well studied. Though some literature exists regarding the combustion of aerosolized thermite sprays [114], [115], it does not ignite the particles in an aerosolized form; the particles are consolidated into a solid charge and ignited using a NiCr wire, then ejected through a nozzle to create the aerosol spray. The lack of literature on this topic is likely a result of the limitations of traditional physically mixed thermite powders, since contact between both fuel and oxidizer powders must exist for combustion, therefore individual suspended particles become inert. However, the recent development of core-shell thermites has

removed this limitation, and a recent paper by Rahman et al. [116] evaluates the physics of group combustion of gas-dispersed core-shell thermite particles. The study focuses on the theory and numerical modelling of aerosol combustion of core-shell Al@CuO, so experimental results for the combustion of dispersed thermites remain missing in literature.

1.9 True Microscale EMEMS

Only a limited amount of research combining the fields of microfluidic MEMS and energetic materials has been performed. In the past, energetics could not achieve full, self-sustained combustion in narrow, sub-millimeter geometries. However, thermites have proved to be usable at these small scales, and therefore present an opportunity for even further miniaturization of energetic systems.

Many of the aforementioned MEMS devices operate at mesoscales, defined as those with characteristic dimensions in the millimeters [117]. The capabilities of modern thermites are smaller, as demonstrated by a handful of studies that have pushed the operating scales into true microscale geometries, with both unconfined and confined thermite charges with micron dimensions. As previously discussed, deposition techniques such as magnetron sputtering can be used to create multilayered laminate thermites. Zhu et al. deposited Al/CuO laminate films between two conductive layers, creating a capacitor with an energetic dielectric gap [118]–[120], and Fu et al. demonstrated it in the form of a 400 μ m square micro-initiator [121]. Alternatively, by first sputter-depositing platinum onto glass, Sullivan et al. used electrophoretic deposition (EPD) to deposit, ignite, and study unconfined, micro- and nanothermite films with a variety of micrometric geometries and thicknesses [122], [123], as shown in Figure 5A. The electrodes, and subsequently the thermite geometry, can also be shaped by laser-cutting, as was demonstrated in a recent paper [124]. Similarly, sub-millimeter scale electrodes can be 3D printed using conductive inks, then thermite can be deposited by EPD to create a freestanding 3D energetic structure [125], [126]. When the EP deposited thermites were combusted, flame speeds varied between 1.5-150 m/s, depending on the composition, thickness, and geometry of the patterned thermite [122]–[126].

Subtractive methods have also been used to selectively machine trenches into substrates for thermite deposition. One study used a patterned etching process to create porous trenches on a

silicon wafer, then filled it with oxidizer to create a semi-enclosed, Si-based energetic trace [39], shown in Figure 5B. To demonstrate the practical usefulness of microenergetics, Ervin et al. used thermites in 50-200 μ m semi-confined trenches as heat sources to activate shape-memory alloy-based actuators [127], shown in Figure 5C.

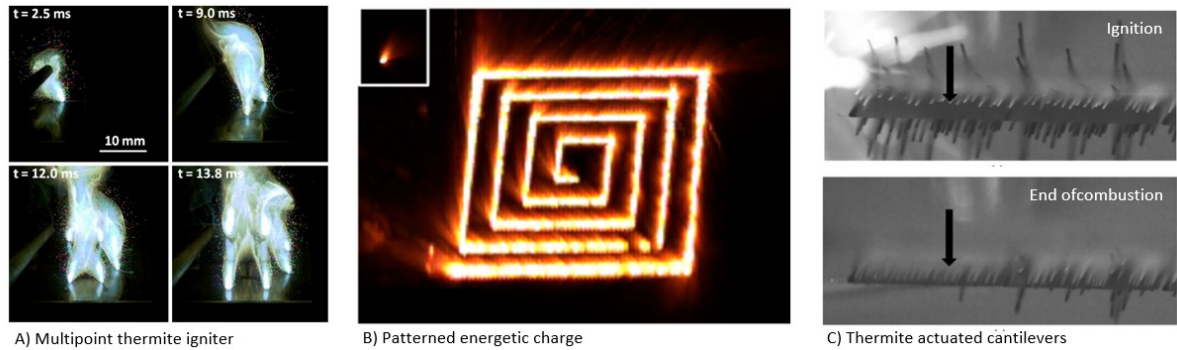


Figure 5: Previously published microchannel-based thermite MEMS including: multipoint ignitors (A) as published by Sullivan et al. [122], patterned Si/NaClO₄ energetic charge published by Piekiet et al. [39], and shape-memory alloy-based actuator using thermite heat source as published by Ervin et al. [127].

Some research also has been performed to characterize and demonstrate nanothermite combustion in confined microchannels [128]–[131]. The flame speed of Al/MoO₃ was observed to decrease as the channel size grew smaller due to increased thermal and viscous effects at the walls, but speed still exceeded 250m/s in 300 μ m square channels [128]. The same trend was observed for Al/CuO mixtures in microchannels with 100 μ m thickness [129]. Studies by Tappan et al. used a 100x300 μ m microchannel loaded with Al/MoO₃ nanothermite found that flame speed was greater when a sliding piston was used to create a confined but expandable combustion chamber when compared to a single open-ended rectangular tube [130]. Once the flame filled the entire volume of the confined chamber the flame speed decreased from 450m/s to values between 100 – 200 m/s [131]. The thermite was also enriched with the explosive CL-20 but resulted in failure of the microchannel wall. This study demonstrated that thermite combustion in small scales could be used to preform mechanical work, though quantitative results of work output are not available. Gangopadhyay et al. have used these concepts to patent a thermite MEMS combustor as a shock

wave and power source for microchips [132]. These studies show the state of the art for true microscale solid energetic, but there also exist microfluidic devices using energetic liquids.

Use of energetic liquids at microfluidic scales has been studied since the late 1990's. The main interest in microfluidic liquid fuels is their high energy density when compared to current battery technology, enabling for increased operational duration of microdevices [117], [133]. This has led to the development of microcombustion based power generation devices for MEMS applications, such as a small silicon-based gas turbine developed by Spadaccini et al. with a footprint of 21mm in diameter and 3.7mm in thickness and capable of thermal efficiencies of 90% when used with H₂ gas and 60% when used with hydrocarbon fuels [134]. Thermoelectric and thermophotovoltaic based power generation with liquid fuel microcombustion has also been demonstrated [117].

Microcombustion has also been demonstrated in the field of actuators and robotics, often as a gas generating source. The operating principle behind many of the proposed devices is the use of flexible membrane balloon actuators, similar to those shown in Figure 4A. Liquid fueled balloon actuators have been used as pumps for micropneumatic devices [135] as well as actuators for tactile interfaces for the visually impaired [136], [137]. More energetic reactions have been used in soft robots to provide fast actuation of a jumping mechanism, as demonstrated by Shephard et al. [138] and Tolley et al. [139].

The works presented here represent the smallest scale footprints for energetic MEMS and demonstrate the practical usefulness and limits of modern thermite compositions. In addition, the field of liquid-based microcombustion shows a diversity of devices where novel thermite compositions may be useful. An energetic material that could be used in both solid and fluid forms would have broad reaching applicability, and new thermite microstructures may have enabled this.

Chapter 2

Microfluidics, Joule Heating, and Electrical Breakdown Physics

Over the last 30 years, advances in electronics and microfluidics have created great interest in microfluidic devices, often in the form of MEMS. These include complex fluid devices with micro-pumps, valves, and fluid conditioning structures which are often used in lab-scale procedures, especially in life-science and wet-chemistry settings [140].

2.1 Microfluidic fundamentals

Microfluidics is the study of fluid flows with microscale length or volume properties, usually realized by liquid, gas, or multiphase flows in sub-millimeter domains. Though relatively small when compared to traditional fluid flows, the length scales of microfluid flows are still orders of magnitude larger than molecular scale. In practice, most microfluidic flows can be described by continuum regime flow equations, though sometimes in simulation discrete Monte-Carlo and molecular dynamics techniques are used [141]. They differ from traditional flows because, in addition to well-established body forces, small scale interactions (van der Waals, h-bonding) that can be ignored in large scale flows have a large impact on fluids in micro-scale interactions. Interface and surface forces become more significant due to the increase in surface area to volume ratio, giving rise to capillary forces and other surface tension effects. Small length-scales also give rise to electrical, molecular, and ionic gradients which can be manipulated to move the fluid [141]. Because the length scales are so small, surface/interface induced viscous forces typically dominate over momentum forces, leading to low Reynolds number laminar flows. The Reynolds number is a nondimensional value which compares inertial forces to viscous forces in a flow, and is computed as:

$$Re = \frac{\rho u L}{\mu} \quad (4)$$

Where ρ , u , and μ are the density, velocity, and viscosity of the flow [142]. L is a length that is characteristic to the flow; for flows within channels or pipes the hydraulic diameter is typically used. The hydraulic diameter is defined as:

$$D_h = \frac{4A}{S} \quad (5)$$

Where A is the cross-sectional area of the duct and S is the wetted perimeter [142].

The micro-scale geometries in microfluidic flows also mean that diffusion lengths are low, and since turbulent flows are less common, diffusion is important for mixing and heat-transfer in microfluidic flows [141]. Heat transfer in microfluidics is not dissimilar to larger scale flows, though the high surface-to-volume ratio means surface fluxes typically play a more dominant role. At micron scales and smaller, thermal conductivity in solids begins to be affected by the microstructure, such as defects and grain boundaries in crystalline materials, as well as by surface-based effects that can typically be neglected for bulk materials [143]. As a result, anisotropic thermal properties have been observed for films with submicron thicknesses. Some change to thermal properties also occurs in liquids with decreasing size, but for water, these effects only become relevant at length scales below 100nm [144], and are resultantly not significant for most microfluidic devices.

2.2 Mass transport and electrokinetic flows

Mass transport in microfluidics can be achieved in a multitude of ways to transport a fluid species of interest, bubbles, droplets, or solid particles. Aside from diffusion, typical methods of mass transport such as gravity, pressure, and temperature driven flows can be used, but the increased prevalence of interfacial and molecular forces in microfluidics enables more control over the flows.

Microchannel devices with liquid flows are commonly used to transport and act on some secondary phase of interest, either gas (bubble), liquid (droplet), or solid (particle) [141]. These suspensions are referred to as colloidal dispersions, where an insoluble phase is stably dispersed into a solvent phase. These solutes can be manipulated with momentum as with larger scale flows, but also with intermolecular, thermal, magnetic, and electrokinetic techniques [141], [145]. An important quantity in dispersed-phase particle transport is the Stokes number, which is a quantification of the inertia of the particle compared to the inertia of the suspending medium [141]. The Stokes number is defined as:

$$Stk = \frac{\tau u_0}{d_c} \quad (6)$$

Where τ is the relaxation time of the particle, u_0 is the flow velocity, and d_c is a characteristic length scale; for particle flows d_c is typically set as the particle diameter. In a Stokes flow, where $Re < 1$, the relaxation time can be computed as:

$$\tau = \frac{\rho_p d_p^2}{18\mu_g} \quad (7)$$

Where ρ_p and d_p are the particle density and diameter, respectively, and μ_g is the density of the suspending fluid [146]. A Stokes number below 1 generally indicates that particles will closely follow streamlines in the flow, whereas Stokes numbers above 1 generally indicate that particles will prefer to travel in straight lines due to the dominance of their inertia. In practice, other parameters that are not considered in the Stokes number can affect whether particle follow streamlines, especially in microfluidic flows where the effects of surface and electrokinetic forces are prevalent [141], [146], [147].

A simple and popular method for transportation of liquids and suspended secondary phases through microchannels is electro-osmosis, whereby flow can be achieved by applying a voltage across a fluid channel. The direction and magnitude of the imposed velocity depends on the applied voltage potential as well as the material properties of the electrolyte and the channel walls. Along liquid-solid interfaces such as the walls of a microchannel, ionization and adsorption causes charge dissociation in the form of ion gradients near the wall, called the electric double-layer or Debye layer. The polarity of which depends on the interfacing materials, and the strength of electric potential across this gradient is described by the zeta potential, ζ . The size of this finite non-uniform charge layer is quantified by the Debye length:

$$\lambda_D = \sqrt{\frac{\epsilon_r \epsilon_0 \kappa_b T}{2n_0 e^2}} \quad (8)$$

Where ϵ_r and ϵ_0 are the relative and vacuum permittivity, κ_b is the Boltzmann constant, T is the temperature, n_0 is the ion concentration, and e is the elementary charge [141]. For water-based solutions, the Debye length is on the scale of nanometers[141]. Outside the Debye length, in the centre of a microscale flow column, the charge balance remains neutral. When an external voltage is

applied across the channel, the fluid at the walls experiences an electrically induced force parallel to the electric field lines; the direction depends on the polarity of the ions at the wall. Cohesive viscous forces in the liquid cause the fluid in the channel to move with the fluid along the walls [148]. One important and desirable trait of electro-osmotic flow (EOF) is a plug flow with uniform velocity magnitude across the section of the channel [141], [148]. This allows for samples to be transported together in groups, often desirable for preventing sample smearing as well as particle, bubble, or droplet transport processes. So long as the Debye layers are not self-intersecting, the velocity magnitude of the plug flow can be computed using the Helmholtz-Smoluchowski equation [141], [148]:

$$\mathbf{u}_{HS} = -\frac{\epsilon_r \epsilon_0 \zeta \mathbf{E}}{\mu} \quad (9)$$

Where ϵ_r and ϵ_0 are the relative and vacuum permittivity, ζ is the zeta potential, $\mathbf{E}$ is the electric field, and μ is the dynamic viscosity of the fluid. The same charge dissociation which causes flow along the walls of a liquid-filled microchannel occurs at the interfaces of suspended or dispersed particles. The application of an external electric field then causes the particles to experience an electric force as well as cause electro-osmotic flow along the particle-liquid interface. The velocity of the particles is also described by the Helmholtz-Smoluchowski equation, though only if the particle is substantially larger than the Debye length and when surface conductivity can be ignored [148]. This phenomenon is called electrophoresis and is used to transport particles within liquids in microchannels. This technique can be used to sort particles by size and is prominent in biological processes for protein and DNA sorting and analysis [140].

2.3 Joule heating in liquids

For EOF to occur, current must flow through the electrolyte solution. As a result, the fluid acts as a conductor and can be described by Ohm's law.

$$V = IR \quad (10)$$

As with all other conductors, the passage of current causes Ohmic or Joule heating. The power loss due to Joule heating across a conductor is described by Ohm's power law:

$$P = VI = \frac{V^2}{R} = I^2 R \quad (11)$$

Where V is voltage across the conductor, I is current through the conductor, and R is the resistance of the conductor. Joule heating is a volumetric energy conversion process and can be written in differential form as:

$$\dot{q}_j = \mathbf{J} \cdot \mathbf{E} = \frac{\mathbf{J} \cdot \mathbf{J}}{\lambda} = \lambda [\mathbf{E} \cdot \mathbf{E}] \quad (12)$$

Where $\mathbf{J}$ is the current density vector [A/m²], $\mathbf{E}$ is the electric field vector [V/m], and λ is the specific conductance of the material, also known as conductivity [S/m]. For water-based symmetric electrolyte solutions, the conductivity of a solution can be calculated using the following equations [149]:

$$\lambda = \lambda_+ \eta_+ + \lambda_- \eta_- \quad (13)$$

Where λ_+ and λ_- are the ionic conductivities for each ionic component in the solution. Temperature dependence can be approximated using the following linear relation:

$$\lambda_+ = \lambda_{+0} + 0.025 \lambda_{+0} (T - 298) \quad (14)$$

$$\lambda_- = \lambda_{-0} + 0.025 \lambda_{-0} (T - 298) \quad (15)$$

Where λ_{+0} and λ_{-0} are the reference ionic conductivities for each ionic component in the solution at 298K.

Joule heating acts a source term in a control-volume based energy balance equation [149]:

$$\rho C_p (\mathbf{u} \cdot \nabla T) = \nabla \cdot [k \nabla T] + \lambda |\mathbf{E} \cdot \mathbf{E}| \quad (16)$$

Joule heating in microchannels can be desirable or problematic, depending on the application. Joule heating is a simple and reliable method for controlling heat input into a microchannel, particularly for straight-section channels where electric field is uniform. However, in cases where plug flow is desired, Joule heating can act to distort the flow [149], [150]. In these cases, Joule heating can be avoided by using either low-conductivity liquid or by reducing the electric field strength.

Once an aqueous electrolyte reaches its boiling point, its electrical properties change since steam is an electrical insulator, thus Joule heating does not occur in the vapor phase. Similarly, EOF only occurs in liquid phases, so once a solution is heated to the point of vaporization, both EOF and Joule heating cease, even though an electric field may still be present. If the electric field across the gas phase is high enough, current flow may be induced by means of electrical breakdown.

2.4 Electrical breakdown of liquids

Dielectric materials, known more commonly as electric insulators, may still conduct current if a large enough potential is imposed upon them; this process is called electrical breakdown [151]. This process can occur in solid, liquid, or gas insulators and leads to generation of a plasma, producing very high temperatures and bright emissions. The resistance of a material to the breakdown process is measured by the dielectric strength with units of voltage per unit length [V/m] [151]. This property is a measurement of the maximum electric field that the material can sustain before it undergoes the breakdown process.

In many cases, electrical breakdown is not desirable as it can lead to material erosion and high electrical loads on peripheral equipment [152]. However, some applications require dielectric breakdown, including for shock-wave production [153], water purification [154], and material fabrication [155]. Erosion due to the electrical breakdown process is the basis of electrical discharge machining (EDM) processes and is one technique that can be used to produce dimensionally accurate micro-scale features [156], including for microchannel fabrication [128]. Aside from the manufacturing process, electrical breakdown of fluids is relevant in electrically active microfluidic flows since microchannel geometries can focus electric fields.

The breakdown process for liquids is not fully understood, and behavioral differences exist between polar and non-polar fluids. There are currently two theories that are used to explain the mechanism of electrical breakdown of water-based solutions [151], [152]: one which assumes that breakdown initiates in a gas bubble, 'bubble theory,' and the other which assumes the breakdown occurs in a liquid phase, 'direct impact ionization theory.'

Typically, the breakdown mechanism of liquids assumes streamer propagation from solid electrodes within the liquid. If the streamers create a connection between the electrodes, a short

circuit is formed, and an arc or spark is produced. Additionally, the electrolytic liquid itself can act as one or both electrodes, as can be achieved by placing a gas phase between the solid electrode and the liquid electrolyte. In this case, gas-phase breakdown causes an arc to form between the solid and liquid electrodes. Similarly, if both electrodes are liquid and are separated by a gas phase, breakdown can occur in the gas phase exclusively; this can be achieved by introducing bubbles into a conducting electrolyte [157]. The breakdown within these bubbles has been shown to stabilize along the interface of the bubble (either gas-liquid or gas-solid) [158]–[160].

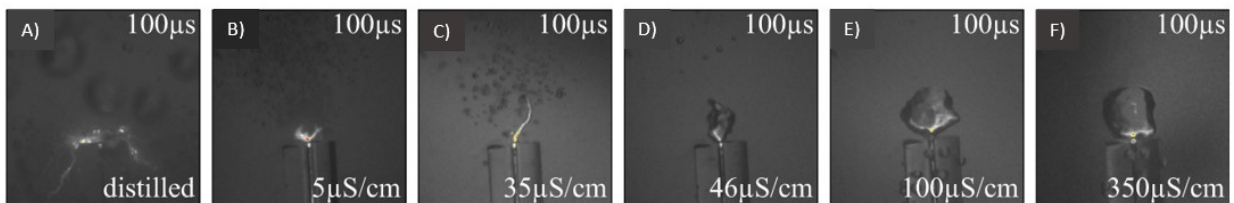


Figure 6: Electrical breakdown of aqueous KCl with a solid electrode, showing transition from direct liquid breakdown into gas-phase breakdown as solution conductivity increases. Reproduced from Bruggeman et al. [160].

For a solid-liquid electrode system, it has been shown that the conductivity of the liquid medium changes the streamer behavior [160]. In low conductivity cases, such as in distilled water, the streamers are formed within the liquid itself, with only small bubbles present (either from electrolysis or mild Joule heating). Increasing the conductivity of the liquid results in more current flow for a given electric field, so Joule heating is also increased. As a result, higher conductivity solutions first produce a bubble via Joule heating, then electric breakdown occurs within the bubble along its surface. The influence of the conductivity on breakdown strength in aqueous solutions is not fully understood but has been shown to depend on the polarity of the electrodes. For solid-liquid and liquid-gas electrode configurations, it has also been shown that increasing the conductivity decreases the required electric field for complete breakdown [158], [160]–[164].

The plasma produced by electrical breakdown of water can be considered nonthermal because its presence is short and so heat transfer into the surrounding environment is low [157], [165], [166]. The methods of determining plasma temperature are non-trivial and often produce differing results depending on the species considered. However, the local temperature of the arc is on the order of

thousands of Kelvin; depending on the electrolyte, concentration, electrode configuration, and power, temperatures have been estimated to range from 1600K [160] to 4900K [167].

Chapter 3

Research Gap, Objective, and Scope

3.1 Research gap

Microfluidics has primarily been used as a tool for fabrication in the field of energetics, either for the direct manufacture of energetic particles or for fabrication of devices based on micro-deposition techniques. The direct use and ignition of solid energetics at microfluidic device scale has been limited to a handful of studies, often because of limitations of energetic materials at the necessary scales. Despite some works demonstrating the useful nature of thermites in microchannels, works combining the two fields are limited. Additionally, advances in thermite structures and coatings have removed the obstacle of particle-particle contact for reactivity, so combustion in a dispersed phase is believed to be achievable. This presents an opportunity for integration of these materials in a microfluidic flow based EMEMS device.

Core-shell thermites can act as an energy source by providing heat and pressure at micro- and nano-metric particle scales in the absence of environmental oxygen, unlike many conventional energy sources. In addition, the self-contained energetic nature of the core-shell particle means that it can be ignited as a dispersed phase, unlike physically mixed thermites. Microfluidic techniques can reliably transport, sort, deposit, heat, and/or irradiate their working fluids and any dispersed phase. By combining the knowledge in these two areas of study, we aim to develop a system which can transport and deposit core shell thermites in inert environments. These particles can then be ignited to produce heat and pressure for a variety of applications.

3.2 Objective and scope

To close this research gap, an EMEMS device is designed, characterized, and evaluated. A core-shell Al@CuO thermite is selected for use because the Lab for Emerging Energy Research is expertly familiar with the fabrication process. To fabricate the Al@CuO particles, the wet-chemistry method described by Zhang et al. [38] is used. It has been shown that the coating quality of microparticles is much better than that of nanoparticles using this methodology, so for improved performance of the

particle mixture in the channel a microparticle composition is selected over the nanoparticle composition.

These particles are introduced into salt-water to create a dispersion. An NaCl solution is used to increase the liquid conductivity, increasing Joule heating ability, and reducing breakdown strength. The ignition system to be used will be prioritized for design simplicity. Introducing a hot-wire, laser, or microwave ignition system adds complexity to the fabrication of the microchannel. Instead, the microchannel will be designed to focus the electric field to a small region where ignition is to occur. The suspended particles are intended to be ignited by either direct Joule heating due to current flow, or by proximity to electrical breakdown of the liquid phase. A higher conductivity liquid results in a lower breakdown threshold but reduced zeta potential, so a balance between particle mobility and ignition capability is needed.

The device, in principle, seeks to ignite core-shell thermites in a dispersed phase at microscopic scale. The energetic particles will be transported by the flow of the fluid and be collected along the walls of a constriction in the channel geometry. The same constriction will be used to produce a concentrated electrical field to ignite the particles. Upon ignition, it is expected that light, heat, and a gas phase will be produced and observed. The scope of the project will be limited to the design, characterization, and evaluation of such a device, but will not include application-specific refinement or adaptation of the device.

In the development of such a device, several key questions arise:

- Is it possible to ignite thermite microparticles in a dispersed phase? Publications in this topic focus on the theoretical and numerical analysis of dispersed-phase thermite reaction, but experimental studies showing successful ignition have not been published.
- If the thermite reaction is achieved, is it a result of temperature or electric potential? If it is a thermal process, is it the Joule heating of the solution or the particles that is important?
- How repeatable and useful is the process within the microchannel? What are its capabilities and limitations?

The intent of this thesis is to document the design and characterization of a novel thermite based microfluidic device, provide answers to the above questions, and provide recommendations for future studies.

3.3 Research Methodology

COMSOL 5.6 is used to create a model of a microchannel and conductive fluid. For simplicity, particle transport and heating effects are neglected; the particles are not modelled in the flow. This model is used to evaluate the performance of different microchannel geometries by showing the distribution of the voltage field, EOF, and Joule heating within the channel. These results are then extracted to an axisymmetric model of a single core-shell particle to get an idea of the distortions of the voltage field resulting from particle presence, and the subsequent heating effects.

High speed microscopy is used to directly observe the microchannel during operation. It is used to make observations about flow, particle transport, phase changes, and optical emission sources. A single monochrome Phantom v2012 camera is used, so pyrometry is not possible.

Infrared (IR) microscopy is also used to observe thermal emissions during microchannel operation. This technique allows comparative measurements of temperature within the channel, including phase changes. It does not have the ability to distinguish details within the flow and has limited frame rate to make clear observations regarding the detailed sequence of events (at microsecond scales).

The microchannel chip consists of five independent microchannels on a single glass slide. Each channel has its own inlet and outlet reservoirs. The microchannel is fabricated by soft-lithography casting of PDMS which is plasma-bonded to a glass slide. Chip quality is checked under a microscope by pumping deionized (DI) water from the inlet to the outlet; once quality is assured, acrylic tubes (acting as reservoirs) are glued to the inlet and outlet using Momentive RTV118 silicone sealant. Figure 7 shows the assembled microchannel chip (B), and a microchannel as observed under microscope operating in dark-field mode (D). Note that the acrylic reservoirs have copper tape at the top; these act as the electrodes in the channel through which a current path is created in the channel. The reservoirs are filled such that the electrodes are submerged in the electrolyte solution.

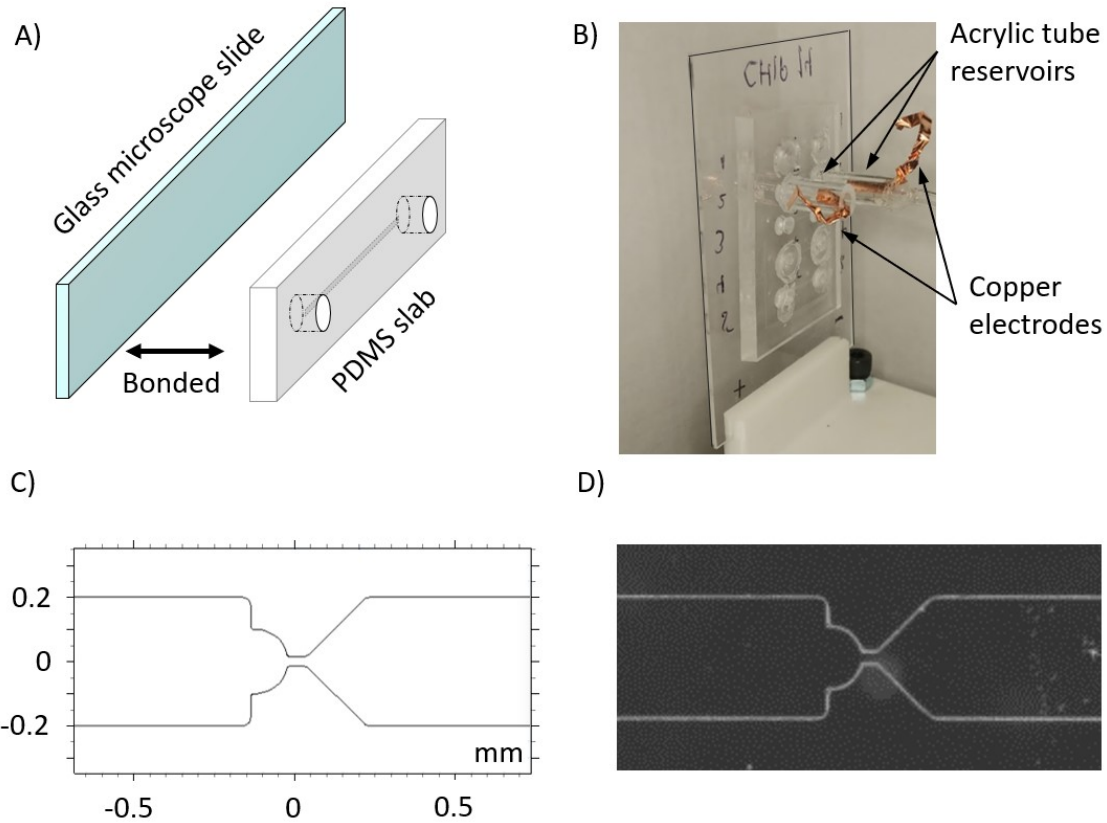


Figure 7: Schematic diagram of microchannel assembly (A), as-fabricated microchannel chip showing 5 channels per chip and attached reservoirs and copper electrodes (B), CAD used for microchannel throat geometry (C), and as fabricated microchannel geometry imaged using dark-field microscopy (D).

A converging-diverging channel geometry is used, as shown in Figure 7C. The 30 μ m throat is used to create an area of high electric gradient as well as to concentrate particles to a small region. In preliminary tests, it was observed that particles tended to stick to the channel walls, so it is expected that the throat could be used to collect particles into an area where they can be heated.

Chapter 4

Numerical Modelling

4.1 Setup and methodology

A steady-state 3-dimensional model is used to evaluate the performance of the microchannel using COMSOL 5.6. A half-channel geometry is used with a symmetry boundary to reduce computational load. Three domains are modelled: the glass slide, the PDMS casting, and a liquid water domain in the microchannel. Boundary and initial conditions are described in Figure 8. The modelling work is intended to be used primarily as a design tool and so is kept simple. For this model, the complexity of the physics is limited by neglecting phase change and neglecting particle transport and the associated disturbances to the electric field because of particle presence.

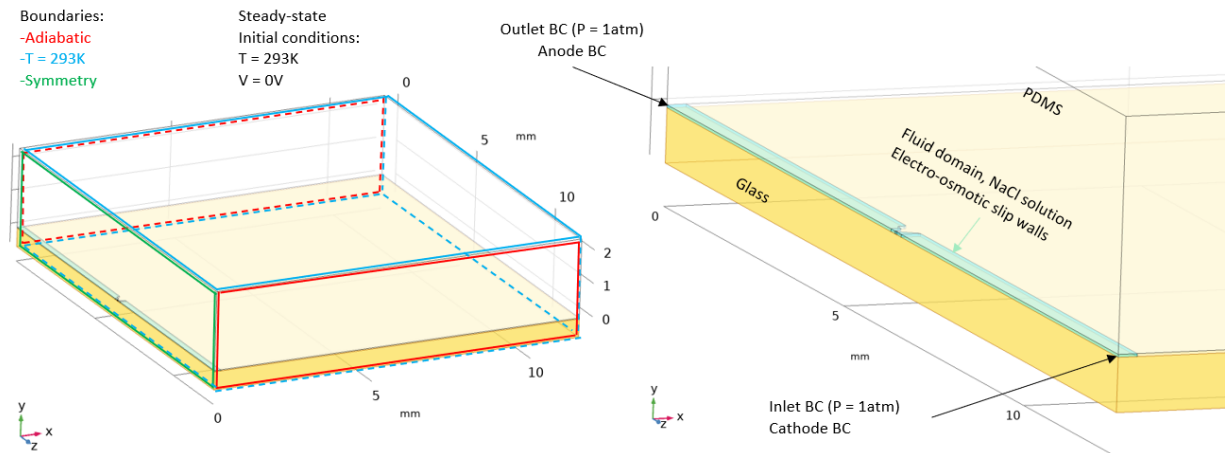


Figure 8: Schematic diagram of modelled domains showing domain geometry, material selections, boundary conditions, and thermal and electrical initial conditions.

The simulation is performed for cross-channel voltages ranging from 50V to 500V and dissolved NaCl concentrations ranging from 0.1 [mM] to 1 [M]. The conductivity of the solution at various concentrations is considered uniform and temperature independent and is presented in Table 3. A sufficiently fine mesh is used such that the model is grid independent (details provided in Appendix B).

Table 3: Conductivity used for liquid phase in numerical model for various NaCl solution concentration cases

Solution Concentration [M]	Solution Conductivity [$\mu\text{S}/\text{cm}$]
1.0 E-4	11.1 E0
2.2 E-4	16.2 E0
4.6 E-4	27.1 E0
1.0 E-3	50.7 E0
2.2 E-3	10.2 E1
4.6 E-3	21.1 E1
1.0 E-2	44.7 E1
2.2 E-2	95.5 E1
4.6 E-2	20.5 E2
1.0 E-1	44.1 E2
2.2 E-1	94.9 E2
4.6 E-1	20.4 E3
1.0 E0	44.0 E3

4.2 Electric field, Joule heating, and their effects on temperature and velocity distribution

The electric field drives the particle transport, Joule heating, and plasma generation process, and so is an important metric to consider. The electric field produced within the channel is dependent only on the channel geometry and the magnitude and polarity of the electric potential across the channel. For the converging-diverging geometry, Figure 9 shows the electric field magnitude for a 500V applied voltage.

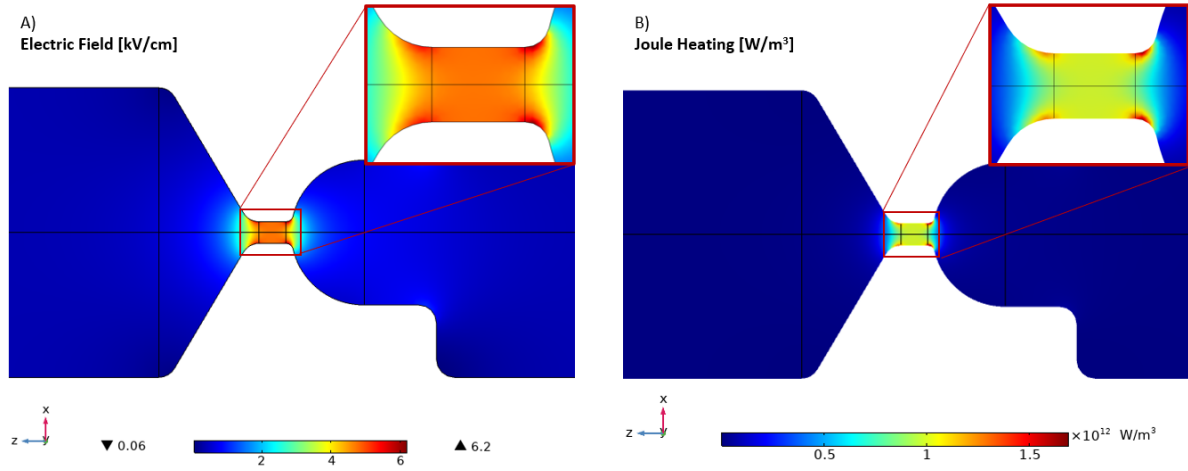


Figure 9: Numerical results for a 500V, 1E-03 [M] case taken at midplane of channel (equidistant between top and bottom walls) showing A) electrical field distribution with detailed view of throat section, and B) corresponding Joule heating source term magnitude.

As expected, the electric field magnitude is nearly constant and comparatively low in most of the straight channel, with major increases around the geometric changes. The strongest electric field occurs at the throat of the channel, with maxima occurring at the corners that transition between the throat and semi-circle areas. The distribution of electric field is dependent only on the geometry of the conductor, so the electric field contour plots of all simulated cases appear identical to that shown in Figure 9a, albeit with different values for maximum and minimum magnitudes. The electric field is directly proportional to the voltage, so 50V will result in a tenth of the field compared to 500V. The maximum electric field magnitude predicted by the model is 6.4 kV/cm for the 500V case.

The volumetric Joule heating generation term is squarely proportional to the electric field magnitude but is also affected by the conductivity of the solution. The result is that the Joule heating contour plot strongly resembles the electric field magnitude plot, but with maximum and minimum values that vary linearly with conductivity (NaCl concentration), and squarely with voltage. Within the channel, the conductivity for each tested concentration is modelled as uniform, so the Joule heating power contour plot shown in Figure 9B is essentially the square of the electric field plot seen in Figure 9A. The distribution of Joule heating power within the channel is concentrated at the throat, with increased power areas observed at the corners of the throat where the electric field

is strongest. Like the electric field distribution, the Joule heating distribution remains the same across all tested cases, with magnitude scaled based on the solution concentration and applied voltage. Since Joule heating power is squarely proportional to the electric field magnitude, the 500V simulation predicts heating powers 100 times greater than the 50V simulation. These results suggest that phase change and combustion due to heating should occur close to the corners of the throat, with preference towards the right-side (outlet-side) of the channel. However, due to heat transfer through the liquid and walls, the temperature contours do not follow the Joule heating and electric field contours.

Instead, it is shown in Figure 10 that maximum temperatures occur at the centre of the throat because of the high negative heat flux at the walls. With increasing voltage, the EOF causes the hot-spot at the throat to shift farther towards the outlet as heat is advected away from the heat-generation zones shown in the Joule heating plot. The difference in thickness and conductivity of the glass and PDMS layers affect the cross-sectional temperature distribution within the channel, with higher temperatures expected at the PDMS walls. This results is expected since the PDMS layer is twice as thick and nearly 10 times less thermally conductive than the glass layer.

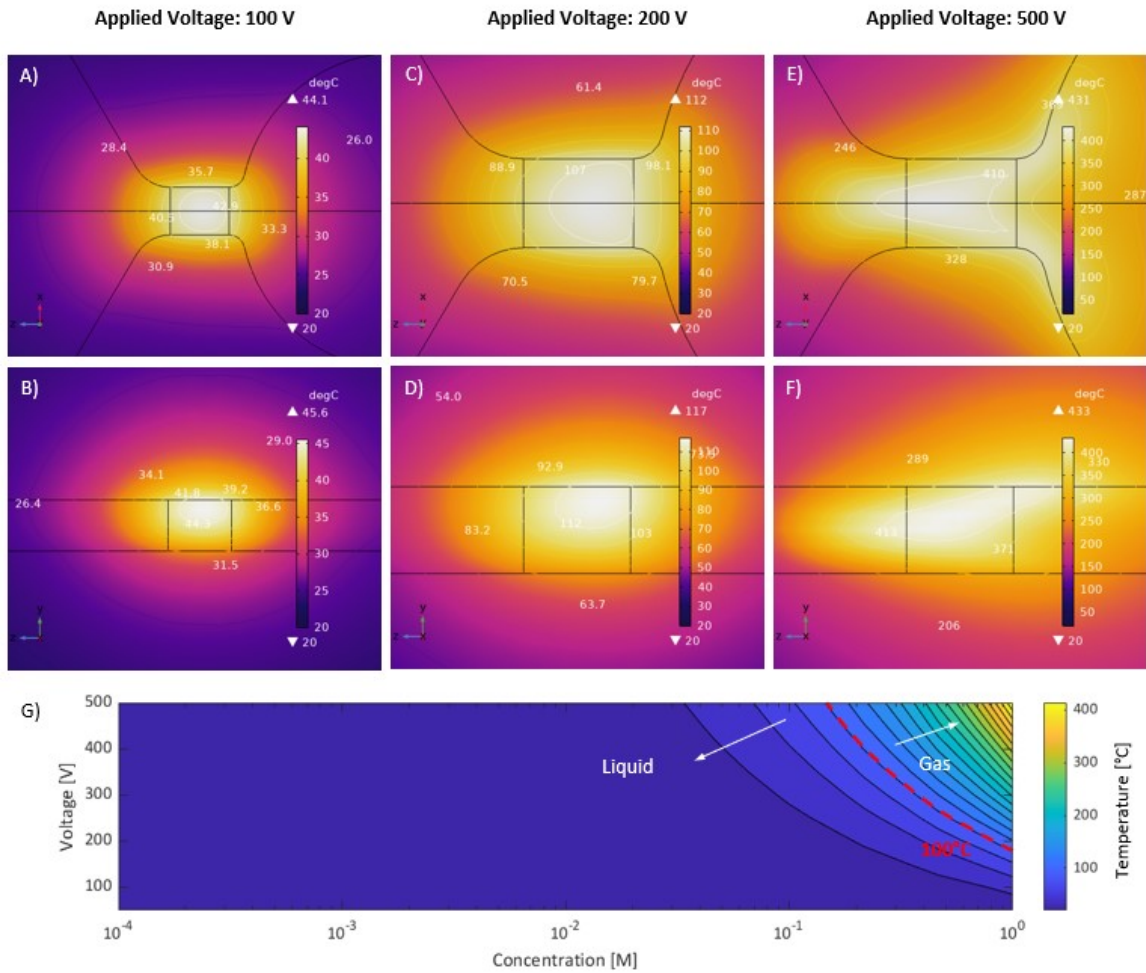


Figure 10: Numerical results showing temperature distribution for 1[M] solution at A) and B): 100V, C) and D): 200V, and E) and F): 500V applied voltage cases, alongside G) contour plot of maximum temperatures obtained from simulated results with highlighted 100°C isotherm to denote electrolyte boiling threshold.

A contour plot showing the predicted maximum temperatures is shown in Figure 10G, with the 100C isothermal line highlighted to show in which conditions boiling is expected. The threshold of boiling for the 1M concentration case occurs at just below 200V, and this case is shown in Figure 10. In this case, the hottest spot is shifted to the right side of the throat (towards the outlet), rather than the central location observed in the 100V, 1[M] case. The cross-sectional view also shows that fluid near the glass wall is near but slightly under 100°C, but most of the channel falls within

isotherms that exceed 100°C. This result is interesting because it shows that, even though the Joule heating effect is maximized locally at the corners of the throat, the entire channel volume is predicted to reach and exceed boiling temperature. This means steam bubbles can be expected to nucleate anywhere in the throat, with a preference towards the PDMS-side upper wall.

However, it is important to note that the simulation results become non-physical at high voltage-concentration combinations because phase change is not accounted for, and temperatures substantially higher than the boiling point of the electrolyte are predicted (431°C for 1 [M] at 500V). In this case, the temperature profile changes shape compared to the lower voltage cases tested, where the maximum temperature contour shifts towards the inlet/left side of the throat and two high-temperature 'wings' can be observed at the right-side corners where Joule heating is maximized. In the cross-section plot, the same leftward smearing of the hottest region is observed. Though it may be possible to superheat the water in the microchannel, reaching temperatures higher than 400°C is not realistic. In addition, the flow of the liquid combined with the channel geometry are factors which promote bubble nucleation/ boiling and preventing superheating to such a high degree.

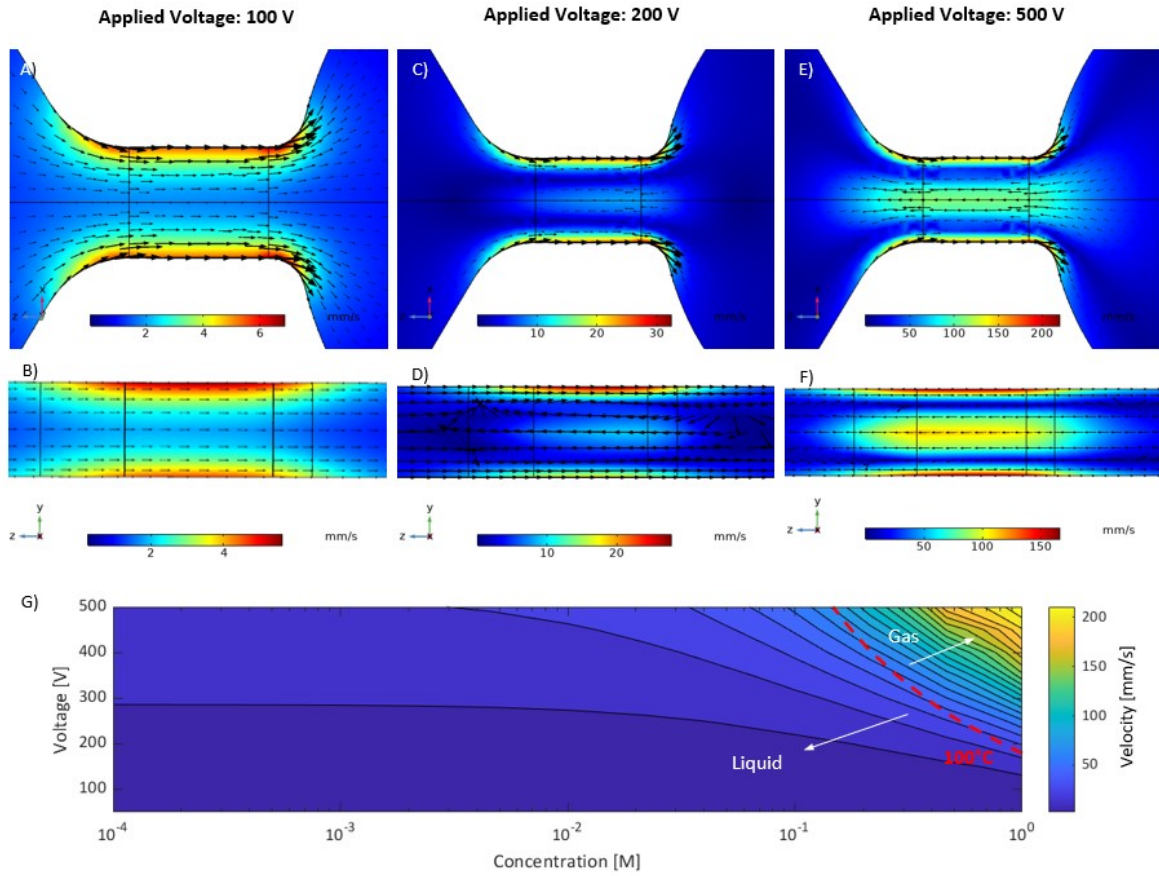


Figure 11: Numerical results showing velocity distribution for 1[M] solution at A) and B): 100V, C) and D): 200V, and E) and F): 500V applied voltage cases, alongside G) contour plot of maximum velocity obtained from simulated results with highlighted 100°C isotherm to denote electrolyte boiling threshold.

As previously discussed, a defining aspect of EOF is that the velocity across the channel is uniform, except near the walls. This is generally observed in the simulation results where heating effects at the throat are small such as at the 400 μ m straight channel sections preceding and following the throat. As the concentration and voltage increases, the velocity profiles are distorted such that the flow at the walls is greater than that at the symmetry plane of the channel, as shown in Figure 11. This result agrees well with literature that investigates EOF distortion with Joule heating [149], [150]. At 100V and 1[M], velocities are 1.9mm/s at the centre of the throat and 5.2mm/s at the walls. The channel is 37.5 μ m long, so this results in residence times of 19.7ms and 7.2ms at the

centre and walls of the throat, respectively. Increasing the distortion causes the flow at the centre of the throat to stagnate and eventually, the results predict that backflow will occur. This stagnation and backflow begin to occur as the liquid reaches boiling point, at slightly less than 200V for the 1[M] case. For the 500V case, the results are even more exaggerated, with most of the volume in the channel taken up by backflow.

4.3 The role of Joule heating on velocity profile distortion

Considering the same 500V, 1[M] case but removing the volumetric Joule heating term, we observe in Figure 12 that the flow returns to the expected plug flow produced by EOF. So, the source of the velocity profile distortion is the Joule heating source term. A similar result can be produced by using a low conductivity solution as shown for the 500V, 10 [mM] case in Figure 12. In that case though, even a 6°C temperature increase can be seen to produce substantial distortion from the plug flow. In these cases, flows are 15.2mm/s and 18.7mm/s at the centre and walls of the throat, respectively. These are likely too high for particle deposition or residence in the throat, so for practical applications a lower voltage may be more desirable.

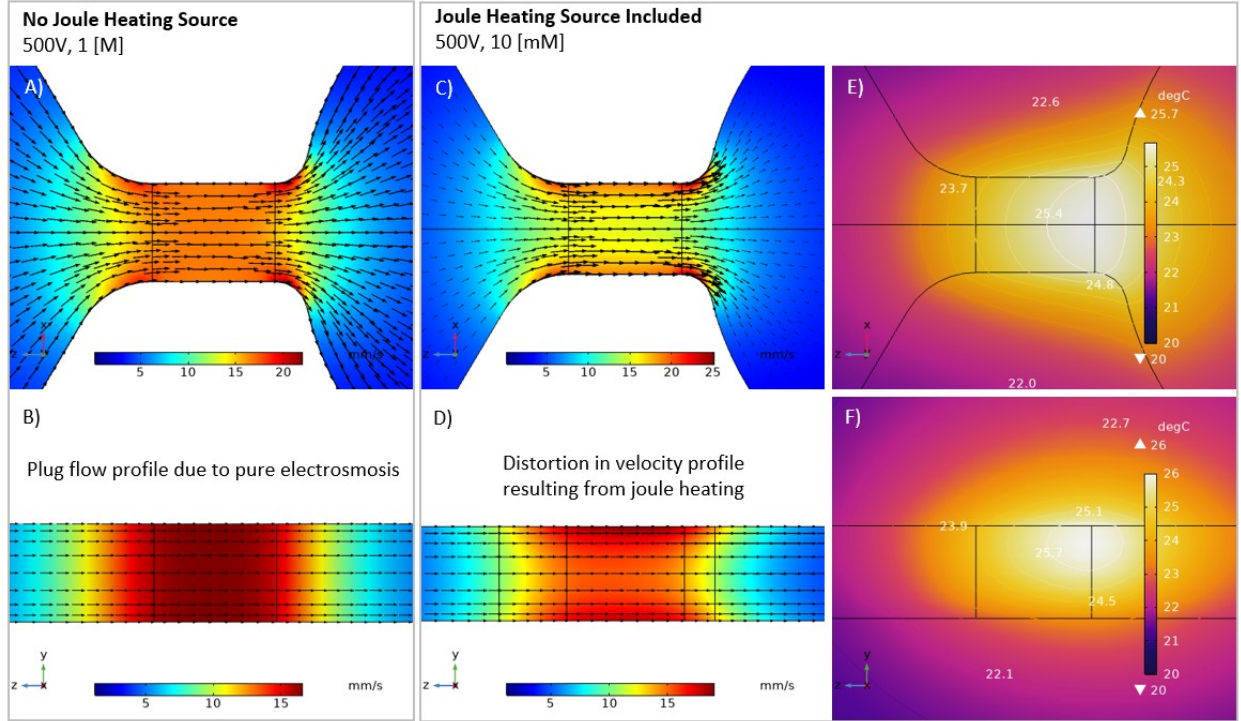


Figure 12: Numerical results 500V applied channel voltage showing A) and B): velocity profile for 1[M] NaCl solution without Joule heating term, C) and D): velocity profile for 10[mM] NaCl solution with Joule heating term, and E) and F) temperature profile for 10[mM] NaCl solution with Joule heating term.

It is important to note the limitations of this numerical result since the backflow occurs when voltage-concentration combinations are high; in these scenarios the lack of phase change in the model results in temperature overprediction so the flow results are also unreliable. Additionally, an assumption was made that zeta potential does not vary with temperature and concentration. This assumption is valid only at high concentrations of NaCl, where zeta potential is low. A more robust model taking this into account would show that EOF with increasing NaCl concentration would reduce, and the effects of thermally induced flow would become even more dominant in high concentration cases.

4.4 Input power and prediction of breakdown strength

Though the dependence of breakdown strength on conductivity is not fully understood, several studies show that, for a DC-induced electrical breakdown in a symmetric electrolyte, increasing the solution conductivity decreases the breakdown strength. For diaphragm-based DC excited discharges in NaCl, it has been suggested that, though the breakdown voltage decreases with increasing conductivity, the breakdown current increases such that the power required to achieve breakdown is independent of solution conductivity [161]. The breakdown strength of NaCl solution at 66.7mS/cm (around 1 [M] concentration) has been reported at around 10 kV/cm for a hemisphere-plate electrode configuration [164]. Based on this value, the model predicts that electrical breakdown will not occur within the microchannel. However, more detailed experimental work has shown that, in a capillary, breakdown of NaCl can occur as low as 6 kV/cm for solutions around 20 μ S/cm (around 0.3 [mM] NaCl concentration) [159], which is exceeded in the 500V simulation condition. If we assume that breakdown power is independent of solution concentration, then we can use the input power for the 500V - 20 μ S/cm case to make a low-fidelity estimation of the expected conditions for breakdown. A contour plot of the average power within the channel is shown in Figure 13, showing the estimated breakdown contour.

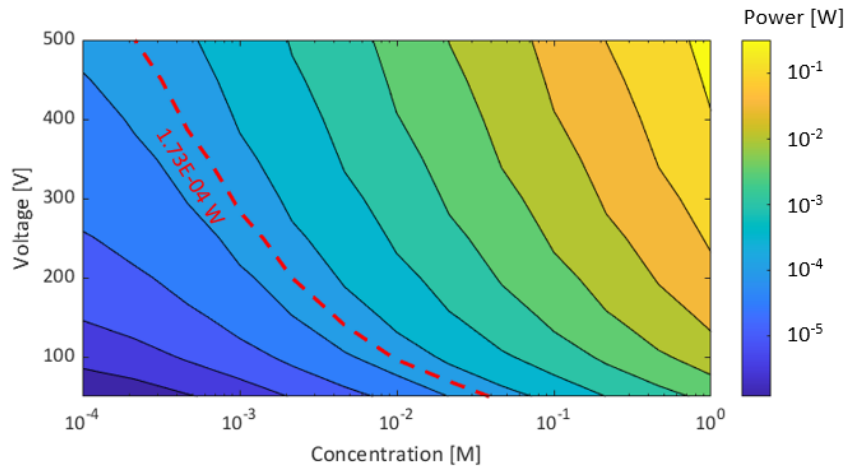


Figure 13: Numerically predicted log-scale input power contour plot for range of voltage and concentration combinations considered, showing estimated breakdown contour at 1.73 E-04 W (dotted red line).

The breakdown threshold contour suggests that in most of the simulated test conditions, electrical breakdown will occur. However, the temperature results shown in Figure 10 show that, for 1[M] solutions, the solution will remain in a liquid state. The first stage of the electrical breakdown process for high conductivity liquids such as 1[M] NaCl is the generation of a bubble by Joule heating, but the Joule heating model predicts this will not happen until 200V. Therefore, the threshold shown in Figure 13 is contradictory to the results presented in Figure 10. This is a result of the low-fidelity nature of the breakdown threshold prediction, since the constant breakdown-power relation applies only at high conductivities, and at conductivities below $150 \mu\text{S}/\text{cm}$ the power requirement decreases; so, the threshold shown in Figure 13 is an overprediction. However, it is difficult to refine the prediction since breakdown strengths in capillary or diaphragm configurations are not well reported in literature, especially for high conductivity solutions such as 1[M] NaCl.

With these limitations in mind, the model can provide some interesting insight into the physical behavior of the microchannel. The distribution of the electric field in the channel shows that the region where interesting phenomena will take place is the throat, with local maxima in magnitude occurring at the transition between the throat and converging and diverging sections. At these corners, it is observed that Joule heating is maximised. Due to heat flux out of the channel at the

walls, temperature maxima are observed along the centreline of the channel rather than the corners where Joule heating is maximised, with higher temperatures expected along the PDMS walls than the glass wall. For combinations of high-concentration and high voltage, temperatures are predicted to exceed the electrolyte boiling point and the model begins to breakdown because phase change effects are not captured. These results are helpful in selecting appropriate voltage-concentration parameters for experiments as well as showing what regions we can expect interesting phenomena such as boiling and bubble formation.

4.5 Stokes number analysis and single particle model

The velocity data produced by the model, shown in

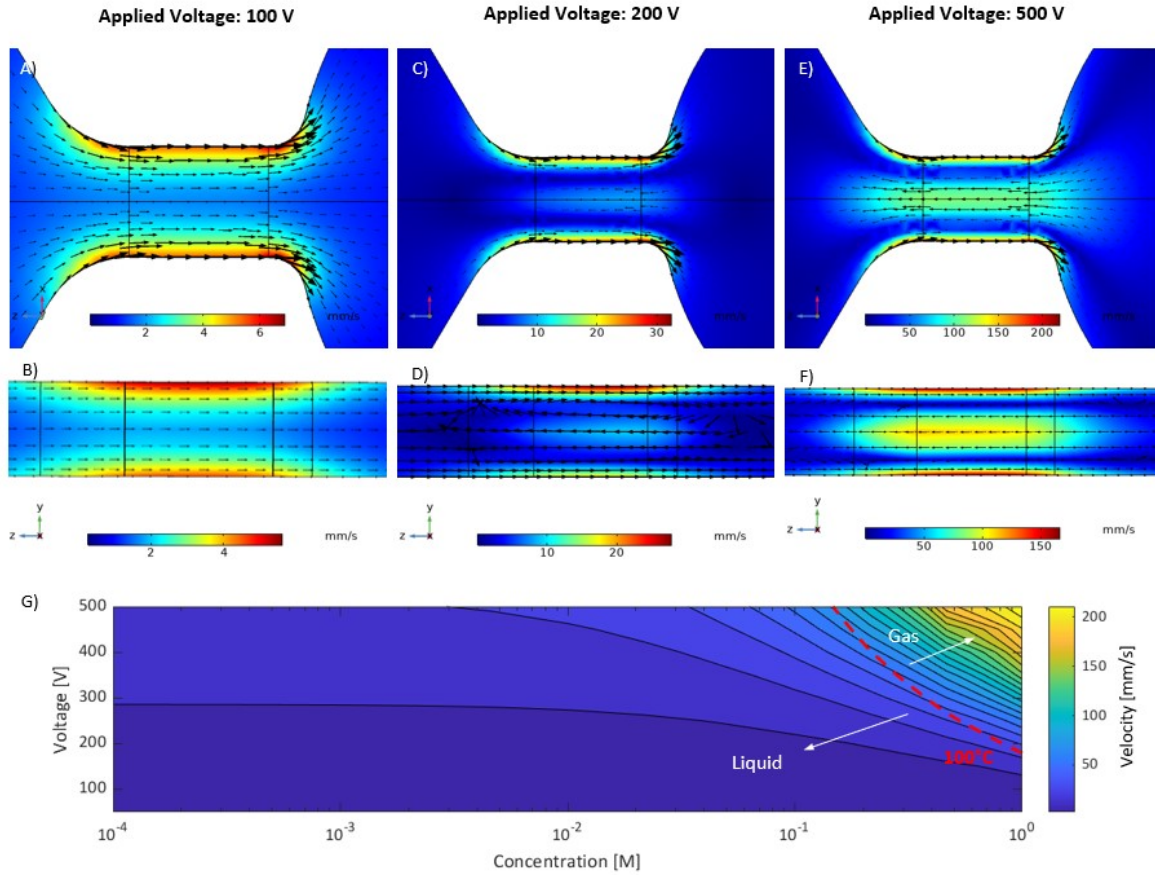


Figure 11G, can be used to predict an upper bound for the Stokes number for a dispersed particle flow using equations (6) and (7). The density of core-shell particles can be computed for a $1\mu\text{m}$

diameter Al particle coated by a fully monolithic CuO shell with 100nm thickness, and an alumina layer of 2-5nm in between, as observed in Zhang et al. [38]. Using material densities of 2.7g/cm^3 , 4.0g/cm^3 , and 6.3g/cm^3 for the Al, Al_2O_3 , and CuO, respectively, the calculated density of the core-shell structure is $4.0\text{-}4.3\text{g/cm}^3$. The higher bound for the core-shell particle density (4.3g/cm^3) is used in the Stokes number calculation. The liquid viscosity was set to $1\text{mPa}\cdot\text{s}$ (water at 20°C). The results of the calculation are presented in Figure 14.

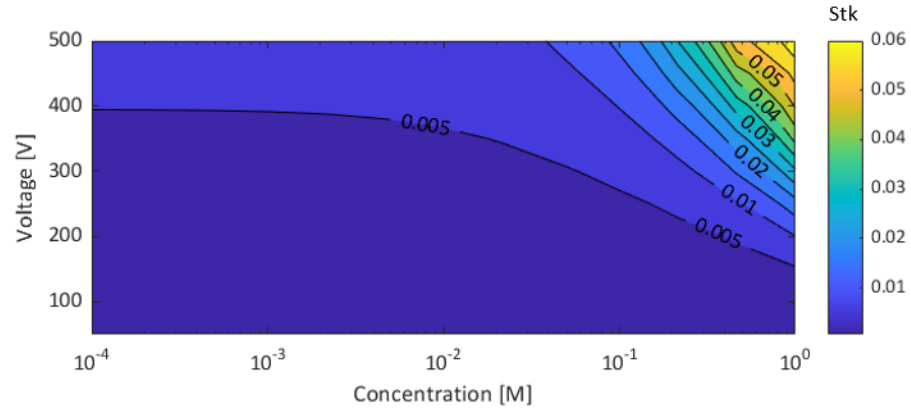


Figure 14: Numerically predicted Stokes number (Stk) contour plot for range of voltage and concentration combinations considered.

The Stokes number contour plot shown in Figure 14 is effectively a rescaled version of the velocity plot shown in

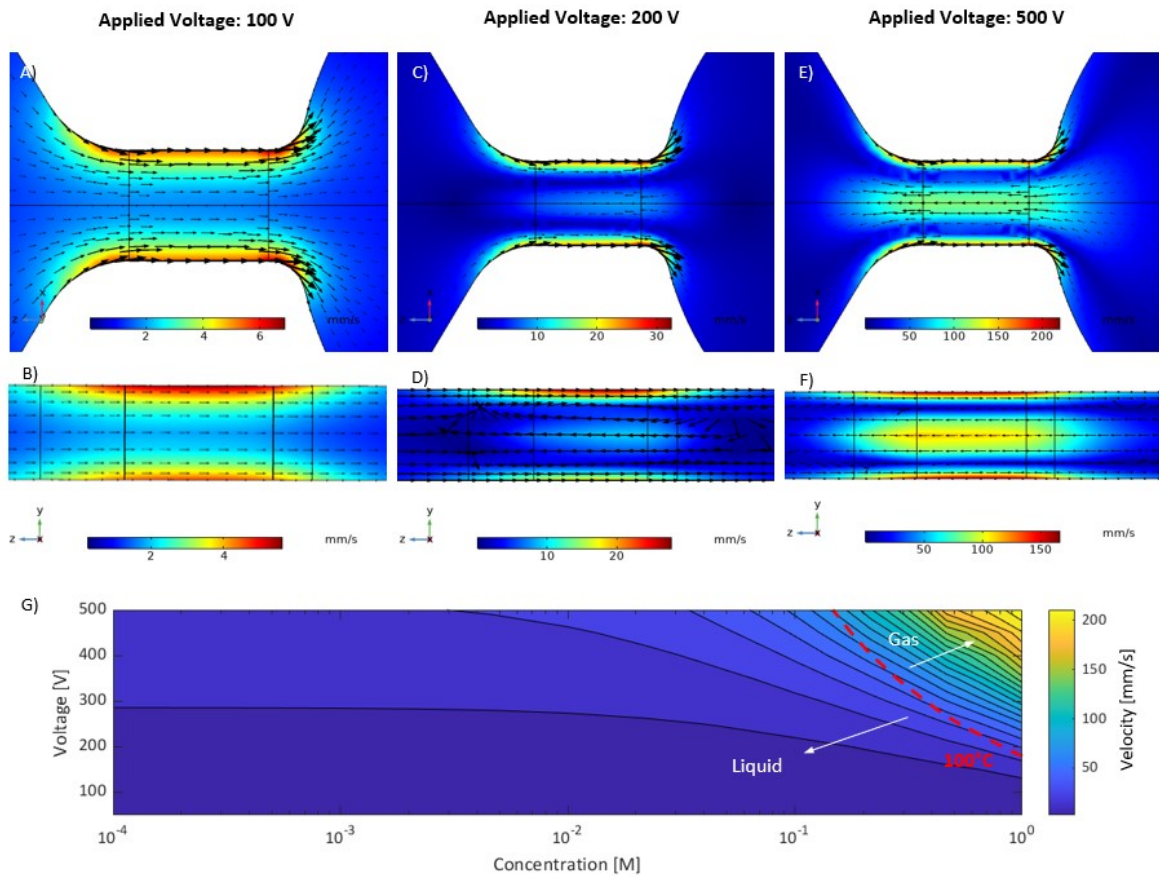


Figure 11. The maximum value of Stokes number predicted is 0.063 at 1[M], 500V and indicates that, even at the highest predicted flow values, the inertia of particles remains small enough that they follow the streamlines of the flow.

To help understand the influence of particles on the electrical field, an axisymmetric representation of the microchannel was modelled with a 1 μ m diameter Al@CuO core-shell particle located at the centre. The particle was modelled as a 1 μ m Al core coated uniformly by with a 100nm thick CuO shell. The magnitude of the electric field within the throat was volume-averaged for each voltage case modelled in the full-channel model (50-500V in 50V increments), and these average electric field magnitudes were applied within the axisymmetric channel model by applying an equivalent voltage across the domain. Since the Stokes numbers of the flows are low, there is little relative motion between the particle and surrounding fluid. Therefore, it is reasonable to simplify the simulation to a stationary particle within a liquid domain. A schematic diagram of the model is shown in Figure 15.

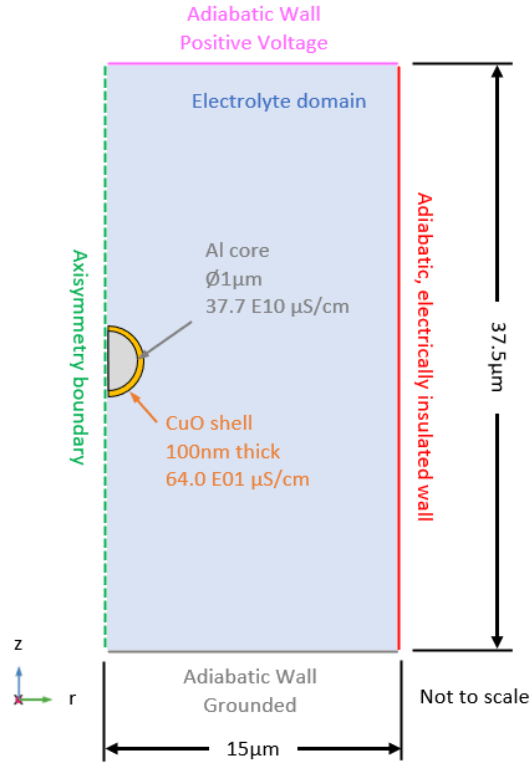


Figure 15: Schematic diagram of modelled domains showing domain geometry, material selections, and boundary conditions for single-particle model.

The initial temperature and voltage within the domain are set to 20°C and 0V, respectively, and a time-dependent study is run for 30ms to model the heat generation, but all material parameters were kept constant and temperature independent. An insulated wall boundary was applied at $r = 15\mu\text{m}$ to represent the microchannel walls. Since the focus of this study is to observe the focusing effects of particles on the electric field, the thermal model is kept very simple and is not a good reproduction of the true physics. For this reason, temperature results are not included in the following text.

The electric field results for several solution conductivities are presented in Figure 16.

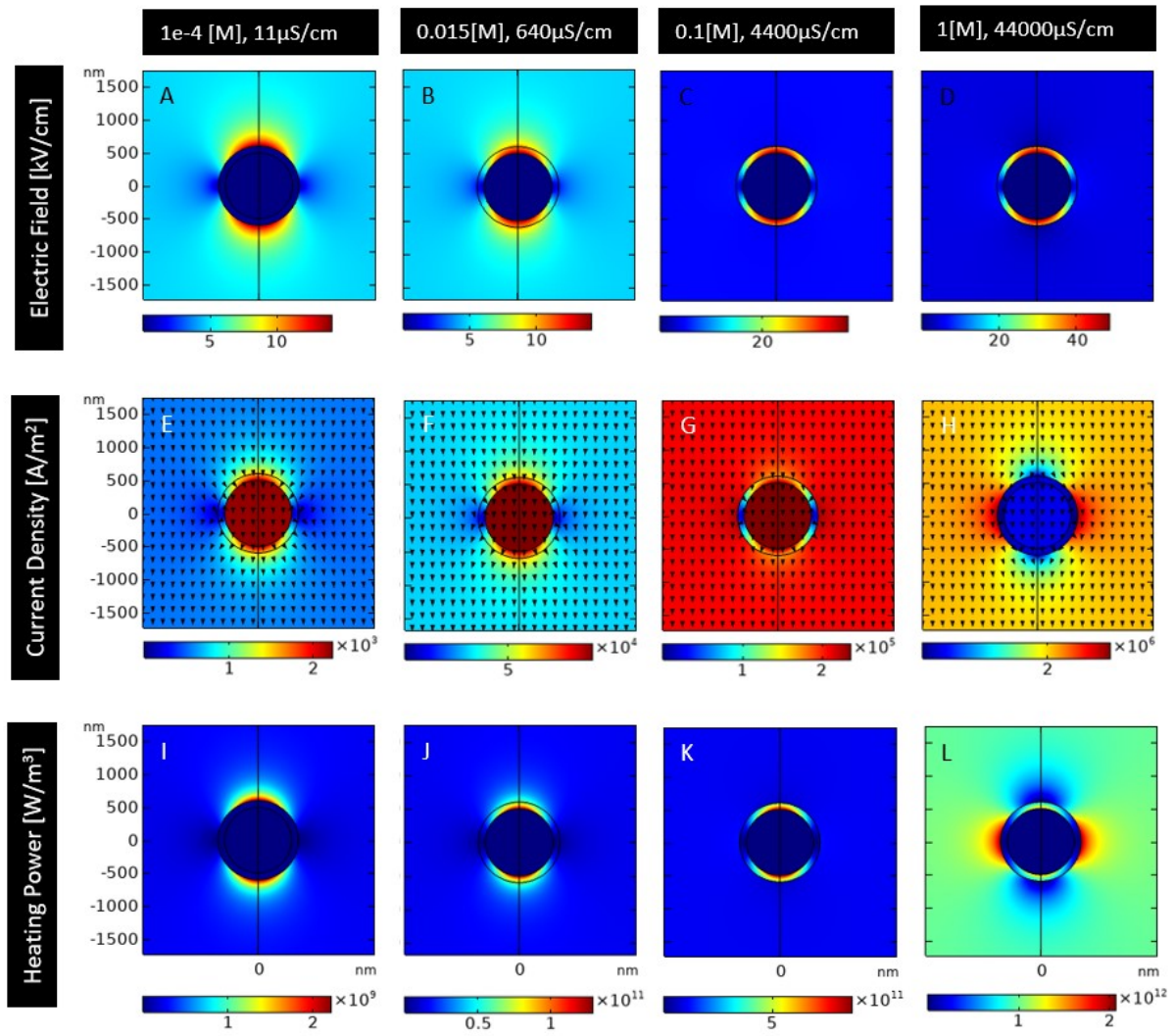


Figure 16: Electric field (A-D), current density (E-H), and Joule heating power (I-L) surface plots for solutions conductivities varying from $11\mu\text{S/cm}$ to $44000\mu\text{S/cm}$ showing transition from liquid heating to oxide-layer heating to combined heating modes. Results shown are for an applied voltage gradient of 4.75kV/cm (corresponding to 500V results from full channel model).

As was the case for the full microchannel model discussed earlier, changing the applied voltage across the domain only changes the magnitude of the electric field but does not change the distribution. Of more interest are the effects of solution conductivity on the electric field, shown in Figure 16. Increasing the conductivity of the solution results in an increase in the maximum

observed electric field magnitude. For the $1\text{e-}4[\text{M}]$ case, the presence of the particle results in a 3x intensification of voltage gradient, from 4.7 to 14.1kV/cm, with the maximum occurring in the liquid phase. For the $1[\text{M}]$ case, the intensification is 10-fold, producing a maximum gradient of 48.8kV/cm within the CuO shell. Additionally, the electric field distribution also changes, as can be seen in Figure 16A-D. At low conductivity, there are distinct potential gradient lobes above and below the particle; as the conductivity increases, those lobes disappear, and new lobes appear on either side of the particle. As conductivity increases, the CuO shell layer shows a strong voltage gradient at the top and bottom of the particle. When the conductivity of the solution matches that of the CuO shell layer (Figure 16C), the gradient in the liquid matches that in the CuO shell. The conductivity of Al is many orders of magnitude higher than the CuO and NaCl solution, so no voltage drop occurs across the particle core.

These changes occur because the conductivity of the solution affects the relative proportion of current through and around the particles; this can be seen in Figure 16E-H. Since the conductivity of the particle remains the same, increasing the solution conductivity diverts more current around the particle due to the low conductivity of the oxide shell, as shown by the arrows indicating current flow direction in Figure 16E-H. Between $0.1[\text{M}]$ and $1[\text{M}]$, the current density maximum switches from within the particle (Figure 16G) to the liquid phase (Figure 16H).

The Joule heating power is presented in Figure 16I-L. If the liquid conductivity is lower than the CuO conductivity, heating in the liquid is dominant. As the conductivity of the solution increases above that of CuO, heating within the CuO shell becomes more prominent (Figure 16I-K). The switch in current density distribution between $0.1[\text{M}]$ and $1[\text{M}]$ results in substantial heating in both liquid and CuO phases (Figure 16L). The diversion of current around the particle also results in two low-heating lobes in the liquid phase above and below the particle.

These results suggest that, even at low solution conductivity, the presence of particles may intensify the electric field and induce electrical breakdown. It is also shown that increasing the concentration of the solution can shift the Joule heating maximum from the liquid into the CuO shell, potentially acting as a heat source for particle ignition.

It is important to understand the limitations of the model in this case. Firstly, it is assumed that the particle be perfectly advected by the electro-osmotic flow, however it is possible that electrophoresis may result in particles moving independently of the flow, invalidating the main simplifying assumption. We also assume that only one particle travels through the channel at a time, but this is challenging to replicate experimentally. The particles will travel in clusters or clouds and the limitations of the experimental hardware prevent reliable imaging of individual particles within the channel. The thermal aspects are also not considered, especially temperature changes in the liquid by self-heating, as well as heat transfer into and from adjacent particles, and cooling through the channel walls. These factors affect the accuracy and usefulness of the model, but the discussed results help to develop insights on the system behaviour based on fundamental physics.

Chapter 5

Experimental Methodology

A glass-PDMS microchannel chip is produced to test the effects of core-shell particles within high-voltage electric fields. This is done by first laser-cutting a mask with the desired microchannel geometry. The mask is then used to create a ~30 μ m thick master on a silicon wafer via photolithography. PDMS is then deposited onto the silicon master, creating the desired negative geometry. Once the PDMS is released from the master, holes are punched at the ends of the microchannel geometry to enable injection of liquid into the channel; these holes were approximately 3mm in diameter. Next, the PDMS is bonded to a glass slide to create enclosed microchannels, and polycarbonate reservoirs (20mm in length) are bonded to the PDMS using Momentive RTV118 silicon sealant. Copper tape is inserted into the microchannel reservoirs to provide an electrical connection from the Labsmith HVS448-3000V power supply to the electrolyte.

The 1 [M] salt-water solution is selected for use in the experimental tests to reduce the voltage required to initiate breakdown as well as to maximize heating in the liquid and in the particle, as was observed from in the single-particle model. This comes at the expense of effective EOF control, but preliminary tests at this concentration proved to be sufficient for the scope of this work. The solution prepared by adding 2.92g of NaCl to 50mL of DI water. The mixture is shaken vigorously until the salt grains dissolve, then placed in an ultrasonic bath for at least 30 minutes to remove any entrapped air or gas. A warm water bath is used (40°C or higher) to further reduce gas solubility within the sample. After degassing, the solution is cooled to room temperature by placing the sample containers under running cool water or in a cool-water bath.

To prepare the energetic particle solution, 1 μ m Al@CuO core-shell particles are fabricated using the wet-chemistry method described by Zhang et al. [38]. The fabricated particles are measured and mixed into 10mL of 1M NaCl solution (already degassed) for the appropriate particle concentration in a glass vial. The mixture is dispersed in a cool ultrasonic bath for a few seconds until the fluid appears uniform in color and opacity. It is important to limit the time of sonication for the energetic mixture as active content of the core-shell particle may be reduced within an aqueous suspension.

Sonication may accelerate the oxidation process between the core and shell of the particles themselves.

The saltwater solution is then injected into one of the microchannel reservoirs via pipette, leaving a small air pocket at the top of the reservoir. The inlet side is typically filled first because the inlet-side convergence provided less trapped air bubbles. Compressed air is used to pressurize the air pocket in the reservoir and drive the fluid slowly through the microchannel, and out into the opposite-side reservoir. It is important not to let all the fluid be pushed into the microchannel to prevent reintroduction of air bubbles. Once the channel is filled, it is inspected under a microscope for the presence of contaminants or trapped bubbles. These must be removed or will act as nucleation sites for bubbles which may cause an open circuit across the microchannel and will reduce repeatability of the test. To remove the contaminants, both reservoirs are filled as previously described, and liquid is pushed through the channel via compressed air to loosen and transport bubbles and contaminants. For stubborn bubbles and contaminants, the microchannel chip can be semi-submerged in the sonication bath such that the microchannel inlets/outlets are above the water level. The channel is then reinspected, and the process is repeated until no bubbles or contaminants are present in the channel. Then the microchannel reservoirs are filled so that the electrodes on the reservoir are submerged.

The microchannel is locked into the microscope stage, and the microchannel is connected to the power supply. The inlet is connected to the positive electrode and the outlet to the negative. To test the electrical connection, a small current is applied from the power supply (100-200uA). If the power supply does not provide a steady current flow, then there is an open circuit condition somewhere in the chip. The chip must be reinspected and rebled as necessary.

Two heating modes are used in this study: high and low power modes. For high-power tests, 500V is applied across the electrodes. Low power tests aim to slow down the events in the microchannel to make them easier to observe with the hardware used. Low power tests are run using a heating current of 2500uA, corresponding to approximately 120V across electrodes. In low power tests, the power supply is operated in constant current mode for convenience. This is because, at comparatively low voltages, the power supply substantially overshoots the requested voltage when powered on, then slowly drops until the requested voltage is met; this does not happen in constant

current mode. Heating current is supplied until a bubble is formed and/or optical emission is observed.

A schematic of the experimental setup is shown in Figure 17.

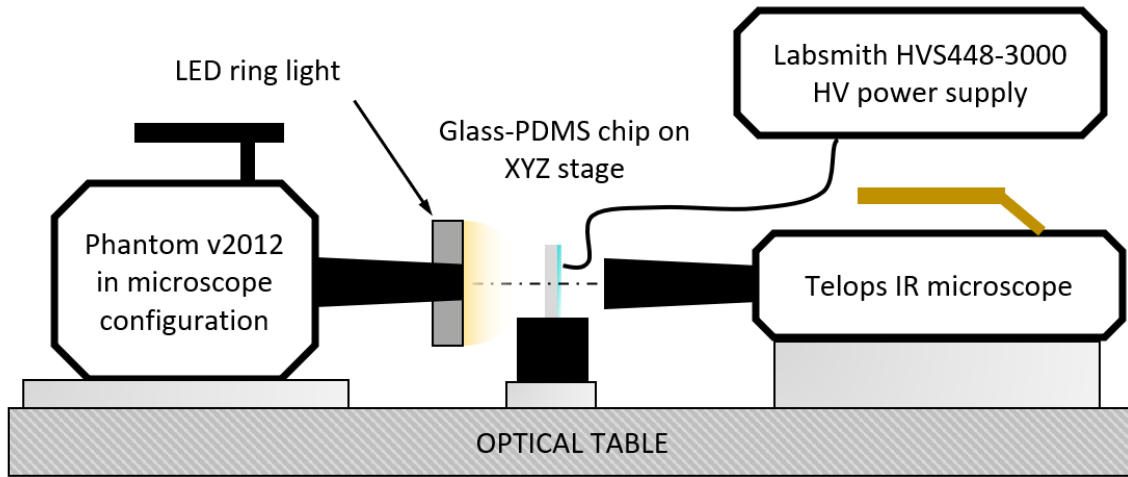


Figure 17: Schematic diagram of simultaneous high-speed + IR imaging system used to collect experimental results.

The image observed by the Telops IR camera can be presented in units of temperature [K] or irradiative flux [W/m^2]. In this work, infrared imaging is always performed through the glass-side of the microchannel assembly. Due to the unaccounted IR absorbance of glass, the temperature predicted by the IR camera is not the true temperature within the channel, so the IR data is presented in the form of irradiative flux. An increase in irradiative flux is observed as an increase in temperature, as this is the operating principle of IR thermography.

Note that running both cameras simultaneously is possible but the resulting high-speed camera image quality is low due to a lack of light. So, typically, one camera is used at a time and a backlight is used to illuminate the sample.

Chapter 6

Experimental Results and Discussion

To characterise the behaviour of the microchannel, the 1 [M] electrolyte solution is first considered without addition of particles. Applying a 2.5mA input current corresponds to approximately 120V across the channel and is hereafter referred to as the slow-heating operation mode for the microchannel chip.

6.1 Characteristic results of particle-free operation of the microchannel in slow-heating mode

The characteristic results for particle-free operation of the microchannel in slow-heating mode are shown in Figure 18.

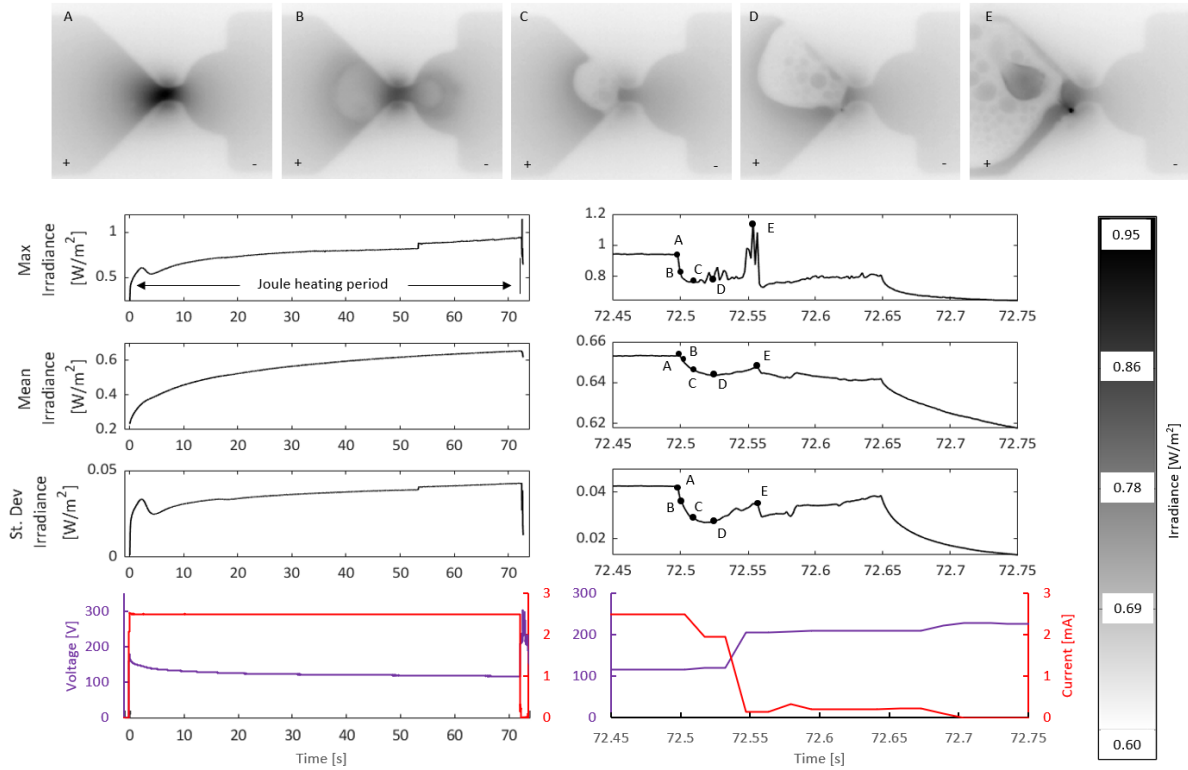


Figure 18: Maximum, mean, and standard deviation of irradiance flux profiles, and voltage-current profiles for 1 [M] electrolyte-only microchannel test run in slow-heating mode (2.5mA input current), showing full test timescale (left-column plots), bubble formation timescale (right-column), and IR image snapshots (top, A-E).

The irradiative flux plots show a Joule heating period (72s long), during which the liquid within the entire channel heats up. In this period, the fluid within the channel remains in a continuous liquid phase, and a constant current flow is present. The conductivity of the electrolyte solution increases with temperature, and this can be observed as the voltage across the channel decreases with time. Since input current is kept constant, heating power is therefore reduced as temperature increases, resulting in the declining heating rate observed in the first 20s shown in Figure 18. Afterwards, the rate of input power decrease is low, so it can be treated as quasi-steady. Small anomalies can be observed in the maximum radiative flux plot, such as those observed around 2s and 53s in Figure 18. The presence of a local maxima early in the Joule heating period ($t = 2\text{s}$) is likely a result of the

transients in power/conductivity, whereas the step in max irradiance flux around 53s is likely due to an uncontrolled event far from the throat, such as gas generation at the electrodes or some phenomena due to unobserved contaminants within the channel.

In these tests, flow is not observed directly in the video data because there is no visible phase within the liquid. Simulation results predict EOF in these testing conditions, and in analogous tests with particles, a flow is observable. Snapshot A of Figure 18 shows the temperature field observed through IR microscopy at event A marked in the radiative flux profile. The fluid is hottest at the throat of the channel, a result which agrees with the numerically predicted results. Joule heating at the throat is most substantial, and so with continued heating it is expected that phase change will occur at this location once the local temperatures exceed the boiling point of the electrolyte. During this period, the average heat flux throughout the image increases, with the heating rate decreasing as the system stabilizes. The standard deviation of radiative flux within the channel remains nearly constant after the initial transience in power, indicating that the observed area of the channel heats at nearly the same rate. The maximum observed heat flux value at A is 0.95W/m^2 . The continued heating of the liquid eventually leads to the formation of a bubble as observed at snapshot B.

Snapshot B of Figure 18 corresponds to a drop in maximum and average measured flux because a gas phase is formed. This is due to the reduced IR emissivity of steam compared to the liquid electrolyte, which enables the observation of separate phases within the microchannel and shows that the bubble formation process begins with a rapid expansion of the gas phase. At this stage, the current through the channel begins to drop and heating power is reduced by a factor of 10, seen in the voltage-current plot in Figure 18. As a result of this, cooling through the channel walls promotes uniformity in the temperature distribution, observed in Figure 18 as a decrease in the standard deviation throughout the image until snapshot C.

The rapid expansion produces a largely symmetric dog-bone shaped geometry centred around the throat of the channel. The implication of this symmetry is that the bubble nucleation site is near the centre of the throat. Since this test is performed without particles, the bubble likely nucleates at a site on one of the channel walls, though it is possible a contaminant (PDMS, insoluble material, or microbubble) acts as a nucleation site. It cannot be determined from the video whether the bubble nucleates within the fluid volume or along either the front or rear wall, though numerical results

suggest higher temperature towards the PDMS-side and highest electrical field at the walls. The bubble nucleation and expansion processes occur in less than 1.5ms and cannot be observed in detail due to frame-rate limitations of the IR imaging system. The area-rate of expansion of the initial bubble process shown in Figure 18 is $10.1 \text{ mm}^2/\text{s}$. The bubble then undergoes a rapid contraction, shown in snapshot C.

At this stage, the simulation results are no longer useful in predicting the behaviour of the system. The introduction of a gas phase results in changes to the surface and electrical properties in the liquid, affecting EOF and the electric field. If we assume the gas is effectively insulating and that electrical conduction occurs only in the liquid phase, then the 'effective geometry' of the channel is governed by the volume filled with the liquid phase and so the electric field becomes a function of the bubble geometry. As a result, thin liquid volumes and films surrounding the bubble may experience higher local electrical field and subsequent heating if a liquid pathway between electrodes exists.

The contraction of the gas phase, as shown in snapshot C of Figure 18, is consistent among all trials which show the dog-bone bubble expansion; in some cases, slower nucleation occurs at the wall either due to trapped bubbles, presence of contaminants, or manufacturing variation between channels. For the case shown in the Figure 18, the bubble contracts and settles for 5ms after the dog-bone expansion. This settling period varies in length between tests depending on the geometry of the settled bubble. If the bubble spans the entire width of the channel, as is the case in Figure 18, the non-conductive gas phase causes an open-circuit condition and Joule heating is paused. This can be seen in the voltage-current plot as a rapid drop in current alongside an increase in voltage as the power supply tries to meet the imposed constant-current input condition. The result is a net cooling of the channel caused by the reduced current, as observed in the average irradiative flux trace. As the bubble settles, a visible thin liquid film may develop along the gas-solid interface that reconnects the anode and cathode and reenables Joule heating. This is observed in snapshot D of Figure 18, accompanied by an increase in maximum and average temperature measurement. In some cases, Joule heating may continue at a lower capacity and either increase or maintain temperature in the channel via a liquid link across or around the bubble.

As the film heats up, vaporization resumes and the bubble expands. This process is observed after snapshot C of Figure 18 in the max irradiative flux profile as a series of small peaks accompanied by an increase in average flux across the image, and as a small peak or peaks in the current/power input profile. The jagged shape of the peaks is likely a result of the unsteady nature of the expansion process, and the local IR emissivity change as the bubble-liquid interface shifts. During this stage, the bubble expands at less than a tenth of its initial formation rate, with a maximum rate of $0.50 \text{ mm}^2/\text{s}$ for the trial shown in Figure 18. The expansion process continues until the bubble spans the entire cross section of the channel, at which point the system becomes an open circuit again and heating stops. As the gas phase cools and the fluids settle, fluid films may reconnect the two electrodes on either side of the channel and restart the Joule heating process. This cycle repeats until the power supply is shut-off. In the experiments conducted, power was typically shut off after the completion of the first bubble formation-contraction-expansion cycle.

On rare occasions, a local area of substantially higher temperature is observed at the location of bubble expansion. This can be seen in snapshot E of Figure 18 which shows a bright spot corresponding to a large peak in the maximum flux profile and a clearly discernable peak in the average flux profile, though the events occur too rapidly to be observed in the voltage/current plot. The trial chosen for Figure 18 is the only particle-free test which shows a peak with such a localized flux peak. Generally, the maximum irradiative flux observed in electrolyte solution testing occurs just before bubble formation, shown at snapshot A. However, in the case shown in Figure 18, the overall maximum irradiative flux is observed after bubble formation. Typically for particle-free flows, small hot-spots are not easily observed on the average flux trace since the long heating period results in a uniformly high temperature throughout the channel, and though the presence of a peak is noticeable, it is not as obvious as in particle flows, as will later be discussed.

It is hypothesised that, in this case, Joule heating was stronger due to an unusually thin film resulting in a high voltage gradient. However, if the voltage gradient is high enough, electrical breakdown becomes a possibility. It is not clear which mechanism is responsible for this peak from the data collected, but high-speed video shows that dielectric breakdown is possible even in low voltage tests of the electrolyte solution. The IR data shows that this breakdown typically does not produce large peaks in the heat flux measurements, behaving as a non-thermal plasma. If the hot

spot observed in Figure 18 was produced by dielectric breakdown, it is possible that either an unusually bright or long-lasting arc occurred. Though electrical discharges can produce temperatures exceeding 1000°C [160], [167], such high temperature peaks are not observed in the IR videos. The absence of these peaks suggests that the dielectric breakdown process does not produce a strong enough IR signal, either by low intensity or short duration, to be measured with the hardware used.

It is noted that the maximum irradiant heat flux observed at E reaches a value of 1.15W/m²; it will later be shown that addition of particles results in radiant heat flux values which exceed the maximum of 1.15W/m² as observed for electrolyte-only tests.

Apart from the observation of high irradiative heat flux hot-spots, the general trends described by snapshots A-D in Figure 18 are repeatable and easily reproducible. Variation in the Joule-heating periods, maximum heat flux, and rates of bubble expansion is observed throughout the tests as can be seen in Table 4, but the general profiles of the plots in Figure 18 are characteristic of the operation of the channel at low voltages and without particles.

6.2 Characteristic results of Al@ CuO particle-laden operation of the microchannel in slow-heating mode

The slow-heating mode 2.5mA constant current tests are repeated with energetic particles dispersed in the 1 [M] electrolyte solution at 0.5g/L concentration. The characteristic behaviour of the microchannel is like that observed in the previously discussed tests, albeit with some distinct differences. Figure 19 shows the irradiation flux profiles for one trial, with IR image snapshots for key events.

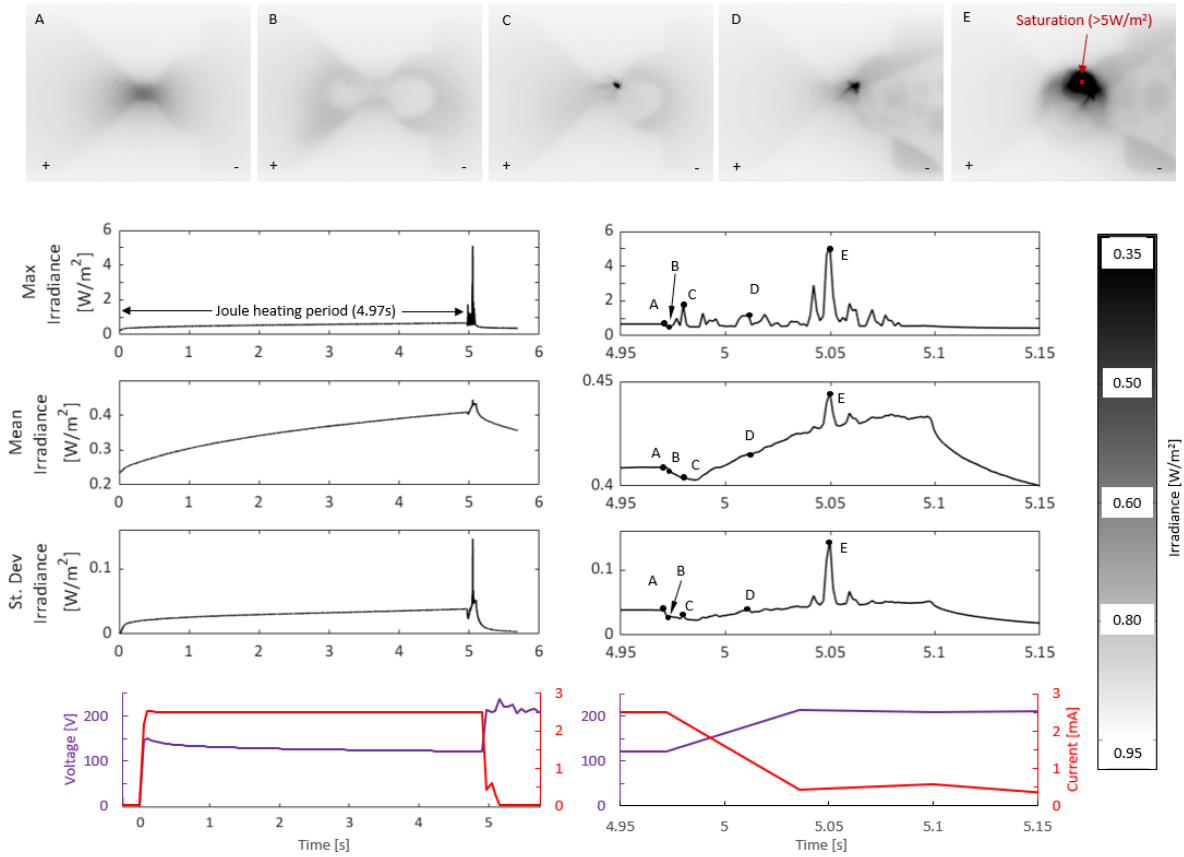


Figure 19: Maximum, mean, and standard deviation of irradiant flux profiles, and voltage-current profiles for a particle-laden flow (0.5g/L particle conc., 1 [M] electrolyte conc.) microchannel test run in slow-heating operating mode (2.5mA), showing full test timescale (left plots), bubble formation timescale (right), and IR image snapshots (top, A-E).

As was observed in the electrolyte-only tests, the application of power to the microchannel first leads to a continuous liquid-phase heating period. The duration of Joule heating prior to bubble formation varies across tests; in the case shown in Figure 19 it is 4.97s. In general, the addition of particles to the liquid results in shorter Joule-heating periods prior to bubble formation compared to the no-particle case (5s vs. +60s). The shorter heating period means that average measured irradiance within the channel is lower at the moment of bubble formation compared to the electrolyte-only tests, indicating that the average temperature in the channel is also lower for the particle laden tests. For the cases shown, the measured maximum flux prior to bubble nucleation is

0.67W/m² when particles are present, whereas the solution alone measured at 0.94W/m² prior to bubble formation. The presence of insoluble particles within the liquid phase likely plays a large role in bubble formation as they act as nucleation points. The heat distribution in the continuous phase liquid as shown in snapshot A of Figure 19 is like that observed in Figure 18, showing highest temperature at the throat, as expected.

Snapshot B of Figure 19 shows the formation of a bubble at the throat. The same dog-bone shape is seen as was observed for the electrolyte solution tests (Figure 18). Likewise, a dip is observed in the radiation flux profiles at Snapshot B and the current/heating power drops too. For both the particle-free and particle laden test conditions, the bubble expansion process is typically symmetric and occurs at rates on the order of 10 mm²/s, with the trial shown in Figure 19 expanding at 12.6 mm²/s. When a bubble is formed, particles occupying the volume are pushed by along liquid-gas interface. This can result in a collection of particles at the surface of the bubble, seen in Figure 20.

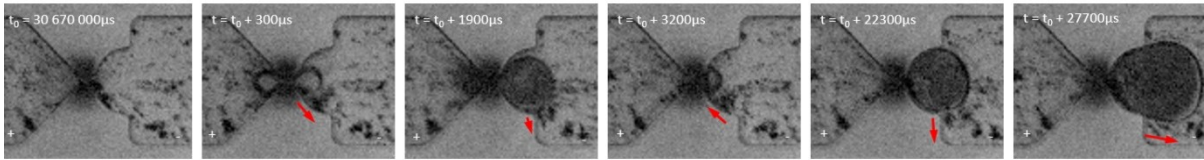


Figure 20: Microchannel operating in slow-heating mode (2.5mA) showing displacement of particle agglomerations and their collection at the liquid-gas interface. Red arrows indicate direction of particle motion as a result of the bubble expansion process. Particles used are 1μm Al@CuO at 0.5g/L concentration in 1 [M] NaCl.

Next, the bubble contracts as was shown in snapshot C of Figure 18. For the particle-laden channel shown in Figure 19, the contraction phase is very short (1.5-3ms). The bubble expansion process then begins, shown in snapshot C of Figure 19. A difference is noted here between the particle-laden and particle-free flows; the expansion process is accompanied by a localized hot-spot. These hot spots remain present throughout the expansion process (snapshots C, D, E), and are visible on the maximum irradiance profile in the form of peaks. Most of the peaks exceed the 0.67W/m² observed in the continuous liquid prior to bubble formation (snapshot A); these high-flux spots are commonly observed in particle laden tests but not in particle-free tests. The localized heating events cause the average temperature of the entire channel to increase and its standard

deviation to continue climbing past bubble formation; this is also not observed in electrolyte-only tests. Additionally, the hot spots observed are generally produce higher radiant flux than those observed in particle-free tests (1.15W/m^2). In fact, the hotspots reach fluxes high enough that the thermal camera dynamic range is insufficient to observe the cool and hot areas of the image, and so some pixels saturate (red pixels in Figure 19E); saturation occurs at approximately 5W/m^2 for the 300us exposure time used. These hot-spot events are strong enough to be visible even after spatial averaging of the channel temperature, observed as distinct individual peaks in the mean irradiance profile; this is not observed in the electrolyte-only tests. Fluxes this high cannot be achieved by Joule heating of the water alone, otherwise they would be observed in electrolyte-only tests, so some other heat-release mechanism must be the source of these localized hot-zones.

These hot-spots occur within thin structures and interfaces along the liquid-gas boundaries and liquid-gas-wall boundaries, and this is the case in both Figure 18 and Figure 19. The interfacial nature suggests that these hot spots are a result of changing electric fields; as was mentioned before, the liquid in the channel is the primary conducting phase and so it acts as the domain in which the electric field is conducted. It is important to note that particles collect at the liquid-gas boundary, as shown in Figure 20. The movement of the liquid-gas boundary can act to push particles away from an area of high temperature, but in some cases can bring particles towards regions of high electric field, even higher than those produced by the base geometry of the microchannel itself. This may be an explanation for the observed hot spots.

The presence of such high irradiant heat fluxes in particle-laden flows (and the absence of such temperatures from particle-free flows) implies that these thermal events are related to the particles. Since the particles used are energetic, the most basic hypothesis would be to state that the particles are igniting and the hotspots are an observation of thermite combustion. However, it is known that the Al/CuO thermite combustion in micro-core-shell particles occurs between $580\text{-}600^\circ\text{C}$ [38], [168]. Since the Joule heating of the liquid electrolyte should only produce temperatures up to the boiling point of water, there appears to be an explanatory gap as to why combustion is occurring. Joule heating in thin films might be able to produce higher temperatures, but an inability to study the temperature profile within these films in higher fidelity means no data is available to quantify the temperature. On the contrary, if these temperatures were being produced, one would expect still a

strong IR signal to be emitted and so a high temperature spot should be observable. So, it is unlikely Joule-heating causes the hotspots themselves and likely does not directly cause particle combustion; the latter is not easily evaluated.

Observations of electrical breakdown in the particle-free tests, shown in Figure 21, introduce more doubt towards the thermite-combustion explanation. Just as they act as nucleation sites for gas-phase formation, the particles also act as nucleation sites for breakdown of either the liquid or gas phases. So, it can only be concluded that the introduction of particles results in higher temperature hotspots, either by acting as nucleation for more intense electrical breakdown or through thermite combustion, or some combination of the two.

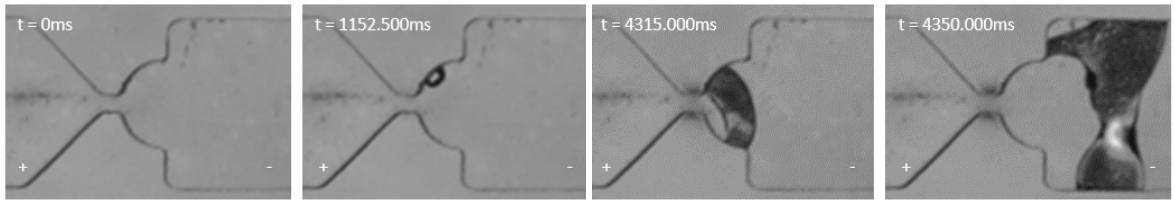


Figure 21: Slow-nucleation bubble formation process followed by electrical discharge in a 1 [M] NaCl solution in a slow-heating operating mode microchannel.

The bubble expansion process and accompanying hot-spotting continue until the bubble reaches a size that prevents current flow through the channel, at which point an open-circuit is formed. As with the electrolyte-only tests, the gas-liquid system cools and settles until a liquid bridge is formed between the two electrodes and current flow can resume. The process of bubble expansion then resumes, typically accompanied by more hot spotting. This process continues until the bubble is large enough to cause an open-circuit post-cooling, or until power is disconnected from the microchannel.

6.3 Comparison between particle-free and particle-laden operation of the microchannel in slow heating mode

The processes described here are characteristic to the microchannel operation, although the locations, rates, and intensities of bubble expansion and hot-spots are not controllable so there is a

large variance in peak-shapes and lengths throughout the IR data. Table 4 summarizes the variation observed during experimental testing.

Table 4: Summary of characteristic results for particle-free and particle-laden solutions in microchannel operating in slow-heating mode (2.5mA)

Particle concentration [g/L]	Joule heating time [s]	Maximum local radiative flux [W/m ²]	Maximum average radiative flux [W/m ²]	Maximum bubble growth rate [mm ² /s]
0	62.5 ± 47.1	1.12 ± 0.44	0.57 ± 0.19	0.37 ± 0.46
0.5	17.6 ± 25.6	3.96 ± 1.70	0.49 ± 0.19	2.1 ± 2.1

The summary results support the previous discussions of characteristic operation of the microchannel with and without particles. Addition of particles results in shorter heating times, higher local fluxes (and therefore temperatures), and higher maximum bubble growth rates. Though the Joule heating period is shorter in particle-laden operation, there is substantial overlap in the average irradiance data for particle-free and particle-laden tests, suggesting that the difference may be insignificant. This indicates that, at a concentration of 0.5g/L, any thermite combustion in the channel is highly localized and does not produce large thermal influence on the larger scale throat region.

6.4 Operation of the microchannel in fast-heating mode and comparison with slow-heating results

Increasing the voltage from approximately 120V to 500V shows a stark difference in the behaviour of the channel. The fast-heating operating mode refers to this 500V constant voltage application across the microchannel, as opposed to the slow-heating operating mode where 2.5mA of constant current is applied. The first case considered is the electrolyte-only case as was previously discussed. The Figure 22 shows high speed video captured for the two different cases.

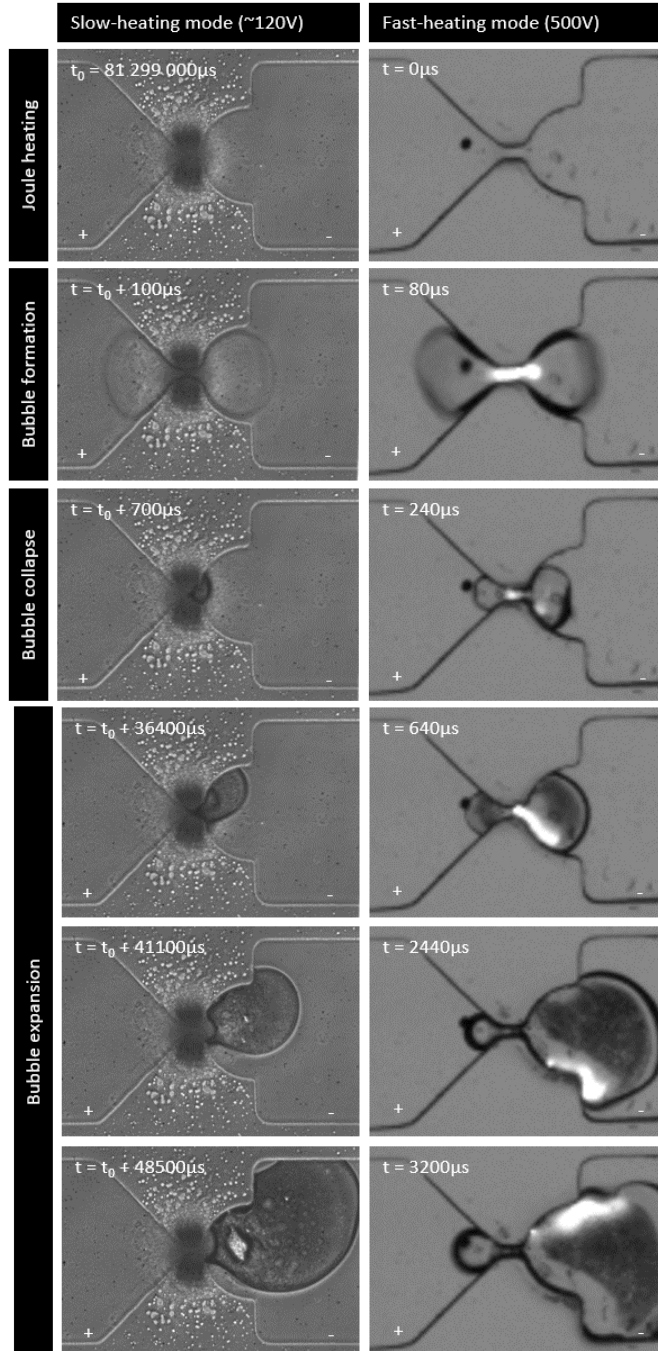


Figure 22: Bubble formation process in 1 [M] NaCl solution for two heating modes: slow heating mode (2.5mA, 120V, left column) showing damage of PDMS layer, and fast-heating mode (500V, right column) showing clear presence of electrical discharge.

The slow-heating mode tests show the same results as previously discussed as characteristic to the microchannel at low voltage (slow Joule heating, dog-bone bubble formation, bubble collapse, and subsequent expansion and open circuit cycle). It is noted that when bright spots are observed (Figure 21), in either visible or IR spectra, they always occur after the formation of the dog-bone bubble shape. Additionally, the dog-bone formation is preceded by a long Joule heating period, during which geometric deformation of the PDMS walls at the throat due to thermal expansion, and even PDMS degradation as seen in Figures Figure 20, Figure 21, and Figure 22, is observable.

When high voltage is applied, there is no distinct, observable heating period. Instead, we see the dog-bone bubble form instantly with power application. This is expected since the increased power will lead to faster Joule heating, and the rate of temperature increase is highest at the moment that power is applied (Figure 18 and Figure 19). However, we also typically see a distinct bright spot in the centre of the channel, which appears to originate collocal and simultaneously with the bubble. The absence of particles in the flow indicates that this emission is a result of some electrical breakdown phenomenon. Due to the rapid nature of this event, the high-speed video cannot provide detail towards the sequence of events, however it has been shown that bubble formation occurs prior to breakdown in highly conductive solutions.

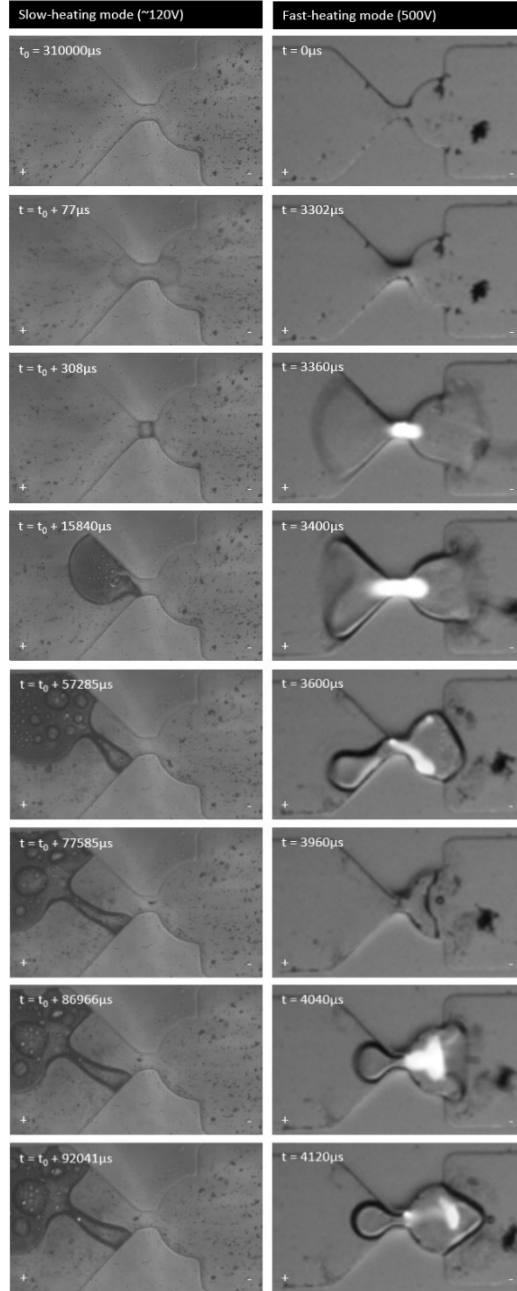


Figure 23: Bubble formation process in energetic particle-laden flow showing optical emission for two heating modes: s heating mode (2.5mA, 120V, left column) showing damage of PDMS layer, and fast-heating mode (500V, right column) showing clear presence of electrical discharge. Particles are $1\mu m$ Al@CuO core-shell at 0.5g/L concentration dispersed in 1[M] NaCl solution.

Most importantly, the presence of an optical emission in the particle-free tests present serious challenges since it becomes impossible to distinguish dielectric breakdown from the combustion of particles from the video and IR footage alone. This is shown in the comparative Figure 23 which shows low and high voltage power application with presence of suspended energetic particles. The same rapid bubble and bright-spot formation appear as were previously discussed for electrolyte-only tests. These videos demonstrate the inability to distinguish between light sources. In some cases, as shown in the slow-heating mode trial presented in Figure 23 at $t = t_0 + 92041\mu\text{s}$ (bottom left), small scale point-source bright spots can be seen. These are likely combustion events because they are highly localized and do not appear to bridge across any structures. In contrast, sometimes the emission takes the form of a bridging structure across the length of the bubble, as seen in Figure 22 (right column) at $t = 640\mu\text{s}$ and Figure 23 (right column) after $t = 3600\mu\text{s}$; this is reminiscent of plasma bridges seen in literature and indicates a strong likelihood of dielectric breakdown. Based only on the high-speed video, these distinctions are hard to make and cannot provide much certainty. As such, it becomes necessary to develop a method to confirm or validate the presence of thermite ignition.

6.5 Confirmation of optical and thermal emission sources by combined IR and narrow-band visible imaging

The results shown in the fast-heating-mode tests show a problem in our ability to distinguish combustion from electrical breakdown. While the IR results suggest that electrical breakdown does not produce significant temperature increase, this alone cannot be used to state that combustion occurs. Therefore, it is necessary to introduce a methodology to differentiate between thermite combustion and electrical breakdown more easily.

This is achieved by spectroscopic filtering; in principle, a narrow band-pass filter may be used to differentiate between particle reactions and other light sources, including electrical breakdown. This technique is commonly used in thermite combustion to confirm thermite ignition [20]. Spectroscopy of aluminum dust combustion with oxygen is shown in Figure 24 as obtained from Peuker et al. [169]. In the oxidation process of aluminum, an intermediate product in the reaction is aluminum monoxide (Al-O) and is thought to be responsible for the spectral peaks at 483 – 488nm. To separate

this response from other light sources, a band-pass filter centred around 488nm can be used to transmit only the light produced by Al-O to the camera sensor. The transmissive response of a Thorlabs 488nm laser line filter is shown in Figure 24; the peaks produced by Al-O fall within the passband of the filter.

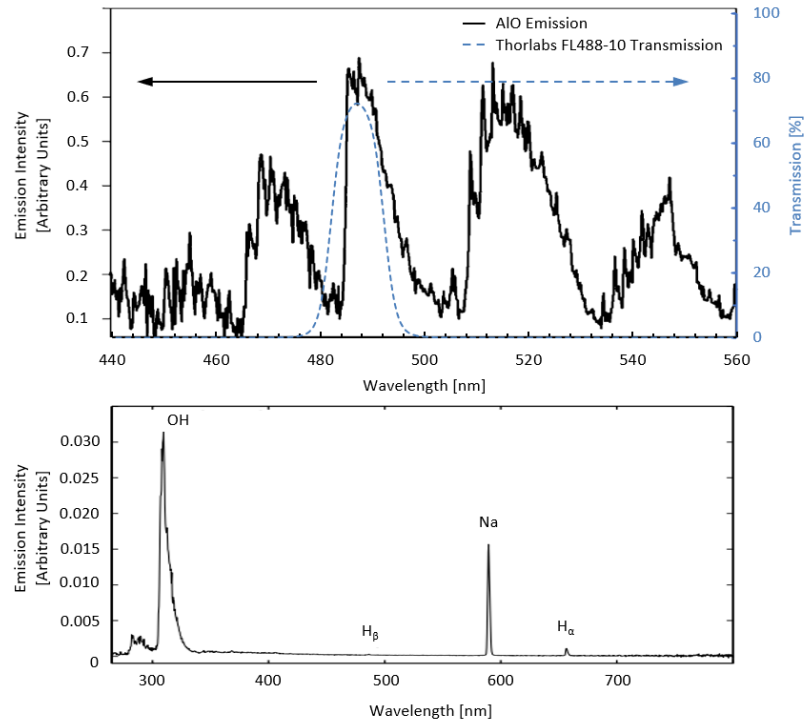


Figure 24: Emission spectrum of Al particles showing AIO characteristic peaks as obtained from Peuker et al. [169] with overlaid transmission band of Thorlabs FL488-10 laser line filter (top) and characteristic spectrum of electrical breakdown of aqueous NaCl solution as obtained from Bruggeman et al. [170] (bottom).

The emission spectrum of electrical breakdown of and aqueous NaCl solution in a capillary is also shown in Figure 24. Many species contribute to the visible spectral signal produced in steam breakdown but only the Balmer-series hydrogen beta (H_{β}) peak at 486.1nm falls within the transmission band of the Al-O filter. Importantly, the relative magnitude of the H_{β} peak is less than that of the other peaks produced by electrical breakdown. So, while the presence of the H_{β} emission may be observable through the filter, an assumption is made that the emission will be dim upon

observation. Additionally, it is assumed that the intensity of the Al-O signal will be significantly brighter since it plays a larger role in the overall emission spectra of Al/CuO thermite compared to H_{β} in the electrical breakdown. This assumption is based on the qualitative similarities of optical emissions between the electrolyte-only and particle-laden microchannels regarding size, duration, and intensity.

The filter is integrated into the high-speed microscopy setup between the sample and the objective lens. Due to the narrow transmittance of the filter, the image becomes very dim; this is observable in the camera images shown in Figure 25.

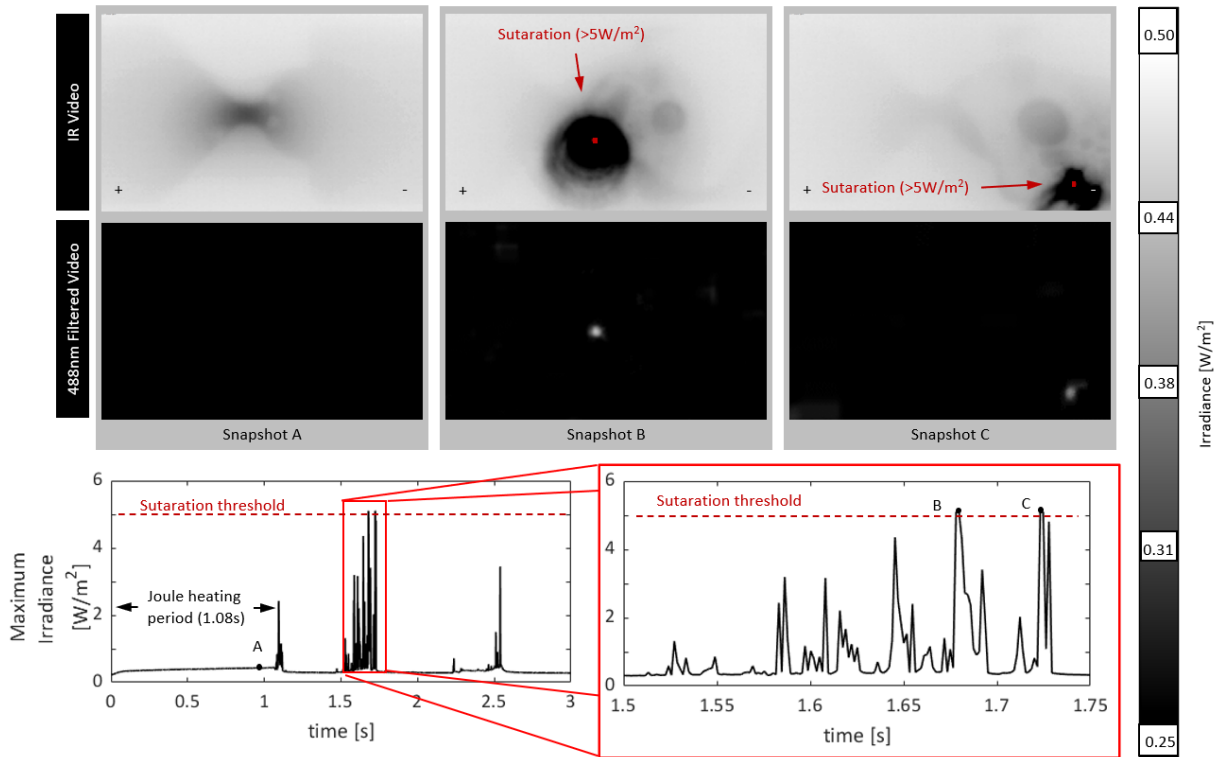


Figure 25: Simultaneous IR and 488nm filtered VIS imaging showing maximum irradiant heat flux trace and spatial and temporal correlation between hot-spots and AlO signal bright-spots for a 2.5mA heating current, 0.5g/L concentration of $1\mu\text{m}$ Al@CuO particles dispersed in 1 [M] NaCl solution.

The figure shows snapshots captured simultaneously via IR and visible spectrum cameras for a particle-dispersed microchannel. The irradiant flux profile is also shown below the snapshots; many high flux peaks are produced throughout the duration of the test. Although many peaks are visible in the thermal camera video, they do not always correlate well to the visible spectra video. Only at peak A is there observation of any activity in the filtered camera video, apparent as a dim point light source. The next observable light source occurs a few frames later, and correlates temporally to peak B in the maximum irradiance plot. It is apparent that the spots also correspond well spatially in both the IR and 488nm datasets, indicating that the same events are being observed. For the IR camera settings used in this test, the peaks reach sensor saturation (5W/m^2), and only the peaks corresponding to sensor saturation can be observed through the bandpass filter. As previously discussed, these IR sensor saturation events occur only in particle-laden tests, so the light observed through the filter indicates a particle related event. It is hypothesised that either the particles are enhancing or augmenting the duration, strength, and spectra of an electrical breakdown process, or they are combusting and emitting light. It is also possible that a combination of the two processes is occurring, where the particles facilitate arcing, then combust because of the produced high temperature.

When the test was repeated for the particle-free electrolyte solutions, bright spots were not observed in the filtered camera video. This result supports the assumption that the Al-O emission will be dominant over the H_β emission in the passband of the filter since emission through the filter was observed only when particles were present. As previously discussed, extensive IR imaging on the electrolyte solution showed that temperatures produced were insufficient in magnitude to saturate the sensor. The combination of these results further supports the correlation between IR saturation and thermite combustion, as validated using a spectral bandpass filter.

6.6 Post-test analysis of PDMS microchannel walls using SEM imaging and EDS elemental mapping

Further investigation regarding the thermite combustion was performed by analysing the microchannels post-test. The microchannels are disassembled by using a single-edged blade to separate the PDMS layer from glass. The channel walls are gently rinsed with DI water to dilute the

NaCl solution and left to dry. Then, the samples are mounted to an SEM sample stub with carbon tape. Since PDMS is not conductive, the carbon tape is wrapped to the top surface of the sample to provide a conductive path to the sample stub, and then the stub and sample are gold coated. This enables SEM and EDS observation of the microchannel and any remaining particles in the channel. It is noted that, due to the disruptive nature of the disassembly process, the position of particles within the channel may not be directly related to any physical or electrochemical property of the channel at that location. Particles will undoubtedly be disturbed in sample handling, flushing, mounting, and during transportation.

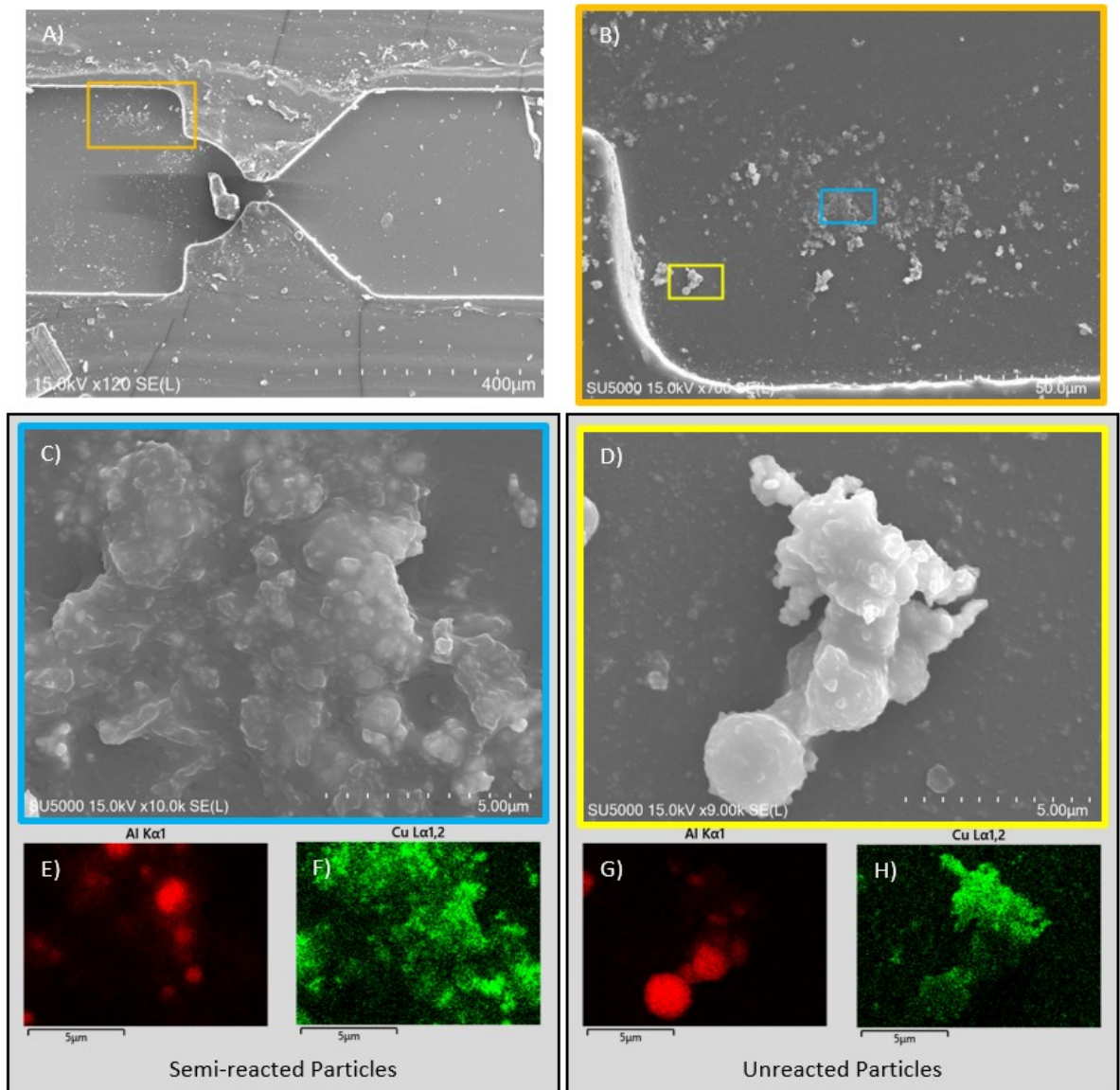


Figure 26: SEM images showing: A) overview of microchannel post-test, B) region of interest where optical emission was observed post 2.5mA applied current particle test, C) reacted or partially-reacted particles, D) unreacted particles, and EDS mapping showing: E) Al distribution in image C, F) Cu distribution in image C, G) Al distribution in image D, H) Cu distribution in image D.

Figure 26A shows the general overview of the throat of a used microchannel. The large grain to the left of the throat is a segment of PDMS that was introduced into the channel during the

disassembly and sample mounting process. This image shows that there are still many particles along the walls of the channel, even after rinsing of the channel.

At higher magnifications such as in Figure 26B, some particles are visible in the channel that appear qualitatively like as-fabricated unreacted core-shell particles. These particles appear in agglomerations; this corroborates the large particles seen in the high-speed video. As observed in the video results, it is clear that the fluid itself does not combust, but rather only particles and clusters can be used as energetic carriers which may be useful for delivering heat.

Figure 26B shows a region of interest (as highlighted in A) where a bright spot was observed during chip operation. Within this region, two distinct particle morphologies can be observed, and are presented in Figure 26C and D.

A particle cluster is presented in Figure 26D. The cluster shows clear spherical particles with some roughness along the surface consistent with SEM images of as-fabricated Al@CuO particles made by the same wet-chemistry method. The EDS analysis plots seen in Figure 26G shows that the spherical particles are aluminum, as expected for the core-shell particles. Similarly, Figure 26H shows that Cu is distributed along the Al particle surfaces and is responsible for the rough structures observed in Figure 26D. These images show an unreacted Al@CuO particle agglomeration within the microchannel.

The morphology seen in Figure 26C does not show the spherical structure expected from an unreacted particle. Instead, the structure looks embedded into the PDMS wall of the channel and appears to have a rough, granular appearance. EDS analysis for this region is presented in Figure 26E and F for elemental Al and Cu content, respectively. Figure 26E shows a relatively diffuse concentration of aluminum with distinct aluminum-rich pockets. Copper is more uniformly distributed throughout the structure compared to the aluminum, seen in Figure 26F. The diffuse Al concentration and uniform Cu concentrations suggest that this structure may be a combination of intermetallic compounds and/or alumina. The concentrated Al regions may either correspond to alumina droplets or, less likely but possible, some unreacted aluminum particles; if, for example, the agglomeration was Al rich.

It would seem unlikely that unreacted aluminum would remain in the vicinity of combustion, or the high temperatures observed at the throat. This is because any exposed aluminum surface on the aluminum particles will react with water at these temperatures. However, Figure 26B and D shows that there are indeed unreacted particles in the vicinity of the throat and other high-temperature areas. It is important to note though, that the unreacted particle may have ended up at its location during the SEM preparation process of the microchannel rather than during operation. This is unlikely to be the case for the cluster in Figure 26C since it appears fused to the wall, likely due to high temperatures. Though definite conclusions cannot be made from these results, it is fair to state that the structure seen in Figure 26C represents at least partial combustion but the extent of completion of the reaction is unclear.

6.7 Evaluation of thermite reaction plausibility

These results confirm that, in general, the particles travel in the flow as clusters. Well-coated particles may even be able to travel through areas of comparatively high temperature without reaction, demonstrating their robustness in particle delivery applications. From the depositions left on the walls of the channel, it appears that there is strong evidence of thermite combustion, so the power applied to the channel is indeed combusting the particles, but the mechanism is unclear.

The evidence collected appears to confirm the presence of thermite combustion. The spectral responses of steam plasma and aluminum combustion were considered and showed that a narrow band-pass optical filter could be used to observe only combustion and not electrical breakdown. Without the filter, bright flashes are observable regardless of whether particles are present or not. Repeated testing of the microchannel showed that bright flashes were only observable through the filter when particles were present in the flow, this supports the underlying assumption that the filter can be used to observe combustion. The presence of emission signal with the presence of particles is an important indicator that aluminothermic reaction occurs.

Simultaneous imaging of infrared and filtered visible spectrum shows that hot spots correlate with bright spots. Hot spots which produce irradiant fluxes exceeding 5W/m^2 occur only when particles are present in the microchannel; this finding suggests that these hot spots result from thermite

combustion. These results further support aluminothermic reaction. Furthermore, this correlation can be used to predict whether combustion occurs in the rest of the IR data set.

SEM images show a distinction between unreacted particles and reacted particle agglomerations, both of which can be found in the microchannel post-test. Results suggest that particles travel in agglomerations and can travel through relatively high temperature zones without reacting. The presence of rough, non-spherical geometries embedded in the walls of the PDMS suggest some reaction has occurred. Chemical analysis via EDS shows these structures have well distributed copper and diffuse aluminum throughout. Several aluminum-rich particles still exist within the structure, either corresponding to unreacted aluminum or alumina particles.

6.8 Particle cluster collection techniques and large-scale ignition attempts

For the results discussed thus-far, deliberate attempts to collect particles at a specific position in the channel were not attempted. However, it was noted during experimentation that simple methodologies could be used to create large particle clusters at the throat of the channel. These clusters, in principle, should enable the control of energy deposition at the throat once combusted; a large cluster releases more heat than small agglomerations or single particles.

These clusters can be created by slowly cycling fluid through the channel by either electrokinetic or traditional flow techniques. The particles have a natural tendency to adhere to the walls of the channel and to each other, so with enough flow-time clusters will form at the throat. In practice, this was achieved by either inducing a gravity flow or a low-current EOF. It was also achieved using pressure driven flows which produced large blockages at the throat; these often contained undesirable non-thermite contaminants. Gravity and EOF flows were preferred due to their simplicity but pump-driven flows using peristaltic or syringe pumps can be used if the channel inlet is designed in a way which accommodates a tube from the pump as well as an electrode.

Figure 28 shows a microchannel with a particle agglomeration at the throat. This was achieved by applying a low EOF (5V) within the channel for an extended duration and monitoring until an agglomeration was observed.

Agglomerations occur naturally with enough time. However, ignition of these agglomerations is challenging to achieve due to a lack of control with the microchannel design and hardware available. Of over 100 tests performed, only three cases of agglomeration-ignition were observed. Of these three cases, two of the ignitions occurred in the continuity-check step of channel setup; the voltages used for this step range between 5-10V. Video data for these two events was not recorded because they occurred unexpectedly, however they were powerful enough to be seen with the naked eye.

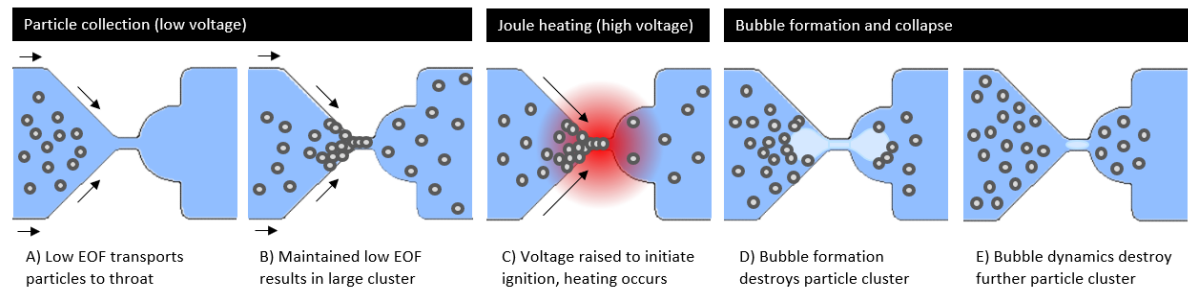


Figure 27: Schematic diagram detailing the incompatibility of particle agglomeration and ignition method.

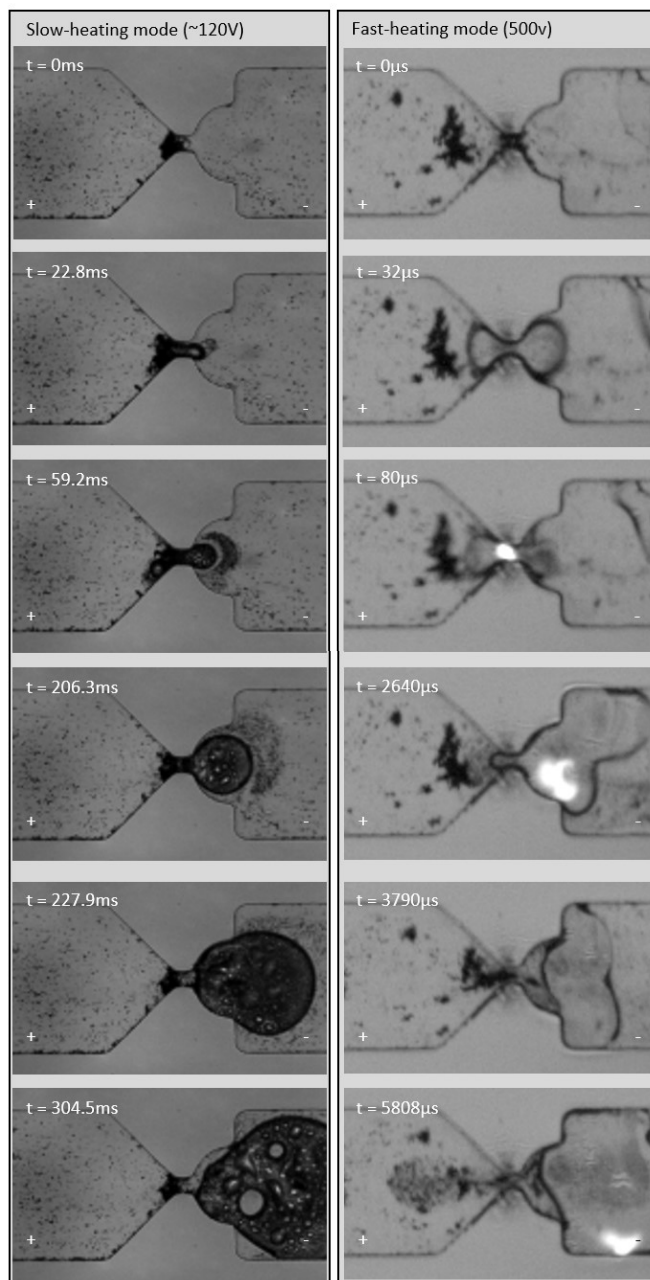


Figure 28: Attempts to ignite particle accumulation at throat produced by low EOF cycling using slow-heating mode (2.5mA, left) and fast-heating mode (500V, right), both resulting in characteristic behavior without large-scale particle ignition. Particles are $1\mu\text{m}$ Al@CuO at 0.5g/L concentration in 1 [M] NaCl solution, $t = 0$ corresponds to frame before first bubble is observed.

In the cases where an agglomeration was successfully formed, both high and low voltages were used in attempts to achieve ignition. For low voltages it was hypothesised that a slow bubble formation process nucleating at the clusters would keep the agglomeration from breaking, like the process shown in Figures Figure 20 and Figure 23. For high voltages it was hypothesised that the instantaneous arc could induce ignition of the particles prior to the large-scale growth of a bubble and subsequent particle displacement. In practice, the process of bubble formation necessary for electrical discharge proved to be incompatible with the particle agglomeration-based flame modulation method. A schematic diagram is presented in Figure 27.

High-speed video results are presented in Figure 28. In most cases, the bubble formation process created enough force to break-up and displace the particle clusters from the throat. The microchannel system then behaved in the typical characteristic way, as previously discussed. In the low-voltage trial shown in Figure 28 (left), the cyclical nature of the bubble expansion and contraction effectively breaks down some of the large agglomerations, and at 59.2ms and onwards, a cloud of particle can be seen surrounding the bubble. Similar particle clouds can also be seen in the right column of Figure 28 at 5808 μ s. Neither of the hypotheses held true and, in most cases, ignition of aggregates was not achieved.

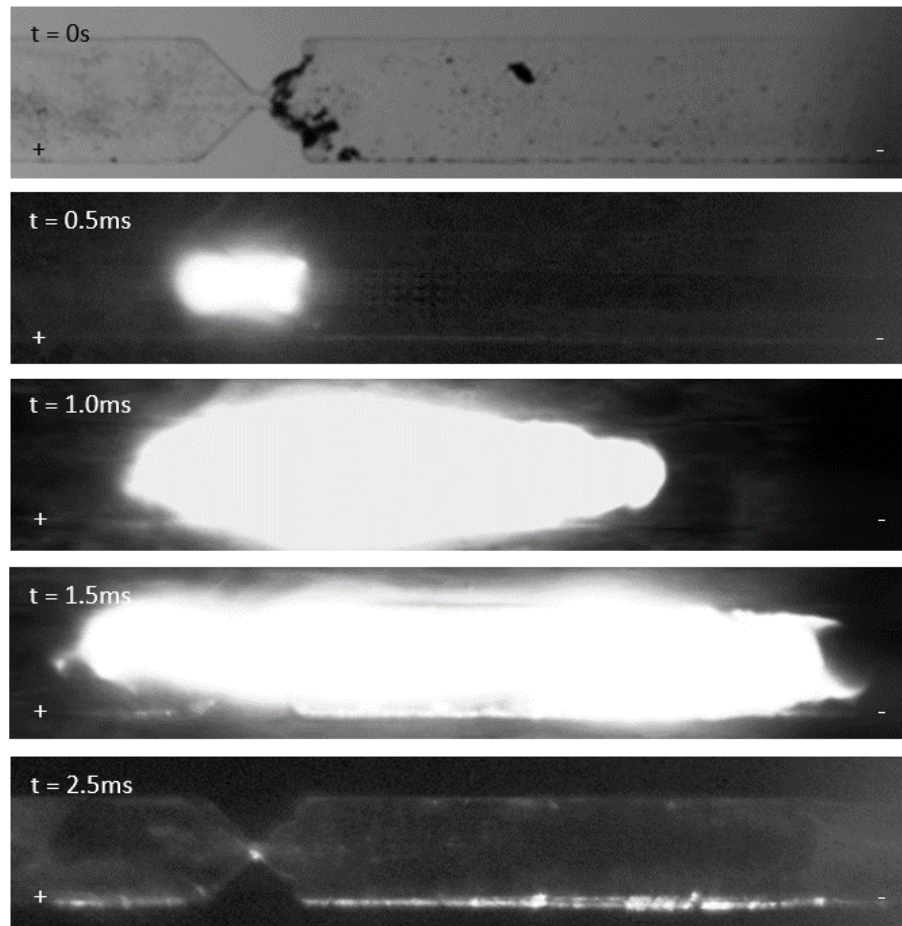


Figure 29: Successful ignition of large particle accumulation at throat produced by low EOF cycling, ignition occurring during 10V microchannel circuit continuity check. Particles are $1\mu\text{m}$ Al@CuO at 0.5g/L concentration in 1 [M] NaCl solution, $t = 0$ corresponds to frame before first ignition is observed.

In one case, ignition was achieved and recorded as shown in Figure 29. This video shows clear large scale thermite combustion; the duration and size of the light source exceeds any electrical breakdown emission. The frame-by-frame evolution of the flame shows the origin as the particle agglomeration observed pre-test and flame front speeds reaching 1.875m/s in the outlet direction. The ignition delay was less than 0.5ms and the entire flame was observed over 1.5ms. Once the flame is completed, the channel is mostly filled with a gas phase gap that is too large to support any further heating or electrical processes.

Further attempts to reproduce this result were unsuccessful. However, this result remains important as it demonstrates that some level of tunability within the microchannel is feasible. The results show clear difference between small- and large-scale combustion events because of differences in the energetic mass. This demonstrates that, although normally combustion is limited to the scale of a small particle cluster, it can be scaled up by selective aggregation and still produce large scale combustion. With refinement of the microchannel system to improve particle deposition and ignition techniques, it is anticipated that finer control can be achieved, and larger scale combustion can be more easily reproduced.

Chapter 7

Conclusion and Recommendations

7.1 Summary

The objective of the work was to create a system which uses microfluidic transport techniques to deposit core-shell thermites in dispersed phase and ignite it in an inert, aqueous environment. This was realized by designing a microchannel device with a converging-diverging geometry for the collection of dispersed $1\mu\text{m}$ Al@CuO particles. Using electrodes at the inlet and outlet, an ignition system was introduced by means of electrical discharge produced by capillary breakdown of the liquid at the throat.

The microchannel geometry was modelled in COMSOL to determine the effects of applied voltage and solution conductivity on the electrical field, velocity, and temperature within the channel. Maxima were observed in the magnitude of the electric field at the throat, specifically at the transitions of the converging and diverging sections. Heating power is also maximized at these locations due to the square nature of Ohm's power law. It was found that using a highly conductive solution results in higher observed temperatures for a given voltage, eventually resulting in boiling of the liquid phase. When the model predicted temperatures exceeding the boiling point of water, it was also observed that the velocity prediction began to breakdown and backflow was predicted; this was deemed a limitation of the practical usefulness of the model. A single particle suspended in the electrolytic solution was also modelled. The presence of a particle in the liquid increased the maximum electric field magnitude by 3 to 10 times. Because a large spread of conductivity was considered, several heating modes are predicted by the model: heating at the liquid-shell interface for solutions less conductive than CuO, heating within the shell for solutions more conductive than CuO, and heating in the liquid and the shell when the solution was significantly more conductive than CuO. These results suggested that a higher solution concentration results in increased heating in both the electrolyte and particle phases, so experimentally, a high conductivity solution was used.

The microchannel was experimentally characterized using 1[M] NaCl solution using IR imaging and high-speed microscopy techniques. When operated in slow-heating mode, the liquid in the channel

undergoes a long Joule heating stage and eventually result in the formation of a bubble. Once the bubble fills the cross-section of the channel current flow is halted and the bubble cools and shrinks. If the bubble shrinks enough, a conductive path may be re-established around the bubble and Joule heating may begin again. When $1\mu\text{m}$ Al@CuO particles are added to the channel in slow-heating mode, the Joule heating stage is shortened. Additionally, thermal hot spots are more readily observed in the IR video and maximum irradiant heat flux increases.

In fast-heating mode, a Joule heating stage is not observed. Instead, capillary discharge occurs, where bubble formation is nearly instantaneous and closely followed by visible electrical discharge once power is applied. When $1\mu\text{m}$ Al@CuO particles are added to the channel in high-power/fast-heating mode, the difference is more difficult to observe because the presence of particle combustion is masked by the bright electrical discharge.

Attempts to modulate the combustion size were made by purposeful collection of large particle aggregations at the channel throat with the intent of increasing the flame by increasing energetic mass. It was found that the capillary ignition technique used was generally incompatible with this method because the bubbles formed by Joule heating destroy the particle clusters. A large-scale combustion event was observed when particles were clustered at the throat, demonstrating that flame-size is tunable, but the event could not be reproduced due to limitations with the ignition system.

7.2 Conclusion

Overall, a system was designed with the capability to ignite thermite core-shell particles in inert, aqueous, microscale environments. The numerical work showed that tuning the solution conductivity can change the location of maximum Joule heating, either in the liquid, at the core-shell interface, or in the liquid and shell phases. In-liquid temperatures are limited by the boiling point of the solution though, so it is hypothesised that either heating within the particles or proximity to electrical breakdown discharge is responsible for thermite ignition. Small combustion events can be readily reproduced with the designed system, but the usefulness of this combustion process is difficult to quantify due to the dominance of Joule heating on the bubble dynamics, masking the influence of combustion. Extensive work was performed to confirm that the video data observed

was indeed combustion, and there is a high degree of confidence that combustion takes place in the channel. The device design does not lend itself well to large-scale combustion since the breakdown process produces a bubble that destroys and displaces energetic agglomerates.

7.3 Recommendations

To improve the performance of the design, several changes are recommended:

Numerical:

1. A temperature dependent conductivity model, as described by equations (14) and (15), was implemented into the microchannel model but led to convergence issues. If these problems can be addressed by tuning of the solver parameters, then a more accurate numerical result is expected.
2. The zeta potential was kept constant across all simulations. In reality, it decreases with increased ionic concentration and different materials result in different potentials. Performing an experimental study of the zeta potential with glass, PDMS, and Al@CuO interfaces at different NaCl concentrations would allow a more accurate picture of the EOF. In addition, this would reveal the electrophoretic properties of the core-shell particles.
3. Incorporating phase change in the numerical model would remove the non-physical temperature values observed in the model. Additionally, the focussing of electrical field along the bubble edge would be quantifiable and electrical breakdown could be more accurately predicted.
4. Including dispersed particles within the microchannel model would show the evolution of the electric field as particles travel through the channel. Multiple dispersed particles within the flow could be used to predict the effects of groups of particles on the intensification of the electric field, providing more insight into the state of the channel during operation.

Experimental:

1. Simplifying the microchannel geometry would reduce issues with trapped bubbles in the channel. The corners at the semi-circular transition of the channel, as highlighted in Figure 30, tend to trap and hold air that is difficult to remove, smoothing the geometry would eliminate this problem without substantially changing the geometry.

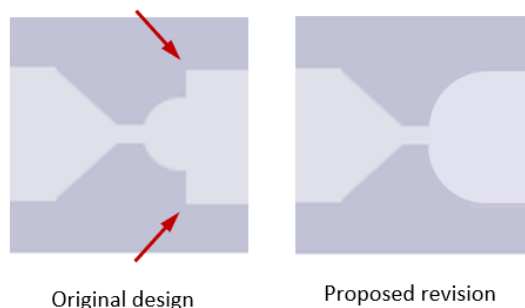


Figure 30: Proposed geometry change for future microchannels, red arrows indicating corners that trap bubbles during filling process.

2. Using a lower conductivity solution would result in less bubble formation during electrical breakdown. It is hypothesized that this could be leveraged to create a discharge near the energetic particle aggregations without disrupting their structure. This may improve the repeatability of large-scale combustion tests, but higher voltages will need to be used since lower conductivity solutions have greater breakdown strength.
3. For the fabrication methodology used in this study, the core-shell structure of microscale particles was observed to be better than the nanoparticle equivalent. However, the focussing effects of nanoparticles on the electric field within the channel may reduce the energy required to initiate breakdown. This, combined with reduced solution conductivity, may prove to be an important refinement in the controllability of the combustion scale.
4. Using inert micro- and nanoparticles could help to isolate the electric field focussing effects from the combustion effects. This was attempted as part of this work, but data could not be collected because of the instability of the CuO particles in the NaCl solution.

If the dispersion stability can be improved without addition of surfactants to the solution, then a good comparison between energetic and inert particles can be made.

5. The 0.5g/L concentration of particles used in this study was insufficient to produce group combustion within the liquid suspension. Increasing the particle concentration may make the dispersion more reactive while maintaining its transportable, fluid nature.
6. The IR data was presented in the form of irradiance flux [W/m^2] but presenting the data in temperature form would be more intuitive for readers. However, the IR video temperature calibration is inaccurate due to the attenuation of the IR wavelength signal through the glass. This problem can be solved by using IR transparent slides, such as those made of CaF_2 , which are readily available but more expensive than glass slides. Alternatively, an inverse analysis of the radiation heat transfer through the glass may provide more accurate temperature measurements for the existing setup, while also being applicable for all the existing IR data.
7. The electrical data was logged using the logger built into the Labsmith power supply. Recording was limited to 60Hz, but events in the microchannel occur at ms and μs scales, so the temporal fidelity of the voltage and current data is insufficient to provide detail regarding the power input and breakdown of the solution. An external data logging setup with kHz to MHz sampling rates could be used to solve this problem and better characterize the breakdown of the liquid.
8. Higher magnification microscopy would allow the observation of individual microparticles within the channel. Combined with high-speed video, this may enable the observation of the ignition events of small clusters and provide insight on the ignition mechanism.

Implementing these changes would provide further insight into the operation of the microchannel and the mechanism of thermite ignition, which could then drive the design of the next iteration of the thermite-based MEMS device.

Letters of Copyright Permission

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Nov 03, 2022

This Agreement between Alex Baranovsky ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number 5412710338980

License date Oct 19, 2022

Licensed Content
Publisher John Wiley and Sons

Licensed Content
Publication Propellants, Explosives, Pyrotechnics

Licensed Content
Title Nanothermites: A short Review. Factsheet for Experimenters, Present and Future Challenges

Licensed Content
Author Marc Comet, Cédric Martin, Fabien Schnell, et al

Licensed Content
Date Nov 15, 2018

Licensed Content
Volume 44

Licensed Content
Issue 1

Licensed Content
Pages 19

Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title	Student
Institution name	University of Waterloo
Expected presentation date	Oct 2022
Portions	Table 1
Requestor Location	Alex Baranovsky 200 University Ave W Waterloo, ON N2L 3G1 Canada Attn: Alex Baranovsky
Publisher Tax ID	EU826007151
Total	0.00 CAD
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.
- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. **For STM Signatory Publishers clearing permission under the terms of the [STM Permissions Guidelines](#) only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts**, You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right,

license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.
- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.
- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.
- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.
- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\) License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License](#) (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library
<http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE TERMS AND CONDITIONS

Nov 03, 2022

This Agreement between Alex Baranovsky ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	5412670354164
License date	Oct 19, 2022
Licensed Content Publisher	Elsevier
Licensed Content Publication	Thermochimica Acta
Licensed Content Title	Energetic characteristics of the Al/CuO core-shell composite micro-particles fabricated as spherical colloids
Licensed Content Author	Yiqi Zhang,Hongtao Sui,Yuning Li,John Z. Wen
Licensed Content Date	Jul 1, 2020
Licensed Content Volume	689
Licensed Content Issue	n/a
Licensed Content Pages	1
Start Page	178656
End Page	0
Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Title	Student
Institution name	University of Waterloo
Expected presentation date	Oct 2022
Portions	Figure 4
Requestor Location	Alex Baranovsky 200 University Ave W Waterloo, ON N2L 3G1 Canada Attn: Alex Baranovsky
Publisher Tax ID	GB 494 6272 12
Total	0.00 CAD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier's permissions helpdesk [here](#)). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must

be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript
 - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
 - directly by providing copies to their students or to research collaborators for their personal use
 - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.

Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a [CrossMark logo](#), the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's [posting policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.10

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

This is a License Agreement between Alex Baranovsky ("User") and Copyright Clearance Center, Inc. ("CCC") on behalf of the Rightsholder identified in the order details below. The license consists of the order details, the Marketplace Order General Terms and Conditions below, and any Rightsholder Terms and Conditions which are included below.

All payments must be made in full to CCC in accordance with the Marketplace Order General Terms and Conditions below.

Order Date	19-Oct-2022	Type of Use	Republish in a thesis/dissertation
Order License ID	1281142-1	Publisher	INSTITUTE OF PHYSICS PUBLISHING
ISSN	0960-1317	Portion	Image/photo/illustration

LICENSED CONTENT

Publication Title	Journal of micromechanics and microengineering : structures, devices, and systems	Country	United Kingdom of Great Britain and Northern Ireland
Author/Editor	Institute of Physics (Great Britain)	Rightsholder	IOP Publishing, Ltd
Date	01/01/1991	Publication Type	Journal
Language	English		

REQUEST DETAILS

Portion Type	Image/photo/illustration	Distribution	Canada
Number of Images / Photos / Illustrations	2	Translation	Original language of publication
Format (select all that apply)	Electronic	Copies for the Disabled?	No
Who Will Republish the Content?	Academic institution	Minor Editing Privileges?	Yes
Duration of Use	Life of current edition	Incidental Promotional Use?	No
Lifetime Unit Quantity	Up to 499	Currency	CAD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Master's Thesis	Institution Name	University of Waterloo
Instructor Name	Prof. John Wen	Expected Presentation Date	2022-10-19

ADDITIONAL DETAILS

Order Reference Number	N/A	The Requesting Person/Organization to Appear on the License	Alex Baranovsky
-------------------------------	-----	--	-----------------

REUSE CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 6, Figure 12	Title of the Article/Chapter the Portion Is From	N/A
Editor of Portion(s)	N/A	Author of Portion(s)	Institute of Physics (Great Britain)
Volume of Serial or Monograph	N/A	Issue, if Republishing an Article From a Serial	N/A
Page or Page Range of Portion	4-6	Publication Date of Portion	2008-11-27

RIGHTSHOLDER TERMS AND CONDITIONS

These special terms and conditions are in addition to the standard terms and conditions for CCC's Reproduction Service and, together with those standard terms and conditions, govern the use of the Works. As the User you will make all reasonable efforts to contact the author(s) of the article which the Work is to be reused from, to seek consent for your intended use. Contacting one author who is acting expressly as authorised agent for their co-author(s) is acceptable. User will reproduce the following wording prominently alongside the Work: the source of the Work, including author, article title, title of journal, volume number, issue number (if relevant), page range (or first page if this is the only information available) and date of first publication; and a link back to the article (via DOI); and if practicable, and IN ALL CASES for new works published under any of the Creative Commons licences, the words "© IOP Publishing. Reproduced with permission. All rights reserved" Without the express permission of the author(s) and the Rightsholder of the article from which the Work is to be reused, User shall not use it in any way which, in the opinion of the Rightsholder, could: (i) distort or alter the author(s)' original intention(s) and meaning; (ii) be prejudicial to the honour or reputation of the author(s); and/or (iii) imply endorsement by the author(s) and/or the Rightsholder. This licence does not apply to any article which is credited to another source and which does not have the copyright line '© IOP Publishing Ltd'. User must check the copyright line of the article from which the Work is to be reused to check that IOP Publishing Ltd has all the necessary rights to be able to grant permission. User is solely responsible for identifying and obtaining separate licences and permissions from the copyright owner for reuse of any such third party material/figures which the Rightsholder is not the copyright owner of. The Rightsholder shall not reimburse any fees which User pays for a republication license for such third party content. This licence does not apply to any material/figure which is credited to another source in the Rightsholder's publication or has been obtained from a third party. User must check the Version of Record of the article from which the Work is to be reused, to check whether any of the material in the Work is third party material. Third party citations and/or copyright notices and/or permissions statements may not be included in any other version of the article from which the Work is to be reused and so cannot be relied upon by the User. User is solely responsible for identifying and obtaining separate licences and permissions from the copyright owner for reuse of any such third party material/figures where the Rightsholder is not the copyright owner. The Rightsholder shall not reimburse any fees which User pays for a republication license for such third party content. User and CCC acknowledge that the Rightsholder may, from time to time, make changes or additions to these special terms and conditions without express notification, provided that these shall not apply to permissions already secured and paid for by User prior to such change or addition. User acknowledges that the Rightsholder (which includes companies within its group and third parties for whom it publishes its titles) may make use of personal data collected through the service in the course of their business. If User is the author of the Work, User may automatically have the right to reuse it under the rights granted back when User transferred the copyright in the article to the Rightsholder. User should check the copyright form and the relevant author rights policy to check whether permission is required. If User is the author of the Work and does require permission for proposed reuse of the Work, User should select 'Author of requested content' as the Requestor Type. The Rightsholder shall not reimburse any fees which User pays for a republication license. If User is the author of the article which User wishes to reuse in User's thesis or dissertation, the republication licence covers the right to include the Version of Record of the article, provided it is not then shared or deposited online. User must include citation details. Where User wishes to share their thesis or dissertation online, they should remove the Version of Record before uploading it. User may include a Preprint or the Accepted Manuscript (after the embargo period) in the online version of the thesis or dissertation, provided they do so in accordance with the Rightsholder's policies on sharing Preprints or Accepted Manuscripts. User may need to obtain separate permission for any third party content included within the article. User must check this with the copyright owner of such third party content. Any online or commercial use of User's thesis or dissertation containing the article, including publication via ProQuest, would need to be expressly notified in writing to the Rightsholder at the time of request and would require separate written permission from the Rightsholder. As well as CCC, the Rightsholder shall have the right to bring any legal action that it deems necessary to enforce its rights should it consider that the Work infringes those rights

in any way. For content reuse requests that qualify for permission under the STM Permissions Guidelines, which may be updated from time to time, the STM Permissions Guidelines supplement the terms and conditions contained in this license.

Marketplace Order General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on

duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) **Books and Records; Right to Audit.** As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content**, which grants authorizations to import requested material in electronic format, and allows electronic access to this material

to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Confirmation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and

- o a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any

such resizing, reformatting, resolution modification or “clipping” does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) Miscellaneous.

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Nov 03, 2022

This Agreement between Alex Baranovsky ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	5412681503944
License date	Oct 19, 2022
Licensed Content Publisher	Elsevier
Licensed Content Publication	Sensors and Actuators A: Physical
Licensed Content Title	Fast circuit breaker based on integration of Al/CuO nanothermites
Licensed Content Author	Andréa Nicollet,Ludovic Salvagnac,Vincent Baijot,Alain Estève,Carole Rossi
Licensed Content Date	Apr 15, 2018
Licensed Content Volume	273
Licensed Content Issue	n/a
Licensed Content Pages	7
Start Page	249
End Page	255

Type of Use	reuse in a thesis/dissertation
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Title	Student
Institution name	University of Waterloo
Expected presentation date	Oct 2022
Portions	Figure 4
Requestor Location	Alex Baranovsky 200 University Ave W Waterloo, ON N2L 3G1 Canada Attn: Alex Baranovsky
Publisher Tax ID	GB 494 6272 12
Total	0.00 CAD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions

apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier's permissions helpdesk [here](#)). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following

clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. For journal authors: the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
 - via their non-commercial person homepage or blog
 - by updating a preprint in arXiv or RePEc with the accepted manuscript
 - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
 - directly by providing copies to their students or to research collaborators for their personal use
 - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- After the embargo period
 - via non-commercial hosting platforms such as their institutional repository
 - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.

Policies for sharing publishing journal articles differ for subscription and gold open access articles:

Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.

Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.

Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a [CrossMark logo](#), the end user license, and a DOI link to the formal publication on ScienceDirect.

Please refer to Elsevier's [posting policy](#) for further information.

18. For book authors the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

19. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our [open access license policy](#) for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by/4.0>.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-sa/4.0>.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at <http://creativecommons.org/licenses/by-nc-nd/4.0>. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. Other Conditions:

v1.10

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

JOHN WILEY AND SONS LICENSE
TERMS AND CONDITIONS

Nov 03, 2022

This Agreement between Alex Baranovsky ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	5412690427975
License date	Oct 19, 2022
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Propellants, Explosives, Pyrotechnics
Licensed Content Title	Influence of Stoichiometry on the Thrust and Heat Deposition of On-Chip Nanothermites
Licensed Content Author	Steven F. Son, Ibrahim E. Gunduz, Jeffrey F. Rhoads, et al
Licensed Content Date	Jan 29, 2018
Licensed Content Volume	43
Licensed Content Issue	3
Licensed Content Pages	9

Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title	Student
Institution name	University of Waterloo
Expected presentation date	Oct 2022
Portions	Figure 8
Requestor Location	Alex Baranovsky 200 University Ave W Waterloo, ON N2L 3G1 Canada Attn: Alex Baranovsky
Publisher Tax ID	EU826007151
Total	0.00 CAD
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.
- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. **For STM Signatory Publishers clearing permission under the terms of the [STM Permissions Guidelines](#) only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts**, You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right,

license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.
- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.
- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.
- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.
- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\) License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License](#) (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library
<http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

This is a License Agreement between Alex Baranovsky ("User") and Copyright Clearance Center, Inc. ("CCC") on behalf of the Rightsholder identified in the order details below. The license consists of the order details, the Marketplace Order General Terms and Conditions below, and any Rightsholder Terms and Conditions which are included below.

All payments must be made in full to CCC in accordance with the Marketplace Order General Terms and Conditions below.

Order Date	03-Nov-2022	Type of Use	Republish in a thesis/dissertation
Order License ID	1281153-2	Publisher	Begell House Inc. Publishers
ISSN	2150-766X	Portion	Image/photo/illustration

LICENSED CONTENT

Publication Title	International journal of energetic materials and chemical propulsion	Country	United States of America
Date	01/01/1991	Rightsholder	Begell House Inc., Publishers
Language	English	Publication Type	Journal

REQUEST DETAILS

Portion Type	Image/photo/illustration	Distribution	Canada
Number of Images / Photos / Illustrations	1	Translation	Original language of publication
Format (select all that apply)	Electronic	Copies for the Disabled?	No
Who Will Republish the Content?	Academic institution	Minor Editing Privileges?	No
Duration of Use	Life of current edition	Incidental Promotional Use?	No
Lifetime Unit Quantity	Up to 499	Currency	CAD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Master's Thesis	Institution Name	University of Waterloo
Instructor Name	Dr. John Wen	Expected Presentation Date	2022-11-03

ADDITIONAL DETAILS

Order Reference Number	N/A	The Requesting Person/Organization to Appear on the License	Alex Baranovsky
-------------------------------	-----	--	-----------------

REUSE CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Fine patterning of thermites for mechanistic studies and microenergetic applications	Title of the Article/Chapter the Portion Is From	N/A
Editor of Portion(s)	N/A	Author of Portion(s)	N/A
Volume of Serial or Monograph	N/A	Issue, if Republishing an Article From a Serial	N/A
Page or Page Range of Portion	522	Publication Date of Portion	2013-01-01

RIGHTSHOLDER TERMS AND CONDITIONS

User is responsible for identifying and seeking separate licenses (under this service or otherwise) for, any of such third party materials which are identified anywhere in the works by permission without a separate license, such third party materials may not be used.

Marketplace Order General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER

WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) Additional Terms for Specific Products and Services. If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the

numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content**, which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text**, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content**, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Confirmation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) *Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).* For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republishing date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) Miscellaneous.

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Small-Scale, Self-Propagating Combustion Realized with On-Chip Porous Silicon



Author: Nicholas W. Piekiet, Christopher J. Morris

Publication: Applied Materials

Publisher: American Chemical Society

Date: May 1, 2015

Copyright © 2015, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms and Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from {COMPLETE REFERENCE CITATION}. Copyright {YEAR} American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your RightsLink request. No additional uses are granted (such as derivative works or other editions). For any uses, please submit a new request.

If credit is given to another source for the material you requested from RightsLink, permission must be obtained from that source.

[BACK](#)

[CLOSE WINDOW](#)



Evaporation Driven Assembly of On-Chip Thermite Devices

Author: Matthew H. Ervin

Publication: Journal of Microelectromechanical Systems

Publisher: IEEE

Date: December 2017

Copyright © 2017, IEEE

Thesis / Dissertation Reuse

The IEEE does not require individuals working on a thesis to obtain a formal reuse license, however, you may print out this statement to be used as a permission grant:

Requirements to be followed when using any portion (e.g., figure, graph, table, or textual material) of an IEEE copyrighted paper in a thesis:

- 1) In the case of textual material (e.g., using short quotes or referring to the work within these papers) users must give full credit to the original source (author, paper, publication) followed by the IEEE copyright line © 2011 IEEE.
- 2) In the case of illustrations or tabular material, we require that the copyright line © [Year of original publication] IEEE appear prominently with each reprinted figure and/or table.
- 3) If a substantial portion of the original paper is to be used, and if you are not the senior author, also obtain the senior author's approval.

Requirements to be followed when using an entire IEEE copyrighted paper in a thesis:

- 1) The following IEEE copyright/ credit notice should be placed prominently in the references: © [year of original publication] IEEE. Reprinted, with permission, from [author names, paper title, IEEE publication title, and month/year of publication]
- 2) Only the accepted version of an IEEE copyrighted paper can be used when posting the paper or your thesis online.
- 3) In placing the thesis on the author's university website, please display the following message in a prominent place on the website: In reference to IEEE copyrighted material which is used with permission in this thesis, the IEEE does not endorse any of [university/educational entity's name goes here]'s products or services. Internal or personal use of this material is permitted. If interested in reprinting/republishing IEEE copyrighted material for advertising or promotional purposes or for creating new collective works for resale or redistribution, please go to http://www.ieee.org/publications_standards/publications/rights/rights_link.html to learn how to obtain a License from RightsLink.

If applicable, University Microfilms and/or ProQuest Library, or the Archives of Canada may supply single copies of the dissertation.

[BACK](#)

[CLOSE WINDOW](#)

This is a License Agreement between Alex Baranovsky ("User") and Copyright Clearance Center, Inc. ("CCC") on behalf of the Rightsholder identified in the order details below. The license consists of the order details, the Marketplace Order General Terms and Conditions below, and any Rightsholder Terms and Conditions which are included below.

All payments must be made in full to CCC in accordance with the Marketplace Order General Terms and Conditions below.

Order Date	03-Nov-2022	Type of Use	Republish in a thesis/dissertation
Order License ID	1286649-1	Publisher Portion	IOP Publishing
ISSN	1361-6595		Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Plasma Sources Science and Technology	Country	United Kingdom of Great Britain and Northern Ireland
Author/Editor	Institute of Physics (Great Britain)	Rightsholder	IOP Publishing, Ltd
Date	01/01/1996	Publication Type	e-Journal
Language	English	URL	http://iopscience.iop.org/0963-0252

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	Distribution	Canada
Number of Charts / Graphs / Tables / Figures Requested	1	Translation	Original language of publication
Format (select all that apply)	Electronic	Copies for the Disabled?	No
Who Will Republish the Content?	Academic institution	Minor Editing Privileges?	Yes
Duration of Use	Life of current edition	Incidental Promotional Use?	No
Lifetime Unit Quantity	Up to 499	Currency	CAD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Master's Thesis	Institution Name	University of Waterloo
Instructor Name	Dr. John Wen	Expected Presentation Date	2022-11-03

ADDITIONAL DETAILS

Order Reference Number	N/A	The Requesting Person/Organization to Appear on the License	Alex Baranovsky
-------------------------------	-----	--	-----------------

REUSE CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 2	Title of the Article/Chapter the Portion Is From	Characterization of a direct dc-excited discharge in water by optical emission spectroscopy
Editor of Portion(s)	N/A	Author of Portion(s)	Institute of Physics (Great Britain)
Volume of Serial or Monograph	N/A	Issue, if Republishing an Article From a Serial	N/A
Page or Page Range of Portion	3	Publication Date of Portion	2009-03-04

RIGHTSHOLDER TERMS AND CONDITIONS

These special terms and conditions are in addition to the standard terms and conditions for CCC's Republication Service and, together with those standard terms and conditions, govern the use of the Works. As the User you will make all reasonable efforts to contact the author(s) of the article which the Work is to be reused from, to seek consent for your intended use. Contacting one author who is acting expressly as authorised agent for their co-author(s) is acceptable. User will reproduce the following wording prominently alongside the Work: the source of the Work, including author, article title, title of journal, volume number, issue number (if relevant), page range (or first page if this is the only information available) and date of first publication; and a link back to the article (via DOI); and if practicable, and IN ALL CASES for new works published under any of the Creative Commons licences, the words "© IOP Publishing. Reproduced with permission. All rights reserved" Without the express permission of the author(s) and the Rightsholder of the article from which the Work is to be reused, User shall not use it in any way which, in the opinion of the Rightsholder, could: (i) distort or alter the author(s)' original intention(s) and meaning; (ii) be prejudicial to the honour or reputation of the author(s); and/or (iii) imply endorsement by the author(s) and/or the Rightsholder. This licence does not apply to any article which is credited to another source and which does not have the copyright line '© IOP Publishing Ltd'. User must check the copyright line of the article from which the Work is to be reused to check that IOP Publishing Ltd has all the necessary rights to be able to grant permission. User is solely responsible for identifying and obtaining separate licences and permissions from the copyright owner for reuse of any such third party material/figures which the Rightsholder is not the copyright owner of. The Rightsholder shall not reimburse any fees which User pays for a republication license for such third party content. This licence does not apply to any material/figure which is credited to another source in the Rightsholder's publication or has been obtained from a third party. User must check the Version of Record of the article from which the Work is to be reused, to check whether any of the material in the Work is third party material. Third party citations and/or copyright notices and/or permissions statements may not be included in any other version of the article from which the Work is to be reused and so cannot be relied upon by the User. User is solely responsible for identifying and obtaining separate licences and permissions from the copyright owner for reuse of any such third party material/figures where the Rightsholder is not the copyright owner. The Rightsholder shall not reimburse any fees which User pays for a republication license for such third party content. User and CCC acknowledge that the Rightsholder may, from time to time, make changes or additions to these special terms and conditions without express notification, provided that these shall not apply to permissions already secured and paid for by User prior to such change or addition. User acknowledges that the Rightsholder (which includes companies within its group and third parties for whom it publishes its titles) may make use of personal data collected through the service in the course of their business. If User is the author of the Work, User may automatically have the right to reuse it under the rights granted back when User transferred the copyright in the article to the Rightsholder. User should check the copyright form and the relevant author rights policy to check whether permission is required. If User is the author of the Work and does require permission for proposed reuse of the Work, User should select 'Author of requested content' as the Requestor Type. The Rightsholder shall not reimburse any fees which User pays for a republication license. If User is the author of the article which User wishes to reuse in User's thesis or dissertation, the republication licence covers the right to include the Version of Record of the article, provided it is not then shared or deposited online. User must include citation details. Where User wishes to share their thesis or dissertation online, they should remove the Version of Record before uploading it. User may include a Preprint or the Accepted Manuscript (after the embargo period) in the online version of the thesis or dissertation, provided they do so in accordance with the Rightsholder's policies on sharing Preprints or Accepted Manuscripts. User may need to obtain separate permission for any third party content included within the article. User must check this with the copyright owner of such third party content. Any online or commercial use of User's thesis or dissertation containing the article, including publication via ProQuest, would need to be expressly notified in writing to the Rightsholder at the time of request and would require separate written permission from the Rightsholder. As well as CCC, the Rightsholder shall have the right to

bring any legal action that it deems necessary to enforce its rights should it consider that the Work infringes those rights in any way. For content reuse requests that qualify for permission under the STM Permissions Guidelines, which may be updated from time to time, the STM Permissions Guidelines supplement the terms and conditions contained in this license.

Marketplace Order General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-

transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) Third Party Materials. In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) Copyright Notice. Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) Indemnity. User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) Limitation of Liability. UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) Limited Warranties. THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) Effect of Breach. Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) **Books and Records; Right to Audit.** As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content**, which grants authorizations to import requested material in electronic format, and allows electronic access to this material

to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Confirmation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and

- o a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

- i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;
- ii) the input of Works or reproductions thereof into any computerized database;
- iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;
- iv) reproduction for resale to anyone other than a specific customer of User;
- v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

- i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.
- ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any

such resizing, reformatting, resolution modification or “clipping” does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) Miscellaneous.

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

JOHN WILEY AND SONS LICENSE TERMS AND CONDITIONS

Nov 03, 2022

This Agreement between Alex Baranovsky ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	5421431440686
License date	Nov 03, 2022
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Propellants, Explosives, Pyrotechnics
Licensed Content Title	On AIO Emission Spectroscopy as a Diagnostic in Energetic Materials Testing
Licensed Content Author	Nick Glumac, Herman Krier, Patrick Lynch, et al
Licensed Content Date	Feb 11, 2013
Licensed Content Volume	38
Licensed Content Issue	4
Licensed Content Pages	9
Type of Use	Dissertation/Thesis
Requestor type	University/Academic
Format	Electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title	Student
Institution name	University of Waterloo
Expected presentation date	Nov 2022
Portions	Figure 1
Requestor Location	Alex Baranovsky 200 University Ave W Waterloo, ON N2L 3G1 Canada Attn: Alex Baranovsky
Publisher Tax ID	EU826007151
Total	0.00 CAD
Terms and Conditions	

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a "Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at <http://myaccount.copyright.com>).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.

- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order**, is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.
- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner. **For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts**, You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.
- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto
- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.
- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.
- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.
- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.
- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.
- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or

excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.
- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.
- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.
- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.
- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.
- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The [Creative Commons Attribution License \(CC-BY\)](#) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The [Creative Commons Attribution Non-Commercial \(CC-BY-NC\) License](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The [Creative Commons Attribution Non-Commercial-NoDerivs License \(CC-BY-NC-ND\)](#) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Use by commercial "for-profit" organizations

Use of Wiley Open Access articles for commercial, promotional, or marketing purposes requires further explicit permission from Wiley and will be subject to a fee.

Further details can be found on Wiley Online Library <http://olabout.wiley.com/WileyCDA/Section/id-410895.html>

Other Terms and Conditions:

v1.10 Last updated September 2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

This is a License Agreement between Alex Baranovsky ("User") and Copyright Clearance Center, Inc. ("CCC") on behalf of the Rightsholder identified in the order details below. The license consists of the order details, the Marketplace Order General Terms and Conditions below, and any Rightsholder Terms and Conditions which are included below.

All payments must be made in full to CCC in accordance with the Marketplace Order General Terms and Conditions below.

Order Date	03-Nov-2022	Type of Use	Republish in a thesis/dissertation
Order License ID	1286562-1	Publisher Portion	IOP Publishing
ISSN	1361-6595		Chart/graph/table/figure

LICENSED CONTENT

Publication Title	Plasma Sources Science and Technology	Country	United Kingdom of Great Britain and Northern Ireland
Author/Editor	Institute of Physics (Great Britain)	Rightsholder	IOP Publishing, Ltd
Date	01/01/1996	Publication Type	e-Journal
Language	English	URL	http://iopscience.iop.org/0963-0252

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	Distribution	Worldwide
Number of Charts / Graphs / Tables / Figures Requested	1	Translation	Original language of publication
Format (select all that apply)	Electronic	Copies for the Disabled?	No
Who Will Republish the Content?	Academic institution	Minor Editing Privileges?	Yes
Duration of Use	Life of current edition	Incidental Promotional Use?	No
Lifetime Unit Quantity	Up to 499	Currency	CAD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Master's Thesis	Institution Name	University of Waterloo
Instructor Name	Dr. John Wen	Expected Presentation Date	2022-11-03

ADDITIONAL DETAILS

Order Reference Number	N/A	The Requesting Person/Organization to Appear on the License	Alex Baranovsky
-------------------------------	-----	--	-----------------

REUSE CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	DC-excited discharges in vapour bubbles in capillaries	Title of the Article/Chapter the Portion Is From	N/A
Editor of Portion(s)	N/A	Author of Portion(s)	Institute of Physics (Great Britain)
Volume of Serial or Monograph	N/A	Issue, if Republishing an Article From a Serial	N/A
Page or Page Range of Portion	5	Publication Date of Portion	2008-03-10

RIGHTSHOLDER TERMS AND CONDITIONS

These special terms and conditions are in addition to the standard terms and conditions for CCC's Republication Service and, together with those standard terms and conditions, govern the use of the Works. As the User you will make all reasonable efforts to contact the author(s) of the article which the Work is to be reused from, to seek consent for your intended use. Contacting one author who is acting expressly as authorised agent for their co-author(s) is acceptable. User will reproduce the following wording prominently alongside the Work: the source of the Work, including author, article title, title of journal, volume number, issue number (if relevant), page range (or first page if this is the only information available) and date of first publication; and a link back to the article (via DOI); and if practicable, and IN ALL CASES for new works published under any of the Creative Commons licences, the words "© IOP Publishing. Reproduced with permission. All rights reserved" Without the express permission of the author(s) and the Rightsholder of the article from which the Work is to be reused, User shall not use it in any way which, in the opinion of the Rightsholder, could: (i) distort or alter the author(s)' original intention(s) and meaning; (ii) be prejudicial to the honour or reputation of the author(s); and/or (iii) imply endorsement by the author(s) and/or the Rightsholder. This licence does not apply to any article which is credited to another source and which does not have the copyright line '© IOP Publishing Ltd'. User must check the copyright line of the article from which the Work is to be reused to check that IOP Publishing Ltd has all the necessary rights to be able to grant permission. User is solely responsible for identifying and obtaining separate licences and permissions from the copyright owner for reuse of any such third party material/figures which the Rightsholder is not the copyright owner of. The Rightsholder shall not reimburse any fees which User pays for a republication license for such third party content. This licence does not apply to any material/figure which is credited to another source in the Rightsholder's publication or has been obtained from a third party. User must check the Version of Record of the article from which the Work is to be reused, to check whether any of the material in the Work is third party material. Third party citations and/or copyright notices and/or permissions statements may not be included in any other version of the article from which the Work is to be reused and so cannot be relied upon by the User. User is solely responsible for identifying and obtaining separate licences and permissions from the copyright owner for reuse of any such third party material/figures where the Rightsholder is not the copyright owner. The Rightsholder shall not reimburse any fees which User pays for a republication license for such third party content. User and CCC acknowledge that the Rightsholder may, from time to time, make changes or additions to these special terms and conditions without express notification, provided that these shall not apply to permissions already secured and paid for by User prior to such change or addition. User acknowledges that the Rightsholder (which includes companies within its group and third parties for whom it publishes its titles) may make use of personal data collected through the service in the course of their business. If User is the author of the Work, User may automatically have the right to reuse it under the rights granted back when User transferred the copyright in the article to the Rightsholder. User should check the copyright form and the relevant author rights policy to check whether permission is required. If User is the author of the Work and does require permission for proposed reuse of the Work, User should select 'Author of requested content' as the Requestor Type. The Rightsholder shall not reimburse any fees which User pays for a republication license. If User is the author of the article which User wishes to reuse in User's thesis or dissertation, the republication licence covers the right to include the Version of Record of the article, provided it is not then shared or deposited online. User must include citation details. Where User wishes to share their thesis or dissertation online, they should remove the Version of Record before uploading it. User may include a Preprint or the Accepted Manuscript (after the embargo period) in the online version of the thesis or dissertation, provided they do so in accordance with the Rightsholder's policies on sharing Preprints or Accepted Manuscripts. User may need to obtain separate permission for any third party content included within the article. User must check this with the copyright owner of such third party content. Any online or commercial use of User's thesis or dissertation containing the article, including publication via ProQuest, would need to be expressly notified in writing to the Rightsholder at the time of request and would require separate written permission from the Rightsholder. As well as CCC, the Rightsholder shall have the right to bring any legal action that it deems necessary to enforce its rights should it consider that the Work infringes those rights

in any way. For content reuse requests that qualify for permission under the STM Permissions Guidelines, which may be updated from time to time, the STM Permissions Guidelines supplement the terms and conditions contained in this license.

Marketplace Order General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on

duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is defamatory, violates the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) **Books and Records; Right to Audit.** As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content**, which grants authorizations to import requested material in electronic format, and allows electronic access to this material

to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content, which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Confirmation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and

- o a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

- i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;
- ii) the input of Works or reproductions thereof into any computerized database;
- iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;
- iv) reproduction for resale to anyone other than a specific customer of User;
- v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

- i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.
- ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any

such resizing, reformatting, resolution modification or “clipping” does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) Miscellaneous.

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

References

- [1] T. M. Klapötke, "2. Classification of Energetic Materials," in *Chemistry of High-Energy Materials*, 2012, pp. 33–78. doi: 10.1515/9783110624571-002.
- [2] M. Comet, C. Martin, F. Schnell, and D. Spitzer, "Nanothermites: A short Review. Factsheet for Experimenters, Present and Future Challenges," *Propellants, Explosives, Pyrotechnics*, vol. 44, no. 1, pp. 18–36, 2019, doi: 10.1002/prep.201800095.
- [3] William Gurstelle, "Hans Goldschmidt and the Invention of Thermite," in *ReMaking History, Volume 3*, First Edit., R. Stewart, Ed. San Francisco: Maker Media, 2017.
- [4] B. Schwartz, N. Southern, and R. Company, "Thermite Welding," vol. 6, pp. 291–293, 1933, doi: 10.1361/asmhba000.
- [5] S. H. Fischer and M. H. Grubelich, "A survey of combustible metals, thermites, and intermetallics for pyrotechnic applications," in *32nd AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, 1996.
- [6] C. Yu *et al.*, "The super-hydrophobic thermite film of the Co_3O_4 / Al core / shell nanowires for an underwater ignition with a favorable aging-resistance," *Chemical Engineering Journal*, vol. 338, no. September 2017, pp. 99–106, 2018, doi: 10.1016/j.cej.2017.12.129.
- [7] Y. Meir and E. Jerby, "Underwater microwave ignition of hydrophobic thermite powder enabled by the bubble-marble effect," *Appl Phys Lett*, vol. 107, no. 5, pp. 5–8, 2015, doi: 10.1063/1.4928110.
- [8] E. Nixon, M. L. Pantoya, G. Sivakumar, A. Vijayasai, and T. Dallas, "Effect of a superhydrophobic coating on the combustion of aluminium and iron oxide nanothermites," *Surf Coat Technol*, vol. 205, no. 21–22, pp. 5103–5108, 2011, doi: 10.1016/j.surfcoat.2011.05.014.
- [9] H. Zhang *et al.*, "Electrophoretic Deposition of Superhydrophobic Al / Fe_2O_3 Nanothermite with Long – Term Storage Stability," vol. 15, pp. 5133–5143, 2020, doi: 10.20964/2020.06.21.
- [10] D. S. Hacker, "Thermodynamic Performance Evaluation of a Hydroduct Using a Thermite Fuel," vol. 3, no. 3, pp. 139–144, 1969.

- [11] J. H. Kim *et al.*, “Flash-ignitable nanoenergetic materials with tunable underwater explosion reactivity: The role of sea urchin-like carbon nanotubes,” *Combust Flame*, vol. 162, no. 4, pp. 1448–1454, Apr. 2015, doi: 10.1016/j.combustflame.2014.11.011.
- [12] S. C. Stacy, M. L. Pantoya, D. J. Prentic, E. D. Steffer, and M. A. Daniels, “Nanocomposites for underwater deflagration,” *Advanced Materials & Processes*, pp. 33–35, 2009.
- [13] E. Koch and S. Knapp, “Thermites – Versatile Materials,” *Propellants, Explosives, Pyrotechnics*, vol. 44, no. 1, pp. 7–7, Jan. 2019, doi: 10.1002/prep.201980131.
- [14] D. Sundaram, V. Yang, and R. A. Yetter, “Metal-based nanoenergetic materials: Synthesis, properties, and applications,” *Prog Energy Combust Sci*, vol. 61, pp. 293–365, 2017, doi: 10.1016/j.pecs.2017.02.002.
- [15] F. Saceleanu, “Heterogeneous Reactions of Micro and Nano Aluminum Particles with Various Oxidizers,” University of Waterloo, 2019.
- [16] S. Fischer and M. Grubelich, “Theoretical energy release of thermites, intermetallics, and combustible metals,” 1998. [Online]. Available: <http://journals.pepublishing.com/openurl.asp?genre=article&id=doi:10.1243/09544097F01505>
- [17] S. Bhattacharya, A. K. Agarwal, T. Rajagopalan, and V. K. Patel, Eds., *Nano-Energetic Materials*. Singapore: Springer Singapore, 2019. doi: 10.1007/978-981-13-3269-2.
- [18] E. Lafontaine and M. Comet, *Nanothermites*. Hoboken, NJ: John Wiley & Sons, 2016. doi: 10.1002/9781119283553.
- [19] M. L. Pantoya and J. J. Granier, “Combustion behavior of highly energetic thermites: Nano versus micron composites,” *Propellants, Explosives, Pyrotechnics*, vol. 30, no. 1, pp. 53–62, 2005, doi: 10.1002/prep.200400085.
- [20] A. Fahd, A. Baranovsky, C. Dubois, J. Chaouki, and J. Z. Wen, “Superior performance of quaternary NC/GO/Al/KClO₄ nanothermite for high speed impulse small-scale propulsion applications,” *Combust Flame*, vol. 232, p. 111527, 2021, doi: 10.1016/j.combustflame.2021.111527.

- [21] D. T. Osborne and M. L. Pantoya, "Effect of al particle size on the thermal degradation of Al/teflon mixtures," *Combustion Science and Technology*, vol. 179, no. 8, pp. 1467–1480, Jul. 2007, doi: 10.1080/00102200601182333.
- [22] Y. Hu *et al.*, "Fabrication and mechanistic study of AP/nAl/PTFE spherical encapsulated energetic materials with enhanced combustion performance," *Chem Eng Sci*, vol. 222, p. 115701, Aug. 2020, doi: 10.1016/j.ces.2020.115701.
- [23] J. Ji *et al.*, "Facile solvent evaporation synthesis of core-shell structured Al@PVDF nanoparticles with excellent corrosion resistance and combustion properties," *Combust Flame*, vol. 238, p. 111925, Apr. 2022, doi: 10.1016/j.combustflame.2021.111925.
- [24] Z. yang Wu *et al.*, "Enhanced thermal- and impact-initiated reactions of PTFE/Al energetic materials through ultrasonic-assisted core-shell construction," *Defence Technology*, vol. 18, no. 8, pp. 1362–1368, 2022, doi: 10.1016/j.dt.2021.08.003.
- [25] T. Wu, X. Wang, J. B. DeLisio, S. Holdren, and M. R. Zachariah, "Carbon addition lowers initiation and iodine release temperatures from iodine oxide-based biocidal energetic materials," *Carbon N Y*, vol. 130, pp. 410–415, Apr. 2018, doi: 10.1016/j.carbon.2018.01.001.
- [26] M. Zhang, H. Ren, Q. Cui, H. Li, and Y. Chen, "Effects of Different Nanocarbon Materials on the Properties of Al/MoO₃/NCM Thermite Prepared by Electrostatic Spinning," *Nanomaterials*, vol. 12, no. 4, p. 635, Feb. 2022, doi: 10.3390/nano12040635.
- [27] R. Thiruvengadathan *et al.*, "Enhanced Combustion Characteristics of Bismuth Trioxide-Aluminum Nanocomposites Prepared through Graphene Oxide Directed Self-Assembly," *Propellants, Explosives, Pyrotechnics*, vol. 40, no. 5, pp. 729–734, Oct. 2015, doi: 10.1002/prep.201400238.
- [28] A. Wang *et al.*, "Reactive nanoenergetic graphene aerogel synthesized by one-step chemical reduction," *Combust Flame*, vol. 196, pp. 400–406, Oct. 2018, doi: 10.1016/j.combustflame.2018.06.034.

- [29] D. L. Hastings and E. L. Dreizin, "Reactive Structural Materials: Preparation and Characterization," *Adv Eng Mater*, vol. 20, no. 3, p. 1700631, Mar. 2018, doi: 10.1002/adem.201700631.
- [30] M. C. Rehwoldt *et al.*, "Ignition and combustion analysis of direct write fabricated aluminum/metal oxide/PVDF films," *Combust Flame*, vol. 211, pp. 260–269, Jan. 2020, doi: 10.1016/j.combustflame.2019.08.023.
- [31] K. Meeks, M. L. Pantoya, and C. Apblett, "Deposition and characterization of energetic thin films," *Combust Flame*, vol. 161, no. 4, pp. 1117–1124, Apr. 2014, doi: 10.1016/j.combustflame.2013.10.027.
- [32] X. Li, P. Guerieri, W. Zhou, C. Huang, and M. R. Zachariah, "Direct Deposit Laminate Nanocomposites with Enhanced Propellant Properties," *ACS Appl Mater Interfaces*, vol. 7, no. 17, pp. 9103–9109, May 2015, doi: 10.1021/acsami.5b00891.
- [33] K. J. Kim, M. H. Cho, J. H. Kim, and S. H. Kim, "Effect of paraffin wax on combustion properties and surface protection of Al/CuO-based nanoenergetic composite pellets," *Combust Flame*, vol. 198, pp. 169–175, Dec. 2018, doi: 10.1016/j.combustflame.2018.09.010.
- [34] C. S. Staley *et al.*, "Fast-Impulse Nanothermite Solid-Propellant Miniaturized Thrusters," *J Propuls Power*, vol. 29, no. 6, pp. 1400–1409, Nov. 2013, doi: 10.2514/1.B34962.
- [35] E. Collins, M. Pantoya, A. Vijayasai, and T. Dallas, "Comparison of engineered nanocoatings on the combustion of aluminum and copper oxide nanothermites," *Surf Coat Technol*, vol. 215, pp. 476–484, Jan. 2013, doi: 10.1016/j.surfcoat.2012.07.094.
- [36] F. Saceleanu, M. Idir, N. Chaumeix, and J. Z. Wen, "Combustion Characteristics of Physically Mixed 40 nm Aluminum/Copper Oxide Nanothermites Using Laser Ignition," *Front Chem*, vol. 6, no. SEP, pp. 1–10, Oct. 2018, doi: 10.3389/fchem.2018.00465.
- [37] L. LeSergent, "Tailoring the Ignition and Reaction Properties of Cu₂O Thermite Nanolaminates," University of Waterloo, 2018.

- [38] Y. Zhang, H. Sui, Y. Li, and J. Z. Wen, "Energetic characteristics of the Al/CuO core-shell composite micro-particles fabricated as spherical colloids," *Thermochim Acta*, vol. 689, no. December 2019, p. 178656, 2020, doi: 10.1016/j.tca.2020.178656.
- [39] N. W. Piekiet and C. J. Morris, "Small-Scale, Self-Propagating Combustion Realized with On-Chip Porous Silicon," *ACS Appl Mater Interfaces*, vol. 7, no. 18, pp. 9889–9897, May 2015, doi: 10.1021/acsami.5b01964.
- [40] H. Sui, L. LeSergent, and J. Z. Wen, "Diversity in Addressing Reaction Mechanisms of Nano-Thermite Composites with a Layer by Layer Structure," *Adv Eng Mater*, vol. 20, no. 3, p. 1700822, Mar. 2018, doi: 10.1002/adem.201700822.
- [41] M. Polis, A. Stolarczyk, K. Glosz, and T. Jarosz, "Quo Vadis, Nanothermite? A Review of Recent Progress," *Materials*, vol. 15, no. 9, p. 3215, Apr. 2022, doi: 10.3390/ma15093215.
- [42] X. Zhou, M. Torabi, J. Lu, R. Shen, and K. Zhang, "Nanostructured Energetic Composites: Synthesis, Ignition/Combustion Modeling, and Applications," *ACS Appl Mater Interfaces*, vol. 6, no. 5, pp. 3058–3074, Mar. 2014, doi: 10.1021/am4058138.
- [43] L. Qin, T. Gong, H. Hao, K. Wang, and H. Feng, "Core-shell-structured nanothermites synthesized by atomic layer deposition," *Journal of Nanoparticle Research*, vol. 15, no. 12, p. 2150, Dec. 2013, doi: 10.1007/s11051-013-2150-z.
- [44] Q. Wang *et al.*, "Facile fabrication of highly exothermic CuO@Al nanothermites via self-assembly approach," *Nanotechnology*, vol. 31, no. 5, p. 055601, Jan. 2020, doi: 10.1088/1361-6528/ab4ed0.
- [45] X. Ke *et al.*, "Tuning the Reactivity of Al/NiO@C Nanoenergetic Materials through Building an Interfacial Carbon Barrier Layer," *ACS Appl Mater Interfaces*, vol. 11, no. 38, pp. 35394–35403, Sep. 2019, doi: 10.1021/acsami.9b09723.
- [46] X. Ke *et al.*, "Superhydrophobic Fluorine-Containing Protective Coating to Endow Al Nanoparticles with Long-Term Storage Stability and Self-Activation Reaction Capability," *Adv Mater Interfaces*, vol. 6, no. 19, p. 1901025, Oct. 2019, doi: 10.1002/admi.201901025.

- [47] Y. Wang *et al.*, "Thermite reactions of Al/Cu core-shell nanocomposites with WO₃," *Thermochim Acta*, vol. 463, no. 1–2, pp. 69–76, Oct. 2007, doi: 10.1016/j.tca.2007.07.017.
- [48] X. Ma, Y. Li, I. Hussain, R. Shen, G. Yang, and K. Zhang, "Core–Shell Structured Nanoenergetic Materials: Preparation and Fundamental Properties," *Advanced Materials*, vol. 32, no. 30, p. 2001291, Jul. 2020, doi: 10.1002/adma.202001291.
- [49] A. Chen *et al.*, "Pushing the Limits of Energy Performance in Micron-Sized Thermite: Core–Shell Assembled Liquid Metal-Modified Al@Fe₂O₃ Thermites," *ACS Appl Energy Mater*, vol. 4, no. 10, pp. 11777–11786, Oct. 2021, doi: 10.1021/acsaem.1c02549.
- [50] K. Xue, H. Li, L. Pan, Y. Liu, X. Zhang, and J.-J. Zou, "Bifunctional core-shell nAl@MOF energetic particles with enhanced ignition and combustion performance," *Chemical Engineering Journal*, vol. 430, no. P2, p. 132909, Feb. 2022, doi: 10.1016/j.cej.2021.132909.
- [51] K. Shi *et al.*, "Alcohol-thermal synthesis of approximately core-shell structured Al@CuO nanothermite with improved heat-release and combustion characteristics," *Combust Flame*, vol. 228, pp. 331–339, Jun. 2021, doi: 10.1016/j.combustflame.2021.02.008.
- [52] Y. Chen, W. Zhang, C. Yu, D. Ni, K. Ma, and J. Ye, "Controllable synthesis of NiCo₂O₄/Al core-shell nanowires thermite film with excellent heat release and short ignition time," *Mater Des*, vol. 155, pp. 396–403, 2018, doi: 10.1016/j.matdes.2018.06.025.
- [53] C. Yu *et al.*, "A facile preparation and energetic characteristics of the core/shell CoFe₂O₄/Al nanowires thermite film," *Micromachines (Basel)*, vol. 11, no. 5, p. 516, May 2020, doi: 10.3390/mi11050516.
- [54] X. Zhou *et al.*, "Highly Exothermic and Superhydrophobic Mg/Fluorocarbon Core/Shell Nanoenergetic Arrays," *ACS Appl Mater Interfaces*, vol. 6, no. 13, pp. 10497–10505, Jul. 2014, doi: 10.1021/am502078e.
- [55] Y. Wang *et al.*, "Fabrication of energetic aluminum core/hydrophobic shell nanofibers via coaxial electrospinning," *Chemical Engineering Journal*, vol. 427, no. June 2021, p. 132001, Jan. 2022, doi: 10.1016/j.cej.2021.132001.

- [56] Y. Zhu, X. Zhou, C. Wu, H. Cheng, Z. Lu, and K. Zhang, "Si Wire Supported MnO₂/Al/Fluorocarbon 3D Core/Shell Nanoenergetic Arrays with Long-Term Storage Stability," *Sci Rep*, vol. 7, no. 1, p. 6678, Dec. 2017, doi: 10.1038/s41598-017-07148-1.
- [57] J.-L. Pouchairet and C. Rossi, "PyroMEMS as Future Technological Building Blocks for Advanced Microenergetic Systems," *Micromachines (Basel)*, vol. 12, no. 2, p. 118, Jan. 2021, doi: 10.3390/mi12020118.
- [58] C. Rossi, K. Zhang, D. Esteve, P. Alphonse, P. Tailhades, and C. Vahlas, "Nanoenergetic Materials for MEMS: A Review," *Journal of Microelectromechanical Systems*, vol. 16, no. 4, pp. 919–931, Aug. 2007, doi: 10.1109/JMEMS.2007.893519.
- [59] C. Rossi and D. Estève, "Micropyrotechnics, a new technology for making energetic microsystems: review and prospective," *Sens Actuators A Phys*, vol. 120, no. 2, pp. 297–310, May 2005, doi: 10.1016/j.sna.2005.01.025.
- [60] J. J. Allen, *Micro Electro Mechanical System Design*. Boca Raton: Taylor & Francis, 2005. doi: 10.1201/9781420027754.
- [61] M. Kaisti *et al.*, "Clinical assessment of a non-invasive wearable MEMS pressure sensor array for monitoring of arterial pulse waveform, heart rate and detection of atrial fibrillation," *NPJ Digit Med*, vol. 2, no. 1, p. 39, Dec. 2019, doi: 10.1038/s41746-019-0117-x.
- [62] G. A. Ardila Rodríguez *et al.*, "A microactuator based on the decomposition of an energetic material for disposable lab-on-chip applications: fabrication and test," *Journal of Micromechanics and Microengineering*, vol. 19, no. 1, p. 015006, Jan. 2009, doi: 10.1088/0960-1317/19/1/015006.
- [63] A. Nicollet, L. Salvagnac, V. Baijot, A. Estève, and C. Rossi, "Fast circuit breaker based on integration of Al/CuO nanothermites," *Sens Actuators A Phys*, vol. 273, pp. 249–255, Apr. 2018, doi: 10.1016/j.sna.2018.02.044.
- [64] R. Ramachandran, V. S. Vuppuluri, T. J. Fleck, J. F. Rhoads, I. E. Gunduz, and S. F. Son, "Influence of Stoichiometry on the Thrust and Heat Deposition of On-Chip Nanothermites,"

Propellants, Explosives, Pyrotechnics, vol. 43, no. 3, pp. 258–266, Mar. 2018, doi: 10.1002/prop.201700132.

- [65] C. Rossi, D. Estève, P. Temple-Boyer, and G. Delannoy, “Realization, characterization of micro pyrotechnic actuators and FEM modelling of the combustion ignition,” *Sens Actuators A Phys*, vol. 70, no. 1–2, pp. 141–147, Oct. 1998, doi: 10.1016/S0924-4247(98)00136-8.
- [66] C. Rossi, P. Millot, D. Estève, C. Mikler, and E. Teillaud, “Miniature Valve for Filling the Reservoir of an Apparatus for the Transdermal Administration of Medicine,” WO 98/22719, 1998
- [67] M. Korampally *et al.*, “Transient pressure mediated intranuclear delivery of FITC-Dextran into chicken cardiomyocytes by MEMS-based nanothermite reaction actuator,” *Sens Actuators B Chem*, vol. 171–172, pp. 1292–1296, 2012, doi: 10.1016/j.snb.2012.06.081.
- [68] P. Pennarun, C. Rossi, D. Esteve, and V. Conedera, “Development of MEMS based safe electro-thermal pyrotechnic igniter for a new generation of microfuze,” *Smart Sensors, Actuators, and MEMS II*, vol. 5836, no. July 2005, pp. 558–569, 2005, doi: 10.1117/12.608082.
- [69] P. Pennarun, C. Rossi, D. Estève, and D. Bourrier, “Design, fabrication and characterization of a MEMS safe pyrotechnical igniter integrating arming, disarming and sterilization functions,” *Journal of Micromechanics and Microengineering*, vol. 16, no. 1, pp. 92–100, Jan. 2006, doi: 10.1088/0960-1317/16/1/013.
- [70] A. M. de Aragón, “Space applications of micro/nano-technologies,” *Journal of Micromechanics and Microengineering*, vol. 8, no. 2, pp. 54–56, Jun. 1998, doi: 10.1088/0960-1317/8/2/003.
- [71] A. R. Tummala and A. Dutta, “An Overview of Cube-Satellite Propulsion Technologies and Trends,” *Aerospace*, vol. 4, no. 4, p. 58, Dec. 2017, doi: 10.3390/aerospace4040058.
- [72] D. H. Lewis, S. W. Janson, R. B. Cohen, and E. K. Antonsson, “Digital micropropulsion,” *Sens Actuators A Phys*, vol. 80, no. 2, pp. 143–154, Mar. 2000, doi: 10.1016/S0924-4247(99)00260-5.

- [73] B. Larangot, V. Conédéra, P. Dubreuil, T. do Conto, and C. Rossi, "Solid Propellant MicroThruster: an alternative propulsion device for nanosatellite," in *Aerospace Energetic ...*, 2002, vol. 40, no. 5, pp. 24–27. [Online]. Available: [http://www.norlandprod.com/Applicationpages/solidpropellantmicrothruster mems.pdf](http://www.norlandprod.com/Applicationpages/solidpropellantmicrothruster%20mems.pdf)
- [74] W. N. Sawka, A. Katzakian, and C. Grix, "Solid State Digital Propulsion Cluster Thrusters For Small Satellites Using High Performance Electrically Controlled Extinguishable Solid Propellants," in *19th Annual AIAA/USU Conference on Small Satellites*, 2005.
- [75] K. Sathiyathan et al., "Solid Propellant Microthruster Design for Nanosatellite Applications," *J Propuls Power*, vol. 27, no. 6, pp. 1288–1294, Nov. 2011, doi: 10.2514/1.B34109.
- [76] C. Ru et al., "Superior performance of a MEMS-based solid propellant microthruster (SPM) array with nanothermites," *Microsystem Technologies*, vol. 23, no. 8, pp. 3161–3174, Aug. 2017, doi: 10.1007/s00542-016-3159-x.
- [77] C. Rossi, B. Larangot, D. Lagrange, and A. Chaalane, "Final characterizations of MEMS-based pyrotechnical microthrusters," *Sens Actuators A Phys*, vol. 121, no. 2, pp. 508–514, Jun. 2005, doi: 10.1016/j.sna.2005.03.017.
- [78] C. Rossi et al., "Solid Propellant Microthrusters on Silicon: Design, Modeling, Fabrication, and Testing," *Journal of Microelectromechanical Systems*, vol. 15, no. 6, pp. 1805–1815, Dec. 2006, doi: 10.1109/JMEMS.2006.880232.
- [79] S. Romero-Diez, L. Hantsche, J. Pearl, D. Hitt, M. McDevitt, and P. Lee, "A Single-Use Microthruster Concept for Small Satellite Attitude Control in Formation-Flying Applications," *Aerospace*, vol. 5, no. 4, p. 119, Nov. 2018, doi: 10.3390/aerospace5040119.
- [80] A. Trevino, M. A. Hobosyan, I. Davila, K. S. Martirosyan, and S. E. Lyshevski, "Design and Characterization of Thermoplastic Microthrusters With Nanothermite Intermolecular Composites," in *2020 IEEE 40th International Conference on Electronics and Nanotechnology (ELNANO)*, Apr. 2020, pp. 662–666. doi: 10.1109/ELNANO50318.2020.9088782.

- [81] S. J. Apperson *et al.*, "Characterization of nanothermite material for solid-fuel microthruster applications," *J Propuls Power*, vol. 25, no. 5, pp. 1086–1091, 2009, doi: 10.2514/1.43206.
- [82] C. S. Staley *et al.*, "Effect of Nitrocellulose Gasifying Binder on Thrust Performance and High-g Launch Tolerance of Miniaturized Nanothermite Thrusters," *Propellants, Explosives, Pyrotechnics*, vol. 39, no. 3, pp. 374–382, Jun. 2014, doi: 10.1002/prep.201400011.
- [83] M. Hobosyan, K. S. Martirosyan, and S. E. Lyshevski, "Design and Evaluations of 3D-Printed Microthrusters with Nanothermite Propellants," in *2018 IEEE 38th International Conference on Electronics and Nanotechnology (ELNANO)*, Apr. 2018, pp. 478–482. doi: 10.1109/ELNANO.2018.8477521.
- [84] J. Dai *et al.*, "Ammonium Perchlorate as an Effective Additive for Enhancing the Combustion and Propulsion Performance of Al/CuO Nanothermites," *The Journal of Physical Chemistry C*, vol. 122, no. 18, pp. 10240–10247, May 2018, doi: 10.1021/acs.jpcc.8b01514.
- [85] T. Jr. Barbee, R. L. Simpson, A. E. Gash, and J. H. Jr. Satcher, "NANO-LAMINATE-BASED IGNITORS," WO 2005/016850 A2
- [86] G. Taton, D. Lagrange, V. Conedera, L. Renaud, and C. Rossi, "Micro-chip initiator realized by integrating Al/CuO multilayer nanothermite on polymeric membrane," *Journal of Micromechanics and Microengineering*, vol. 23, no. 10, p. 105009, Oct. 2013, doi: 10.1088/0960-1317/23/10/105009.
- [87] J. Y. Ahn *et al.*, "A micro-chip initiator with controlled combustion reactivity realized by integrating Al/CuO nanothermite composites on a microhotplate platform," *Journal of Micromechanics and Microengineering*, vol. 26, no. 1, p. 015002, Jan. 2016, doi: 10.1088/0960-1317/26/1/015002.
- [88] A. Nicollet *et al.*, "Investigation of Al/CuO multilayered thermite ignition," *J Appl Phys*, vol. 121, no. 3, p. 034503, Jan. 2017, doi: 10.1063/1.4974288.
- [89] J. Dai *et al.*, "From nanoparticles to on-chip 3D nanothermite: electrospray deposition of reactive Al/CuO@NC onto semiconductor bridge and its application for rapid ignition," *Nanotechnology*, vol. 31, no. 19, p. 195712, May 2020, doi: 10.1088/1361-6528/ab6fd8.

- [90] T. Hu, Y. Zhao, K. Wang, K. Fang, and W. Ren, "The development of an on-chip microinitiator with a built-in safety-and-arming device," *Review of Scientific Instruments*, vol. 92, no. 2, p. 025007, Feb. 2021, doi: 10.1063/5.0032550.
- [91] L. Glavier *et al.*, "Nanothermite/RDX-Based Miniature Device for Impact Ignition of High Explosives," *Propellants, Explosives, Pyrotechnics*, vol. 42, no. 3, pp. 308–317, Mar. 2017, doi: 10.1002/prep.201600154.
- [92] J. Zhou *et al.*, "Accurate and efficient droplet microfluidic strategy for controlling the morphology of energetic microspheres," *Journal of Energetic Materials*, vol. 00, no. 00, pp. 1–18, Sep. 2021, doi: 10.1080/07370652.2021.1980152.
- [93] M. F. Coelho, M. A. Rivas, G. Vilão, E. M. Nogueira, and T. P. Iglesias, "Permittivity and electrical conductivity of copper oxide nanofluid (12 nm) in water at different temperatures," *J Chem Thermodyn*, vol. 132, pp. 164–173, May 2019, doi: 10.1016/j.jct.2018.12.025.
- [94] X. E. L. Pan, F. Wang, L. Wang, X. Zhang, and J.-J. Zou, "Al-Nanoparticle-Containing Nanofluid Fuel: Synthesis, Stability, Properties, and Propulsion Performance," *Ind Eng Chem Res*, vol. 55, no. 10, pp. 2738–2745, Mar. 2016, doi: 10.1021/acs.iecr.6b00043.
- [95] X. Zhang, L. Pan, L. Wang, and J. J. Zou, "Review on synthesis and properties of high-energy-density liquid fuels: Hydrocarbons, nanofluids and energetic ionic liquids," *Chem Eng Sci*, vol. 180, pp. 95–125, 2018, doi: 10.1016/j.ces.2017.11.044.
- [96] M. R. Mitchell, R. E. Link, M.-J. Kao, C.-C. Ting, B.-F. Lin, and T.-T. Tsung, "Aqueous Aluminum Nanofluid Combustion in Diesel Fuel," *J Test Eval*, vol. 36, no. 2, p. 100579, 2008, doi: 10.1520/JTE100579.
- [97] G. Liu and D. Liu, "Combustion characteristics of nanofluid fuels in a half-opening slot tube," *Sci China Technol Sci*, vol. 60, no. 7, pp. 1075–1087, Jul. 2017, doi: 10.1007/s11431-016-9012-8.
- [98] H. Tyagi *et al.*, "Increased Hot-Plate Ignition Probability for Nanoparticle-Laden Diesel Fuel," *Nano Lett*, vol. 8, no. 5, pp. 1410–1416, May 2008, doi: 10.1021/nl080277d.

- [99] R. N. Mehta, M. Chakraborty, and P. A. Parikh, "Nanofuels: Combustion, engine performance and emissions," *Fuel*, vol. 120, pp. 91–97, Mar. 2014, doi: 10.1016/j.fuel.2013.12.008.
- [100] S. Sharma, "Fabricating an experimental setup to investigate the performance of an automobile car radiator by using aluminum/water nanofluid," *J Therm Anal Calorim*, vol. 133, no. 3, pp. 1387–1406, Sep. 2018, doi: 10.1007/s10973-018-7224-9.
- [101] N. Ali, J. A. Teixeira, and A. Addali, "Aluminium Nanofluids Stability: A Comparison between the Conventional Two-Step Fabrication Approach and the Controlled Sonication Bath Temperature Method," *J Nanomater*, vol. 2019, pp. 1–9, Oct. 2019, doi: 10.1155/2019/3930572.
- [102] J. Petrovic and G. Thomas, "Reaction of Aluminum with Water to Produce Hydrogen: A Study of Issues Related to the Use of Aluminum for On-Board Vehicular Hydrogen Storage," 2008.
- [103] G. Ilyes, Y. Shiwei, and W. Haixing, "Energy generation from metal-water reaction for power systems, underwater and aerospace propulsion applications," in *Proceedings of 2019 16th International Bhurban Conference on Applied Sciences and Technology, IBCAST 2019*, 2019, pp. 49–54. doi: 10.1109/IBCAST.2019.8667177.
- [104] Z.-Y. Deng, J. M. F. Ferreira, and Y. Sakka, "Hydrogen-Generation Materials for Portable Applications," *Journal of the American Ceramic Society*, vol. 91, no. 12, pp. 3825–3834, Dec. 2008, doi: 10.1111/j.1551-2916.2008.02800.x.
- [105] T. Miller and J. Herr, "Green Rocket Propulsion by Reaction of Al and Mg Powders and Water," no. July, pp. 1–10, 2004, doi: 10.2514/6.2004-4037.
- [106] G. A. Risha, S. F. Son, R. A. Yetter, V. Yang, and B. C. Tappan, "Combustion of nano-aluminum and liquid water," *Proceedings of the Combustion Institute*, vol. 31, no. 2, pp. 2029–2036, Jan. 2007, doi: 10.1016/j.proci.2006.08.056.
- [107] E. I. Shkolnikov, A. Z. Zhuk, and M. S. Vlaskin, "Aluminum as energy carrier: Feasibility analysis and current technologies overview," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 9, pp. 4611–4623, Dec. 2011, doi: 10.1016/j.rser.2011.07.091.

- [108] J. L. Sabourin, G. A. Risha, R. A. Yetter, S. F. Son, and B. C. Tappan, "Combustion characteristics of nanoaluminum, liquid water, and hydrogen peroxide mixtures," *Combust Flame*, vol. 154, no. 3, pp. 587–600, Aug. 2008, doi: 10.1016/j.combustflame.2008.05.015.
- [109] J. M. Bergthorson *et al.*, "Metal-water combustion for clean propulsion and power generation," *Appl Energy*, vol. 186, pp. 13–27, 2017, doi: 10.1016/j.apenergy.2016.10.033.
- [110] G. Risha *et al.*, "Aluminum-ICE (ALICE) Propellants for Hydrogen Generation and Propulsion," in *45th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit*, Aug. 2009, no. August 2009, pp. 1–16. doi: 10.2514/6.2009-4877.
- [111] T. L. Pourpoint, T. D. Wood, M. A. Pfeil, J. Tsohas, and S. F. Son, "Feasibility study and demonstration of an aluminum and ice solid propellant," *International Journal of Aerospace Engineering*, vol. 2012, 2012, doi: 10.1155/2012/874076.
- [112] J. Jun, B.-J. Lee, and D. J. Song, "Measurement of burning velocity for bare strand casted with a frozen mixture of nano/micro-aluminum particles and water," *Journal of Mechanical Science and Technology*, vol. 30, no. 5, pp. 2409–2413, May 2016, doi: 10.1007/s12206-016-0451-8.
- [113] T. R. Sippel, T. L. Pourpoint, and S. F. Son, "Combustion of nanoaluminum and water propellants: Effect of equivalence ratio and safety/aging characterization," *Propellants, Explosives, Pyrotechnics*, vol. 38, no. 1, pp. 56–66, Feb. 2013, doi: 10.1002/prep.201200143.
- [114] C. A. Crane, E. S. Collins, M. L. Pantoya, and B. L. Weeks, "Nanoscale investigation of surfaces exposed to a thermite spray," *Appl Therm Eng*, vol. 31, no. 6–7, pp. 1286–1292, 2011, doi: 10.1016/j.applthermaleng.2011.01.001.
- [115] E. S. Collins, M. L. Pantoya, M. A. Daniels, D. J. Prentice, E. D. Steffler, and S. P. D'Arche, "Heat Flux Analysis of a Reacting Thermite Spray Impinging on a Substrate," *Energy & Fuels*, vol. 26, no. 3, pp. 1621–1628, Mar. 2012, doi: 10.1021/ef201954d.
- [116] M. M. Rahman, A. Saieed, M. F. Khan, and J. Hickey, "Group Combustion of Dispersed Spherical Core–Shell Nanothermite Particles," *Thermo*, vol. 2, no. 3, pp. 209–231, Aug. 2022, doi: 10.3390/thermo2030016.

- [117] N. S. Kaisare and D. G. Vlachos, "A review on microcombustion: Fundamentals, devices and applications," *Prog Energy Combust Sci*, vol. 38, no. 3, pp. 321–359, 2012, doi: 10.1016/j.pecs.2012.01.001.
- [118] P. Zhu, R. Shen, Y. Ye, X. Zhou, Y. Hu, and L. Wu, "Fabrication and electrical explosion of igniters based on Al/CuO reactive multilayer films," *Science and Technology of Energetic Materials*, vol. 73, no. 5–6, pp. 127–131, 2012.
- [119] P. Zhu, R. Shen, N. N. Fiadosenka, Y. Ye, and Y. Hu, "Dielectric structure pyrotechnic initiator realized by integrating Ti/CuO-based reactive multilayer films," *J Appl Phys*, vol. 109, no. 8, p. 084523, Apr. 2011, doi: 10.1063/1.3576138.
- [120] P. Zhu, R. Shen, Y. Ye, S. Fu, and D. Li, "Characterization of Al/CuO nanoenergetic multilayer films integrated with semiconductor bridge for initiator applications," *J Appl Phys*, vol. 113, no. 18, p. 184505, May 2013, doi: 10.1063/1.4804315.
- [121] S. Fu, R. Shen, P. Zhu, and Y. Ye, "Metal–interlayer–metal structured initiator containing Al/CuO reactive multilayer films that exhibits improved ignition properties," *Sens Actuators A Phys*, vol. 292, pp. 198–204, 2019, doi: 10.1016/j.sna.2019.04.019.
- [122] K. T. Sullivan, J. D. Kuntz, and A. E. Gash, "Fine patterning of thermites for mechanistic studies and microenergetic applications," *International Journal of Energetic Materials and Chemical Propulsion*, vol. 12, no. 6, pp. 511–528, 2013, doi: 10.1615/IntJEnergeticMaterialsChemProp.2013005289.
- [123] K. T. Sullivan, J. D. Kuntz, and A. E. Gash, "Electrophoretic deposition and mechanistic studies of nano-Al/CuO thermites," *J Appl Phys*, vol. 112, no. 2, p. 024316, Jul. 2012, doi: 10.1063/1.4737464.
- [124] L. Sorokina, R. Ryazanov, Y. Shaman, and E. Lebedev, "Electrophoretic deposition of Al-CuO x thermite materials on patterned electrodes for microenergetic applications," *E3S Web of Conferences*, vol. 239, p. 00015, Feb. 2021, doi: 10.1051/e3sconf/202123900015.
- [125] K. T. Sullivan *et al.*, "Controlling Material Reactivity Using Architecture," *Advanced Materials*, vol. 28, no. 10, pp. 1934–1939, Mar. 2016, doi: 10.1002/adma.201504286.

- [126] K. T. Sullivan, C. Zhu, D. J. Tanaka, J. D. Kuntz, E. B. Duoss, and A. E. Gash, "Electrophoretic deposition of thermites onto micro-engineered electrodes prepared by direct-ink writing," *Journal of Physical Chemistry B*, vol. 117, no. 6, pp. 1686–1693, Feb. 2013, doi: 10.1021/jp306440t.
- [127] M. H. Ervin, S. S. Bedair, C. R. Knick, H. Tsang, B. Isaacson, and N. W. Piekiet, "Evaporation driven assembly of on-chip thermite devices," *Journal of Microelectromechanical Systems*, vol. 26, no. 6, pp. 1408–1416, 2017, doi: 10.1109/JMEMS.2017.2757149.
- [128] S. F. Son, B. W. Asay, T. J. Foley, R. A. Yetter, M. H. Wu, and G. A. Risha, "Combustion of Nanoscale Al/MoO₃ Thermite in Microchannels," *J Propuls Power*, vol. 23, no. 4, pp. 715–721, Jul. 2007, doi: 10.2514/1.26090.
- [129] V. v. Gordeev, M. v. Kazutin, and N. v. Kozyrev, "Effect of additives on CuO/Al nanothermite properties," in *Journal of Physics: Conference Series*, Oct. 2017, vol. 894, no. 1, p. 012116. doi: 10.1088/1742-6596/894/1/012116.
- [130] A. S. Tappan, "Microenergetics: Combustion and detonation at sub-millimeter scales," in *AIP Conference Proceedings*, 2008, vol. 955, pp. 997–1002. doi: 10.1063/1.2833299.
- [131] A. S. Tappan, "Microenergetics: Combustion and detonation at sub-millimeter scales," 2007. [Online]. Available: <https://www.osti.gov/servlets/purl/1147844>
- [132] S. Gangopadhyay *et al.*, "Shock wave and power generation using on-chip nanoenergetic material," WO 2007/053543 A2, 2007 [Online]. Available: <http://www.google.com/patents/US8066831>
- [133] J. E. J. Ding, J. Chen, G. Liao, F. Zhang, and B. Luo, "Process in micro-combustion and energy conversion of micro power system: A review," *Energy Convers Manag*, vol. 246, no. May, p. 114664, 2021, doi: 10.1016/j.enconman.2021.114664.
- [134] C. M. Spadaccini, A. Mehra, J. Lee, X. Zhang, S. Lukachko, and I. A. Waitz, "High Power Density Silicon Combustion Systems for Micro Gas Turbine Engines," *J Eng Gas Turbine Power*, vol. 125, no. 3, pp. 709–719, Jul. 2003, doi: 10.1115/1.1586312.

- [135] C. Stergiopoulos *et al.*, “A Soft Combustion-Driven Pump for Soft Robots,” in *Volume 2: Mechanics and Behavior of Active Materials; Integrated System Design and Implementation; Bioinspired Smart Materials and Systems; Energy Harvesting*, Sep. 2014, vol. 2, no. September. doi: 10.1115/SMASIS2014-7536.
- [136] R. H. Heisser *et al.*, “Valveless microliter combustion for densely packed arrays of powerful soft actuators,” *Proceedings of the National Academy of Sciences*, vol. 118, no. 39, pp. 1–7, Sep. 2021, doi: 10.1073/pnas.2106553118.
- [137] R. Heisser, R. Shepherd, and C. Aubin, “Microscale Combustion for High Density Soft Actuation,” US 11353046 B2, 2022
- [138] R. F. Shepherd *et al.*, “Using Explosions to Power a Soft Robot,” *Angewandte Chemie International Edition*, vol. 52, no. 10, pp. 2892–2896, Mar. 2013, doi: 10.1002/anie.201209540.
- [139] M. T. Tolley *et al.*, “An untethered jumping soft robot,” in *2014 IEEE/RSJ International Conference on Intelligent Robots and Systems*, Sep. 2014, no. Iros, pp. 561–566. doi: 10.1109/IROS.2014.6942615.
- [140] K. F. Lei, “Introduction: The Origin, Current Status, and Future of Microfluidics,” in *Microfluidics: Fundamental, Devices and Applications*, Y. Song, D. Cheng, and L. Zhao, Eds. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2018, pp. 1–18. doi: 10.1002/9783527800643.ch1.
- [141] Y. Song, X. Zhao, Q. Tian, and H. Liang, “Fundamental Concepts and Physics in Microfluidics,” in *Microfluidics: Fundamental, Devices and Applications*, Y. Song, D. Cheng, and L. Zhao, Eds. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2018, pp. 19–111. doi: 10.1002/9783527800643.ch2.
- [142] F. M. White, *Fluid Mechanics*, 8th Editio. New York: McGraw-Hill Education, 2016.
- [143] C. Dames, “Measuring the Thermal Conductivity of Thin Films: 3 Omega And Related Electrothermal Methods,” in *Annual Review of Heat Transfer*, vol. 16, no. 1, Begell House, 2013, pp. 7–49. doi: 10.1615/AnnualRevHeatTransfer.v16.20.

- [144] L. Jin and L. Zhou, "Investigation on Thermal Conductivity and Viscosity of Thin Water Film by Molecular Dynamics Simulation," in *ASME 2019 6th International Conference on Micro/Nanoscale Heat and Mass Transfer*, Jul. 2019, pp. 1–8. doi: 10.1115/MNHMT2019-4087.
- [145] S. K. Mitra and S. Chakraborty, Eds., *Microfluidics and Nanofluidics Handbook: Chemistry, Physics, and Life Science Principles*. Boca Raton: CRC Press, 2012. [Online]. Available: https://books.google.com/books/about/Microfluidics_and_Nanofluidics_Handbook.html?hl=tr&id=eRXOBQAAQBAJ
- [146] C. E. Brennen, *Fundamentals of Multiphase Flow*. Cambridge University Press, 2005. doi: 10.1017/CBO9780511807169.
- [147] A. Saieed, M. M. Rahman, and J. P. Hickey, "Role of viscosity in the preferential concentration of heated, bidispersed particles," *International Journal of Multiphase Flow*, vol. 155, no. June, p. 104185, 2022, doi: 10.1016/j.ijmultiphaseflow.2022.104185.
- [148] G. Karniadakis, A. Beskok, N. Aluru, and S. S. Antman, "Electrokinetic Flows," in *Microflows and Nanoflows*, New York: Springer New York, 2005, pp. 255–239. doi: 10.1007/0-387-28676-4.
- [149] G. Tang, D. Yan, C. Yang, H. Gong, J. C. Chai, and Y. C. Lam, "Assessment of Joule heating and its effects on electroosmotic flow and electrophoretic transport of solutes in microfluidic channels," *Electrophoresis*, vol. 27, no. 3, pp. 628–639, Feb. 2006, doi: 10.1002/elps.200500681.
- [150] K. Horiuchi and P. Dutta, "Joule heating effects in electroosmotically driven microchannel flows," *Int J Heat Mass Transf*, vol. 47, no. 14–16, pp. 3085–3095, Jul. 2004, doi: 10.1016/j.ijheatmasstransfer.2004.02.020.
- [151] M. Szklarczyk, "Electrical Breakdown of Liquids," in *Modern Aspects of Electrochemistry*, no. 25, 1993, pp. 253–296. doi: 10.1007/978-1-4615-2876-0_5.
- [152] P. Wedin, "Electrical breakdown in dielectric liquids-a short overview," *IEEE Electrical Insulation Magazine*, vol. 30, no. 6, pp. 20–25, Nov. 2014, doi: 10.1109/MEI.2014.6943430.

- [153] H.-C. Ham and J. J. Yoh, "Electronegative microchannel guided streamer propagation for in-liquid spark breakdown applications," *Appl Phys Lett*, vol. 118, no. 10, p. 103905, Mar. 2021, doi: 10.1063/5.0042591.
- [154] P. Lukes *et al.*, "High Power DC Diaphragm Discharge Excited in a Vapor Bubble for the Treatment of Water," *Plasma Chemistry and Plasma Processing*, vol. 33, no. 1, pp. 83–95, Feb. 2013, doi: 10.1007/s11090-012-9432-6.
- [155] W. Chiang, D. Mariotti, R. M. Sankaran, J. G. Eden, and K. (Ken) Ostrikov, "Microplasmas for Advanced Materials and Devices," *Advanced Materials*, vol. 32, no. 18, p. 1905508, May 2020, doi: 10.1002/adma.201905508.
- [156] G. Kibria, M. P. Jahan, and B. Bhattacharyya, Eds., *Micro-electrical Discharge Machining Processes*. Singapore: Springer Singapore, 2019. doi: 10.1007/978-981-13-3074-2.
- [157] P. J. Bruggeman *et al.*, "Plasma–liquid interactions: a review and roadmap," *Plasma Sources Sci Technol*, vol. 25, no. 5, p. 053002, Sep. 2016, doi: 10.1088/0963-0252/25/5/053002.
- [158] P. Bruggeman, C. Leys, and J. Vierendeels, "Experimental investigation of dc electrical breakdown of long vapour bubbles in capillaries," *J Phys D Appl Phys*, vol. 40, no. 7, pp. 1937–1943, Apr. 2007, doi: 10.1088/0022-3727/40/7/016.
- [159] P. J. Bruggeman, C. A. Leys, and J. A. Vierendeels, "Electrical breakdown of a bubble in a water-filled capillary," *J Appl Phys*, vol. 99, no. 11, p. 116101, Jun. 2006, doi: 10.1063/1.2199748.
- [160] P. Bruggeman, D. Schram, M. Á. González, R. Rego, M. G. Kong, and C. Leys, "Characterization of a direct dc-excited discharge in water by optical emission spectroscopy," *Plasma Sources Sci Technol*, vol. 18, no. 2, p. 025017, May 2009, doi: 10.1088/0963-0252/18/2/025017.
- [161] Z. Stara, F. Krčma, P. Slavíček, and V. Aubrecht, "Creation of DC diaphragm discharge in electrolytes," in *28th International Conference on Phenomena in Ionized Gases*, 2007, pp. 1082–1085.

- [162] F. Krcma, Z. Stara, and J. Prochazkova, "Diaphragm discharge in liquids: Fundamentals and applications," in *Journal of Physics: Conference Series*, Jan. 2010, vol. 207, p. 012010. doi: 10.1088/1742-6596/207/1/012010.
- [163] Z. Kozáková, F. Krčma, M. Vašíček, L. Hlavatá, and L. Hlochová, "Generation of dc pin-hole discharges in liquids: comparison of discharge breakdown in diaphragm and capillary configuration," *The European Physical Journal D*, vol. 69, no. 4, p. 100, Apr. 2015, doi: 10.1140/epjd/e2015-50331-6.
- [164] J. Bernardes and M. F. Rose, "Electrical Breakdown Characteristics of Sodium Chloride - Water Mixtures," Dahlgren, VI, 1983.
- [165] B. R. Locke, M. Sato, P. Sunka, M. R. Hoffmann, and J.-S. Chang, "Electrohydraulic Discharge and Nonthermal Plasma for Water Treatment," *Ind Eng Chem Res*, vol. 45, no. 3, pp. 882–905, Feb. 2006, doi: 10.1021/ie050981u.
- [166] P. Bruggeman and C. Leys, "Non-thermal plasmas in and in contact with liquids," *J Phys D Appl Phys*, vol. 42, no. 5, p. 053001, Mar. 2009, doi: 10.1088/0022-3727/42/5/053001.
- [167] J. Wang, M. S. Simeni, M. Rong, and P. J. Bruggeman, "Absolute OH density and gas temperature measurements by laser induced fluorescence in a microsecond pulsed discharge generated in a conductive NaCl solution," *Plasma Sources Sci Technol*, vol. 30, no. 7, p. 075016, Jul. 2021, doi: 10.1088/1361-6595/abf71c.
- [168] Y. Zhang, "Fabrication and energetic characterization of micro and nano sized Al/CuO core-shell particles," University of Waterloo, 2019. [Online]. Available: <http://hdl.handle.net/10012/14707>
- [169] J. M. Peuker, P. Lynch, H. Krier, and N. Glumac, "On AIO emission spectroscopy as a diagnostic in energetic materials testing," *Propellants, Explosives, Pyrotechnics*, vol. 38, no. 4, pp. 577–585, 2013, doi: 10.1002/prep.201200144.
- [170] P. Bruggeman, J. Degroote, J. Vierendeels, and C. Leys, "DC-excited discharges in vapour bubbles in capillaries," *Plasma Sources Sci Technol*, vol. 17, no. 2, p. 025008, May 2008, doi: 10.1088/0963-0252/17/2/025008.

Appendices

Appendix A

Details of bubble growth rate analysis

Video data was used to analyse the rate of bubble growth in the microchannel upon nucleation. The analysis is performed in Matlab using functions from the image processing toolbox and the Telops custom toolbox. The process looks for dark regions within the microchannel using a series of image segmentation processes, then those dark regions are labelled, and the area of the labelled regions is calculated and logged. A block diagram describing the process is shown in Figure 31. The mask is generated using the frame just before a bubble is visible and is used to ensure that future segmentation considers only data within the confines of the microchannel. Images at different stages of processing are presented for two time-snapshots in Figure 32, alongside the computed bubble area evolution with time.

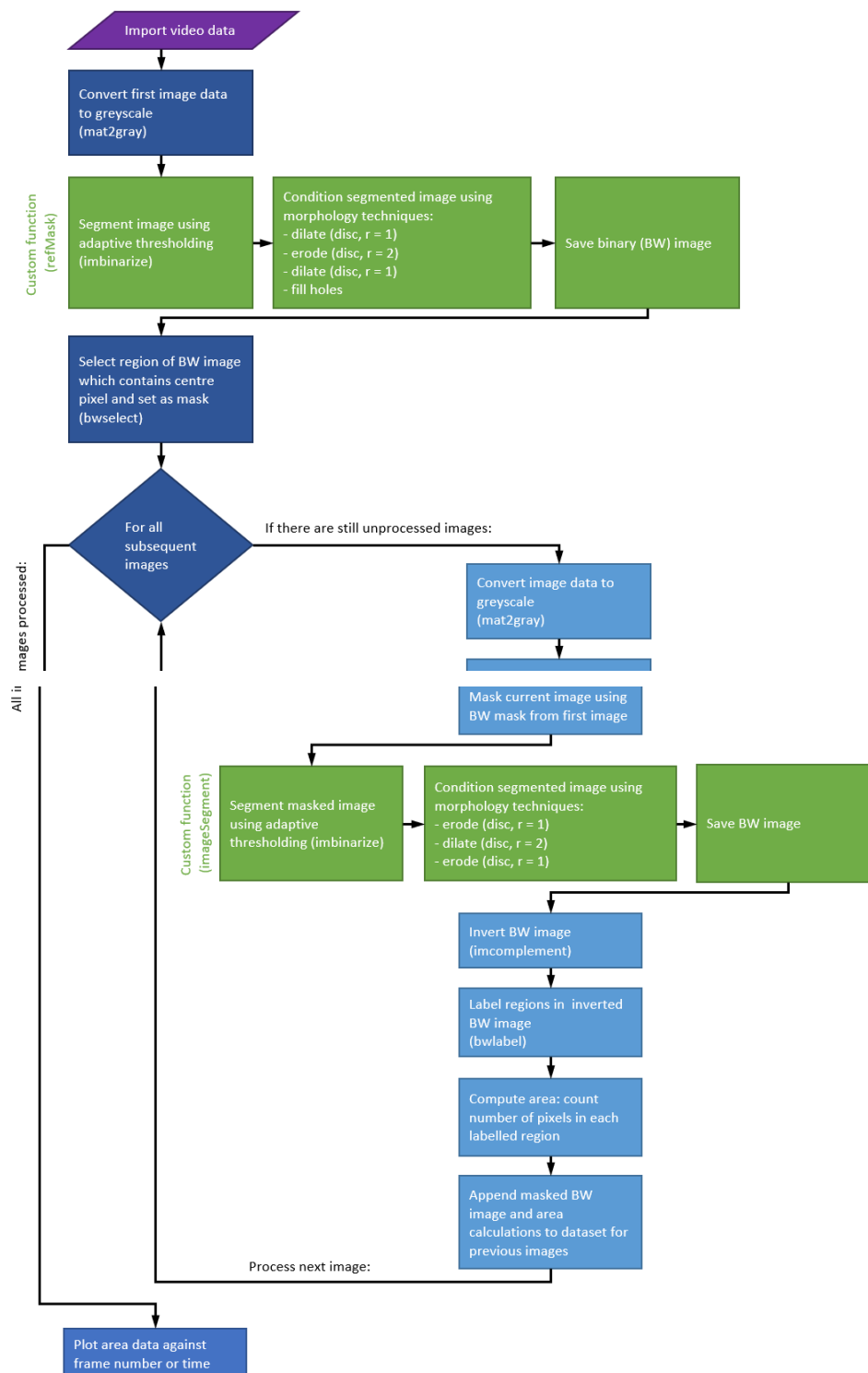


Figure 31: Block diagram of bubble growth rate analysis image process.

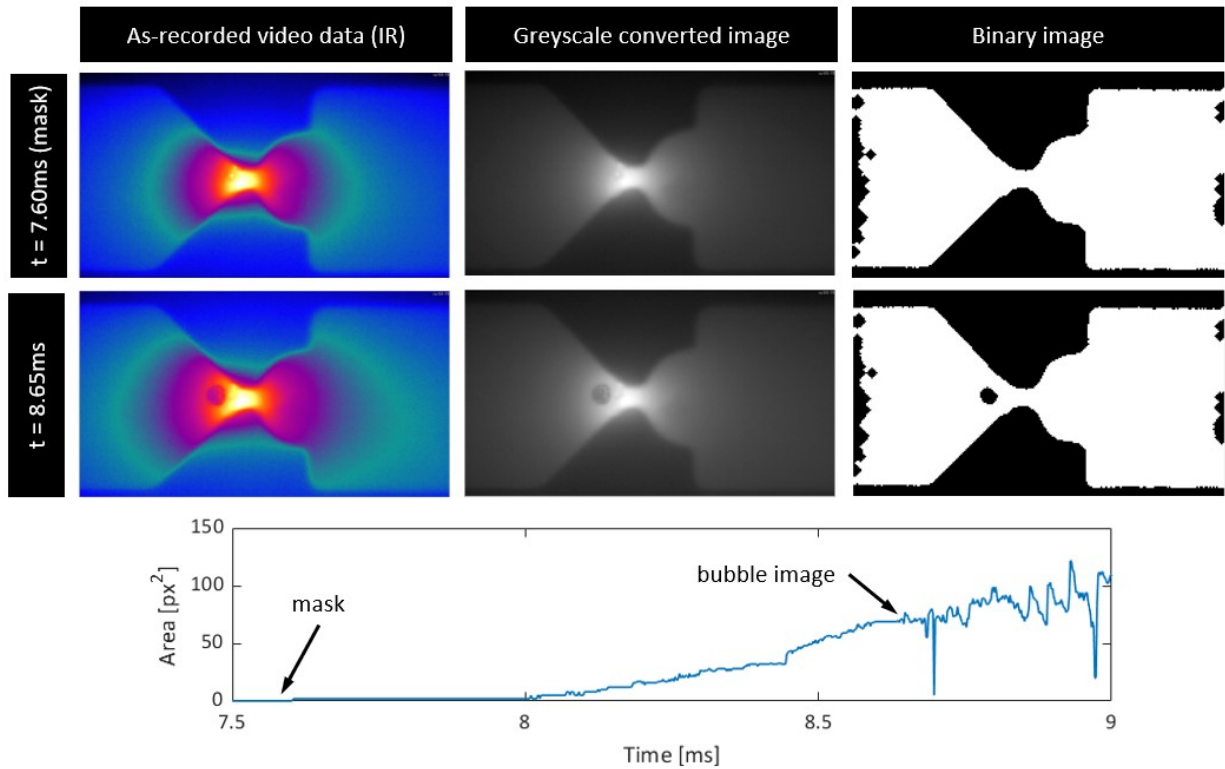


Figure 32: Snapshots from bubble analysis process, showing as-recorded IR video, converted greyscale, and binary masked images taken before bubble formation ($t = 7.60\text{ms}$, top row) and after bubble formation ($t = 8.65\text{ms}$, middle row), as well as calculated bubble area plotted against time (bottom row).

Appendix B

Details of COMSOL Models

A steady-state 3-dimensional model was used to evaluate the performance of the microchannel using COMSOL 5.6. A half-channel geometry was used with a symmetry boundary to reduce computational load. Three domains were modelled: the glass slide (1mm thick), the PDMS casting (2.4mm), and a liquid water domain in the microchannel. Heat transfer was considered across all domains, but only the liquid domain was considered electrically conductive. Boundary and initial conditions are described in Figure 8. As was previously mentioned, the modelling work was used primarily as a design tool and so was kept simple. For this model, the complexity of the physics was limited by neglecting phase change and neglecting particle transport and the associated disturbances to the electric field because of particle presence.

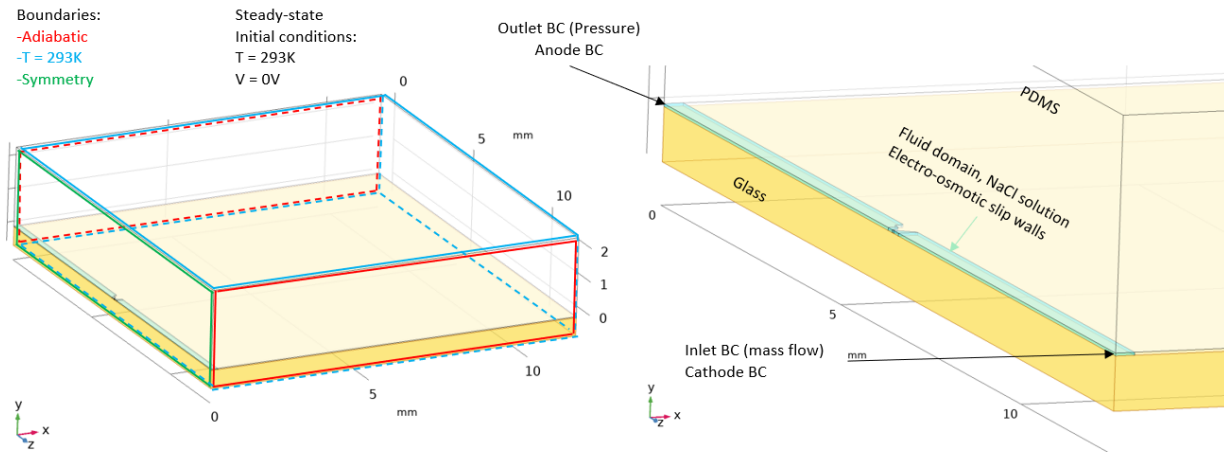


Figure 33: Schematic diagram of modelled domains showing domain geometry, material selections, boundary conditions, and thermal and electrical initial conditions for full-channel model.

Material properties were obtained from the materials library built-into COMSOL 5.6; 'Glass (quartz),' 'PDMS – Polydimethylsiloxane,' and 'Water, liquid' were used for the glass, PDMS, and liquid phases respectively. The electrical conductivity of the solution at various concentrations was considered uniform and temperature independent and is presented in Table 5.

Table 5: Conductivity used for liquid phase in numerical model for various NaCl solution concentration cases

Solution Concentration [M]	Solution Conductivity [$\mu\text{S}/\text{cm}$]
1.0 E-4	11.1 E0
2.2 E-4	16.2 E0
4.6 E-4	27.1 E0
1.0 E-3	50.7 E0
2.2 E-3	10.2 E1
4.6 E-3	21.1 E1
1.0 E-2	44.7 E1
2.2 E-2	95.5 E1
4.6 E-2	20.5 E2
1.0 E-1	44.1 E2
2.2 E-1	94.9 E2
4.6 E-1	20.4 E3
1.0 E0	44.0 E3

The simulation was performed for cross-channel voltages ranging from 50V to 500V and dissolved NaCl concentrations ranging from 0.1mM to 1M.

A convergence study was performed using several mesh densities, which were methodically controlled by using distribution functions along key geometric boundaries. Figure 34A shows the distribution parameters for the grid spacing. Distribution, n , was varied from 2 to 16 for the grid refinement study.

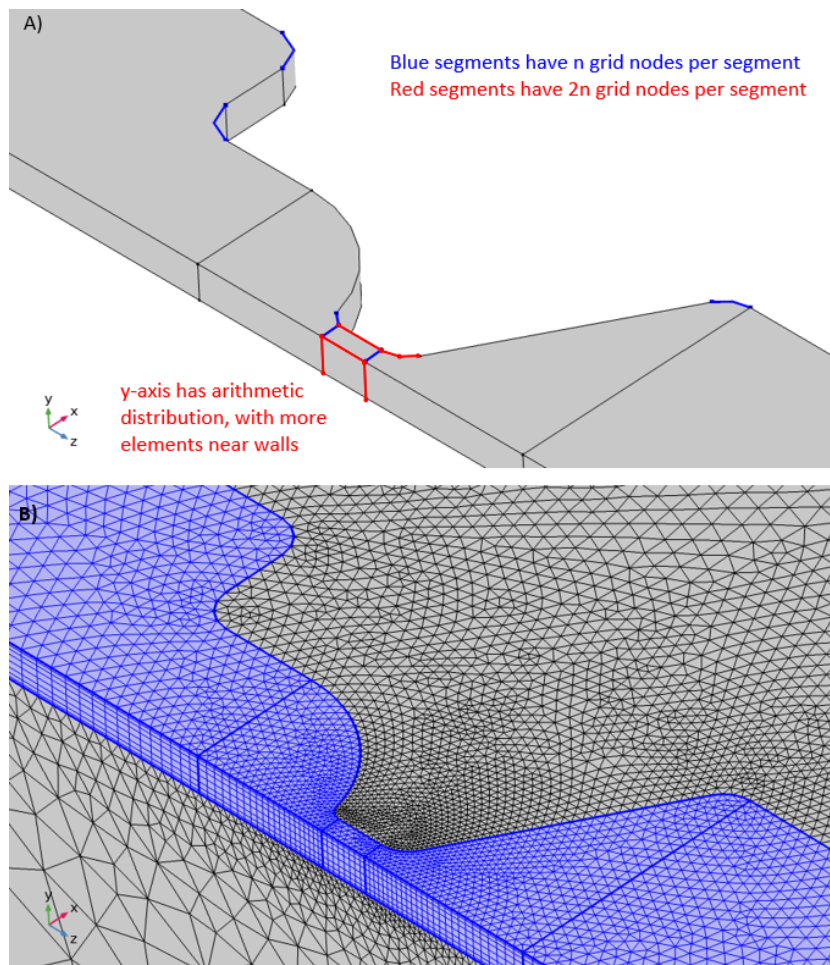


Figure 34: Diagram of microchannel domain showing the location and type of applied grid node distribution control functions (A), and resultant grid for $n = 4$ (B, blue domain is liquid, grey domain is PDMS, glass domain not shown).

The grid convergence study considered the maximum temperature, velocity, and electric field within the liquid domain for the 1[M], 500V condition. The grid was considered converged once the difference between grid spacings was less than 5% for all parameters of interest. The results are

presented in Table 6, and it can be seen that between $n = 4$ and $n = 16$ there is less than a 5% difference in temperature, velocity, and electric field. Therefore, $n = 4$ produces a sufficiently fine grid spacing and is selected for all subsequent analysis.

Table 6: Microchannel model predicted maximum temperature, velocity, and electric field results for the 500V, 1[M] NaCl case at increasing mesh density.

Number of divisions, n	Maximum temperature [K]	Maximum velocity [m/s]	Maximum electric field magnitude [V/m]
16	2173.4	0.71394	2.03 E06
8	2173.1	0.71319	2.04 E06
4	2163	0.70695	2.06 E06
2	2110	0.66542	1.91 E06

The velocity data produced by the model, shown in Figure 11g, can be used to predict an upper bound for the Stokes number for a dispersed particle flow using equations (6) and (7). The density of core-shell particles can be computed for a $1\mu\text{m}$ diameter Al particle coated by a fully monolithic CuO shell with 100nm thickness, and an alumina layer of 2-5nm in between, as observed in Zhang et al. [38]. Using material densities of 2.7g/cm^3 , 4.0g/cm^3 , and 6.3g/cm^3 for the Al, Al_2O_3 , and CuO, respectively, the calculated density of the core-shell structure is $4.0\text{-}4.3\text{g/cm}^3$. The higher bound for the core-shell particle density (4.3g/cm^3) is used in the Stokes number calculation. The viscosity liquid was set to $1\text{mPa}\cdot\text{s}$ (water at 20°C). The results of the calculation are presented in Figure 14.

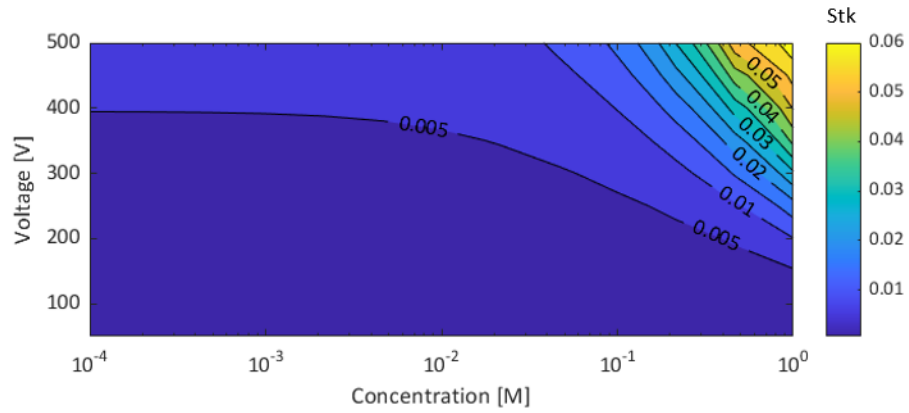


Figure 35: Numerically predicted Stokes number (Stk) contour plot for range of voltage and concentration combinations considered.

The Stokes number contour plot shown in Figure 14 is effectively a rescaled version of the velocity plot shown in Figure 11. The maximum value of Stokes number predicted is 0.063 at 1[M], 500V and indicates that, even at the highest predicted flow values, the inertia of particles remains small enough that they follow the streamlines of the flow.

To help understand the influence of particles on the electrical field, an axisymmetric representation of the microchannel was modelled with a 1 μ m diameter Al@CuO core-shell particle located at the centre. The particle was modelled as a 1 μ m Al core coated uniformly by with a 100nm thick CuO shell. Material properties for all considered phases were obtained from the built-in COMSOL material library. The electrical conductivity of CuO was obtained from Coelho et al. The magnitude of the electric field within the throat was volume-averaged for each voltage case modelled in the full-channel model (50-500V in 50V increments), and these average electric field magnitudes were applied within the axisymmetric channel model by applying an equivalent voltage across the domain. Since the Stokes numbers of the flows are low, there is little relative motion between the particle and surrounding fluid. Therefore, it is reasonable to simplify the simulation to a stationary particle within a liquid domain. A schematic diagram of the model is shown in Figure 15.

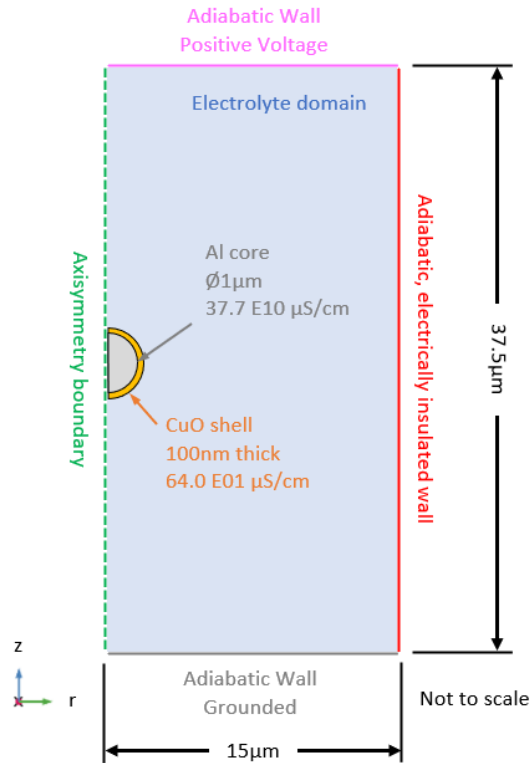


Figure 36: Schematic diagram of modelled domains showing domain geometry, material selections, and boundary conditions for single-particle model.

The initial temperature and voltage within the domain were set to 20°C and 0V , respectively, and a time-dependent study was run for 30ms to model the heat generation, but all material parameters were kept steady and temperature independent. An insulated wall boundary was applied at $r = 15\mu\text{m}$ to represent the microchannel walls. Since the focus of this study is to observe the geometric focussing effects of particles on the electric field, the thermal model was kept very simple and is not a good reproduction of the true physics. For this reason, temperature results are not included.

The grid convergence study was performed for the single particle model by observing the maximum electric field, current density, and heating power at different grid densities. The grid was controlled by dictating the number of divisions at the interfaces of the CuO shell domain. The grid control functions are shown in Figure 37A, and the grid produced when $n = 2$ is shown in B.

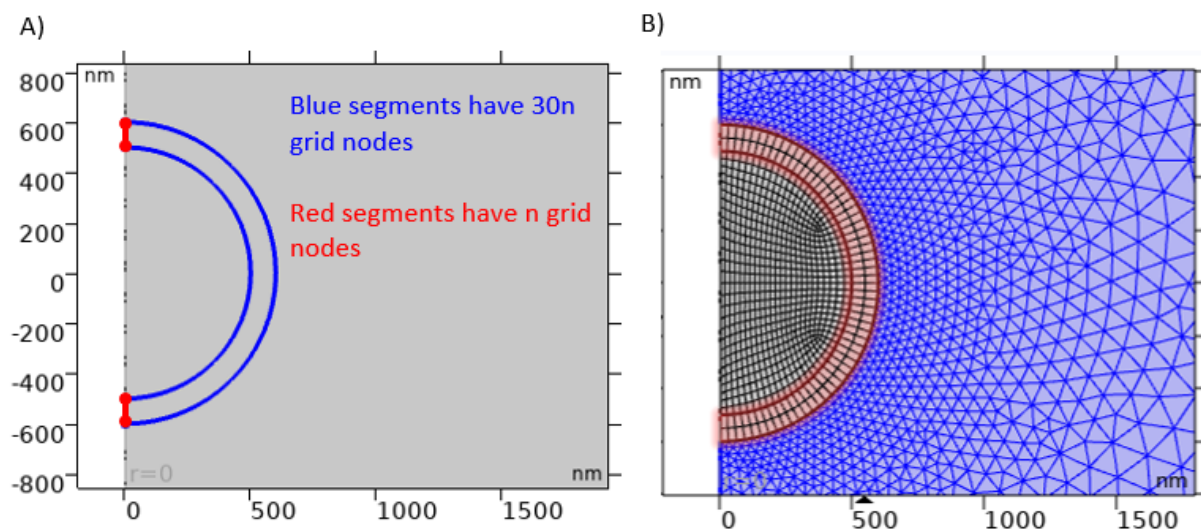


Figure 37: Diagram of single-particle model domains showing the location and type of applied grid node distribution control functions (A), and resultant grid for $n = 2$ (B, grey domain is Al, red domain is CuO, blue domain is water).

The convergence study was run for n ranging from 1 to 16, and the results are presented in Table 7. The results show that grid independence is reached (<5% error) even at $n = 2$, but $n = 4$ was used for all simulations to reduce the grid-error to below 1%.

Table 7: Single particle model predicted maximum electric field, current density, and Joule heating power results for the 500V, 1[M] NaCl case at increasing mesh density.

Number of divisions, n	Maximum electric field magnitude [V/m]	Maximum current density [A/m^2]	Maximum Joule heating power [W/m^3]
16	5.00 E6	7.80 E6	5.47 E12
8	5.00 E6	7.80 E6	5.47 E12
4	4.99 E6	7.80 E6	5.47 E12
2	4.97 E6	7.94 E6	5.47 E12
1	4.90 E6	7.79 E6	5.47 E12