

Development of Multifunctional Fiber Optic Sensors for Lithium Ion-Battery Monitoring

by

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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.

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ABSTRACT

The objective of this thesis is to develop a fiber optic sensor that is capable of simultaneously measuring temperature and the optical properties of lithium ion batteries. The ultimate goal of the project is the integration of this sensor inside of the pouch of a lithium ion battery cell. Estimation of the state-of-charge (SOC) yields a lot of useful information about the properties of the lithium ion battery. However, in moving towards a completed battery management system, the monitoring of temperature is an important aspect. In this thesis, a fluorescence- based fiber optic temperature sensor is developed such that it can be integrated to a previously developed fiber optic sensor for SOC estimation of lithium ion battery cells.

The fluorescence-based fiber optic methodology developed for the measurement of temperature and presented in this thesis is compatible with the current fiber optic sensing methodology for SOC estimation developed in our laboratory, which uses Near Infrared (NIR) transmittance through a partially cladded optical fiber. It is also impervious to harsh environments such as the ones existing in an automobile. This new temperature sensor is fabricated in the same fiber optic cable as the SOC sensor by etching away the cladding of a section of the fiber to form the temperature sensing region. A temperature sensitive film is then used to coat this sensing region which was developed using a double dye system of fluorescein and rhodamine B. Poly(methyl methacrylate) (PMMA) was chosen as a suitable matrix in which the fluorophore are dispersed in. The fluorescence signal of these dyes is exhibited around 570 nm when excited by a 470 nm LED. This allows for wavelength based separation of the signal coming from the SOC sensor and the temperature sensitive signal. The coating developed was optimized for high sensitivity to temperature as well as to ensure a uniform high quality coating. During testing, the temperature sensor was mounted outside of the battery cell while the SOC sensor was embedded inside in between the battery electrodes. The sensor thus obtained, allows for real-time monitoring of the optical properties of graphite and simultaneous monitoring of its temperature while

the battery is in operation. A resolution of roughly $0.868\text{ }^{\circ}\text{C}$ and a sensitivity of $9.738\text{ lx}/^{\circ}\text{C}$ was obtained for this sensor.

Further work to be performed in order to allow for its embedded use in a lithium ion battery is presented. Also presented is the development of a fully integrated photodetector based sensor for dual parameter monitoring in an automotive environment without a spectrometer.

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Table of Contents

List of Figures	ix
Chapter 1 Introduction.....	1
1.1 Motivation	3
1.1.1 Need for improved state-of-charge (SOC) estimation methods	3
1.1.2 Temperature monitoring of batteries	4
1.2 Thesis Objective	5
1.3 Thesis Organization.....	6
Chapter 2 Background and Literature Review	8
2.1 Background.....	8
2.1.1 Fiber based SOC sensing.....	10
2.1.2 Temperature dependence of lithium ion batteries	11
2.2 Literature Review	13
2.2.1 Traditional battery temperature monitoring.....	13
2.2.2 Optical temperature sensing mechanisms.....	14
2.2.3 Fiber Bragg Gratings	14
2.2.4 Fabry Perot Etalon	16
2.2.5 Optical Time Domain Reflectometry	17
2.2.6 Polymer Thermo-Optic Transition	18

2.2.7	Fluorescent Temperature Sensing	19
Chapter 3 Design of the Sensor		20
3.1	Principle of operation	20
3.2	Two-dye fluorescence	22
3.2.1	Optimization of the composition	22
3.3	Fiber based fluorescent thermometry	25
3.4	Coating of the thermometric coating on the optical fiber.....	27
3.5	Signal acquisition and processing.....	28
Chapter 4 Sensor Fabrication and Experimental Results		30
4.1	Coating preparation	30
4.2	Thermal characterization of coating.....	31
4.3	Fiber preparation and etching.....	35
4.4	Coating Process	37
4.4.1	Influence of optical fiber cleaning.....	39
4.4.2	Effect of pull rate.....	40
4.5	Fiber optic temperature sensing.....	42
4.6	Multiplexed Sensing.....	45
Chapter 5 Sensor performance and characteristics.....		52
5.1	Analysis of dedicated temperature sensor	52
5.1.1	Sensitivity and noise of the temperature sensor	52
5.1.2	Transient analysis of the temperature sensor.....	54
5.2	Analysis of the multifunctional sensor	56

5.2.1	SOC Sensing.....	56
5.2.2	Temperature sensing.....	57
5.2.3	Temperature transient behaviour	63
Chapter 6 Contributions, Future Work and Conclusions		65
6.1	Contributions	65
6.1.1	Development of a novel multifunctional sensor system.....	65
6.1.2	Development of a novel temperature sensitive coating	65
6.1.3	Development of a complementary system for signal acquisition	65
6.2	Future Work.....	66
6.2.1	Fiber coating optimization.....	66
6.2.2	Barrier material coating.....	66
6.2.3	Optimization of materials	67
6.2.4	Computer controlled coating	68
6.2.5	Signal acquisition system design.....	68
6.2.6	Circuit design.....	68
6.2.7	Optical coupling	70
6.2.8	Improving signal-to-noise ratio	70
6.3	Conclusions	70
Bibliography.....		72
Glossary.....		75

List of Figures

Figure 1 Voltage behaviour of a commercial lithium iron phosphate batteries (adapted from [7])	3
Figure 2 Schematic of a lithium ion battery showing the its components (adapted from[14])	9
Figure 3 The experimental reflectance spectrum of graphite as a function of state-of-charge (adapted from [18])	10
Figure 4 (a) Schematic of the experimental setup for fiber evanescent wave spectroscopy with a detailed illustration of the pouch cell (modified from [19]) and (b) Transmittance of the fiber SOC sensor at 850 nm in a pouch cell plotted as a function of the voltage of the cell	11
Figure 5 Illustration of a Fiber Brag Grating structure use for temperature sensing.....	14
Figure 6 Left: Illustration of Fabry-Perot Temperature Sensor; Right: Temepature Response fo a Fabry-Perot Sensor (extracted from [30])	16
Figure 7 (a) Illustration of distributed temperature sensing using an OTDR(extracted from [33]) and (b) Illustration of the Raman spectrum of silica showing strong dependence of anti-stokes shift in temperature (extracted from [34])	17
Figure 8 Illustration of temperature dependence of refractive indices of some common polymeric materials (extracted from [32]).....	18
Figure 9 Fluorescence emission spectrum of a fluorescein as a function of temperature (extracted from [35]).....	19
Figure 10 Schematic Illustration of electronic energy transitions in a fluorescent molecule (adapted from [37])	20

Figure 11 The absorption spectrum of fluorescein (Fabs) and Rhodamine (Rabs) in ethanol and emission spectrum of LED (430 nm and 470 nm), Fluorescein (Fems) and Rhodamine B (Rems) in ethanol (extracted from [41]).....	24
Figure 12 The fluorescence quantum yield of fluorescein (pH 12) at various concentrations(adapted from [42])	25
Figure 13 The structure of an optical fiber illustrated showing its construction	26
Figure 14 Schematic of the dip-coating process showing the forces acting on the meniscus determining the thin film coating thickness (extracted from [44])	27
Figure 15 Block diagram of proposed multifunctional sensor showing the two sensing regions and their effect on the output signal	28
Figure 16 Reflectance of graphite anode retrieved from a commercial cell as a function of SOC (adapted from [19])	28
Figure 17 Diagrammatic illustration of thermal cycler setup for testing the temperature sensitivity of the fluorescent coating.....	31
Figure 18 Reflectance spectrum of the fluorescent coating with 0.38% w/w fluorescein and 0.38% w/w rhodamine B showing one peak for the excitation source and the next peak with the emission spectrum of the fluorophore	33
Figure 19 Results of thermal cycling for a sample composition of 0.32% w/w fluorescein and 0.38%w/w rhodamine B (a) showing the time dependent response of the fluorescent intensity and temperature and (b) showing the correlation between the temperature and the fluorescent intensity illustrating the sensor sensitivity.....	34
Figure 20 Result of concentration optimization experiments for the selection of the optimum concentration for fluorescent thermometry	35
Figure 21 (a) Custom Teflon [®] etching apparatus with fiber secured in place and (b) the portion of the fiber shown extending below the etcher to be etched by hydrofluoric acid (HF)	36

Figure 22 (a) Dip coating system used for the coating of the optical fiber displaying parts of the apparatus and (b) A close-up view displaying the fiber extending on the bottom side of the fiber holder into the solvent	38
Figure 23 (a) Microscope image of the untreated fiber coated showing non-uniform coating (shown in pink) and (b) Microscope image of the ozone treated fiber coated showing a uniform coating	40
Figure 24 Coating Thickness Dependence on pull rate	41
Figure 25 Microscope images showing the effect of pull rate with (a) beading observed at fast pull rates (0.03 mm/s); (b) optimal coating observed at preferred pull rate (0.02 mm/s) and (c) gaps and cracks observed at slow pull rates (0.005 mm/s)	42
Figure 26 Image of setup used to test the temperature response of the fibers	42
Figure 27 (a) Optical spectrum of un-optimized fluorescent temperature sensing fiber showing saturation of the excitation source (b) Optical spectrum of optimized temperature sensing fiber showing a much weaker excitation source with a strong emission observed at the output end	43
Figure 28 (a) Fluorescent intensity and temperature versus time showing the fluorescent signal tracking the measured temperature reading from the measurement thermocouple	45
Figure 29 Temperature responsivity of the temperature sensing portion of the multifunctional fiber optic sensor obtained prior to the embedding inside of a battery. This test is used for calibration and to compare the performance before and after the battery is introduced.	46
Figure 30 Cross Sectional illustration of fiber placement in pouch cell (adapted from [43])	47
Figure 31 Pouch cell constructed with multifunctional sensor	48
Figure 32 (a) The intensity of the signal at 850 nm plotted versus time compared to the voltage of a lithium ion battery charged at 0.1C displaying a state-of-charge dependent behaviour (b) the intensity of the fluorescent signal around 560 nm plotted as a function of time compared to the temperature measured by a thermocouple displaying a temperature dependent behaviour and long term signal drift	50

Figure 33 The fluorescent intensity of a temperature sensing fiber plotted as a function of the temperature measured by the thermocouple to obtain the sensitivity of the sensor	53
Figure 34 Data distribution about the linear fit of the model	53
Figure 35 Temperature transition displaying sensor lag by the fluorescent temperature sensor.....	55
Figure 36 The averaged optical signal from the multifunctional sensor compared to the charge capacity of the battery obtained by coulomb counting	56
Figure 37 Fluorescent intensity vs thermocouple temperature in a multifunctional fiber sensor showing the variance in the fluorescent intensity as a function of the temperature.....	58
Figure 38 (a) Data corrected using the above presented algorithm displaying little long-term drift (b) The temperature vs corrected fluorescent intensity shows a large improvement in the goodness-of-fit to the linear model	60
Figure 39 Data distribution about the linear fit of the model after data correction	61
Figure 40 (a) Intensity at 850 nm during the cycling of a battery without a temperature sensor (b) Intensity at 470 nm during the cycling of a battery without a temperature sensor showing a similar trend to 850 nm.....	62
Figure 41 Comparison of the multifunctional SOC and fiber sensor response with the transient behaviour of a thermocouple	63
Figure 42 Optical micrograph of epoxy coated temperature sensor	67
Figure 43 (a) Board layout of multifunctional OSI (b) Schematic view for multifunctional OSI	69

Chapter 1

Introduction

Owing to socio-economic circumstances in the middles of the 2000s, there has been a renewed interest in electric vehicles. Since 2010, all major automotive companies have released electric vehicles. Initially, hybrid electric vehicles (HEV) were the primary type of electric vehicles. Hybrid electric vehicles consist of two motors; electric and internal combustion. In HEVs, electric motors are engaged to retrieve (otherwise wasted) energy using regenerative braking. The electric motors also drive the vehicle at lower speeds (where internal combustion is less desired).

However, in more recent times, there has been an emergence of battery electric vehicles (BEV). In Canada, BEVs form around 50.8% of electric vehicles sold [1]. Some reports predict more than a two-fold increase in the global sales of BEVs from 2.7 million sales in 2014 to 6.4 million sales in 2023 [2]. In the past, BEVs on-board energy supply has been primarily based on lead-acid or nickel metal hydride (NiMH) batteries. In more recent times, lithium-ion (Li-ion) batteries are preferred.

The successful mass adoption of EVs is however hindered by two major psychological factors; *range anxiety* and *resale anxiety*. Range anxiety is the concern generated by driving an electric vehicle owing to its limited energy storage. Unlike traditional internal combustion vehicles, the range on an electric vehicle is constrained by the energy stored in the battery since it is not possible to the quickly “top-up” the energy source in the vehicle. Resale anxiety is the concern regarding the lack of confidence in the future value of the vehicles. The degradation of more traditional internal combustion vehicles is better

understood owing to their relatively much longer history on the market. However, electric vehicles are perceived as less durable owing to the degradation of the capacity in the battery of the vehicle [3].

Lithium iron phosphate (LFP) has been identified as a more favourable positive electrode (cathode) for use in an electric vehicle. Its battery chemistry has been identified to ease some of these psychological concerns by improving the performance of the battery. Furthermore, lithium iron phosphate batteries are inherently more safe due to their lower likelihood to experience thermal runaway due to their better thermal performance [4]. Despite its initial lower energy density than the more widespread Lithium Manganese Oxide (LMO) or Lithium Nickel Manganese Cobalt Oxide (NMC); LFP is likely to catch up and have the same energy density after a couple years of use [5].

The inherent benefits of lithium iron phosphate chemistry translate to a battery that has the following advantages for EV applications:

- **Lighter:** Owing to the improved thermal performance, the battery does not require more complicated liquid cooling. It may instead be air cooled. Furthermore, owing to its improved inherent safety, fewer additional safety features leads to a lighter battery
- **Long-lasting:** Compared to LMO and NMC batteries, LFP batteries perform better and exhibit lesser capacity fade in the long term. This means that in a car, the energy storage mechanism degrades to a lesser degree with use (thus providing a higher resale value).
- **Fast-charging:** Owing to the higher power capacity of LFP, higher currents can be used to charge and discharge the battery. This helps alleviate range anxiety by allowing rapid charging of the batteries.
- **Chemically Stable:** when compared to other types of lithium ion chemistries, lithium iron phosphate is an extremely stable cathode chemistry. This stability is manifested in its higher possible operating temperature before thermal runaway is experienced [6]

1.1 Motivation

1.1.1 Need for improved state-of-charge (SOC) estimation methods

LFP however does face some significant challenges that prevents its widespread adoption. LFP batteries show a mostly flat response for open-circuit voltage (OCV) vs state-of-charge (SOC) as shown in Figure 1 [7]. This relative flat voltage response in the ~30%-80% induces the challenge of estimating the state of charge of LFP batteries using more traditional electrochemical methods, especially during partial cycling (like in an automotive application).

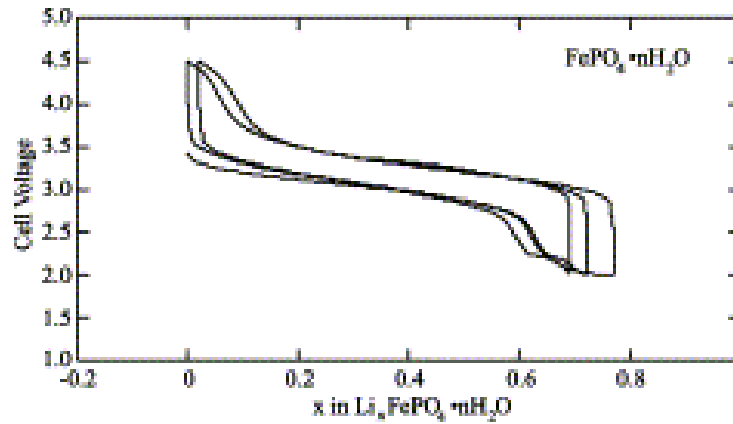


Figure 1 Voltage behaviour of a commercial lithium iron phosphate batteries (adapted from [7])

Researchers have demonstrated several novel ways to estimate state-of-charge of LFP batteries [8][9]. However, there is still a lot of room for improvement as those methods are challenging to implement in a vehicular application.

Another important consideration is the operating temperature of the battery. Although elevated temperatures improve the kinetics of the lithium intercalation process, it adversely affects the morphology of the Solid Electrolyte Interface (SEI) and causes its degradation. Low temperatures result in the plating of lithium metal on the electrodes owing to the low diffusion rate of ions [10]. Thus the operating temperature of lithium ion batteries is limited. Accelerated aging is observed at non-optimal operating temperatures which adversely affects its state-of-health (SOH). In an automotive environment, there is expected to be large temperature variations reflecting the environment of use.

Additional sensors to estimate the SOC and the SOH of lithium ion batteries are highly desirable. Additional information about the temperature of the battery is essential for improved SOH estimation. This research work presents an approach to tackle these problems by implementing a multifunctional fiber optic sensor.

1.1.2 Temperature monitoring of batteries

Temperature of a lithium ion battery strongly influences its performance. In an automotive environment, it is possible for the temperature of the battery to vary with the temperature of its surroundings. One of the highest profile incidents highlighting the importance of thermal management of lithium ion batteries is the incident involving Boeing's Dreamliner 787. In early 2013, the entire fleet of Boeing 787 Dreamliners were grounded by the US Federal Aviation Agency just 18 days after its first commercial flights owing to unexpected fires. The culprit turned out to be poor thermal management of lithium ion batteries thus causing thermal runaway [11]. Better temperature monitoring could have easily prevented this \$600 million disaster.

The use of lithium iron phosphate batteries based systems are often pushed to extreme limits. Owing to its relative stability, it is becoming more common to charge and discharge lithium iron phosphate batteries at a much higher current. This process is less efficient than charging at a slow rate. Due to the lack of efficiency, there is a lot of heat produced in the process, thus causing rapid heating of the battery. This needs to be monitored in order to ensure that a safe margin is maintained to prevent the battery from experiencing thermal runaway.

The internal temperature of lithium ion batteries is typically measured using thermocouples. However, as power densities of batteries rise, thermocouples lead to inaccurate readings. The internal temperature of batteries can often deviate significantly enough from the measured surface temperature (thus leading to accumulated errors in the SOC and SOH estimation). This could damage the battery in the long run. Often times, thermal modelling of the battery is performed in order to obtain a more reliable estimate of the internal temperature of the battery [12]. This approach can tend to be error prone. Furthermore,

it requires additional computing power which in a real-time scenario like a vehicle can be hard to come by. Other approaches to estimate the internal temperature of the battery with higher confidence include microelectromechanical system (MEMS) based temperature sensors embedded inside the battery [13]. However, these sensors tend to be expensive owing the complex fabrication processes used to produce them.

There is thus a need for an embedded temperature sensor that can detect changes in the internal temperatures of the battery and report it externally. An optical sensor lends well to use in such a scenario owing to its robustness from electromagnetic interference as well as tolerance to the relatively harsh environments of the interior of a lithium ion battery.

1.2 Thesis Objective

This thesis presents a fluorescence based fiber optic temperature sensor for monitoring the temperature of lithium ion batteries. The design of such temperature sensor further allows for a multifunctional sensor which can effectively measure multiple parameters namely SOC monitoring and temperature sensing simultaneously. This work represents further development towards an embedded multifunctional temperature and SOC sensor. This allows for a relatively unsophisticated instrumentation for the optical interrogation for temperature estimation and SOC estimation using one fiber. The system for this interrogation are sufficiently simplistic to allow for a cost-effective integration in an automotive environment. Although the work is aimed at the embedding of both of the sensors inside the battery, there is more work required in order to accomplish that goal. The sensor presented here is designed to meet the following objectives:

- **Multifunctional:** The new technology developed must be compatible to a high degree with the existing technology for fiber optic SOC estimation. Thus the choice of wavelength and the effect of cross-talk are important factors that need to be optimized against.

- **Cost-Effective:** Due to the nature of the use of the sensor, it is essential that this sensor be cost-effective. An average electric vehicle has well over 300 individual cells. In order to enable the accurate monitoring of each of them, it is essential to remain somewhat competitive with rival technologies to accomplish the same task.
- **Simple Sensor Readout:** In addition to the actual sensor requiring to be cost effective, it is also necessary that the readout electronics for this system be unsophisticated. The main reasons for this are the cost as well as the harsh environment of an automotive product. The readout should be able to be fed with ease to the car's on board computers.
- **Mass production:** Although a sensor may be easy to produce and cost effective when produced in a one off manner, it is important that the fabrication process used to produce this sensor be scalable. In order to implement this system in a real world, the ability to scale up its production is necessary
- **Embeddable:** The sensor produced here must be able to be adapted to be embedded inside the battery in order to obtain a true readout of temperature that will aid in the determination of the SOC..

1.3 Thesis Organization

This thesis is divided into six chapters. Chapter 2 presents the necessary background to understand the current SOC estimation sensor and explores possible methods to integrate a fiber optic temperature sensor on the same fiber. Several different methods of fiber optic based temperature sensing are discussed with the context of being integrated with the existing SOC sensing methodology and embedded inside a battery.

Chapter 3 provides the more specific design considerations taken into account while designing a thermometric fluorescence based evanescent wave sensor. The specific design decisions made are explored more in depth and the anticipated challenges are presented. Lastly, a design of the proposed sensor is presented.

Chapter 4 presents the experimental methodology used to develop a multifunctional temperature sensor. The chapter first describes the methodology used to prepare the coating solution. Following this, a design of experiment is undertaken to further optimize the coating formulation so that a high degree of sensitivity is obtained. The preparation of the fiber for coating using wet etching is discussed. The dip coating process for the deposition of a good quality film for the sensing is then optimized. The factors influencing the quality of the film in a dip coating process are investigated. The fiber obtained from an optimized dip coating process is then tested in a custom fixture obtain a fiber optic temperature sensor. The sensor is then calibrated and data about the temperature sensor is thus obtained. Lastly a multifunctional sensor that simultaneously senses the SOC of a battery and the temperature is presented.

Chapter 5 analyzes the data obtained from the sensor. The sensor characteristics of the fiber temperature sensor proposed above is analyzed. The sensitivity is obtained and an analysis on the noise obtained is performed. The resulting accuracy of the sensor is then obtained. The temporal response of the sensor is also analyzed. A sensor acceptable for application in an electric vehicle scenario is thus obtained. Lastly, the data obtained from the multifunctional sensor is presented. The cross sensitivity between the temperature and the SOC is analyzed.

Chapter 6 presents the conclusions obtained from this work. The contributions are discussed here. Lastly future work is proposed in order to progress the sensor to a more commercially viable product.

Chapter 2

Background and Literature Review

This chapter provides an overview of the requisite background in order to understand the specifics of the project. Presented initially is background pertaining to the construction and operation of a battery. State-of-charge estimation using the optical properties of graphite in lithium ion battery is then presented. The effect of temperature on the performance of a lithium ion battery is then presented. Existing methodology for temperature estimation in batteries is studied and the trend for battery temperature estimation are presented. Lastly, a variety of different fiber optic temperature sensing mechanisms are presented.

2.1 Background

This chapter reviews the relevant literature pertinent to the development of a multifunctional fiber optic sensor for SOC and temperature estimation. In order to understand the background established by the literature, it is important to understand the architecture of a lithium ion battery (LIB) as shown below in Figure 2.

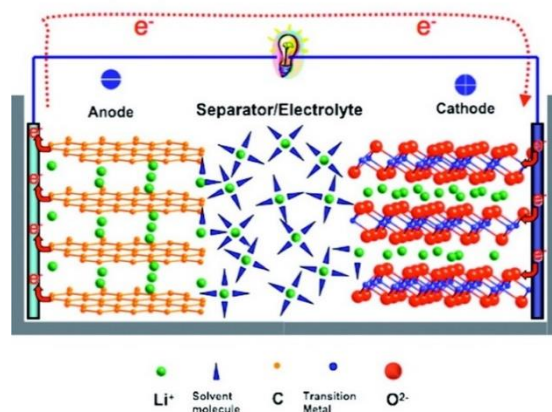


Figure 2 Schematic of a lithium ion battery showing the its components (adapted from[14])

A lithium ion battery consists of the following parts

- **Anode (Negative electrode):** The anode is most commonly a carbon based electrode. The anode of the cell normally stores lithium ions when in a charged state. A range of factors impact the performance of the anode. At the interface between the anode and the electrolyte, a passivating surface reaction occurs. This reaction is irreversible and creates a layer known as the solid electrolyte interface (SEI) [15].
- **Electrolyte/Separator:** There is a layer of a porous insulating layer between the anode and the cathode. This layer is called a separator and serves the purpose to electrically insulate the anode from the cathode but allow for lithium ion transport across it. The porous material of the separator is normally soaked with a liquid known as the electrolyte. This electrolyte is responsible for the mobility of the lithium ion between the electrodes. The electrolyte consists of an lithium salts and organic solvents [16].
- **Cathode:** The cathode material of an LIB consists of a transition metal oxide [17]. The composition of the cathode can strongly determine the performance of the battery. The cathode may be optimized for high power (using materials like Lithium Iron Phosphate) or high energy (Nickel Manganese Spinel). As with the anode, a passivation reaction at the surface occurs and the cathode also forms a solid electrolyte interface layer (SEI).

2.1.1 Fiber based SOC sensing

The intercalation of lithium in graphite electrodes of a lithium ion battery causes a change in the optical properties of graphite. The monitoring of this lithiation process in graphite can reveal a lot about the behaviour of the battery that cannot be gleaned using traditional SOC estimation processes. As shown in Figure 3 the reflectance of graphite at 850 nm is strongly dependent on the amount of lithium intercalation exhibited [17]. This property of graphite can be monitored to obtain more information of the intercalation process in a battery

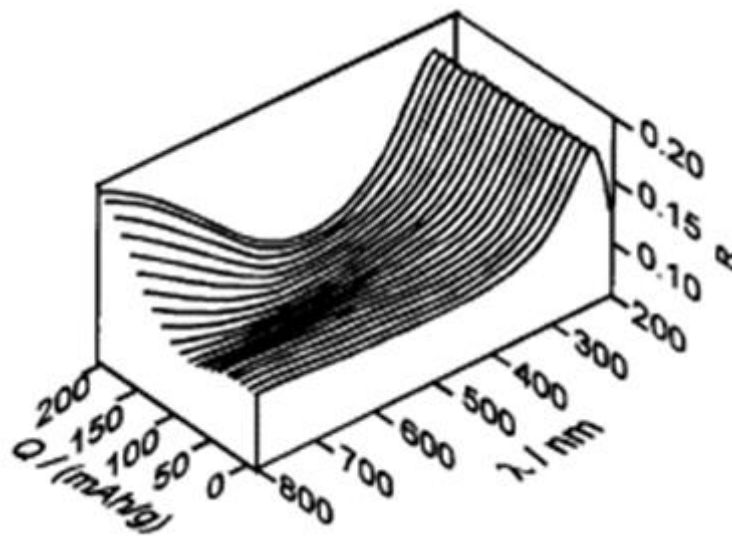


Figure 3 The experimental reflectance spectrum of graphite as a function of state-of-charge (adapted from [18])

This property has been exploited in prior work done at the Sensors and Integrated Microsystems Lab to develop an in-situ real time characterization tool to understand the lithiation process [19]. In this case a Fiber Optic Evanescent Wave Sensor (FEWS) is embedded in close contact inside of a lithium ion battery to monitor its optical properties.

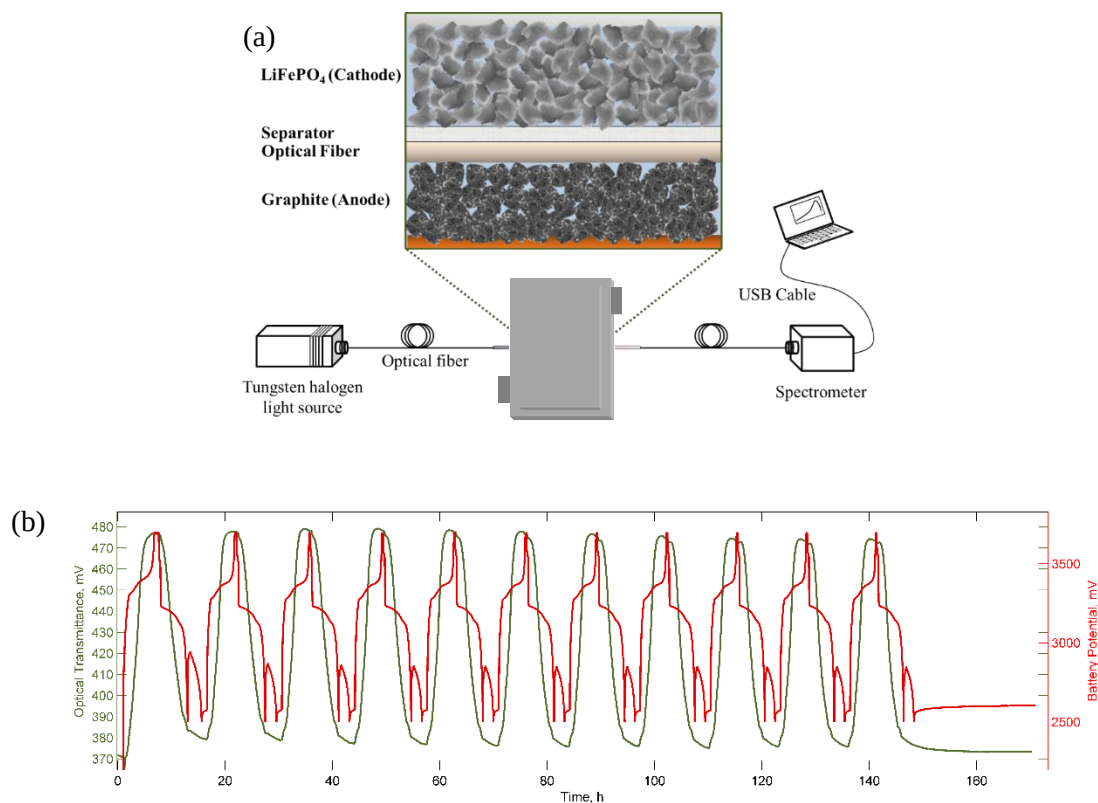


Figure 4 (a) Schematic of the experimental setup for fiber evanescent wave spectroscopy with a detailed illustration of the pouch cell (modified from [19]) and (b) Transmittance of the fiber SOC sensor at 850 nm in a pouch cell plotted as a function of the voltage of the cell

An unjacketed multimode fiber is wet etched in hydrofluoric (HF) acid to thin out the cladding. This thinned out portion of the fiber is embedded within a lithium ion battery in close proximity with the electrode as shown in Figure 4 (a). The optical interaction between the electrode and FEWS allows for non-invasive monitoring of the properties inside the battery in a robust manner. The fiber optic is placed in transmission mode and an 850 nm LED is used to illuminate one end of the fiber. The intensity of light at the other end is monitored in real-time. The intensity of the transmitted light is dependent on the lithiation state of the graphite that it is in contact with. A temperature sensor designed would have to be compatible with this form of battery monitoring.

2.1.2 Temperature dependence of lithium ion batteries

The performance of a lithium ion battery is strongly dependent on the temperature. In an electric vehicle (EV) there are many factors contributing to the greater contribution of temperature on the battery performance. Unlike consumer devices, EVs face a high density of lithium ion batteries stored together. Thus when high current is supplied to or drawn from the battery pack, low heat dissipation causes localized heating the battery pack. Secondly, owing to exposure to environmental factors, battery packs in an electric vehicle are more likely to experience a wide spread of temperatures depending on the weather conditions.

In a harsh winter like that in Canada (-40°C), the capacity of a lithium ion battery can fall to as low as 5% of the energy density provided at 20°C [20]. Additionally, although the cell can be discharged, the charging process at low temperatures can lead to irreversible degradation thus leading to a high degree of inefficiency. High temperature of the lithium ion battery can also irreversibly damage the battery. Operating a battery at an elevated temperature leads to capacity fade. In more traditional lithium ion cell architectures (lithium cobalt oxide cells), the biggest factor contributing to this capacity fade is the degradation of the cathode [21]. This capacity fade effect is less pronounced in lithium iron phosphate cathodes which makes them a likely candidate for automotive applications [22]. The anode (most commonly graphite) also displays a pronounced degradation in its capacity when cycled at an elevated temperature. At higher temperatures, the growth of the SEI layer is assisted. This thick SEI layer causes a barrier to the diffusion of lithium between the graphite particles and the electrolyte [23] [22] [21]. This degradation in the performance of the battery translates directly to the capacity of the battery and determines the SOH of the battery. Temperature measurement is thus necessary for maintaining optimum battery performance.

Lastly good thermal management is necessary for batteries especially in an automotive context. Due to the near-instantaneous torque response of electric vehicles, during acceleration, there can be large peaks in the current draw from the battery. In order to better estimate the temperature of the battery, temperature sensors must be placed as close to the source of heat as possible (thus allowing for faster

readout and preventing catastrophic thermal runaway). Furthermore, a faster temperature readout combined with a more precise measurement of the state-of-charge of the battery is essential for better thermal behaviour analysis of lithium-ion batteries [25]. Integration of these two parameters of the battery on one sensor is thus a desirable area of work.

2.2 Literature Review

2.2.1 Traditional battery temperature monitoring

Electric vehicles often have a dedicated system to ensure the correct operating conditions for their battery pack [26]. These systems consist of sophisticated controllers that read out temperature from strategically placed thermistors around the battery pack. This is necessary to extend the life of the battery pack throughout the service life of the vehicle by maintaining optimum temperature conditions. These systems use strategically placed thermistors or thermocouples near the current collectors of the battery. The location is owing to the fact that the battery is most likely to heat up near to current collectors owing to high current density [27].

In practical applications however, the heating process of batteries is in-homogenous. Due to defects present in the battery, it is possible that there are highly localized hot-spots within the battery. These localized hot-spots can often not be picked up by the thermocouples used traditionally for battery monitoring owing to their location. Furthermore, it is experimentally observed that the surface temperature of a lithium ion battery can often be different from the internal temperature [28]. Owing to the relatively poor thermal conductivity of the electrodes used in a lithium-ion cell, accidental short-circuits or overcharges cannot be estimated rapidly using surface temperature measurements.

It is thus important to develop embedded temperature sensors that can quickly detect the thermal performance of a battery. Some work has been done to demonstrate the viability of embedded temperature sensors inside the battery [13]. At the time of this research however, there is no demonstrated temperature sensor embedded inside a lithium ion cell for temperature monitoring.

2.2.2 Optical temperature sensing mechanisms

Optical sensing of temperature is a viable option for automotive use owing to their robust nature. Optical sensors are used owing to their resistance to harsh environments (such as the corrosive nature of batteries). Furthermore, they are functional in areas with vastly varying electromagnetic fields (such as an electric vehicle) and are less prone to electromagnetic noise. Furthermore, optical temperature sensors present the possibility of integrating multiple functionalities onto one fiber. In addition to previously demonstrated optical SOC and SOH estimation using fiber optic sensors, the internal temperature may also be estimated using such a sensor.

There are several different methods to measure temperature using a fiber optic transducer. Not all technologies may be applicable for this use scenario. The selection of the candidate technologies was based on literature review and assessment based on the design objectives outlined in section 1.2. The most prevalent technologies are outlined below with their inherent benefits and faults for the intended application.

2.2.3 Fiber Bragg Gratings

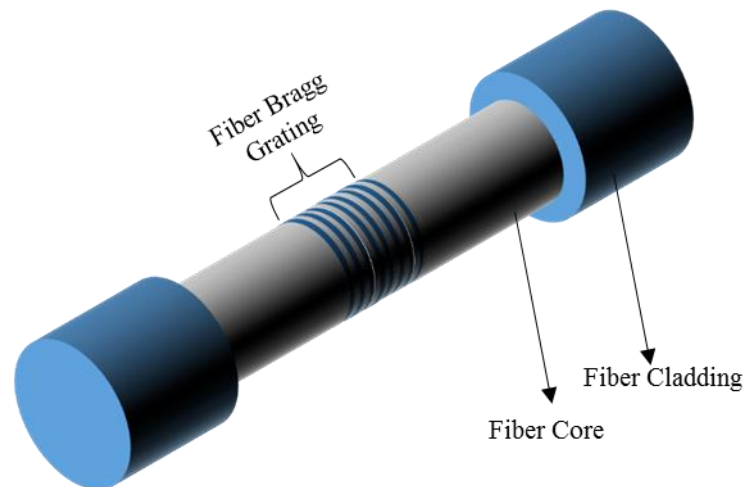


Figure 5 Illustration of a Fiber Bragg Grating structure use for temperature sensing

Fiber Bragg Gratings (FBG) are a specialized type of fiber in which systematic gratings are inscribed as shown in Figure 5. The periodicity of these gratings causes some wavelengths to be reflected very

strongly while other wavelengths are transmitted through. It thus behaves as an optical filter. This periodicity strongly influences the transmittance properties of the FBG. Thus when the periodicity increase (because of linear expansion due to temperature or strain), the peak wavelength of the optical filter system changes significantly. The FBG is normally encapsulated in a housing with a large thermal coefficient which causes a strain exerted on the FBG. This change is described by Equation (1).

$$\frac{\Delta\lambda}{\lambda} = (1 - p_e) \cdot \varepsilon + [\alpha + \zeta + (1 - p_e) \cdot (a_s + \alpha)] \cdot \Delta T \quad (1)$$

In the above equation, $\Delta\lambda$ describes the shift from the original peak position of the FBG optical filter from the original peak position of λ with a_s and α are the thermal expansion coefficients of the substrate and the optical fiber respectively, p_e is the elastic-optic coefficient of the FBG, ζ the Poisson's ratio for the optical fiber and ε describes the Young's modulus of the optical fiber.

FBG based sensors are used in a variety of commercial applications and have a market exceeding \$1 billion annually. They are most often used in scenarios where traditional electrical readout is not possible or poses significant challenges due to the harsh nature of the measurand [29]. FBGs have been used in aerospace applications, medical applications, oil exploration and other similar applications where signal integrity is expected to be maintained over large distances with high tolerance to electromagnetic variances.

Despite their widespread adoption, FBG based sensing is still expensive. Although fabrication of these devices is possible economically, the necessary instrumentation required for interrogation is a hurdle. The instrumentation used for this purpose is normally a complex opto-mechanical assembly which is expensive and delicate.

2.2.4 Fabry Perot Etalon

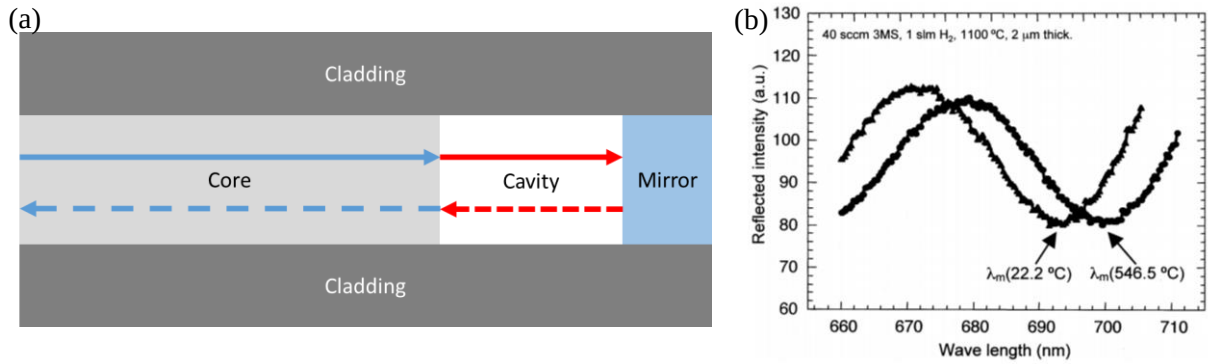


Figure 6 Left: Illustration of Fabry-Perot Temperature Sensor;
Right: Temperature Response for a Fabry-Perot Sensor (extracted from [30])

Fabry-Perot Etalons consist of a cavity whose thickness is around the order of magnitude of the wavelength of light (shown in Figure 6). Constructive and destructive interference occurs in this cavity and certain wavelengths can be reflected more strongly (owing to the supporting of electromagnetic standing waves). The wavelength of light is strongly dependent on the path length of light in the cavity (which in turn depends on the thickness of the film and the refractive index of the film). This principle may be used for sensing in a fiber. Such a sensor has a construction which consists of the sensing area as a thin film on the tip of a fiber. Two main types of Fabry-Perot based temperature sensors exist and they use two different phenomena to perform sensing.

- **Thermal Deformation:** Thermal deformation based Fabry-Perot sensors use the property of solid to expand upon increases in temperature. These changes in temperature cause a change in the thickness of the Fabry-Perot cavity. This change in thickness translates to a change in the interference condition [31].
- **Thermo-optic Transduction:** These kind of sensors rely more on the change in the optical properties of the film that forms the cavity. An embodiment of this type of sensor uses sapphire owing to its high thermo-optic coefficient in the Fabry-Perot cavity [32]. The refractive index change causes a change in the path length of the light in the medium thus causing a temperature dependent response which is then monitored.

Fabry-Perot based fiber temperature sensors are challenging to produce on a large scale. However, over the past few years, the industrial usage of Fabry-Perot sensors has expanded (primarily owing to its fast response time). Furthermore, owing to relatively simpler optics required for the readout, Fabry-Perot based sensors can be used in harsh environments with the accompanying readout device. Fabry-Perot sensors, however, have an inherent disadvantage owing to the nature of their construction. Due the mirrored end, these sensors can only be used in reflectance mode measurements. Transmittance type measurements along with Fabry Perot type measurements are challenging to perform. This thus poses a significant difficulty in integrating with the SOC sensor (which relies on transmittance)

2.2.5 Optical Time Domain Reflectometry

Optical Time Domain Reflectometry (OTDR) may be used to perform temperature sensing. Short and narrow pulses of a laser is shone into the fiber and the reflected light from the fiber is studied in an interferometric setup as shown in Figure 7 (a). This allows for distributed temperature sensing along any part of the fiber (thus allowing for a one dimensional map of the temperature of the fiber along its length. The temperature is estimated by studying the anti-Stokes shift of the backscattered light in the silica fiber as shown in Figure 7 (b).

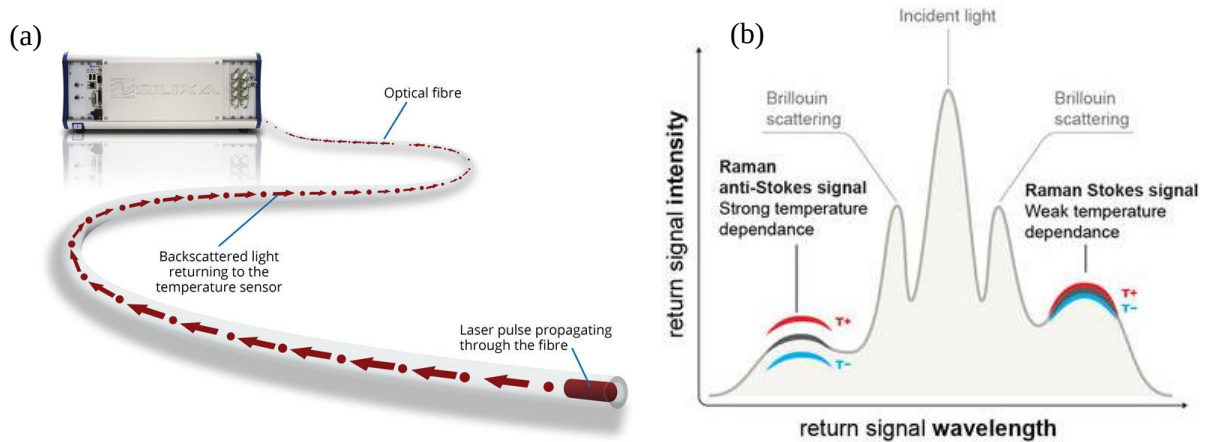


Figure 7 (a) Illustration of distributed temperature sensing using an OTDR(extracted from [33]) and (b) Illustration of the Raman spectrum of silica showing strong dependence of anti-stokes shift in temperature (extracted from [34])

This methodology of temperature sensing forms a strong candidate for a robust sensor. Without the need for modification of commercial fiber, this type of sensor can be integrated on an existing SOC sensor without any modifications to the fiber. Furthermore, the ability to perform distributed temperature sensing allows the studying of temperature along different points of the fiber simultaneously. This thus allows to study the homogeneity of temperature distribution along the fiber.

A big challenge with this method for estimation of the temperature is the readout instrumentation required. An OTDR is normally a very expensive piece of equipment. Due to the delicate optical components in an OTDR, it is not an instrument that is robust enough for integration in an automotive environment.

2.2.6 Polymer Thermo-Optic Transition

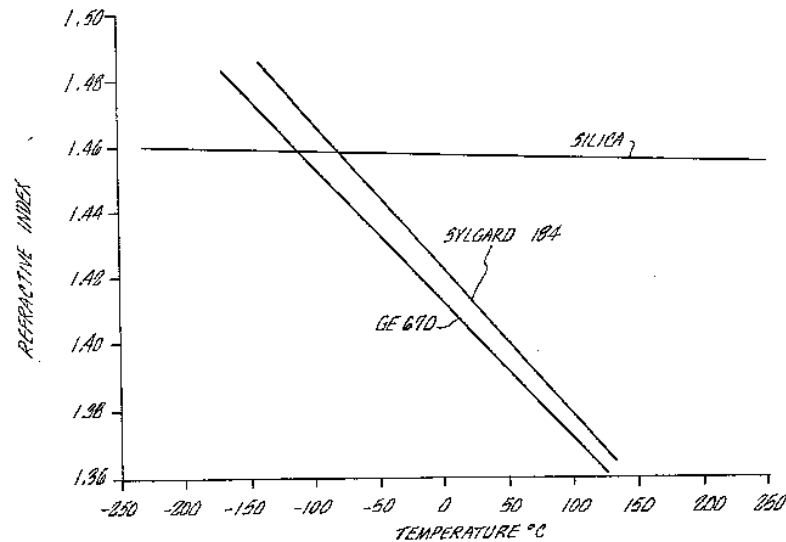


Figure 8 Illustration of temperature dependence of refractive indices of some common polymeric materials (extracted from [32])

Polymers are known to have a high thermo-optic coefficient of refractive index as shown in Figure 8. This property may be used for temperature sensing. The total internal reflection into the fiber is strongly dependent on the refractive index of the cladding. Thus, when the polymer is used as a cladding for

silica core fiber optics, a temperature dependent response may be observed. This has been established as a methodology for sensing since 1980 [32].

This type of sensor is plausible for integration with our system owing to its low cost. Interrogation of this system is fairly straightforward as this is an intensity based measurement. However, owing to the fact that this causes an overall attenuation of the signal, there would be a high degree of cross-sensitivity between the temperature signal and the SOC signal at 850 nm.

2.2.7 Fluorescent Temperature Sensing

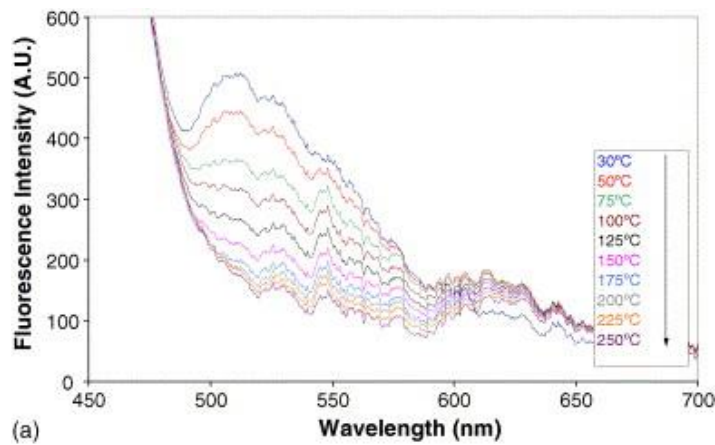


Figure 9 Fluorescence emission spectrum of a fluorescein as a function of temperature (extracted from [35])

Fluorescence based sensing relies on the temperature dependent fluorescence of certain fluorescent compounds. Coating impregnated with these fluorescent molecules forms the cladding. Fluorescence uses a high energy light source (~450 nm) to excite electrons in the fluorescent molecule into a singlet state. This state then relaxes emitting energy at a lower wavelength in the process. The efficiency of down conversion is strongly dependent on temperature.

This system uses a simple blue light source to excite the electrons and senses the fluorescence at a lower wavelength. This system relies on an intensity based measurement thus allowing for lower cost. The ability to separate the temperature transduction and the SOC monitoring on different wavelengths makes this a likely candidate for low-cost integration with the existing sensor.

Chapter 3

Design of the Sensor

In this chapter, the various factors that determine the final outcome of the design are presented. The ideal architecture of the sensor is then selected and implemented.

3.1 Principle of operation

Luminescence is the emission of light from any substance as a result of electronically excited states. Luminescence may be divided broadly into two categories: fluorescence and phosphorescence, depending on the nature of the excited state. Fluorescence is characterized by singlet states with a spin counter to the electron in the ground state. As a result, the singlet state is not very stable and the return to the ground state is rapid with a resulting photon emitted [36].

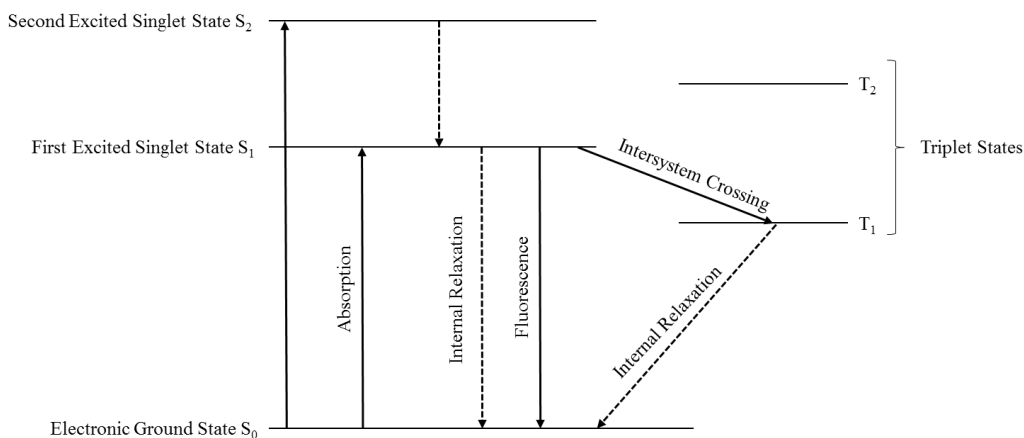


Figure 10 Schematic Illustration of electronic energy transitions in a fluorescent molecule (adapted from [37])

As shown in Figure 10 when an electron is excited by a photon of a given energy, the fluorescent molecule (fluorophore) absorbs the energy from the photon and the molecule transitions from ground

state to a higher electronic state. The energy of the electron is then dissipated thermally until the electron reaches the lowest excited energy state (denoted as S_1). From this state, the molecule can reach the ground state through many processes. The mechanisms of de-excitation can be categorized into radiative and non-radiative processes. In radiative processes, the remaining energy is dissipated by the return of the electron to the ground state along with the emission of a photon in the process. This is known as fluorescence. In a real scenario, only a fraction of decay events occurs radiatively. Most of the energy of the excited state is dissipated non-radiatively through internal conversions and intersystem crossings. The efficiency of a fluorophore is characterized by its quantum efficiency

$$\phi = \frac{k_r}{k_r + k_{nr}} \quad (2)$$

where k_r is the rate of emission of photons radiatively through fluorescence and k_{nr} is the rate of non-radiative relaxation. For a dye of a given concentration C and quantum efficiency ϕ , the intensity of the fluorescence energy emitted per unit volume (I) is given by the expression

$$I = I_0 C \phi \epsilon \quad (3)$$

where ϵ is the absorption coefficient of the dye, I_0 is the flux of incident light. Thus variations in the intensity of the fluorescent light is a direct result of variations in the quantum efficiency ϕ of the dye. Temperature has a strong effect on the quantum efficiency of a dye. For example, Rhodamine B has a temperature coefficient of quantum efficiency of 2.3%/K compared to its temperature coefficient of absorption coefficient of about 0.05%/K [38]. This modulation of quantum efficiency as a function of temperature allows for fluorescence based thermometry as it modulates the intensity of the fluorescent intensity as a function of the temperature.

The simplest embodiment of fluorescent uses a single dye based measurement. The intensity of the excitation source is kept constant and the intensity of the emission is monitored. This intensity is compared to the intensity at a known temperature to obtain the measured temperature.

3.2 Two-dye fluorescence

Although single dye fluorescent thermometry is widely used, a significant problem with such an implementation is the effect of photobleaching. Bleaching is the irreversible conversion of a fluorescent molecule or particle into a non-fluorescent species. Commonly observed degradation mechanisms for bleaching are mostly dominated by photon mediated bleaching (photobleaching). The occurrence of photobleaching is accelerated by higher temperature [39].

This phenomenon can be countered by the use of two dyes in a FRET (Forster Resonant Energy Transfer) based system. FRET uses two different dyes in order to produce fluorescence. FRET based systems normally have a donor dye and an acceptor. The donor dye is a larger bandgap molecule than the acceptor. When illuminated with the excitation source, the donor is excited (normally owing to its higher absorption coefficient at the excitation wavelength). The energy from the excited donor fluorophore is transferred to the acceptor fluorophore through FRET. The acceptor is thus excited indirectly. This acceptor then comes down to its ground state thus emitting photons in the process. For use in thermometry, the donor is normally a more stable (less likely to photo-bleach) molecule with a low temperature coefficient of quantum efficiency and the acceptor is a molecule with a higher temperature coefficient of quantum efficiency (which correlates to a lower stability). In the system described in this thesis, the donor used is Fluorescein and the acceptor used is Rhodamine B.

An additional benefit of using a double dye based fluorescent thermometry system is the fact the energy transfer process between the two molecules also tends to be dependent on temperature. Although using such a system causes a much lower quantum efficiency, the temperature coefficient of the quantum efficiency is observed to be higher

3.2.1 Optimization of the composition

Optimization of the concentrations of the two dyes for this application is necessary. There are three components of the PMMA based thermochromic coating. For the coating, PMMA was used owing to its optical properties and its wide utility as a matrix for the doping of fluorophores. The fluorophores used were fluorescein as the donor owing to its accessibility and precedent as a donor in such a system. For the acceptor, rhodamine B was used owing to its high temperature coefficient of quantum efficiency.

The exact composition of the mixture required optimization in order to ensure a high fluorescent yield as well as high sensitivity. According to the Förster theory [40], the radius of 50% energy transfer (in Å) via FRET is described by

$$R_0^6 = 9.78 \times 10^3 [\kappa^2 n^{-4} Q_D J(\lambda)]^{\frac{1}{6}} \quad (4)$$

where κ is an orientation factor of dipole-dipole interaction (assumed to be 2/3 for random orientations of the donor and acceptor), n is the refractive index of the medium that the donor and acceptor are distributed in, Q_D is the quantum yield of the donor and J is the degree of spectral overlap between the donor and the acceptor. As shown in Figure 11, the use of a 470 nm LED with fluorescein and rhodamine B is ideal [41]. This is primarily due to the low absorption of the excitation source by rhodamine B (thus minimizing photobleaching). Most of the excitation occurs in fluorescein. Due to the good spectral overlap between the emission spectrum of fluorescein and the absorbance spectrum of rhodamine B, efficient energy transfer using FRET is possible.

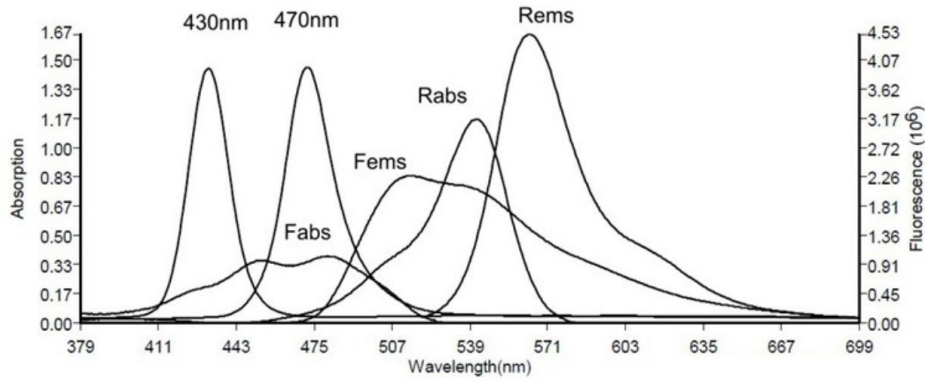


Figure 11 The absorption spectrum of fluorescein (Fabs) and Rhodamine (Rabs) in ethanol and emission spectrum of LED (430 nm and 470 nm), Fluorescein (Fems) and Rhodamine B (Rems) in ethanol (extracted from [41])

Furthermore, the efficiency of energy transferred E from the donor to the acceptor for a FRET based system is given by

$$E = \frac{R_0^6}{R_0^6 + r^6} \quad (4)$$

where r is the intermolecular spacing and R_0 is the Forster distance (distance at which 50% energy transfer occurs). The intermolecular spacing of the compounds is determined by the doping concentration of the coating. Thus, by optimizing the doping concentration, a high efficiency of energy transfer via FRET can be observed. The R_0 of a system is based on several factors including the spectral overlap of the molecules, the lifetime of the excited species and the refractive index of the material. All of those factors vary significantly as a function of temperature leading to a change in the R_0 as a function of temperature.

According to the above equation, it would be highly beneficial to have the fluorophores as close to each other as possible in order to have the highest energy transfer possible. However, when the fluorophores get too close to one another, the quantum yield is observed to reduce. This is due to the phenomenon of self quenching where two fluorophores placed close to each other will experience a higher probability of intersystem crossing owing to their proximity. This intersystem crossing contributes to the non-radiative decay of the excited molecule thus leading to a reduced quantum yield.

As shown in Figure 12 it is evident that a higher concentration of the fluorophore leads to a reduction in the quantum yield. In order to obtain a high sensitivity fluorescent coating, it is necessary to perform the requisite optimization processes empirically.

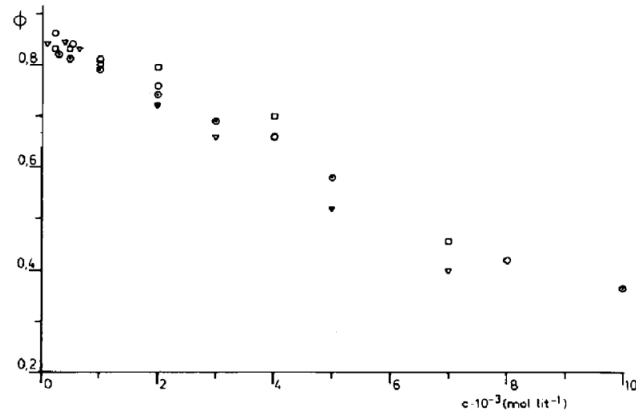


Figure 12 The fluorescence quantum yield of fluorescein (pH 12) at various concentrations(adapted from [42])

3.3 Fiber based fluorescent thermometry

The use of optical fibers in this application is important because it facilitates the usage of two different sensors on the same compact form factor. The current generation SOC and SOH sensors developed by Zdravkova et al [43] uses a multimode fiber that is etched in a certain region and embedded inside a lithium ion battery. This is primarily motivated by the fact that optical fibers are typical of a very small diameter (125 μm in our case) and allow for conduction of optical signals in a robust manner which are impervious to electromagnetic interference.

Optical fibers generally consist of a central core material with a high index of refraction surrounded by a cladding of low refractive index. As shown in Figure 13, the fibers used in this research were a silica core with a fluoride doped silica cladding. Around the silica components is an acrylate coating which provide further mechanical protection to the fiber. Light is introduced in the core and propagates along the length of the fiber by total internal reflection (TIR).

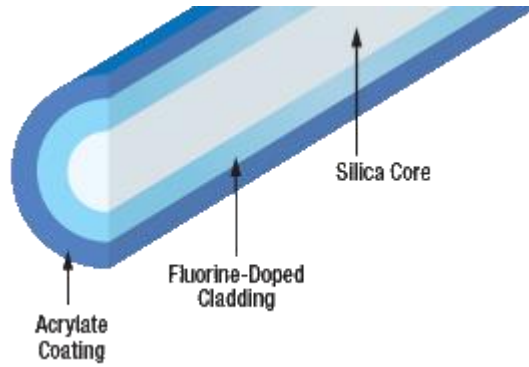


Figure 13 The structure of an optical fiber illustrated showing its construction

At the interface between the core and cladding, a part of the electromagnetic wave in the core extends into the cladding. This electromagnetic wave decays exponentially as the distance from the core-cladding interface increases. This exponentially decaying stationary electromagnetic field is known as an evanescent wave. Evanescent waves have been harvested as a development of in-line optical sensors. When a portion of the cladding is removed, the evanescent field can escape the cladding and interact with the surrounding material. When the material surrounding the thinned-out portion of the cladding (henceforth referred to as the sensing region of the fiber) absorbs the evanescent wave propagating through the fiber, the intensity of the light propagating through the fiber reduces. This phenomenon may be used to develop sensors that measure a materials optical properties based on its absorbance. This technique allows for effective measurement of optical properties coupled with the ease of conduction of the signal over the length of the fiber.

For the work demonstrated in this thesis, evanescent wave sensors are coupled with the aforementioned fluorescent thermometry in order to measure temperature using transmission mode measurements in a fiber. This allows for in-line integration with the existing transmission based SOC sensor. Although fluorescence based fiber optic temperature sensors have been established, evanescence based fluorescent thermometry as presented here is novel.

3.4 Coating of the thermometric coating on the optical fiber

There are a variety of ways for coating the thermometric coating on the optical fiber. Due to its simplicity, dip coating was used as the preferred methodology. Dip coating consists of withdrawing a substrate from a solution leaving behind a film of the solute. Dip coating a cost effective method to coat a surface in a rapid and predictable manner.

In order to dip coat a substrate, it is immersed in a solution containing a solvent and a solute. In our case, the solution is formed by the PMMA and fluorescent dye solution in acetic acid. The substrate is then withdrawn in a controlled manner to promote film formation on the surface of the substrate by solvent evaporation. Due to the Newtonian behaviour of solution, there is normally a layer of fluid that is dragged along the surface of the substrate owing to viscous drag. This forms an asymptotically tangential film of liquid parallel to the surface of the substrate. At the same time as this liquid film is formed, solvent evaporation occurs. This solvent evaporation causes a decrease in film thickness and an increase in the concentration of PMMA locally. Eventually, the concentration increases to a point that concentration of PMMA in the solution allows for the crosslinking of the PMMA chains. This leads to a uniform coating of cross-linked PMMA on the optical fiber. It is thus important to optimize and chose the correct conditions for depositing a sound dip coating on a fiber

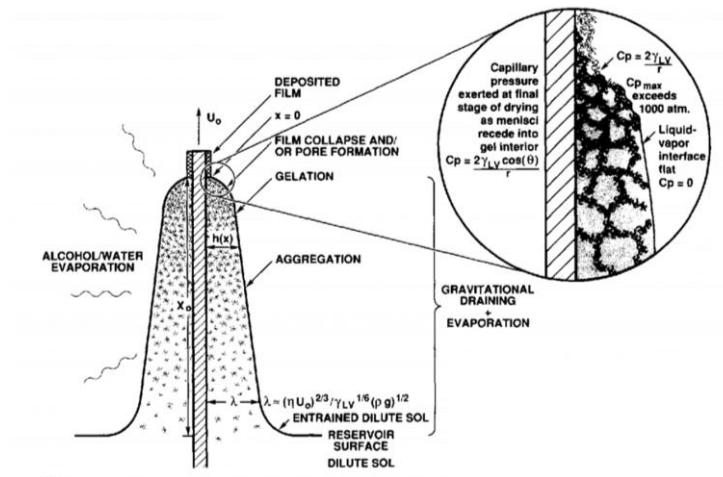


Figure 14 Schematic of the dip-coating process showing the forces acting on the meniscus determining the thin film coating thickness (extracted from [44])

3.5 Signal acquisition and processing

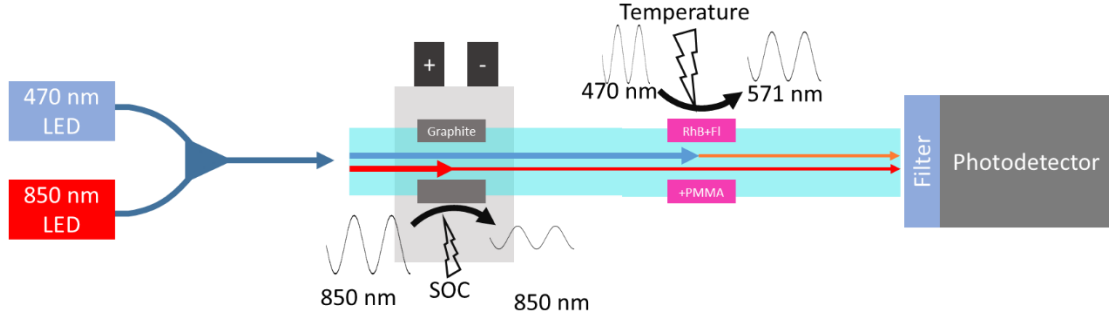


Figure 15 Block diagram of proposed multifunctional sensor showing the two sensing regions and their effect on the output signal

The block diagram of the proposed multifunctional sensor is shown above in Figure 15. The system consists of 2 LED sources at 2 different wavelengths coupled to the same fiber (which acts as a multifunctional sensor). One LED at 850 nm is used in order to monitor the SOC of the battery. This wavelength is chosen as a result of prior work shown in Figure 16 which demonstrates that at 850 nm the reflectance of graphite is more sensitive to the state of charge (when compared to other wavelengths). Thus monitoring the transmittance of the fiber at 850 nm is demonstrated to display good correlation between the state-of-charge and the optical transmittance through a fiber optic evanescent wave sensor.

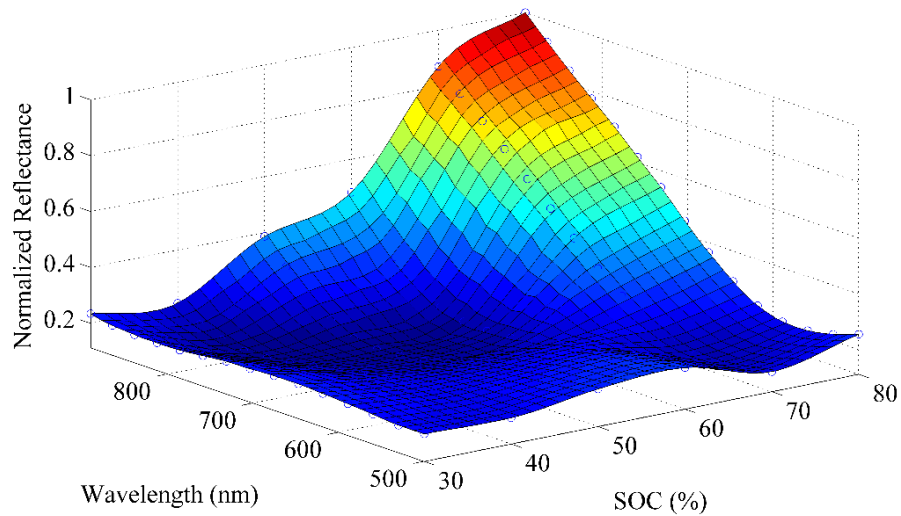


Figure 16 Reflectance of graphite anode retrieved from a commercial cell as a function of SOC (adapted from [19])

The reflectance of graphite shows some dependence on the SOC at 600 nm. Thus the temperature sensor is placed in-line after the SOC sensing section of the fiber. This is primarily done to avoid cross-sensitivity between the temperature readout and the SOC readout. The temperature sensor consists of a thermochromic fluorescent coating coated on a partially etched optical fiber. At excitation source is the second LED used in the system. The excitation source is chosen to be at 470 nm due to the high absorbance of the fluorescent dyes at the given wavelength. The light at 470 nm passes through the SOC sensing section of the fiber before proceeding to the temperature sensing section. As shown from studies above in Figure 16, only a small amount of optical activity is displayed by graphite at 470 nm. The excitation light then proceeds to excite the fluorescent coating. The fluorescent coating then down-converts this excitation source to light at 570 nm. The efficiency of conversion of the 470 nm light to light at 570 nm is temperature dependent. Thus when the temperature changes, the fluorescent intensity changes.

The temperature sensing portion is placed in close proximity with the battery in order to pick up the temperature of the battery. In the final embodiment of the device, only one of the LEDs is turned on at a given time. When the 850 nm is turned on, the intensity thus captured by the photodetector is representative of the SOC of the battery. When the LED at 470 nm is turned on, the intensity thus obtained would be correlated to the temperature signal. This therefore allows for switching between temperature acquisition and SOC acquisition simply by choosing which LED is shone through the multifunctional sensor. This thus represents a simplistic system that appears to be a good candidate for integration in a ruggedized automotive environment.

Chapter 4

Sensor Fabrication and Experimental Results

4.1 Coating preparation

The first step for the fabrication of the sensor is the preparation of the coating. The solvent chosen for the coating is acetic acid owing to the good solubility of PMMA in acetic acid as well as its environmental compatibility [45]. Additionally, acetic acid has been shown to introduce fewer contaminants and demonstrates better surface properties [46]. The use of acetic acid to prepare a PMMA coating on optical fibers has been demonstrated in prior work [41]. The use of acetic acid and PMMA allows for simpler solvent evaporation based polymer film deposition thus requiring little processing of the coating once deposited.

The PMMA (Alfa Aesar Part no) was measured out and dispensed into a glass vial. Glacial acetic acid was then dispensed into this vial using a micropipette. The weight of the vial was carefully monitored in order to ensure a predictable concentration of a PMMA solution was obtained. For the given molecular mass of PMMA, a 5% w/w solution was determined to be appropriate. Concentrations much higher than this were found too difficult to dissolve easily in acetic acid. In order to promote the dissolution of the PMMA in acetic acid, a stir bar was introduced and the vial was stirred for 3 hours.

The donor used for the double dye fluorescence system is fluorescein owing to its popularity as a fluorophore. The acceptor used for these experiments are rhodamine B (Sigma Aldrich Part no) owing to its high thermal coefficient of quantum efficiency. In order to ensure a high fluorescent yield without self-quenching, a design-of-experiment based optimization was conducted in order to obtain the optimum concentration of the materials to create the fluorescent thermometric coating.

Stock solutions of Rhodamine B (0.014w/w in ethanol) and fluorescein (0.06% w/w) were made. The concentrations were chosen based on the solubility of the fluorophores in ethanol. These solutions were then mixed with the 5% PMMA to obtain a range of 5 different doping concentrations between 0.3% (w/w of the PMMA) and 0.4% (w/w of the PMMA) for both fluorescein and rhodamine B of the cast coating.

Glass slides were sonicated in acetone followed by ethanol to remove contamination. An ozone cleaner was then used into to further get rid of surface contamination and induce oxygen passivation in order to ensure a low contact angle. These solutions were then drop cast onto this glass slide. 5 μ L of the mixtures prepared were dispensed onto the cleaned glass slides using a micropipette. The drop was allowed to spread and air dry for 15 minutes.

4.2 Thermal characterization of coating

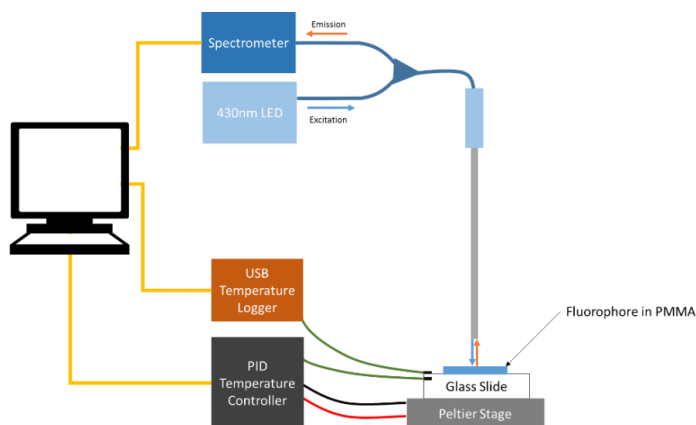


Figure 17 Diagrammatic illustration of thermal cycler setup for testing the temperature sensitivity of the fluorescent coating

The thermal properties of the coating were monitored using a custom experimental apparatus as shown in Figure 17. These glass slides were then secured onto a Peltier stage (Ferrotec 9501/128/040B) using thermal paste to ensure good thermal conductivity. The Peltier stage is controlled using a PID temperature controller (Ferrotec FTC 100) which is computer controlled. There are 2 thermocouples secured onto the glass slide using thermally conductive tape (3M 363). One of the thermocouples is used to provide feedback to the control loop of the temperature controller in order to maintain a steady temperature. The second thermocouple is connected to a computer using a USB thermocouple reader (National Instruments USB-TC01). The excitation light is shone on this coating covered slide using a reflectance probe (Ocean Optics R200-7-UV-VIS). The reflecting fibers of the probe are connected to a spectrometer which feeds data in real time to a computer (Ocean Optics USB 2000). The system is controlled by a custom MATLAB software. The entire setup is placed in a blacked out glovebox in order to isolate the contribution of external light sources.

A dark spectrum is acquired with the light source turned off in order to compensate the nonlinearity of the CCD based light sensor. A light spectrum is then taken in a part of the glass slide where there is no coating. This allows for a measurement of a baseline from which the contribution of the reflection of the excitation source can be isolated. The probe is then moved to the region where coating is present and illuminates the coating. The result of such a setup is shown below in figure 17 displaying a saturated signal for the excitation wavelength and the emission of the coating (which appears to match the emission of rhodamine).

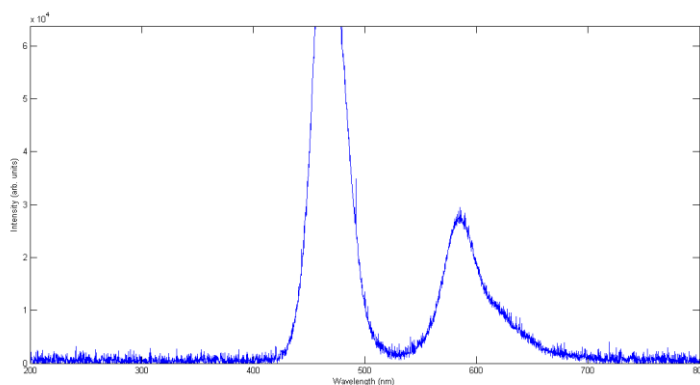


Figure 18 Reflectance spectrum of the fluorescent coating with 0.38% w/w fluorescein and 0.38% w/w rhodamine B showing one peak for the excitation source and the next peak with the emission spectrum of the fluorophore

A reflectance spectrum is taken every 10 seconds from this point on. The coating is heated and maintained at around 40°C for 30 minutes in order to make sure that the solvent is evaporated and to allow for the annealing of the coating. After the annealing step, the coating is brought down to 15°C and maintained at that temperature for 30 minutes in order to ensure that the coating is at thermal equilibrium. The temperature is then ramped up in 5 °C increments and held for 30 minutes. Once the 30-minute period at 35°C is finished, the test is considered complete and the user is sent a notification.

From the spectra obtained above, post-processing is performed by MATLAB and results are plotted. Some degree of electrical noise is isolated using boxcar averaging. Boxcar averaging was implemented by using exponentially weighted moving averages on each pixel (i.e. wavelength). Owing to the lack of any sharp features in the spectrum, the averaging did not alter any features or trends from the spectrum. Following the averaging step, the response of an optical filter and a photodetector were implemented. A low-pass filter was simulated which allowed only wavelengths greater than 500 nm to pass through the filter. The curve thus obtained was then processed using the cumulative trapezoidal function from MATLAB to integrate the area under the curve in order to simulate the photon flux incident on a photodetector. This cumulative trapezoidal function outputs a value in arbitrary units that corresponds to the net photon flux (greater than 500 nm) incident on the spectrometer. This should thus

correspond roughly to the current produced by a photodetector in a similar system as a result of the fluorescent intensity of the coating.

This output (henceforth referred to as the fluorescent intensity) is then plotted as a function of time and correlated to the temperature read by the USB thermocouple reader. This correlation is then plotted and a linear regression analysis is performed. This analysis gives us an idea of the important sensor characteristics of sensitivity and signal to noise ratio.

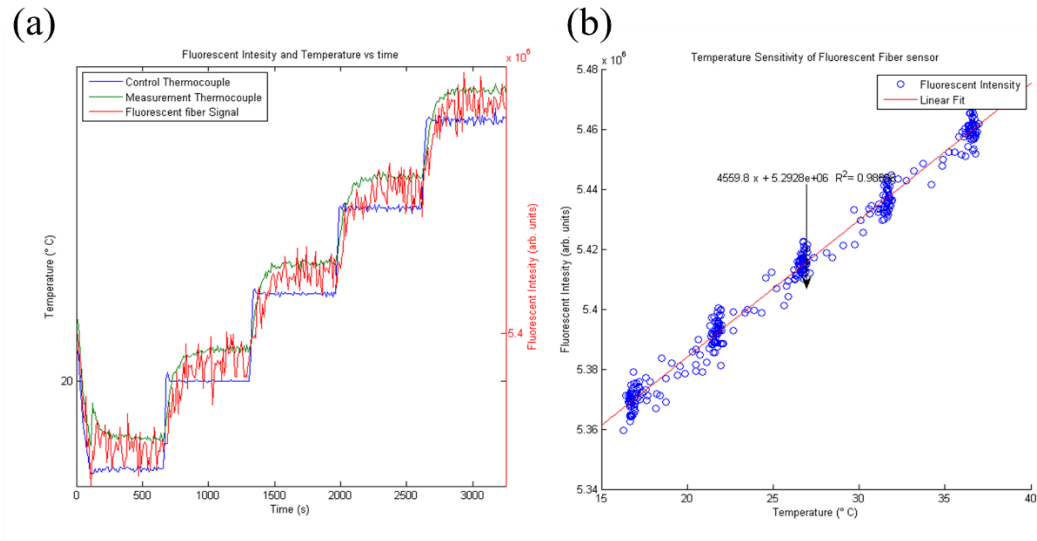


Figure 19 Results of thermal cycling for a sample composition of 0.32% w/w fluorescein and 0.38%w/w rhodamine B (a) showing the time dependent response of the fluorescent intensity and temperature and (b) showing the correlation between the temperature and the fluorescent intensity illustrating the sensor sensitivity

The data obtained from the design-of-experiment above is analyzed. Each of the 25 different samples were analyzed in a similar manner. The noise performance was characterized by the goodness-of-fit (i.e. the R^2 value of the linear regression). It was found that for all of the samples, an R^2 value of between 93% and 95% was obtained thus indicating that a linear regression is sufficient for first order analysis of the sensor response. The sensitivities of each of the samples in the design-of-experiment study were compared.

As shown below in Figure 20, there is variation in the sensitivity as a function of the composition. A peak in observed at around 0.32% w/w Fluorescein with 0.38% w/w Rhodamine B. This is consistent

with compositions reported in literature for two dye fluorescent thermometry [41]. This composition was then chosen going forward to comprise the temperature sensitive coating for fiber optical fluorescent thermometry.

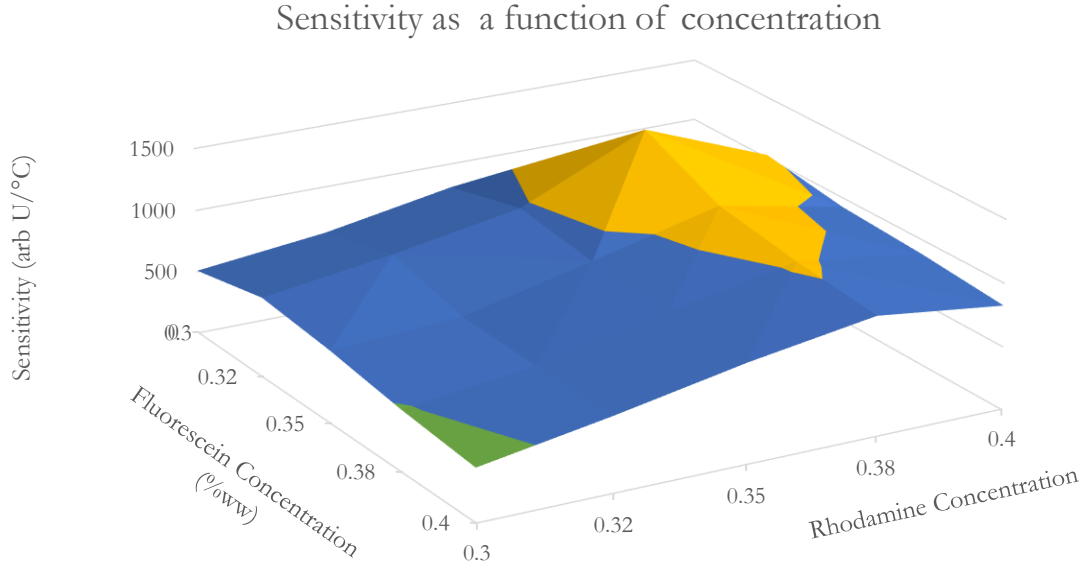


Figure 20 Result of concentration optimization experiments for the selection of the optimum concentration for fluorescent thermometry

4.3 Fiber preparation and etching

Following the optimization of the sensor, the immediate following step is the preparation of the optical fiber for sensing. The sensing area is formed by the incomplete wet etching of the cladding using buffered oxide etchant containing 7% w/w hydrofluoric acid with 34% w/w ammonium fluoride(VWR JT5569-3). The optical fiber used to make these sensors are multimode fibers (Thorlabs FG105LCA) with a core thickness of 105 μm and a cladding thickness of 125 μm .

The optical fiber has a 120 μm thick acrylate coating around them. This coating provides the fiber with mechanical strength and strain relief. However, in order to access the cladding and etch it, this coating needs to be removed. This is performed by making incisions 4 cm apart near the center of a 70 cm long fragment of the fiber. The section between incisions is surrounded with a wipe that is folded to be the same length. This wipe is then saturated with acetone and the coating is allowed to soak the acetone for about 5 minutes. The coating is then removed by gently wiping it off using the same wipe thus exposing the cladding.

The fiber is then fixed in a custom fixture machined from Teflon, owing to its chemical stability (see Figure 20a). The custom fixture supports the fiber mechanically in place as it is descended into a beaker containing hydrofluoric acid. The fixture is designed to etch 3 fibers simultaneously while minimizing the stress that the optical fiber experiences during the etching process. The portion of the fiber that has its coating removed is curved and extends from below the fixture. This fixture is then immersed in a beaker containing HF. The amount of HF in the beaker is adjusted such that only the central part of the exposed region is immersed in the etchant leaving about 1 cm of room of the fiber not immersed. The fiber is then left undisturbed for 48 minutes.

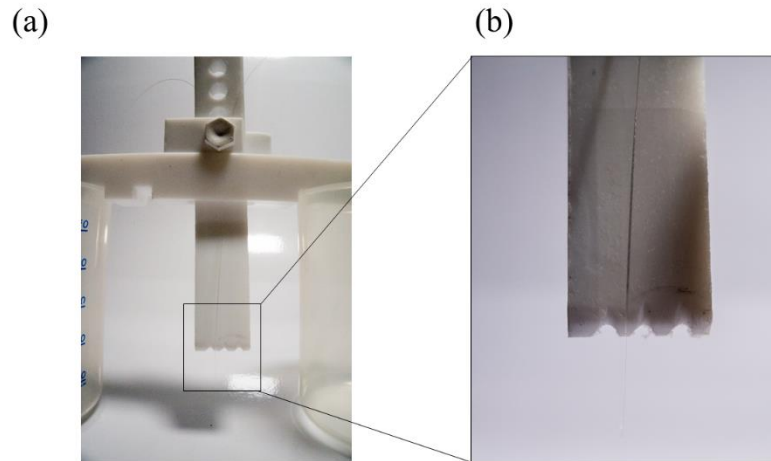


Figure 21 (a) Custom Teflon[®] etching apparatus with fiber secured in place and (b) the portion of the fiber shown extending below the etcher to be etched by hydrofluoric acid (HF)

The resulting de-cladded optical fiber is then removed from the beaker containing HF and transferred to a beaker containing water. It is then rinsed for 5 minutes under running water in order to ensure no HF remains are present on the etched region. Following the etching step, the etched fibers are characterized to test their functionality as a fiber optic evanescent wave sensor (FEWS). For this purpose, a white LED is shone through the fiber to detect the presence of any visible cracks in the FEWS. If such cracks are seen, the resulting optical fiber is not used further and is discarded. The next step of characterization involves measuring the diameter of the etched region of the FEWS. A microscope is used to measure this thickness. This is compared to the thickness of the un-etched optical fiber to gain a rough estimate of the etch depth. The final step of characterization is the estimation of the loss in the FEWS upon immersion in glycerol. The FEWS is connected to a near-infrared (NIR) LED and the intensity of light coming out the other end is monitored by recording the current emitted from a silicon photodetector. Glycerol of a known volume is then dispensed on the central sensing region. The intensity drop at the photodetector end is then compared to the intensity in air. This intensity loss is then characterized as the transmittance loss in glycerol which forms the primary figure of merit for the FEWS. In fibers that exhibit a loss less than 80%, an insufficient fluorescent signal is obtained. This may be because of good confinement of the excitation light within the fiber. In fibers with losses greater than 95%, there is an insufficient fluorescence signal. This is primarily because the fluorescence light thus emitted leaks out of the fiber to a large degree. Further work is necessary to more fundamentally understand the effect of the cladding thickness on the temperature sensor.

4.4 Coating Process

Dip coating is a common industrial process used in optical fiber preparation to deposit the protective sheathing around the otherwise delicate silica optical fiber. This process may also be adapted to easily apply functional coatings on the etched region of the FEWS for sensing purposes. In the work proposed, dip-coating is used as the preferred methodology for depositing the coating of PMMA on the sensing region.

A custom dip coater was designed in order to coat the fiber with the fluorescent thermometric coating. A motorized linear stage (Zaber LML25) was secured to an aluminum frame and held in a vertical position. The stage was controlled using a computer controlled motor controller (Zaber T-MCA). The optical fiber is secured to the motorized linear stage using a custom machined holder. The sensing region extends in a U-shape past the bottom end of the holder. A container for the acetic acid containing the PMMA and the fluorescent dyes is then placed below the optical fiber holder. The sensing region is then descended into the solution. The stage is then withdrawn at a controlled speed from the solution and the coating is produced at the meniscus of the sensing region and the liquid.

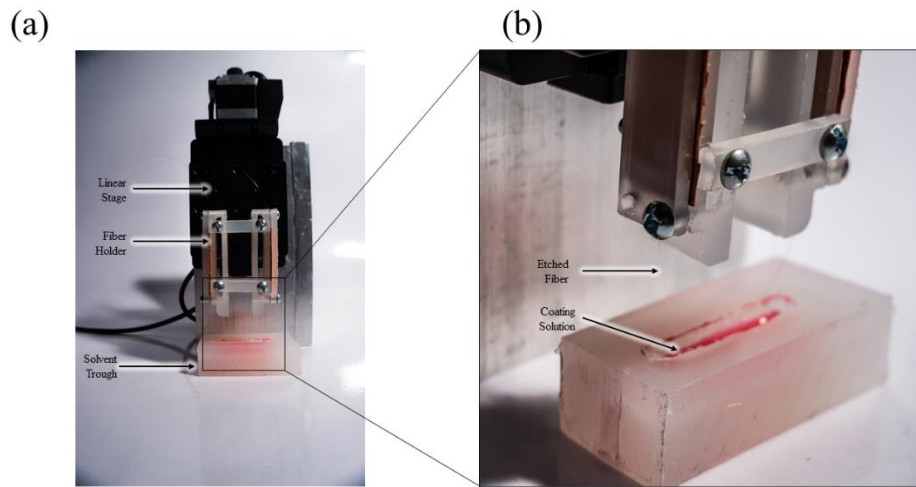


Figure 22 (a) Dip coating system used for the coating of the optical fiber displaying parts of the apparatus and (b) A close-up view displaying the fiber extending on the bottom side of the fiber holder into the solvent

After the FEWS is dip coated, it is placed in a metal support on a hot plate maintained at 125°C. This temperature was chosen because it is higher than the reported glass transition temperature for the PMMA used (i.e 550 kDa molecular weight PMMA) but lower than the melting point thus allowing the PMMA to anneal the deposited film. This annealing step is important to improve adhesion to the glass and reduce porosity of the film. The annealing step reduces the surface roughness of the PMMA film. This surface roughness reduction is important in an FEWS sensor as it reduces air pockets and

improves degree of contact between the film and the optical fiber (thus increasing the degree of optical interaction between the sensor and the coating).

4.4.1 Influence of optical fiber cleaning

Initially, the FEWS were mounted in the fiber holder after the etching process. However, the quality of the film pulled thusly was remarkably poor. There were many pores and gaps in the coated film as observed under the microscope as shown in Figure 23 (a). These pores are indicative of poor adhesion of the film to the silica. Despite varying the pull rate to a very slow pull, the coating was observed to be patchy and incomplete. After some root cause analysis, it was determined that the problem could be owing the buildup of siloxinated and/or fluorocarbon species at the surface (as a result of the HF etching process) [47], [48]. These entities lead to a reduction in the surface energy (contact angle) thus causing breaks in the film formation.

In order to alleviate the problem, the fiber was ozone treated to oxidize the siloxane species into silicon dioxide. The optical fiber as a whole with the exposed sensing region was placed in a UV/Ozone treatment chamber (Novascan PSDP-UVHT) and treated for 10 minutes to ensure that the surface is appropriately oxidized. After this, the coating was performed as described earlier. A drastic improvement in film quality was observed with the film being uniform and without the aforementioned patchiness as seen in Figure 23 (b).

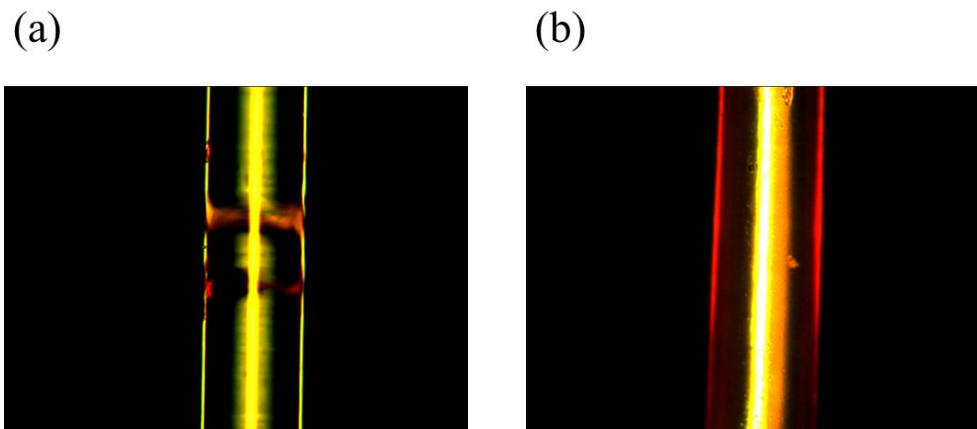


Figure 23 (a) Microscope image of the untreated fiber coated showing non-uniform coating (shown in pink) and (b) Microscope image of the ozone treated fiber coated showing a uniform coating

4.4.2 Effect of pull rate

After the annealing step, the thickness of the coating is measured roughly using optical microscopy. Images of the sensing region of the fiber were taken prior to the dip coating process under optical magnification at 400x magnification. The sensing region was again imaged after the dip coating process. Both these images are compared to images of unetched region of bare optical fiber (i.e with the polymer sheathing removed). The bare optical fiber is used as a reference measurement as its diameter is known to be 125 μ m based on the datasheet provided. This calculation yields the thickness of the coating applied. Although the resolution of such a methodology is poor, it is deemed satisfactory for this purpose.

The rate of withdrawal of the optical fiber from the solution (pull rate) must be chosen to be as fast as possible to obtain a sufficient coating without a lengthy processing time. Owing to the length of sensing region of about 25mm a maximal pull rate is desired. As the pull rate reduces, the thickness of the film deposited increases as shown below in Figure 24.

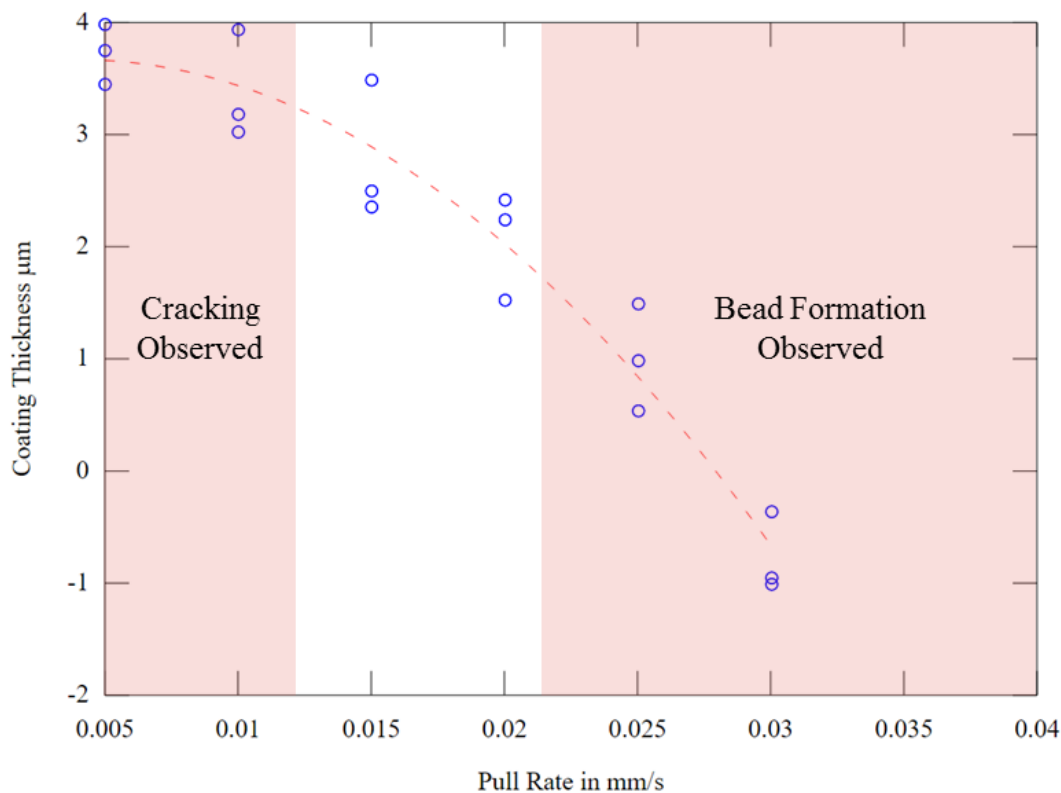


Figure 24 Coating Thickness Dependence on pull rate

At high pull rates above 0.01 mm/s, there is beading observed on the fiber owing to the pull rate. This is due to the viscous drag retaining fluid on the fiber while the capillary forces cause a meniscus to be formed in a spherical manner causing beading. At slightly higher speeds, the capillary forces that causes beading, are low owing to the evaporation of the solvent as shown in Figure 25 (c). At speeds that are too low, the coating is observed to be rather thick. In this thick coating, cracks are observed Figure 25 (a). This could be because of solvent evaporation from a thick film. Thus an ideal pull rate of approximately 0.01mm/s was chosen for the coating of the fiber due to the good quality film observed from this pull rate as shown in Figure 25 (b).

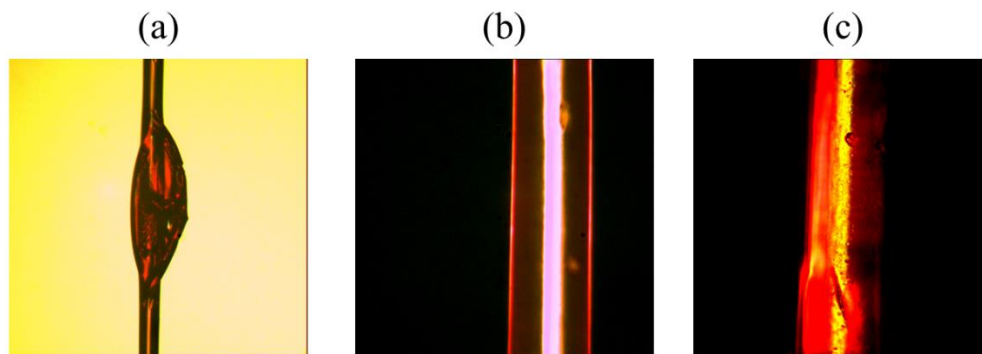


Figure 25 Microscope images showing the effect of pull rate with (a) beading observed at fast pull rates (0.03 mm/s); (b) optimal coating observed at preferred pull rate (0.02 mm/s) and (c) gaps and cracks observed at slow pull rates (0.005 mm/s)

4.5 Fiber optic temperature sensing

Experiments were carried out to establish the viability of the fiber optic fluorescence based temperature sensor. The experiments were carried out in a custom designed apparatus for testing the fiber optic sensor response as shown in Figure 26. The holder was designed to sit flush atop the Peltier stage and it is secured to the Peltier stage using thermal joint compound. A cavity formed in the holder contains water. Owing to its high specific heat capacity, the water acts as a thermal mass. The sensor is then immersed in the water and the fluorescence signal is monitored using a spectrometer. The temperature of the water is monitored and measured using a thermocouple immersed in the water. The setup is then cycled at different temperatures while the fluorescence is monitored in real-time.

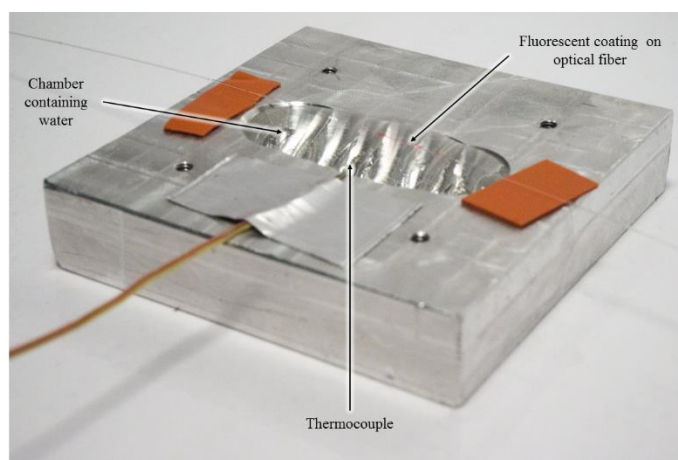


Figure 26 Image of setup used to test the temperature response of the fibers

The spectrum of the sensor is collected in real-time. The performance of these sensors corresponded roughly to the quality of the coating. The spectrum shown in Figure 27 (a) shows the spectrum of an un-optimized fiber optic temperature sensor pulled at 0.005 mm/s. This spectrum displays a strong signal from the excitation source at 470 nm (which saturates the spectrometer) with a very small signal that corresponds to the fluorescent emission of rhodamine B. This is possibly due to the thickness of the coating being high thus causing air gaps between the coating and the sensing region thus promoting total internal reflection without interaction with the fluorescent coating. The spectrum shown in Figure 27 (b) is of an optimized fiber optic sensor pulled at 0.015 mm/s. In contrast to the spectrum shown in Figure 27 (a), the spectrum, shows a strong fluorescent emission spectrum corresponding to rhodamine B. The spectrum is collected in real-time and co-related to the temperature of the water. It is shown that at the chosen sensing length, despite losses from the sensing region due to the etching process, a good fluorescent signal is obtained. The elongation of the fiber sensing length is enough to cause the decay of the excitation source to a large degree. This is manifested in the low intensity of the excitation source in the output spectrum. This allows for a less noisy signal to be obtained.

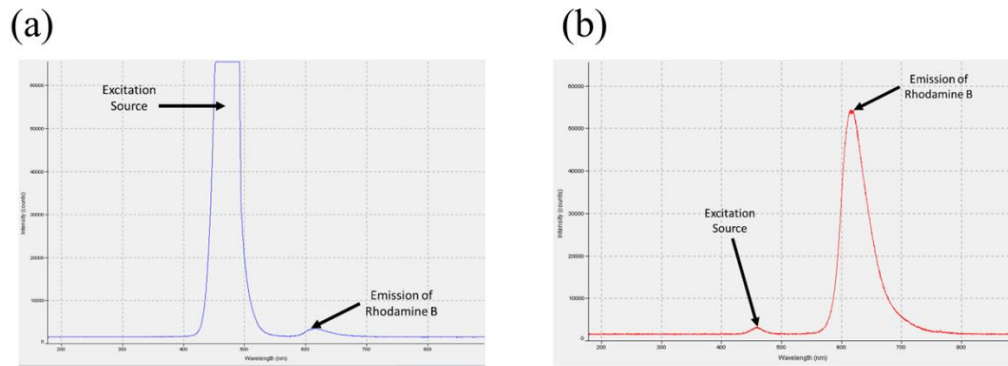


Figure 27 (a) Optical spectrum of un-optimized fluorescent temperature sensing fiber showing saturation of the excitation source (b) Optical spectrum of optimized temperature sensing fiber showing a much weaker excitation source with a strong emission observed at the output end

It may thus be demonstrated that the performance of the fiber is highly sensitive to the parameters of the coating process. Upon optimum coating parameters however, a fiber sensor with excellent performance can be obtained.

Upon the observation of a satisfactory spectrum after coating, the sensors are put through a temperature calibration process in which they are cycled at different temperatures. An appropriate integration time (183 ms) is chosen to allow for a maximum fluorescent intensity and reducing the noise introduced by analog to digital conversion. The Peltier stage is used to heat and cool the custom holder for the fiber sensor. A PID controller uses a thermocouple to adjust the temperature of the apparatus to a set point determined by a computer. A second thermocouple immersed in the water along with the sensor is used for readout of the true temperature. The fluorescent intensity is then obtained in MATLAB by performing trapezoidal integration between 550 nm and 800 nm. This intensity is then compared to temperature to obtain the temperature dependent performance of the fiber optic sensor shown below in Figure 28(a). Upon optimization, the fluorescent signal appears to closely track the temperature measured by the thermocouple immersed in the water. However, the noise in the measurement of fluorescent intensity is greater than that of the thermocouples. It should however be noted that the measured temperature from each of the thermocouples is different. The temperature output is different primarily due to the poor readout ability of the PID controller. Testing performed in the lab shows that the same thermocouple when compared to other thermocouple readout instrument shows the same temperature as the USB thermocouple data acquisition device while the PID controller displays this permanent offset.

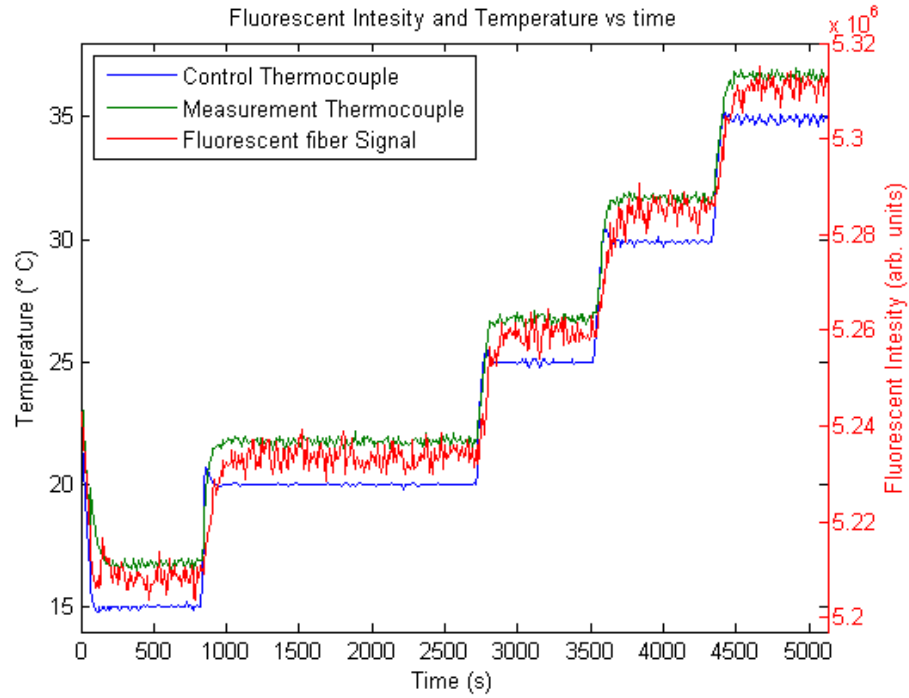


Figure 28 (a) Fluorescent intensity and temperature versus time showing the fluorescent signal tracking the measured temperature reading from the measurement thermocouple

4.6 Multiplexed Sensing

The final experiment in the work presented here revolves around the integration of 2 discrete sensors on the same fiber optic cable. Owing to the different active wavelengths of the temperature sensor and the battery sensor, the temperature sensor was integrated in-line with the battery SOC sensor. The fiber was etched in HF for 48 minutes and 30 seconds according the procedure described above. The loss obtained in glycerol for both of these sensors was similar at around 89%. This loss is a function of the amount of cladding left behind as described above.

The temperature sensing region was then coated and tested. This testing process is important in order to obtain the calibration of the temperature sensitive coating. The calibration yielded the graph shown in Figure 29 exhibits good linearity as evident from the close tracking of the thermocouple temperature by the fluorescent signal and a similar performance to prior temperature sensors built. This fiber optic

temperature sensor was thus deemed appropriate for use in the multifunctional fiber optic sensor system setup.

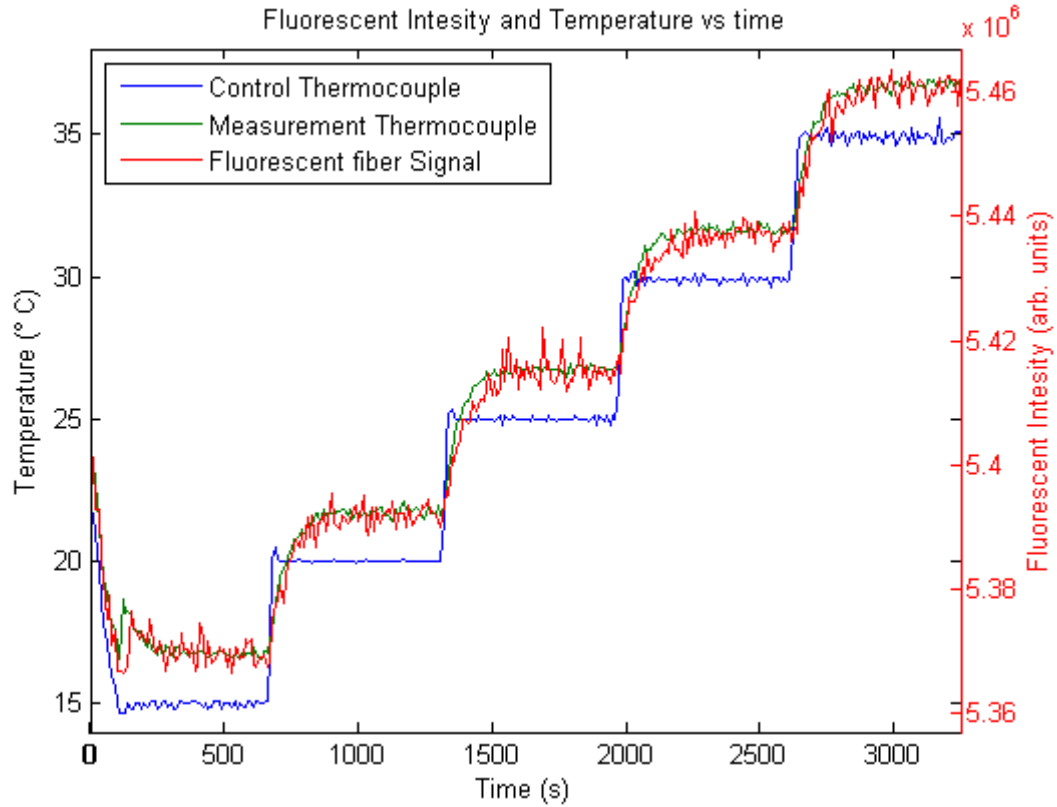


Figure 29 Temperature responsivity of the temperature sensing portion of the multifunctional fiber optic sensor obtained prior to the embedding inside of a battery. This test is used for calibration and to compare the performance before and after the battery is introduced.

The SOC sensor is a bare fiber without any coating with a portion of the cladding etched off. This sensor was embedded in a battery right above the anode section of a lithium iron phosphate pouch cell as shown below in Figure 30. The purpose of this sensor is to allow for in-line monitoring of the optical properties of the underlying graphite as it undergoes various lithiation states [43].

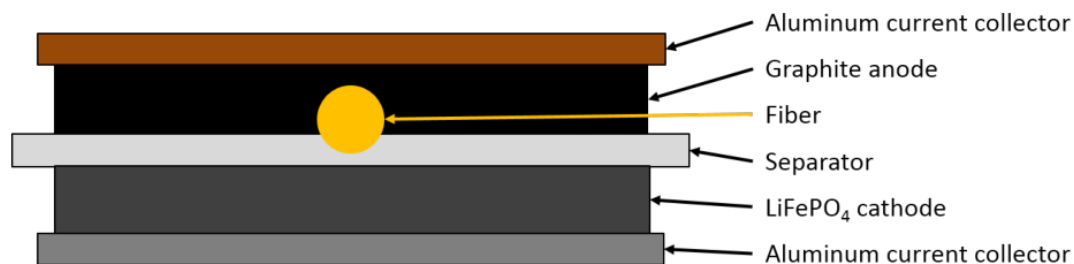


Figure 30 Cross Sectional illustration of fiber placement in pouch cell (adapted from [43])

In order to allow for a good seal around the fiber, the region where the fiber emerges from the pouch cell is covered by a thermoplastic polymer at the transition between the bare fiber and the sheathed portion of the fiber. This sealant polymer is then melted in an impact sealer to allow for good adhesion to the fiber. This polymer sheet on the fiber is then lined up with aluminium coated sheet that form the outer construct of the lithium ion pouch cell. The exposed portion of the fiber is then placed in a pocket made from separator material. This material is a polymer that allows for lithium ions to freely flow from the anode to the cathode while preventing electrical shorts. The graphite is then placed on top the fiber on one side of the separator while the lithium iron phosphate is placed on the other side. The current collectors have been welded to these electrode prior to assembly and protrude on either side right above the fiber. The aluminium backed polymer sheets are then lined up to the optical fiber and the current collectors of the cell to form the pouch that the cell rests in. This pouch is then temporarily sealed using the impact sealer followed by a more permanent seal on two sides using a Compacting Heat Sealer (MTI corporation MSK-140).

Following this step, the assembly was taken into an inert argon environment glove box. The battery was left in the vacuum chamber overnight to ensure that no water vapour or oxygen was introduced into the glovebox. In the glovebox, the electrolyte was injected into the pouch. Excess electrolyte was removed from the pouch and the pouch was mechanically sealed using a custom assembly in order to minimize exposure to ambient air or water vapour (which degrade the battery upon exposure to the

electrolyte). The last remaining side of the battery is then sealed under vacuum to create a permanently sealed cell with the optical fiber embedded in it.

After this stage, the fiber is connectorized and placed in a plastic enclosure. A set amount of weight is placed on this enclosure in order to secure the battery in the enclosure. This is done to ensure that the battery is placed under pressure. This pressure is necessary not only for optimal battery performance but also to embed the optical fiber into the graphite anode. The temperature sensor is configured such that it forms a u-shape on top of the battery. This is done to maintain close proximity of the battery to the temperature sensor. A thermocouple is then placed in the enclosure. This enclosure is then placed on a Peltier stage and cycled at different temperatures similar to before.

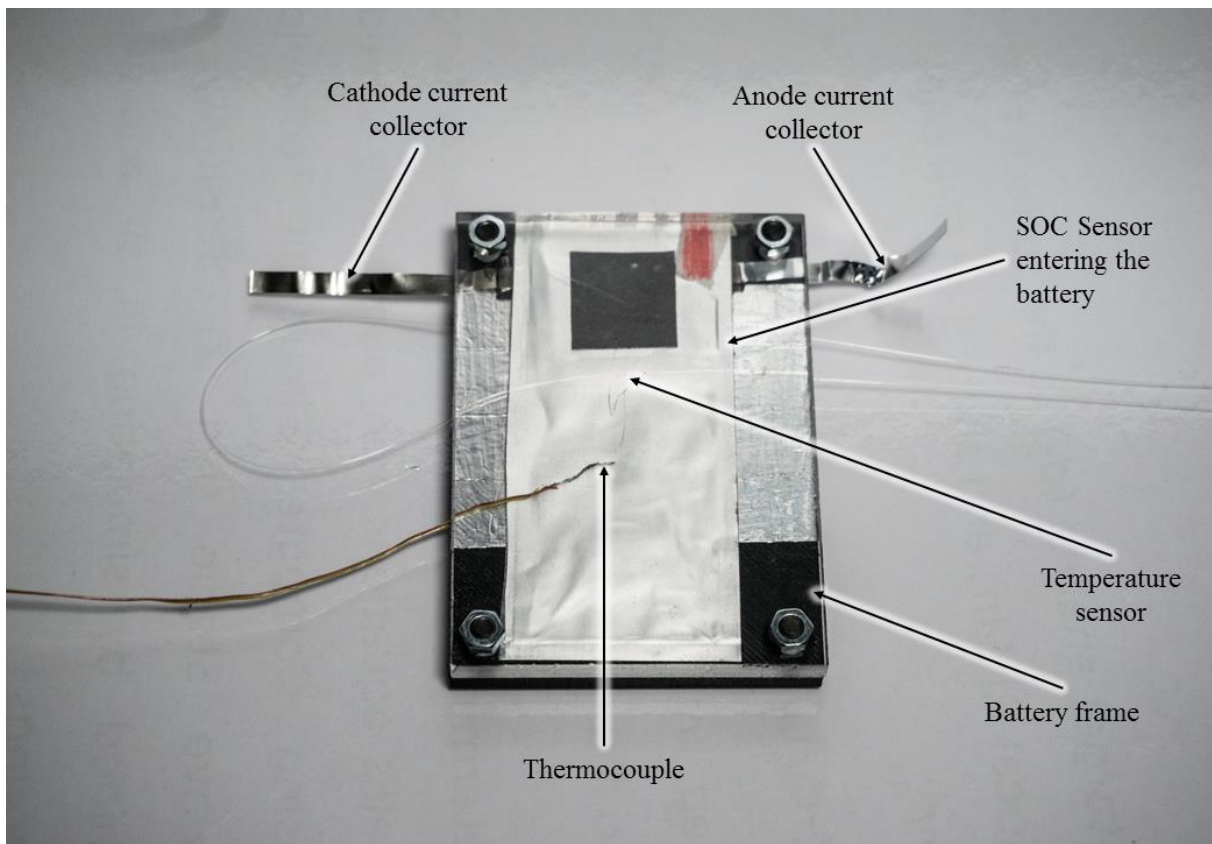


Figure 31 Pouch cell constructed with multifunctional sensor

A y-fiber coupler is used to couple light from two different light sources into the fiber. The first light source is an 850 nm LED (Optek OPF370A) used to measure the transmittance signal through the SOC

sensing portion of the fiber. The SOC sensor relies on the decay in transmission of this light to interrogate the optical properties of the graphite. The other source connected to the y-fiber coupler (FIS MMC28550122C) is a 470 nm LED used to excite the fluorescent coating. These LEDs are run at a constant current and are controlled by a power supply (Agilent 3631A). The power supply in turn is controlled using a custom MATLAB script.

The other end of the fiber is connected to a UV-Vis spectrometer (Ocean Optics USB 2000). The spectrometer is also interfaced with the computer. The data obtained from the spectrometer is fed to the same MATLAB script that controls the power supply. The script is used to turn on only one LED at a time with a 1 second break in between to ensure a complete transition between sources of light. This should be sufficient to allow the LED to reach optimum full brightness. At this point, the spectrum is obtained using MATLAB. When the UV LED is turned on, the fluorescent signal (around 600nm) is monitored and when the NIR LED is turned on, the intensity of the light at the other end (at 850 nm) is monitored. The integration time is chosen automatically to ensure a high intensity of the signal. Owing to the relatively brighter NIR signal compared to the fluorescence signal, the integration time for the NIR signal is much lower (21 ms) than the fluorescence signal integration time (194 ms). Real-time integration of the peaks is then carried out and this value is then written to a text file. While this is occurring, the MATLAB script also controls the PID controller which, in turn, heats and cools the battery maintaining a constant ramp up and down of temperature in increments of 5 degrees between 15°C and 35°C.

At this point, the battery cyclier is turned on. A constant current charge is carried out at 0.1 mA until the voltage limit of 3.7 V is reached at which point the cyclier changes to a constant voltage charge (until the current decays down to 0.01 mA). Once the constant current and constant voltage steps are completed, the battery is allowed to undergo a constant current discharge at 0.1 mA until the lower voltage limit of 2.5 V is reached. The battery is then allowed to rest for 20 minutes and a constant current discharge at a much lower current of 0.01 mA is carried out at that point. The battery is allowed

to come down to 2.5V with this current (trickle discharge) and the battery is allowed to rest for 1 hour after which the charging cycle, as described above, resumes.

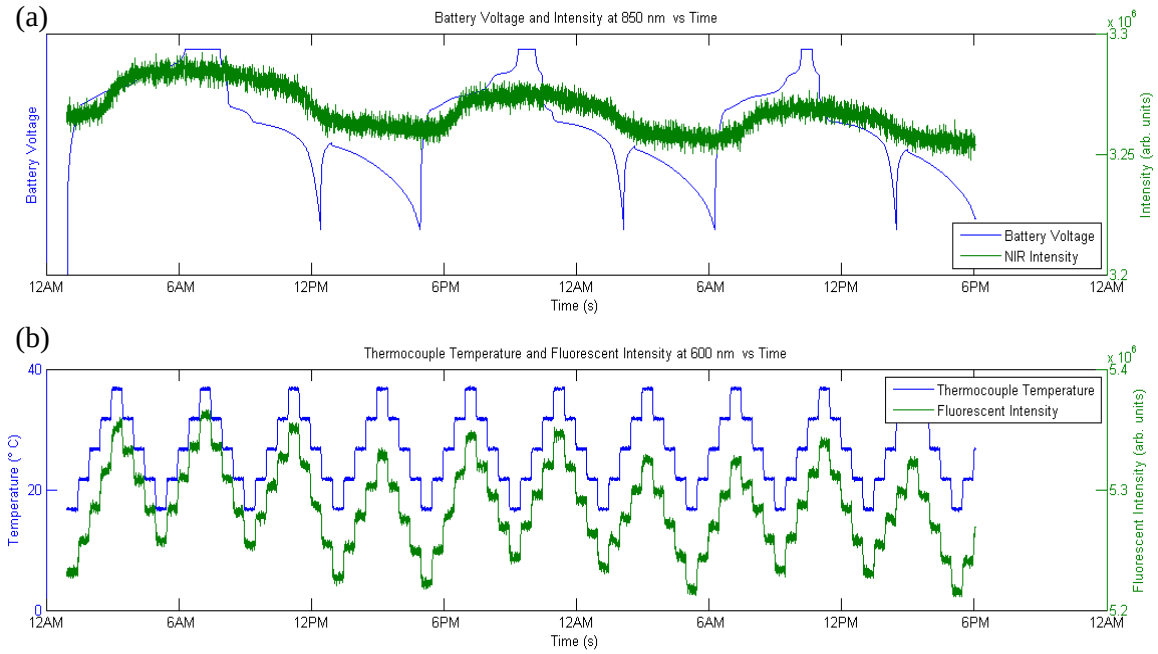


Figure 32 (a) The intensity of the signal at 850 nm plotted versus time compared to the voltage of a lithium ion battery charged at 0.1C displaying a state-of-charge dependent behaviour (b) the intensity of the fluorescent signal around 560 nm plotted as a function of time compared to the temperature measured by a thermocouple displaying a temperature dependent behaviour and long term signal drift

The post-processed signal from the spectrometer is shown in Figure 32 (a). The data shows the intensity of the signal at $850 \text{ nm} \pm 20 \text{ nm}$ when the NIR LED is turned on. Figure 32 (b) shows the measured fluorescent intensity at $600 \text{ nm} \pm 30 \text{ nm}$ integrated using trapezoidal integration over the denoted span of wavelengths. There seems to be a clear correlation between the signal at 850 nm and the voltage of the lithium battery. This trend is comparable to previous experimentation performed. The signal measured by the SOC fibre optic sensor is not exactly like previously reported trends. This is likely due to a misalignment of the electrode in the battery during the assembly phase. It is observed that the duration of the trickle discharge is much longer than previously observed. This may be attributable to the fact that the lithium ion transport by charge transfer occurs only in the region of overlap (thus leaving a portion of the electrode incompletely lithiated or delithiated). At a lower charging rate

however, the role of mass transfer limited regime increases, thus allowing for diffusion of the lithium ions to previously lithiated or unlithiated areas.

The temperature signal shown in Figure 32 (b) displays a much greater variation in the data when compared to the calibration stage. Despite this long term variation, the temperature shows good correlation between the thermocouple readout and the fluorescent intensity. The source of the long term drift is likely due to the absorbance of light at 470 nm by the graphite electrode. This increase in absorbance dims the intensity of the excitation source consequently having an effect on the fluorescence output flux. This hypothesis is tested in the following chapter.

Chapter 5

Sensor performance and characteristics

In this chapter, the results from experiments described in Chapter 4 are presented. Post processing is performed on the sensor data and the noise is analyzed. The characteristics of the sensor such as hysteresis, accuracy and sensitivity are analyzed and discussed as a temperature sensing platform.

5.1 Analysis of dedicated temperature sensor

5.1.1 Sensitivity and noise of the temperature sensor

The data obtained from one of the optimized temperature sensor is shown in Figure 33. A linear regression based model was chosen for this data as a first degree approximation of its behaviour. The correlation between the temperature and the fluorescent intensity data appears to be linear with good correlation. However, between points of rest, it is evident that there is some sensor lag present.

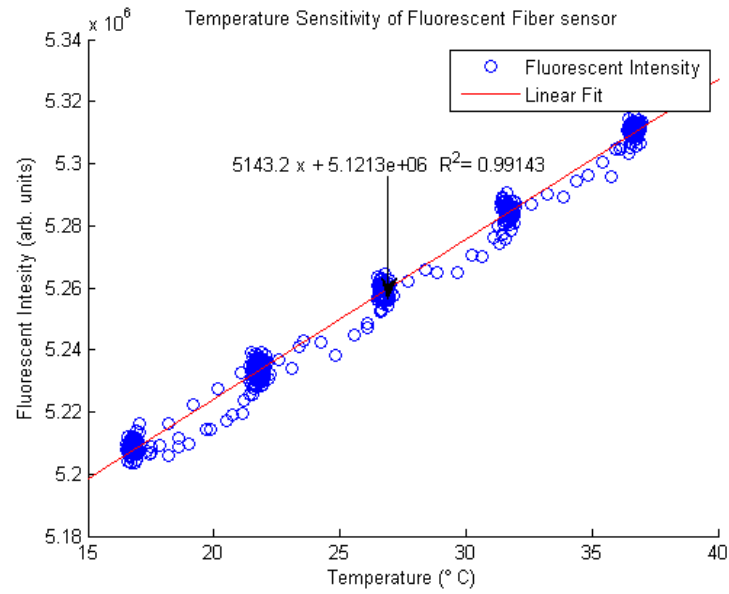


Figure 33 The fluorescent intensity of a temperature sensing fiber plotted as a function of the temperature measured by the thermocouple to obtain the sensitivity of the sensor

There is some noise present in the signal thus contributing to the overall sensor noise. The origin of this noise is most likely owing the methodology of signal acquisition and is electronic in nature. Shown below in Figure 34 is the deviation of the sensor signal from the model fit of linearity.

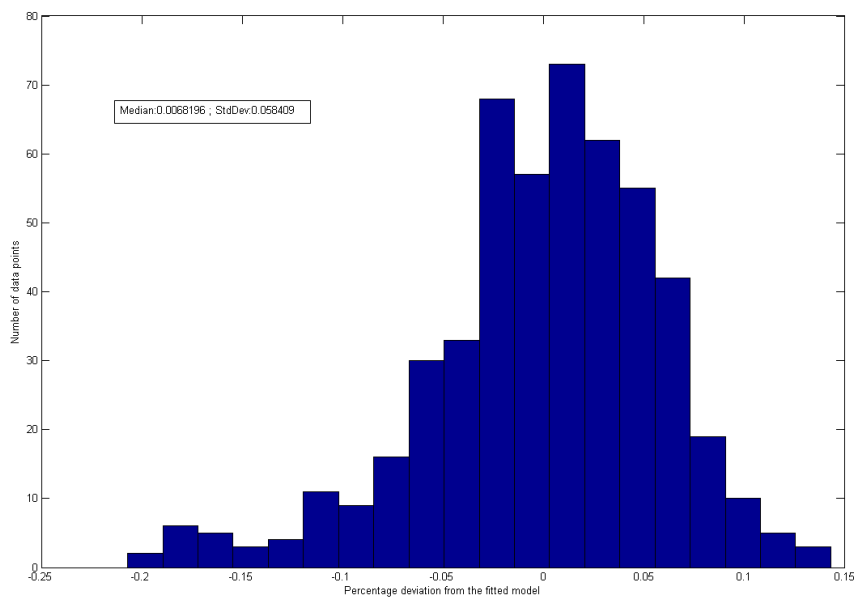


Figure 34 Data distribution about the linear fit of the model

As seen above, the distribution of the data appears roughly normal. The z-score of the distribution is 0.68 which represents a normal distribution with a slight skew to the right. The skew to the right can be explained by the relatively slower response time of the fiber sensor when compared to the thermocouple used. The accuracy of the sensor is estimated using the standard deviation of the Gaussian distribution above and comparing that to the linear fit of the model obtained earlier. It may thus be concluded that 67% of the data points lie within a band of $\pm 0.168^{\circ}\text{C}$ of the temperature estimated with the help of the linear fit model.

The estimation of sensitivity is performed by the conversion of arbitrary units to watts. In order to convert between the units, it is important to understand the characteristics of the spectrometer and the CCD sensor utilized. The responsivity of the sensor is reported to be $2000 \text{ V}/(\text{lx.s})$ [49]. Assuming a similar sensitivity at 570 nm, the maximum intensity of the signal is obtained to be 3.3 V according to the data sheet of the spectrometer [50]. The 16-bit resolution means that each arbitrary unit corresponds to roughly 0.01 lx.s. At the integration time used of 183 ms, each arbitrary unit corresponds to 0.00184 lx. Thus, from the slope obtained above, the sensitivity of the sensor is obtained to be $9.478 \text{ lx}/^{\circ}\text{C}$.

5.1.2 Transient analysis of the temperature sensor

While the thermocouple readout quickly picks up changes in the temperature of the water that the fiber is immersed in, there is a lag in the response of the fiber. The thermocouple readouts stabilize in about 100 seconds, but the amount of time taken by the temperature sensor to achieve stability is higher and it is around 200 seconds as shown in Figure 35. The response time τ (s) of a temperature sensor can be estimated from the physical properties of the sensor by the following equation

$$\tau = \frac{\rho C_p V}{hA} \quad (5)$$

where ρ is the density of the material (kg m^{-3}), C_p is the specific heat capacity of the sensor ($\text{J m}^{-2} ^{\circ}\text{C}^{-1}$), V is the volume of the sensor (m^3), h is the surface heat transfer coefficient ($\text{W m}^{-2} ^{\circ}\text{C}^{-1}$) and A is the surface area of the sensor (m^2).

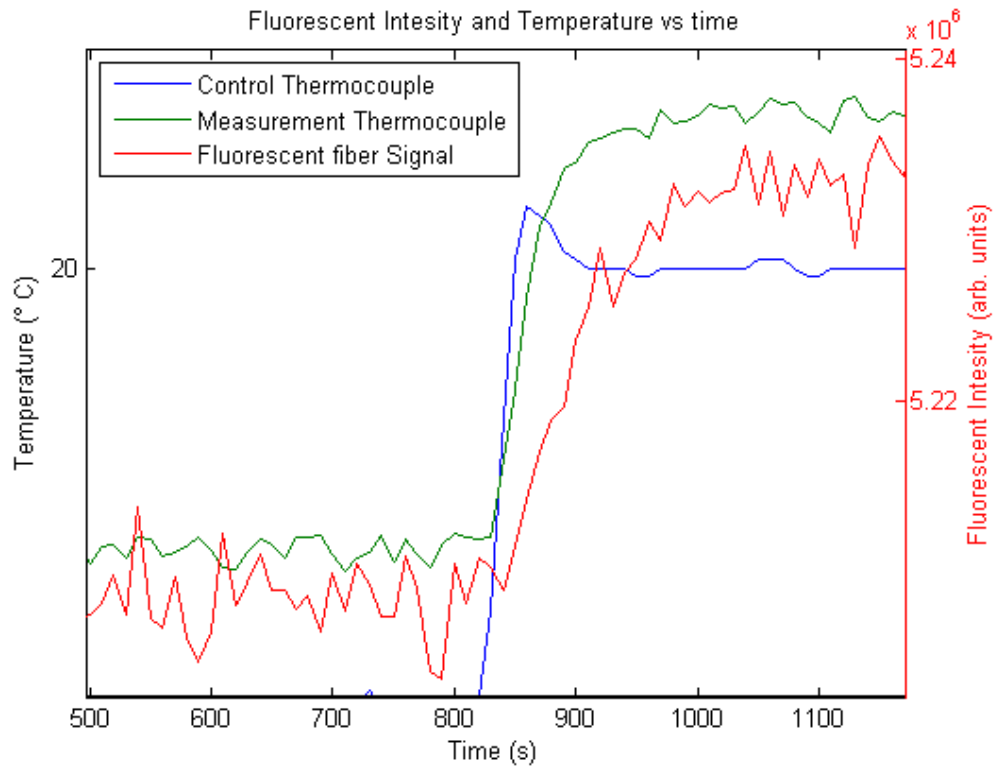


Figure 35 Temperature transition displaying sensor lag by the fluorescent temperature sensor

Although the sensing area of the fiber optic sensor is much greater than that of the thermocouple based sensor, the sensor response times are slower. This can be explained by the fact that locations of the thermocouple and the fiber temperature sensor were slightly spatially apart. The fiber temperature sensor was closer to the top surface of the water reservoir while the thermocouple was closer to the bottom.

Although this sort of sensor response time is not good enough for certain applications, this response is sufficient for the pick-up of temperature related data from lithium ion batteries owing to their much slower rate of heat generation when compared to the Peltier stage used in this experiment [25] [12]. Furthermore, the construction of the fiber based sensor allows for the embedding of this fiber into a battery which makes it much closer to the source of heat generation (thus more accurately estimating the temperature of a battery when compared to a thermocouple on the surface).

5.2 Analysis of the multifunctional sensor

5.2.1 SOC Sensing

The SOC sensing functionality of the sensor was validated through empirical experimentation. The signal shown in figure below is a plot of the optical signal from the multifunctional sensor overlayed on the charge capacity of the battery. A significant amount of high frequency noise was observed. The likely origin of this noise is electronic in nature. The noise has the appearance of high frequency Gaussian noise. The noise was reduced by using an exponential moving average over a windows of 20 samples. The results are shown below in Figure 36 comparing the amount of charge computed using coulomb counting to the optical signal outputted by the spectrometer.

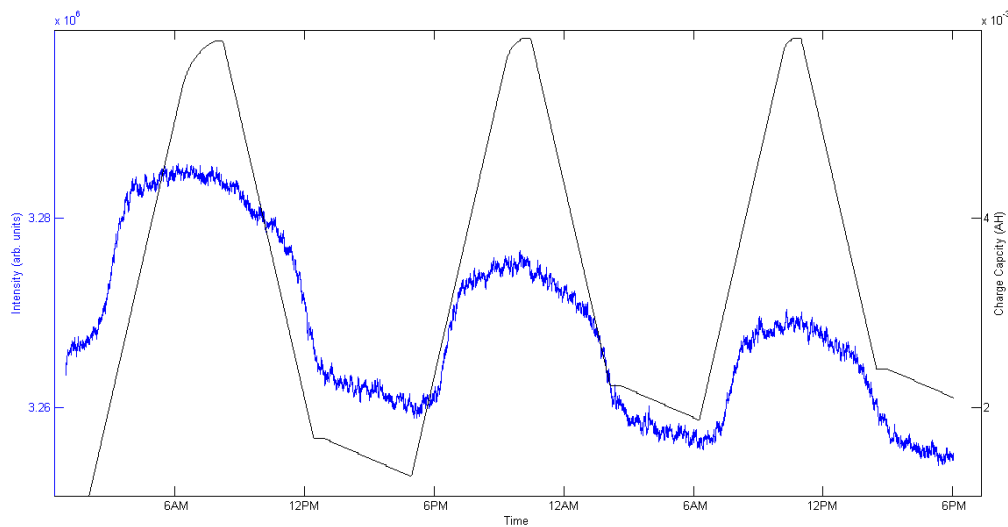


Figure 36 The averaged optical signal from the multifunctional sensor compared to the charge capacity of the battery obtained by coulomb counting

Although only 3 cycles of charging and discharging were performed, they were sufficient to observe trends similar to previously observed trends for other fiber optic SOC sensors. It can be seen that each cycle varies slightly from another. There are several hypotheses for the overall decay of the optical signal. Although initially, it may seem to be correlated to the charge capacity of the battery, further experimentation is necessary to understand this decay. This is however outside the scope of the work presented in this thesis.

The results shown here are consistent with previously reported [43]. The charging shows a lower slope near the beginning and the end of the cycle with a large slope in the middle. The discharging shows a trend that is roughly the reverse of the charging. However, it is visible that there is a sizable hysteresis present in the signal. These trends were also observed in the standalone SOC sensors subject of previous study. It is visible that similar trends are observed in previously reported data obtained using a simple LED and photodetector in a simple transmission loss type measurement setup [43].

It can thus be concluded that a temperature sensitive coating on a fiber optic cable does not interfere with the state-of-charge measurements. This validates that previous observations that the fluorescent coating does not exhibit significant activity in the 850 nm region. The fluorescent temperature sensitive coating is therefore a suitable candidate for integration with the SOC sensor.

5.2.2 Temperature sensing

The temperature sensor used in the multifunctional sensor shows a long term drift in the baseline of the signal. This drift negatively affects the sensitivity to a large degree by introducing uncertainty to the signal. The sensitivity graph is shown below in Figure 37. The fitted linear regression model still seems to hold up as a valid approximation for the behaviour of the sensor. The spread of the points about the fitted model is however very large. This is further evident from the relatively poor goodness of fit (R^2 of about 0.86).

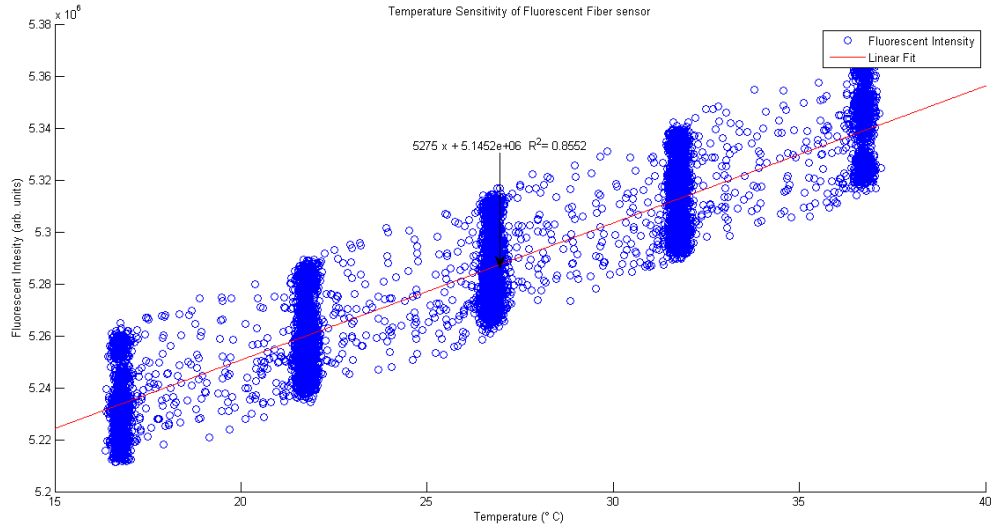


Figure 37 Fluorescent intensity vs thermocouple temperature in a multifunctional fiber sensor showing the variance in the fluorescent intensity as a function of the temperature

A root cause analysis reveals that the only thing introduced between the initial temperature calibration of the sensor and the multifunctional sensor is the presence of the electrode material in the SOC sensing regions of the battery. Thus, it may be hypothesized that the SOC of the battery influences the temperature signal.

This is possibly owing to the absorbance of graphite at 470 nm being dependent on the state-of-charge. Just like the change of the transmittance through the fiber at 850 nm, there may be a similar effect at the excitation wavelength (470 nm). The change in the absorbance of graphite causes a change in the amount of blue light getting passed the battery. This consequently causes a reduction in the intensity of the excitation light incident on the fluorescent layer. Therefore, despite no change in the photoluminescent flux, there is a reduction in the output of fluorescent intensity.

The following model was proposed to investigate the correlation between the SOC signal and the fluorescence signal.

$$Fluorescent\ Intensity_{modified} \quad (6)$$

$$= Fluorescent\ Intensity_{original} - \zeta$$

$$\cdot NIR\ Intensity_{original}$$

The fluorescent intensity was modified from the original by subtracting a constant, ζ , times the NIR intensity. From trial and error, an optimum value for the constant was chosen to be 1.4. This does not represent a scalar modification of the intensity at 850 nm due to the different integration times of the signal acquired at 850 nm and the integration time of the fluorescent signal at 571 nm. When this equation is used to isolate the effect of the change in the photoluminescent yield (due to temperature) from the net change in fluorescent intensity. The corrected data displays a much lower long term drift in the fluorescent intensity. Thus it may be plausibly concluded that the aforementioned hypothesis holds true.

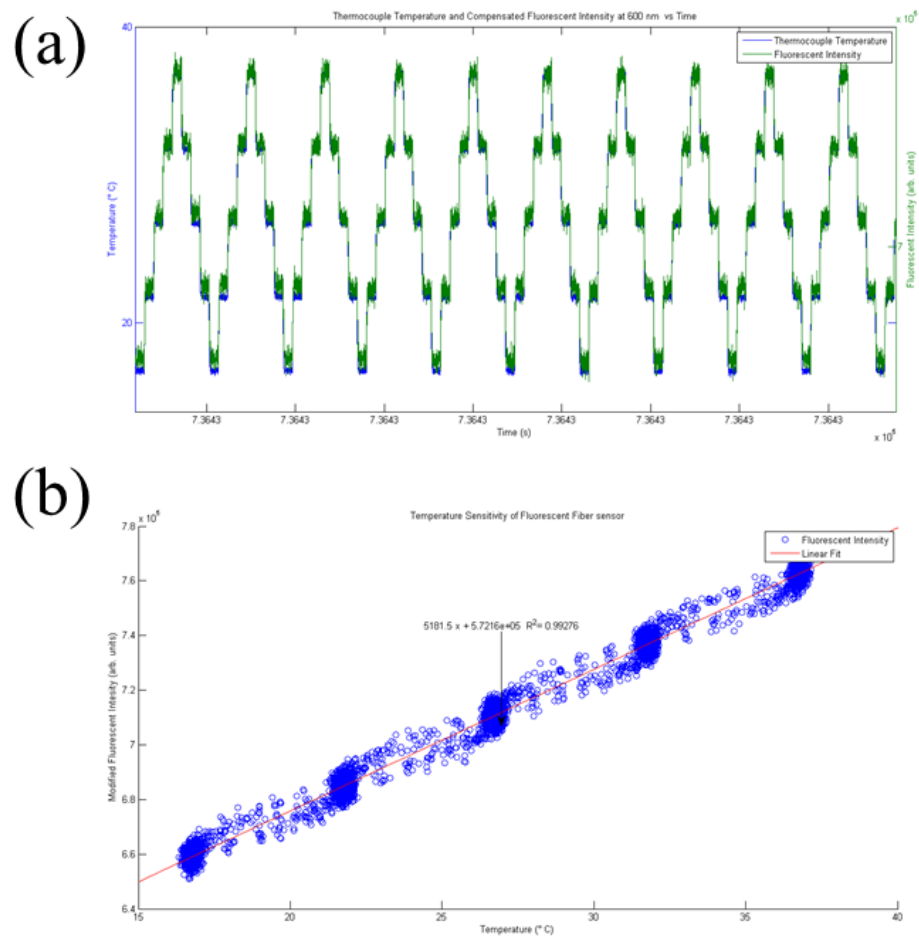


Figure 38 (a) Data corrected using the above presented algorithm displaying little long-term drift (b) The temperature vs corrected fluorescent intensity shows a large improvement in the goodness-of-fit to the linear model

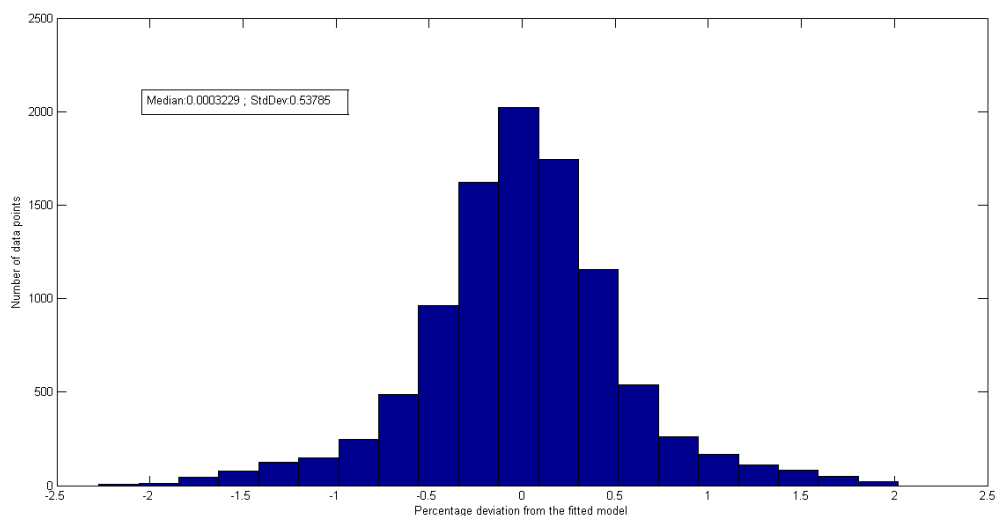


Figure 39 Data distribution about the linear fit of the model after data correction

As seen above, the distribution of the data is roughly normal. This skew to the right seen in the prior set of data is only slightly visible. This is likely due to the fact that temperature is changed by both ramping up and ramping down, thus causing an equal amount of lag in both directions of the linear model. It may thus be concluded that 67% of the data points lie within a band of $\pm 0.868^{\circ}\text{C}$ of the temperature estimated with the help of the linear fit model. The sensitivity of the sensor was obtained in a manner similar to the process described in section 5.1.1. The sensitivity thus obtained is $9.738 \text{ lx}/^{\circ}\text{C}$.

The validity of the aforementioned approximation is verified by the real-time monitoring of the transmittance of light through the battery at 850 nm and 470 nm. A battery without a temperature sensor was used to test and observe the absorbance of graphite as a function of SOC. The results are shown below in Figure 40 as the battery is allowed to cycle. As shown above, the 850 nm signal displays a trend similar to the trends observed in the multifunctional sensor above. Without the fluorescent coating on the fiber, the trends observed at 850 nm are similar to the trends observed at 850 nm (although the numerical value of the change is significantly different owing to different integration times). More importantly however, the trends displayed at 470 nm show a similar trend to the signal at 850 nm albeit

at a much lower intensity with a much lower difference between the SOC states. It may thus be concluded that the simple correction factor described above of a scaling factor is adequate as a first degree correction. More work is necessary to identify the behaviour of the battery at 470nm.

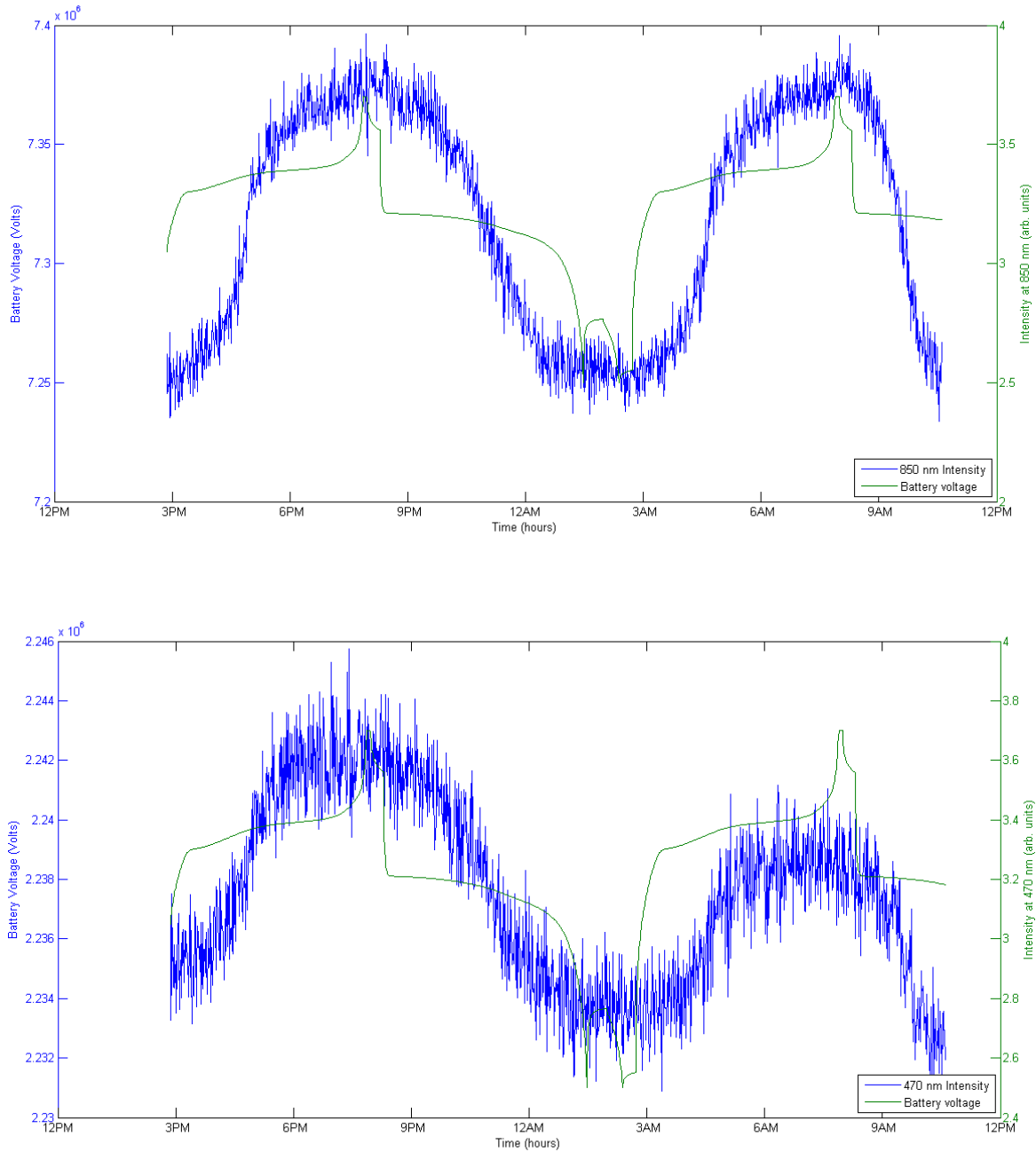


Figure 40 (a) Intensity at 850 nm during the cycling of a battery without a temperature sensor (b) Intensity at 470 nm during the cycling of a battery without a temperature sensor showing a similar trend to 850 nm

5.2.3 Temperature transient behaviour

Like in the standalone fiber optic temperature sensor, a delay in the response of the fiber optic temperature sensor is observed when compared to the thermocouple placed adjacent to it.

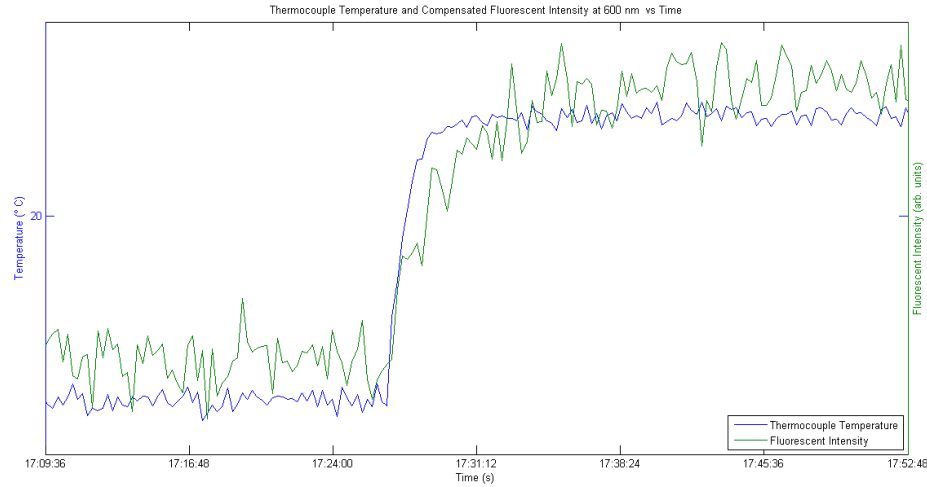


Figure 41 Comparison of the multifunctional SOC and fiber sensor response with the transient behaviour of a thermocouple

As seen in Figure 41, there is a delay of about 2 minutes between the time the thermocouple reaches a steady state temperature and the fluorescent temperature sensor. This is primarily owing to the plastic enclosure that the battery is encased in acts as a thermal barrier between rapid heat transfer between the battery and the Peltier stage. This reduces the rate of change of temperature for the battery when compared to the aluminium enclosure used for testing the prior temperature sensor. Furthermore, the temperature distribution along the surface of the Peltier stage may be non-uniform thus leading to a slight difference in achieving thermal equilibrium. As a result, the difference in behaviour between the thermocouple and the fluorescent temperature sensor is reduced further to an acceptable level. Further experimentation is required to study the thermal properties of the battery and the heat generation of the battery during high current charges or discharges.

It may thus be shown that temperature sensing with a multifunctional SOC fiber can perform to degree deemed acceptable for applications in battery monitoring. The proposed post-processing measures to

isolate the effect of battery lithiation processes on the fluorescent intensity demonstrates the ability to remove long-term drift otherwise seen in the data. A multifunctional SOC and temperature sensor for battery monitoring has thus been demonstrated to perform to an adequate degree. There is additional work required in order to be able to embed this fiber inside of a battery. More work is also necessary to understand the relation between the transmittance at 850nm and the true SOC of the battery.

Chapter 6

Contributions, Future Work and Conclusions

6.1 Contributions

6.1.1 Development of a novel multifunctional sensor system

The use of fluorescence based thermometry for the monitoring of temperature when coupled with a NIR SOC sensor provides for a powerful tool for battery management. The accuracy of the existing SOC sensor when coupled with the additional functionality of a temperature sensor allows for a more reliable method for the estimation of the state-of-charge of a lithium ion battery while additionally integrating another functionality to the battery management system; temperature monitoring and compensation.

6.1.2 Development of a novel temperature sensitive coating

The development of a novel temperature sensitive coating is necessary for the development of a fluorescence based temperature sensor. Although similar compositions have been demonstrated before for temperature sensing, development of the optimum composition using empirical design of experiment has enabled the selection of a highly temperature sensitive coating

6.1.3 Development of a complementary system for signal acquisition

In the prototype phase, commercially available spectrometers were used. However, the multifunctional sensor is designed to enable simple readout with unsophisticated electronics. A system was designed

for low-cost interrogation of both sensors. Although it was never tested, it is presented in the section 6.2.

6.2 Future Work

The fiber optic temperature sensor demonstrated in this work serves as a good candidate for an embedded multifunctional temperature and SOC monitor. This opens up new methodology to characterize the cycling behaviour of graphitic lithium ion cells. However, there are several improvements to be made in to current embodiment of the sensor system in order to enable commercial viability.

6.2.1 Fiber coating optimization

In this study, fluorescein and rhodamine B were used as fluorescent markers with PMMA chosen as the matrix. However, the PMMA coating was observed to be corroded by the harsh environment of the battery. With the ultimate goal of embedding the fiber inside of the battery, further work is necessary.

6.2.2 Barrier material coating

In order to promote the chemical compatibility of the fiber temperature sensor in the harsh battery environment, a protective coating may be employed in order to protect against corrosion. Some work was carried out in order to promote corrosion resistance. A two-part transparent epoxy coating (EpoTek 353ND) was investigated (see figure 42). However, owing to its relatively high viscosity, the coating thus obtained was observed to be extremely thick and non-uniform.

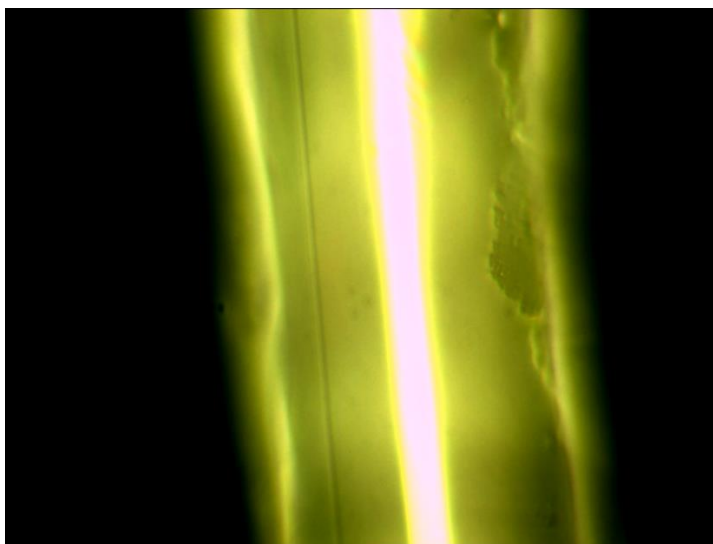


Figure 42 Optical micrograph of epoxy coated temperature sensor

When tested, this epoxy coating was also proven to be inadequate. The underlying fluorescent temperature sensing coating was found to be corroded when placed in a lithium ion battery. Further work is required to optimize the coating process for this barrier layer.

6.2.3 Optimization of materials

In this work, PMMA was chosen as the bulk component for the fluorescent coating. Furthermore, fluorescein and rhodamine B were chosen as the fluorescent dyes. There are a wide variety of dyes that can be used for this purpose. Although long-term testing was not carried out, the lifetime of the rhodamine B and fluorescein might be an issue that needs further optimization. Furthermore, in this study, only organic dyes were chosen owing to safety concerns and limited access to equipment. Inorganic dyes should also be considered owing to their better long term stability.

Only PMMA was studied as a host material. A variety of other hosts may also be used in order to combat the corrosion problem. Other polymers such as siloxanes or epoxies may be used due to their superior chemical resistance and optical properties. Another avenue that might be worth exploring is the using of sol-gel methods to cast thin films of silica impregnated with the fluorescent dye. These studies were not performed owing to time and equipment constraints.

6.2.4 Computer controlled coating

The coating process used for these studies were extremely simplistic with a constant pull-rate for the coating. However, further optimizations are possible to further improve the coating process. These improvements would improve the coating adhesion.

The biggest improvement to the coating process would be dynamic pull rates. Owing to the curvature of the fiber extending into the trough used for the dip coating process, the rate at which the fiber is pulled out of the solution is non-constant. Using a more sophisticated computer control can enable the compensation of this curvature thus promoting a more uniform coating over the entire fiber sensing region.

6.2.5 Signal acquisition system design

The signal acquisition system in its current implementation is not suitable for use in an automotive environment. The use of a spectrometer means that the system would be priced out of any commercially viable system. In order to combat this, a system was designed to enable simultaneous multifunctional sensor readout at a low-cost.

6.2.6 Circuit design

A circuit was designed based on an earlier design of an optical sensor interrogator (OSI). The new circuit was designed to be a multifunctional OSI which would allow for the readout of both temperature and battery SOC. The circuit is designed as a shield to a microcontroller (Arduino Nano). The circuit is designed to house 2 different light sources; one for the excitation of the temperature sensitive coating (Superbright LED RL5-B5515) and another NIR LED for the sensing of the battery SOC (Optek OPV370). Each of the LEDs has its own linear regulator (Linear Technology LT3092) to isolate noise from the power supply and provide a stable constant current drive. Furthermore, the circuit has 2 NPN transistors (ON Semi P2N2222A) configured as a high side switch controlled with the microcontroller. The microcontroller can thus individual address these LEDs using the digital input and output pins without having to provide a stable supply of power.

For the acquisition, a general purpose silicon based photodetector (Optek OPF480) is used. This photodetector is configured in photovoltaic mode (i.e. no bias applied). The voltage output from this photodetector is amplified using a general purpose op-amp (Texas Instruments TLC272). The amplified readout is then read by an ADC IC (Microchip MCP3425) with programmable gain in order to be able to switch between fluorescent yield (high gain) and NIR readout (low gain). The digital bitstream is fed to the microcontroller over the I²C bus. This data is then captured, stored to buffer and then transmitted over USB to a host computer which processes the data.

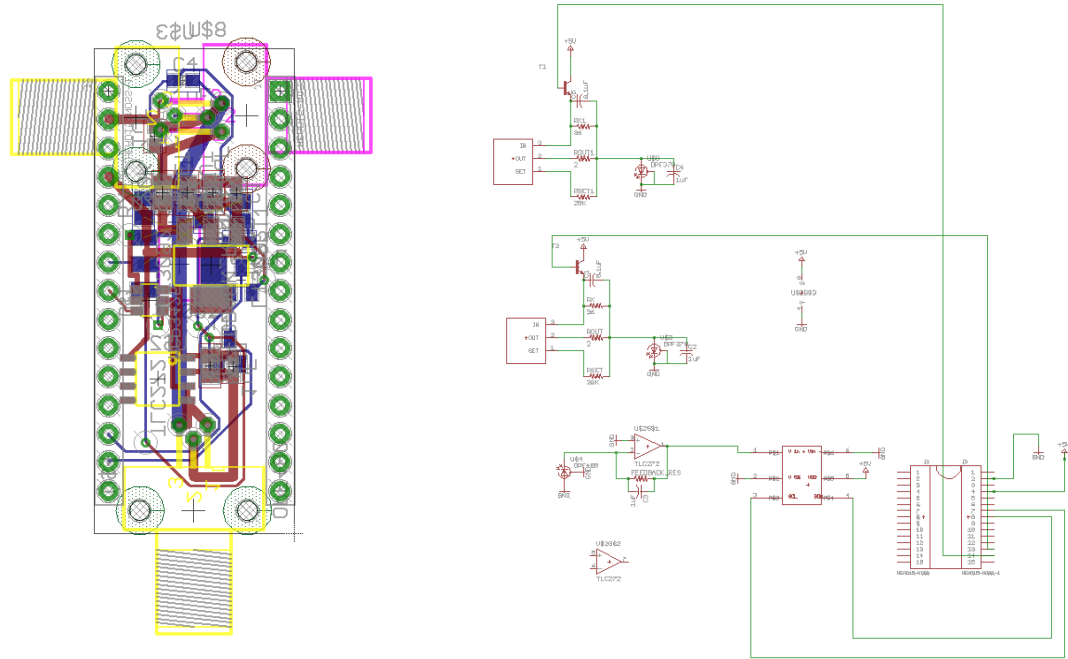


Figure 43 (a) Board layout of multifunctional OSI (b) Schematic view for multifunctional OSI

Thus, this circuit allows for rapid switching between the sources and being able to interrogate both functions of the fiber using the same device. This allows for a low-cost signal processing platform the readout from the multifunctional sensor. Although this circuit was designed, it has not been fabricated or tested yet.

6.2.7 Optical coupling

Although for the prototype stage, a y-fiber coupler was used to couple both of the LEDs together, this may not be a commercially feasible option. Low-cost options for LED light coupling such as polymer optical fiber based y-couplers or injection moulded light pipes may be used to couple both LED sources into one fiber.

In order to have a commercially feasible product, the integration of the UV-LED die and the IR-LED dye on the same LED substrate is necessary. This would thus cut the price of the OSI module significantly. However, this is only commercially plausible when high volumes are being produced.

6.2.8 Improving signal-to-noise ratio

It is anticipated that some of the excitation light source will be received at the other end. Although the responsivity of silicon is much lower at 470 nm, it is proposed that an optical filter be used to filter the lower wavelengths of light and separate the excitation source from the emission of fluorescence.

6.3 Conclusions

In this thesis, a sensor was developed that is capable of sensing two important battery parameters simultaneously; state-of-charge and temperature. Both sensors are fiber optic based in nature providing a unique and robust methodology to gather information about a lithium ion battery

The temperature sensitive coating is a polymer based coating which contains temperature fluorescent molecules to convert the stimulus of temperature to observable data. A double dye system was used to enhance the expected lifespan of the sensor. Widely available fluorescent dyes, fluorescein and rhodamine B were used to transduce the temperature stimulus to an optical signal. The sensitivity of the coating was studied and its composition was optimized to provide maximum sensitivity.

A process was developed to coat this coating on a silica optical fiber using dip coating. The influence of dip-coating parameters was studied and an optimum process was developed to enable good quality coatings.

A temperature sensor was constructed on a silica optical fiber using this methodology. The behaviour of this sensor was observed to be linear and the sensor displayed a theoretical resolution of $0.168\text{ }^{\circ}\text{C}$ when used with a spectrometer and compared to a thermocouple. Owing to its larger sensing region when compared to the thermocouple, a response time of roughly 200 seconds was observed. This accuracy and response is sufficient for applications in lithium ion battery monitoring systems.

Finally, a multifunctional temperature and SOC sensor was developed and demonstrated. The methodology for temperature sensing was coupled with a fiber optic SOC sensing methodology to invent a novel strategy for more accurate battery monitoring of lithium ion pouch cells which allows for the monitoring of temperature and the SOC of the battery simultaneously using optical interrogation techniques. A resolution of $0.86\text{ }^{\circ}\text{C}$ was observed when the performance of this multifunctional sensor is compared to the performance of a thermocouple with a sensitivity of $9.738\text{ lx}/^{\circ}\text{C}$. The response time of 2 minutes observed was also shown to be plenty adequate for application in battery temperature monitoring.

The embedding of this sensor inside of a lithium ion battery will allow for a better measurement of temperature while simultaneously measuring the battery SOC. Furthermore, the use of a dual-function interrogation system will allow for a low cost addition to a battery management system. The work done in this thesis is aimed at better understanding the limitation of a battery and improving the amount of performance that can be obtained from a lithium ion battery without causing permanent damage thus allowing for a more efficient electric vehicle.

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Glossary

SOC	State-of-charge of a battery
SOH	State-of-health of a battery
OCV	Open circuit voltage
LFP	Lithium iron phosphate battery
SEI	Solid electrolyte interface
MEMS	Microelectromechanical systems
LIB	Lithium ion battery
FEWS	Fiber optic evanescent wave sensor
EV	Electric vehicle
FBG	Fiber Bragg grating
OTDR	Optical Time Domain Reflectometry
FRET	Forster Resonance Energy Transfer
PMMA	Poly(Methyl Methacrylate)
LED	Light emitting diode
TIR	Total internal reflection
CCD	Charge Coupled Device
HF	Hydrofluoric acid
NIR	Near-infrared
I ² C	Inter instrument Communication