

Modeling and Experimental Studies of Electrolyte for Zinc Battery Systems

by
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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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

Statement of Contribution

All experimental results, figures, and text are generated from my own work during this Ph.D. research. The thesis is based on the following papers that I have submitted or published.

1- Study Of Zn (TFSI)₂-H₂O Electrolyte System For Using In Zinc Batteries, **A Mashayekhi**, Materials Chemistry And Physics, 343, 131077 (2025).

2- Effect Of Hydration Level On Zinc Electrolyte Properties, **A Mashayekhi**, Journal Of Solid-State Ionics, 430, 117011 (2025).

3- Early-Stage Lifetime Classification For Batteries: Machine-Learned Features Vs Human-Selected Features, **A Mashayekhi**, Under Review.

4- Accelerating The Discovery Of Ionic Liquids For Zinc Electrochemical Applications, **A Mashayekhi**, Computational And Theoretical Chemistry, 1251, 115340 (2025).

5- Machine Learning For Catalyst Optimization: Outlier Detection And Material Innovation, **A Mashayekhi**, et al., Applied Catalysis A: General 705, 120434 (2025).

6- Chemical Space Exploration For SSEs: Data-Driven Insights Into Structure-Property Relationships, **A Mashayekhi**, et al., Journal Of Energy Storage, Minor Revision Under Review.

Abstract

Zinc-based batteries have emerged as promising alternatives to lithium-ion systems due to their low cost, inherent safety, and sustainability. However, challenges in electrolyte stability, dendrite formation, and limited lifetime have constrained their practical deployment. Addressing these barriers requires both experimental innovation and data-driven approaches for electrolyte and materials design.

This thesis aims to advance zinc battery technologies through four interconnected directions: (i) development of novel electrolyte systems, (ii) optimization of zinc deposition and cycling performance, (iii) machine learning methods for early-stage lifetime prediction, and (iv) accelerated discovery of functional ionic liquids.

Molten salt-derived $\text{Zn}(\text{TFSI})_2$ electrolytes were investigated for zinc–oxygen batteries across a wide temperature range. Electrochemical, spectroscopic, and microscopy analyses revealed the structural evolution of zinc oxide nanosheets during cycling and highlighted that $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ suppresses parasitic reactions more effectively than $\text{Zn}(\text{TFSI})_2 \cdot 18\text{H}_2\text{O}$, enabling improved reversibility and energy storage potential. Complementary studies on hydrated ZnCl_2 electrolytes demonstrated how temperature and hydration level influence zinc nucleation, morphology, and cycling stability. $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ achieved 99.2% coulombic efficiency over 50 cycles, while higher operating temperatures increased discharge capacity from 17 mAh g⁻¹ at -10 °C to 72 mAh g⁻¹ at 40 °C.

Artificial intelligence approaches were developed to classify and predict battery lifetime from early cycling data. Machine-learned models achieved up to 96% accuracy after only two cycles and 98% with additional data, while human-selected electrochemical features showed strong generalizability across chemistries. Deep learning methods reached 99.5% accuracy with extended cycling data but proved less transferable to systems with distinct degradation profiles. In parallel, convolutional and generative adversarial neural networks were applied to accelerate the discovery of ionic liquids for zinc batteries. These models improved property prediction and successfully generated new candidate electrolytes with enhanced performance at room temperature.

Overall, this work provides an integrated experimental–computational framework for electrolyte optimization, electrochemical performance improvement, and AI-driven materials discovery. The findings pave the way toward more durable, efficient, and scalable zinc-based energy storage technologies.

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Dedication

I dedicate this thesis to my beloved father, who passed away recently, and to my dear mother.

My father always believed in me and wished to see me graduate.

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List of Abbreviations

Ar – Argon (inert gas)

O₂ – Oxygen

H₂ – Hydrogen

Zn(TFSI)₂ – Zinc Di[bis(trifluoromethylsulfonyl)imide]

ZnCl₂ – Zinc Chloride

ZnO – Zinc Oxide

ZnO₂ – Zinc Peroxide

Zinc Triflate – Zinc Trifluoromethanesulfonate

ZnSO₄ – Zinc Sulfate

K₃Fe(CN)₆ – Potassium Ferricyanide

WiSE – Water in Salt Electrolyte

OTf – Trifluoromethanesulfonate

TFSI – Bis(trifluoromethanesulfonyl)imide)

MD – Molecular Dynamics

Zn – Zinc

Cu – Copper

KOH – Potassium Hydroxide

CE – Columbic Efficiency

Zn(OH)₂ – Zinc Hydroxide

LDH – Layered Double Hydroxides

ZnHCF – Zinc Hexacyanoferrate (Prussian Blue)

MAH – Milliampere Hour

DSC – Differential Scanning Calorimetry

DTA – Differential Thermal Analysis

EIS _ Electrochemical Impedance Spectroscopy

HER – Hydrogen Evolution Reaction

OER – Oxygen Evolution Reaction

OCV – Open Circuit Voltage (rest potential of electrochemical cell)

OEMS – Online Electrochemical Mass Spectrometry (Instrument)

DEMS – Differential electrochemical mass spectrometry

ORR – Oxygen Reduction Reaction

PTFE – Polytetrafluorethylene

PVDF – Polyvinylidene fluoride

SEM – Scanning Electron Microscopy

SHE – Standard Hydrogen Electrode

TGA – Thermal Gravimetric Analysis

XRD – X-ray Diffraction

EDX – Energy Dispersive X-ray Spectroscopy

MPM – Melting Point Meter

RT – Room Temperature

ML – Machine Learning

DL – Deep Learning

CC – Constant Current

CV – Constant Voltage

IR – Internal Resistance

RF – Random Forests

GBDT – Gradient Boosting Decision Trees

DNN – Deep Neural Network

CNN – Convolutional Neural Network

LFP – Lithium Iron Phosphate

IC – Incremental Capacity

SOH – State-of-Health

RNN – Recurrent Neural Networks

IL - Ionic Liquid

SMILES - Simplified Molecular Input Line Entry System

VAE - Variational Autoencoder

GAN - Generative Adversarial Network

CNN - Convolutional Neural Network

BF₄⁻ - Tetrafluoroborate

PF₆⁻ - Hexafluorophosphate

TFSI - Bis(trifluoromethanesulfonyl)imide

Cl⁻ - Chloride

mPa·S - Millipascal-second

mS cm⁻¹ - Millisiemens per centimeter

MOF – Metal Organic Framework

Chapter 1: Introduction

1.1 Electrochemical Energy Storage

Electrochemical energy storage systems, such as the batteries in many electronic devices, are key to an increasingly electric-powered world.¹ These systems store electricity in chemical form and then convert it back to electricity when needed.² At their core, they work using a simple idea: they turn chemical energy into electrical energy using electrochemical cells.³ These cells are made of two electrodes (anode and cathode) and an electrolyte in between.⁴ This setup is not only for small gadgets; it is also essential for larger applications such as electric vehicles and the storage of solar and wind energy.⁵

The performance of these batteries heavily depends on the materials used for the electrodes and the electrolyte.⁶ Researchers are always trying to find and improve these materials to make cost-effective batteries with a long cycle life.⁷ As the demand for clean and sustainable energy sources increases, these batteries are becoming more important. They help maximize the use of renewable energy sources such as solar and wind by storing excess energy and releasing it when needed, thereby keeping the energy supply steady and reliable.⁸

Electrochemical energy storage plays a critical role in the automotive industry, particularly with the transition toward electric vehicles (EVs). EVs need batteries that can store a great amount of energy, charge quickly, last a long time, and be safe.⁸ Lithium-ion batteries are widely used in electric vehicles because they offer high energy storage and long cycle life.⁹ But there are still challenges, including obtaining the materials needed for these batteries, addressing the impact of manufacturing and disposal, and developing even better batteries capable of powering cars for longer distances.^{10,11}

The environmental impact of batteries is becoming increasingly significant, and as battery usage grows, consideration must be given to how they are manufactured, utilized, and disposed of.¹² Efforts are being directed toward developing batteries that are more environmentally friendly and easier to recycle.¹³ Therefore, it is important to make sure that the benefits of using batteries don't come with too high of an environmental cost.

Also, new technologies such as artificial intelligence (AI) and machine learning are starting to play a role in battery technology.¹⁴ They are helping to find new materials, make batteries

last longer, and predict when they will need to be replaced.¹⁵ These improvements could make batteries last longer and work better, which is a big step forward for electrochemical energy storage.¹⁶

1.2 Divalent Metal Batteries

In the evolving landscape of battery technology, divalent metal batteries, particularly those using zinc, are gaining notable interest. These batteries utilize metals with a +2 charge in their ionic form, offering a unique approach to energy storage compared to the conventional lithium-ion batteries that operate with monovalent ions.¹⁷ Zinc batteries, leveraging the divalent nature of zinc, provide two positive charges per ion, suggesting the potential for higher energy storage within the same volume.^{18,19}

Zinc batteries are characterized by their use of zinc as the anode material, while the cathode can be composed of various materials depending on the desired battery characteristics. A significant feature of these batteries is the use of water-based electrolytes, which contribute to their safety and environmental benefits.^{20–23} The working mechanism of zinc batteries involves the shuttling of zinc ions between the anode and cathode during discharge and charging cycles, thereby generating and storing electrical energy.²³

The scalability and adaptability of zinc batteries make them suitable for a broad spectrum of applications, from small electronic devices to large-scale energy storage systems.²⁴ They are particularly advantageous in the context of renewable energy storage, such as for solar and wind power. Zinc batteries are capable of handling high-power requirements and can provide long-duration energy storage, making them ideal for integrating into energy grids to store excess renewable energy and help stabilize supply and demand.²⁴

While zinc batteries currently do not match the reversible energy density of the more advanced lithium-ion batteries, there is intense ongoing research aimed at enhancing their energy storage capacity and efficiency.²⁵ This research is centered on developing new electrode materials and optimizing battery designs to improve the energy density and capacity of zinc batteries, which could make them a more viable option for energy-intensive applications.²⁶

One of the primary challenges in the development of zinc batteries is overcoming issues such as dendrite formation during the charging process.²⁶ Dendrites can cause short circuits and

significantly reduce the battery's lifespan and safety. Researchers are exploring innovative electrolyte compositions and electrode designs that can inhibit dendrite growth, thereby enhancing the safety and durability of zinc batteries.^{27,28}

The environmental and economic aspects of zinc batteries contribute significantly to their unique features. Zinc is more readily available and less environmentally damaging in its extraction and use compared to some other battery materials, thus positioning zinc batteries as a sustainable energy storage solution.²⁹ Their cost-effectiveness is also advantageous, particularly for large-scale energy storage applications where the cost is a critical factor.³⁰

Current research in zinc battery technology extends beyond improving energy capacity and charging efficiency. It also includes efforts to enhance the operational life and reliability of these batteries. Advanced battery management systems are being developed to optimize the performance and extend the lifespan of zinc batteries, aiming to maximize their potential in various applications.^{31,32}

Overall, divalent metal batteries, with an emphasis on zinc-based batteries, represent an important and promising area in the field of energy storage. Their unique characteristics, such as the potential for higher energy density, safety, and environmental sustainability, position them as key players in the future of battery technology.³³ As research continues to address their limitations and enhance their capabilities, zinc batteries are poised to play a significant role in a wide range of applications, from portable electronics to the large-scale storage of renewable energy.

1.2.1 Aqueous Zinc Batteries

Aqueous zinc batteries use water-based electrolytes, which is a key distinguishing feature from their non-aqueous counterparts. This characteristic offers several advantages, making them attractive for various applications. The use of water as an electrolyte solvent not only makes these batteries safer and less flammable than those with organic solvents but also more environmentally friendly.^{34–36}

One of the primary benefits of aqueous zinc batteries is their safety profile.³⁴ The water-based electrolyte significantly reduces the risk of fire and explosion, a concern often associated

with non-aqueous batteries. This safety aspect makes aqueous zinc batteries suitable for a wide range of applications, including consumer electronics and large-scale energy storage systems.

Moreover, the materials used in aqueous zinc batteries, particularly zinc, are abundant and inexpensive.^{22,37} This cost-effectiveness is a major advantage, especially for large-scale deployments such as grid energy storage. The environmental impact of these batteries is also generally lower compared to non-aqueous batteries, as they use less toxic and less environmentally harmful materials.^{38–40}

Despite their advantages, aqueous zinc batteries face certain challenges. One significant issue is the limited energy density compared to non-aqueous batteries.^{41–43} This can be a drawback for applications requiring compact and high-energy storage solutions, such as in electric vehicles. Additionally, the aqueous nature of the electrolyte can lead to issues such as water electrolysis and dendrite formation, which can affect the battery's lifespan and performance.^{40,44,45}

1.2.2 Non-Aqueous Zinc Batteries

Non-aqueous zinc batteries use an electrolyte that is not water-based, typically involving organic solvents. This difference in electrolyte composition allows a wider operational temperature range compared to aqueous zinc batteries.^{44,46,47}

The primary advantage of non-aqueous zinc batteries is their higher energy density.^{40,44–50} This makes them more suitable for applications where space and weight are critical factors, such as in portable electronics and electric vehicles. Additionally, the use of non-aqueous electrolytes expands the temperature range in which these batteries can operate effectively, making them more versatile in different environmental conditions.^{21,51,52}

Non-aqueous zinc batteries also tend to have a longer lifespan and better performance stability compared to their aqueous counterparts.^{18,51–53} This is partly due to the reduced issues with water electrolysis and dendrite formation, which are more prevalent in aqueous systems.¹⁸

The challenges associated with non-aqueous zinc batteries primarily relate to their cost and safety. The organic solvents used in the electrolyte can be more expensive and less environmentally friendly than water-based electrolytes.^{54,55} There is also an increased risk of flammability, which necessitates stringent safety measures in their design and use.^{17,54,55}

Ongoing research and development are focused on improving their cost-effectiveness and safety profile, aiming to broaden their applications in the future.

1.3 Zinc-Oxygen Batteries

Zinc-oxygen batteries, emerging as a category within the metal-air battery family, are gaining significant interest in the field of energy storage.⁵⁶ These batteries leverage the chemical reaction between zinc and atmospheric oxygen, distinguishing them from conventional battery systems.⁵⁶ The core operation involves the oxidation of zinc at the anode and the reduction of oxygen at the cathode during discharge, a process that is reversed during recharging in rechargeable variants.^{57,58} This operation principle offers a theoretical energy density that surpasses many conventional batteries, primarily due to the utilization of atmospheric oxygen as a reactant, which dramatically reduces the weight and potentially increases the energy density of these batteries.¹⁸

Despite their potential, zinc-oxygen batteries face several challenges. The primary issue is the formation of zinc dendrites during charging, which can bridge the gap between the anode and cathode, leading to short circuits and potential battery failure.^{59,60} This dendritic growth presents a significant safety risk and is a key focus of ongoing research.³¹ Furthermore, the stability of cathode materials is another critical challenge.⁶¹ The cathode, particularly when carbon-based materials are used, can degrade over time, leading to reduced efficiency and a shorter lifespan for the battery.⁶¹

Aqueous electrolytes are widely used in zinc-oxygen batteries due to their inherent safety and low cost.^{62,63} These electrolytes typically include alkaline or neutral solutions, which effectively conduct ions between the anode and cathode.⁶²⁻⁶⁴ However, the use of aqueous electrolytes presents certain limitations, including a narrow electrochemical stability window.⁶²⁻⁶⁵ This limited window can lead to water electrolysis and hydrogen gas formation, posing a risk to the battery's safety and efficiency.⁶⁵⁻⁶⁷ Additionally, aqueous systems may suffer from corrosion and zinc dissolution issues, which can further limit the lifespan and efficiency of the battery.⁶²

Non-aqueous electrolytes offer a potential alternative to the challenges posed by aqueous electrolytes.^{62,65,66} These electrolytes, typically consisting of organic solvents, provide a

broader electrochemical stability window and potentially higher energy densities.^{62,65} Non-aqueous electrolytes help to mitigate issues related to water electrolysis and corrosion.^{59,62,63} However, they introduce their own set of challenges, such as higher costs, flammability, and the need for more complex sealing and packaging to prevent solvent evaporation and moisture ingress.^{68,69} The development of stable and safe non-aqueous electrolytes that can effectively support the zinc-oxygen electrochemistry is an ongoing area of research and development.

In addition to these electrolyte-related challenges, research in zinc-oxygen batteries is also focused on enhancing their overall energy density, safety, and longevity.⁶⁹ Efforts include innovations in electrode materials to prevent dendrite formation, identification of stable cathode materials, and the introduction of novel electrolyte formulations.⁶² Advancements in cathode catalysts, which are crucial for the oxygen reduction reaction during discharge and the oxygen evolution reaction during charging, are also being actively researched.⁷⁰ These catalysts can significantly enhance the overall performance and rechargeability of zinc-oxygen batteries.⁷¹

The potential applications for zinc-oxygen batteries are vast and varied, extending from portable electronic devices to large-scale energy storage systems.⁷² Their capability to handle high-power requirements and provide long-duration energy storage makes them particularly suitable for renewable energy storage, such as for solar and wind power.^{63,72,73} In these applications, zinc-oxygen batteries could play a crucial role in integrating into energy grids, storing excess renewable energy, and helping to stabilize the supply and demand of electricity.⁷³

The development of zinc-oxygen batteries, both with aqueous and non-aqueous electrolytes, is part of the broader effort to find sustainable, safe, and efficient energy storage solutions. Addressing the challenges related to dendrite formation, cathode degradation, electrolyte stability, and rechargeability remains central to the advancement and application of this promising battery technology.⁷³ As research continues, zinc-oxygen batteries are expected to become a more viable and competitive option in the field of energy storage, offering solutions that align with the growing demand for sustainable and high-performing energy systems.⁷³ crucial for meeting diverse energy storage needs across various sectors.

1.4 Zinc-Ion Batteries

Multivalent ion batteries, especially zinc-ion batteries, emerge as a promising solution for large-scale energy storage, thanks to zinc's environmentally friendly nature, affordability, abundant availability, low redox potential, compatibility with aqueous electrolytes, and high volumetric capacity.²⁴

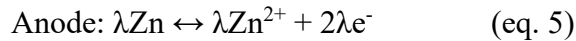
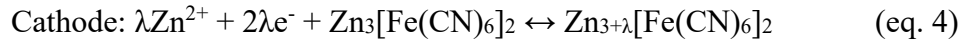
However, challenges such as limited capacity, cycling instability, and dendrite formation in zinc batteries remain obstacles to their practical application.²³ A water-in-salt electrolyte (WiSE) of 30 m ZnCl_2 has been developed for consistent and dendrite-free zinc plating/stripping, showing dense and uniform zinc morphology as opposed to the irregular formations seen in dilute aqueous solutions.⁷⁴

The capacity retention in zinc batteries, particularly using a cathode of $\text{Ca}_{0.20}\text{V}_2\text{O}_5 \cdot 0.80\text{H}_2\text{O}$, improves significantly by increasing the ZnCl_2 electrolyte concentration, demonstrating enhanced cycling stability.⁷⁵ Similarly, concentrated $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ electrolyte offers superior properties for zinc-air batteries compared to its diluted aqueous counterpart, benefiting from the strong hydration effect of molten salt.⁷⁵

Recognizing the need for zinc batteries to function under extreme temperatures. For instance, a study on lithium nucleation shows that higher temperatures lead to more compact lithium layers, suggesting the influence of temperature on nucleation properties.⁷⁵ This concept is applied to zinc, where the role of temperature in zinc nuclei size, density, and compact growth is critically important yet underexplored. It is also shown that by adjusting the ZnCl_2 electrolyte structure and lowering its freezing point, the electrolyte becomes suitable for low-temperature applications, such as polyaniline/Zn batteries.⁷⁶

Focusing on rechargeable zinc-ion cells, ZnHCF ($\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$) nanostructures are employed as the cathode electrode. These nanostructures, known for their large surface area and increased diffusion rates, enhance the cycling performance of zinc cathodes.⁷⁷ Prior studies have demonstrated the successful application of ZnHCF nanoparticles as reversible cathodes in zinc-ion battery systems, highlighting their stability and effectiveness in facilitating Zn^{2+} intercalation and deintercalation.^{77,78} The impact of ZnHCF particle morphology on electrochemical behavior, with particular focus on polyhedral and rhombohedral structures has

also been studied.⁷⁸ Improvements in the performance of the ZnHCF cathode have been achieved using a concentrated zinc nitrate electrolyte, attributed to the smaller hydration number of zinc ions and reduced structural stress on the ZnHCF.⁷⁹ This zinc-ion battery system, comprising Zn/ZnCl₂/ZnHCF-NPs, operates based on the following electrochemical reactions, showcasing the potential for high-efficiency, temperature-adaptable zinc-ion batteries:⁷⁷



where λ represents the number of Zn^{2+} that can be reversibly inserted into ZnHCF-NPs. As seen, the reaction at the cathode electrode involves zinc ions (Zn^{2+}) moving in and out of the Zn hexacyanoferrate (ZnHCF) material, while at the anode, the process is about zinc depositing and dissolving. Zn^{2+} ions shuttle back and forth between the anode and cathode, carried through the electrolytes. These advancements highlight the growing potential of zinc-ion batteries as sustainable and efficient energy storage systems. Continued research into electrolyte optimization, electrode material design, and thermal adaptability will be essential to unlock their full commercial viability.

1.5 Lifetime Classification for Batteries

Rechargeable batteries are extensively utilized in a variety of applications owing to their attractive features such as low cost, extended lifespan, superior high-power density, and impressive energy density.^{1,80,81} However, with the passage of time and continued use, these batteries tend to exhibit a decline in performance, leading to heightened concerns regarding their safety and reliability.^{1,81} The accurate prediction of a battery's lifespan is a critical aspect, essential for evaluating the quality of the battery, enhancing the effectiveness of long-term planning, and ensuring the safety of the systems that rely on these batteries.^{82–84}

A diverse range of techniques has been suggested for the prediction of battery lifespan. These techniques include model-based methods, mechanism-based methods, and approaches based on machine learning (ML).^{82,83,85} The model-based methods primarily utilize detailed mathematical models and adaptive filtering techniques to track and understand the dynamics of battery degradation.^{82,83,85} However, these methods often face challenges in generating

precise predictions, particularly in the early stages of a battery's life.^{16,86,87} The mechanism-based methods, in contrast, concentrate on deciphering the aging processes of batteries through detailed chemical and physical equations.^{16,86} Despite their detailed approach, these methods are limited by the complex nature of the chemical reactions within the batteries.¹⁶

In the last few years, there has been a noticeable shift towards ML approaches, spurred by significant advancements in the field of computational technology.^{16,88} These methods involve the process of correlating specific features of batteries to their expected lifespan using various ML models.⁸⁹ In several past studies, methods such as the elastic net model, neural networks, Gaussian process regression, and gradient boosting regression tree models have been employed.⁸⁹ These methods aim to predict the lifespan of batteries by analyzing data extracted from parameters such as voltage, capacity curves, temperature profiles, among other factors.^{82,83,89} While these methods have shown promising results in predicting battery lifespan, they often require access to extensive historical data on battery degradation, which can slow down the process of development and validation. Furthermore, basing predictions on a single set of training and testing data can lead to inaccurate assessments and does not provide a complete picture of a network's capabilities. A single dataset might show high accuracy, sometimes over 90 %, but this may not be consistent across various sets of training and testing data. By conducting assessments over a wide range of random datasets and averaging these results, a more accurate and comprehensive evaluation of the performance could be achieved. This approach minimizes the risk of overfitting to a particular dataset and ensures that the conclusions are based on a broader and more representative range of scenarios. In contrast, previous studies that relied on a single fixed set of training and testing data may not have fully captured the network's applicability and generalization capabilities in real-world scenarios.⁹⁰

Researchers have been exploring a blend of traditional machine learning techniques and advanced deep learning technologies, which can use both human-selected and data-driven features to predict battery lifespan.⁹¹⁻⁹⁵ Traditional machine learning methods have been used for predicting the remaining lifespan of batteries and classifying them based on factors such as charge-discharge cycles, temperature, and usage patterns.^{92,96} Meanwhile, deep learning methods have shown their ability to identify complex patterns and temporal dependencies in

battery data.^{91,92,97} These deep learning models are adaptable and can use data-driven features, enabling them to extract complex information from raw data and thereby enhance prediction and classification accuracy. The comparison of these two types of approaches is key to improving the understanding of battery performance and longevity, providing flexibility in feature selection, and leading to more efficient and reliable energy storage solutions.

A notable challenge in applying machine learning for predicting the lifespan of batteries is the limited availability of samples of degraded cells for training purposes. Predicting battery lifetime with sparse data presents a crucial challenge across multiple sectors, including electric vehicles and renewable energy systems. Precise predictions of battery life are vital for optimizing resource use and reducing operational interruptions. Conventional wisdom has long held that substantial datasets are pivotal for precise predictive modeling.^{98–100} Yet, in practical scenarios, the availability of battery cells for model training is often restricted. This constraint underscores the need for methodologies that can achieve high accuracy despite limited data. Models based on neural networks require large datasets for training to prevent overfitting,¹⁰¹ while simpler algorithms such as K Nearest Neighbor, Naïve Bayes, and decision trees tend to be less effective when dealing with a large number of features.¹⁰² Modified tree-based ensemble models such as random forests (RF)^{103,104} and gradient boosting decision trees (GBDT)^{105,106} have shown better results in predicting battery lifespan because of their flexibility, ease of training, and their ability to manage multiple correlated features without the risk of overfitting. As research continues to evolve, developing reliable, data-efficient predictive tools is essential for advancing the safe deployment and operational efficiency of rechargeable battery technologies across various real-world applications.

1.6 Accelerated Electrolyte Discovery

The integration of AI into battery research represents a pivotal advancement in the field, offering more efficient and accurate methods for material discovery and lifetime prediction. As AI technology continues to evolve, it is poised to play a crucial role in the development of next-generation battery technologies, potentially leading to batteries that are more sustainable, efficient, and capable of meeting the growing demands of various energy storage applications.

Ionic liquids (ILs) are a unique class of compounds known for their ability to remain liquid at low temperatures, often below 100 °C.¹⁰⁷ Unlike conventional salts that require high temperatures to melt, ILs consist of bulky, asymmetric organic cations paired with either organic or inorganic anions.^{107,108} This structural characteristic leads to low melting points and notable properties such as non-volatility, non-flammability, and high thermal stability. These attributes make ILs ideal for various applications that benefit from their liquid state at room temperature, particularly as solvents in chemical processes and electrochemical applications.^{107–109}

Recent advancements in artificial intelligence and machine learning have significantly propelled the research and development of ionic liquids, particularly in their application to electrochemical systems and battery technologies.¹¹⁰ AI techniques have been increasingly utilized to predict and optimize the properties and behaviors of ILs, addressing some of the traditional challenges faced in electrochemistry and battery design.¹¹⁰ One significant breakthrough is the use of AI to predict the formation and growth of dendrites in lithium-air batteries.¹¹¹ By applying transfer learning methods, researchers have developed predictive models that accurately simulate dendrite growth. These models leverage existing datasets of compound properties significantly speeding up the research process and reducing reliance on costly and time-consuming experimental methods.

The application of AI and ML in this field not only enhances the fundamental understanding of ILs but also accelerates the development of solutions to problems in energy storage technologies.^{111,112} This integration promises to unlock new possibilities in the customization and application of ILs. Ongoing research continues to highlight the versatility of ILs and their vast potential across various technological applications, supported by advancements in computational chemistry and data-driven approaches.

The versatility of ILs allows for the customization of their cationic and anionic components. This is highly beneficial in the field of electrochemistry. In applications such as zinc electrochemical systems and zinc batteries, the properties of ILs are particularly advantageous. They stabilize zinc ions and prevent dendrite formation, thus enhancing both the safety and efficiency of these batteries.^{113–115} The ongoing development of ILs aims to address specific

industrial challenges, such as improving the reversibility and efficiency of metal deposition and stripping processes in batteries.¹¹³

However, the widespread adoption of ILs faces several challenges. The synthesis of ILs can be costly, and their environmental impact requires careful consideration.^{108,109,116} Issues such as high viscosity and complex synthesis processes hinder their broader application. Further research into ILs has also explored their use in solid-state batteries, where they are integrated with polymer matrices to enhance safety and energy density.^{117–119} Achieving a balance between high ionic conductivity and mechanical stability is challenging but crucial for the advancement of solid-state battery technologies.^{117–119} The wide electrochemical windows and good thermal stability of ILs contribute positively, although issues such as higher viscosity compared to traditional electrolytes affect ion mobility and performance. The application of machine learning in this domain not only accelerates the search for new materials but also opens a pathway to systematically overcoming long-standing challenges in electrolyte design for metal-based batteries.

1.7 Knowledge Gaps and Research Needs

This thesis aims to fill the following gaps in the current literature:

- 1- The thermal behavior and stability of hydrated electrolytes remain insufficiently explored, particularly under molten conditions, and it is still unclear whether the reversibility of zinc–oxygen cells can be demonstrated through zinc oxide oxidation across different temperatures.
- 2- There is still limited understanding of how different hydration levels influence zinc nucleation and growth, plating and stripping behavior, and overall reversibility of zinc cells at subzero temperatures (e.g., $-10\text{ }^{\circ}\text{C}$) and elevated temperatures (e.g., $40\text{ }^{\circ}\text{C}$), compared with room-temperature performance. It also remains unclear which conditions can deliver more than 1000 stable cycles with less than 20 % capacity loss.
- 3- No early-stage battery lifetime classifiers have yet been optimized or validated specifically for zinc-based systems. Therefore, it is necessary to develop predictive machine learning models that can classify battery failure using data from fewer than 200 initial cycles, and to systematically compare the performance of traditional

machine learning approaches with deep learning methods, including an assessment of data-driven versus hand-crafted features.

- 4- The field currently lacks a generative design framework for ionic liquids specifically tailored to zinc battery applications, targeting thermal and electrochemical properties that enable stable operation at room temperature with melting points below 25 °C.

Chapter 2: Motivations and Objectives

2.1 Motivation

Zinc-based batteries offer a promising platform for sustainable energy storage due to the abundance, low cost, and environmental benignity of zinc. Among them, zinc-oxygen and zinc-ion batteries have shown potential for high energy density applications. However, a key barrier to their advancement lies in the limitations of commonly used alkaline electrolytes, which suffer from carbonation, instability in ambient conditions, and poor compatibility with certain electrode materials. These challenges motivate the search for alternative electrolytes that can enhance device stability and lifetime.

Molten hydrated salts, such as $\text{Zn(TFSI)}_2\text{-H}_2\text{O}$ and $\text{ZnCl}_2\text{-H}_2\text{O}$ systems, have recently emerged as viable candidates for zinc battery electrolytes due to their high ionic conductivity, low volatility, and intrinsic stability under moderately elevated temperatures. Their tunable hydration levels offer a promising pathway to control zinc plating/stripping behavior and reduce side reactions such as dendrite formation and gas evolution. Despite these advantages, a systematic understanding of their electrochemical behavior, particularly under various hydration states and temperature regimes, is lacking.

At the same time, the field of battery research is increasingly benefiting from data-driven approaches that complement experimental efforts. Machine learning models can be used to predict battery degradation from early-cycle measurements, offering a powerful tool for assessing long-term performance. Furthermore, generative AI frameworks now enable the discovery of electrolytes tailored for zinc-based systems, potentially accelerating the design of next-generation batteries. This thesis is driven by the dual motivation of:

- Investigating molten hydrated salt systems as stable alternatives to alkaline electrolytes in zinc-oxygen batteries and effective mediums for zinc-ion transport.
- Leveraging machine learning to predict battery life and discover novel ionic liquid candidates.

Together, these goals aim to enhance the understanding and performance of zinc-based electrochemical energy storage systems.

2.2 Objective

The main objective of this thesis is to investigate the interplay between electrolyte composition, temperature, and hydration level in zinc-based batteries and to develop data-driven frameworks for predicting battery performance and discovering new materials. This objective is pursued through four distinct but interconnected tasks:

1- Investigate the electrochemical behavior of hydrated $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ electrolytes in symmetric zinc and full zinc–oxygen cells. This includes:

- Characterizing zinc plating/stripping reversibility at elevated temperatures using $\text{Zn}(\text{TFSI})_2\cdot 18\text{H}_2\text{O}$ and $\text{Zn}(\text{TFSI})_2\cdot 8\text{H}_2\text{O}$.
- Evaluating discharge product morphology and reversibility on nanostructured Co_3O_4 cathodes.
- Quantifying parasitic reactions and electrolyte decomposition during long-term cycling.

2- Examine the influence of temperature on zinc deposition using ZnCl_2 -based electrolytes at multiple hydration levels. This involves:

- Visualizing nucleation and growth morphology across different temperatures and water contents.
- Identifying conditions that suppress dendrite formation and promote uniform zinc deposition.

3- Develop machine learning models for early prediction of battery failure based on early-cycle voltage, impedance, and capacity data. This objective includes:

- Extracting and comparing human-selected versus machine-learned features across different battery chemistries.
- Building interpretable and transferable models for predicting battery lifespan at early stages of operation.

4- Design and implement a generative deep learning model for the discovery of ionic liquids suitable for zinc battery applications. This task involves:

- Training convolutional neural networks to predict melting point and decomposition temperature from SMILES strings.

- Using a generative adversarial network to propose new cation-anion pairs with optimized thermal and electrochemical stability.

Through these objectives, this work seeks to bridge the gap between experimental battery development and computational design, paving the way for more robust and scalable zinc-based energy storage systems.

2.3 Organization of the Thesis

This thesis is organized into seven chapters, each addressing an aspect of the experimental and computational investigation of zinc-based battery systems:

- Chapter 1 introduces the research topic, presenting the background, and significance of zinc-based energy storage systems and the challenges this work aims to address.
- Chapter 2 outlines the motivation behind the study, defines the specific objectives pursued, and explains the overall organization of the thesis.
- Chapter 3 investigates the electrochemical behavior of $\text{Zn}(\text{TFSI})_2$ -based hydrated molten salts in zinc symmetric and zinc–oxygen cells. The impact of hydration level and temperature on reversibility, gas evolution, and discharge product morphology is studied in detail.
- Chapter 4 explores zinc nucleation and growth behavior using ZnCl_2 -based electrolytes under controlled temperature and hydration conditions. Morphological and electrochemical analyses are performed to identify optimal deposition parameters.
- Chapter 5 presents machine learning models for early-stage battery lifetime prediction. It evaluates the performance of models trained on human-engineered and machine-learned features, providing insights into the key indicators of zinc battery degradation.
- Chapter 6 introduces a deep learning framework for the discovery of new ionic liquids. A neural network is used to predict thermal properties of ionic liquids, while a generative adversarial network proposes novel candidates tailored for zinc electrolyte applications.
- Chapter 7 concludes the thesis by summarizing the major findings and proposing future directions for experimental electrolyte optimization and AI-driven material discovery in zinc-based batteries.

Chapter 3: Study of $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ Electrolyte System for Using in Zinc Batteries

This chapter was published in Materials Chemistry and Physics, A. Mashayekhi, “Study of $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ Electrolyte System for Use in Zinc Batteries”, Vol. 343, 131077, Copyright Elsevier (2025).

The focus of Chapter 3 is placed on zinc-oxygen batteries, increasingly recognized as potential next-generation energy storage solutions for electric vehicles and grid storage.^{120–123} Earlier research predominantly targeted catalyst materials and their durability over cycles in these batteries.⁵⁶ Yet, the oxidation process of zinc oxide (ZnO) during charging in zinc-oxygen cells remains unclear. Additionally, comprehensive data on gas formation in secondary zinc-oxygen battery systems is limited, both in quality and quantity. To address these gaps, a zinc-oxygen battery employing a $\text{Zn}(\text{TFSI})_2$ -based molten salt electrolyte is introduced in this study. This electrolyte is crafted through a straightforward method, allowing control over water removal. By adjusting the drying and hydrating conditions, a hydrated system with melting points ranging from 139 °C to -35 °C can be achieved. This range is significant for accommodating various operational temperatures. Electrochemical tests, spectroscopy, and microscopy are combined in this approach to track the structural changes of ZnO nanosheets during charging. Reversible zinc plating/stripping is also examined in symmetric Zn cells with $\text{Zn}(\text{TFSI})_2 \cdot 18\text{H}_2\text{O}$ and $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolytes at -15 °C and 80 °C. The versatility of $\text{Zn}(\text{TFSI})_2 \cdot 18\text{H}_2\text{O}$ and $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolytes is further demonstrated in a zinc-oxygen cell with an O_2 cathode. In summary, this chapter presents an exploration into these hydrated liquids for zinc-oxygen batteries and how they perform at different temperatures. The findings are considered important for making these batteries a practical option for storing substantial amounts of energy, such as from solar panels or wind turbines. Several tools and techniques, including electron microscopy, X-ray tests, and various electrical measurements, were used to obtain a comprehensive picture of how these batteries charge and discharge.

3.1 Experimental and Methods

3.1.1 Preparation of Molten Salt Electrolyte

For the zinc-oxygen batteries, zinc di[bis(trifluoromethylsulfonyl)imide] ($\text{Zn}(\text{TFSI})_2$) salt at 98 % purity from TCI was used to create the hydrated electrolyte. We filled this electrolyte into glass fiber pores using a technique where we drop-cast the electrolyte at a concentration of 1 g L^{-1} . We placed the wet glass fiber discs, each 12 mm in diameter, in an oven set at 80°C for 15 minutes. This step helped evaporate extra water and allowed the absorbed hydrated salt to form a network within the glass fiber. We repeated this four times to ensure all pores were filled with hydrated electrolytes. We achieved an electrolyte-filled glass fiber mass of approximately $70 \pm 5 \text{ mg}$. After preparation, these fibers were dried under vacuum at 100°C for 24 hours and stored in an argon-filled glovebox, where we exposed them to different humidity levels (20 % and 75 %).

To create hydrated states of $\text{Zn}(\text{TFSI})_2 \cdot n\text{H}_2\text{O}$ with melting points below room temperature, we mixed inorganic $\text{Zn}(\text{TFSI})_2$ salt, previously dried and stored in an argon-filled glovebox, with ultrapure water in a predetermined ratio and in a dry chamber. We ensured complete salt dissolution by sealing and stirring the solutions overnight.

3.1.2 Cathode Electrode Preparation

We synthesized Cobalt oxide (Co_3O_4) nanowires (NWs) following a previously established method.¹²⁴ In a typical synthesis, 10 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98 %, Sigma-Aldrich) and 5 mmol of NH_4NO_3 (98 %, Sigma-Aldrich) were introduced into a 50 mL aqueous solution with 9 % ammonium hydroxide. After the complete dissolution of the precursors, stainless steel mesh pieces (SS316, Alfa-Aesar) were immersed in the precursor solution. The system was then held static at a temperature of 90°C . Upon completion of a 10-hour reaction period, the now black-colored SS meshes were washed with DI water. A final heat treatment was conducted at 300°C for 2 hours in an atmospheric environment to yield the Co_3O_4 -coated-SS electrode.

The Pt/C– IrO_2 (1:1) hybrid electrocatalyst combined 10 wt % Pt/C (Sigma-Aldrich), 10 wt % graphitized carbon-supported Pt (10 % Pt/Vulcan, Sigma-Aldrich), and iridium (IV) oxide (IrO_2 , 99.9 %, Sigma-Aldrich) with a polytetrafluoroethylene (PTFE) binder (Sigma-Aldrich).

The synthesis approach involved creating a slurry composed of 50 % catalyst by weight (equally divided between Pt/C and IrO₂), 45 % Vulcan XC-72, and 5 % PTFE binder in NMP (99.5 %, Sigma-Aldrich). This slurry was then evenly spread over carbon paper. The electrodes were subjected to a drying process at 60 °C for 10 minutes to eliminate any excess solvent. The carbon paper, now coated, was cut into disc-shaped electrodes, and further dried under vacuum at 120 °C for a duration of 12 hours.

The Super P air-cathode fabrication employed a standard slurry coating method. The slurry consisted of 70 % Super P conductive carbon black and 30 % PTFE binder in NMP solvent. This slurry was then applied to carbon paper, which was subsequently cut and dried using the same protocol established for the Pt/C–IrO₂ electrodes.

3.1.3 Physical Characterization

We conducted SEM studies using a Zeiss Ultra field emission SEM equipped with an Oxford EDX attachment. Powder XRD was performed on a Bruker D8-Advance powder diffractometer with Cu K α radiation. For DSC and TGA analysis, we used TA Instruments in sealed crucibles, and we monitored modified Swagelok®-type cells with an OEMS system to measure gas evolution rates during cell operation.

3.1.4 Cell Assembly and Electrochemical Characterization

For electrochemical impedance spectroscopy (EIS), we measured ionic conductivities of molten electrolyte systems using an MTZ-35 Biologic impedance analyzer. We assembled the zinc-oxygen cells in a modified Swagelok stainless steel cell, stacking a zinc metal anode, electrolyte-filled glass fiber, and the cathode electrocatalyst. After purging with pure oxygen and sealing the cell, we allowed it to equilibrate at the operating temperature before further testing with a multi-channel Arbin instrument.

3.2 Results and Discussion

Zn(TFSI)₂ has been recently reported as the electrolyte for high performance aqueous zinc batteries.¹²⁵ More importantly, a water-in-salt mixture of 1 M Zn(TFSI)₂ and 20 M Li(TFSI) was introduced as a high performance electrolyte for hybrid zinc-lithium systems and zinc-oxygen batteries.¹²⁶ In this chapter, a concentrated Zn(TFSI)₂-based electrolyte for zinc-oxygen cells is explored and the performance of the two different hydration levels is evaluated.

To date, many inorganic molten hydrated salts are recognized.^{127,128,129} This molten hydrated state is not an aqueous solution nor a water-in-salt system anymore, but rather a solid Zn(TFSI)_2 -based salt below the melting point temperature and a liquid electrolyte without free water molecules at its melting point temperature. The liquid–solid phase diagram of the Zn(TFSI)_2 – H_2O binary system in the range of (0, 0.6) mol of Zn(TFSI)_2 is summarized in **Figure 1a**. The graph exhibits a variety of $\text{Zn(TFSI)}_2 \cdot n\text{H}_2\text{O}$ hydrates at hydration levels of $n=2$, $n=4$, $n=6$, and $n=8$, as well as the Zn(TFSI)_2 – H_2O eutectic composition. The binary phase diagram also shows the melting points of these hydrates varies from 139 °C to -35 °C (139 °C, 108 °C, 75 °C, 62 °C, -35 °C) depending on the hydration levels, and the melting point mostly increases as the hydration level within the electrolyte decreases. To characterize the hydrates, the XRD patterns of the anhydrous salt along with the hydrated salt after 12 h exposure to 20 % humidity are shown in **Figure 1b**, indicating the formation of a new crystalline phase of hydrated Zn(TFSI)_2 . The sequential room temperature XRD analysis at time intervals of air exposure in **Figure 2** reveals that the crystal structure starts changing upon holding in 20 % air humidity. The inset of **Figure 1c** demonstrates the variation in the melting point of hydrated Zn(TFSI)_2 salt versus time of exposure to 20 % humidity. The melting point could be further reduced to an even lower value than room temperature (-35 °C) by further exposing the electrolyte-filled glass fiber to 20 % humidity or using a high humidity environment (75 % humidity) to enhance the speed of the hydration process. This could also be accomplished by

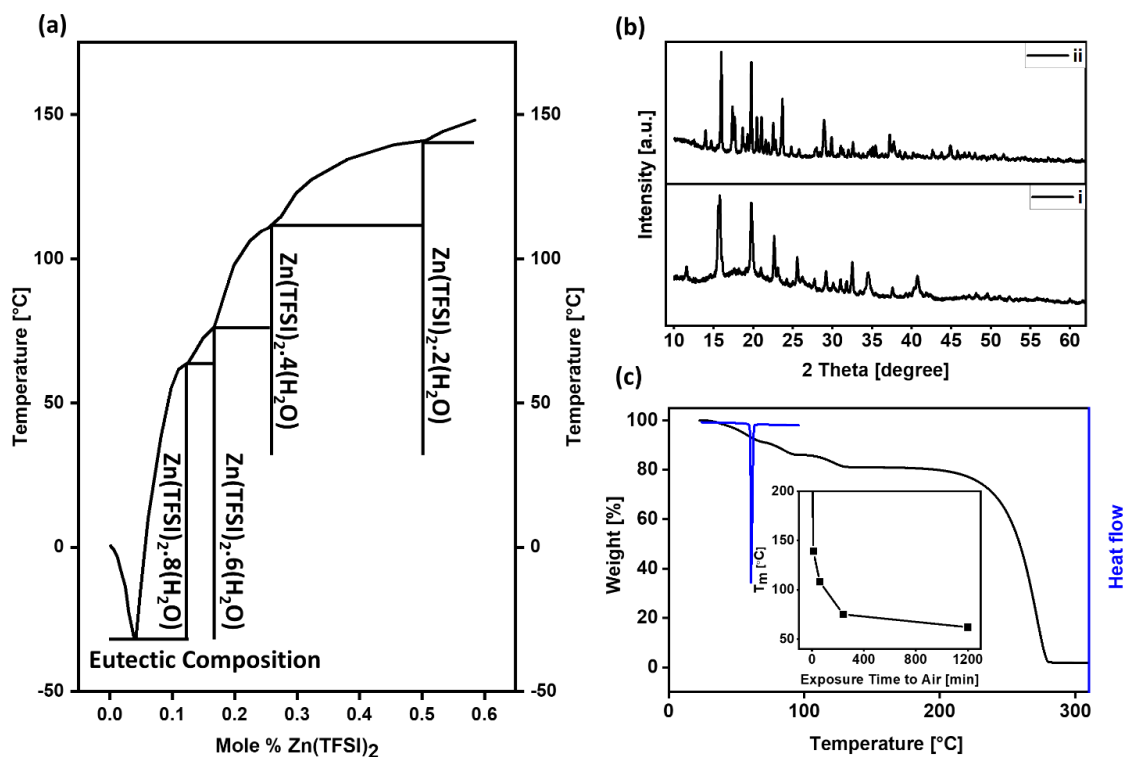


Figure 1: Thermal behavior and phase composition of $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ electrolytes. a) Liquid–solid phase diagram of the $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ binary system. b) XRD patterns of inorganic molten salt before (i) and after (ii) 12 h of exposure to 20 % air humidity. c) TGA and DSC result of hydrated $\text{Zn}(\text{TFSI})_2$ salt after 12 h of air exposure. The inset shows the effect of holding time in 20 % air humidity on the melting point of $\text{Zn}(\text{TFSI})_2$ salt, evaluated by the melting point meter (mpm).

dissolving $\text{Zn}(\text{TFSI})_2$ salt in ultrapure H_2O with a molar ratio of 1:18 so that the $\text{Zn}(\text{TFSI})_2\cdot 18\text{H}_2\text{O}$ with a melting point of $-35\text{ }^\circ\text{C}$ be obtained (**Figure 3a**).

Thermogravimetric analysis was used to measure the amount of crystalline water in a $\text{Zn}(\text{TFSI})_2$ hydrate after 12 h exposure to 20 % air humidity (**Figure 1c**). Weight loss of hydrated $\text{Zn}(\text{TFSI})_2\cdot n\text{H}_2\text{O}$ after 12 h exposure to 20 % air humidity occurs over two steps at $60\text{ }^\circ\text{C}$ and $105\text{ }^\circ\text{C}$. The 18.8 % mass loss corresponds to the 8 molecules of water per formula unit (the octahydrate $\text{Zn}(\text{TFSI})_2\cdot 8\text{H}_2\text{O}$). The huge mass loss starting at $200\text{ }^\circ\text{C}$ represents a starting point for the thermal degradation of the $\text{Zn}(\text{TFSI})_2$ salt. DSC analysis was also

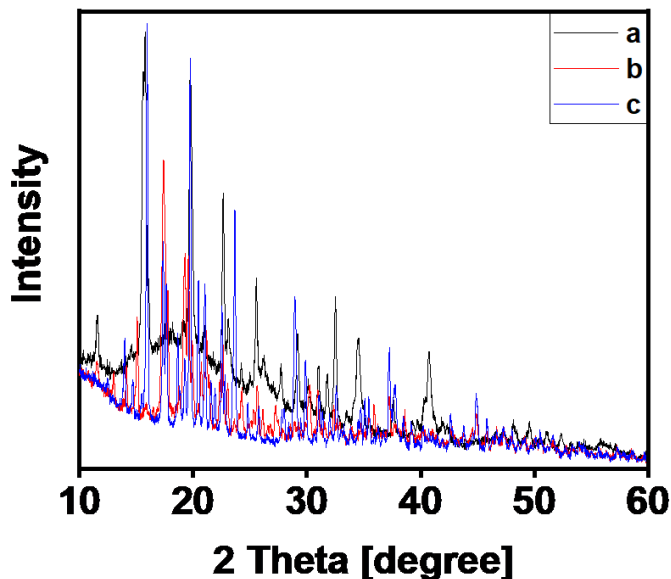


Figure 2: Room temperature sequential XRD analyses at certain time intervals of exposure to 20 % humidity: a) Anhydrous Zn(TFSI)₂, b) Hydrated Zn(TFSI)₂ upon 10 min of air exposure, c) hydrated Zn(TFSI)₂ upon 12 h of exposure to 20 % humidity level.

performed in a sealed aluminum crucible (**Figure 1c**). It confirms the melting point of 62 °C for Zn(TFSI)₂·8H₂O, while anhydrous Zn(TFSI)₂ decomposes starting at 200 °C, signaled by a significant mass loss in the TGA and as also confirmed by the DSC curve of anhydrous Zn(TFSI)₂ (**Figure 3b**). The existence of the octahydrate Zn(TFSI)₂ with a conductivity of 22 mS cm⁻¹ at 80 °C and a eutectic composition with a conductivity of 5 mS cm⁻¹ at -15 °C, makes the opportunities for the operation of batteries employing molten hydrates Zn(TFSI)₂-H₂O electrolytes.

Electrochemical plating/stripping experiments in the Zn(TFSI)₂·18H₂O and Zn(TFSI)₂·8H₂O molten electrolytes were conducted in the Zn/Zn symmetric cells with a sweep duration of 1 h at 0.25 mA cm⁻² at operating temperatures of -15 °C and 80 °C. At each operating temperature, a molten hydrated electrolyte with a lower melting point needs to be used to ensure the complete melting of the electrolyte. Both cells exhibit stable plating/stripping with the potentials of 16 mV in Zn(TFSI)₂·8H₂O molten electrolyte at 80 °C, to 120 mV in Zn(TFSI)₂·18H₂O molten electrolyte at -15 °C, shown in **Figure 4a, b**. The low zinc deposition potentials of the Zn/Zn symmetric cells compared to a previous study on a

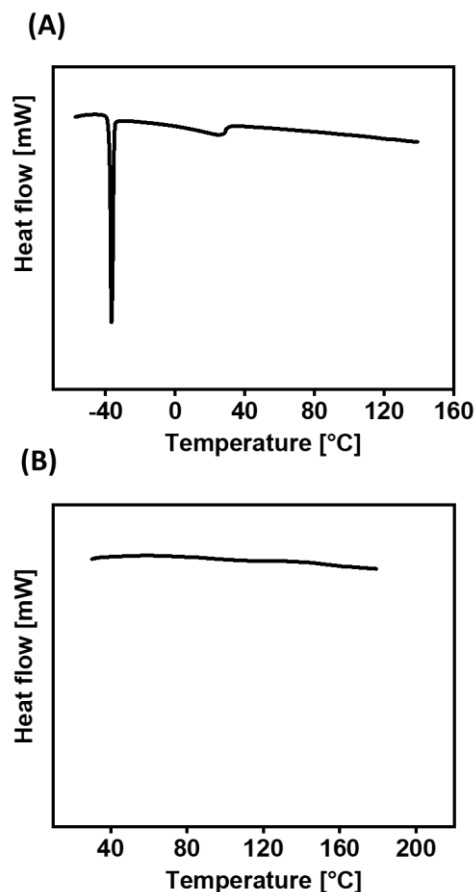


Figure 3: DSC analysis comparing fully hydrated and dried Zn(TFSI)₂ electrolytes. DSC characterizations of a) Zn(TFSI)₂.18H₂O and b) Buchi dried Zn(TFSI)₂.

Zn(TFSI)₂-based electrolyte¹²⁶ indicate molten electrolyte reliability at different hydration levels. The Zn(TFSI)₂.18H₂O molten electrolyte cell shows a more stable voltage profile during extended cycling than the Zn(TFSI)₂.8H₂O molten electrolyte cell. However, the Zn(TFSI)₂.8H₂O electrolyte is the selected electrolyte for the next steps of this chapter, as it offers low plating/stripping potential and stable cycling at once.

The ability of the molten salt electrolyte to support reversible zinc-oxygen chemistry was assessed using either nanostructured Co₃O₄ NWs, a Pt/C–IrO₂ hybrid electrocatalyst, or a Super P air electrode as the established zinc-oxygen cathodes at different temperatures. Nanostructured materials have recently attracted significant attention due to their exceptional physical and electrical properties. They are believed to provide high specific surface area,

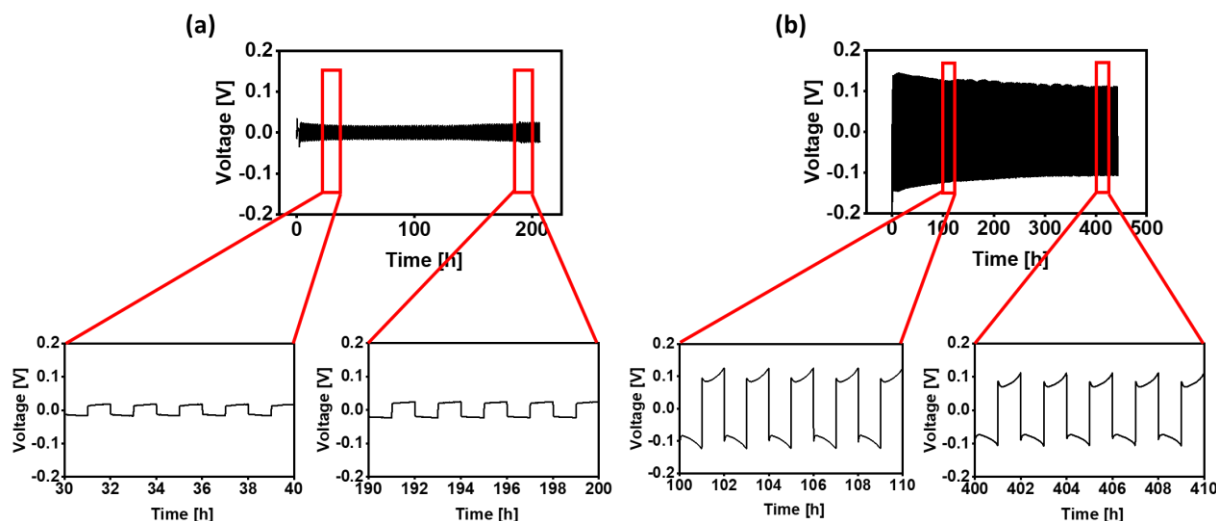


Figure 4: Long-term stability of zinc symmetric cells in molten Zn(TFSI)₂ electrolytes. a) and b) Long term galvanostatic plating/stripping of zinc in the Zn/Zn symmetric cell in the Zn(TFSI)₂.8H₂O and Zn(TFSI)₂.18H₂O molten electrolytes at 0.25 mA cm⁻² current density with a sweep duration of 1 hour at 80 °C and -15 °C, respectively.

ample free volume, improved structural integrity and an increased diffusion rate,^{40,130,131} leading to the superior performance of the zinc-oxygen battery catalysts made from nanostructures compared to bulk materials. Cobalt-based nanomaterials, in particular, in zinc-oxygen batteries, provide a binder-free electrocatalyst with a large specific surface area along with improved structural integrity, which leads to an enhanced electrochemical oxygen reduction reaction (ORR) activity and better longevity in comparison to commercially available air cathodes.^{132,133} SEM images (**Figure 5a, b**) of Co₃O₄ NWs on a SS mesh current collector show the presence of densely packed NWs with a roughened surface structure and an average diameter of 300 nm. The growth of Co₃O₄ NWs does not block the surface of the SS mesh, and no further processing is needed to use the electrodes as the O₂ cathode in rechargeable zinc-oxygen batteries. The open mesh structure also helps to maximize the spectroscopic gas evolution signals of the oxidation process within the cell. Hence, this study employs directly grown Co₃O₄ NWs onto the SS mesh current collector as the air electrode to

trace the ZnO discharge product's structural evolution and determine the amount of gas evolution upon the charge in the secondary zinc-oxygen battery.

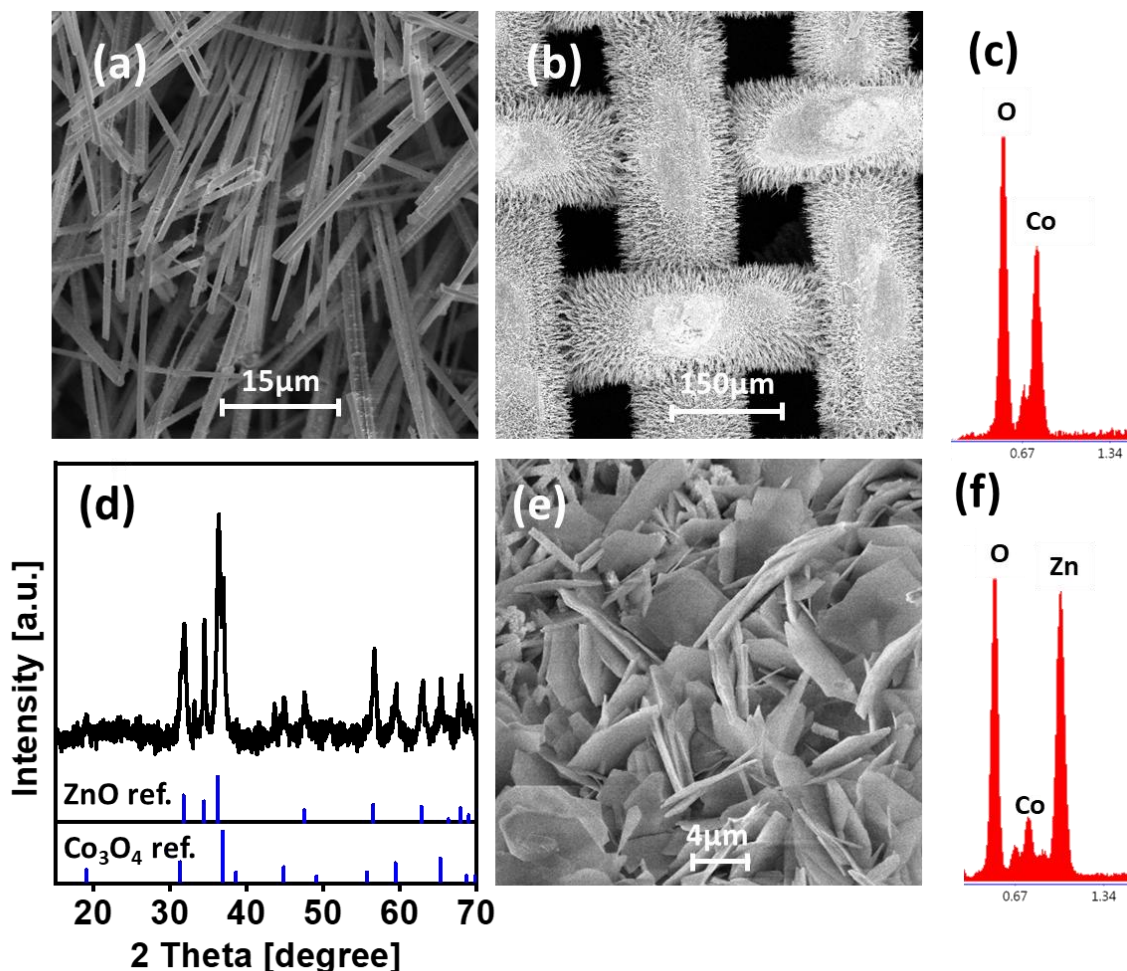


Figure 5: Structural characterization of Co_3O_4 nanowire cathodes before and after discharge. a) and b) Top view, high and low magnification SEM images of Co_3O_4 NWs grown on SS substrate as the current collector. c) The EDX analysis of Co_3O_4 NWs. d) and e) XRD pattern and high magnification SEM image of Co_3O_4 NWs grown on SS substrate after 1st discharge in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolyte with a capacity of 1000 mAh g^{-1} (based on O_2 cathode) at 80°C (The current density is 100 mA g^{-1}). f) The EDX analysis of Co_3O_4 NWs electrode after 1st discharge in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolyte with a capacity of 1000 mAh g^{-1} (based on O_2 cathode) at 80°C .

EDX analysis on the Co_3O_4 nanostructured wires shows the presence of Co and O in the expected ratio (**Figure 5c**). Experimental analyses methods were conducted to elucidate the

formation and oxidation processes of ZnO as the discharge product of the zinc-oxygen cells. The XRD pattern of **Figure 5d** depicts that the ZnO nanosheets were formed after the first discharge process in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ electrolyte, and the high magnification image of **Figure 5e** corroborates that the ZnO products possess hexagonal-shaped morphologies with 150 nm thickness and about 10 μm width. The morphology of ZnO species is hexagonal with various aspect ratios, depending on the ORR catalyst used in the cell. **Figure 6** provides ex-situ SEM, EDX and XRD analyses of the ZnO nanostructures in the zinc-oxygen batteries with some of the main available catalysts and cathode materials, which serve as the evidence of crystallinity and elemental distribution of ZnO hexagonal structures as the discharge product of oxygen cells. Because Super P-based cathode is not a high-performance ORR catalyst, this cell can only be operated at temperatures as high as 150 °C to attain a reasonable amount of capacity (**Figure 7**). The morphology of ZnO structures is also correlated with the operating temperature of the cells and the levels of hydration within the electrolyte system. **Figure 6f-h** demonstrates this correlation by providing the microscopy images of the discharge product at three different temperatures of -15 °C, room temperature and 80 °C using molten hydrated electrolyte system with $n=18$, $n=8$ and the dilute aqueous electrolyte with a concentration of 1 M. Hexagonal ZnO sheets with different aspect ratio were formed in all cases, which is a proof of concept for the relevance of operating temperature, level of hydration and ORR catalyst properties with the aspect ratio of ZnO structures. These findings challenge the previous understanding that electrolytes with large hydrophobic anions such as OTF^- favor the formation and oxidation of zinc peroxide via a $2e^-$ reaction mechanism.^{134,135} Hence, other factors must be also involved in enabling the $2e^-$ (final product ZnO_2) and $4e^-$ (final product ZnO) reaction pathways. Free energy diagrams predicted that the formation of zinc oxide is thermodynamically favoured in the electrolytes with large hydrophobic anions, while kinetics favor the zinc peroxide formation.¹³⁴ Consequently, it is speculated that zinc oxide formation is favored when sufficient energy is available for the slow and difficult process of cleaving hydrogen bonds in electrolytes containing large hydrophobic anions.

ZnO nanosheets could effectively undergo oxidation reaction and will start disappearing upon the charging process, ensuring the reversible formation and oxidation of ZnO in the

rechargeable zinc-oxygen cell utilizing the molten hydrated electrolyte in various hydration

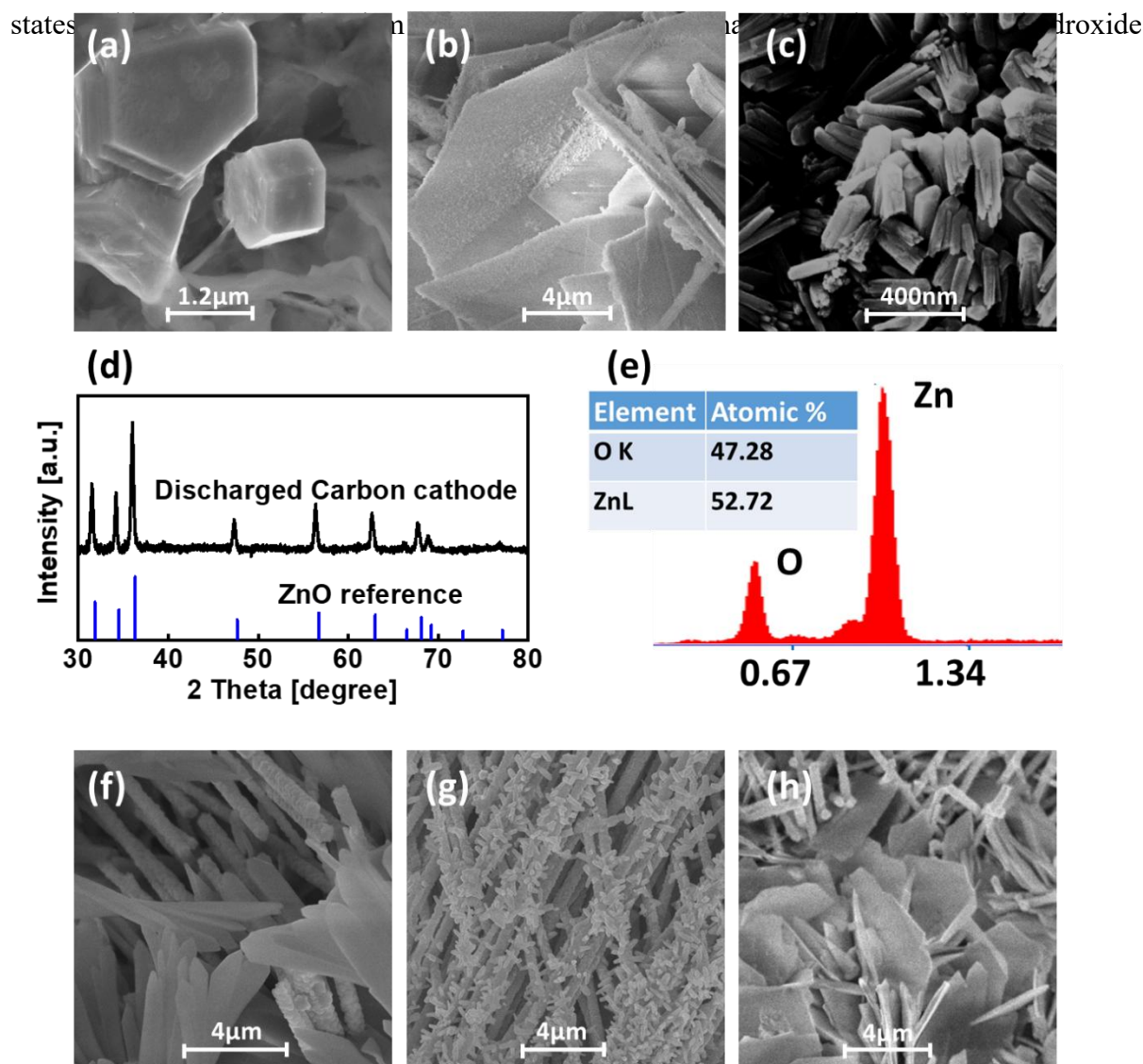


Figure 6: ZnO discharge product morphologies under different catalysts and electrolytes. Microscopy images of ZnO species as the discharge products of the zinc-oxygen cells in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolyte with the capacity of 1000 mAh g^{-1} (based on O_2 cathode) at a current density of 100 mA g^{-1} and a) Pt/C at 80°C , b) Co_3O_4 at 80°C , c) Super P at 150°C as the ORR catalyst. d) XRD pattern and e) EDX results of ZnO nanorods as the discharge product of the zinc-oxygen cell with Super P cathode. Microscopy images of ZnO species as the discharge products of zinc-oxygen cells with the capacity of 1000 mAh g^{-1} at a current density of 100 mA g^{-1} in f) $\text{Zn}(\text{TFSI})_2 \cdot 18\text{H}_2\text{O}$ molten hydrated electrolyte system at -15°C , g) dilute aqueous electrolyte system (1 M) at room temperature and h) $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolyte system at 80°C .

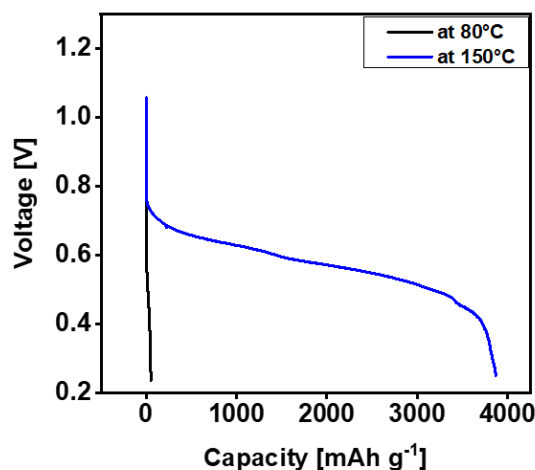


Figure 7: Initial discharge profiles of zinc-oxygen cells at elevated temperatures. 1st discharge profile of zinc-oxygen cell in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ electrolyte at 80 °C and 150 °C with Super P cathode. (KOH)-based electrolytes, in which ZnO would be precipitated on the anode surface after zincate ions supersaturation.¹³⁶

To trace the structural evolution of ZnO nanosheets and confirm its oxidation through the charging process, electrodes at different states of charge (SOC) have been examined by the ex-situ SEM and EDX analyses. Based on the obtained galvanostatic charge curve in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten electrolyte at 80 °C in **Figure 8a**, SEM photographs of ZnO nanosheets at 0, 30, 60 and 100 SOC are collected in **Figures 8b**. The thinning of nanosheets occurs at the basal plane of hexagonal ZnO structures, and the plot of ZnO nanosheets thicknesses versus SOC (Figure 8c) proves the ZnO nanosheets are being oxidized during the charging process. The ratio of zinc atoms to cobalt atoms within the cathode electrodes is also collected at several points of the charge curve, as indicated by the arrows in **Figure 8a** plot. The data are consistent with the measured thickness values with the SEM evaluation method, confirming the complete oxidation of ZnO nanosheets after a full charge.

Online gas analyses experiments have been employed to extend the study of ZnO conversion to Zn and understand the amount of oxygen evolution during the charging process of the zinc-oxygen cells in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolyte (**Figure 9a**). The first charge profile of the zinc-oxygen cell with the molten hydrated electrolyte in the open cell setup of

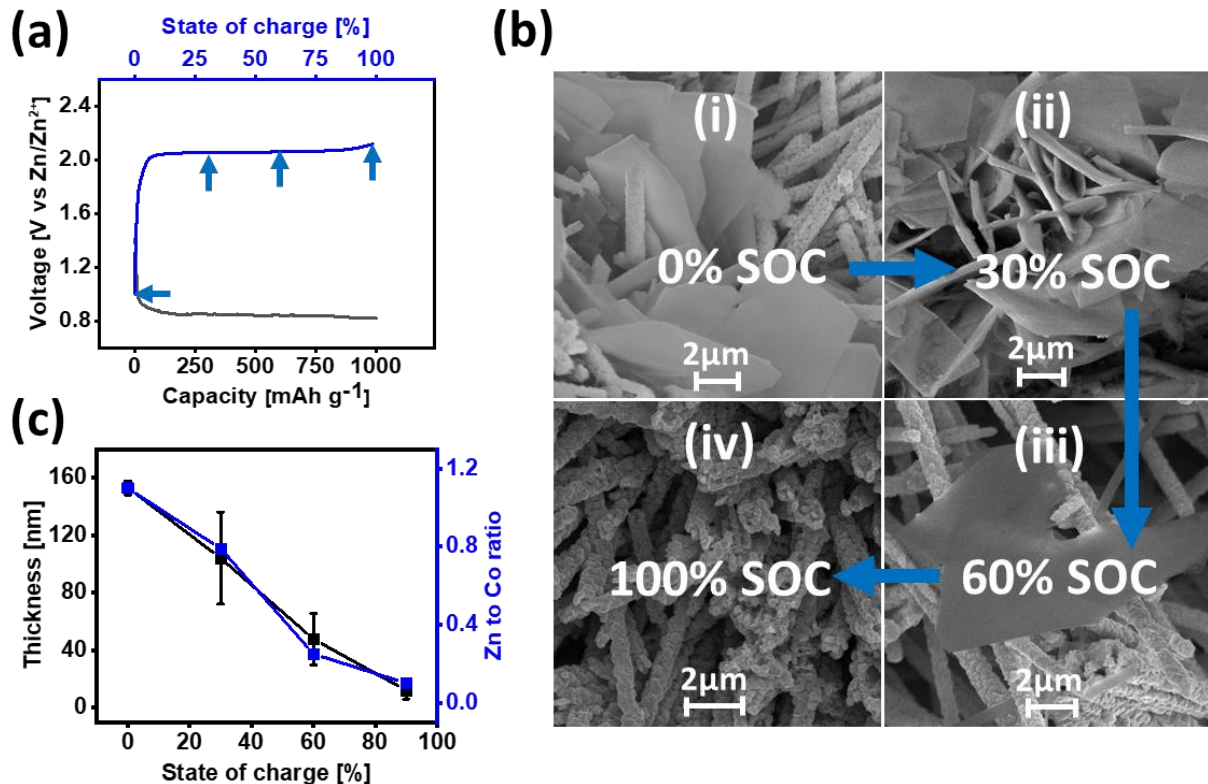


Figure 8: ZnO oxidation dynamics in Co₃O₄ cathodes during charging. a) Galvanostatic discharge/charge curves of the zinc-oxygen cell in Zn(TFSI)₂·8H₂O molten electrolyte with Co₃O₄ cathode electrode and a capacity limited to 1000 mAh g⁻¹ (based on O₂ cathode) at 80 °C (The current density is 100 mA g⁻¹). The arrows indicate the points that SEM images of part b are collected. b) Top view high magnification SEM images of Co₃O₄ NWs cathode electrodes at different states of charge (SOC) of 0 %, 30 %, 60 %, 100 %, respectively, to visualize ZnO nanosheets oxidation process when charging the cells. c) The plot for thickness of ZnO nanosheets versus SOC including the associated error bars, as well as the plot of Zn atom to Co atom ratio versus SOC, obtained from the microscopy images and EDX analyses, respectively.

the online mass spectrometer system exhibits two distinct plateaus at 2.0-2.1 V and 2.2-2.3 V (**Figure 10**). The ion current ascribed to O₂ ($m/z = 32$) is observed during the first plateau of 1st charge as the only major mass spectroscopy signal below 2.1 V. However, at around 100 % SOC, corresponding to the total delivered capacity of the discharge phase, an increase of evolved H₂ (ascribed to the ion current of $m/z = 2$) (**Figure 11**) indicates more hydrogen species are produced at the second charge plateau in comparison to the first one. It is speculated that

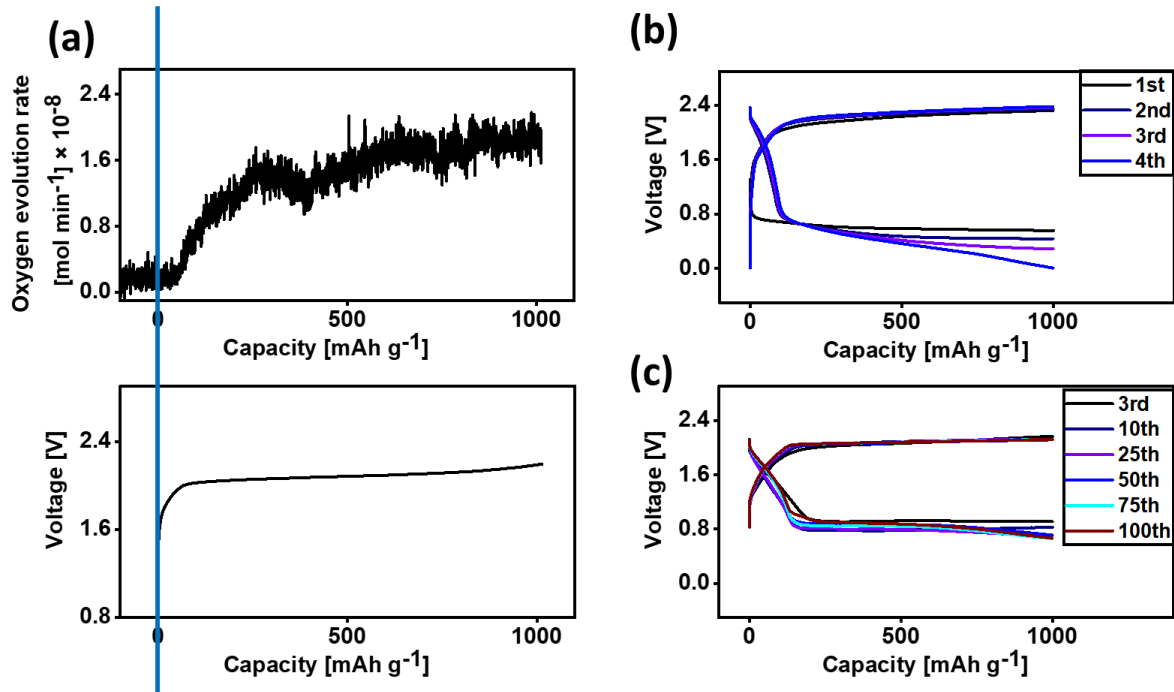


Figure 9: Online detection of O₂ evolution and cycling stability at different temperatures. a) Galvanostatic charge curve of zinc-oxygen cell in Zn(TFSI)₂·8H₂O molten hydrated electrolyte at 80 °C and the associated online gas analysis data with ion current ascribed to O₂ gas. b) and c) Cycling stability evaluation of zinc-oxygen cell in Zn(TFSI)₂·18H₂O molten hydrated electrolyte and Zn(TFSI)₂·8H₂O molten hydrated electrolyte with Co₃O₄ cathode electrode at -15 °C and 80 °C, respectively, with a capacity limited to 1000 mAh g⁻¹ (based on O₂ cathode) (The current density is 100 the O₂ evolution on the first plateau indicates the electrochemical oxidation of ZnO. In contrast, the higher charge plateau at around 2.3 V corresponds to the dominance of parasitic reactions. Therefore, it can be presumed that a portion of the electrons used to charge the zinc-oxygen batteries can be consumed by side reactions that decompose water and produce hydrogen. The calibration procedure of evolved O₂ species was conducted by introducing a series of Ar /O₂ gas mixtures with the known concentrations into the MS through the separated lines. The total gas flow was maintained at 20 mL min⁻¹ while the Ar/O₂ ratio was changed, and a linear fit was obtained from the calibration data (**parts a and b of Figure 12**). A similar procedure using a mixture of Ar/H₂ gas was applied to calibrate the H₂ ion signal to determine the actual flow of hydrogen species. The final amounts of evolved O₂ and H₂ in the OEMS setup were

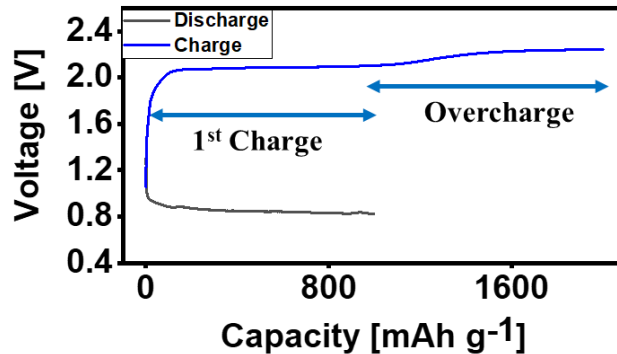


Figure 10: Charge efficiency behavior without coulombic constraints. Galvanostatic discharge/charge curves of zinc-oxygen cell in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolyte at 80°C with Co_3O_4 cathode and a discharge capacity of 1000 mAh g^{-1} , without limitation on charge parameters so that the CE seems to be over 100 %.

determined based on the slope of the obtained linear fits of flux versus the function of the MS signal.

The parasitic reactions potential can be varied with respect to the amount of free H_2O molecules and the characteristics of the air cathode electrode. An experiment was conducted by introducing additional H_2O molecules into the molten electrolyte, and the results are collected in **Figure 13**. As a result, a substantial decrease of about 0.2V in parasitic reactions potential occurs when the electrolyte system contains a non-negligible amount of free H_2O molecules. This serves as evidence for the confinement of H_2O molecules within the molten salt system. Another scenario was designed to highlight the effect of cathode properties, particularly the current collector, on parasitic reactions potential, in which SS current collector was substituted with titanium (Ti) mesh. As a result, hydrogen evolution potential was pushed to more positive values. More experiments are currently under development to further expand the potential window by enhancing hydrogen evolution overpotential.

To evaluate the functionality of $\text{Zn}(\text{TFSI})_2$ -based electrolyte under the hydrated condition with $n=18$ and $n=8$, cycling experiments within a limited capacity of 1000 mAh g^{-1} (based on O_2 cathode) at a current density of 100 mA g^{-1} have been performed on the zinc-oxygen cells with molten hydrated electrolytes and the dilute aqueous electrolyte (1 M). The resulting data are collected in **Figure 9b, c** and **Figure 14**, respectively. The system with the dilute aqueous

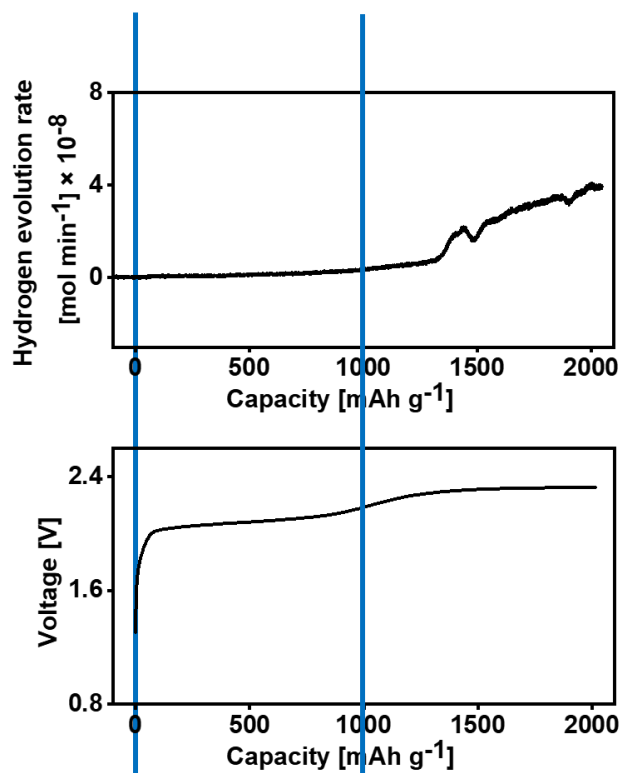


Figure 11: Hydrogen evolution monitoring during zinc–oxygen cell charging. Galvanostatic charge curve of the zinc-oxygen cell in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten hydrated electrolyte at 80 °C with Co_3O_4 cathode and a discharge capacity of 1000 mAh g^{-1} and the associated online gas analysis data with ion current ascribed to H_2 gas.

electrolyte $\text{Zn}(\text{TFSI})_2$ experienced unstable cycling behavior (**Figure 14**). After only the first discharge, signs of short circuit fault are detected in the voltage curve, and this cell could not play the role of a secondary battery. However, the zinc-oxygen cells with molten salt electrolyte systems of $n=18$ and $n=8$ were able to show further reversible cycling stability. The cells in $\text{Zn}(\text{TFSI})_2 \cdot 18\text{H}_2\text{O}$ molten electrolyte show a significant increase in overpotential as the intrinsically sluggish OER/ORR slowed down even more by lowering the operating temperature. The cell in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten electrolyte shows reversible behavior. The slight increase in the discharge potential could be attributed to the parasitic reaction between $\text{Zn}(\text{TFSI})_2$ salt and zinc electrode surface and degradation of Co_3O_4 catalyst. The results indicate an enhanced cyclability of the zinc-oxygen cells in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten electrolyte compared with that cells reported in the traditional alkaline electrolytes, which show a sudden

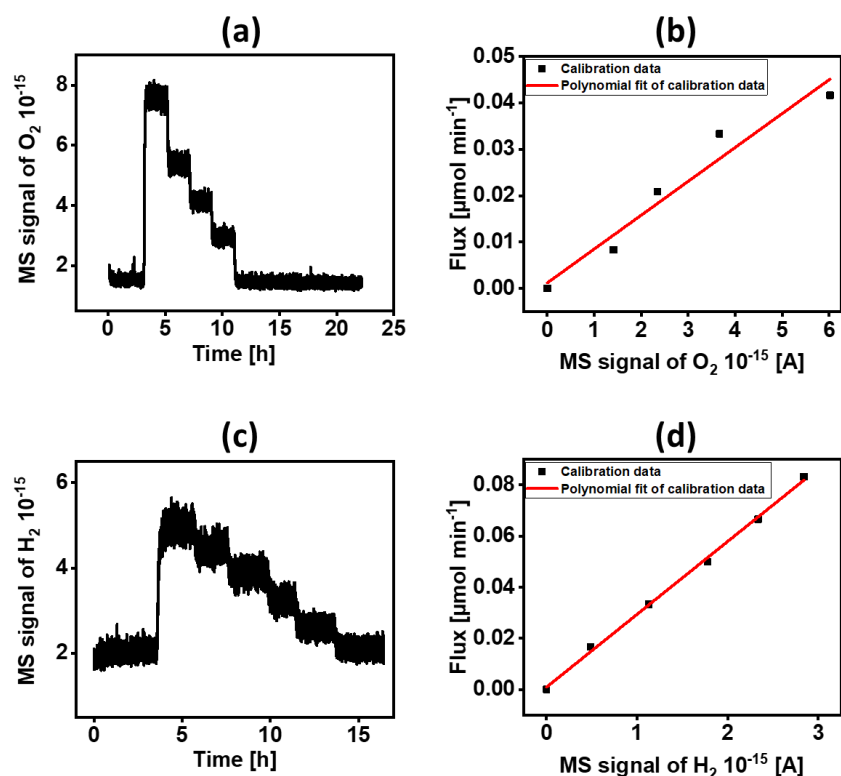


Figure 12: Calibration of OEMS system for O_2 quantification. a) Online MS signals responses to different ratio of Ar/ O_2 mixture with predetermined concentrations. b) Linear calibration fit of the O_2 ion signal obtained from the standard Ar/ O_2 mixture and the values of part a.

increase in ORR/OER overpotentials and severe capacity fading in only the first few cycles.^{134,129} The electrochemical data on the traditional KOH-based zinc-air cells were usually obtained in the flooding cells, where the gap between the cathode and anode is 1.0 cm or more,^{137,138} leading to a low volumetric energy density of the resultant zinc-oxygen cells. More recent studies on the novel electrolyte systems have also applied 200 μl (~ 240 mg),¹³⁴ and 500 μl (~ 1000 mg)¹²⁹ of electrolyte to the cell, which lowers the overall energy density of the zinc cells. Therefore, of interest here is the fact that the described performance in $\text{Zn}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ molten electrolyte was achieved under a limited amount of electrolyte, as the total weight of the electrolyte-filled glass fiber is determined to be 70 mg on average. This system utilizes the minimum total amount of electrolyte, which is a critical step toward building potentially high energy density zinc-oxygen batteries.

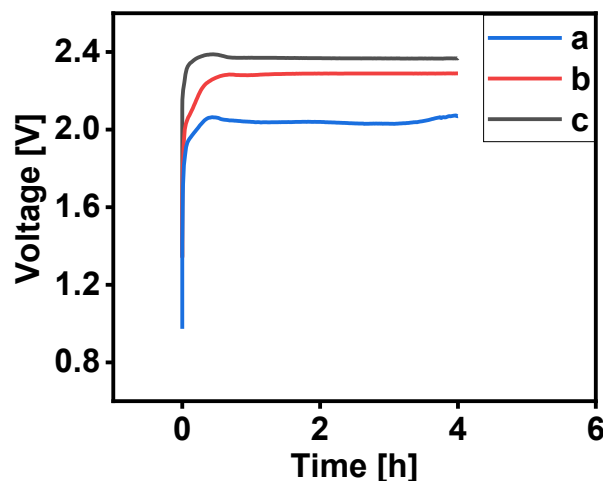
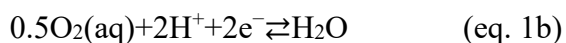


Figure 13: Impact of water content and electrode material on hydrogen evolution overpotential. The evaluation of hydrogen evolution overpotential in molten hydrated electrolyte system a) with additional H₂O molecules within the system, b) no additional water in the system and c) Ti mesh as the current collector with no additional water content.

The discrepancy between the rechargeability of the cells in the molten hydrated electrolyte system and the primary cells in the dilute 1 M electrolyte should be explained based on the operating temperature and the reaction mechanism in different electrolyte pH values. As discussed, the reaction rates increase with increasing temperature for the intrinsically slow-moving OER/ORR. Therefore, it is expected to obtain lower discharge/charge overpotentials for the cells in Zn(TFSI)₂·8H₂O molten electrolyte. It is known that during the discharge process, oxygen adsorbs on the surface of the cathode, and then it is electrochemically reduced to H₂O (eq. 1a, 1b).^{18,139} Meanwhile, the metallic zinc undergoes oxidation to produce Zn²⁺ ions, which dissolve in the electrolyte (eq. 2).¹³⁹ The equations of 1 and 2 are the fundamental reactions of the zinc–oxygen cell in the Zn(TFSI)₂–H₂O electrolyte system. When the concentration of Zn²⁺ ions reaches its solubility limit in the Zn(TFSI)₂–H₂O electrolyte system, zinc oxide will precipitate according to precipitation reaction in equation 3. The reverse of these reactions occurs during the charging process.



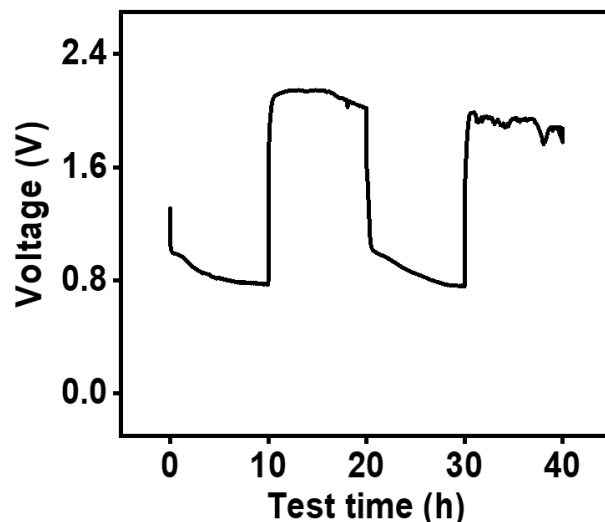
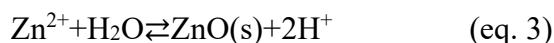


Figure 14: Stability of zinc–oxygen cells in dilute $\text{Zn}(\text{TFSI})_2$ aqueous electrolyte. Cycling stability evaluation of zinc-oxygen cell in the $\text{Zn}(\text{TFSI})_2$ -based dilute aqueous electrolyte (1 M) with Co_3O_4 cathode electrode under the limited capacity of 1000 mAh g^{-1} (based on O_2 cathode) at a current density of 100 mA g^{-1} .



However, it is observed that the cells in the dilute 1 M electrolyte could not play the role of a secondary battery, and the charging mechanism cannot be driven in an aqueous $\text{Zn}(\text{TFSI})_2$ -based electrolyte. **Figure 15** exhibits that the ZnO nanostructures did not completely disappear after a charging process limited to 1000 mAh g^{-1} capacity. Therefore, the discharge products could not effectively undergo oxidation during the charge step in the dilute 1 M electrolyte, and ZnO nanostructures could not solubilize in the 1 M $\text{Zn}(\text{TFSI})_2$ - H_2O acidic media to form Zn^{2+} ions (eq. 3). The reason is believed to be related to the pH and temperature of the electrolyte environment. **Figure 16** depicts the variation of pH in the $\text{Zn}(\text{TFSI})_2$ - H_2O electrolyte system based on the salt concentration. The amount of H^+ ions could be enhanced by increasing the electrolyte concentration, which results in a decrease in the total pH of the electrolyte. Previous studies showed that the solubility of ZnO in aqueous media is enhanced by lowering the total pH of the solution or equivalently raising the amount of H^+ ions in the solution.^{140,141} Therefore, the high concentration electrolyte system of $\text{Zn}(\text{TFSI})_2$ - H_2O

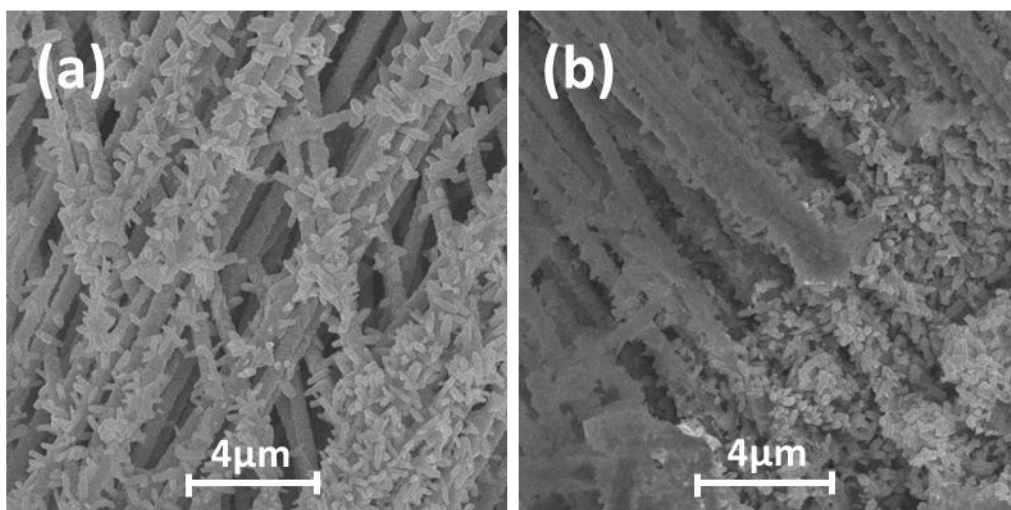


Figure 15: Morphological changes in Co_3O_4 cathodes after charging in aqueous electrolyte. Microscopy images of Co_3O_4 NWs cathode electrode a) before and b) after the charge process in dilute aqueous electrolyte system of $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ with a concentration of 1 M and a capacity limited to 1000 mAh g^{-1} (based on O_2 cathode) at a current density of 500 mA g^{-1} .

provides a more effective media for the ZnO oxidation mechanism, leading to the high reversibility of the zinc-oxygen cells.

Ongoing research is focused on enhancing cycling stability and mitigating the evolution of additional gases, particularly hydrogen species. Exploring electrolyte optimization through the incorporation of additives to alter the overpotential of hydrogen evolution in zinc-oxygen cells, utilizing ionic liquid-based electrolytes to curb hydrogen evolution, and refining the design of both anode and cathode electrodes are potential avenues for future studies.

3.3 Conclusions

Considerable progress has been made in creating special liquid electrolytes ($\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$) for zinc batteries. These electrolytes, with varying water contents, are crucial for the functioning of both zinc-zinc cells and zinc-oxygen batteries. By adjusting humidity levels during preparation, the weight of the electrolyte can be controlled and its melting point set within a range from 139°C to -35°C .

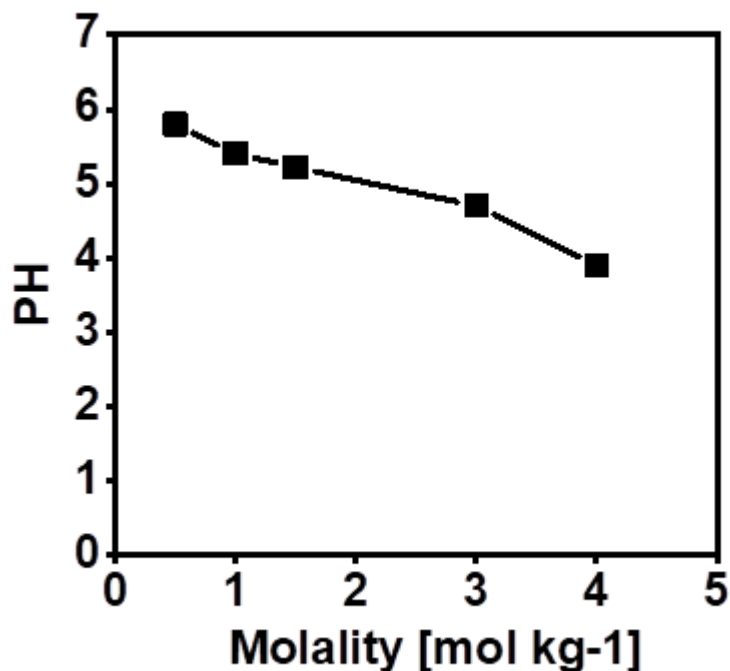


Figure 16: Variation of pH in the $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ electrolyte system with varied concentrations.

The study highlighted the effective performance of these electrolytes, especially in $\text{Zn}(\text{TFSI})_{2.8}\text{H}_2\text{O}$ and $\text{Zn}(\text{TFSI})_{2.18}\text{H}_2\text{O}$ versions, at temperatures of 80 °C and -15 °C. Notably, a zinc-oxygen battery using the $\text{Zn}(\text{TFSI})_{2.8}\text{H}_2\text{O}$ electrolyte at a moderate temperature showed promising results, performing better than batteries with the dilute $\text{Zn}(\text{TFSI})_2$ electrolyte.

Detailed analyses, including discharge product examination and Online Electrochemical Mass Spectrometry (OEMS) measurements, were conducted. These analyses helped in understanding the release of hydrogen and oxygen during charging. The study also linked the battery's electrical activity with structural changes, particularly observing the shape changes of ZnO hexagonal nanosheets as the battery was used.

One key finding was that when all the ZnO is used up in the battery, there is a notable increase in hydrogen release, depending on the electrode materials and the water content in the electrolyte. This information is important because using an electrolyte with just the right amount of water can improve the energy storage capacity of rechargeable zinc batteries.

In summary, this chapter has provided valuable insights into developing new electrolytes for zinc batteries. These findings are a step forward in improving rechargeable zinc batteries, making them more efficient for storing energy.

Chapter 4: Effect of Hydration Level on Zinc Electrolyte Properties

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Chapter 4 focuses on the mechanisms of zinc metal nucleation and growth in various temperature and current conditions, utilizing Zn/Zn symmetric and Zn/Cu asymmetric cells within a zinc chloride-based hydrated electrolyte. The study aims to shed light on the different ways zinc metal layers form under these specific conditions.

Scanning electron microscopy is employed to examine the morphologies of zinc nuclei layers. A fixed areal capacity, favorable to initiating zinc nucleation, is maintained to observe changes in the size and density of zinc nuclei at different temperatures. This method is crucial for understanding the zinc metal plating process within the cells' capacity limits. The investigation also includes an analysis of deposited zinc layers with high areal capacities at temperatures of -10 °C, room temperature (RT), and 40 °C. The focus is on evaluating the compactness and smoothness of these layers on electrode surfaces, which influences factors such as surface area, dendrite growth, conductivity, and solid electrolyte interphase formation on the anode in zinc batteries.

The electrochemical performance of zinc electrodes in Zn/Cu asymmetric cell configurations is assessed at varying temperatures. This involves comparisons of key parameters such as cyclability, coulombic efficiency, and plating/stripping potentials at different operational conditions.

Additionally, the effectiveness of a chloride-based molten salt electrolyte is demonstrated in a full-cell zinc-ion battery, employing nanoparticles of zinc hexacyanoferrate (ZnHCF-NPs) as the cathode. The study includes zinc plating and stripping processes in zinc half-cells with various compositions of hydrated $\text{ZnCl}_2 \cdot n\text{H}_2\text{O}$ electrolyte ($n=10, 2.33, 1.5$) across a range of temperatures. Detailed microscopy investigations are conducted to analyze how deposition temperature affects nuclei size, density, and the growth of deposited zinc metal.

Performance of hydrated ZnCl_2 electrolytes with different hydration levels is also evaluated in zinc-ion batteries with ZnHCF nanostructured cathodes. The current study contributes

valuable insights into the development of temperature-dependent molten hydrated electrolyte systems for zinc batteries, advancing the understanding of zinc-based battery systems.

4.1 Experimental and Methods

4.2.1 Preparation of the Electrolyte:

For creating different hydrated forms of $\text{ZnCl}_2 \cdot n\text{H}_2\text{O}$, with hydration levels of $n = 10, 2.33$, and 1.5 , ZnCl_2 salt of high purity (99.999 %, from Sigma Aldrich) was first dried at 140°C under vacuum conditions and then stored in an argon-filled glovebox. In a dry environment, precise amounts of this dried ZnCl_2 were measured and mixed with ultrapure water in specific molar ratios. These mixtures were sealed and stirred overnight to ensure complete dissolution of the salt.

4.2.2 Making the Zinc Hexacyanoferrate Cathode:

The zinc hexacyanoferrate (ZnHCF) was produced using a standard coprecipitation method.⁷⁷ For this, equal volumes of 0.1 M ZnSO_4 and $0.05\text{ M K}_3\text{Fe}(\text{CN})_6$ solutions were simultaneously added to a heated water solution. The resulting mixture was aged for several hours, then filtered, and washed. Drying at 70°C produced a bright green powder. To make the cathode, a slurry containing this active material, Super P, and Polytetrafluoroethylene was spread on a current collector and dried at 120°C . The finished cathode was then shaped into 10 mm discs.

4.2.3 Physical Characterization:

Physical characterization involved SEM and EDX analyses using a Zeiss Ultra field emission SEM equipped with an EDX detector. X-ray diffraction (XRD) was performed on a PANalytical Empyrean diffractometer using $\text{Cu K}\alpha$ radiation. Both DSC and TGA analyses were conducted using TA Instruments (DSC Q2000, SDT Q600).

4.2.4 Electrochemical Characterization:

Ionic conductivities of hydrated and diluted aqueous ZnCl_2 electrolytes were measured through electrochemical impedance spectroscopy (EIS). These measurements, conducted over a frequency range from 100 kHz to 1 Hz at a voltage of 100 mV, utilized an MTZ-35 impedance analyzer controlled by MT-Lab software. For zinc half-cells, zinc metal electrodes and glass fiber separators were stacked with 100 μl of the electrolytes and zinc or copper foil as the counter electrode, operating at a current density of 0.25 mA cm^{-2} . For full-cell setups, a zinc

metal anode, electrolyte-soaked glass fiber, ZnHCF cathode, and titanium mesh current collectors were assembled. After equilibrating in an oven for two hours, the cells' electrochemical performance was assessed using an Arbin instrument at a current density of 0.1 mA cm^{-2} within a voltage range of 1.0 to 2.0 V versus Zn/Zn^{2+} .

4.2 Results and Discussions

ZnCl_2 has been reported as the MHE for room temperature zinc-oxygen batteries.¹²⁹ A concentrated state of $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ was determined to offer superior properties to the dilute aqueous counterpart due to the strong hydration effect of molten salt. Here, three hydrate compositions of the ZnCl_2 molten electrolyte are used to study zinc metal batteries at -10°C , 25°C and 40°C . Differential scanning calorimetry analysis was used to determine the melting points of the selected hydrated electrolytes ($\text{ZnCl}_2 \cdot n\text{H}_2\text{O}$) with $n=10$, $n=2.33$, and $n=1.5$ compositions (**Figure 17a**). The observed melting points at around -40°C , 0°C and 28°C are consistent with the previously reported values.¹²⁹ The ionic conductivities of these ZnCl_2 -based MHEs and the dilute aqueous ZnCl_2 electrolyte (1 M) were measured at -10°C to $+60^\circ\text{C}$ to choose the appropriate temperature range for the operation of each electrolyte (**Figure 17b**). Molten hydrated electrolytes of $n=1.5$ and $n=2.33$ get partially frozen at 28°C and 0°C , respectively. The existence of solid ice hinders ionic conduction at temperatures slightly lower than the melting point. However, these two systems still possess some degree of ionic conduction at low temperatures, resulting from the ionic conduction supported by the remaining concentrated electrolyte network. On the other hand, the $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte shows a high ionic conductivity of 145 mS cm^{-1} at 60°C and 42 mS cm^{-1} at -10°C .

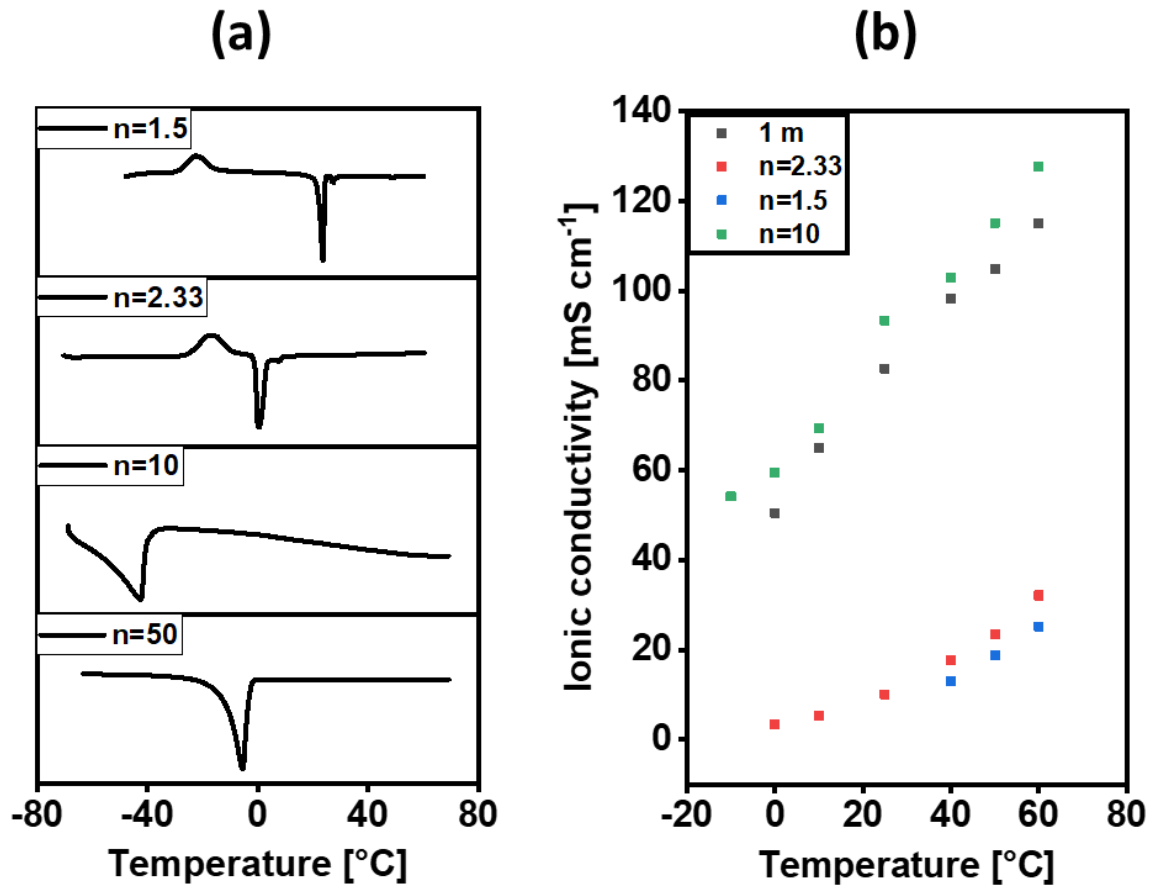


Figure 17: Thermophysical and conductive properties of ZnCl₂·nH₂O systems. Study of the ZnCl₂·nH₂O electrolytes. a) DSC measurements of ZnCl₂·nH₂O system at different hydration states, showing the melting point changes. b) The plot of ionic conductivities versus temperature for 1 M ZnCl₂ electrolyte (RT), ZnCl₂·2.33H₂O electrolyte (RT), ZnCl₂·1.5H₂O electrolyte (40 °C) and

To understand the electrochemical performance of zinc cells in MHE at different temperatures, electrochemical experiments were conducted using Zn/Zn and Zn/Cu half-cells by plating and stripping zinc metal for 1 h at 0.25 mA cm⁻² current density, and the relevant stability and potential were studied (**Figure 18**). The Zn/Zn symmetric cells exhibit stable zinc electrodeposition potentials of 12 mV at 40 °C, 7 mV at RT and 30 mV at -10 °C in MHE systems with n=10, n=2.33 and n=1.5, respectively. The plating/stripping potentials are decreased by increasing the operating temperature of the cells, and all the symmetric cells operated in MHEs exhibit a long-life span (**Figure 18a**). This is unlike the unstable

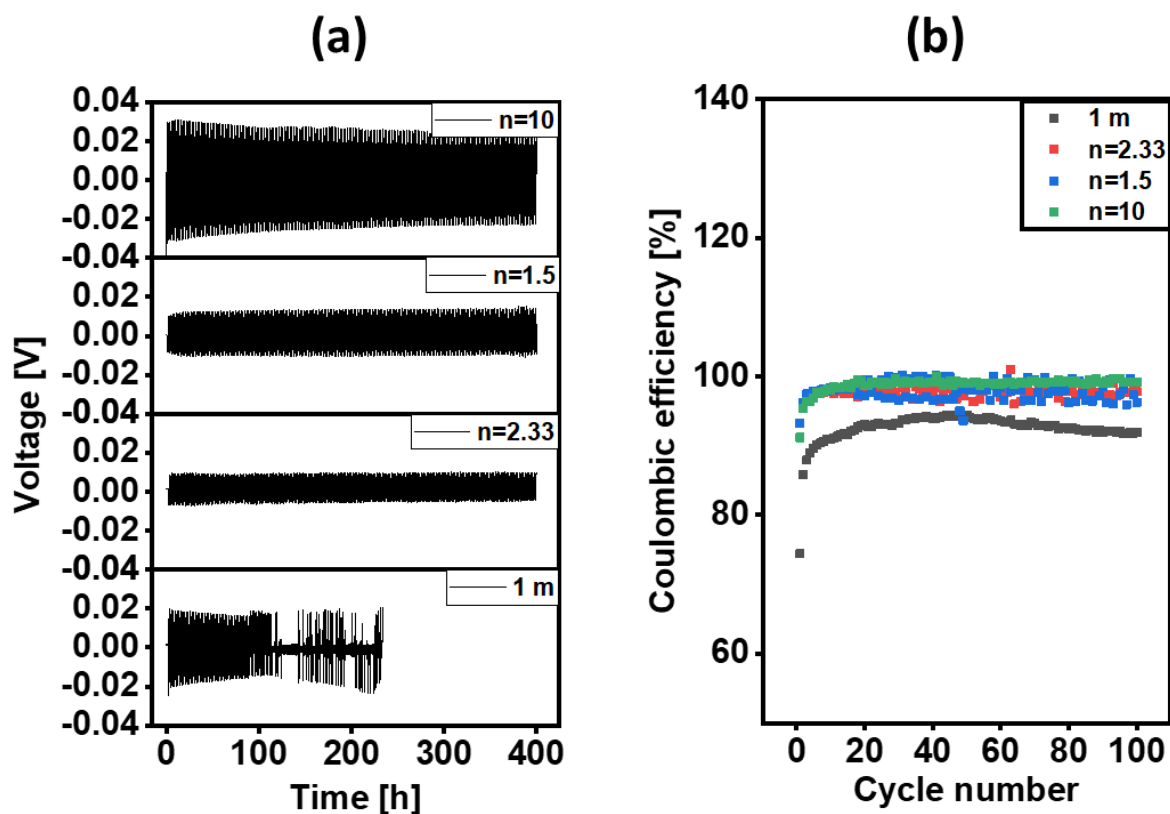


Figure 18: Galvanostatic zinc deposition-stripping in Zn/Zn and Zn/Cu cells. a) The cycling performance of Zn/Zn symmetric cells in 1 M ZnCl₂ electrolyte (RT), ZnCl₂·2.33H₂O electrolyte (RT), ZnCl₂·1.5H₂O electrolyte (40 °C) and ZnCl₂·10H₂O electrolyte (−10 °C) at a current density of 0.25 mA cm^{−2} with a sweep duration of 1 hour. b) The plot of coulombic efficiencies versus cycle number for asymmetric Zn/Cu cells in 1 M ZnCl₂ electrolyte (RT), ZnCl₂·2.33H₂O electrolyte (RT), ZnCl₂·1.5H₂O electrolyte (40 °C) and ZnCl₂·10H₂O electrolyte (−10 °C) at a current density of 0.25 mA cm^{−2} with a sweep duration of 1 hour.

plating/stripping process in Zn/Zn symmetric cells in the dilute aqueous ZnCl₂ electrolyte (1 M). Coulombic efficiency is also a vital factor in determining whether the plating/stripping of Zn is reversible.

Accordingly, the Zn/Cu half-cells were used to evaluate the actual coulombic efficiency of hydrated electrolytes for the first 100 cycles (**Figure 18b**, **Figure 19**,). The average coulombic efficiency of the last 50 cycles in the molten hydrates decreased from 99.1 % at −10 °C to 97.9 % at 40 °C, indicating the high reversibility of Zn plating/stripping in MHE.

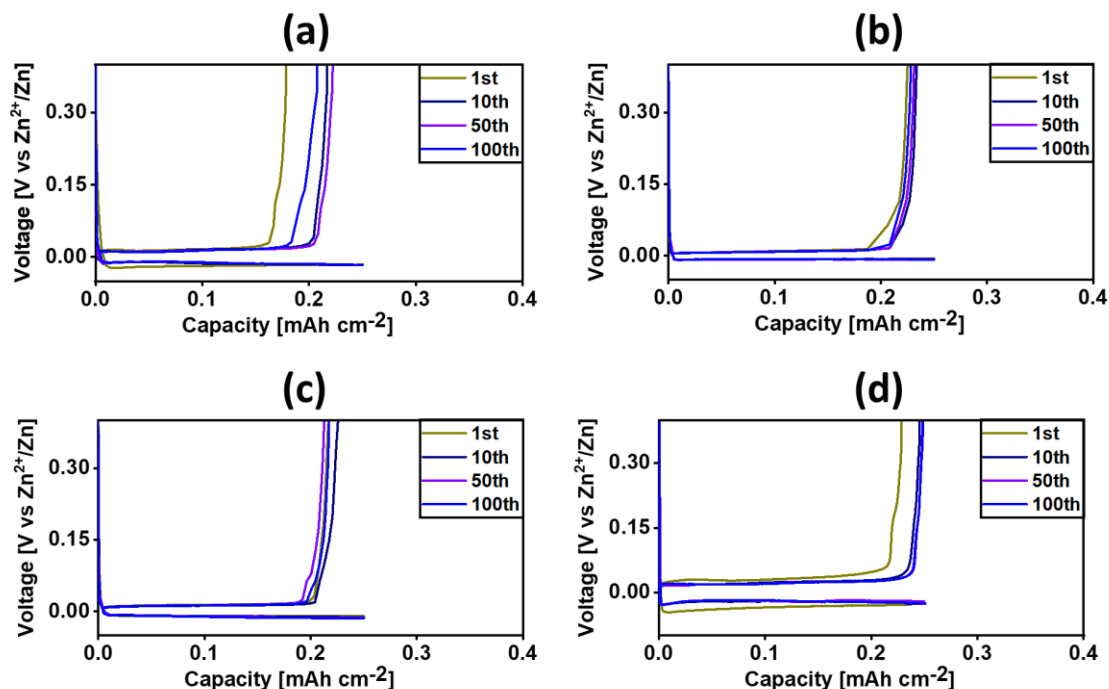


Figure 19: Discharge-charge curves of asymmetric Zn/Cu cells during different cycles in a) 1 M ZnCl_2 electrolyte (RT), b) $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ electrolyte (RT), c) $\text{ZnCl}_2 \cdot 1.5\text{H}_2\text{O}$ electrolyte (40 °C) and d) $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte (-10 °C) at a current density of 0.25 mA cm^{-2} with a sweep duration of 1 hour.

A series of SEM imaging tests are done to understand the difference in zinc deposition and dissolution behavior in hydrated and diluted electrolytes. The extracted zinc anode surfaces after 100 cycles in Zn/Cu cells containing MHEs and the dilute aqueous ZnCl_2 electrolyte (1 M) are studied in **Figure 20**. The cycled zinc surface exhibits significant cracking and dendritic growth in the electrolyte containing 1 M ZnCl_2 . On the other hand, **Figure 20b-d** shows that the cycled zinc electrodes in the MHE systems have a smooth surface. Almost no cracking was observed for the extracted zinc electrode from the cells operated at -10 °C in the $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ MHE. The significantly improved electrochemical performances of Zn/Cu half-cells at MHE systems are consistent with the obtained results of Zn/Zn symmetric cells. The SEM imaging results indicate that the hydrated electrolytes, especially the ones operating at low temperature benefit reversible zinc plating/stripping.

The differences between zinc metal layers deposited at various temperatures are also studied to investigate the zinc nucleation and growth process in hydrated and diluted electrolytes. First,

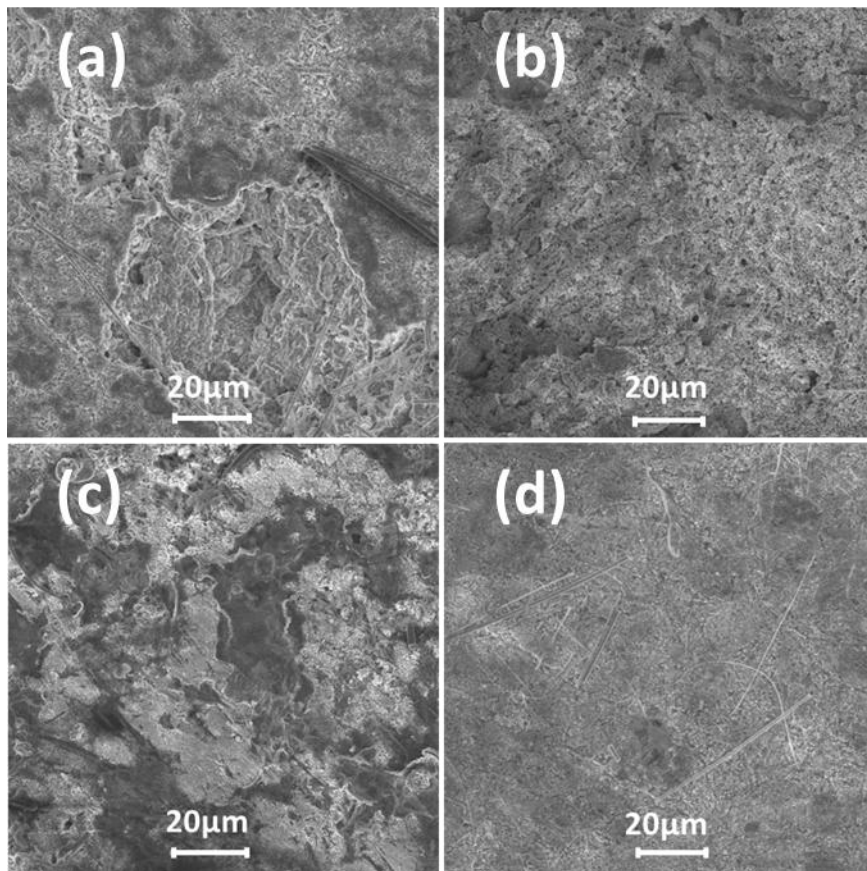


Figure 20: SEM imaging of Zn metal electrodes after 100 plating/stripping cycles in Zn/Cu asymmetric cells in a) 1 M ZnCl_2 electrolyte (RT), b) $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ electrolyte (RT), c) $\text{ZnCl}_2 \cdot 1.5\text{H}_2\text{O}$ electrolyte (40 °C) and d) $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte (-10 °C) at 0.25 mA cm^{-2} and 0.25 mAh cm^{-2} .

a fixed areal capacity of $0.075 \text{ mAh cm}^{-2}$ was used, which fulfilled the initial nucleation of zinc metal on the surface of copper electrodes. The SEM images of **Figure 21a-d** reveal that the size of zinc metal nuclei increases in the molten systems noticeably, while zinc nucleation density decreases. Second, the zinc deposition layers with areal capacities of 1.25 mAh cm^{-2} at different temperatures were also observed (**Figure 21e-h**). This areal capacity allows a significant amount of zinc deposition on the surface of copper electrodes. A compact and smooth zinc layer was deposited at -10 °C (**Figure 21h**), indicating the influence of temperature on zinc deposition behaviour.

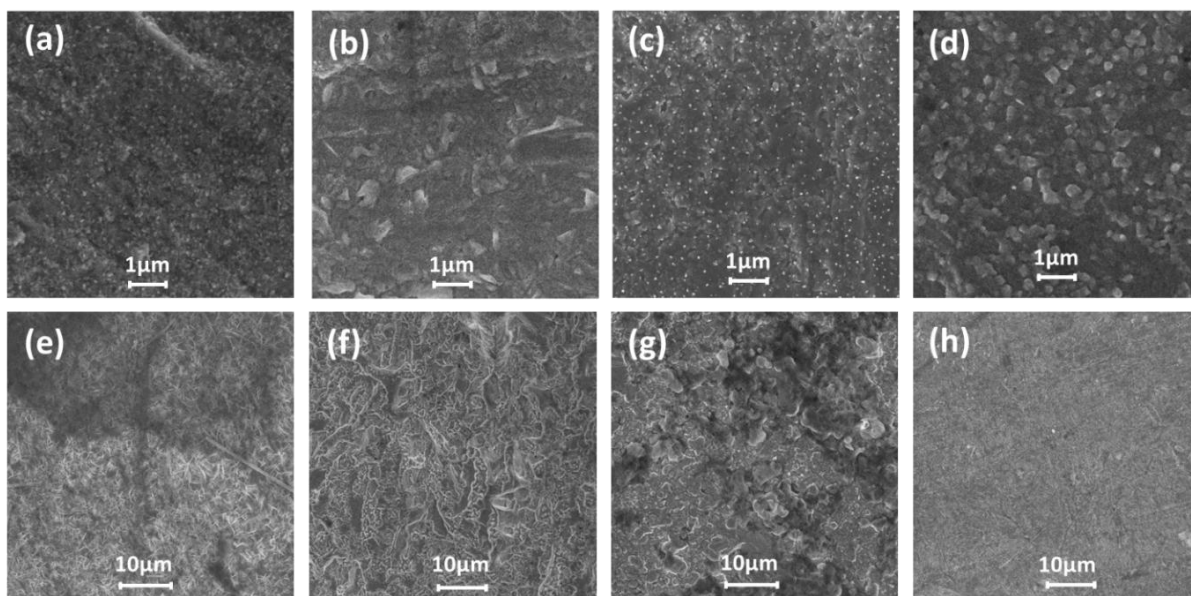


Figure 21: Nucleation and growth of zinc at varied electrolyte and current conditions. SEM imaging of zinc nuclei layers at varied temperatures in a) 1 M ZnCl_2 electrolyte (RT), b) $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ electrolyte (RT), c) $\text{ZnCl}_2 \cdot 1.5\text{H}_2\text{O}$ electrolyte (40 °C) and d) $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte (−10 °C) at 0.25 mA cm^{-2} and 0.075 mAh cm^{-2} . SEM imaging of zinc deposited layers at varied temperatures in e) 1 M ZnCl_2 electrolyte (RT), f) $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ electrolyte (RT), g) $\text{ZnCl}_2 \cdot 1.5\text{H}_2\text{O}$ electrolyte (40 °C) and h) $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte (−10 °C) at 0.25 mA cm^{-2} and 1.25 mAh cm^{-2} .

The collected photographs of zinc-deposited Cu electrodes in **Figure 22** also show that a large area of blank Cu foil was still visible for the cells operated in the dilute aqueous ZnCl_2 electrolyte (1 M), unlike the Cu foils extracted from the cells assessed in molten hydrates. Therefore, the low temperature establishes the growth of large and sparse zinc nuclei layers until a compact zinc deposition layer forms after further plating, which prevents zinc dendrite growth during repeated cycling. As a result, Zn/Zn and Zn/Cu half-cells exhibit higher reversibility in hydrated electrolytes especially at $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte (−10 °C).

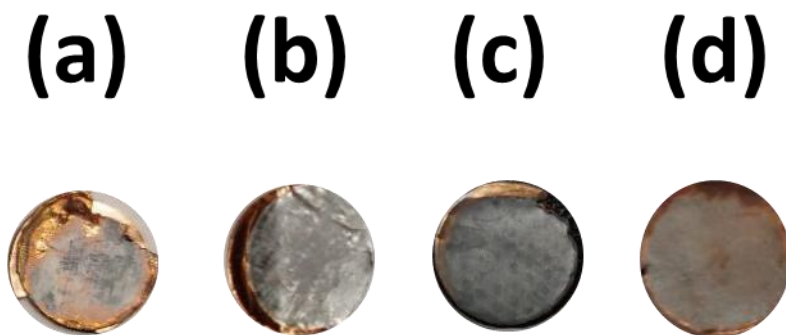


Figure 22: Collected photographs of zinc-deposited Cu electrodes in a) 1 m ZnCl_2 electrolyte (RT), b) $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ electrolyte (RT), c) $\text{ZnCl}_2 \cdot 1.5\text{H}_2\text{O}$ electrolyte (40 °C) and d) $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte (−10 °C) at 0.25 mA cm^{-2} and 1.25 mAh cm^{-2} . (The capacities are based on the mass of active cathode materials.)

In general, the temperature can affect the deposition of metals by influencing the diffusion rates of ions, the viscosity of the electrolyte, the side reactions, and the kinetics of the electrochemical reactions. For lithium, higher temperatures might improve ion mobility and reduce the formation of dendritic structures.¹⁴² For zinc, lower temperatures might help in achieving a more uniform deposition by preventing the undesired side reactions.

The zinc-ion batteries were assembled by employing ZnHCF (ZnHCF-NPs) nanoparticles as the cathode electrode to establish the proof-of-concept in the full cells. The nanoparticles have been characterized using X-ray diffraction (XRD) measurements to determine their crystal structure (**Figure 23a**). The XRD pattern shows that the synthesized ZnHCF has a rhombohedral structure, and the XRD peaks are well assigned to $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (JCPDS # 38–0688). The microscopy image of **Figure 23b** reveals that the ZnHCF nanostructure exhibits irregular shapes with a broad particle size distribution. The zinc-ion full cells were assessed at varied temperatures to investigate the electrochemical performance of hydrated electrolytes.

Figure 24 illustrates the discharge/charge curves of the ZnHCF electrodes in the dilute aqueous ZnCl_2 electrolyte (1 M) and the molten hydrates systems. The comparison reveals the superior electrochemical performance of the ZnHCF electrode assessed by the MHE system over the electrode tested with a dilute aqueous ZnCl_2 electrolyte (1 M). Rechargeable metal-ion batteries naturally experience significant performance reduction at subzero temperatures,

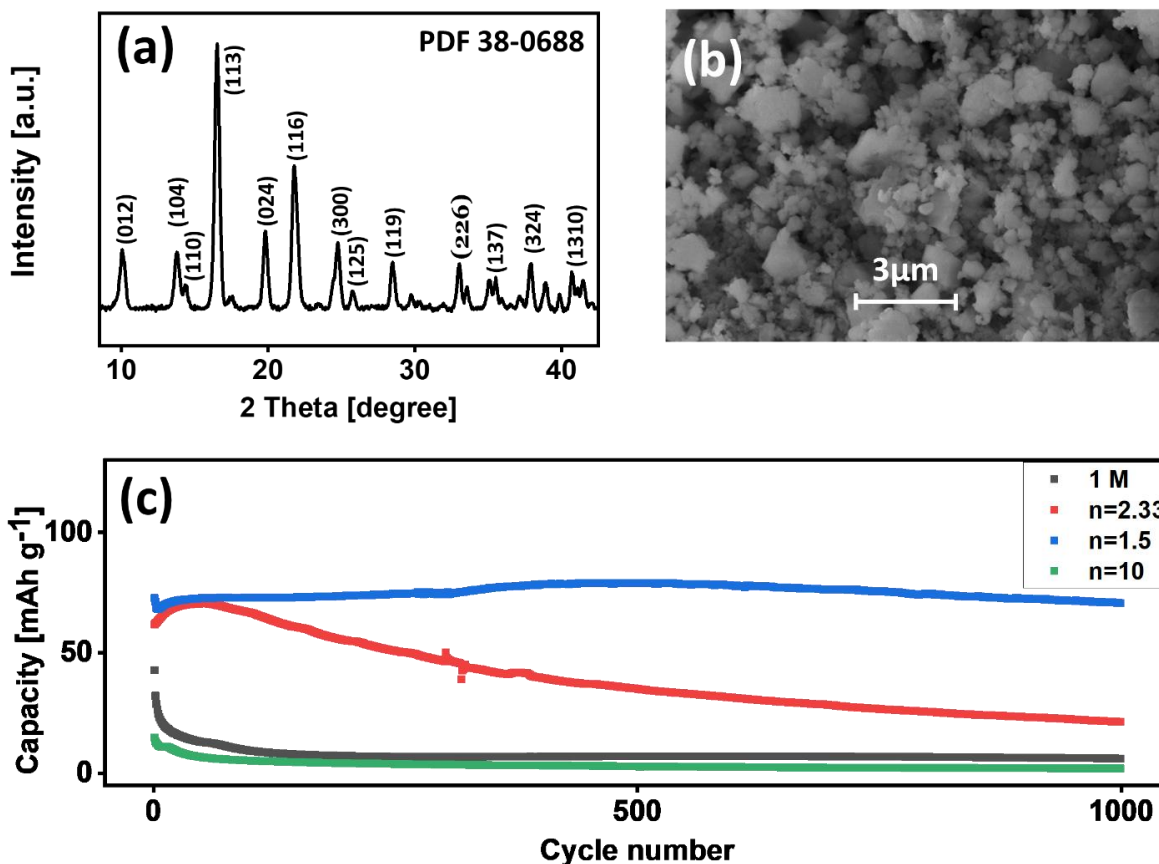


Figure 23: Study of ZnHCF-NPs as the cathode of zinc-ion full cells. a) XRD pattern of ZnHCF-NPs indexed to JCPDS #38-0688. b) Top view SEM image of ZnHCF-NPs cathode electrode. c) The cycling performance of ZnHCF-based cathode electrodes in 1 M ZnCl₂ electrolyte (RT), ZnCl₂.2.33H₂O electrolyte (RT), ZnCl₂.1.5H₂O electrolyte (40 °C) and ZnCl₂.10H₂O electrolyte (-10 °C) at 1C rate (The capacities are based on the mass of active cathode materials).

primarily due to deterioration in electrolyte wettability, diminished electronic conductivity, slow ionic diffusion of electrode materials, and reduced chemical reaction rates.¹⁴³ This causes the ZnCl₂.10H₂O electrolyte to perform poorly in a full cell design. However, the specific capacity was improved by increasing the operating temperature from -10 °C to 40 °C in a less hydrated composition, and the cycle life of the zinc-ion cell was prolonged in ZnCl₂.1.5H₂O MHE. As a result of the high capacity in ZnCl₂.1.5H₂O MHE, its specific energy is approximately 125 Wh kg⁻¹ (based on the mass of active cathode materials). The high energy density remains stable for almost 1000 cycles, superior to the previous reports.⁷⁷⁻⁷⁹

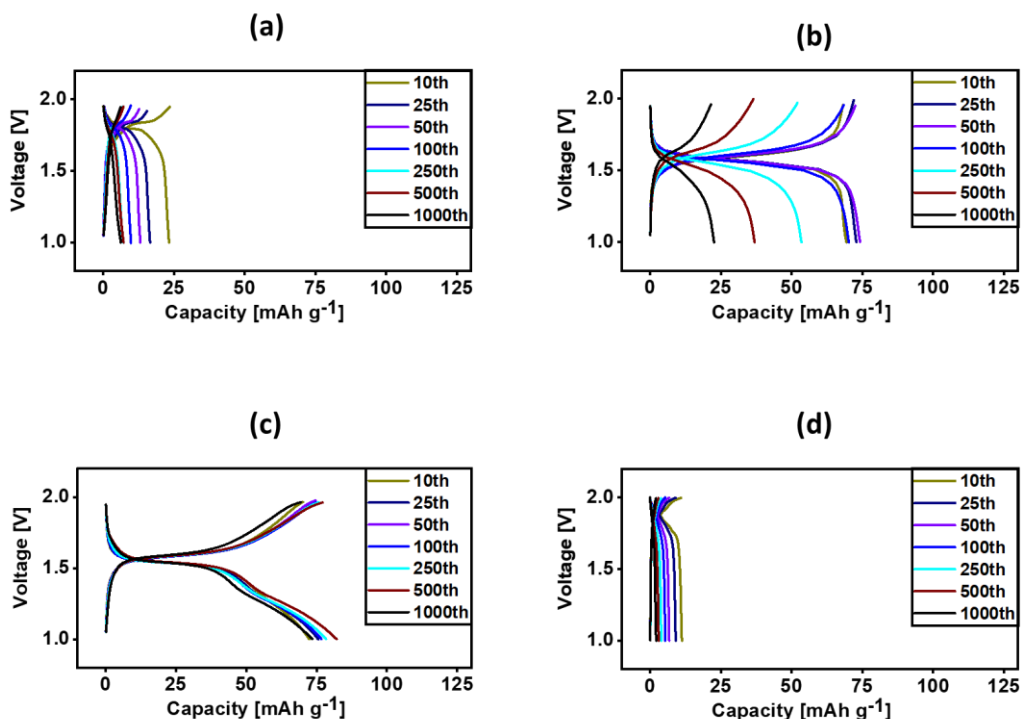


Figure 24: Discharge-charge curves of ZnHCF cathode during different cycles in a) 1 m ZnCl_2 electrolyte (RT), b) $\text{ZnCl}_2 \cdot 2.33\text{H}_2\text{O}$ electrolyte (RT), c) $\text{ZnCl}_2 \cdot 1.5\text{H}_2\text{O}$ electrolyte (40 °C) and d) $\text{ZnCl}_2 \cdot 10\text{H}_2\text{O}$ electrolyte (−10 °C) at 1C. (The capacities are based on the mass of active cathode materials.)

The zinc-ion cells demonstrated remarkable performance under an extremely low amount of electrolyte solvent. Further improvements in cycling stability and suppressing side reactions should be investigated. Electrolyte optimization by adding additives and improving the electrode design could be effective methods to improve the energy efficiency of zinc-ion cells.

4.3 Conclusions

The research in Chapter 4 concludes that temperature plays a critical role in influencing the deposition behavior of zinc and the overall electrochemical performance of zinc metal anodes. Electrochemical tests conducted on zinc chloride-based hydrated electrolyte systems, with compositions $n=10$, $n=2.33$, and $n=1.5$, demonstrated how varying operating temperatures of −10 °C, 25 °C, and 40 °C affect battery performance. These results were contrasted with those obtained from a dilute aqueous ZnCl_2 electrolyte (1 M) system.

The findings revealed that zinc half-cells, both Zn/Cu and Zn/Zn, in MHE systems, exhibited longer cycling life and higher average coulombic efficiencies compared to the cells in the 1 M ZnCl₂ electrolyte. Notably, the highest average coulombic efficiency was recorded at -10 °C. Ex-situ scanning electron microscopy (SEM) further illustrated that zinc deposited at lower temperatures forms a more compact and smoother layer, contributing to higher efficiency. In contrast, SEM images showed significant cracking on zinc electrodes cycled in the 1 M ZnCl₂ electrolyte, whereas electrodes from cells in ZnCl₂·10H₂O at -10 °C maintained better structural integrity.

The study also observed larger zinc nuclei with lower nucleation densities forming on the copper foil at reduced temperatures. The Zn/MHE/ZnHCF-NP full cells showed remarkable performance at 40 °C over 1000 cycles, outperforming the cells in more hydrated electrolytes at lower temperatures. In addition, the zinc-ion battery system achieved an impressive capacity of 76.3 mAh g⁻¹ at 40 °C, surpassing both the dilute aqueous system and other MHE configurations.

From these results, elevated temperatures up to 40 °C are a straightforward and effective method to enhance the performance of zinc-ion batteries. This approach, focusing on temperature optimization, could potentially be applied to other multivalent metal-based rechargeable batteries to extend their cycle life and improve overall performance. The chapter underscores the importance of temperature as a key factor in the development of high-performance zinc batteries and opens new possibilities for extending this strategy to a broader range of battery technologies.

Chapter 5: Early-Stage Lifetime Classification for Batteries: Machine-Learned Features vs Human-Selected Features

In Chapter 5, the application of both shallow machine learning tools and deep learning algorithms to early battery lifetime prediction is explored. An extensive evaluation of these algorithms was conducted using selected features by experts and features derived directly from the data across three distinct battery datasets (A, B, and C). Traditional machine learning approaches, which rely on expert-selected features, were contrasted with deep learning methods that automatically extract features from the data for classification.

The study discovered that two traditional learning techniques achieved impressive accuracy rates. Specifically, a 96 % accuracy rate in classifying batteries that retained over 80 % of their initial capacity after 550 cycles was obtained using data from just the first two cycles. Remarkably, a 94 % accuracy rate was achieved even with data from only one cycle. The accuracy of these shallow learning methods improved progressively with more cycle data, reaching 98 %. An analysis of the importance of the selected features revealed that changes in internal resistance during the initial two cycles were crucial for early predictions of battery life. The study also highlighted the impact of temperature fluctuations during charging and discharging, alongside the importance of features from the capacity fade curve, due to minimal initial capacity degradation.

These models were also applied to classify battery lifetimes in additional datasets, notably predicting the lifetime of lithium batteries in dataset B. It is important to note that while data-driven features excel in specific scenarios, their adaptability may be limited to battery types with distinct charge/discharge profiles in dataset C to those in the studied datasets A, B. On the other hand, the flexibility of expert-selected features offers a significant advantage, allowing for adjustments to accommodate various battery types and chemistries.

The layout of this thesis chapter is structured as follows: Section 5.1 introduces the experimental data, outlines the methodology used for feature extraction, and details the shallow machine learning and deep learning models. Section 5.2 is dedicated to the classification of battery lifetimes, considering the diverse datasets. It includes a thorough discussion of the

results obtained from training both the shallow machine learning and deep learning models, and how these trained models are then applied to classify the lifetimes of the batteries in dataset B and selected in-house batteries. In addition, this section includes a supplementary analysis focused on feature selection using a genetic algorithm, which leads to a reduction in the number of features while maintaining their relevance and importance. The chapter concludes by offering a comparative analysis of the strengths of both shallow machine learning and deep learning approaches, summarizing the key findings, and discussing the potential applications and future directions of this research.

5.1 Experimental

5.1.1 Data Description

This chapter incorporates three separate datasets for its experimental analysis. The batteries within each dataset are grouped into two categories based on their lifespan: those with "High lifetime" and those with "Low lifetime." A battery is considered to have failed once its cycle capacity falls below 80 % of its original capacity. Those classified under "High lifetime" managed to endure over 550 cycles before failing, whereas the others were labeled as "Low lifetime."

Dataset A encompasses 124 commercial lithium iron phosphate/graphite batteries, each with a rated capacity of 1.1 Ah, provided by Severson et al.⁹⁰ These batteries were subjected to testing in a controlled environment, maintained consistently at 30 °C. They underwent a testing protocol involving multi-step fast charging and constant current discharging. This chapter explores various parameters such as capacity, temperature, voltage, and current across numerous cycles, revealing a wide range of battery lifetimes spanning from 150 to 2300 cycles.

Figures 25a and 25b present the discharge capacity trends over the first 1,000 cycles for Dataset A, with color coding to highlight cycle life. It is noted that capacity fade is minimal in the first 200 cycles, increasing as the batteries approach their end of life – a characteristic trait of lithium-ion batteries. The intersection of capacity fade trajectories in **Figure 25a** underscores the weak correlation between initial capacity and overall battery life. **Figure 25b** further delineates the lifespan distribution of the 124 batteries, with a significant portion

surpassing 500 cycles. To assess classification accuracy, the dataset is split into varying training and testing batches.

Dataset B comprises commercial high-power lithium iron phosphate (LFP)/graphite cylindrical cells, each with a nominal capacity of 1.1 Ah and voltage of 3.3 V.¹⁴⁴ While charging protocols varied, the discharge process was consistent, operating between cutoff voltages of 2.0 V and 3.6 V.¹⁴⁴ **Figures 25c and 25d** illustrate the discharge capacity trends over the first 1,000 cycles and the lifespan distribution for these batteries. The dataset is carefully examined by hand to identify and exclude any batteries with issues.

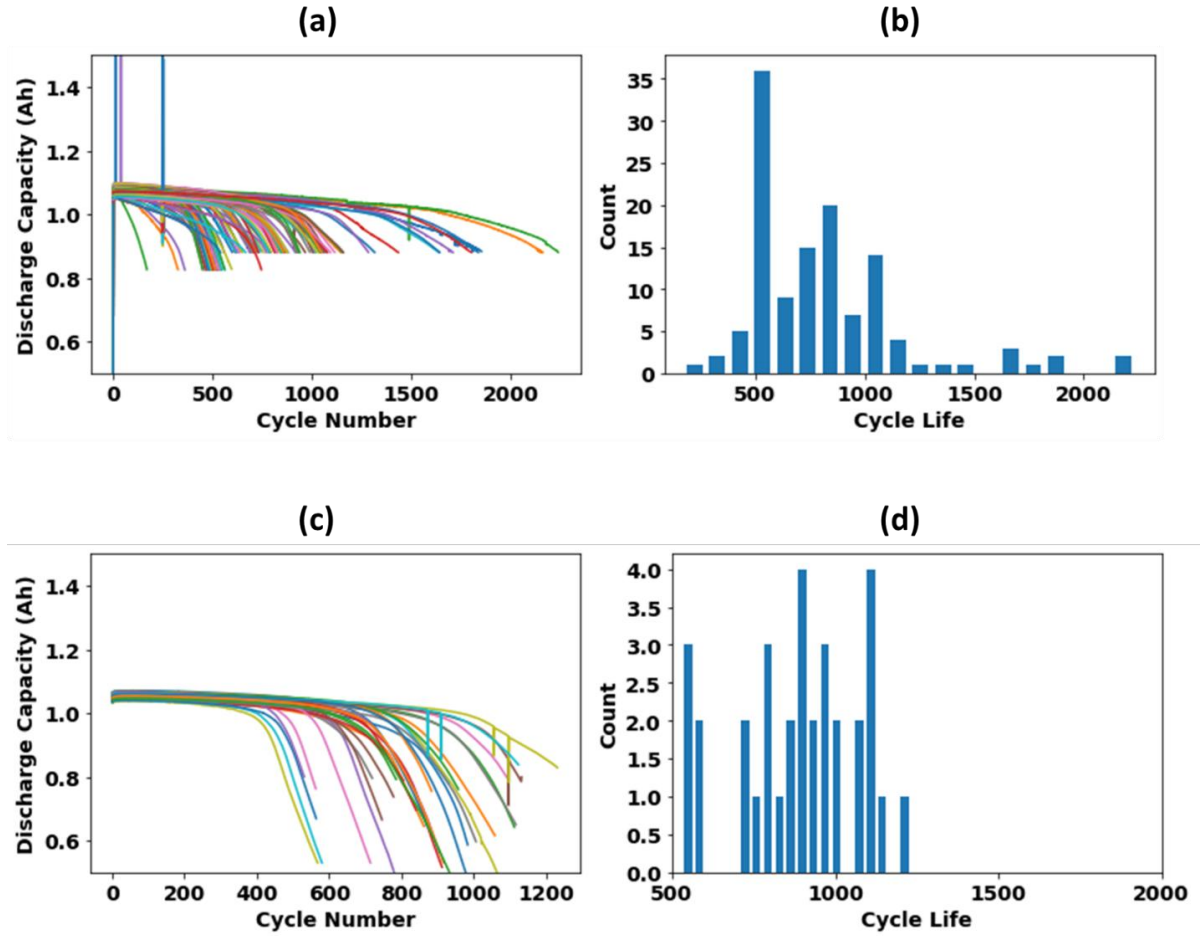


Figure 25: Data description. a) Capacity fade curves of cell samples in Dataset A. b) Cycle life of the battery cells in the dataset A. Most cells lasted around 500 charging cycles before they were considered broken. c) Capacity fade curves of cell samples in Dataset B. d) Cycle life of the battery cells in the dataset B.

Dataset C focuses on homemade zinc ion batteries, which serve as a unique test case to evaluate model prediction capabilities for a different type of battery. These batteries underwent testing in cylindrical fixtures with 3-point contacts, using an Arbin Laboratory Battery Testing cyclers within a temperature-controlled oven at 30 °C and 80 °C. The testing protocol included single step charging and constant current discharging, with capacity, voltage, and current measurements taken over numerous cycles. **Figure 26** displays the discharge capacity versus cycle number for the first 1,000 cycles of Dataset C, revealing contrasting fading patterns between batteries in the initial 100 cycles. This dataset provides crucial insights into

classification accuracy across different battery types. Notably, the initial cycle data has been omitted from all datasets, treating the second cycle as the initial one. This adjustment was necessitated by the incomplete parameter recording during the first cycle in the original datasets.¹⁴ distribution of the 124 batteries, with the majority having a lifetime exceeding 500 cycles. The dataset is divided into training and testing batches with different ratios to explore the classification accuracies.

Dataset B consists of commercial high-power lithium iron phosphate (LFP)/graphite cylindrical cells provided by Attia et al.¹⁴⁴ These cells have a nominal capacity of 1.1 Ah and a nominal voltage of 3.3 V. Charging protocols were varied, while the discharge process remained identical. The lower and upper cutoff voltages were set at 2.0 V and 3.6 V, respectively. **Figure 25c** and **Figure 25d** display the discharge capacity as a function of cycle number for the first 1,000 cycles, and the life distribution of the batteries. The dataset is screened manually and automatically to identify problematic batteries, including experiment log information and visual analysis of curves. Batteries exhibiting significant curve shifts between cycles, unusual voltage drops, irregular curve patterns, and unreasonable negative values in the time log were excluded from the analysis.

Dataset C comprises homemade zinc ion batteries, serving as a test to assess the prediction capabilities of models for a distinct battery type. The batteries were tested using cylindrical fixtures with 3-point contacts on an Arbin Laboratory Battery Testing battery cycler, placed inside an oven chamber at temperatures of 30 °C and 80 °C. The testing involved a single step charging policy and constant current discharging, with measurements of capacity, voltage, and current recorded over multiple cycles. **Figure 26** shows the discharge capacity plotted against the cycle number for the first 1,000 cycles, revealing minimal capacity fading in one battery and significant fading in the other during the initial 100 cycles. This dataset provides valuable insights for exploring classification accuracy in different battery types. The data from the initial cycle in all datasets has been excluded, and the second cycle is regarded as the initial cycle. This adjustment is necessary because not all parameters were recorded during the first cycle of the original dataset.⁹⁰

5.1.2 Human-Picked Feature Extraction

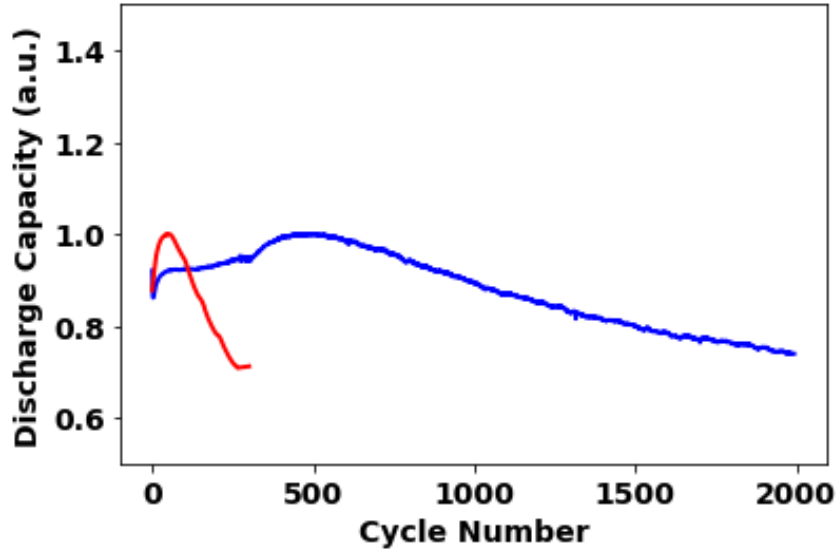


Figure 26: Data description. Capacity fade curves of cell samples in Dataset C.

In this project, the focus is on early detection in lithium-ion batteries, with key features from the first few cycles identified based on existing knowledge in the area. These features include how the battery charges and discharges, its internal resistance, temperature, and how much power it can hold. The charge and discharge details are essential, while internal resistance tells us about build and condition of the battery. The temperature indicates how the environment affects the battery, and the capacity shows its wear and tear. We compare data from a certain cycle (Nth cycle) with the first cycle's data to spot early changes in the battery.

An analysis of the batteries was conducted across multiple cycles, specifically the 2nd, 5th, 10th, 20th, 50th, 100th, and 200th cycles. We created groups of these key features (see **Table 1**). This study includes 312 carefully chosen features from battery data over the first 2, 5, 10, 20, 50, 100, and 200 cycles. These features are divided into five categories: related to charging, discharging, capacity, temperature, and internal resistance. This helps us get a full picture of how the battery ages. We based the choice of features on numerous studies, each for a specific reason. The next sections give a brief overview of each category.

5.1.2.1 Charge-related features

In **Figure 27a**, we see the charging voltage curves for a sample battery from the current study plotted against time. The first part of the curve, going up, shows the CC (Constant Current) charging phase, and the flat part is the CV (Constant Voltage) phase. These curves help us see how the battery changes as it gets older. As the battery goes through more cycles, the curve

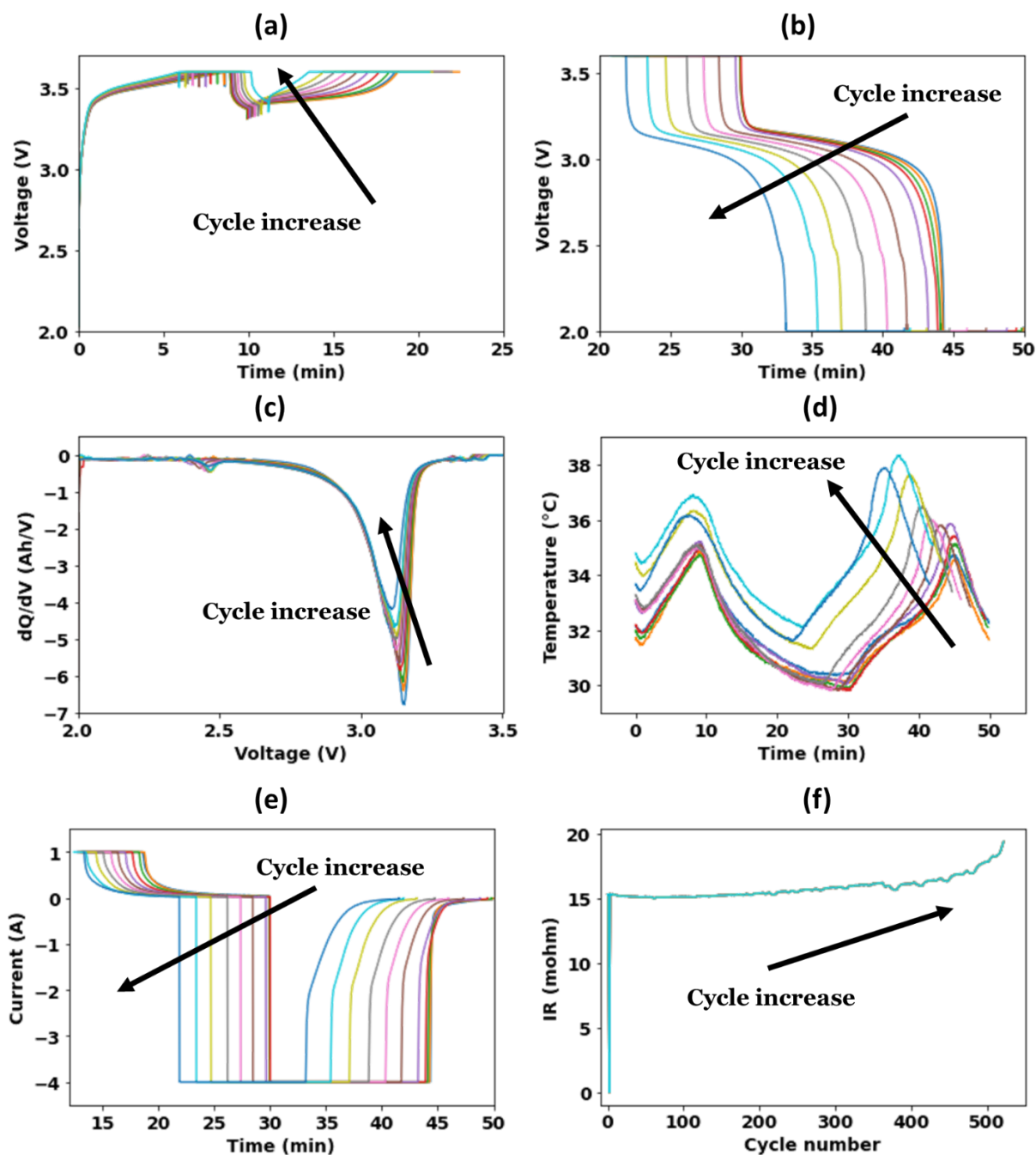


Figure 27: Feature evolution across battery cycles. Cycle-to-cycle evolution of a) charge voltage (V), b) discharge voltage (V), c) dQ/dV (Ah V^{-1}), d) temperature (T), e) current (I), and f) internal resistance (IR) of a cell from dataset A. The peak in (c) moves towards the top left in **Figure 27a**. This move means the CC phase gets shorter and the CV phase gets longer. This is because of battery polarization, which gets worse as the battery

gets older.

To track these changes, we made several features, named Ch1 to Ch12 as listed in **Table 1**. We look at how the CC phase time changes from the 1st cycle to cycle N. We do the same for the CV phase. We also use the charging time, which we can measure easily, including how it changes from the 1st cycle to cycle N and the average charging time from the 1st to cycle N. We compare these from the 1st cycle to cycle N to spot significant changes over time.

5.1.2.2 Discharge-Related Features

The features related to discharging are based on the discharge voltage curves and their changes. These are crucial for figuring out how the battery gets worse over time. In **Figure 27b**, we see discharge voltage curves for a sample battery from the current study, shown against the time it was charging. Also, in **Figure 27c**, there is an incremental capacity (IC) curve. We get this by looking at minor changes in how much power the battery can hold as the voltage changes a little. This IC curve is really useful for spotting how the battery ages and guessing its online State-of-Health (SOH).^{145,146}

From the IC curve, we made features D1 to D3. These look at how the peak and voltage of the IC curve change from the 1st cycle to cycle N. We also made a feature that looks at how the area under the IC peak changes from the 1st cycle to cycle N, by measuring the change in the total amount under this peak.

As the battery goes through more cycles, both the power it can hold and the area under the voltage curve usually gets smaller. The difference in the area under the $Q_i(V)$ and $Q_j(V)$ curves ($\Delta Q(V)$) tells us about how much energy the battery loses between two cycles. This is helpful for figuring out how long the battery will last.⁹⁰ Features D4 to D11 include measures of discharge capacity changes, the minimum, average, and maximum values, as well as the distribution and skewness of these values.

There are also features based on how the discharge capacity changes over cycles. Feature D10 looks at the discharge capacity at a certain cycle, and feature D11 looks at how the discharge capacity changes from the 1st cycle to cycle N, giving us more clues about how long the battery will last.^{90,94,147}

5.1.2.3 Capacity-Related Features

Understanding how battery capacity changes is key to knowing how the battery gets worse over time. We look at two models often used in lithium-ion battery studies: a simple linear model and a square-root-of-time model.^{90,148} We use these models to understand the capacity changes in the first N cycles. These models help us see how the capacity of the battery changes over time during the initial cycles.

We created four features based on these models. C1 and C2 come from the slope and the starting point of the linear model applied to capacity change curves from cycle 1 to cycle N. C3 and C4 are the slope and starting point from the square root model for the same curves. We speculate these features from the changing capacity curves might be important for predicting how long the battery will last.

5.1.2.4 Temperature-Related Features

Temperature is a crucial indicator to how a battery ages.^{14,87,91,149,150} In **Figure 27d**, we see temperature changes over several cycles. There are two high points: one during charging and one during discharging. The temperature goes up when the battery charges and discharges. As the battery goes through more cycles, these high points get higher, and it takes less time to reach them.

To track these changes, we defined eighteen temperature-related features. T1 to T4 are about how the lowest, highest, average, and total temperature change between cycles. T5 to T12 are similar but look at the temperature changes during charging and discharging. T13 to T18 are about the lowest, highest, average, and total temperature from cycle 1 to cycle N. T17 and T18 show how fast the temperature peaks during charging and discharging change over cycles.

5.1.2.5 Internal Resistance-Related Features

As a battery gets older, its internal resistance (IR) tends to go up.^{87,91,150} In **Figure 27f**, we see how IR changes over 500 cycles in one battery from the selected datasets. To capture this, we made IR1, the change in IR from the 1st cycle to cycle N, and IR2, the IR at a certain cycle. IR3 to IR5 are about the lowest, highest, and average IR from cycle 1 to cycle N. IR6 shows the cycle with the lowest IR.

These five categories of features, from charging and discharging data, help us predict how long a battery will last. But it is important to remember that the secondary test set we used is about a year older than the main test and training sets.⁹⁰ This age difference can affect the initial capacity of the cells due to calendar aging. So, we should think about including calendar aging as another feature for a full picture. Overall, these features give us valuable information about how batteries get degraded over time and help us guess their lifespan.

5.1.3 Traditional (Shallow) Machine Learning Models

A wide range of classification and regression algorithms are available in data science, such as logistic regression, support vector machines, naive bayes classifiers, and decision trees.^{16,151–153} Particularly notable are the random forest classifier and the gradient boosting decision tree classifier, which are advanced forms of decision trees.^{15,96,153–156} Decision Trees play a critical role in supervised machine learning, replicating human decision-making via rule-based selections.^{157,158} These adaptable models are used for both classification and regression tasks, resembling inverted trees with nodes representing features, branches for decision paths, and leaves as output results. For tasks such as battery modeling, decision trees are highly effective, providing continuous data for fitting models and quick predictions.^{157,158}

The Random Forest (RF) model is a collective of various decision trees (**Figure 28a**).¹⁰⁴ It utilizes the principle of majority voting, leveraging the combined strength of different, independent models.¹⁰³ This technique is particularly effective in estimating battery lifetimes, where it builds numerous trees with randomly selected features and averages their lifespan predictions.¹⁰³ Another method, the Gradient Boosting Decision Trees (GBDT), systematically improves weaker models by reducing residual errors (**Figure 28b**).¹⁰³ This method incrementally improves predictions by adding trees that contribute to minimizing overall loss. Both methods, through hyperparameter tuning and introducing randomness in features, excel in enhancing performance and reducing the interdependence of trees in the ensemble.

Table 1: Human-picked features for shallow machine learning classification.

Feature category	Selected feature
Charge features	Ch1: Time duration of CC charging mode, difference between two cycles
	Ch2: Time duration of CV charging mode, difference between two cycles
	Ch3-5: Min/Max/Mean of CC charging time from cycle 1 to cycle N
	Ch6-8: Min/Max/Mean of CV charging time from cycle 1 to cycle N
	Ch9: Charging time, difference between two cycles
	Ch10-12: Min/Max/Mean of charging time from cycle 1 to cycle N
Discharge features	D1: Height of IC peak, difference between two cycles
	D2: Voltage of IC peak, difference between two cycles
	D3: Covering area of IC peak, difference between two cycles
	D4-9: Variance/Min/Mean/Max/Skewness/Kurtosis of cycle-to-cycle evolution of $Q(V)$ ($\Delta Q(V)$)
	D10: Discharge capacity at specific cycle
	D11: Difference between maximum discharge capacity and the discharge capacity at specific cycle
Capacity features	C1: Slope of linear model, fit to the capacity fade curve from cycle 1 to cycle N
	C2: Intercept of linear model, fit to the capacity fade curve from cycle 1 to cycle N
	C3: Slope of square-root-of-time model, fit to the capacity fade curve from cycle 1 to cycle N
	C4: Intercept of square-root-of-time model, fit to the capacity fade curve from cycle 1 to cycle N
Temperature features	T1-4: Surface temperature, difference between Min/Max/Mean/Integral of two cycles
	T5-8: Surface temperature of discharge process, difference between Min/Max/Mean/Integral of two cycles
	T9-12: Surface temperature of charge process, difference between Min/Max/Mean/Integral of two cycles
	T13-16: Surface temperature, mean of Min/Max/Mean/Integral from cycle 1 to cycle N
	T17-18: Surface temperature, time of reaching peak temperature during charge and discharge
IR features	IR1: Internal resistance, difference between two cycles
	IR2: Internal resistance, value at latest cycle
	IR3-5: Internal resistance, Min/Max/Mean from cycle 1 to cycle N
	IR6: The cycle of minimum internal resistance

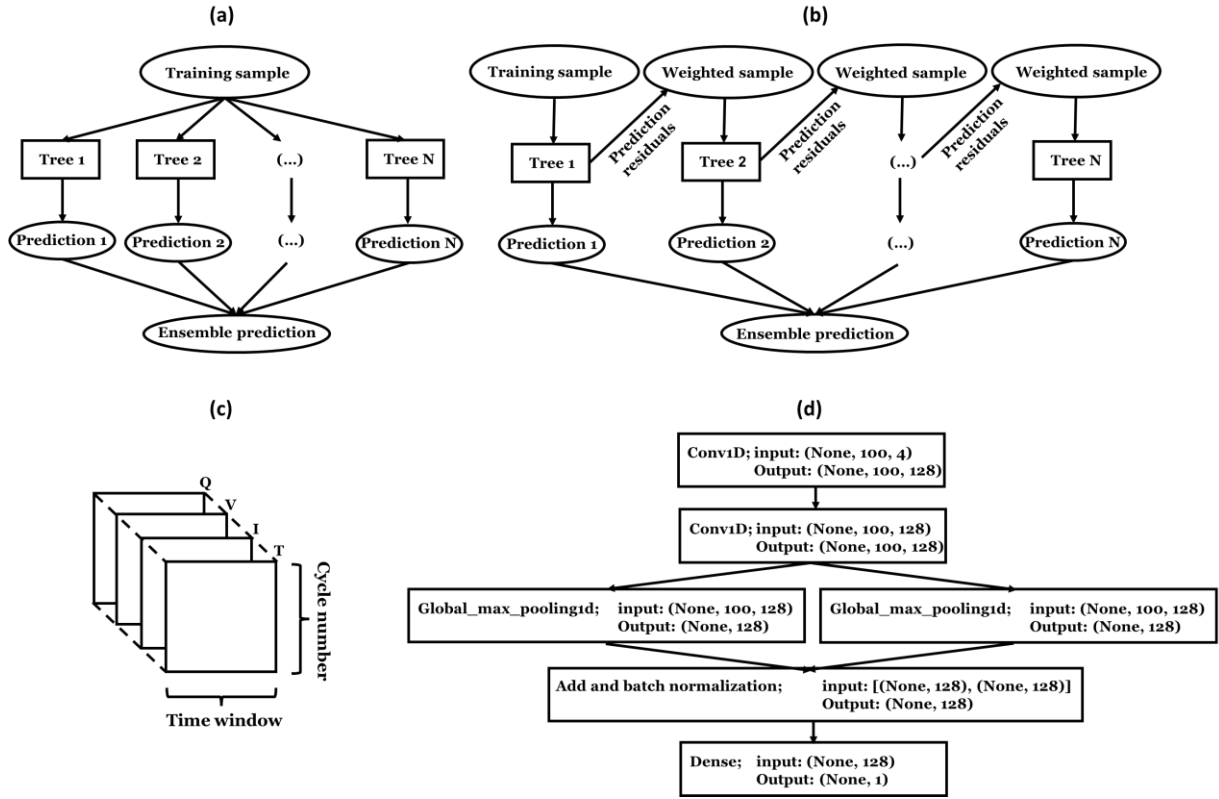


Figure 28: Shallow and deep learning models. a) Flow diagram of RF model making a prediction. b) Visualization of a gradient boosting machine learning method. c) Input tensor structure for DL network. d) Structure of the CNN classifier.

5.1.4 Deep Learning Model

Deep learning models have emerged as invaluable assets in the realm of battery lifetime prediction, markedly transforming the landscape of energy storage management.^{159–162} These sophisticated models harness the power of historical data to meticulously analyze and understand complex patterns and influencing factors that contribute to a battery's gradual degradation over time.^{160,162,163} Employing advanced techniques such as recurrent neural networks (RNNs) and convolutional neural networks (CNNs), these models are adept at capturing even the most subtle details in raw measurement data, which is often riddled with noise and inconsistencies.¹⁶²

The challenge with raw measurement data is manifold. It can be extremely noisy, with irregular distances between measurements.⁹⁸ Additionally, data that is expected to decrease monotonically might exhibit unexpected increases, and there are instances where hardware

issues cause interruptions, leading to measurements resuming at arbitrary points in time.^{98,101} These anomalies necessitate rigorous preprocessing to ensure that the data fed into the deep learning model is clean and properly formatted.

In the selected datasets, a significant challenge was the variability of time due to diverse charging policies, resulting in cycles completing at different rates. This discrepancy meant that time measurements for charge and temperature could not be directly compared. To overcome this, the continuous time data was discretized into vectors of uniform dimensions using linear interpolation.

The current study involved utilizing the initial 50, 100, and 200 cycles of charging and discharging data, represented as Q/V/I/T, to construct a tensor-shaped structure suitable for CNN feature extraction, as illustrated in **Figure 28c**. The performance of these data-driven models is heavily influenced by the volume of training samples. The tensor channels were designated for each of the Q/V/I/T measurements, with the vertical dimension corresponding to the cycle number (ranging from 1 to 200) and the horizontal dimension correlating to equidistant steps during each charging and discharging cycle.

The tensors were then processed through CNN feature extractors, following the architecture outlined in **Figure 28c**, to identify trends and patterns in the charging and discharging steps. To capture valuable patterns and dependencies within the data, early stopping methods were implemented during the training phase of these feature extractors to prevent model overfitting.^{101,164} The CNNs were tasked with processing the input tensors and extracting two features each related to charging and discharging. This process involved down-sampling to yield two distinct sets of $1 \times 1 \times 2$ outputs. These data-driven features are projected as compact representations of the batteries' end-of-life characteristics.

For the classification phase, these extracted features from the charge and discharge curves were inputted into the final CNN classifier. The classifier, as shown in **Figure 28d**, was

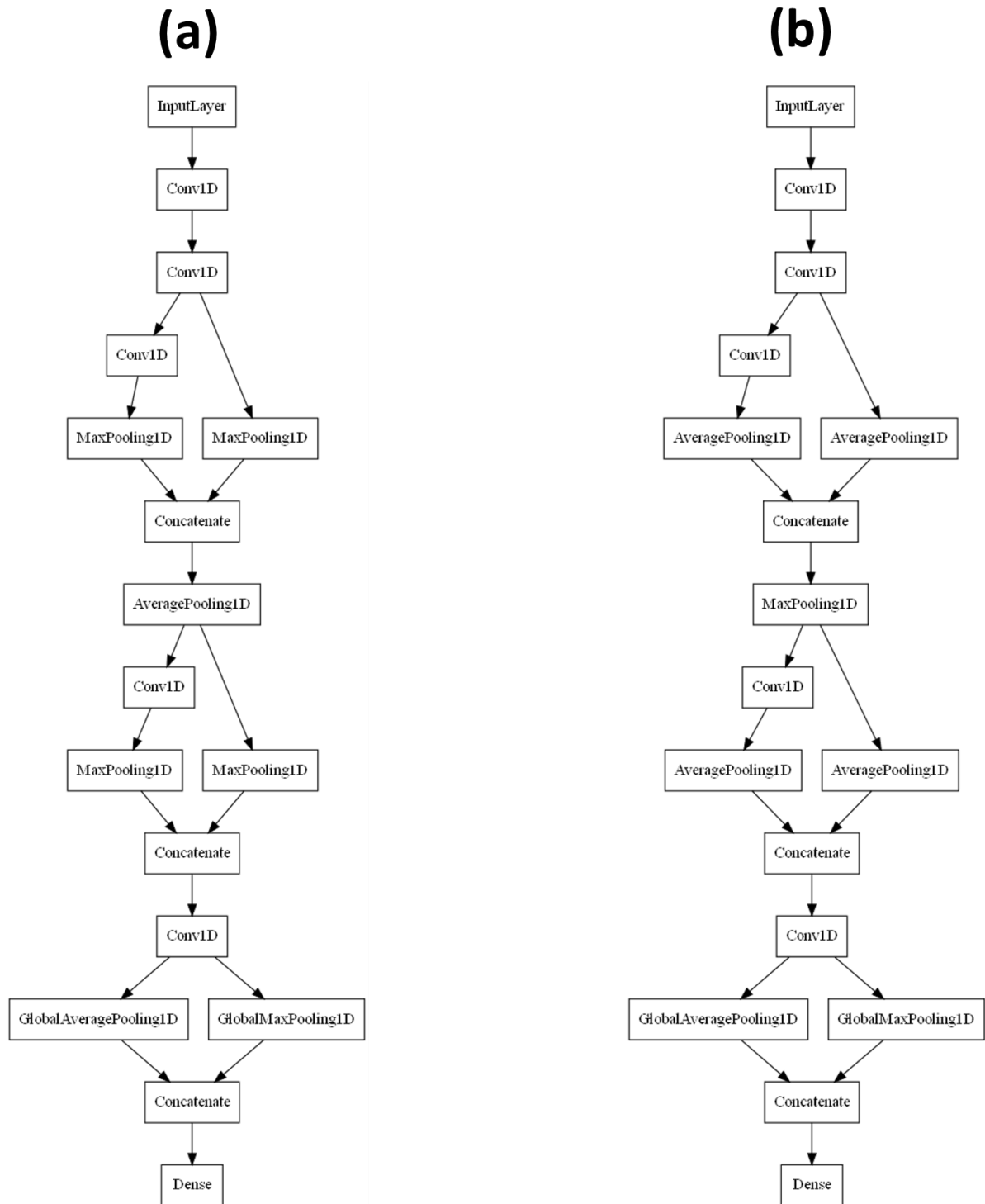


Figure 29: The general architecture of charge and discharge feature extractors.

comprised of a series of layers: two convolutional layers, two global max pooling layers, add

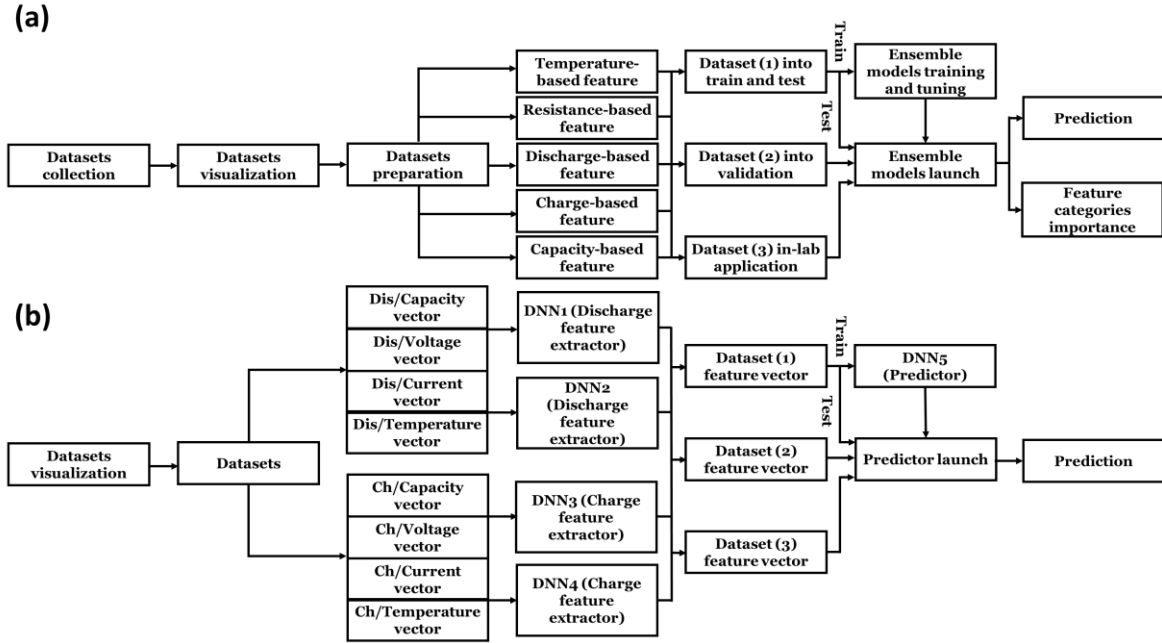


Figure 30: Comparative workflow of traditional and deep learning-based lifetime prediction. a) The traditional (shallow) machine learning algorithm, and b) The deep learning-based framework for the early-stage battery lifetime prediction.

and batch normalization layers, and a concluding dense layer.^{165–168} This arrangement, {conv, conv, (global max-pooling, global max-pooling), add and batch normalization, dense}, is a common configuration in CNNs, further optimized for performance based on the specific task and dataset.⁹¹ The global max pooling layers, with a 2×2 window size, were instrumental in reducing the spatial feature size,¹⁰¹ while the dense layer at the end was critical in enabling the neural network to transform the learned features into meaningful classifications (**Figure 29**).¹⁶⁹

Our strategy initiates with the methodology in **Figure 30a**, extracting numerical features from data points for model input. Progressing from this foundational approach, the strategy evolves as depicted in **Figure 30b**. Here, the deep learning framework marks a significant development by employing input data encompassing capacity, voltage, current, and temperature measurements from consecutive cycles to extract data-driven features. This progression illustrates a commitment to refining analytical methods, leveraging advanced techniques to harness the full potential of the data for more sophisticated and accurate models.

To execute DNN training and testing, the Google Colab environment, integrated with Keras and the TensorFlow GPU backend, was chosen for its robustness and efficiency.¹⁷⁰ Through grid search optimization, settings for all DNNs are carefully fine-tuned, including the number of filters, kernel sizes, pooling methods, and the best regularization weights for each layer.¹⁷¹ Following this optimization phase, all DNNs underwent training using the Adam optimizer.¹⁷² This comprehensive approach allowed us to effectively capture the correlations of battery Q/V/I/T signals over various early life cycles and different periods within a cycle, paving the way for more accurate and reliable battery lifetime predictions.

5.1.5 Experimental Methods for Zinc-Ion Batteries

5.1.5.1 Cathode Fabrication Process

The zinc hexacyanoferrate (ZnHCF) cathode material was synthesized through a coprecipitation method, as established in prior studies.⁷⁷ We combined 50 ml of a 0.1 M ZnSO₄ solution (99 % purity, from Sigma Aldrich) with 50 ml of a 0.05 M K₃Fe(CN)₆ solution (also 99 % pure, Sigma Aldrich) into 25 ml of water at 60 °C, stirring continuously. This mixture was left to age for several hours, followed by filtration and rinsing with deionized water. The resulting substance was then dried at 70 °C in an open environment, yielding a vibrant green powder. To prepare the cathode slurry, we mixed the active ZnHCF material (60 % by weight), Super P carbon black (30 % by weight), and Polytetrafluoroethylene binder (10 % by weight) in n-methyl-2-pyrrolidinone. This slurry was spread over the current collector and dried at 120 °C for 12 hours, after which the cathode was shaped into discs of 10 mm diameter.

5.1.5.2 Electrolyte Formulation

For the electrolyte, we prepared ZnCl₂·nH₂O with hydration levels n = 2.33 and 1.5. This began with drying ZnCl₂ salt (99.999 % pure, Sigma Aldrich) at 140 °C under the vacuum, followed by storage in an argon-filled glovebox to prevent moisture absorption. In a moisture-free environment, precise amounts of dried ZnCl₂ were weighed and mixed with ultrapure water to achieve the desired hydration levels.

5.1.5.3 Electrochemical Testing

The assembly of zinc-ion full cells involved layering a 10 mm zinc metal anode, an electrolyte-saturated glass fiber separator, the prepared ZnHCF cathode, and titanium mesh current

collectors. These cells were then placed in an oven for two hours under open circuit conditions to stabilize. The cells were evaluated at a current density of 0.1 mA cm^{-2} within a voltage range of 1.0 to 2.0 V versus Zn/Zn^{2+} . This testing was conducted at controlled temperatures of 25 °C and 40 °C, evaluating the performance of the cells with both electrolyte compositions.

5.2 Battery Lifetime Classification

The analysis of batteries using machine learning involves three essential steps: (a) data collection and feature selection, (b) constructing machine learning models, and (c) analyzing the target systems. In this study, a shallow machine learning-based framework and a deep neural network (DNN) workflow are presented for early lifetime classification of batteries. The shallow ML-based framework operates by inputting human-picked features derived from battery characteristics. Two ensemble ML models, namely GBDT and RF, are investigated for their application to battery lifetime classification. The performance of two algorithms is compared using the accuracy metric. Surprisingly, by utilizing data from only the initial two cycles, battery lifetime could be classified with an impressive accuracy of approximately 96 %. This surpasses the classification accuracy achieved in the original paper, which relied on data from the first five cycles.⁹⁰ Furthermore, all the accuracies in this study are derived from 50 random train and test sets, ensuring a precise evaluation of the network's performance while averting potential inaccuracies from a single train and test set. This method enhances the comprehensiveness and reliability of the evaluation, minimizing the risk of overfitting and delivering a more expansive insight into the network's capabilities. The accuracy of classifications linearly increases as the number of cycles used in the analysis increases, which is intuitive (**Figure 31a**). The classification accuracies can reach up to 98 % when employing data from 200 cycles in either of the two shallow machine learning models. Single-cycle classification can achieve an impressive accuracy rate of up to 94.5 %, even when not

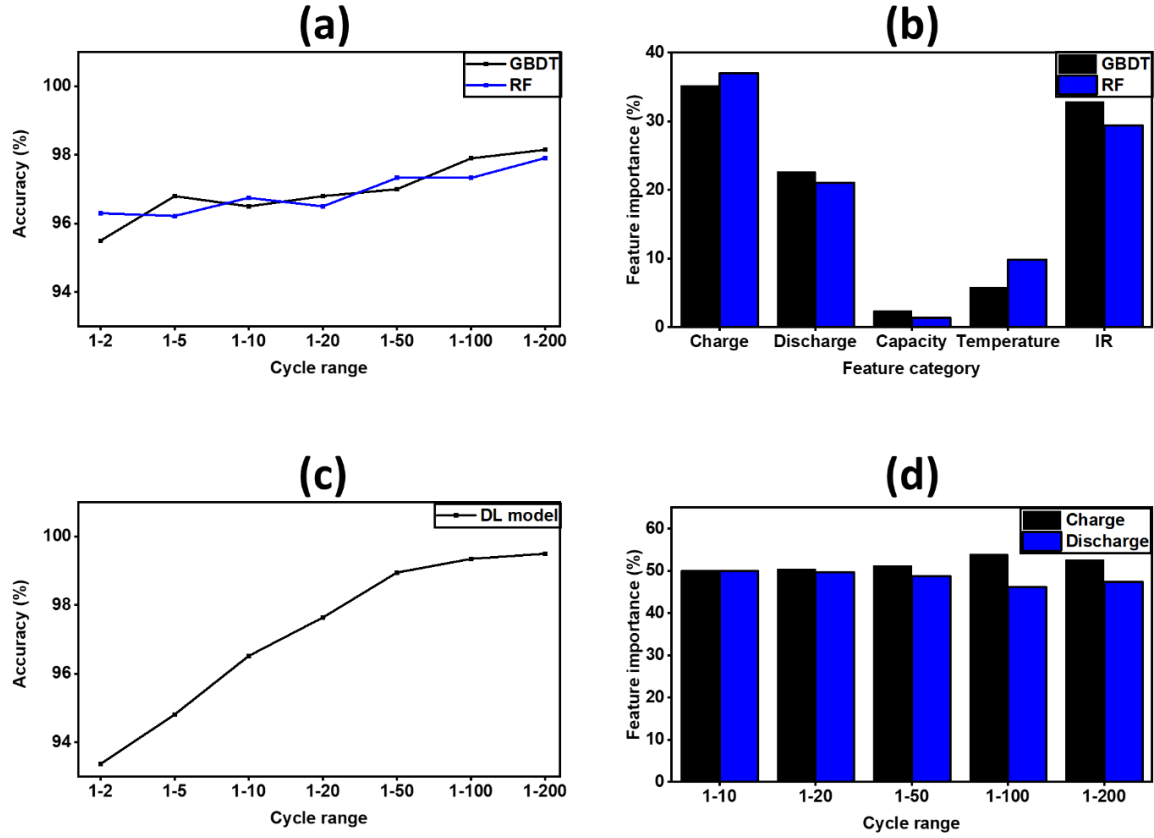


Figure 31: Battery lifetime classification accuracies using a) the traditional (shallow) machine learning framework, and c) the deep learning framework. The feature importance in b) the trained traditional machine learning models, and d) the trained deep learning classifier.

incorporating some of the human-picked features that measure the disparity between two cycles.

The relative importance of human-picked input features is studied and analyzed based on the classification results of determined optimal models. The mean importance scores of five feature categories across the two ensemble models are summarized in **Figure 31b**. To select the most influential human-picked features, feature dimensions are scored based on their contributions to classification accuracy. Charge features emerge as the most important feature in predicting battery life, indicating the potential of the CC-CV charging policy as a guiding parameter for estimating battery life. This ranking process also identifies the most important charge features, with six features selected as the most significant: Minimum/Maximum/Mean

of CC charging time (Ch3-5), and Minimum/Maximum/Mean of CV charging time (Ch6-8). It is observed that features related to the CC (constant current) mode held greater importance than those related to the CV (constant voltage) mode. To gain a better understanding, research has demonstrated that under the influence of an external power source, the CC phase facilitates the movement of reversible lithium ions from the cathode/electrolyte interface to the anode/electrolyte interface, resulting in an increased concentration of lithium ions at the solid/electrolyte interface.¹⁷³ Subsequently, during the CV phase, lithium ions diffuse, moving from the anode/electrolyte interface into the bulk of the anode and from the bulk of the cathode to the cathode/electrolyte interface.¹⁷³ Therefore, it becomes evident that these parameters play the most significant role in battery degradation mechanisms.

The internal resistance features and the discharge features are the next important feature categories in both models. Notably, the maximum internal resistance in the cycle range (IR4 feature) plays the most important feature role in this category. The following important IR features are the average of internal resistance during cycling, the internal resistance at the latest cycles and the minimum internal resistance in the training data of each cell (IR5,2,3). The internal resistance of a battery signifies the hindrance to electric current flow within it. When a battery is connected to a load, its voltage drops due to various polarization sources, stemming from the resistance within the battery's components and internal processes. Specifically, ohmic polarization losses result from the ionic resistance of the electrolyte and the electronic resistance of the electrodes' terminals and contacts, adhering to Ohm's law. Furthermore, charge transfer or activation polarization relates to the energy involved in chemical reactions on the electrodes, while diffusion polarization arises from limitations in mass transport within the electrolyte and electrode materials.^{174–176} Both charge transfer and diffusion polarizations adhere to the generalized Butler–Volmer equation.¹⁷⁴ The cumulative impact of these polarization sources contributes to the battery's total internal resistance, which can be influenced by both internal and external factors. It is established as the second critical category in the selected lithium-ion battery dataset affecting battery lifetime. This result emphasizes that the small variations in the internal resistance of the cell significantly impact aging and degradation of batteries, and it is the second critical category of key features in the lithium-ion

battery dataset. Subsequently, the discharge features are the next significant, highlighting the minimum and variance of $\Delta Q(V)$ as the most crucial discharge-related attributes (D4-5). The maximum and average of $\Delta Q(V)$ over the cycle range rank the next two important discharge features, underscoring the importance of tracking the difference in discharge capacity versus voltage, which provides essential insights into battery behavior during cycles. Previously, the minimum and variance of $\Delta Q(V)$ have been ranked among the highest-scoring features in the entire feature map in several recent studies.^{90,144} However, this study reveals that while the discharge parameters are indeed significant, there exist even more crucial factors that determine battery lifecycle. The temperature-related features, in contrast to earlier findings emphasizing their significance in very-early-cycle prediction tasks, appear to have relatively lower importance than the charge, IR, and discharge features.⁹⁰ This result is consistent with what was anticipated, as the initial research paper noted that there was some degree of inconsistency in temperature control, resulting in fluctuations in the baseline chamber temperature.^{90,144} Additionally, it was discovered that there was an accidental swap of the thermocouples for channels 15 and 16.⁹⁰ Nevertheless, it is essential to recognize that the differences in minimum, maximum, and average temperatures during charge and discharge steps continue to hold significance in determining battery lifetime within the temperature-related category. The next category of features obtained from the capacity fade curve exhibit a notably low importance score, and they may not provide accurate predictions of cycle life, particularly when dealing with batteries characterized by extended cycle longevity. This limitation stems from the observation that most batteries in dataset A undergo minimal capacity degradation during their initial few cycles. This chapter has employed two distinct fits to the capacity curves. The first involves a straightforward linear fit to the capacity fade curve. In contrast, the square-root-of-time model represents active material loss by modeling the thickening of the solid electrolyte interface film, as it has been observed that the film thickness increases proportionally to the square root of time.¹⁴⁸ Features extracted from the square root of time model excel at capturing more vital data from the cells and achieve higher rankings when compared to the basic linear fit of the capacity curve. These represent the primary human-

selected features within each category, offering valuable insights into the underlying mechanisms of battery degradation.

While the ensemble models demonstrate competitive accuracy and versatility in handling different battery types, the DNN workflow yields a slight improvement in accuracy at the cost of being computationally intensive and sensitive to data anomalies. The results highlight the potential of deep learning for battery life prediction and underscore the importance of large datasets for further advancements in the field. However, it is worth noting that the training sample size utilized in this study is limited for a deep learning network with more than 9 million parameters (**Table 2**). It is anticipated that incorporating additional training samples will result in an improved performance in life prediction. This effect becomes more apparent, especially when the number of cycles employed in the training process of the DNN classifier is reduced, leading to a noticeable drop in the accuracy of the deep learning network (**Figure 31c**).

In CNNs, feature importance means understanding which parts of data are essential for the computer to make decisions. This importance could be found by looking at the numbers that the computer learns when it processes the data. If a number is big, it means that part of the data is crucial, and if it is small, it is less important. The method presented here examines the first step the computer takes when processing features in the final classifier and checks which parts are important by analyzing these numbers. Then, these important parts were grouped into two charge and discharge categories. This helps us get a basic idea of what the computer pays attention to when making decisions. This approach reveals that the charge features exerted more considerable influence and played a more crucial role in predicting properties within the DNNs, especially in comparison to the extracted discharge features when utilizing input data from 50, 100, and 200 cycles for network training. Notably, it becomes apparent that the importance of charge features and discharge features becomes more balanced when the quantity of training data is reduced to 2, 5, and 10 cycles (**Figure 31d**). Traditional learning techniques similarly indicated that charge parameters hold more significance than discharge ones. However, the examination of the deep learning classifier reveals that despite the increased complexity of networks with

Table 2: The specification of the algorithms.

Component	Objective	Parameters
RF	EOL classification with human-selected features	~1 K
GBDT	EOL classification with human-selected features	~10 K
DL feature selectors	Data-driven features extraction	~8700 K
DL predictor	EOL classification with data-driven features	~400 K

numerous parameters, it struggles to discern hidden patterns in the data when the training cycle count is below 20 cycles.

To further validate the robustness of the proposed framework, testing was conducted on dataset B and C using the trained models from dataset A. Notably, some cells in dataset B and dataset C do not contain temperature signal and IR signals, which means temperature-related and IR-related features were not included in the verification. The trained models were used to classify the end-of-life of 39 batteries from a different dataset provided by Attia et al. in 2020.¹⁴⁴ These 39 batteries were selected based on the availability of data from the first few cycles. The machine learning model trained on data from the first two cycles achieved a remarkable 90 % accuracy in predicting the end-of-life for the 39 batteries. In contrast, the deep learning framework demonstrated impressive accuracy in predicting the lifespan of all batteries in the dataset B. Therefore, the deep learning framework stands out as the superior choice for predicting the lifecycle of lithium-ion batteries under different testing conditions.

Now, this is the time to evaluate the generalizability of the present research by implementing the models developed from the lithium-ion battery datasets to classify the lifespan of custom-made zinc-ion batteries under different testing conditions. The batteries in the dataset C featured entirely distinct chemical compositions, resulting in significantly divergent current and voltage profiles compared to the batteries in the lithium-ion battery datasets. **Figure 26** illustrates the discharge capacity plotted against the cycle number, demonstrating minimal capacity degradation in one of the zinc-ion batteries and pronounced degradation in the other, over the initial 200 cycles. The trained traditional machine learning and deep learning models are applied to forecast the lifecycle of these two batteries using data from two cycles and one cycle, respectively. The results yield a surprising revelation: despite the superior performance of deep learning models in the case of lithium-ion batteries, they prove inadequate in

classifying the lifecycle of zinc-ion batteries. Conversely, the machine learning model effectively classifies both new batteries into their respective categories. The explanation for this phenomenon lies in the following insight. In the domain of battery lifetime classification, two distinct frameworks have been introduced, each employing distinct approaches to feature extraction: the human-selection approach and the data-driven approach. In the first framework, the process of feature extraction is initiated by domain experts who analyze the changing patterns of informative parameters, including voltage, capacity, temperature, internal resistance (IR), and capacity curve during the charge-discharge process. Drawing from the understanding of battery characteristics, the human-picked features manually selected and designed to incorporate battery aging dynamics. The human-selection approach promotes the advantage of interpretability and transparency. The transparency of human-picked features allows for a clear understanding of how specific parameters influence battery lifetime, thus facilitating targeted improvements in battery design and optimization. Therefore, the adaptability of human-picked features is a notable strength. By adjusting the profiles of the informative parameters, this approach can be generalized to different battery types and various operation conditions. The versatility of human-picked features enables researchers to apply the framework across diverse battery chemistries and technologies, making it a valuable tool for studying battery lifetime prediction in a wide range of real-world scenarios. Additionally, the insights gained from exploring different feature selection techniques and shallow ML algorithms can be extended to address other battery-related challenges beyond lifetime prediction. The knowledge acquired in this stage can be leveraged for state-of-health estimation, anomaly detection, and performance optimization in various battery applications.

In contrast, the second framework adopts a data-driven approach, where features are extracted using advanced deep learning techniques. These data-driven features are derived from parameters such as charge and discharge voltage, current, temperature, and capacity curves. These parameters serve as input tensors for the network. This approach excels in capturing non-linear relationships within the data, providing the framework with a powerful predictive capability. The data-driven features are deeply learned from lithium-ion battery curves, allowing the model to uncover hidden patterns that might not be immediately apparent

to human experts. However, data-driven features have inherent limitations in terms of generalizability. The reason may also be that the amount of training samples is quite limited and is insufficient to train a high-quality CNN containing many parameters from different battery systems. Therefore, for a simple classification target task with a limited sample size, simpler models with fewer parameters, such as ensemble techniques, may achieve satisfactory performance, while also being adaptable to other types of batteries. As the data-driven features are deeply learned from specific datasets, these features cannot be directly applied to different battery types and operation conditions without further adaptation. Therefore, it is essential to exercise caution when deploying data-driven approaches in scenarios with battery technologies not well-represented in the training dataset.

The comparative analysis between the two frameworks highlights a fundamental trade-off between interpretability, generalizability, and predictive power. The human-picked features approach offers interpretability and adaptability to diverse battery types, making it well-suited for cases where domain expertise is critical, and the understanding of underlying degradation mechanisms is essential. On the other hand, the data-driven features approach excels in predictive power and complexity capture, providing valuable insights when specific degradation patterns are difficult to discern manually. However, training an effective CNN structure from scratch is computationally expensive.

While deep learning models have seen extensive success in a range of applications, they are not the best fit for scenarios with limited data, such as battery lifetime prediction with a small number of cells. The issue with deep learning in these cases is overfitting, where the model over-learns the specifics and noise in the training data, adversely affecting its ability to perform well on new, unseen data. These models often have a substantial number of parameters, making them less efficient and more prone to overfitting in situations with smaller datasets.

In contrast, the presented methods employing Gradient Boosting Decision Trees (GBDT) and Random Forest (RF) exhibit remarkable performance under these conditions. These techniques have proven highly effective in delivering accurate predictions with minimal data availability. For instance, the presented GBDT and RF models, when trained with only five battery cells, achieve impressive average classification accuracies of 90.4 % and 92.5 %,

respectively (**Figure 32**). This accuracy markedly increases with larger training sets. Such results highlight that GBDT and RF are not just viable for small-scale projects with limited data but may also offer superior estimation accuracy in these contexts compared to deep learning models.

To strike an optimal balance, researchers might consider a hybrid approach, leveraging the strengths of both methodologies. Combining human-picked features with data-driven features can potentially harness interpretability and domain knowledge while benefiting from the predictive performance of data-driven techniques.⁹⁷ Furthermore, ongoing research and advancements in both feature extraction methodologies hold promise for improving generalizability and transferability, leading to more robust and versatile battery lifetime classification frameworks in real-world conditions. Another suggestion could involve interpreting the extracted data-driven features to gain insights into the underlying parameters influencing these four data-driven characteristics.

5.3 Feature Selection Using Genetic Algorithms

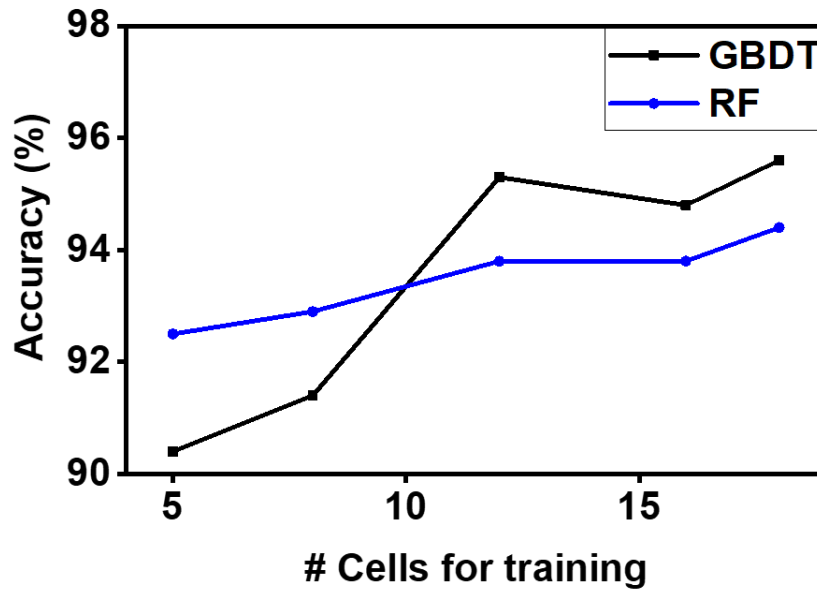


Figure 32: Graphical representation of battery lifetime classification accuracies using traditional (shallow) machine learning models, highlighting the correlation with the number of cells utilized in training.

Feature selection is a crucial data preprocessing technique.⁹³ Its aim is to reduce the number of features for reasons including simplifying model interpretation for researchers, achieving shorter training times, and mitigating the curse of dimensionality.⁹² The genetic algorithm is a search heuristic inspired by Charles Darwin's theory of natural evolution that can be used for the feature selection purpose.⁹⁵ It mimics the process of natural selection, where the fittest individuals are chosen for reproduction, creating offspring for the next generation.¹⁷⁷

Starting with a population, the algorithm selects the fittest individuals to produce offspring that inherit their parents' characteristics. If parents have higher fitness, their offspring will be even better, increasing their chances of survival. This iterative process continues, eventually leading to a generation with the fittest individuals, applied to a search problem where the best solutions are selected from a set of possibilities.

With a dataset containing tens of features for each shallow machine learning model, the application of a genetic algorithm provides the flexibility to select any number of high-importance features, effectively reducing dimensionality to enhance any model performance.

Therefore, within the pool of the features, the algorithm exclusively identifies and highlights the significance of three key features in the initial cycle: timeCCmode_1, time_CVmode_1, and IR_1, showcasing their primary role in extending battery lifespan. Notably, these three pivotal features align with the outcomes of feature importance analysis conducted on trained shallow machine learning models. This approach not only aids in enhancing predictive accuracy but also simplifies the interpretability of the resulting models.

5.4 The Specifications of the Algorithms

The specifications of the traditional machine learning algorithms, such as Random Forest (RF) and Gradient Boosting Decision Trees (GBDT), along with the deep learning algorithm, are detailed in **Table 2**. While the former relies on manually selected features for end-of-life prediction, the latter leverages four data-driven features. **Table 2** also provides the specifications of the data-driven feature selectors. Notably, the analysis reveals that the number of parameters in traditional machine learning algorithms is approximately two orders of magnitude fewer than the parameters needed for predicting single value properties in deep learning frameworks. This implies that current Deep Neural Networks (DNNs) have significantly higher computational requirements compared to traditional algorithms.

5.5 Conclusions

The current study introduces two frameworks: a traditional machine learning (ML)-based framework and a deep learning-based framework. These are designed to enhance early battery lifetime classification, with the ML framework consisting of three pivotal modules: feature extraction, feature selection, and ML-based classification.

In this framework, 312 features were selected from the degradation data of the initial 200 cycles, during which most cells show minimal capacity degradation. The evaluation included two shallow models, Random Forest and Gradient Boosting Decision Tree, applied to the selected features. Remarkably, when applying ensemble ML models and using data from just the first two cycles, a classification accuracy of 96.2 % is achieved. This accuracy impressively increased to 98 % as training data were expanded to include more cycles. The key contributor to this high accuracy was identified as the change in internal resistance, particularly in the initial cycles. Additionally, charge features, notably from CC-CV charging, emerged as crucial

in estimating the life of commercial lithium-ion cells. Among these, six charge features - including aspects of CC and CV charging time - were particularly influential.

Contrastingly, the trained deep learning framework, leveraging only four data-driven features, demonstrated remarkable accuracy. It achieved an average accuracy rate of 98.5 % with data from the first 100 cycles and astonishingly increased to 99.5 % with data from the first 200 cycles. When applied to two additional datasets, the traditional ML model showed 90 % accuracy in predicting end-of-life for 39 batteries, while the deep learning framework accurately predicted the lifespan of all batteries in dataset B. Thus, for lithium-ion batteries under various testing conditions, the deep learning framework proved superior.

However, when applying these models to zinc-ion batteries, a distinct trend was observed. The deep learning model, effective with lithium-ion batteries, faltered in predicting the lifespan of zinc-ion batteries. In contrast, the traditional ML model, with its human-selected features, was successful in categorizing zinc-ion batteries as well. This underscores the adaptability of human-selected features in battery lifespan categorization, adaptable to various battery types and operating conditions through parameter profile modifications. In contrast, the data-driven features, tailored to lithium-ion batteries, lacked such generalizability.

This research underscores the vast potential of both shallow machine learning and deep learning methods in battery technology. The proposed frameworks exhibit robustness and accuracy in predicting battery lifetimes for diverse datasets and chemistries. This work, therefore, not only contributes valuable insights for battery lifetime prediction but also paves the way for future advancements in battery technology and energy storage systems.

Chapter 6: Accelerating the Discovery of Ionic Liquids for Zinc Battery Applications

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In Chapter 6, the use of advanced machine learning techniques, specifically generative adversarial networks (GANs), is examined for their ability to predict and create new ionic liquids (ILs) that are effective in zinc batteries. This chapter builds upon previous research by integrating computational methods to tackle the complex challenges in battery materials innovation.

The approach begins with the development of predictive models using CNNs to estimate key IL properties such as melting and clearing temperatures. These models were trained on a comprehensive dataset of IL properties, utilizing molecular fingerprints and compound images. To achieve this, three distinct datasets were utilized. The first dataset includes data on 2938 ILs, detailing their thermal decomposition temperature, glass transition temperature, electrical conductivity at specific temperatures, viscosity at specific pressures and temperatures, and melting points. The second dataset consists of data on 510 ILs, focusing on their varied melting points and thermal stability. The third dataset contains SMILES strings of 36 ILs specifically for zinc electrochemical systems and zinc batteries, sourced from literature.

GANs were then employed to generate innovative combinations of anions and cations, aiming to discover new IL electrolytes that function effectively at room temperature. This generative approach advances the practicality and sustainability of zinc electrochemical systems. The generative approach yielded 15 new ILs after filtering, some of which are already used in zinc systems, validated by literature citations. The utility of the established ILs is thereby affirmed, and the potential of the model to suggest new ILs with promising properties such as melting point, decomposition temperature, conductivity, and viscosity is also demonstrated. The criteria focused on selecting ILs with melting points below room temperature to ensure they remain liquid under standard conditions, viscosities between 10 to 100 mPa·S for enhanced ion mobility, and conductivities ranging from 5 to 50 mS cm⁻¹ at

higher temperatures such as 200 °C. By comparing the predictions with established data, the effectiveness of the generative approach in identifying viable ILs for zinc battery applications was validated. This comprehensive evaluation of both well-documented and newly proposed ionic liquids enhances the selection process for creating efficient zinc electrochemical cells.

This study highlights the potential of combining advanced machine learning models with domain-specific knowledge to drive innovations in battery materials technology. This integrative approach not only enhances the fundamental understanding of zinc ILs but also showcases the immense potential of machine learning in revolutionizing materials discovery for technological advancements.

6.1 Experimental

6.1.1 Data Description

The initial phase of this study involved creating datasets of various ionic liquids, each characterized by unique combinations of anions and cations. These ionic liquids were chosen for their relevance to electrochemical systems and battery technology, particularly their potential use in electrochemical systems. This research utilized three distinct datasets:

Dataset 1: This dataset includes 2938 ionic liquids, along with data on their thermal decomposition temperature, glass transition temperature, electrical conductivity at specific temperatures, viscosity at specific pressures and temperatures, and melting points.¹⁷⁸

Dataset 2: Comprising data on 510 ionic liquids, this dataset provides information on their varied melting points and thermal stability.

Dataset 3: Consisting of 36 ionic liquids specifically for zinc electrochemical systems and zinc batteries, this dataset was sourced from literature. Not all possible zinc-compatible ionic liquids from the literature were included in this dataset. This strategic decision allows us to validate the generative network model by seeing if it can independently identify some of these established ILs. By comparing the predictions with established data, the effectiveness of the generative approach in identifying viable ionic liquids for zinc battery applications can be assessed.

These datasets are crucial for understanding the performance characteristics of ionic liquids in electrochemistry and battery applications. Each IL was preprocessed to standardize the data

format and scale, ensuring compatibility of subsequent analyses. Generational procedures were adapted to produce new ionic liquids.

6.1.2 SMILES Representations

SMILES (Simplified Molecular Input Line Entry System) is a notation system that encodes molecular structures into ASCII strings, allowing for a compact and easily interpretable representation of chemical species.¹⁷⁹ Each SMILES string uniquely describes the structure of a molecule using letters for atoms, numbers for ring structures, and symbols to denote different types of bonds. Additionally, branches are represented with parentheses and special symbols, respectively, allowing complex molecules to be described in a straightforward, linear format.¹⁸⁰ This is pivotal for database searches and storage, facilitating efficient query and retrieval processes that are much less computationally intensive compared to other molecular representation methods.

Thus, SMILES notations serve as inputs for machine learning models designed to predict molecular properties and behaviors.¹⁸¹ By applying machine learning algorithms directly to SMILES strings or their derived numerical features such as fingerprints, patterns and relationships within chemical data can be uncovered.¹⁸¹ To ensure the data was optimal for machine learning analysis, all the inputs were converted to SMILES strings, and each SMILES string was augmented into 50 randomized variants using the RDKit library to account for the structural variability of ionic liquids.¹⁸² This augmentation reflects possible stereochemical configurations, providing a more comprehensive representation of potential structural diversity.

6.1.3 Morgan Fingerprinting

Fingerprinting techniques in cheminformatics transform complex molecular structures into abstract known as fingerprints.^{183,184} Each bit in these vectors represents the presence or absence of specific substructures within the molecule, standardizing compound representation. Among these, Morgan fingerprints are particularly valuable for machine learning and computational chemistry applications.^{183,184} This method captures both specific chemical groups and the broader context of their interconnections. Their binary, fixed-size nature aligns

well with various machine learning algorithms, especially those involved in classification and clustering.^{184,185}

Generating Morgan fingerprints from SMILES strings involves using the RDKit library, a popular tool in cheminformatics.¹⁸³ A Morgan fingerprint is created by specifying the molecule, the radius of the environment to consider, and the number of bits in the resulting fingerprint. These parameters directly influence the size of the fingerprint, affecting both the level of molecular detail captured and the computational demands of the model.^{186,187} The Morgan fingerprint can then serve multiple purposes: as input for machine learning models, for quick database searches, or in similarity assessments between different molecules.

6.1.4 Data Augmentation for SMILES Representations

Data augmentation plays a crucial role in cheminformatics by building more robust machine learning models.^{188,189} The primary goals of employing data augmentation include enhancing the diversity of chemical datasets, which often contain limited examples of rare or newly synthesized molecules. By artificially expanding this diversity, models are provided with a broader range of data on which to train, which is particularly beneficial in scenarios where data collection is expensive.^{188,189}

Another significant advantage of data augmentation is its ability to mitigate overfitting.¹⁹⁰ By introducing variations in the training examples, data augmentation forces the model to avoid memorizing specific data patterns.

In the context of SMILES data, data augmentation can be particularly effective. Techniques used include random shuffling of branches within the SMILES strings, and random rotation of ring structures.¹⁹¹ These modifications generate new, valid SMILES strings that represent the molecule in different forms.

6.1.5 Variational Autoencoder (VAE)

An autoencoder consists of two main components: the encoder and the decoder.^{192,193} The encoder compresses the input data into a smaller, dense representation called the latent space or latent representation.¹⁹⁴ The decoder then reconstructs the input data from this latent representation, with the quality of this reconstruction serving as a measure of how well the autoencoder has understood the input data.¹⁹⁴

Variational autoencoders introduce a probabilistic approach to this architecture.¹⁹⁵ This approach involves sampling from the distribution defined by the encoder outputs to generate new inputs or reconstruct existing ones.¹⁹⁵

The architecture of a VAE involves several layers in both the encoder and the decoder.¹⁹⁶ The encoder processes the input data through multiple neural network layers to produce the latent space. This latent space is not a fixed point but rather a statistical distribution for each input. The decoder, comprising several layers of neural networks as well, takes a sampled vector from this distribution and reconstructs the input data, aiming to minimize the difference between the original and the reconstructed data. Each layer within both the encoder and the decoder typically consists of dense or convolutional layers, depending on the type of input data.^{196,197}

6.1.6 Property Prediction Network within a Variational Autoencoder

In the implementation of a VAE, a significant enhancement is the integration of a property prediction network.^{198–200} This network utilizes the latent representation of input molecules to predict specific chemical properties such as melting points and decomposition temperatures. The property prediction network employs a series of dense layers to map these latent representations to desired chemical properties.²⁰⁰

The integration of this property prediction network within the VAE framework transforms it into a dual-output model that facilitates simultaneous training.^{201,202} This model architecture not only learns to encode and decode the molecular structures but also predicts chemical properties directly from the encoded information. By training on both reconstruction and property prediction concurrently, the model develops more robust and meaningful latent representations.

The overall loss function of the model is a composite of the reconstruction loss (typically mean squared error between the input and its reconstruction) and the property prediction loss (which could be mean squared error for regression tasks), ensuring that the learning is balanced and effective.^{203,204}

During training, backpropagation considers gradients from both the reconstruction and property prediction losses,²⁰⁵ meaning that updates to the model parameters optimize both the

accuracy of the molecular reconstruction and the correctness of the property predictions. This dual-output configuration not only enhances the practical utility of the VAE in cheminformatics applications but also expands the capabilities of the framework by incorporating elements of supervised learning directly into the latent space learning process.²⁰⁶

6.1.7 Model Training and Validation

Training a sophisticated model such as a variational autoencoder with a property prediction network requires careful planning to ensure effective learning while avoiding overfitting. The training process begins with the dataset dividing into training and testing sets with an 80/20 ratio.^{207–209}

The selection of batch size is a critical step that influences the training dynamics.²¹⁰ Smaller batch sizes can lead to noisier gradients, potentially helping the model to escape local minima but risking unstable training dynamics. Conversely, larger batch sizes provide more accurate gradient estimates but increase computational demands. The batch size for this work is set at 256, determined empirically based on the available hardware capabilities and model requirements.

The number of epochs is set based on preliminary observations of validation loss convergence.^{211,212} Too few epochs might undertrain the model, while too many can lead to overfitting. For this work, the number of epochs has been established at 100. Early stopping is also implemented to halt training if there is no improvement in validation loss after a predetermined number of epochs.^{211,212}

6.1.8 Evaluation and performance metrics

The evaluation of a variational autoencoder with a property prediction network is pivotal to ensuring precision and reliability. By concentrating on key evaluation metrics such as mean squared error (MSE) and R^2 values, we systematically assess the ability to generalize across diverse datasets. The formula for calculating MSE and R^2 are provided in equations 5 and 6.

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (\text{eq. 6})$$

where y_i is the actual value, $\hat{y}_i$ is the predicted value, and n is the number of observations.^{213,214}

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \quad (\text{eq. 7})$$

where SS_{res} is the sum of squares of residuals, and SS_{tot} is the total sum of squares.²¹⁵

6.1.9 Generating Molecular Structures with Variational Autoencoders

We employ a series of techniques to enhance the diversity of molecular structures and explore potential new combinations of cations and anions. These methods effectively leverage the encoded latent space of the VAE to create variations of molecular structures that are both plausible and new, thus moving beyond the limitations of the initial data.

Each modified SMILES string is encoded into the latent space using the encoder. This latent space acts as a compressed database of molecular information, capturing the essential features that define the chemical properties. By manipulating this latent space, we can explore a broad spectrum of molecular characteristics that may not be explicitly present in the original dataset.

A technique for generating new molecular structures is the interpolation between two latent vectors. This method involves linearly interpolating or blending the features encoded within these vectors, resulting in the creation of new latent vectors that potentially correspond to viable, yet unexplored, molecular structures. Additionally, variation is introduced through methods such as Gaussian sampling, where new latent vectors are generated by adding Gaussian noise to existing vectors,^{216,217} altering their properties. Another method, Laplacian sampling, adds Laplacian noise to the latent vectors,^{218,219} offering a different statistical approach to introduce variability and potentially leading to a broader diversity in the generated molecular structures.

Once new latent vectors are created, they are decoded back into SMILES strings using the decoder. This crucial step reconstructs the molecular structures from the latent space, translating the encoded features back into chemical notations. The last step involves validating these newly generated SMILES strings using cheminformatics tools such as the RDKit library to ensure their chemical validity and plausibility. This validation confirms that the generated structures are chemically sound and potentially synthesizable, paving the way for their practical application in areas such as materials science, particularly ionic liquids for zinc batteries and zinc-based energy storage applications.

6.2 Ionic Liquids Property Prediction and Generation

Predicting chemical properties using machine learning presents a significant challenge due to the complexity of chemical structures.²²⁰ The primary goal is to develop a model capable of accurately predicting chemical properties, such as melting points and decomposition temperatures. These properties are crucial for various applications in material science and battery science, as they influence the development of new materials. Enhancing the accuracy of these predictions can improve the efficiency of experimental processes, reduce costs, and accelerate research and development efforts in these critical industries. Furthermore, generating new SMILES strings with appropriate anions and cations adds another layer of complexity to this task. Therefore, a secondary objective of this research involves generating ILs specifically for zinc battery applications. These ILs must have melting points below room temperature to ensure functionality at ambient conditions, while also possessing high decomposition temperatures for enhanced stability. This objective will be addressed using generative models that have been developed and tuned specifically for zinc-based ILs (**Table 3**). The generation of new anions and cations will employ methods such as adding noise and interpolation, which are then validated using the existing dataset of 2938 ILs (Supplementary file named Dataset 1). Once generated, these anions and cations will be evaluated to determine their potential for use in zinc electrochemical systems and zinc batteries.

Table 3: SMILES Strings of Anions and Cations in Ionic Liquids. This table compiles SMILES strings extracted from literature, detailing the structural diversity of ionic liquids used in dataset 3.

Cation	Anion	Ref.
<chem>CCCC[n+](c1)C</chem>	<chem>F[B-](F)(F)F</chem>	221
<chem>CCCC[N+](C)CCCC1</chem>	<chem>C(#N)[N-]C#N</chem>	222
<chem>CC[n+](c1)C</chem>	<chem>C(C)(=O)[O-]</chem>	223
<chem>CC[n+](c1)C</chem>	<chem>C(C)OS(=O)(=O)[O-]</chem>	224
<chem>CCCC[n+](c1)C</chem>	<chem>C(C)(=O)[O-]</chem>	115
<chem>CC[n+](c1)C</chem>	<chem>C(#N)[N-]C#N</chem>	222,225
<chem>CC[n+](c1)C</chem>	<chem>FC(S(=O)(=O)[N-]S(=O)(=O)C(F)(F)F)(F)F</chem>	114,118
<chem>CC[n+](c1)C</chem>	<chem>FC(S(=O)(=O)[O-])(F)F</chem>	114,118
<chem>CCCC[n+](c1)C</chem>	<chem>C(#N)[N-]C#N</chem>	226
<chem>CCCC[n+](c1)C</chem>	<chem>[F-]</chem>	221

<chem>CCCC[N+](C)(CCCC)1</chem>	<chem>FC(S(=O)(=O)[N-]S(=O)(=O)C(F)(F)F)(F)F</chem>	227
<chem>CCCC[n+](c1)C</chem>	<chem>Cl(=O)(=O)(=O)[O-]</chem>	221
<chem>CCC[N+](C)(CCCC)1</chem>	<chem>FC(S(=O)(=O)[N-]S(=O)(=O)C(F)(F)F)(F)F</chem>	228
<chem>CCCC[N+](C)(CCCC)1</chem>	<chem>FC(S(=O)(=O)[O-])(F)F</chem>	229
<chem>CCCC[n+](c1)C</chem>	<chem>F[P-](F)(F)(F)F</chem>	221
<chem>CC[n+](c1)C</chem>	<chem>FC(S(=O)(=O)[O-])(F)F</chem>	230
<chem>CC[n+](c1)C</chem>	<chem>F[B-](F)(F)F</chem>	117
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>N(=O)[O-]</chem>	221
<chem>CCCCCCCCCN1CC[N+](C1)C</chem>	<chem>[Cl-]</chem>	231
<chem>CCCC[n+](c1)C</chem>	<chem>S(=O)(=O)(O)[O-]</chem>	221
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>[Cl-]</chem>	221
<chem>CCCC[n+](c1)C</chem>	<chem>N(=O)[O-]</chem>	221
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>OP(=O)(O)[O-]</chem>	221
<chem>CCCC[N+](C)(CCCC)1</chem>	<chem>S(=O)(=O)(O)[O-]</chem>	221
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>[F-]</chem>	221
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>S(=O)(=O)(O)[O-]</chem>	221
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>F[B-](F)(F)F</chem>	221
<chem>CC[n+](c1)C</chem>	<chem>F[P-](F)(F)(F)F</chem>	232
<chem>CCCC[n+](c1)C</chem>	<chem>[Cl-]</chem>	233,234
<chem>C[N+](C)(C)C</chem>	<chem>C(C)(=O)[O-]</chem>	235,236
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>Cl(=O)(=O)(=O)[O-]</chem>	221
<chem>CCCC[N+](C)(CCCC)1</chem>	<chem>C(C)(=O)[O-]</chem>	221
<chem>CCCC[P+](C)(CCCC)CCCC</chem>	<chem>S(=O)(=O)(O)[O-]</chem>	221
<chem>OCC[N+](C)(C)C</chem>	<chem>C(C)(=O)[O-]</chem>	237,238
<chem>CCCC[N+](C)(CCCC)1</chem>	<chem>F[B-](F)(F)F</chem>	221
<chem>CCCC[N+](C)(CCCC)1</chem>	<chem>P(=O)(O)(O)[O-]</chem>	221

In this study, a variational autoencoder integrated with a property prediction network is employed to generate SMILES strings for ILs. The workflow consists of several distinct phases, each crucial for the development and application of the model. **Figure 33** visually represents the various stages involved in employing a VAE for predicting ionic liquid thermal properties and generating SMILES strings for ionic liquids, particularly for zinc battery applications. This diagram depicts each critical step, from data preparation to the output and analysis of generated chemical structures.

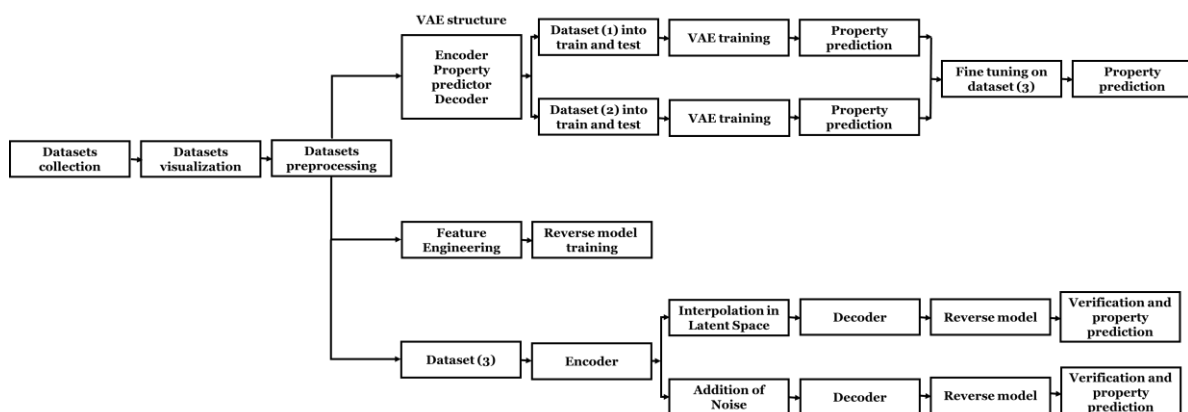


Figure 33: Visual representation of the VAE workflow, illustrating the sequential steps from data input through model training and adaptation, to the generation and analysis of new chemical entities, effectively conveying the systematic approach employed in the study.

Initially, the data comprising the representations of cations and anions are loaded and converted to SMILES strings. These representations are then augmented to introduce variability, simulating diverse molecular configurations. Each SMILES string is converted into a numerical format using molecular fingerprinting techniques, facilitating computational handling.

The core of the VAE is structured into three main components: an encoder, a decoder, and a property predictor. The encoder compresses the input features into a latent space, capturing essential information in a reduced dimensionality. The decoder attempts to reconstruct the input data from this latent representation, ensuring the model learns a meaningful encoding of the data. Concurrently, the property predictor estimates physical properties such as melting points from the latent space, adding a layer of functional prediction to the model. The model is trained using a loss function that combines errors from both reconstruction and property prediction, optimizing the model to balance between accurate SMILES reconstruction and reliable property estimation.

The reverse model plays a crucial role in generating new SMILES strings. It is designed to take numerical feature representations and predict the corresponding SMILES sequences. Without the reverse model, the latent space representations could not be converted back into SMILES strings, which are essential for understanding and validating the chemical structures. The reverse model bridges the gap between abstract numerical features and concrete chemical

representations. The reverse model is then trained with these augmented features. The model architecture includes dense layers, bidirectional LSTM layers, and dropout for regularization.^{239–241} It is compiled with a focal loss function to handle class imbalance and improve accuracy.^{242–244}

Next, the VAE undergoes fine-tuning with a dataset specific to zinc electrochemical applications and zinc batteries.²⁴⁵ This step adjusts the encoder and decoder to better represent and generate SMILES for zinc ILs, enhancing their applicability to this domain. With the fine-tuned model, new SMILES strings are generated using two techniques: interpolation between known latent vectors to discover intermediate chemical structures, and the addition of Gaussian or Laplacian noise to explore nearby chemical space, potentially leading to viable ILs for zinc batteries. During the generation phase, latent vectors are sampled or interpolated to produce new numerical feature representations. These features are fed into the reverse model, which predicts the corresponding SMILES sequences.

The last step involves validating these newly generated SMILES strings using cheminformatics tools such as RDKit library to ensure their chemical validity and plausibility. This validation confirms that the generated structures are chemically sound and potentially synthesizable.

In analyzing multiple datasets related to ionic liquids, the diversity of compositions is evident through the number of unique cations and anions. Dataset 1, the most extensive, includes 2,129 unique cations and 325 unique anions, indicating a broad chemical space covered, suitable for exploring a wide range of properties and applications of ionic liquids. In contrast, dataset 2, while smaller, contains 242 unique cations and 87 unique anions, aimed at specific ionic liquids with reported melting point and decomposition temperature. The third dataset is smaller, featuring only 15 unique cations and anions each, pointing to a targeted study focusing on zinc electrochemical applications.

Figures 34a-d depict the data distribution and key characteristics of datasets 1 and 2, including the melting points and decomposition temperatures of ionic liquids. **Figures 34a and 34c** illustrate the actual melting points and decomposition temperatures for the ionic liquids in

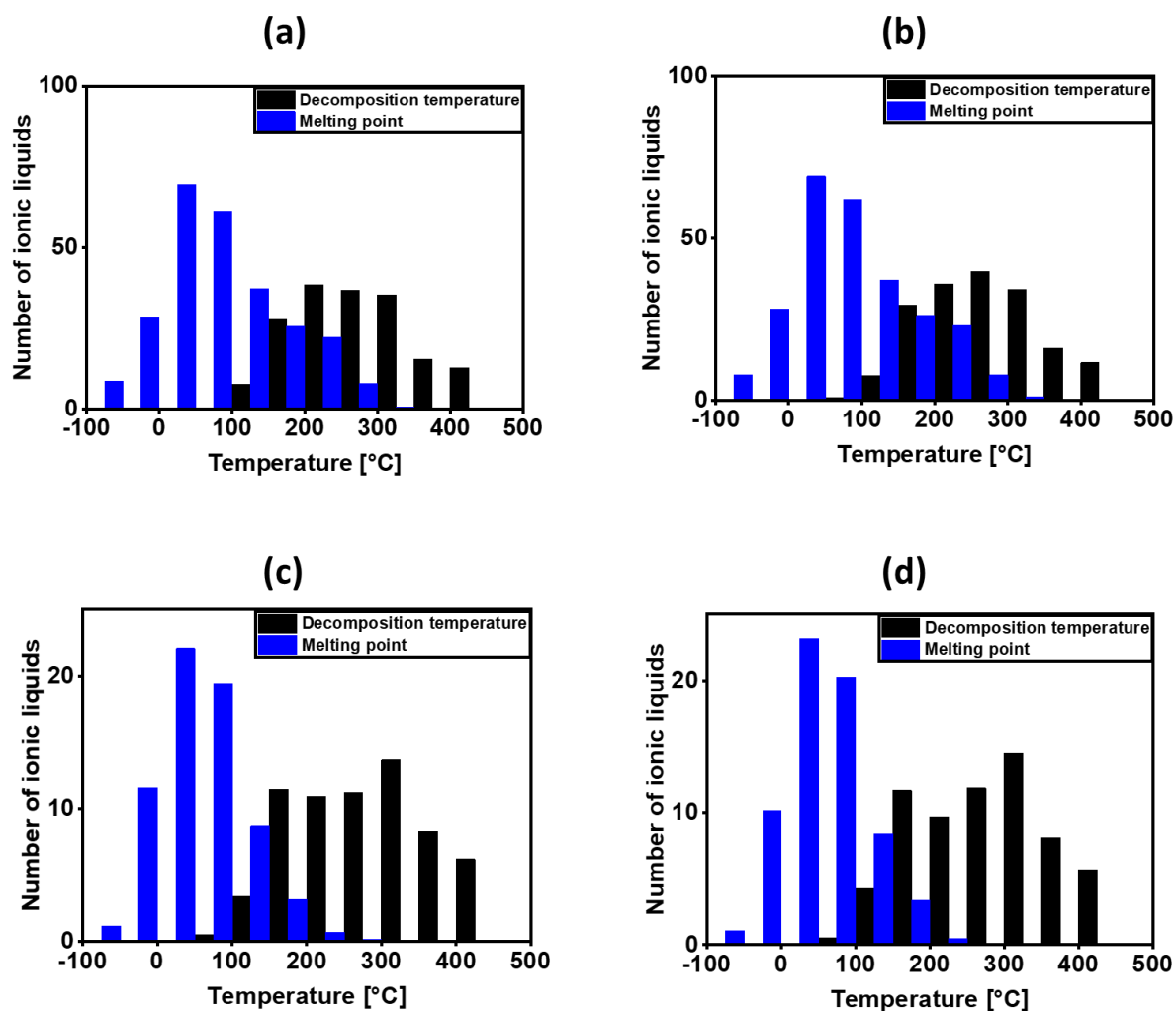


Figure 34: Comparison of experimental versus predicted melting points and decomposition temperatures of ionic liquids for datasets 1 and 2. Parts a and c display the actual melting points and decomposition temperatures for the ionic liquids in these datasets, respectively. Parts b and d show the predicted values for these thermal properties on the test sets, derived using a generative modeling approach, respectively.

these datasets. **Figures 34b and 34d** present the predicted values for these thermal properties on the test sets, calculated using the generative modeling approach. The consistency between the observed and predicted values showcased in these charts underscores the accuracy in simulating the thermal behavior of these compounds. This alignment not only validates the effectiveness but also provides deep insights into the thermal stability and behavior of the ionic liquids, which are essential for assessing their practical applications.

Figure 35 provides a comprehensive visualization of the thermal properties of the most prevalent cation and anion types in dataset 2. **Panels a and c** highlight the range of melting points observed, suggesting variability in ionic liquid stability and potential applications based on temperature thresholds. Similarly, **panels b and d** detail the decomposition temperatures, crucial for understanding the thermal limits of these substances. This data is instrumental in identifying which ionic liquids may be suited for high-temperature applications or require stabilization measures under thermal stress.

The performance metrics summarized in **Table 4** reflect the accuracy of the variational autoencoder model in predicting the melting point and decomposition temperature for datasets 1 and 2. Analyzing the mean squared error (MSE) and the coefficient of determination (R^2) values offers insights into the predictive accuracy of the model on the test sets.^{246,247}

For dataset 1, the MSE for melting point prediction is 79.9586, with a corresponding R^2 value of 0.9884, indicating that the model explains approximately 98.84 % of the variance in the melting point data. The decomposition temperature predictions show a similarly prominent level of accuracy, with an MSE of 76.7548 and an R^2 value of 0.9880, suggesting that the model accounts for about 98.80 % of the variance in the decomposition temperature data.

Dataset 2 demonstrates impressive performance as well, particularly in the prediction of decomposition temperature. The MSE for melting point prediction stands at 65.4463, with an R^2 of 0.9805, reflecting that the model captures 98.05 % of the variance. The decomposition temperature predictions are also precise, with an MSE of 60.5056 and a remarkable R^2 of 0.9921, indicating that the model explains nearly 99.21 % of the variance in these measurements. These high R^2 values across both datasets confirm the robust predictive capability, as supported by **Figure 34**.

The predicted values displayed in **Figure 36** provide predictive insights into the properties of the ionic liquids studied in dataset 3. This analysis employs predictive modeling to connect experimental observations with theoretical results. **Figure 36a** uses predictive modeling to estimate these properties, enabling valuable comparisons between dataset 3 predictions and established data from the other two datasets. The models utilize features derived from the

chemical structures of the cations and anions to predict how new or less-studied ionic liquids

Table 4: Summary of Performance Metrics for Property Prediction in Dataset 1 and Dataset 2

	Melting point		Decomposition temperature	
	Test set MSE	Test set R ²	Test set MSE	Test set R ²
Dataset 1	79.9586	0.9884	76.7548	0.9880
Dataset 2	65.4463	0.9805	60.5056	0.9921

might behave under similar conditions. Dataset 3 favors ionic liquids with low melting points and high decomposition temperatures compared to the general data of ionic liquids in datasets 1 and 2. This preference for low melting points facilitates their use in practical applications without the need for much heating. High decomposition temperatures contribute to the thermal stability of the ionic liquids, making them suitable for use in devices that may experience occasional temperature spikes.

The scatter plot in **Figure 36b** illustrates the relationship between predicted and actual values for melting points and decomposition temperatures of different ionic liquids used in zinc electrochemical systems and zinc batteries. Each point on the plot represents an ionic liquid, with its position determined by the predicted and actual thermal properties. The diagonal line represents perfect prediction accuracy. This plot helps assess the accuracy of predictive models used in ionic liquid research. The plot demonstrates that the trained model has high accuracy in predicting the thermal properties of ionic liquids. The high accuracy of the model underscores its reliability and effectiveness in predicting ionic liquid properties.

Figure 36c shows the frequency of different cation types found in zinc electrochemical systems and zinc battery ionic liquids. The most common cations identified are imidazolium, pyrrolidinium, and phosphonium. Imidazolium-based ionic liquids are popular because they offer high thermal stability, good ionic conductivity, and low volatility, making them suitable for high-temperature applications and enhancing the safety of zinc electrochemical systems.^{248,249} Pyrrolidinium ionic liquids are favored for their electrochemical stability and low viscosity, which contribute to better ion mobility and overall zinc electrochemical systems efficiency.^{107,250} Phosphonium-based ionic liquids are known for their excellent chemical stability and resistance to hydrolysis, which is crucial for maintaining long-term

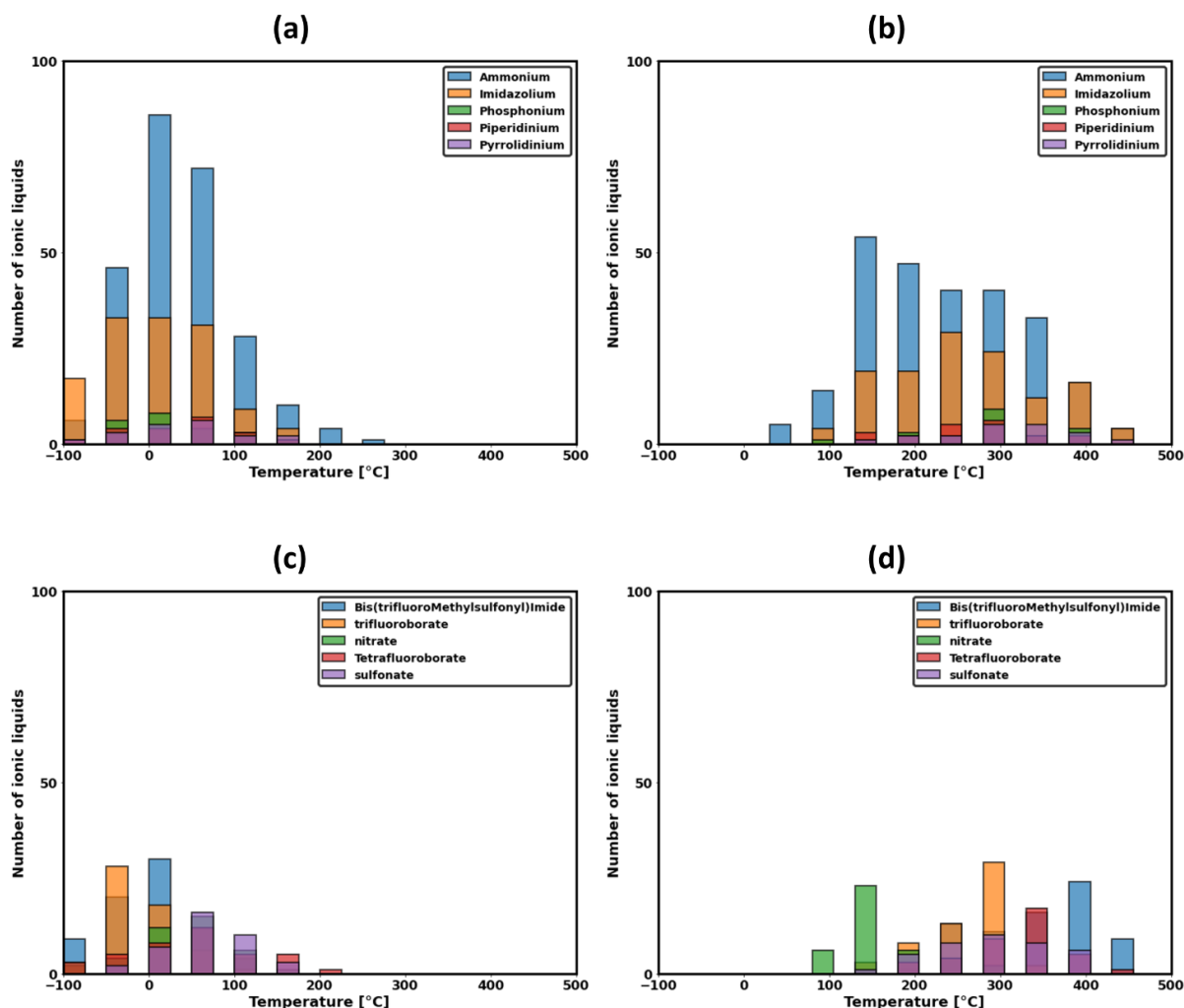


Figure 35: Thermal property distributions by cation and anion types in dataset 2. Distribution of melting points (a, c) and decomposition temperatures (b, d) for the five most frequent cation and anion types in ionic liquids of dataset 2. These bar charts illustrate the variation and frequency of melting points and decomposition temperatures across selected anions and cations, providing insights into their thermal stability characteristics. ^{107,109,250} Understanding the prevalence of these cation types helps researchers optimize ionic liquid formulations for enhanced zinc battery performance and guides future research efforts to explore new cation types that might offer additional benefits.

The histogram in **Figure 36d** presents the distribution of various anion types used in zinc electrochemical system and zinc battery ionic liquids. There is a wider variety of anions

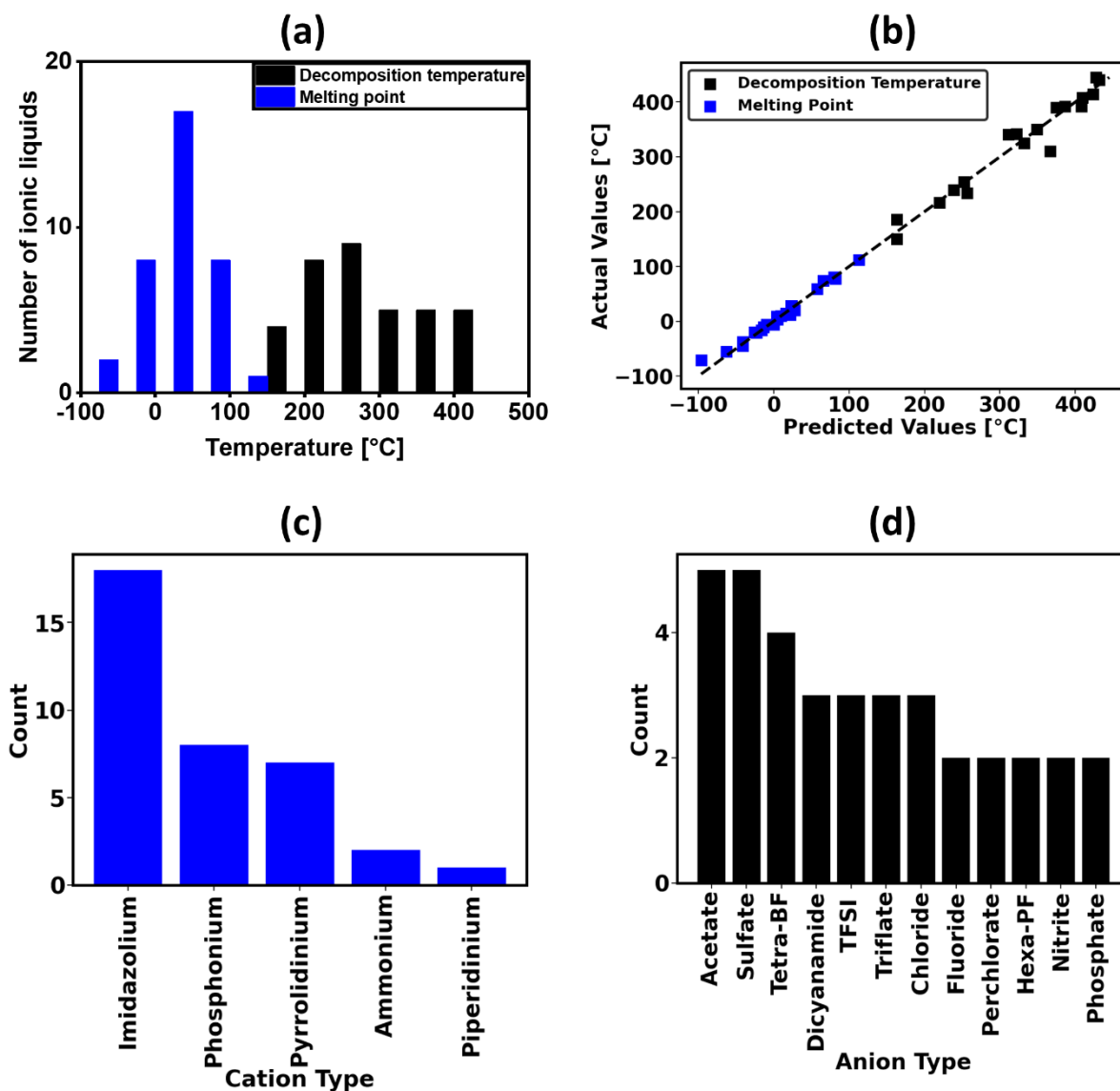


Figure 36: Property and composition summary for dataset 3 ILs. a) Histogram of melting points and decomposition temperature predictions in dataset 3. b) Scatter Plot of predicted vs. actual melting points and decomposition temperatures for diverse types of ILs used in zinc batteries. c) Histogram of cation types: This histogram displays the frequency of different cation types found in zinc battery ionic liquids. d) Histogram of anion types: This histogram presents the distribution of various anion types used in zinc battery ionic liquids.

compared to cations, primarily because anions can significantly influence the solubility, stability, and overall ionic conductivity of the ionic liquids.²⁵¹ The most common anions

identified in the study include sulfate, acetate, tetrafluoroborate (BF_4^-), bis(trifluoromethanesulfonyl)imide (TFSI), triflate, dicyanamide, and chloride. These anions are favored for their specific properties that enhance the performance and stability of ionic liquids in zinc electrochemical systems.

Sulfate anions are among the most frequently used due to their cost-effectiveness and ability to enhance the electrochemical stability of ionic liquids.^{221,224,235} Acetate anions are also commonly utilized for their good ionic conductivity and low toxicity. They help maintain a stable electrochemical environment and contribute to the overall efficiency of zinc electrochemical systems.^{223,249,252} Tetrafluoroborate (BF_4^-) anions are popular due to their excellent electrochemical properties and stability. They are known for their high ionic conductivity and ability to form stable ionic liquids with various cations, which is crucial for the efficient operation of zinc electrochemical systems.^{109,249} These anions are often used in applications that require high performance and reliability, such as zinc batteries, due to their ability to maintain a stable electrochemical environment under various conditions.^{221,230,253–255}

In addition to these anions, TFSI, triflate, dicyanamide, and chloride anions are also widely used. TFSI is favored for its high stability, contributing to low viscosity and high ionic conductivity in ionic liquids.^{248,256} Triflate anions are known for their thermal stability and capacity to form stable ionic liquids, while chloride anions are appreciated for their straightforward chemical structure and effective performance in forming ionic liquids with various cations.^{118,119,254,255,257,258} Understanding the distribution of these anion types in the literature is valuable for researchers aiming to optimize ionic liquid formulations for zinc batteries. The histogram not only highlights the most used anions but also suggests potential areas for further exploration.

Several criteria are applied in selecting suitable ionic liquids for zinc batteries. Ionic liquids with melting points lower than room temperature are prioritized to ensure they remain liquid under standard conditions. Lower viscosity is also preferable to enhance ion mobility, with ideal viscosities ranging from 10 to 100 $\text{mPa}\cdot\text{S}$. For example, certain ionic liquids maintain viscosities around 110 $\text{mPa}\cdot\text{S}$ with conductivities of 3 mS cm^{-1} at 30 °C.^{107,225} At higher temperatures such as 200 °C or 300 °C, ionic liquid conductivity can range from 5 to 50 mS

cm^{-1} , and viscosities typically drop to around 10-20 $\text{mPa}\cdot\text{S}$, enhancing ion transport.^{107,108,118,254,258}

For room temperature ionic liquids, their melting points are ideally below room temperature to ensure they remain liquid during operation. Therefore, those meeting all conditions of conductivity, viscosity, melting point, and decomposition temperature are prioritized to ensure optimal performance and stability for potential applications in zinc batteries. This approach ensures the selection of ionic liquids that not only meet the current requirements but also provide robustness and efficiency under elevated temperatures, making them ideal for advanced zinc battery technologies.

Figure 37 illustrates the essential properties of newly synthesized ionic liquids relevant to their application in zinc batteries. **Figure 37a** displays the thermal properties of the ionic liquids, focusing on their melting points and decomposition temperatures. The blue line indicates the melting points, while the black line shows the decomposition temperatures. Understanding these thermal properties is vital for assessing the stability and usability of ionic liquids under operational conditions. Ionic liquids with lower melting points remain liquid at room temperature, which is beneficial for battery applications. Additionally, higher decomposition temperatures indicate better thermal stability, reducing the risk of degradation at elevated temperatures.

Figure 37b depicts the variations in viscosity and conductivity across different ionic liquids. The blue line represents viscosity, while the black line represents conductivity. These plots help identify ionic liquids with high conductivity and low viscosity, which are optimal conditions for efficient ion transport and enhanced battery performance. This mapping is crucial for selecting ionic liquids that can maintain desirable properties across a range of temperatures, thus ensuring reliable operation in zinc battery applications. This comprehensive analysis of ionic liquid properties supports the development of efficient and stable zinc batteries.

Based on the criteria for selecting suitable ionic liquids for zinc batteries, 15 promising ionic liquids were identified and summarized in **Table 5**. The selection criteria prioritized ionic liquids

Table 5: Suggested ionic liquids for zinc batteries: This table lists 15 ionic liquids chosen for their low melting points, ideal viscosities, and high conductivities. Some are validated by existing zinc battery use and literature; others are proposed based on their promising properties.

Cation	Anion	Ref.
CCCC[N ⁺]1(C)CCCC1	FC(S(=O)(=O)[N ⁻]S(=O)(=O)C(F)(F)F)(F)F	259
CC[n ⁺]1ccn(c1)C	FC(S(=O)(=O)[N ⁻]S(=O)(=O)C(F)(F)F)(F)F	
CC[n ⁺]1ccn(c1)C	C(#N)[N ⁻]C#N	253
CC[n ⁺]1ccn(c1)C	C(C)OS(=O)(=O)[O ⁻]	224
CC[n ⁺]1ccn(c1)C	FC(S(=O)(=O)[O ⁻])(F)F	260
CC[n ⁺]1ccn(c1)C	C(C)(=O)[O ⁻]	223
CCCC[n ⁺]1ccn(c1)C	FC(S(=O)(=O)[N ⁻]S(=O)(=O)C(F)(F)F)(F)F	
CCCC[n ⁺]1ccn(c1)C	C(#N)[N ⁻]C#N	
CCCC[n ⁺]1ccn(c1)C	C(C)(=O)[O ⁻]	221
CCC[N ⁺]1(C)CCCC1	FC(S(=O)(=O)[N ⁻]S(=O)(=O)C(F)(F)F)(F)F	
CCCC[n ⁺]1ccn(c1)C	[I ⁻]	
CCC[n ⁺]1ccn(c1)C	F[B ⁻](F)(F)F	
CCC[n ⁺]1ccn(c1)C	FC(S(=O)(=O)[N ⁻]S(=O)(=O)C(F)(F)F)(F)F	
CCCCCC[n ⁺]1ccn(c1)C	FC(S(=O)(=O)[N ⁻]S(=O)(=O)C(F)(F)F)(F)F	
CCCCCCCC[n ⁺]1ccn(c1)C	F[P ⁻](F)(F)(F)(F)F	

with melting points below room temperature, viscosities between 10 to 100 mPa·S, and conductivities ranging from 5 to 50 mS/cm at higher temperatures, such as 200 °C or 300 °C. At these elevated temperatures, the viscosities typically drop to around 10-20 mPa·S. Among the 15 selected ionic liquids, some are already being used in zinc systems, and the effectiveness is supported by literature citations included in **Table 5**. This approach, drawing from the predictive and generative model as well as existing empirical data, ensures that the selected ionic liquids are robust and efficient for advanced zinc battery technologies. For those ionic liquids that are not yet commonly used in zinc systems, their properties, such as melting point, decomposition temperature, conductivity, and viscosity, suggest they have potential applications in zinc electrochemical cells. This comprehensive analysis validates the existing ionic liquids in use and opens possibilities for new ionic liquids to enhance the performance and stability of zinc batteries, providing a pathway for further research and development. This thorough evaluation aligns with the existing body of research, indicating that some of the selected ionic liquids should meet the demands of zinc battery applications, thus contributing to advancements in energy storage technologies.

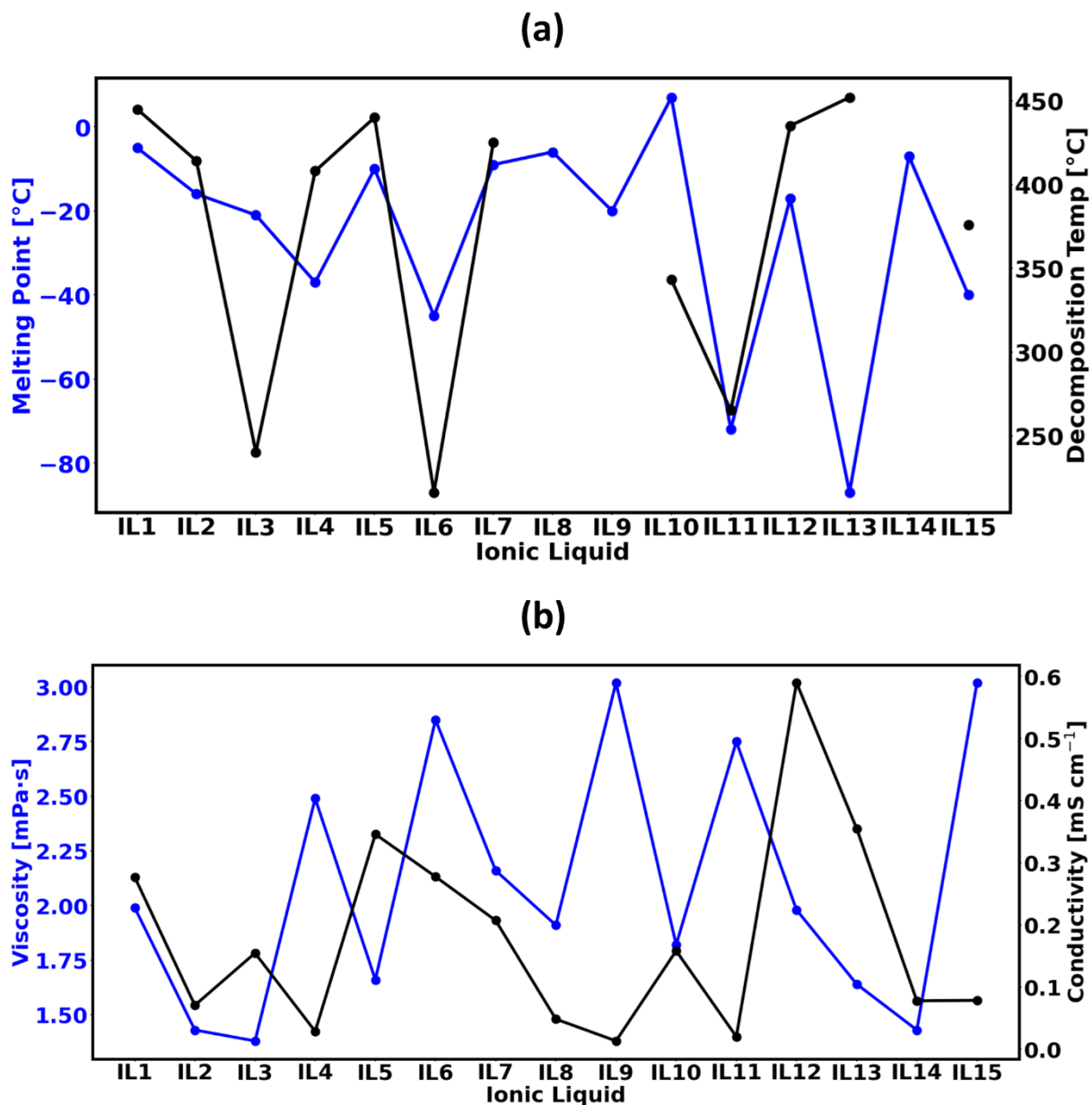


Figure 37: Evaluation of newly generated ILs for zinc battery use. (a) Melting point and Decomposition Temperature: Melting points (blue) and decomposition temperatures (black) of newly selected ionic liquids, showing the thermal stability of generated ionic liquids for zinc battery use. (b) Viscosity and Conductivity: Viscosity (blue) and conductivity (black) variations across newly selected ionic liquids, highlighting optimal conditions for zinc battery applications.

6.3 Conclusions

In this chapter, advanced machine learning models were developed to predict the properties of ionic liquids for zinc electrochemical applications, with a particular focus on their melting points and decomposition temperatures. By utilizing a combination of convolutional neural networks and generative adversarial networks, predictive accuracy for these critical properties was successfully enhanced, which are essential for the practical application of ILs in zinc batteries.

The models were trained on extensive datasets of IL properties and fine-tuned specifically for zinc-based systems, enabling the generation of anion and cation combinations that meet the requirements for zinc battery electrolytes. This approach demonstrated the ability to bridge the gap between theoretical predictions and experimental validation. The integration of variational autoencoders with property prediction networks allowed for the generation of new SMILES strings. These newly generated ILs were validated for their stability and potential applicability in zinc batteries.

Our analysis of the datasets revealed the significant diversity in the cation and anion compositions of ILs. Dataset 1 included 2,129 unique cations and 325 unique anions, providing a broad chemical space for exploration. Dataset 2 contained 242 unique cations and 87 unique anions, aimed at specific ionic liquids with reported melting points and decomposition temperatures. Dataset 3 featured 15 unique cations and 15 unique anions, focusing on zinc electrochemical applications.

The performance metrics for the models showed high predictive accuracy. For dataset 1, the mean squared error for melting point prediction was 79.9586, with a corresponding R^2 value of 0.9884, indicating that the model explains approximately 98.84 % of the variance in the melting point data. The decomposition temperature predictions for dataset 1 had an MSE of 76.7548 and an R^2 value of 0.9880, suggesting that the model accounts for about 98.80 % of the variance. For dataset 2, the MSE for melting point prediction was 65.4463, with an R^2 of 0.9805, while the decomposition temperature predictions had an MSE of 60.5056 and a remarkable R^2 of 0.9921, indicating that the model explains nearly 99.21 % of the variance in these measurements.

The data distribution and key characteristics of datasets 1 and 2, including the melting points and decomposition temperatures of ionic liquids, were illustrated. The consistency between the observed and predicted values underscored the accuracy in simulating the thermal behavior of these compounds. The predicted values provided predictive insights into the properties of the ionic liquids studied in dataset 3. This analysis employed predictive modeling to connect experimental observations with theoretical results. Dataset 3 favored ionic liquids with low melting points and high decomposition temperatures compared to the general data from datasets 1 and 2.

Based on the criteria for selecting suitable ionic liquids for zinc batteries, 15 promising ionic liquids were identified. The selection criteria prioritized ionic liquids with melting points below room temperature, viscosities between 10 to 100 mPa·S, and conductivities ranging from 5 to 50 mS cm⁻¹ at higher temperatures, such as 200 °C or 300 °C. At these elevated temperatures, the viscosities typically drop to around 10-20 mPa·S. Among the 15 selected ionic liquids, some are already being used in zinc systems, and their effectiveness is supported by literature citations. For those ionic liquids not yet commonly used in zinc systems, their properties such as melting point, decomposition temperature, conductivity, and viscosity suggest potential applications in zinc electrochemical cells.

This comprehensive analysis validates the existing ionic liquids in use and opens possibilities for new ionic liquids to enhance the performance and stability of zinc batteries. This thorough evaluation aligns with the existing body of research, indicating that some of the selected ionic liquids should meet the demands of zinc battery applications, thus contributing to advancements in energy storage technologies.

Chapter 7: Conclusion and Future Works

7.1 Conclusions

This work explores four critical areas of energy storage and battery technology, delivering impactful discoveries that enhance scientific understanding.

7.1.1 Electrolyte Advancements for Zinc-Oxygen Batteries

The development of liquid electrolytes based on $\text{Zn}(\text{TFSI})_2\text{-H}_2\text{O}$ for use in zinc-based batteries has been explored. These electrolytes, which vary in water content, play a vital role in the operation of both zinc–zinc and zinc–oxygen cells. By precisely adjusting humidity during their preparation, the electrolyte mass was controlled, and the melting point was tuned over a broad range from 139 °C down to –35 °C. The experimental results demonstrated strong performance, particularly with the $\text{Zn}(\text{TFSI})_2\cdot 8\text{H}_2\text{O}$ and $\text{Zn}(\text{TFSI})_2\cdot 18\text{H}_2\text{O}$ formulations. These versions showed effective operation at elevated and sub-zero temperatures, specifically 80 °C and –15 °C. Among the configurations tested, the zinc-oxygen cell using $\text{Zn}(\text{TFSI})_2\cdot 8\text{H}_2\text{O}$ at a moderate temperature outperformed those employing more dilute $\text{Zn}(\text{TFSI})_2$ electrolytes.

Comprehensive characterization, including discharge product studies and Online Electrochemical Mass Spectrometry, provided a deeper understanding of gas evolution during cycling—especially the release of hydrogen and oxygen during the charging phase. The research also drew connections between electrochemical behavior and structural transformations, such as the morphological evolution of hexagonal ZnO nanosheets during battery use. One notable discovery was that complete consumption of ZnO in the system led to a sharp increase in hydrogen generation. This phenomenon was found to depend significantly on both the electrode composition and the hydration level of the electrolyte. These insights underline the importance of optimizing water content to enhance the energy storage performance of rechargeable zinc batteries.

7.1.2 Temperature Impact on Zinc-ion Batteries

Chapter 4 highlights the crucial influence of temperature on zinc deposition behavior and the electrochemical performance of zinc metal anodes. Through a series of electrochemical tests using zinc chloride-based hydrated electrolytes with varying hydration levels ($n = 10, 2.33, \text{ and } 1.5$), the study examined performance across operating temperatures of –10 °C, 25 °C, and 40 °C. These outcomes were compared to those from a conventional dilute aqueous ZnCl_2 electrolyte (1 M) system.

The experiments demonstrated that zinc half-cells (both Zn/Cu and Zn/Zn) using moderately hydrated electrolytes outperformed those using the 1 M ZnCl₂ solution in terms of cycling stability and average coulombic efficiency. Among all conditions, the highest coulombic efficiency was observed at -10 °C. Surface analysis using ex-situ scanning electron microscopy revealed that zinc plated at lower temperatures formed smoother, denser layers. This morphology contributed to the improved electrochemical efficiency. In contrast, the zinc electrodes cycled in the 1 M ZnCl₂ electrolyte showed extensive surface cracking, whereas those in ZnCl₂·10H₂O at -10 °C retained better structural stability.

Further observations indicated that lower temperatures favored the formation of larger zinc nuclei with lower nucleation density on copper substrates. Full cells comprising Zn anodes, MHE electrolytes, and ZnHCF-NP cathodes delivered outstanding cycling performance at 40 °C, maintaining capacity over more than 1000 cycles and outperforming cells tested at cooler temperatures and in more hydrated electrolytes. Notably, the system achieved a specific capacity of 76.3 mAh g⁻¹ at 40 °C, exceeding the capacities recorded in both dilute aqueous and other MHE setups.

These results suggest that moderately elevated temperatures, such as 40 °C, offer a simple yet effective route to boost the performance of zinc-ion batteries. This temperature-tuning strategy may also be applicable to other rechargeable battery systems based on multivalent metals, offering a path to extend cycle life and improve efficiency. Overall, this chapter emphasizes temperature as a key design parameter in advancing zinc-based battery technologies and encourages further exploration of thermal optimization in broader energy storage systems.

7.1.3 Battery Lifetime Prediction Frameworks

Two distinct approaches were developed in chapter 4: one based on conventional machine learning methods and another utilizing deep learning. Both were designed to improve the early prediction of battery life.

The ML-based approach was structured into three main components: feature extraction, feature selection, and classification using ML algorithms. In this framework, A set of 312 features was engineered from degradation data recorded during the first 200 cycles (a period

when most cells exhibit little capacity loss). This setup was tested using two popular ensemble models, Random Forest and Gradient Boosting Decision Trees, on the selected features. Notably, even with input from only the first two cycles, the ensemble ML models reached an accuracy of 96.2 %. This increased to 98 % as more cycles were incorporated. A key factor behind this performance was the early variation in internal resistance. In addition, specific features related to the constant current-constant voltage (CC–CV) charging process proved especially useful, with six charge features (including timing aspects of CC and CV phases) having the highest impact.

In comparison, the deep learning framework, which relied on just four features automatically derived from the data, achieved even stronger results. It reached an average accuracy of 98.5 % using the first 100 cycles and further improved to 99.5 % when data from the first 200 cycles was used. When tested on two new datasets, the ML-based method successfully predicted the end-of-life for 90 % of the 39 batteries in one of the sets, while the deep learning model delivered perfect predictions for all batteries in the second dataset. Overall, for lithium-ion batteries under varied experimental conditions, the deep learning framework demonstrated superior performance.

However, the situation differed for zinc-ion batteries. The deep learning model, despite its success with lithium-ion cells, was less effective in predicting zinc-ion battery life. On the other hand, the traditional ML approach, built on manually selected features, performed well, successfully classifying the lifespan of zinc-ion batteries. This highlights the versatility of human-engineered features, which can be adjusted to suit different battery chemistries and operating conditions. In contrast, the deep learning features, being more tailored to lithium-ion behavior, did not generalize as effectively to other battery types.

Overall, this section emphasizes the promise of both traditional ML and deep learning methods in battery life prediction. The presented frameworks showed strong performance across diverse battery chemistries and testing protocols. These findings not only provide useful insights into battery degradation modeling but also offer a foundation for future developments in predictive battery diagnostics and advanced energy storage systems.

7.1.4 Accelerating Material Discovery for Zinc Battery Applications

Advanced machine learning models have been introduced to forecast the properties of ionic liquids tailored for zinc electrochemical systems, with particular emphasis on their melting points and decomposition temperatures. By combining convolutional neural networks with generative adversarial networks, improved accuracy was achieved in predicting these essential thermal properties, which play a key role in the practical integration of ILs into zinc batteries. The models were trained using comprehensive datasets that cover a wide range of IL characteristics and were then fine-tuned for systems based on zinc. This allowed the generation of new combinations of anions and cations suited for zinc battery electrolytes. These generated ILs were assessed for stability and their potential suitability in zinc-based electrochemical applications.

Through an in-depth analysis of the datasets, a considerable variety in the structures of both cations and anions was observed. Dataset 1 contained 2129 unique cations and 325 unique anions, offering a vast space for exploration. Dataset 2 was more specific, consisting of 242 unique cations and 87 unique anions, chosen for their reported melting and decomposition data. Dataset 3 was focused on zinc-related ILs, comprising 15 unique cations and 15 unique anions.

The models achieved high performance metrics. For dataset 1, the mean squared error for melting point prediction was 79.96, with an R^2 score of 0.9884, indicating that about 98.84 % of the variance in the data was captured by the model. For decomposition temperature prediction, the model yielded an MSE of 76.75 and an R^2 of 0.9880. Dataset 2 showed even better results, with melting point prediction reaching an MSE of 65.45 and an R^2 of 0.9805. For decomposition temperature, the MSE was 60.51 with an outstanding R^2 of 0.9921, capturing nearly 99.21 % of the variance.

The distributions of key features in Datasets 1 and 2, such as melting and decomposition temperatures, were visualized and analyzed. The strong agreement between predicted and actual values reinforced the reliability of the developed models in simulating the thermal characteristics of ILs. These models were also applied to dataset 3, offering predictive insights into ILs intended for zinc applications. Compared to datasets 1 and 2, dataset 3 favored ILs with lower melting points and higher decomposition temperatures.

To identify optimal ILs for zinc batteries, 15 candidates were selected based on specific performance criteria. These included melting points below ambient temperature, viscosities between 10 and 100 mPa·s, and ionic conductivities in the 5-50 mS·cm⁻¹ range at elevated temperatures (e.g., 200-300 °C), where viscosities tend to drop to around 10-20 mPa·s. Among these 15 ILs, several are already known for use in zinc systems, with supporting literature available. Others, while not yet widely applied in zinc batteries, exhibit favorable physical and electrochemical properties suggesting promising applicability.

This detailed evaluation affirms the suitability of several currently used ILs while also highlighting new candidates that could advance the performance and durability of zinc-based batteries. The findings align with existing research trends and underscore the potential of data-driven methods in guiding electrolyte design for next-generation energy storage.

7.2 Future Works

This research lays the foundation for an expansive array of future works to contribute to the evolution of energy storage systems.

7.2.1 Electrolyte System Refinement

Investigation of hydration levels in Zn(TFSI)₂-based molten electrolytes, aiming for precise tuning of melting points and mass loading for enhanced control and performance. Finding cost-effective substitutes for Zn(TFSI)₂ is also crucial for zinc-oxygen systems.

7.2.2 Temperature-Dependent Electrolyte Systems

Optimize the electrochemical performance of zinc metal anodes by investigating the effects of temperature and examining its broader applicability to other multivalent metal-based rechargeable batteries.

7.2.3 Battery Lifetime Prediction Framework Refinement

Further refine the adaptability of ML and deep learning frameworks to diverse battery types and chemistries to enhance the accuracy of predictions.

7.2.4 Experimental Validation of ILs

Future research should synthesize and experimentally evaluate the newly discovered ILs to validate their application in zinc batteries. Additionally, expanding datasets, exploring ILs

space, and applying these methods to other battery technologies will further advance efficient energy storage solutions.

References

1. Scrosati, B. & Garche, J. Lithium batteries: Status, prospects and future. *Journal of Power Sources* vol. 195 2419–2430 (2010).
2. Winter, M. & Brodd, R. J. What are batteries, fuel cells, and supercapacitors? *Chem. Rev.* **104**, 4245–4269 (2004).
3. Daniel, C. & Besenhard, J. O. *Handbook of battery materials: Second, completely revised and enlarged edition. Handbook of Battery Materials: Second, Completely Revised and Enlarged Edition* (2011). doi:10.1002/9783527637188.
4. Tarascon, J. M. & Armand, M. Issues and challenges facing rechargeable lithium batteries. *Nature* vol. 414 359–367 (2001).
5. S. Rangarajan, S. *et al.* Lithium-Ion Batteries—The Crux of Electric Vehicles with Opportunities and Challenges. *Clean Technologies* vol. 4 908–930 (2022).
6. Choi, N. S. *et al.* Challenges facing lithium batteries and electrical double-layer capacitors. *Angewandte Chemie - International Edition* vol. 51 9994–10024 (2012).
7. Scrosati, B. & Garche, J. Lithium batteries: Status, prospects and future. *J. Power Sources* **195**, 2419–2430 (2010).
8. Nykvist, B. & Nilsson, M. Rapidly falling costs of battery packs for electric vehicles. *Nat. Clim. Chang.* **5**, 329–332 (2015).
9. Tarascon, J. M. Is lithium the new gold? *Nature Chemistry* vol. 2 510 (2010).
10. Lander, L. *et al.* Cost and carbon footprint reduction of electric vehicle lithium-ion batteries through efficient thermal management. *Appl. Energy* **289**, (2021).
11. Mohammadi, F. & Saif, M. A comprehensive overview of electric vehicle batteries market. *e-Prime - Advances in Electrical Engineering, Electronics and Energy* vol. 3 (2023).
12. Notter, D. A. *et al.* Contribution of Li-ion batteries to the environmental impact of electric vehicles. *Environ. Sci. Technol.* **44**, 6550–6556 (2010).
13. Cusenza, M. A., Bobba, S., Ardente, F., Cellura, M. & Di Persio, F. Energy and environmental assessment of a traction lithium-ion battery pack for plug-in hybrid electric vehicles. *J. Clean. Prod.* **215**, 634–649 (2019).
14. Liu, Y., Guo, B., Zou, X., Li, Y. & Shi, S. Machine learning assisted materials design and discovery for rechargeable batteries. *Energy Storage Materials* vol. 31 434–450 (2020).

15. Ng, M. F., Sun, Y. & Seh, Z. W. Machine learning-inspired battery material innovation. *Energy Advances* vol. 2 449–464 (2023).
16. Mao, J., Miao, J., Lu, Y. & Tong, Z. Machine learning of materials design and state prediction for lithium ion batteries. *Chinese Journal of Chemical Engineering* vol. 37 1–11 (2021).
17. Wang, N. *et al.* A review of zinc-based battery from alkaline to acid. *Materials Today Advances* vol. 11 (2021).
18. Mainar, A. R. *et al.* An overview of progress in electrolytes for secondary zinc-air batteries and other storage systems based on zinc. *J. Energy Storage* **15**, 304–328 (2018).
19. Worku, A. K. Engineering techniques to dendrite free Zinc-based rechargeable batteries. *Frontiers in Chemistry* vol. 10 (2022).
20. Fang, G., Zhou, J., Pan, A. & Liang, S. Recent advances in aqueous zinc-ion batteries. *ACS Energy Lett.* **3**, 2480–2501 (2018).
21. Han, C., Li, W., Liu, H. K., Dou, S. & Wang, J. Principals and strategies for constructing a highly reversible zinc metal anode in aqueous batteries. *Nano Energy* vol. 74 (2020).
22. Li, Y. *et al.* Designing Advanced Aqueous Zinc-Ion Batteries: Principles, Strategies, and Perspectives. *Energy and Environmental Materials* vol. 5 823–851 (2022).
23. Li, C., Xie, X., Liang, S. & Zhou, J. Issues and Future Perspective on Zinc Metal Anode for Rechargeable Aqueous Zinc-ion Batteries. *Energy and Environmental Materials* vol. 3 146–159 (2020).
24. Ming, J., Guo, J., Xia, C., Wang, W. & Alshareef, H. N. Zinc-ion batteries: Materials, mechanisms, and applications. *Materials Science and Engineering R: Reports* vol. 135 58–84 (2019).
25. Ma, L. *et al.* Realizing high zinc reversibility in rechargeable batteries. *Nat. Energy* **5**, 743–749 (2020).
26. Wang, Z. *et al.* A Metal-Organic Framework Host for Highly Reversible Dendrite-free Zinc Metal Anodes. *Joule* **3**, 1289–1300 (2019).
27. Zhang, Q., Luan, J., Tang, Y., Ji, X. & Wang, H. Interfacial Design of Dendrite-Free Zinc Anodes for Aqueous Zinc-Ion Batteries. *Angewandte Chemie - International Edition* vol. 59 13180–13191 (2020).
28. Li, C., Wang, H. & Li, X. Strategies to inhibition the dendrites of the anode in zinc ion batteries. *Int. J. Electrochem. Sci.* **17**, (2022).
29. Wu, Y. *et al.* Solar-driven self-powered alkaline seawater electrolysis via multifunctional

- earth-abundant heterostructures. *Chem. Eng. J.* **411**, (2021).
30. Daniel-Ivad, J. Zinc as versatile battery material for energy storage applications. *Metall* **76**, 84–88 (2022).
 31. Li, H. *et al.* Advanced rechargeable zinc-based batteries: Recent progress and future perspectives. *Nano Energy* vol. 62 550–587 (2019).
 32. Mo, F. *et al.* Recent Progress and Challenges of Flexible Zn-Based Batteries with Polymer Electrolyte. *Batteries* vol. 8 (2022).
 33. Wang, R. Y., Wessells, C. D., Huggins, R. A. & Cui, Y. Highly reversible open framework nanoscale electrodes for divalent ion batteries. *Nano Lett.* **13**, 5748–5752 (2013).
 34. Guo, S. *et al.* Fundamentals and perspectives of electrolyte additives for aqueous zinc-ion batteries. *Energy Storage Materials* vol. 34 545–562 (2021).
 35. Han, D. *et al.* A Self-Regulated Interface toward Highly Reversible Aqueous Zinc Batteries. *Adv. Energy Mater.* **12**, (2022).
 36. Liu, C., Chi, X., Yang, C. & Liu, Y. High-Voltage Aqueous Zinc Batteries Achieved by Tri-functional Metallic Bipolar Electrodes. *Energy Environ. Mater.* **6**, (2023).
 37. Zhai, C. *et al.* Electrolyte Additive Strategies for Suppression of Zinc Dendrites in Aqueous Zinc-Ion Batteries. *Batteries* vol. 8 (2022).
 38. Xu, W., Cui, X., Xie, Z. & Wang, Y. Reversible Aqueous Zinc Battery Using Molybdenum-Based Intercalation Cathode. *ECS Meet. Abstr.* **MA2017-01**, 50–50 (2017).
 39. Shi, H.-Y., Ye, Y.-J., Liu, K., Song, Y. & Sun, X. A Self-Doped Polyaniline Cathode for Rechargeable Aqueous Zinc Batteries. *ECS Meet. Abstr.* **MA2019-04**, 227–227 (2019).
 40. Kundu, D., Adams, B. D., Duffort, V., Vajargah, S. H. & Nazar, L. F. A high-capacity and long-life aqueous rechargeable zinc battery using a metal oxide intercalation cathode. *Nat. Energy* **1**, (2016).
 41. Li, G. *et al.* Developing Cathode Materials for Aqueous Zinc Ion Batteries: Challenges and Practical Prospects. *Advanced Functional Materials* vol. 34 (2024).
 42. Tribbia, M., Zampardi, G. & La Mantia, F. Towards the commercialization of rechargeable aqueous zinc ion batteries: The challenge of the zinc electrodeposition at the anode. *Current Opinion in Electrochemistry* vol. 38 (2023).
 43. Yan, J. *et al.* High-Voltage Zinc-Ion Batteries: Design Strategies and Challenges. *Advanced Functional Materials* vol. 31 (2021).
 44. Kundu, D. *et al.* Aqueous: Vs. nonaqueous Zn-ion batteries: Consequences of the desolvation

- penalty at the interface. *Energy Environ. Sci.* **11**, 881–892 (2018).
45. Li, C., Jin, S., Archer, L. A. & Nazar, L. F. Toward practical aqueous zinc-ion batteries for electrochemical energy storage. *Joule* vol. 6 1733–1738 (2022).
 46. Li, C. *et al.* Enabling selective zinc-ion intercalation by a eutectic electrolyte for practical anodeless zinc batteries. *Nat. Commun.* **14**, (2023).
 47. Li, C. *et al.* Highly reversible Zn anode with a practical areal capacity enabled by a sustainable electrolyte and superacid interfacial chemistry. *Joule* **6**, 1103–1120 (2022).
 48. Labbe, M., Cadien, K. & Ivey, D. G. Atomic Layer Deposition of Highly Stable Manganese-Iron Oxide Bifunctional Catalysts for Zinc-Air Batteries. *ECS Meet. Abstr.* **MA2022-01**, 457–457 (2022).
 49. Li, C. *et al.* Tuning the Solvation Structure in Aqueous Zinc Batteries to Maximize Zn-Ion Intercalation and Optimize Dendrite-Free Zinc Plating. *ACS Energy Lett.* **7**, 533–540 (2022).
 50. Shang, Y. & Kundu, D. A path forward for the translational development of aqueous zinc-ion batteries. *Joule* vol. 7 244–250 (2023).
 51. Hwang, B. J. *et al.* Intercalation of Zinc Monochloride Cations by Deep Eutectic Solvents for High-Performance Rechargeable Non-aqueous Zinc Ion Batteries. *ACS Appl. Mater. Interfaces* **14**, 7814–7825 (2022).
 52. Chae, M. S., Heo, J. W., Kwak, H. H., Lee, H. & Hong, S. T. Organic electrolyte-based rechargeable zinc-ion batteries using potassium nickel hexacyanoferrate as a cathode material. *J. Power Sources* **337**, 204–211 (2017).
 53. Dong, Y. *et al.* Non-concentrated aqueous electrolytes with organic solvent additives for stable zinc batteries. *Chem. Sci.* **12**, 5843–5852 (2021).
 54. Zhang, X. *et al.* Comprehensive review on zinc-ion battery anode: Challenges and strategies. *InfoMat* vol. 4 (2022).
 55. Al-Amin, M., Islam, S., Shibly, S. U. A. & Iffat, S. Comparative Review on the Aqueous Zinc-Ion Batteries (AZIBs) and Flexible Zinc-Ion Batteries (FZIBs). *Nanomaterials* vol. 12 (2022).
 56. Li, Y. & Dai, H. Recent advances in Zinc-air batteries. *Chem. Soc. Rev.* **43**, 5257–5275 (2014).
 57. Worku, A. K., Ayele, D. W. & Habtu, N. G. Recent advances and future perspectives in engineering of bifunctional electrocatalysts for rechargeable zinc–air batteries. *Materials Today Advances* vol. 9 (2021).

58. Jamesh, M. I., Moni, P., Prakash, A. S. & Harb, M. ORR/OER activity and zinc-air battery performance of various kinds of graphene-based air catalysts. *Mater. Sci. Energy Technol.* **4**, 1–22 (2021).
59. Li, Y. *et al.* Recent Advances in Flexible Zinc-Based Rechargeable Batteries. *Adv. Energy Mater.* **9**, (2019).
60. Liu, C., Xie, X., Lu, B., Zhou, J. & Liang, S. Electrolyte Strategies toward Better Zinc-Ion Batteries. *ACS Energy Lett.* **6**, 1015–1033 (2021).
61. Wu, J. *et al.* Carbon-based cathode materials for rechargeable zinc-air batteries: From current collectors to bifunctional integrated air electrodes. *Carbon Energy* vol. 2 370–386 (2020).
62. Fu, J. *et al.* Recent Progress in Electrically Rechargeable Zinc–Air Batteries. *Advanced Materials* vol. 31 (2019).
63. Yadav, S. K., Deckenbach, D. & Schneider, J. J. Secondary Zinc–Air Batteries: A View on Rechargeability Aspects. *Batteries* vol. 8 (2022).
64. Fu, J. *et al.* Electrically Rechargeable Zinc–Air Batteries: Progress, Challenges, and Perspectives. *Advanced Materials* vol. 29 (2017).
65. Liu, Q. *et al.* Advanced polymer-based electrolytes in zinc–air batteries. *eScience* **2**, 453–466 (2022).
66. Zhu, M. Cryogenic electrolytes and catalysts for zinc air batteries. *Nano Res. Energy* **2**, (2023).
67. Zhao, C. X. *et al.* Working Zinc–Air Batteries at 80 °C. *Angew. Chemie - Int. Ed.* **61**, (2022).
68. Yi, J. *et al.* Challenges, mitigation strategies and perspectives in development of zinc-electrode materials and fabrication for rechargeable zinc-air batteries. *Energy and Environmental Science* vol. 11 3075–3095 (2018).
69. Chen, P. *et al.* Recent Progress in Electrolytes for Zn–Air Batteries. *Frontiers in Chemistry* vol. 8 (2020).
70. Zhao, J. *et al.* An overview of oxygen reduction electrocatalysts for rechargeable zinc-air batteries enabled by carbon and carbon composites. *Eng. Sci.* **15**, 1–19 (2021).
71. Liu, H. *et al.* Bifunctional carbon-based cathode catalysts for zinc-air battery: A review. *Chinese Chemical Letters* vol. 33 683–692 (2022).
72. Jiao, D. *et al.* Test factors affecting the performance of zinc–air battery. *J. Energy Chem.* **44**, 1–7 (2020).
73. Zhao, Z. *et al.* Challenges in Zinc Electrodes for Alkaline Zinc-Air Batteries: Obstacles to

- Commercialization. *ACS Energy Letters* vol. 4 2259–2270 (2019).
74. Zhang, C. *et al.* A ZnCl₂ water-in-salt electrolyte for a reversible Zn metal anode. *Chem. Commun.* **54**, 14097–14099 (2018).
 75. Zhang, L. *et al.* ZnCl₂ “Water-in-Salt” Electrolyte Transforms the Performance of Vanadium Oxide as a Zn Battery Cathode. *Adv. Funct. Mater.* **29**, (2019).
 76. Zhang, Q. *et al.* Modulating electrolyte structure for ultralow temperature aqueous zinc batteries. *Nat. Commun.* **11**, (2020).
 77. Zhang, L., Chen, L., Zhou, X. & Liu, Z. Towards high-voltage aqueous metal-ion batteries beyond 1.5 V: The zinc/zinc hexacyanoferrate system. *Adv. Energy Mater.* **5**, 1400930 (2015).
 78. Zhang, L., Chen, L., Zhou, X. & Liu, Z. Morphology-Dependent Electrochemical Performance of Zinc Hexacyanoferrate Cathode for Zinc-Ion Battery. *Sci. Rep.* **5**, 1–11 (2015).
 79. Kim, D., Lee, C. & Jeong, S. A concentrated electrolyte for zinc hexacyanoferrate electrodes in aqueous rechargeable zinc-ion batteries. in *IOP Conference Series: Materials Science and Engineering* vol. 284 12001 (2018).
 80. Reddy, M. V., Mauger, A., Julien, C. M., Paoletta, A. & Zaghib, K. Brief history of early lithium-battery development. *Materials (Basel)*. **13**, (2020).
 81. Guo, Y. *et al.* Solid-state lithium batteries: Safety and prospects. *eScience* vol. 2 138–163 (2022).
 82. Zhao, J. *et al.* Review of State Estimation and Remaining Useful Life Prediction Methods for Lithium–Ion Batteries. *Sustainability (Switzerland)* vol. 15 (2023).
 83. Yao, L. *et al.* A review of lithium-ion battery state of health estimation and prediction methods. *World Electr. Veh. J.* **12**, (2021).
 84. Pang, X. *et al.* A lithium-ion battery rul prediction method considering the capacity regeneration phenomenon. *Energies* **12**, (2019).
 85. Jin, S. *et al.* Overview of machine learning methods for lithium-ion battery remaining useful lifetime prediction. *Electron.* **10**, (2021).
 86. Pang, X. *et al.* A Review on the Prediction of Health State and Serving Life of Lithium-Ion Batteries. *Chemical Record* vol. 22 (2022).
 87. Ren, L. *et al.* Remaining Useful Life Prediction for Lithium-Ion Battery: A Deep Learning Approach. *IEEE Access* **6**, 50587–50598 (2018).
 88. Fei, Z., Yang, F., Tsui, K. L., Li, L. & Zhang, Z. Early prediction of battery lifetime via a

- machine learning based framework. *Energy* **225**, (2021).
89. Lv, C. *et al.* Machine Learning: An Advanced Platform for Materials Development and State Prediction in Lithium-Ion Batteries. *Advanced Materials* vol. 34 (2022).
 90. Severson, K. A. *et al.* Data-driven prediction of battery cycle life before capacity degradation. *Nat. Energy* **4**, 383–391 (2019).
 91. Hsu, C. W., Xiong, R., Chen, N. Y., Li, J. & Tsou, N. T. Deep neural network battery life and voltage prediction by using data of one cycle only. *Appl. Energy* **306**, (2022).
 92. Li, J. *et al.* Feature selection: A data perspective. *ACM Computing Surveys* vol. 50 (2018).
 93. Turetskyy, A. *et al.* Toward Data-Driven Applications in Lithium-Ion Battery Cell Manufacturing. *Energy Technol.* **8**, (2020).
 94. Khumprom, P. & Yodo, N. A data-driven predictive prognostic model for lithium-ion batteries based on a deep learning algorithm. *Energies* **12**, (2019).
 95. Rostami, M., Berahmand, K. & Forouzandeh, S. A novel community detection based genetic algorithm for feature selection. *J. Big Data* **8**, (2021).
 96. Paulson, N. H. *et al.* Feature engineering for machine learning enabled early prediction of battery lifetime. *J. Power Sources* **527**, (2022).
 97. Fei, Z., Zhang, Z., Yang, F., Tsui, K. L. & Li, L. Early-stage lifetime prediction for lithium-ion batteries: A deep learning framework jointly considering machine-learned and handcrafted data features. *J. Energy Storage* **52**, (2022).
 98. Najafabadi, M. M. *et al.* Deep learning applications and challenges in big data analytics. *J. Big Data* **2**, (2015).
 99. Whang, S. E. & Lee, J. G. Data Collection and Quality Challenges for Deep Learning. *Proc. VLDB Endow.* **13**, 3429–3432 (2020).
 100. Janiesch, C., Zschech, P. & Heinrich, K. Machine learning and deep learning. *Electron. Mark.* **31**, 685–695 (2021).
 101. Sabiri, B., Asri, B. El & Rhanoui, M. Mechanism of Overfitting Avoidance Techniques for Training Deep Neural Networks. in *International Conference on Enterprise Information Systems, ICEIS - Proceedings* vol. 1 418–427 (2022).
 102. Singh, A., Thakur, N. & Sharma, A. A review of supervised machine learning algorithms. in *Proceedings of the 10th INDIACom; 2016 3rd International Conference on Computing for Sustainable Global Development, INDIACom 2016* 1310–1315 (2016).
 103. Li, Y. *et al.* Random forest regression for online capacity estimation of lithium-ion batteries.

- Appl. Energy* **232**, 197–210 (2018).
104. Couronné, R., Probst, P. & Boulesteix, A. L. Random forest versus logistic regression: A large-scale benchmark experiment. *BMC Bioinformatics* **19**, (2018).
 105. Zhang, Z. *et al.* State-of-health estimation for the lithium-ion battery based on gradient boosting decision tree with autonomous selection of excellent features. *Int. J. Energy Res.* **46**, 1756–1765 (2022).
 106. Liu, W., Fan, H. & Xia, M. Credit scoring based on tree-enhanced gradient boosting decision trees. *Expert Syst. Appl.* **189**, (2022).
 107. Wang, X., Chi, Y. & Mu, T. A review on the transport properties of ionic liquids. *J. Mol. Liq.* **193**, 262–266 (2014).
 108. Giffin, G. A. Ionic liquid-based electrolytes for ‘beyond lithium’ battery technologies. *J. Mater. Chem. A* **4**, 13378–13389 (2016).
 109. Kar, M., Simons, T. J., Forsyth, M. & MacFarlane, D. R. Ionic liquid electrolytes as a platform for rechargeable metal-air batteries: A perspective. *Phys. Chem. Chem. Phys.* **16**, 18658–18674 (2014).
 110. Datta, R., Ramprasad, R. & Venkatram, S. Conductivity prediction model for ionic liquids using machine learning. *J. Chem. Phys.* **156**, (2022).
 111. Yan, A. *et al.* Applying transfer learning with convolutional neural networks to identify novel electrolytes for metal air batteries. *Comput. Theor. Chem.* **1205**, 113443 (2021).
 112. Karakasidis, T. E., Sofos, F. & Tsonos, C. The Electrical Conductivity of Ionic Liquids: Numerical and Analytical Machine Learning Approaches. *Fluids* **7**, (2022).
 113. Chen, J. *et al.* Ionic liquid additive enabling anti-freezing aqueous electrolyte and dendrite-free Zn metal electrode with organic/inorganic hybrid solid electrolyte interphase layer. *Energy Storage Mater.* **53**, 629–637 (2022).
 114. Lv, Y., Xiao, Y., Ma, L., Zhi, C. & Chen, S. Recent Advances in Electrolytes for “Beyond Aqueous” Zinc-Ion Batteries. *Advanced Materials* vol. 34 (2022).
 115. Xiao, T. *et al.* All-Round Ionic Liquids for Shuttle-Free Zinc-Iodine Battery. *Angew. Chemie - Int. Ed.* **63**, (2024).
 116. Huang, S., Zhu, J., Tian, J. & Niu, Z. Recent Progress in the Electrolytes of Aqueous Zinc-Ion Batteries. *Chem. - A Eur. J.* **25**, 14480–14494 (2019).
 117. Ma, L. *et al.* Hydrogen-Free and Dendrite-Free All-Solid-State Zn-Ion Batteries. *Adv. Mater.* **32**, (2020).

118. Xu, J. J., Ye, H. & Huang, J. Novel zinc ion conducting polymer gel electrolytes based on ionic liquids. *Electrochem. commun.* **7**, 1309–1317 (2005).
119. Lv, Y., Xiao, Y., Ma, L., Zhi, C. & Chen, S. Recent Advances in Electrolytes for “Beyond Aqueous” Zinc-Ion Batteries. *Adv. Mater.* **34**, 1–31 (2022).
120. Stock, D. *et al.* Towards zinc-oxygen batteries with enhanced cycling stability: The benefit of anion-exchange ionomer for zinc sponge anodes. *J. Power Sources* **395**, 195–204 (2018).
121. Yan, Z. *et al.* An Exceptionally Facile Synthesis of Highly Efficient Oxygen Evolution Electrodes for Zinc-Oxygen Batteries. *ChemElectroChem* **4**, 2190–2195 (2017).
122. Dongmo, S. *et al.* Reproducible and stable cycling performance data on secondary zinc oxygen batteries. *Sci. Data* **7**, (2020).
123. Yan, Z., Gao, J., Liu, M., Wang, E. & Sun, G. Reducing the Cost of Zinc–Oxygen Batteries by Oxygen Recycling. *Energy Technol.* **6**, 246–250 (2018).
124. Feng, K., Park, H. W., Wang, X., Lee, D. U. & Chen, Z. High performance porous anode based on template-free synthesis of Co₃O₄ nanowires for lithium-ion batteries. *Electrochim. Acta* **139**, 145–151 (2014).
125. Peng, Z. *et al.* Novel layered iron vanadate cathode for high-capacity aqueous rechargeable zinc batteries. *Chem. Commun.* **54**, 4041–4044 (2018).
126. Wang, F. *et al.* Highly reversible zinc metal anode for aqueous batteries. *Nat. Mater.* **17**, 543–549 (2018).
127. Marcus, Y. *Ionic liquid properties: From molten salts to RTILs. Ionic Liquid Properties: From Molten Salts to RTILs* (2016). doi:10.1007/978-3-319-30313-0.
128. Fischer, S., Leipner, H., Thümmeler, K., Brendler, E. & Peters, J. Inorganic molten salts as solvents for cellulose. *Cellulose* **10**, 227–236 (2003).
129. Chen, C. Y., Matsumoto, K., Kubota, K., Hagiwara, R. & Xu, Q. A Room-Temperature Molten Hydrate Electrolyte for Rechargeable Zinc–Air Batteries. *Adv. Energy Mater.* **9**, (2019).
130. Hu, P. *et al.* Highly Durable Na₂V₆O₁₆·1.63H₂O Nanowire Cathode for Aqueous Zinc-Ion Battery. *Nano Lett.* **18**, 1758–1763 (2018).
131. Tang, B. *et al.* Potassium vanadates with stable structure and fast ion diffusion channel as cathode for rechargeable aqueous zinc-ion batteries. *Nano Energy* **51**, 579–587 (2018).
132. Lee, D. U., Choi, J. Y., Feng, K., Park, H. W. & Chen, Z. Advanced extremely durable 3D bifunctional air electrodes for rechargeable zinc-air batteries. *Adv. Energy Mater.* **4**, (2014).

133. Prabu, M., Ketpang, K. & Shanmugam, S. Hierarchical nanostructured NiCo₂O₄ as an efficient bifunctional non-precious metal catalyst for rechargeable zinc-air batteries. *Nanoscale* **6**, 3173–3181 (2014).
134. Sun, W. *et al.* A rechargeable zinc-air battery based on zinc peroxide chemistry. *Science* (80-). **371**, 46–51 (2021).
135. Yang, C. *et al.* All-temperature zinc batteries with high-entropy aqueous electrolyte. *Nat. Sustain.* **6**, 325–335 (2023).
136. Lee, J.-S. *et al.* Metal--air batteries with high energy density: Li--air versus Zn--air. *Adv. Energy Mater.* **1**, 34–50 (2011).
137. Lee, D. U. *et al.* Morphologically controlled Co₃O₄ nanodisks as practical bi-functional catalyst for rechargeable zinc-air battery applications. *Electrochem. commun.* **43**, 109–112 (2014).
138. Chen, Z. & Chen, Z. Highly Active and Stable Core-Corona Structured Bifunctional Catalyst for Rechargeable Metal-Air Battery Application. *ECS Meet. Abstr.* **MA2011-02**, 295–295 (2011).
139. Clark, S., Latz, A. & Horstmann, B. Rational Development of Neutral Aqueous Electrolytes for Zinc–Air Batteries. *ChemSusChem* **10**, 4735–4747 (2017).
140. Li, H. X., Wang, Y. & Cang, D. Q. Zinc leaching from electric arc furnace dust in alkaline medium. *J. Cent. South Univ. Technol. (English Ed.)* **17**, 967–971 (2010).
141. Copur, M. Optimization of dissolution of Zn and Cd metals from Waelz sintering waste by in aqueous (NH₄)₂SO₄ solution. *Energy Educ. Sci. Technol. Part A Energy Sci. Res.* **25**, 17–29 (2010).
142. Yan, K. *et al.* Temperature-Dependent Nucleation and Growth of Dendrite-Free Lithium Metal Anodes. *Angew. Chemie - Int. Ed.* **58**, 11364–11368 (2019).
143. Zhao, Y. *et al.* Aqueous Rechargeable Metal-Ion Batteries Working at Subzero Temperatures. *Advanced Science* vol. 8 (2021).
144. Attia, P. M. *et al.* Closed-loop optimization of fast-charging protocols for batteries with machine learning. *Nature* **578**, 397–402 (2020).
145. Ospina Agudelo, B., Zamboni, W. & Monmasson, E. Application domain extension of incremental capacity-based battery SoH indicators. *Energy* **234**, (2021).
146. Zhang, Y., Liu, Y., Wang, J. & Zhang, T. State-of-health estimation for lithium-ion batteries by combining model-based incremental capacity analysis with support vector regression.

- Energy* **239**, (2022).
147. Yan, L. *et al.* A hybrid method with cascaded structure for early-stage remaining useful life prediction of lithium-ion battery. *Energy* **243**, (2022).
 148. Han, X., Ouyang, M., Lu, L. & Li, J. A comparative study of commercial lithium ion battery cycle life in electric vehicle: Capacity loss estimation. *J. Power Sources* **268**, 658–669 (2014).
 149. Liu, W., Placke, T. & Chau, K. T. Overview of batteries and battery management for electric vehicles. *Energy Reports* vol. 8 4058–4084 (2022).
 150. Mitici, M., Hennink, B., Pavel, M. & Dong, J. Prognostics for Lithium-ion batteries for electric Vertical Take-off and Landing aircraft using data-driven machine learning. *Energy AI* **12**, (2023).
 151. Ara Shaikh, A. *et al.* The Role of Machine Learning and Artificial Intelligence for making a Digital Classroom and its sustainable Impact on Education during Covid-19. *Mater. Today Proc.* **56**, 3211–3215 (2022).
 152. Guo, H., Wang, Q., Stuke, A., Urban, A. & Artrith, N. Accelerated Atomistic Modeling of Solid-State Battery Materials With Machine Learning. *Frontiers in Energy Research* vol. 9 (2021).
 153. Wei, Z., He, Q. & Zhao, Y. Machine learning for battery research. *J. Power Sources* **549**, (2022).
 154. Perezniето, S., Jaafreh, R., Kim, J. gu & Hamad, K. Discovery of solid-state electrolytes for Na-ion batteries using machine learning. *Mater. Lett.* **349**, (2023).
 155. Zhu, Z. W. *et al.* Application of Artificial Intelligence to Lithium-Ion Battery Research and Development. *Journal of Electrochemistry* vol. 28 (2022).
 156. Sai Ramesh, A. *et al.* Artificial intelligence driven hydrogen and battery technologies – A review. *Fuel* **337**, (2023).
 157. Sun, S., Zhang, J., Bi, J., Wang, Y. & Moghaddam, M. H. Y. A Machine Learning Method for Predicting Driving Range of Battery Electric Vehicles. *J. Adv. Transp.* **2019**, (2019).
 158. Tran, M. K. *et al.* Python-based scikit-learn machine learning models for thermal and electrical performance prediction of high-capacity lithium-ion battery. *Int. J. Energy Res.* **46**, 786–794 (2022).
 159. Zheng, C. *et al.* A Deep Reinforcement Learning-Based Energy Management Strategy for Fuel Cell Hybrid Buses. *Int. J. Precis. Eng. Manuf. - Green Technol.* **9**, 885–897 (2022).
 160. Lu, J. *et al.* Battery degradation prediction against uncertain future conditions with recurrent

- neural network enabled deep learning. *Energy Storage Mater.* **50**, 139–151 (2022).
161. Deng, K. *et al.* Deep reinforcement learning based energy management strategy of fuel cell hybrid railway vehicles considering fuel cell aging. *Energy Convers. Manag.* **251**, (2022).
 162. Shahriar, S. M., Bhuiyan, E. A., Nahiduzzaman, M., Ahsan, M. & Haider, J. State of Charge Estimation for Electric Vehicle Battery Management Systems Using the Hybrid Recurrent Learning Approach with Explainable Artificial Intelligence. *Energies* **15**, (2022).
 163. Tian, J., Xiong, R., Shen, W., Lu, J. & Yang, X. G. Deep neural network battery charging curve prediction using 30 points collected in 10 min. *Joule* **5**, 1521–1534 (2021).
 164. Caruana, R., Lawrence, S. & Giles, L. Overfitting in neural nets: Backpropagation, conjugate gradient, and early stopping. in *Advances in Neural Information Processing Systems* (2001).
 165. Ardison, A. C. I., Hutagalung, M. J. R., Chernando, R. & Cenggoro, T. W. Observing Pre-Trained Convolutional Neural Network (CNN) Layers as Feature Extractor for Detecting Bias in Image Classification Data. *CommIT J.* **16**, 149–158 (2022).
 166. Zhang, C. L. & Wu, J. Improving CNN linear layers with power mean non-linearity. *Pattern Recognit.* **89**, 12–21 (2019).
 167. Lu, T. C. CNN Convolutional layer optimisation based on quantum evolutionary algorithm. *Conn. Sci.* **33**, 482–494 (2021).
 168. Saleem, M. A. *et al.* Comparative Analysis of Recent Architecture of Convolutional Neural Network. *Math. Probl. Eng.* **2022**, (2022).
 169. Duwairi, R. & Melhem, A. A deep learning-based framework for automatic detection of drug resistance in tuberculosis patients. *Egypt. Informatics J.* **24**, 139–148 (2023).
 170. Fortuna-Cervantes, J. M., Soubervielle-Montalvo, C., Perez-Cham, O. E., Peña-Gallardo, R. & Puente, C. Experimental Study of the Performance of Convolutional Neural Networks Applied in Art Media Classification. in *Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics)* vol. 13902 LNCS 169–178 (2023).
 171. Nurhopipah, A. & Larasati, N. A. CNN Hyperparameter Optimization using Random Grid Coarse-to-fine Search for Face Classification. *Kinet. Game Technol. Inf. Syst. Comput. Network, Comput. Electron. Control* 19–26 (2021) doi:10.22219/kinetik.v6i1.1185.
 172. Zhang, Z. Improved Adam Optimizer for Deep Neural Networks. in *2018 IEEE/ACM 26th International Symposium on Quality of Service, IWQoS 2018* (2019). doi:10.1109/IWQoS.2018.8624183.

173. Ning, G., White, R. E. & Popov, B. N. A generalized cycle life model of rechargeable Li-ion batteries. *Electrochim. Acta* **51**, 2012–2022 (2006).
174. Aikens, D. A. Electrochemical methods, fundamentals and applications. *J. Chem. Educ.* **60**, A25 (1983).
175. Ratnakumar, B. V., Smart, M. C., Whitcanack, L. D. & Ewell, R. C. The impedance characteristics of Mars Exploration Rover Li-ion batteries. *J. Power Sources* **159**, 1428–1439 (2006).
176. Jossen, A. Fundamentals of battery dynamics. *J. Power Sources* **154**, 530–538 (2006).
177. Mitchell, M. *An Introduction to Genetic Algorithms. An Introduction to Genetic Algorithms* (1996). doi:10.7551/mitpress/3927.001.0001.
178. Venkatraman, V., Evjen, S. & Lethesh, K. C. The ionic liquid property explorer: An extensive library of task-specific solvents. *Data* **4**, (2019).
179. Weininger, D. SMILES, a Chemical Language and Information System: 1: Introduction to Methodology and Encoding Rules. *J. Chem. Inf. Comput. Sci.* **28**, 31–36 (1988).
180. Ucak, U. V., Ashyrmamatov, I. & Lee, J. Improving the quality of chemical language model outcomes with atom-in-SMILES tokenization. *J. Cheminform.* **15**, (2023).
181. Skinnider, M. A. Invalid SMILES are beneficial rather than detrimental to chemical language models. *Nat. Mach. Intell.* **6**, 437–448 (2024).
182. Mokaya, M. *et al.* Testing the limits of SMILES-based de novo molecular generation with curriculum and deep reinforcement learning. *Nat. Mach. Intell.* **5**, 386–394 (2023).
183. Zhong, S. & Guan, X. Count-Based Morgan Fingerprint: A More Efficient and Interpretable Molecular Representation in Developing Machine Learning-Based Predictive Regression Models for Water Contaminants’ Activities and Properties. *Environ. Sci. Technol.* **57**, 18193–18202 (2023).
184. Belenahalli Shekarappa, S., Kandagalla, S. & Lee, J. Development of machine learning models based on molecular fingerprints for selection of small molecule inhibitors against JAK2 protein. *J. Comput. Chem.* **44**, 1493–1504 (2023).
185. Wen, Y., Li, Z., Xiang, Y. & Reker, D. Improving molecular machine learning through adaptive subsampling with active learning. *Digit. Discov.* **2**, 1134–1142 (2023).
186. Zhao, J., Shang, C. & Yin, R. Developing a hybrid model for predicting the reaction kinetics between chlorine and micropollutants in water. *Water Res.* **247**, (2023).
187. Kensert, A., Alvarsson, J., Norinder, U. & Spjuth, O. Evaluating parameters for ligand-based

- modeling with random forest on sparse data sets. *J. Cheminform.* **10**, (2018).
188. Shree Sowndarya, S. V., Kim, Y., Kim, S., St. John, P. C. & Paton, R. S. Expansion of bond dissociation prediction with machine learning to medicinally and environmentally relevant chemical space. *Digit. Discov.* **2**, 1900–1910 (2023).
 189. Ondar, E. & Makarov, I. Chemistry-Wise Augmentations for Molecule Graph Self-supervised Representation Learning. in *Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics)* vol. 14135 LNCS 327–336 (2023).
 190. Shorten, C., Khoshgoftaar, T. M. & Furht, B. Text Data Augmentation for Deep Learning. *J. Big Data* **8**, (2021).
 191. Li, C., Feng, J., Liu, S. & Yao, J. A Novel Molecular Representation Learning for Molecular Property Prediction with a Multiple SMILES-Based Augmentation. *Comput. Intell. Neurosci.* **2022**, (2022).
 192. Guo, C. *et al.* Variational Autoencoder with Optimizing Gaussian Mixture Model Priors. *IEEE Access* **8**, 43992–44005 (2020).
 193. Cai, B., Yang, S., Gao, L. & Xiang, Y. Hybrid variational autoencoder for time series forecasting. *Knowledge-Based Syst.* **281**, (2023).
 194. Zhang, C., Barbano, R. & Jin, B. Conditional variational autoencoder for learned image reconstruction. *Computation* **9**, (2021).
 195. Lin, Y. D. *et al.* Machine Learning with Variational AutoEncoder for Imbalanced Datasets in Intrusion Detection. *IEEE Access* **10**, 15247–15260 (2022).
 196. Lin, E., Mukherjee, S. & Kannan, S. A deep adversarial variational autoencoder model for dimensionality reduction in single-cell RNA sequencing analysis. *BMC Bioinformatics* **21**, (2020).
 197. Shu, X. *et al.* Unsupervised dam anomaly detection with spatial–temporal variational autoencoder. *Struct. Heal. Monit.* **22**, 39–55 (2023).
 198. Lee, C. Data augmentation using a variational autoencoder for estimating property prices. *Prop. Manag.* **39**, 408–418 (2021).
 199. Oliveira, A. F., Da Silva, J. L. F. & Quiles, M. G. Molecular Property Prediction and Molecular Design Using a Supervised Grammar Variational Autoencoder. *J. Chem. Inf. Model.* **62**, 817–828 (2022).
 200. Alperstein, Z., Cherkasov, A. & Rolfe, J. T. All SMILES Variational Autoencoder for

- Molecular Property Prediction and Optimization. in *Challenges and Advances in Computational Chemistry and Physics* vol. 33 85–115 (2023).
201. Rajagopal, D. *et al.* Data-Driven Virtual Material Analysis and Synthesis for Solid Electrolyte Interphases. *Adv. Energy Mater.* **13**, (2023).
 202. Taumoeofolau, G. H. & Best, R. B. Predicting spectroscopic properties of fluorescent proteins with a variational autoencoder. *Biophys. J.* **121**, 156a-157a (2022).
 203. Viatkin, D., Garcia-Zapirain, B., Méndez-Zorrilla, A. & Zakharov, M. Deep Learning Approach for Prediction of Critical Temperature of Superconductor Materials Described by Chemical Formulas. *Front. Mater.* **8**, (2021).
 204. Vinet, L. & Zhedanov, A. A ‘missing’ family of classical orthogonal polynomials. *J. Phys. A Math. Theor.* **44**, (2011).
 205. Baldi, P., Sadowski, P. & Lu, Z. Learning in the machine: Random backpropagation and the deep learning channel. *Artif. Intell.* **260**, 1–35 (2018).
 206. Schmidhuber, J. Deep Learning in neural networks: An overview. *Neural Networks* vol. 61 85–117 (2015).
 207. Luongo, F., Hakim, R., Nguyen, J. H., Anandkumar, A. & Hung, A. J. Deep learning-based computer vision to recognize and classify suturing gestures in robot-assisted surgery. *Surg. (United States)* **169**, 1240–1244 (2021).
 208. Arivazhagan, S., Arun, M. & Rathina, D. Recognition of handwritten characters using deep convolution neural network. *J. Natl. Sci. Found. Sri Lanka* **49**, 503–511 (2022).
 209. Vrigazova, B. The Proportion for Splitting Data into Training and Test Set for the Bootstrap in Classification Problems. *Bus. Syst. Res.* **12**, 228–242 (2021).
 210. Kandel, I. & Castelli, M. The effect of batch size on the generalizability of the convolutional neural networks on a histopathology dataset. *ICT Express* **6**, 312–315 (2020).
 211. Smith, S. L., Kindermans, P. J., Ying, C. & Le, Q. V. Don’t decay the learning rate, increase the batch size. in *6th International Conference on Learning Representations, ICLR 2018 - Conference Track Proceedings* (2018).
 212. Zhang, T., Zhu, T., Gao, K., Zhou, W. & Yu, P. S. Balancing Learning Model Privacy, Fairness, and Accuracy With Early Stopping Criteria. *IEEE Transactions on Neural Networks and Learning Systems* vol. 34 5557–5569 (2023).
 213. Sohil, F., Sohali, M. U. & Shabbir, J. *An introduction to statistical learning with applications in R. Statistical Theory and Related Fields* vol. 6 (2022).

214. Pattern Recognition and Machine Learning. *J. Electron. Imaging* **16**, 049901 (2007).
215. Barnett, V., Neter, J. & Wasserman, W. Applied Linear Statistical Models. *J. R. Stat. Soc. Ser. A* **138**, 258 (1975).
216. Beinecke, J. & Heider, D. Gaussian noise up-sampling is better suited than SMOTE and ADASYN for clinical decision making. *BioData Min.* **14**, (2021).
217. Wei, C., Yu, R., Fan, Y., Chen, W. & Wang, T. Securely Sampling Discrete Gaussian Noise for Multi-Party Differential Privacy. in *CCS 2023 - Proceedings of the 2023 ACM SIGSAC Conference on Computer and Communications Security* 2262–2276 (2021).
doi:10.1145/3576915.3616641.
218. Dorafshan, S., Thomas, R. J. & Maguire, M. Comparison of deep convolutional neural networks and edge detectors for image-based crack detection in concrete. *Constr. Build. Mater.* **186**, 1031–1045 (2018).
219. Han, Y. *et al.* A novel transfer learning for recognition of overlapping nano object. *Neural Comput. Appl.* **34**, 5729–5741 (2022).
220. Galushka, M. *et al.* Prediction of chemical compounds properties using a deep learning model. *Neural Comput. Appl.* **33**, 13345–13366 (2021).
221. Ahmad, M. I. *et al.* Ionic liquids-assisted electrolytes in aqueous zinc ion batteries. *J. Energy Storage* **72**, 108765 (2023).
222. Simons, T. J., Macfarlane, D. R., Forsyth, M. & Howlett, P. C. Zn Electrochemistry in 1-Ethyl-3-Methylimidazolium and N-Butyl-N-Methylpyrrolidinium Dicyanamides: Promising New Rechargeable Zn Battery Electrolytes. *ChemElectroChem* **1**, 1688–1697 (2014).
223. Ghazvini, M. S., Pulletikurthi, G., Cui, T., Kuhl, C. & Endres, F. Electrodeposition of Zinc from 1-ethyl-3-methylimidazolium acetate-water Mixtures: Investigations on the Applicability of the Electrolyte for Zn-Air Batteries. *J. Electrochem. Soc.* **165**, D354–D363 (2018).
224. Ma, Z. & Kan, J. Study of cylindrical Zn/PANI secondary batteries with the electrolyte containing alkylimidazolium ionic liquid. *Synth. Met.* **174**, 58–62 (2013).
225. Simons, T. J., Howlett, P. C., Torriero, A. A. J., MacFarlane, D. R. & Forsyth, M. Electrochemical, transport, and spectroscopic properties of 1-ethyl-3-methylimidazolium ionic liquid electrolytes containing zinc dicyanamide. *J. Phys. Chem. C* **117**, 2662–2669 (2013).
226. Harting, K., Kunz, U. & Turek, T. Zinc-air batteries: Prospects and challenges for future improvement. *Zeitschrift fur Phys. Chemie* **226**, 151–166 (2012).
227. Dilasari, B., Jung, Y. & Kwon, K. Effect of water on the stability of zinc in 1-butyl-1-

- methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid. *J. Ind. Eng. Chem.* **45**, 375–379 (2017).
228. Schuett, F. M. *et al.* Electrodeposition of Zinc onto Au(111) and Au(100) from the Ionic Liquid [MPPip][TFSI]. *Angew. Chemie - Int. Ed.* **60**, 20461–20468 (2021).
 229. Liu, Z., Abedin, S. Z. El & Endres, F. Electrodeposition of zinc films from ionic liquids and ionic liquid/water mixtures. *Electrochim. Acta* **89**, 635–643 (2013).
 230. Liu, Z., Pulletikurthi, G., Lahiri, A., Cui, T. & Endres, F. Suppressing the dendritic growth of zinc in an ionic liquid containing cationic and anionic zinc complexes for battery applications. *Dalt. Trans.* **45**, 8089–8098 (2016).
 231. Goujon, N., Byrne, N., Walsh, T. R. & Forsyth, M. The Influence of Water and Metal Salt on the Transport and Structural Properties of 1-Octyl-3-methylimidazolium Chloride. *Aust. J. Chem.* **68**, 420–425 (2015).
 232. Motlagh, S. R. *et al.* Enhancing electrochemical performance and stabilizing zinc anode in mild acidic electrolyte using combined additive. *Mater. Sci. Energy Technol.* **6**, 178–191 (2023).
 233. Liu, A., Shi, Z. & Reddy, R. G. Electrodeposition of Zinc from Zinc Oxide in 2:1 Urea/1-Butyl-3-methylimidazolium Chloride Ionic Liquid. *J. Electrochem. Soc.* **164**, D666–D673 (2017).
 234. Zhang, Q. G. & Wei, Y. Study on properties of ionic liquid based on ZnCl₂ with 1-butyl-3-methylimidazolium chloride. *J. Chem. Thermodyn.* **40**, 640–644 (2008).
 235. Cao, H. *et al.* An efficient electrolyte additive of tetramethylammonium sulfate hydrate for Dendritic-Free zinc anode for aqueous Zinc-ion batteries. *J. Colloid Interface Sci.* **627**, 367–374 (2022).
 236. Li, L. *et al.* Dual-additive-based electrolyte design for aqueous zinc ion batteries with high plating/stripping efficiency. *Chem. Commun.* **60**, 6809–6812 (2024).
 237. Lahiri, A., Yang, L., Li, G. & Endres, F. Mechanism of zn-ion intercalation/deintercalation in a zn-polypyrrole secondary battery in aqueous and bio-ionic liquid electrolytes. *ACS Appl. Mater. Interfaces* **11**, 45098–45107 (2019).
 238. Deng, Y. P. *et al.* The Current State of Aqueous Zn-Based Rechargeable Batteries. *ACS Energy Letters* vol. 5 1665–1675 (2020).
 239. Graves, A. & Schmidhuber, J. Framewise phoneme classification with bidirectional LSTM and other neural network architectures. in *Neural Networks* vol. 18 602–610 (2005).

240. Ian Goodfellow, Y. B. and A. C. Ian Goodfellow, Yoshua Bengio, and Aaron Courville: Deep learning: The MIT Press, 2016, 800 pp, ISBN: 0262035618 Article. *Genet. Program. Evolvable Mach.* **19**, (2016).
241. Srivastava, N., Hinton, G., Krizhevsky, A., Sutskever, I. & Salakhutdinov, R. Dropout: A simple way to prevent neural networks from overfitting. *J. Mach. Learn. Res.* **15**, 1929–1958 (2014).
242. Li, X. *et al.* Generalized Focal Loss: Towards Efficient Representation Learning for Dense Object Detection. *IEEE Trans. Pattern Anal. Mach. Intell.* **45**, 3139–3153 (2023).
243. Nie, Y., Sommella, P., Carratù, M., O’Nils, M. & Lundgren, J. A Deep CNN Transformer Hybrid Model for Skin Lesion Classification of Dermoscopic Images Using Focal Loss. *Diagnostics* **13**, (2023).
244. Kunang, Y. N., Nurmaini, S., Stiawan, D. & Suprpto, B. Y. Deep learning with focal loss approach for attacks classification. *Telkomnika (Telecommunication Comput. Electron. Control)*. **19**, 1407–1418 (2021).
245. Vrbančič, G. & Podgorelec, V. Transfer learning with adaptive fine-tuning. *IEEE Access* **8**, 196197–196211 (2020).
246. Lee, S. H. Performance Evaluation of Machine Learning and Deep Learning-Based Models for Predicting Remaining Capacity of Lithium-Ion Batteries. *Appl. Sci.* **13**, (2023).
247. Chicco, D., Warrens, M. J. & Jurman, G. The coefficient of determination R-squared is more informative than SMAPE, MAE, MAPE, MSE and RMSE in regression analysis evaluation. *PeerJ Comput. Sci.* **7**, 1–24 (2021).
248. Hawkins, B. E. *et al.* Reversible Zinc Electrodeposition at $-60\text{ }^{\circ}\text{C}$ Using a Deep Eutectic Electrolyte for Low-Temperature Zinc Metal Batteries. *J. Phys. Chem. Lett.* **14**, 2378–2386 (2023).
249. Fortunati, A. *et al.* Understanding the role of imidazolium-based ionic liquids in the electrochemical CO₂ reduction reaction. *Commun. Chem.* **6**, (2023).
250. Xu, M., Ivey, D. G., Xie, Z. & Qu, W. Electrochemical behavior of Zn/Zn(II) couples in aprotic ionic liquids based on pyrrolidinium and imidazolium cations and bis(trifluoromethanesulfonyl) imide and dicyanamide anions. *Electrochim. Acta* **89**, 756–762 (2013).
251. Bambam, A. K., Dhanola, A. & Gajrani, K. K. A critical review on halogen-free ionic liquids as potential metalworking fluid additives. *Journal of Molecular Liquids* vol. 380 (2023).

252. Latifi, M., Ahmad, A., Hassan, N. H., Ben youcef, H. & Kaddami, H. Towards the application of carboxymethyl chitin/ionic liquid blend as polymer electrolyte membrane for aqueous batteries. *Carbohydr. Polym.* **273**, (2021).
253. Cao, J. *et al.* Strategies of regulating Zn²⁺-solvation structures for dendrite-free and side reaction-suppressed zinc-ion batteries. *Energy Environ. Sci.* **15**, 499–528 (2022).
254. Ray, A. & Saruhan, B. Application of ionic liquids for batteries and supercapacitors. *Materials (Basel)*. **14**, (2021).
255. Ilyas, F. *et al.* Recent trends in the benign-by-design electrolytes for zinc batteries. *J. Mol. Liq.* **343**, 117606 (2021).
256. Wang, Y.-S., Yeh, H.-W., Tang, Y.-H., Kao, C.-L. & Chen, P.-Y. Voltammetric Study and Electrodeposition of Zinc in Hydrophobic Room-Temperature Ionic Liquid 1-Butyl-1-methylpyrrolidinium Bis((trifluoromethyl)sulfonyl)imide ([BMP][TFSI]): A Comparison between Chloride and TFSI Salts of Zinc. *J. Electrochem. Soc.* **164**, D39–D47 (2017).
257. Oberholzer, P., Tervoort, E., Bouzid, A., Pasquarello, A. & Kundu, D. Oxide versus Nonoxide Cathode Materials for Aqueous Zn Batteries: An Insight into the Charge Storage Mechanism and Consequences Thereof. *ACS Appl. Mater. Interfaces* **11**, 674–682 (2019).
258. Galiński, M., Lewandowski, A. & Stepniak, I. Ionic liquids as electrolytes. *Electrochim. Acta* **51**, 5567–5580 (2006).
259. Ji, B., Yao, W. & Tang, Y. High-performance rechargeable zinc-based dual-ion batteries. *Sustain. Energy Fuels* **4**, 101–107 (2019).
260. Liu, Z. *et al.* An Ionic Liquid-Surface Functionalized Polystyrene Spheres Hybrid Electrolyte for Rechargeable Zinc/Conductive Polymer Batteries. *ChemElectroChem* **5**, 2321–2325 (2018).