Data-driven understanding and forecasting of electrochemical systems

Penelope Kay Jones

Department of Physics
University of Cambridge

This dissertation is submitted for the degree of

Doctor of Philosophy

Gonville and Caius College

January 2023
Declaration

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the preface and specified in the text. It is not substantially the same as any work that has already been submitted before for any degree or other qualification except as declared in the preface and specified in the text. It does not exceed the prescribed word limit for the Faculty of Physics and Chemistry Degree Committee.

Penelope Kay Jones
January 2023
Table of contents

Acknowledgements ix
Abstract xi
Preface xiii
Nomenclature xv

1 Introduction 1
   1.1 Electrochemical energy systems .................................. 1
   1.2 Research aims and thesis outline ................................ 2

2 Machine learning for electrochemical systems 5
   2.1 Machine learning .................................................. 5
      2.1.1 Big data and machine learning in science ....................... 5
      2.1.2 The importance of uncertainty ................................ 6
   2.2 Machine learning for materials design ............................ 7
      2.2.1 Learning structure-property relationships ...................... 7
      2.2.2 Accelerating simulations with machine learning potentials 13
      2.2.3 Optimal experiment design .................................... 16
      2.2.4 Elucidating microscopic understanding .......................... 17
   2.3 Machine learning for battery analytics ......................... 18
      2.3.1 Applications of battery analytics ............................. 19
      2.3.2 Battery analytics models .................................... 21

3 Uncovering hidden local structure in liquid electrolytes 29
   3.1 Introduction ...................................................... 29
   3.2 Theories of electrolytes .......................................... 31
3.2.1 Debye-Hückel theory ............................................. 31
3.2.2 Liquid state theories ............................................. 32
3.2.3 Scaling analysis .................................................. 32
3.2.4 Ion clustering ..................................................... 33

3.3 Inference of local structure distribution ............................................. 34
3.3.1 Representation of local structure ...................................... 34
3.3.2 Grouping environments using Bayesian inference ..................... 36
3.3.3 Approximate inference ............................................. 37
3.3.4 Bayesian hypothesis testing ........................................ 39

3.4 Data generation ...................................................... 39
3.4.1 Modelling the concentrated electrolyte ................................ 39
3.4.2 Molecular dynamics simulations ...................................... 40

3.5 Results and discussion ............................................... 41
3.5.1 Validation on toy systems .......................................... 41
3.5.2 Bulk monovalent electrolytes ........................................ 41

3.6 Conclusion .......................................................... 45

4 Inferring global dynamics from local structure in liquid electrolytes 47
4.1 Introduction .......................................................... 47
4.2 Theories of ion transport .............................................. 49
4.2.1 Nernst-Einstein relations ......................................... 49
4.2.2 Stefan-Maxwell equations ......................................... 50
4.2.3 Onsager formalism ............................................... 50
4.2.4 Ion clustering ..................................................... 52
4.2.5 Remaining enigmas in ion transport ................................ 53

4.3 Local conductivity field .............................................. 54
4.3.1 Local conductivity hypothesis ...................................... 54
4.3.2 Machine learning model .......................................... 55
4.3.3 Representation of local structure ................................... 55

4.4 Data generation ........................................................ 56
4.4.1 Molecular dynamics simulations .................................... 56

4.5 Results and discussion ............................................... 58
4.5.1 Local structure predicts ionic conductivity of electrolytes ........ 58
4.5.2 Heterogeneity in local conductivity ................................ 59
4.5.3 Local conductivity is spatially correlated ......................... 61
4.5.4 Relating local conductivity to global dynamic properties ........ 63

4.6 Conclusion .......................................................... 64
# Table of contents

5 Forecasting lithium-ion battery performance under uneven usage 67
5.1 Introduction ............................................. 67
5.2 Battery forecasting model .................................. 70
  5.2.1 General framework ..................................... 70
  5.2.2 Generation of battery cycling data ......................... 71
  5.2.3 Representation of battery state .......................... 74
  5.2.4 Representation of future action .......................... 76
  5.2.5 Machine learning model ............................... 76
5.3 Results and discussion ..................................... 77
  5.3.1 Capacity forecasting using EIS ......................... 77
  5.3.2 Data efficiency and robustness to domain shift .......... 78
  5.3.3 Comparison of state representations ...................... 80
  5.3.4 Robustness to different cell manufacturers ............. 82
5.4 Conclusion .............................................. 85

6 Conclusions .................................................. 89
  6.1 Contributions ............................................ 89
  6.2 Open questions .......................................... 91

References ..................................................... 93
Acknowledgements

I will start by expressing my gratitude to my supervisor Dr Alpha Lee. If I hadn’t met Alpha I am not sure I would have found the inner belief to pursue a PhD. This has undoubtedly changed the course of my life. Alpha has an unbounded curiosity about the world, and those who have met him will recognise his ability to inspire the same curiosity in everyone he interacts with. I am grateful that Alpha believed in my scientific ability even when I didn’t believe in myself, gave me the freedom to find my own voice, and has always encouraged my pursuit of truth. Alpha’s mentorship has extended beyond the scope of science and it has been a great privilege to work together.

I will be forever grateful for my education. My high school teachers Lisa Bradshaw, Jane Maher and Dr Cristina Vilela were especially influential: they helped me foster a respect for learning that I hope stays with me for the rest of my life. At Cambridge, I received valued mentorship from my Director of Studies Prof Mike Payne, and later Dr Alex Forse, who patiently taught me how to work in a Chemistry lab. I am fortunate to have had the chance to learn from brilliant collaborators Dr Fabian Coupette, Dr Kara Fong, Dr Andreas Härtel, Prof Kristin Persson and Prof Ulrich Stimming. I appreciate the friends I made studying in the Lee Group, with happy memories of Cambridge during the pandemic spent swimming in Grantchester and having barbecues.

I want to express my appreciation for the Winton Fund, the Oppenheimer Fund and the Alan Turing Institute for their support of my research.

I have spent my adult life to date at Cambridge University and I am grateful for the breadth and depth of experiences that I have had in this city. I am especially grateful for my friends who have been there with me through the highs and lows.

What I am most grateful for is that my life to date has been filled with love. That is in large part because of my family and friends - and especially my brother, Alex, my parents, Sally and Steve, and my partner, Alex. Thank you for showing me by example how to live a life grounded in gratitude, integrity and fun.
Abstract

Electrochemical energy systems such as batteries and supercapacitors have played an important role in society for two centuries. The rise of the consumer electronics industry has been underpinned by innovations in battery technology, and batteries are subject to more public interest now than ever before due to the uptake of electric vehicles and the demand for grid-scale batteries to stabilise an intermittent renewable energy supply.

Most electrochemical energy systems are complex. A multitude of processes over different length- and time-scales drive their realised performance. One source of complexity arises from the enigmatic mechanism by which inter-particle interactions at the atomistic scale give rise to critical macroscopic behaviours. Examples of this can be found in liquid electrolytes, for which electrostatic screening lengths and ion conductivity are both observed to deviate significantly from predictions of classical theories at high concentrations. A second source of complexity is that each system is operated in a different way in practice, and the way a system is used strongly influences both short- and long- term performance, with each system following a unique degradation trajectory.

This thesis will demonstrate that both of these challenges can be tackled through the combination of data, physical intuition and machine learning. Machine learning models can learn from orders of magnitude more data than humans can, and we will see that such models can be trained to make more accurate predictions about how electrochemical systems will perform under different operating conditions. In addition, machine learning can act as a “computational microscope”, offering new ways of understanding the molecular origin of macroscopic properties.

I begin by addressing the enigmatic under-screening effect observed in concentrated electrolytes, and explore whether discrepancies between classical theory and experiment can be explained using the concept of ion pairing, by identifying the number of statistically distinct environments inhabited by ions. The results bring into question the validity of the ion pair hypothesis for concentrated systems, but more importantly they suggest that static properties
of electrolytes, such as screening length, can be explained by studying statistical differences between local ionic environments rather than just the mean local environment as captured by the radial distribution function.

Extending this, I then posit that global dynamic properties such as ion conductivity can also be decomposed into atomistic contributions that are functions of local static structure. The idea is to learn the mapping from local structural motif to a local contribution to conductivity, which effectively generalises ideas first put forward in the ion-pair hypothesis or “cluster Nernst-Einstein” theory. By studying the distributions of local conductivities across electrolytic systems we can decipher what structural motifs are correlated with enhanced or degraded conductivity.

I then turn to address the system level challenge of forecasting how electrochemical systems will respond to different operating conditions. In the growing lithium-ion battery industry, this is a major challenge, since batteries of the same chemistry will respond differently to the same use conditions due to differences in internal state caused by manufacturing heterogeneity and different extents of degradation. We develop a general framework that combines electrochemical impedance spectroscopy with machine learning to predict how a battery will respond to a given use condition, which has relevance for the design of improved battery management systems.

The findings of this thesis help to further our understanding of the fundamental mechanism by which inter-ion interactions give rise to screening and conduction within liquid electrolytes. More broadly, these findings can help to guide the design of novel electrolytes for next-generation systems, to develop optimal fast-charging protocols that do not sacrifice battery life, and to triage batteries towards second-life applications.
Preface

The research presented in Chapter 3 was a collaboration with Dr Andreas Härtel and Dr Fabian Coupette of the University of Freiburg, who conducted several molecular dynamic simulations, and with invaluable insights from Dr Alpha Lee. Prof Joachim Dzubiella, Prof Benjamin Rotenberg and Prof Chanbum Park kindly shared their all-atom simulations data for analysis. I conducted the analysis and I am the principal author on the resulting publication:


I also released the code at https://github.com/PenelopeJones/electrolytes.

The research presented in Chapter 4 was a collaboration with Dr Kara Fong and Prof Kristin Persson of the University of California, Berkeley, and Dr Alpha Lee. Kara conducted molecular dynamics simulations and all offered invaluable insights. I designed and conducted the machine learning methodology and analysis, and I am the principal author on the following pre-print, which is currently under review for publication:


We published the associated data at https://doi.org/10.5281/zenodo.6957888 and released the code at https://github.com/PenelopeJones/conductivity.

The work conducted in Chapter 5 was conducted with supervision by Prof Ulrich Stimming, from the University of Newcastle, and Dr Alpha Lee. I designed the methodology, wrote the code to enable random battery cycling, generated all experimental data, and completed all analysis. I am the principal author on the resulting publication:

Nomenclature

Roman Symbols

\( c \)  Ionic concentration

Greek Symbols

\( \epsilon \)  Relative permittivity

Other Symbols

\( \mathcal{N} \)  The Normal distribution

\( R^2 \)  Coefficient of determination

\( \mathcal{W} \)  The Wishart distribution

Acronyms / Abbreviations

ACSF  Atom-Centered Symmetry Functions

ASI  Area Specific Impedance

BF  Bayes Factor

CC  Constant Current

CT  Capacity Throughput

CVF  Capacity-Voltage Features

DFT  Density Functional Theory
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>Ethylene Carbonate</td>
</tr>
<tr>
<td>ECM</td>
<td>Equivalent Circuit Model</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EKF</td>
<td>Extended Kalman Filter</td>
</tr>
<tr>
<td>ELBO</td>
<td>Evidence Lower Bound</td>
</tr>
<tr>
<td>EMC</td>
<td>Ethyl Methyl Carbonate</td>
</tr>
<tr>
<td>EOL</td>
<td>End of Life</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>ICE</td>
<td>Internal Combustion Engine</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>KF</td>
<td>Kalman Filter</td>
</tr>
<tr>
<td>KL</td>
<td>Kullback–Leibler</td>
</tr>
<tr>
<td>LAM</td>
<td>Loss of Active Material</td>
</tr>
<tr>
<td>LGPS</td>
<td>Li$_{10}$GeP$<em>2$S$</em>{12}$</td>
</tr>
<tr>
<td>LiPON</td>
<td>Li$_x$PO$_y$N$_z$, $2.6 \leq x \leq 3.5, 1.9 \leq y \leq 3.8, 0.1 \leq z \leq 1.3$</td>
</tr>
<tr>
<td>LLI</td>
<td>Loss of Lithium Inventory</td>
</tr>
<tr>
<td>LLZO</td>
<td>Li$_7$La$_3$Zr$<em>2$O$</em>{12}$</td>
</tr>
<tr>
<td>LSTM</td>
<td>Long Short-Term Memory</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>MLP</td>
<td>Machine Learning Potential</td>
</tr>
<tr>
<td>MSA</td>
<td>Mean Spherical Approximation</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>NASICON</td>
<td>$\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}<em>3\text{O}</em>{12}$, $x &lt; 3$</td>
</tr>
<tr>
<td>NMC</td>
<td>$\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>OQMD</td>
<td>Open Quantum Materials Database</td>
</tr>
<tr>
<td>P2D</td>
<td>Pseudo-Two-Dimensional</td>
</tr>
<tr>
<td>PBM</td>
<td>Physics-Based Model</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene Carbonate</td>
</tr>
<tr>
<td>PDF</td>
<td>Pair Distribution Function</td>
</tr>
<tr>
<td>RC</td>
<td>Resistance-Capacitance</td>
</tr>
<tr>
<td>RDF</td>
<td>Radial Distribution Function</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root-Mean-Squared Error</td>
</tr>
<tr>
<td>RPM</td>
<td>Restricted Primitive Model</td>
</tr>
<tr>
<td>RUL</td>
<td>Remaining Useful Life</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid Electrolyte Interphase</td>
</tr>
<tr>
<td>SOAP</td>
<td>Smooth Overlap of Atomic Positions</td>
</tr>
<tr>
<td>SOC</td>
<td>State of Charge</td>
</tr>
<tr>
<td>SOE</td>
<td>State of Energy</td>
</tr>
<tr>
<td>SOH</td>
<td>State of Health</td>
</tr>
<tr>
<td>SOP</td>
<td>State of Power</td>
</tr>
<tr>
<td>SPM</td>
<td>Solvent Primitive Model</td>
</tr>
<tr>
<td>VC</td>
<td>Vinylene Carbonate</td>
</tr>
<tr>
<td>WCA</td>
<td>Weeks-Chandler-Andersen</td>
</tr>
</tbody>
</table>
WLTC  Worldwide Harmonized Light Vehicles Test Cycles
Chapter 1

Introduction

1.1 Electrochemical energy systems

Electrochemical energy systems are ubiquitous in modern society. Lithium-ion batteries, fuel cells and supercapacitors have underpinned technological advancements ranging from smartphones to electric vehicles. These systems have an increasing role to play in tackling climate change, by enabling the transition away from internal combustion engine vehicles (ICE) to electric vehicles, and by stabilising the intermittent supply of renewable energy from solar or wind power [1]. The growth of the lithium-ion battery market reflects this: from 2010 to 2018 global battery demand grew at a 30% annual rate to 0.2 TWh, and by 2030 global battery demand is forecasted to approach 3 TWh [2].

The increasing role of lithium-ion batteries and supercapacitors has incentivised a focus on improving their properties. In electric vehicles, there is demand to further increase energy density and reduce charging time [1], whilst in grid-scale batteries, low cost and high durability are important [3]. Crucially, in all of these applications it is not only the performance of the device at the point of manufacture that is relevant, but also the trajectory to failure. From an environmental perspective, it is important that batteries remain performant for many years: manufacturing electric vehicles contributes more greenhouse gas emissions than ICE vehicles, and only after sufficient use do greenhouse gas emissions from electric vehicles become lower than those from ICE vehicles [4].

Improving the design and use of electrochemical energy systems demands that we have a good grasp of their behaviour. However, most electrochemical energy systems are complex,
with physical and chemical processes taking place on length-scales and time-scales ranging over many orders of magnitude.

A key enigma relates to the molecular origin of macroscopic properties such as screening and transport behaviour. In concentrated liquid electrolytes, a fundamental component of many electrochemical systems, ion conductivities and electrostatic screening lengths have been experimentally observed to deviate by orders of magnitude from predictions of classical theories.

A second challenge is that in the field, each electrochemical system is subject to a range of operating conditions such as temperatures, pressures and charging rates. The operating conditions strongly influence current performance, and future performance due to the differing impacts on degradation. The result is that each system degrades via a unique path.

1.2 Research aims and thesis outline

The aim of this thesis is to demonstrate that both of these challenges can be addressed using machine learning. We will find that machine learning can help to elucidate new scientific understanding of the behaviour of electrochemical energy systems. It is hoped that the frameworks developed here can be used for both “bottom-up” and “top-down” optimisation: to build design-principles for next-generation electrolytes, and to identify optimal usage protocols such as fast-charging strategies that do not compromise health.

Chapter 2 provides a review of some of the ways that machine learning has been used in the field of electrochemical systems, including in high-throughput screening for materials discovery and accelerating simulations. We also review the uses of machine learning for system-level analysis, such as in diagnosing the health of lithium-ion batteries and forecasting their future performance. We motivate the incorporation of uncertainty into machine learning methods and outline the Bayesian framework for quantifying uncertainty.

In the three subsequent chapters, I will demonstrate how probabilistic machine learning, applied carefully, can help us to address remaining enigmas and unravel new insights about electrochemical systems. I will begin by showing in Chapter 3 how Bayesian machine learning methods can reveal hidden structure in concentrated electrolytes, a key component of electrochemical energy systems such as lithium-ion batteries, whose behaviour fundamentally influences the macroscopic properties of the system. I reason that more generally, meaningful physical insights about soft matter systems can be obtained by studying statistical differences between local environments.
I will then build on this approach in Chapter 4, where I posit the hypothesis that global dynamic properties including ion conductivity can be decomposed into local contributions. This framework can be used to identify which structural motifs are correlated with enhanced or suppressed conductivity in concentrated electrolytes.

In Chapter 5, we will turn to look at how machine learning can be used to forecast how a battery will respond to external actions from a top down approach. We provide a general framework that enables the short and longer term performance of the battery to be forecasted under different expected future use conditions, even when no historical performance data is available. This framework is highly generalisable and can be used to develop optimised operation protocols. A key benefit of our forecasting model is its probabilistic nature: we show that it can be acceptable for a model to deliver the wrong predictions provided that it “knows what it doesn’t know”.

Finally in Chapter 6 I will reflect on how the contributions made in this thesis lay the foundations for both “hardware optimisation” of lithium ion batteries through novel next-generation electrolyte discoveries, as well as “software optimisation” through optimal control algorithms that can maximise the utility of each battery over its lifetime.
Chapter 2

Machine learning for electrochemical systems

2.1 Machine learning

2.1.1 Big data and machine learning in science

The rise of “big data” has been ubiquitous in almost all scientific fields as well as in broader society; the five most valuable companies in the United States are fundamentally data-driven. It is hardly surprising then, that media outlets and industrial experts alike have proclaimed that “data is the new oil” in reference to the mass commoditisation of data globally [6–8].

The real value in big data has arisen not only from the data itself, but from the concinnity of this data collection with ever-improving computing power and significant advancements in the tools available for making sense of the data. Many of these tools have been branded by the umbrella term machine learning. At the core of machine learning methodologies is the inference of useful insights from our observations, which can be used to make predictions about unobserved variables, to build models of complex systems and to guide decision-making processes. In science, machine learning is routinely used in a plethora of applications, from designing novel molecules for use as medicinal drugs [9], to aiding conservation of coral reefs [10], and, topically, for forecasting the spread of infectious diseases such as that of the novel coronavirus COVID-19 [11, 12].

[^1]: As of August 2020, the five most valuable publicly traded US companies by market capitalisation are Alphabet, Amazon, Apple, Facebook and Microsoft [5].
2.1.2 The importance of uncertainty

Uncertainty quantification is of fundamental importance in the scientific method and is especially important in applications where we must “know what we do not know”. At the heart of many probabilistic models is the Bayesian framework which, as we shall see, provides a principled mechanism by which one’s degree of belief in any event or model can be iteratively updated, and which enables the quantification of uncertainty in every prediction that one makes.

A scientist recognises and appreciates the success of prevailing theories and models in explaining her observations, but is all the while cognisant that no theory should be above scrutiny. The course of history is testament to this world view; countless theories once considered indubitable truths have been revealed to be flawed. A corollary of this is that no model should ever be considered certain. Instead, one should assess the extent to which they believe that a model is “true” based on the information available to them.

It is on this premise that the Bayesian view of probability naturally arises. Here, anything about which one is uncertain is assigned a probability between zero and one, which quantifies one’s degree of belief that the unobserved quantity will take a specific value. A value close to zero implies a belief that it is unlikely an event will occur. Conversely a probability close to one implies a belief that an event is likely to occur.

No aspect of the scientific method is free of uncertainty. When we make a hypothesis using a model, we consciously or subconsciously assign a prior belief to that hypothesis based on information acquired from previous observations. When this belief is sufficiently great to warrant our time and efforts, we may test the hypothesis by conducting an experiment. Inevitably, even our experimental observations are uncertain - our measurements are subject to noise in part due to the finite precision of our measuring devices. Finally, we use these observations to update our degree of belief in the model, based on its ability to explain the data.

The Bayesian paradigm is to update our degree of belief in a model $M$ in light of new data $X$ using Bayes’ theorem,

$$p(M|X) = \frac{p(X|M)p(M)}{p(X)}.$$  

Here $p(M)$ is the prior, which quantifies our degree of belief in $M$ before observing $X$, and $p(M|X)$ is the posterior, which quantifies our degree of belief in $M$ after observing $X$. The

---

2The uncertainty associated with observation noise is termed *aleatoric*, as against the *epistemic* uncertainty that arises due to a lack of observations.
posterior is related to the prior through the likelihood $p(X|M)$, which measures how well $M$ can explain $X$, and the marginal likelihood $p(X)$, which here serves as a normalising constant. When new observations are made, the previous posterior serves as the new prior, embodying the iterative nature of learning.

In this Chapter, I will first review machine learning approaches to discover new electrochemical materials. I will then discuss applications of machine learning for rapid diagnosis and prognosis of battery health, for use in battery management systems and warranty design.

### 2.2 Machine learning for materials design

Improving electrochemical systems relies on the discovery of novel materials with superior properties to incumbents. Materials space is so vast [13] that finding a material with optimal properties for a particular application through exhaustive random search by manufacturing each material and measuring its properties would be impossible. Given the impracticality of this approach, materials scientists have relied on intuition and previous observations (from reading papers or running their own experiments) to guide decisions about which region of materials space to explore next. Yet no human would be capable of reading the entirety of materials science literature. The challenges of identifying new materials for electrochemical systems are also reflected in the long historical development times on the order of a decade [3, 14, 15].

One of the major contributions of machine learning in the field of materials sciences has been to accelerate the rate of novel materials discovery, by helping scientists to decide which are the most promising materials to test next. Taking inspiration from the more mature field of computational drug discovery [16], machine learning models have been applied to materials science in four main ways: 1) to find structure-property relationships and enable high-throughput screening of millions [17, 18] or billions [19] of material candidates, 2) to accelerate materials simulations through the approximation of molecular force fields [20, 21], 3) to optimally plan and design expensive experiments in an iterative manner [22–24], and 4) to elucidate the molecular origin of macroscopic properties [25, 26].

#### 2.2.1 Learning structure-property relationships

A successful application of machine learning in materials science has been to enable high-throughput virtual screening of materials, by finding relationships between a material’s structure and its bulk properties. Armed with a structure-property relationship, any material
with a known structure can be screened for a particular property, which helps scientists to decide which materials are worthwhile synthesising and characterising experimentally.

The general framework assumes that each material can be represented by a vector and mapped to some location in “materials” space, with each property having an associated field over materials space. Structure-property models aim to identify the mapping between the structural representation to property [27]. This mapping is expected to be highly non-linear and complex: in this regime, machine learning models can offer improvements over more traditional statistics, especially when large quantities of observed data are available.

**Datasets for electrochemical materials**

Building accurate structure-property models relies heavily on having high-quality datasets. Much effort has thus been invested into building datasets containing computed crystal structures and experimentally measured or computationally derived properties, many of which are open source.  

Many structure-property models rely on knowledge of the stable crystal structure to determine a material’s representation. A useful database for finding crystal structures is the Inorganic Crystal Structure Database (ICSD), which has collated almost 300,000 fully characterised crystal structures as of December 2022, including details of the unit cell, space group and atomic parameters [28, 29]. Each entry is scraped from peer-reviewed journals and corresponds to experimentally determined or theoretically calculated structures. Curtarolo et al. presented AFLOW: an open-source database containing DFT-calculated crystal structures of alloys, intermetallic and inorganic compounds [30, 31], as well as total energies and electronic band structures. AFLOW contains measurements for over 3 million compounds as of December 2022. In addition, the Open Quantum Materials Database (OQMD) comprises DFT calculations of 200,000 crystal structures [32], and has been used to screen for novel battery materials including high-capacity lithium-ion anodes from the stannides, phosphides and transition metal silicides classes [33], lithium-ion cathode coatings that inhibit cathode dissolution [34], lithium-air electrodes [35] and solid garnet-oxide electrolytes [36].

Another widely used database is the Materials Project, which comprises millions of DFT-calculated properties such as thermodynamic stability and dielectric tensors, for over 100,000 crystalline materials (as of 2021) [17, 18]. A subset of the Materials Project database (the “Battery Explorer”) is devoted entirely to battery materials (comprising 4000 compositions as

---

3Ab-initio / first-principles calculations have enabled the ground state structure of materials to be computed directly using quantum mechanics via density functional theory (DFT) simulations, with no need for experimental measurements to characterise the crystal structure.
2.2 Machine learning for materials design

of December 2022). Here, for a given battery chemistry, the database contains computed values such as maximum volume changes, gravimetric and volumetric capacity and average cell voltage. Huang and Cole mined 200,000 peer-reviewed publications to generate a database comprising 17,000 battery chemistries and relevant properties including capacity, voltage, conductivity, energy and Coulombic efficiency [37], and noted that biases in datasets can result from the tendency of academics to publish data for their most performant materials. Bligaard et al. also used DFT to compute lattice parameters, bulk moduli and heats of formation for 64,000 ordered metallic alloys that are candidates for battery electrodes. They used the database to identify Pareto-optimal alloy solutions to balance cost, compressibility and stability [38].

Representations of materials

Another challenge in developing an accurate structure-property model is identification of a suitable representation of the material structure. Several pioneering works have considered how to encode the structural motif of crystalline materials, for examples using fingerprints to encode band structure and crystallographic information [39], or using Coulomb matrices, with diagonal elements capturing the nuclear charge of each atom and off-diagonal elements capturing Coulombic repulsion between each pair of atoms [40]. Similarity between two molecules can be ascertained using the Euclidean norm between their respective matrices, which ensures invariance with respect to translations, rotations and index ordering of atoms. Longer-ranged descriptors, such as the size of open channels, can also be developed to capture diffusion channels that are relevant for ion conductivity [41].

In general, a good representation of crystal structure should be unique (for each material structure, there should be only one descriptor), physically interpretable, continuous, in the sense that small changes in environment should correspond to small, continuous changes in descriptor, and the representation should be invariant with respect to symmetries of the system [42]. An example of a representation which satisfies most of these requirements is the Smooth Overlap of Atomic Positions (SOAP) representation [43, 44].

More recently, there has been growing interest in deep learning approaches to learn representations of crystal structures. Here, instead of hand-crafting features based on physical reasoning, neural network architectures are used to learn the representation of crystal structure. Such approaches have achieved high (in some cases, “state-of-the-art”) accuracy on a multitude of property prediction tasks [45–47].

Most methods for obtaining a structural representation of crystalline materials rely on knowledge of the full crystal structure, which means that only materials whose structure
has been characterised can be screened. This means the vast majority of materials space remains unexplored since the stable polymorphs of most materials are unknown due to the expensive cost of running associated DFT calculations. Cubuk et al. tackled this by training an “elemental” machine learning model which takes only atomic number, group, period, boiling and melting temperature, density and ionisation energy as descriptors to predict lithium-ion conductivity of 20 billion lithium-containing materials [19]. Goodall and Lee also addressed this challenge by developing a graph deep-learning framework to learn a suitable material representation using the stoichiometry of the material alone [48]. A challenge here is that two polymorphs of the same stoichiometry could not be distinguished.

The use of structure-property models is arguably more mature for crystalline materials, such as typical battery electrodes or solid electrolytes, than for non-crystalline materials such as liquid electrolytes. This is likely because the existence of a single structural motif for each crystal polymorph makes it feasible to identify what structural motifs are related to high ion conductivity or electrochemical stability. In contrast, the local structure in non-crystalline materials such as liquid electrolytes follows a complex spatio-temporal distribution that is harder to identify and relate to macroscopic properties. In addition, whether local structure can explain macroscopic properties in all non-crystalline materials remains a matter of debate.

Screening battery electrodes

A wide range of potential battery electrode materials have been screened for relevant properties. The Materials Project database was initially used to screen for new lithium-ion battery anode [33] and cathode [49–51] materials with improved specific capacity and specific energy. More recently, the same database was used to identify structurally stable layered cathodes for multi-valent magnesium-ion batteries [52], to screen for stable high-capacity anode materials for potassium-ion batteries [53] and sodium-ion batteries [54], and to predict the average electrode voltage for multivalent-ion batteries [55]. The OQMD has also been used to screen for lithium-ion anode materials predicted to have high capacity, low volume expansion, and “optimal” anode voltage [35]. The same database was used to screen for lithium-air electrodes exhibiting a promising recently identified reaction pathway [35], and to identify lithium-ion battery cathode coatings that will attack the corrosive side-product HF and prevent cathode dissolution [34]. Allam et al. used electronic properties (such as the electron affinity, HOMO, LUMO) of organic electrode materials, computed using DFT simulations, as input to a neural network to predict the redox potential relative to Li/Li$^+$ [56]. The screening rate is inhibited here by the need to run a full DFT simulation for each new molecule being screened.

---

*For anode voltages there is a trade-off between minimising anode voltage to maximise energy density, and maximising anode voltage to reduce the tendency to form lithium metal dendrites.*
At the meso-scale, Kabra used machine learning to investigate the relationship between graphitic electrode microstructure (active material, binder and pore structures) and properties such as tortuosity, electron conductivity and specific surface area [57]. A more niche application has been to help design optimal structures of next-generation graphene electrodes, which are appealing due to their excellent electrical conductivity and mechanical strength, using kirigami [58].

**Screening solid electrolytes**

For several decades most materials development has focused on cathode and anode design. The electrolyte has in contrast been relatively consistent [59, 60]. Yet in recent years the influence of the electrolyte has become increasingly apparent [61, 60, 62–64]. In the bulk, the way that ions in the electrolyte interact with each other and move through the system directly impacts the macroscopic performance of the system. In lithium-ion batteries, the ion conductivity and the transference number limit the maximum cycling rate without resulting in degradation due to lithium plating. In addition, the composition of the electrolyte determines the structure of the solid electrolyte interphase (SEI). Upon assembly of the electrodes and electrolyte, and during the subsequent first charging/discharging cycle (known as the “formation” cycle), a series of reactions take place between the electrodes and the electrolyte [65]. The SEI is a passivating layer between the electrode and electrolyte, formed from the reaction products, which stabilises the battery and inhibits further decomposition of the electrolyte. Properties of the SEI, such as ion conductivity, electronic resistivity, and mechanical stability, critically impact battery performance [66]. The electrolyte chosen determines the distribution of reaction products and the nature of the SEI formed. In supercapacitors, ion interactions influence the lengthscale over which charge is screened, and thus the attainable energy density of the device. Consequently, it is now being recognised that improved electrolyte design could offer an additional route to improved lithium-ion batteries and supercapacitors [67, 68]. Additionally, designing an electrolyte stable enough for operation at the extreme electrode potential of lithium-metal is arguably the biggest hurdle to overcome for lithium-metal batteries [60].

Thus, high-throughput screening has also been recently applied to identify solid electrolytes with high voltage stability [36, 69], high ion conductivity [36, 70, 26] and low electronic conductivity [26]. Several groups have also focused on predicting the Li$^+$ migration barrier which is relevant for understanding ion transport [71, 69]. Ahmad et al. addressed the challenge of dendrite growth in lithium-metal batteries by screening for solid electrolytes with mechanical properties that suppress dendrite initiation [72].
One of the challenges associated with materials discovery is that there are usually several properties that we want to optimise. Optimising multiple parameters simultaneously is difficult, in part because sometimes there is a direct trade-off between two properties that are caused by the same underlying physics. For example, it has been suggested that electrochemical stability and ion conductivity may be related by lattice dynamics [73, 74, 26]. Sendek et al. addressed this challenge by simultaneously screening 13,000 solid electrolyte candidates for several properties including structural and chemical stability, low electronic conductivity, high ion conductivity and low cost, identifying 21 materials which met the criteria [75]. Their results highlight the importance and challenges of optimising for multiple objectives when designing new materials.

The same researchers [26] later approached electrolyte design through a Bayesian lens, placing a prior distribution over each property given all experimental and computational observations so far. They argued that this prior can be used to guide which regions of materials space to search. They calculated formation energy and band gaps for materials in the Materials Project database and used a structure matching algorithm to predict the ion conductivity of solid electrolyte candidates, with structural features including anion coordination number, lithium-lithium bond number, and counter-ion separation distances. They then used Bayesian analysis to calculate the probability that a material with both high ion conductivity and high electrochemical stability will be found in a particular class of materials. Their results suggest a multiple-electrolyte architecture such as that developed by Richards et al. [76] should be used to meet such a multi-objective criteria.

Cubuk et al. used an elegant “transfer learning” approach to screen 20 billion lithium-containing solid electrolyte candidates for high ion conductivity [19], using only a small training dataset of 40 materials. To do this, they first used this small dataset to train a model to predict conductivity from informative structural descriptors that can be computed from crystal structure, and then predicted the conductivity of 12,000 compounds whose crystal structure was already known. They then trained another machine learning model to predict ion conductivity from elemental data alone, using the newly augmented dataset of size 12,000 (rather the original 40). Since this model only required information about atomic number, group, period, boiling and melting temperature, density and ionisation energy (rather than crystal structure), it was then possible to screen 20 billion lithium-containing ternary and quaternary materials.
2.2 Machine learning for materials design

Screening liquid electrolytes

Sodeyama et al. asserted that one of the reasons why innovation in designing new liquid electrolyte materials for lithium-ion batteries has been slow (with commercial electrolytes remaining relatively unchanged since the 1990s), is because it is harder to identify design principles for liquid electrolyte due to the disordered nature of liquids [77]. This has made it more challenging to build local structure–property models than for crystalline materials.

There has been some research attempting to train machine learning models to predict ion conductivity of liquid electrolytes using the formulation alone as a descriptor. This approach was adopted by Krishnamoorthy et al. who built a high-throughput experimental setup to screen electrolyte mixtures of LiPF$_6$, ethylene carbonate (EC), ethyl methyl carbonate (EMC) and vinylene carbonate (VC) at a daily rate of 100 [78]. Similarly, Flores et al. collected thousands of measurements of LiPF$_6$-based electrolytes with propylene carbonate (PC), EC and EMC solvent mixtures at a range of temperatures, and used symbolic regression to fit a phenomenological model of ion conductivity as a function of temperature, salt concentration and PC:EC molar ratio [79]. Sodeyama et al. developed a model to predict the coordination energy between lithium-ion and solvent molecules in liquid electrolytes [77]. They considered 100 solvent molecules used commercially in lithium-ion battery electrolytes. They used descriptors of each solvent including boiling point, flash point, melting point and molecular weight, as well as the Mulliken charge of the coordinating anion and its distance to the cation, and the HOMO and LUMO energies as computed through DFT simulations of clusters. All of these descriptors describe average properties of the liquid rather than encoding information about the local structure distribution. Notwithstanding this, screening liquid electrolytes using structure-property relationships remains a challenge to be addressed.

2.2.2 Accelerating simulations with machine learning potentials

A plethora of methods exist for modelling materials at the atomic scale, ranging from exact quantum methods to DFT to empirical inter-atomic potentials. In general, there is a trade-off between accuracy and computational cost, with accurate and long simulations of large systems being prohibitively expensive. One area where machine learning has offered significant gains is in reducing the computational cost of running simulations to DFT-level accuracy, by training models to learn DFT force-fields. A machine learning potential (MLP) approximates the mapping from electronic structure to the potential energy surface and consequently, force field. At the point of simulation, calculating the forces experienced by an atom then simply requires a forward pass through the model, which is much cheaper than running the equivalent DFT calculation. The generalisability of an MLP depends on the simulation data used to
train the model; predictions will likely only be accurate for systems for which all relevant inter-atomic interactions were also present in the training set.

Behler and Parrinello pioneered the use of neural networks to model the potential energy surface of bulk silicon [20] and presented a novel way to represent local atomic structure using symmetry-invariant transformations of atom coordinates to encode local structure, known as ACSF [21]. Bartok et al. later combined SOAP fingerprints, to encode local atomic structure, with Gaussian processes to model the Born-Oppenheimer potential energy surface [80]. It is important to consider the cut-off distance used for encoding the structural representation when using ACSF and SOAP, since this limits the range of interactions that can be learned: any atoms beyond the cut-off distance are effectively considered not to contribute to the forces experienced by the central atom. Recent innovations in fingerprint representation tackled this, enabling long-ranged effects such as non-local charge transfer to be encoded [81].

More recently, graph neural networks have been used to learn both a suitable representation of local structure and the mapping from local structure to potential energy surface [82]. Here each atom is treated as a node, with edges constructed between all atoms assumed to be interacting. The node and edge vectors are iteratively updated according to a function (learned through training), and the converged vectors are passed through another network to predict the potential. Graph neural networks are typically able to capture longer-ranged structure than possible with the aforementioned techniques [83], depending on the number of permitted message-passing/update steps.

It has also been demonstrated that the above approaches can all be used to accurately model the electron density [84–89], which has been used to study cation migration through solid-state ion conductors [90, 89, 91] and to identify optimal lithium-insertion sites for next-generation cathodes [92]. Direct prediction of the electron density enables chemical reactivity to be investigated without the need for an additional DFT computation after the potential surface has been calculated.

**Simulating energy materials**

MLPs are widely used to study the structural and transport properties of battery electrodes and electrolytes, including for lithium metal anodes [93], crystalline bulk Si [94], titanium dioxide anodes [95] and LiNi$_x$Mn$_y$Co$_z$O$_2$ (NMC) cathodes [96]. The computed force fields have been used to calculate properties relevant for cell design including thermal conductivity [94], lattice expansion upon lithium-insertion and open circuit voltage with respect to lithium-metal [96]. Nishiyama et al. developed a MLP framework to study the structure and energies of grain boundaries in elemental metals [97].
Many electrode materials exhibit disorder in at least one of their phases, such as silicon, which is crystalline in its de-lithiated form, and amorphous once lithiated [98]. Modelling amorphous phases has historically been challenging, because the computational cost of DFT meant only systems with unit cells comprising hundreds of atoms could be sampled. Machine learning thus unlocked a new paradigm for modelling amorphous materials by enabling simulations of much larger systems. For example, Deringer and Csanyi used Gaussian approximation potentials to simulate amorphous carbon [99]. Artrith et al. later developed a framework combining genetic algorithms with a neural network potential to model amorphous materials, and applied the approach to investigate amorphous lithiated silicon [100]. The same researchers later enabled the delithiation of entire amorphous Si nanoparticles to be visualised for the first time by training an MLP using both ab-initio and nanosecond-scale molecular dynamics (MD) simulation data [101].

Diffusion through solid electrolytes has also been extensively studied using MLPs, for systems including Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO), [102], Li$_3$PO$_4$ [103], Li$_{10}$GeP$_2$S$_{12}$ (LGPS) [104–106], $\alpha$-Li$_3$N [107] and Na$_{1+x}$Zr$_2$Si$_x$P$_{3-x}$O$_{12}$, $x < 3$ (NASICON) [108]. Rao et al. used the trained MLP to study the effect of Cl doping, which enabled optimisation of the Cl dopant concentration with respect to transition state energy and conductivity [104]. Eckhoff et al. used MLPs to enable MD simulations of LiMn$_2$O$_4$ over a nanosecond timescale, enabling structural properties such as volume expansion in these materials to be investigated [109].

If machine learning is not used to predict the electron density, DFT can be applied after the base electrode structure has been computed with the MLP [110]. This hybrid approach overcomes two challenges with the MLP approach. Firstly, without a separate model to predict electronic structure, no information about electron density is generated from the MLP, so it is hard to predict chemical reactivity. Secondly, addition of any new species to the simulations reduces the accuracy of MLPs which typically struggle to generalise outside of the training dataset, whereas using DFT to compute electron density makes it easy to add new species, such as Li$^+$ or Na$^+$, into the simulation [111]. This approach was used to study the energetics of Li, Na and K intercalation into disordered hard carbon structures [110, 111], and to calculate the voltage profile associated with metal insertion [111]. They also used clustering to identify the number of statistically relevant local cationic environments.

It is also possible to use MLPs to study diffusion across solid-solid interphases, which is useful for understanding the formation and evolution of the SEI, whose composition, behaviour and evolution has long been enigmatic, in part because it comprises a heterogeneous mixture of reaction products. Wang et al. developed an algorithm to predict the distribution of reaction products that would form at each interface [112], using MLPs to simulate solid-solid
interfaces between eight common solid-state electrolytes including LGPS and Li$_x$PO$_y$N$_z$, $2.6 \leq x \leq 3.5, 1.9 \leq y \leq 3.8, 0.1 \leq z \leq 1.3$ (LiPON) and seven electrode materials including NMC cathodes and lithium-metal anodes. From this they could identify the most favourable diffusion pathways through each of these product phases. The same researchers also used MLPs to model lithium-ion conduction through interfacial cathode coatings used to stabilise the interface between cathodes and liquid electrolytes, which present challenges because simulations must run for longer times since these coatings often exhibit low ion conductivity [113].

In a more limited capacity, MLPs have also been used to simulate liquid electrolytes including aqueous NaOH [114, 115] and zinc ions in water [116] and to investigate the effect of changing temperature on ion conductivity [115].

2.2.3 Optimal experiment design

Machine learning can also be used in conjunction with practical experiments to guide which experiments should be performed next to minimise the number required to identify the optimal material for a particular objective.

One way of achieving this is using Bayesian optimisation. The goal of Bayesian optimisation is to find the global optimum of a black-box function $f(x)$ in as few steps as possible, i.e. to determine

$$x^* = \arg\max_{x \in \mathcal{X}} f(x)$$

where $\mathcal{X}$ is the search space. We obtain information about $f$ by making noisy observations at different locations. Usually homoscedasticity is assumed, such that the observation noise is independent of $x$, although recent work has incorporated heteroscedastic noise [117]. Using Bayesian optimisation to decide where to collect measurements can lead to the optimum being found more quickly than by random sampling or grid search of the input space [118, 119].

Bayesian optimisation has been implemented in a range of applications other than materials design [22], including in drug discovery [120] and the optimisation of neural network hyperparameters for machine learning applications [118]. The method is especially well suited in applications in which the function to be optimised is expensive to evaluate (computationally, temporally or financially), continuous and complicated [121]. The ideal search space is low-dimensional and explorable in the sense that we should be able to make a measurement at all points in the search space [122].
In the field of electrolyte screening, Bayesian optimisation was used to optimise the ionic conductivity and voltage stability window with respect to the composition of an aqueous electrolyte with multiple co-salts [23, 24]. Rahmanian et al. later used one-shot active learning to identify non-aqueous liquid battery electrolytes with high ion conductivity for different operating temperatures, recognising that at extreme temperatures the electrolyte performance can become rate-limiting, and that different temperatures have different optimal electrolytes [123]. Using a similar hardware-in-the-loop setup as Whitacre and Dave et al. [23, 24], they aimed to perform a minimal number of additional experiments to identify electrolyte formulations with the highest ion conductivity over a wide range of operating temperatures. Bayesian optimisation has also been applied to decide which materials should be simulated using DFT. Jalem et al. used this approach to reduce the number of expensive DFT evaluations needed to identify solid favorite electrolytes with low Li\(^+\) and Na\(^+\) migration energies by 70% [71].

### 2.2.4 Elucidating microscopic understanding

Finally, machine learning can help us to elucidate the microscopic origin of macroscopic properties. Armed with this new understanding, we can extract design principles and test those materials whose structure is likely to lead to favourable properties.

A consequence of the development of structure-property relationships for high-throughput screening is the possibility of understanding which structural features are most important for predicting performance. For example, Chen et al. studied the mechanism of lithium transport in the LLZO crystal lattice using unsupervised machine learning to identify the different local structural motifs of cations in MD simulations [25], and investigate their role in diffusion. Sendek et al. found that it is crucial to know the grain size distribution within a solid electrolyte in order to accurately predict its ion conductivity, suggesting that ion transport within and across grain boundaries must be accounted for in theories of solid electrolyte ion conduction [26]. Katcho et al. aimed to develop an understanding of which structural motifs in solid electrolytes are favourable for high ionic conductivities [41]. The results suggested that the best ion conductors are associated with larger channels for diffusion and high cation coordination numbers. A similar approach was taken by Kireeva and Pervov, who explored what structural motifs in garnet-type solid electrolytes are correlated with high ion conductivity [124].

Zhang et al. used unsupervised learning to cluster all lithium-ion containing crystalline structures in the ICSD, representing each material by a modified X-ray diffraction pattern [125]. The premise was that some clusters would contain solid-state lithium-ion conductors
with high ionic conductivity and other clusters will contain poor conductors, and an implicit assumption was that materials with similar diffraction patterns will exhibit similar lithium-ion conduction properties. They found that most known solid-state lithium-ion conductors belonged to the same groups, which was seen as confirmation that anionic lattice structure influences ion conduction. Novel materials could be identified by looking at the materials inhabiting these groups. A downside of this approach is that by only clustering based on anionic geometry, other factors influencing ion conductivity such as electrochemical window and mechanical properties could not be accounted for.

Following our work on ion transport [126], discussed in Chapter 4, Andersson et al. considered the contribution that different local structural motifs in LP30 (1M LiPF₆ in 1:1 DMC/EC) make to lithium-ion diffusivity and noted that the total contribution should be proportional to the number of instances of each motif. They defined motifs using a manually defined cut-off distance to determine if two atoms inhabit the same motif. They highlighted the importance of considering the distribution of local structural motifs, and that a wide range of local structures contribute to the realised macroscopic transport properties [127].

In the field of supercapacitor design, research groups have used machine learning to identify correlations between structural features (such as pore size and shape distribution, specific surface area, and N/O doping percentages) of activated carbon electrodes and in-operando performance properties (e.g. specific capacitance and power density) of electric double layer capacitors [128–130]. Zhu et al. collected data from over 300 peer-reviewed papers on carbon-based supercapacitors to train their models [128]. This could be used to optimise the pore size distribution of electrodes for a given electrolyte composition and expected scan rate. Jha et al. used a neural network model to predict the specific capacitance of lignin-based supercapacitors as a function of the ratio of electrode material constituents and cycle number [131]. In the field of fuel cells, Briceno-Mena et al. developed a machine learning approach to predict ion conductivity of polymer electrolytes, with the goal of designing high temperature polymer electrolyte membranes with increased power density [132].

2.3 Machine learning for battery analytics

Data-driven analysis of batteries is a rapidly growing area serving several purposes. These models can be categorised into two broad remits, namely internal state diagnostics and performance forecasting.

Internal state diagnostics are used for several applications. Firstly, battery state parameters can be used to parameterise simulation models to predict a cell’s voltage response to a
2.3 Machine learning for battery analytics

particular cycling profile. This is relevant for building battery management systems. State estimation is also applied to understand battery degradation; that is, to identify how much the battery’s state has evolved since manufacture. In some diagnostic models, detection of different degradation modes including loss of active lithium, or loss of active electrode material is possible. In industry, these models are used to enable degradation to be detected non-invasively, and for predictive maintenance.

Performance forecasting models are instead focused on predicting how the internal state will evolve under expected use conditions. One class of models focuses on battery lifetime prediction, which is relevant in industry for warranty design. Accurate battery performance forecasts can also significantly accelerate battery research and development, as currently the rate of iteration for cell design is hampered by the need for long-term cycling tests.

2.3.1 Applications of battery analytics

Battery state diagnosis

The most widely used types of battery state are the State of Charge and the State of Health, although other measures such as State of Power and State of Energy are occasionally adopted. The State of Charge (SOC) captures how much charge is available for discharge relative to the fully charged state. A widely used definition is

\[
SOC = \frac{C_N - \int I_d dt}{C_N}
\]  

where \(C_N\) is the nominal capacity of the battery (the capacity provided by the manufacturer), and \(\int I_d dt\) is the net amount of charge discharged through the battery since the battery was last fully charged [133]. SOC estimation is important in battery management systems to enable cell balancing and prevent the cell from becoming over- or under-charged, both of which can result in irreversible damage to the battery [134]. In addition, accurate SOC estimation is useful for range estimation, which is important in practical use to help reduce “range anxiety” [135].

A simple way to determine the SOC is to fully discharge the battery under a low constant current and measure the resulting capacity. This technique is time-consuming and invasive, changing the battery from its current state. Alternatively, Coulomb counting may be used [134]: here, from an initial known SOC, the current SOC may be approximated by subtracting the net total charge discharged due to current flow, \(I_d\) (accounting for current losses \(I_{\text{loss}}\)) as
Machine learning for electrochemical systems

A fraction of the nominal capacity:

\[ SOC_t = SOC_0 - \frac{\int (I_d - I_{loss}) dt}{C_N}. \] (2.4)

Alternatively, the SOC has been estimated from the open circuit voltage (OCV), since there is often a linear relationship between OCV and SOC \[134\]. Once this relationship is known, look-up tables can be used to identify SOC whenever the cell is at equilibrium and its OCV is known.

State of Health (SOH) estimation is designed to quantify the extent of degradation within cells, and to identify cells that have reached their End of Life (in EVs, this is typically defined as the point at which the discharge capacity has reduced to 80% of the nominal capacity \[136, 137\]). The SOH is often defined as the ratio between the discharge capacity (or internal resistance) now relative to its initial value \[138–143\].

Other frequently used measures of a battery’s internal state are State of Energy (SOE) and State of Power (SOP), which are defined as the fraction of total energy and maximum power available relative to the amount that is available when the battery is fully charged \[144\]. SOP and SOE are often used in practice to provide range estimates and indicate the maximum power of a battery pack.

State estimation models can be sub-divided into online and offline estimation methods. Offline methods use the entire set of historical observations for a particular battery to compute the current state. In contrast, online methods iteratively update their estimate of internal state based on real-time measurements of current, voltage, and optionally temperature \[145\]. Online methods do not require storage of historical observations and state estimates, since estimates of battery state depend only on the previous estimate of battery state and the most recent observations of current and voltage. This makes online methods especially well-suited for application in battery management systems, where memory is limited.

Battery health prognostics

Both short \[146–148, 141, 149\] and long \[150–152\] timescale forecasting of battery performance are of interest in battery prognostics. Over a short timescale, predicting how the battery would respond to a particular charging and discharging protocol can be used to develop optimal charging protocols \[146\]. Over a long timescale, a large focus is in predicting the remaining useful life (RUL) \[150\], end of life (EOL) \[151\], or the “knee-point” \[152\]. A common definition of the EOL is the cycle number (under fixed use conditions) when
the discharge capacity will drop to 80% of the initial discharge capacity [153], whilst the RUL is the number of remaining cycles before the battery reaches its EOL. The definition of the knee-point is a matter of debate, but qualitatively refers to the point in the battery’s life trajectory at which degradation accelerates [154]. In addition, there has been recent interest in forecasting the entire degradation trajectory of batteries under a specific use condition [155, 156]. Knowledge of the battery state trajectory can be used to infer the expected degradation mode ahead of time [154].

**Optimal charging protocols**

Whilst materials discovery can be considered a form of “hardware optimisation”, an alternative route to improved systems is through “software optimisation”, which concerns itself with improving how a given system is operated to extract maximal performance.

In the battery field, a challenge is to understand what is the optimal way to charge a battery to minimise the charging time without compromising battery safety or battery life? Or alternatively, for a given charging time, how should I charge the battery to maximise battery lifetime? Attia et al. developed a hardware-in-the-loop approach to learn the optimal fast charging protocol to maximise cycle life [157]. Hardware-in-the-loop optimisation was later used again by Wei et al. who used reinforcement learning to optimise the fast charging protocol, and showed they could extend battery life by 75% for the same charging time [158].

### 2.3.2 Battery analytics models

**Machine learning models**

A variety of machine learning models, including neural networks, random forests, Gaussian processes and support vector machines, have been used to estimate the SOC [159–161], SOH [162, 163, 160, 161], SOE [164] and SOP [165]. A widely used online state estimation algorithm is the Kalman filter (KF) [166], which assumes that the underlying battery state evolves according to a linear relationship of the current battery state $S_t$, the external control $U_t$, with the addition of noise. The goal is to estimate the current battery state, which is achieved by learning the underlying model parameters based on the observed data. The extended Kalman filter (EKF) generalises this such that the state transition function and observation functions can be non-linear:

$$S_{t+1} = f_\theta(S_t, U_{t+1}) + \Sigma. \quad (2.5)$$
Part of the success of the EKF is that it is recursive, such that only the previous estimate of internal state and the observations at the current time step are needed to estimate the current internal state. This means it is not necessary to store all historical observations or estimates, which means in storage-limited battery management systems SOC and SOH can still be estimated. EKFs have been used to estimate SOC and SOH in lead-acid batteries [167] and lithium-ion batteries [168].

Other feature-based data-driven approaches to state estimation transform the historical current voltage time-series data to extract features that are considered to be physically relevant. For example, the input can be the previous cycle capacities [163], or statistical features of the capacity-voltage charge and discharge curve [151], or the electrochemical impedance spectrum measured immediately before charging [150, 169].

In the field of prognostics, a variety of machine learning models have been applied to predict the EOL or RUL of batteries under fixed cycle protocols [163, 142, 151, 150]. Input features can be extracted from charging or discharging curves from early cycling data [151, 152, 155]. Innovations in extracting features from charge/discharge curves [170] and machine learning approaches for modelling time-series data [171, 172] have enabled significant improvements in the accuracy of predictions. Such features can be used to train a generalisable model that can predict the cycle life of a range of chemistries [173]. Other than the charging/discharging curves, features extracted from early cycle Coulombic efficiency [174], electrochemical impedance spectroscopy (EIS) [150], current interruption [175] and acoustic time-of-flight analysis [147, 176] have been used for degradation forecasting. These approaches provide a fuller description of battery state – for example, EIS captures the response of the cell over a broad frequency range, with different frequencies correlating to distinct physical, chemical and mechanical changes in the active material [177–180]. Electrochemical data generated during formation has also recently been used to predict battery life [181]. This is particularly appealing to battery manufacturers, who could use such a model to more accurately grade cells and assign warranties.

Recently, there have been efforts to forecast the entire degradation trajectory, including sudden death [182] or knee-points [152]. Some models take features from a fixed number of previous cycles [183] to forecast the discharge capacity a fixed number of cycles ahead of time. This approach has the drawback that to predict the entire degradation trajectory several iterative forward steps must be made, depending on the size of the rolling window. In addition, the number of available historical cycles is not always fixed. Using a fixed number of input cycles means any relevant information from earlier cycles will not be used to make predictions. Li et al. overcame this challenge, using a long short-term memory (LSTM)
model to forecast the entire capacity [155] and power trajectory [156] from a variable number of input cycles. Strange and dos Reis also built a model aiming to predict the entire capacity fade and impedance rise trajectory from features of the first charge-discharge cycle alone [184]. It should be noted that the data used to train these models is usually generated by repeatedly subjecting cells to the same cycling protocol. This can make it challenging to extrapolate models to batteries in the field, where usage is much more variable.

**Empirical models**

Empirical approaches were amongst the first methods to study lithium-ion battery degradation. In particular, several models focused on the growth of the SEI, which has been asserted to be the most probable cause of capacity loss in long-cycle life lithium-ion batteries [185]. In the 1980s, Peled developed a model of SEI growth suggesting that the SEI should grow with \((\text{time})^{1/2}\) [186]. Later, Bloom et al. fitted an empirical power law model to predict cycle and calendar life, as well as area specific impedance (ASI) rise, as a function of temperature and time [153]. They also observed that ASI rise and power loss scaled with \((\text{time})^{1/2}\) and attributed this to the growth of the SEI. Broussely et al. built a model of SEI degradation and capacity fade using Arrhenius relations. By fitting model parameters to experimental data, they could predict calendar life as a function of temperature [187]. They also noted the capacity loss scales with \((\text{time})^{1/2}\) and attributed this to the growth of the SEI which limits the rate of electrolyte reduction, thus causing sub-linear degradation. Ploehn et al. later developed a diffusion model to explain the \((\text{time})^{1/2}\) dependence of SEI growth and capacity fade [188].

In general, empirical models based on power laws assume fixed operation over battery life, and do not account for intrinsic differences in cell state at start of life. These approaches assume that all cells of the same chemistry will fade in the same way if operated in the same way, which is not observed in practice [153, 189].

**Physics-based models**

Apart from data-driven methods and empirical models, the two main classes of battery models for state diagnostics are physics-based models and equivalent circuit models. Physics-based models (PBM) seek to capture the exact physical and chemical processes taking place within a cell from first principles. They are widely used to predict how battery voltage responds to an externally applied current (or vice versa), which can be used to design battery management systems or predict optimal charging protocols [146].
Because these models are built upon underlying physical principles, they are often expected to be more generalisable than pure machine learning models. In addition, PBM parameters are physically interpretable, and it is generally more straightforward to understand the impact of changing various microscopic properties (such as electrode thickness) on electrochemical performance. However, a major challenge with PBMs is that they are computationally expensive to fit and run at inference time. This means PBMs are rarely implemented in battery management systems. In addition, a new model should be built for each cell, since there can be significant variation in model parameters from cell to cell, even within the same chemistry and batch [189–191]. PBMs can also suffer from non-identifiability, in that the observed data could be explained by multiple sets of model parameters, but each of those selections would result in very different predictions if the cell was cycled under a different set of operating conditions.

Arguably the most widely used PBM is the pseudo-two-dimensional (P2D) model [192], derived from porous electrode theory, which accounts for lithium diffusion through the electrodes under concentration and potential gradients, ion transport through the electrolyte, and electrochemical reactions taking place within the electrodes. Ion transport in the electrolyte is modelled using concentrated solution theory, and the kinetics of electrochemical reactions are modelled using the Butler-Volmer equation. The P2D models the electrode as a single spherical particle, such that radial diffusion into the electrode can be modelled as well as the motion along the central z-axis. Reduced-order models such as single particle models [193–195] can also be adopted to reduce the computational cost, although at risk of compromising accuracy [196].

The majority of PBMs are focused on immediate term modelling of cell performance, not addressing the challenge of parameter evolution due to degradation [197]. However, there are notable exceptions. Pinson and Bazant [185] developed a single particle model accounting for SEI growth, assuming the SEI forms at a rate proportional to electrolyte concentration, and that diffusion through the SEI is limited by electrolyte transport. Yang et al. built upon their original ageing electrochemical-thermal model (ECT) [198] to account for both SEI growth and lithium plating [199]. Jin et al. developed a reduced-order model incorporating capacity fade due to SEI growth and loss of active material [200]. Others have incorporated models of electrode surface cracking using empirical models relating surface concentration and stress [201], or crack growth and capacity throughput [202]. Finally, there has been some work on modelling cathode dissolution using Tafel equations [203]. Reniers et al. combined several of these models into a single framework to enable all degradation mechanisms to be tracked simultaneously, and to study the interrelation of the modes [196].
Another type of reduced-order degradation model aims to track and predict higher-level degradation modes such as (a) loss of active material (LAM), which refers to the reduction of electrode mass available for cycling due to particle cracking, resistive surface layers or loss of electrical contact, or (b) loss of lithium inventory (LLI), which results from lithium ions being expended in SEI formation, side reactions or lithium plating [204–206]. Here, no attempt is made to understand the exact underlying reason why the amount of active electrode material has reduced, and several physical processes, or degradation “mechanisms” can contribute to each degradation mode. The benefits of this approach is that it is much easier to identify a degradation mode than the exact mechanism that caused it [154]. For example, the formation of resistive surface layers can cause both LAM and LLI, whilst LLI can also be caused by side reactions and lithium plating [205]. Such mechanistic models are useful in that they do not require every possible cause of degradation to be explicitly included in the model. However, it is not straightforward to interpret what is the underlying cause of each mode once it has been identified. Smith et al. aimed to bridge the gap between first principles modelling and mechanistic modelling, developing a LLI model accounting for four primary contributions to degradation: a) loss of lithium at the negative electrode due to SEI growth, b) depletion of electrolyte at the positive electrode due to oxidation, c) transition metal ions dissolving into electrolyte at the positive electrode (and potentially depositing on the negative electrode), d) positive electrode cracking [207].

**Equivalent circuit models**

Equivalent circuit models (ECMs) approximate a cell as a circuit comprising an ideal cell voltage source and multiple impedance elements connected in series and parallel [208]. Each impedance element is designed to model a physical or chemical process within the cell, for example charge-transfer resistance at the electrode-electrolyte interface, ohmic resistance of the current collector, and a diffusion element [209, 180].

Often the construction of an ECM utilises the understanding of the physical processes taking place for a particular cell chemistry. A commonly used model is the Randles circuit [210, 212, 134], shown in Figure 2.1a. This circuit can also be extended, for example adding another resistance-capacitance (RC) element to account for the SEI impedance, as shown in Figure 2.1b. Other models add additional RC circuit elements to represent additional physical processes: for example, using separate RC circuit elements to model ion transport through SEI grains, across SEI grain boundaries, and at the electrode/SEI and SEI/electrolyte interfaces [213]. A model with so many parameters is susceptible to overfitting, and a key challenge is to identify the “Occam’s razor” ECM: that is, the simplest model that can
Fig. 2.1 (a) The Randles equivalent circuit [210]. Here, $R_0$ represents the resistance of the electrolyte, $C_{DL}$ is the capacitance of the electric double layer at the electrode interface, $R_{CT}$ is the charge-transfer resistance associated with the chemical reaction at the electrode, and $Z_W$ is a Warburg element which models diffusion [211]. (b) An example of an extended Randles equivalent circuit, which adds an additional RC element in series to model the SEI impedance.

adequately explain the observed data [214, 215]. The parameters of an ECM can be learnt by fitting to current-voltage time-series data [216, 149], or EIS spectra [217, 218].

Once an ECM has been obtained for a particular cell, it is relatively computationally cheap to then predict the cell voltage response to different current profiles [219]. This means ECMs are widely used in battery management systems. An ECM can be fitted at different points in the battery’s life and the cell parameters can be tracked to understand how the battery has degraded [149]. However, it should be remembered that the circuit elements do not actually describe the physical make-up of the cell: each cell is not really divided up into a clear set of fixed capacitors and resistors! Thus interpreting the evolution of the fitted ECM parameters in terms of physical processes can be challenging. An additional challenge is that several ECMs can often explain the same data, and a very small change in the data can cause large changes in the fitted ECM parameters.

**Hybrid models**

There are trade-offs for each of the above classes of models based on computational cost, generalisability and interpretability. Hybrid approaches aim to combine two or more model classes in order to take advantage of the benefits of each whilst overcoming their disadvantages.

Aykol et al. presented several possible model architectures that can be used to combine machine learning with PBMs to predict battery life [197]. For example – PBMs are commonly used to model cell voltage response without incorporating degradation, and assume that the voltage response will remain fixed over the cell lifetime. If a PBM is fitted at the start of a cell’s life, over time the true voltage response will diverge from the predictions of the PBM. The difference between the true voltage response and that predicted by the PBM can
be used to infer how much degradation has taken place. In cases where the quantity of experimental data is limited, PBMs could be used to generate synthetic data and augment the quantity of data available to train a machine learning model [197]. Alternatively, a machine learning model can be trained to predict PBM parameters such as diffusion coefficients and rate constants, which can be allowed to evolve over battery life [220–224].
Chapter 3

Uncovering hidden local structure in liquid electrolytes

3.1 Introduction

Concentrated electrolytes play a role of fundamental importance in the majority of lithium-ion batteries and supercapacitors [225]. The motion of ions through the electrolyte is necessary for energy storage and current flow. In spite of this, inter-ion correlations in concentrated electrolytes remain, to a large extent, enigmatic. Measurements of the interaction force between charged plates immersed in an electrolytic solution, using the Surface Force Balance, show that at sufficiently high concentrations, the electrostatic screening length is orders of magnitude greater than the theoretical Debye length [226–230] for a variety of concentrated inorganic salt solutions and ionic liquids. Further, a scaling relation, shown in Figure 3.1, has been observed between the screening length and Debye length at non-dilute concentrations, which generalises across a wide range of electrolytic systems [229].

Numerous attempts have been made to explain under-screening, but the idea that prevails is the ion-pair hypothesis, which states that a large number of ions are paired up with another ion of the opposite charge, forming effectively neutral ion pairs, which results in a significantly smaller “free” ion concentration [226, 227]. Somewhat unsatisfactorily, the notion of such a pair remains loosely defined as unlike charges being closer than some arbitrary cut-off distance.

If such pairs truly existed, one would expect the existence of two statistically distinct local environments within the electrolyte, corresponding to ions in the “paired” and “free” states.
A notable scaling relationship has been found relating the experimentally determined screening length $\lambda_S$, theoretical Debye length $\lambda_D$, and ionic diameter $a$. When $\lambda_D \gg a, \lambda_S \sim \lambda_D$, but when $\lambda_D < a, \lambda_S > \lambda_D$ according to the scaling $\frac{\lambda_S}{\lambda_D} \sim \left(\frac{a}{\lambda_D}\right)^3$. Figure taken with permission from [229].

In this work, we put this hypothesis to the test by carrying out MD simulations of the bulk electrolyte, and then reframing the problem into a Bayesian hypothesis test. We seek to determine: “Statistically speaking, do multiple local environments exist within the bulk of the electrolyte? If so, how many, and what do they look like?”

We apply the inference technique to data from simulations of models with differing levels of detail: the restricted primitive model, solvent primitive model, and an all-atom model. For all models, at intermediate concentrations we observe the existence of multiple distinct environments within the bulk, whose differences originate in the form of like charge correlations.

This work was carried out with input from collaborators Andreas Härtel and Fabian Coupette of the University of Freiburg, who conducted the majority of MD simulations, and with invaluable insights from Alpha Lee. The work resulted in the publication

3.2 Theories of electrolytes

3.2.1 Debye-Hückel theory

The interaction energy between two charges in a dilute electrolytic solution decays exponentially with separation due to screening by other charges [233]. According to Debye-Hückel theory, the electrostatic potential will decay over the Debye length $\lambda_D$,

$$\lambda_D = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{q^2 c}}$$  \hspace{1cm} (3.1)

where $\varepsilon$ is the dielectric constant, $c$ is the ionic concentration, $T$ is the temperature and $q$ is the ionic charge [234]. The other important length scale is the Bjerrum length,

$$l_B = \frac{q^2}{4\pi \varepsilon \varepsilon_0 k_B T}$$  \hspace{1cm} (3.2)

which is the inter-ion distance at which the electrostatic energy is comparable in magnitude to the thermal energy [235]. The key assumption made in Debye-Hückel theory is that the average inter-ion distance is much greater than the Bjerrum length, such that the electrostatic energy can be treated as a first order perturbation to the thermal energy [229]. In effect, Debye-Hückel theory assumes that all ions in the solution are “free” and can contribute equally to screening. This requires

$$l_B^3 c \ll 1.$$  \hspace{1cm} (3.3)

Debye-Hückel theory is thus only valid for dilute electrolytes. The Debye length can be rewritten in terms of the Bjerrum length to eliminate the concentration-dependent dielectric constant:

$$\lambda_D = \sqrt{\frac{1}{4\pi l_B c}},$$  \hspace{1cm} (3.4)

which suggests that increasing the concentration will reduce the screening length.
3.2.2 Liquid state theories

At high concentrations the mean-field Debye-Hückel theory is no longer valid. The mean spherical approximation (MSA) extended Debye-Hückel theory using a virial correction that accounts for excluded volume effects [236, 237]. The MSA can explain thermodynamic properties of electrolytes, such as osmotic coefficients [238] and mean activity coefficients [239], at significantly higher concentrations than Debye-Hückel theory. Rotenberg et al. developed a liquid state theory using the MSA and fluctuation theory, which predicts a cross-over to a regime in which the screening length increases with concentration [240] with a derived power law

\[ \frac{\lambda_S}{\lambda_D} \sim \left( \frac{a}{\lambda_D} \right)^\alpha, \]  

(3.5)

where \( \lambda_S \) is the screening length, \( \lambda_D \) is the theoretical Debye length, \( a \) is the ionic diameter, and \( \alpha \) is the scaling exponent. However, this power law exhibits a scaling exponent of \( \alpha = 3/2 \), rather than \( \alpha = 3 \) as observed experimentally and shown in Figure 3.1.

Similar power laws have also been derived using classical DFT simulations, which decompose electrostatic forces into a hard sphere contribution, a mean-field Coulombic contribution and an additional correlation term [241, 242]. These theories predict \( \alpha \approx 2 \) [242]. Even fully atomistic MD simulations cannot replicate the order-of-magnitude discrepancy in screening length, predicting \( \alpha \approx 1.3 \) [232].

3.2.3 Scaling analysis

The application of scaling concepts to understand soft matter systems was pioneered by De Gennes [243], who used relatively simple assumptions to derive scaling laws that could explain the behaviour of polymers, including their viscosity, and propensity for segregation and/or gelation. The beauty of his approach is that these laws generalise across polymers of greatly different lengthscales and chemical formulae and can explain why all of these polymers act the way they do, under a range of conditions, independent of chemistry. In general, this is what makes scaling analysis so appealing: the ability to condense a sequence of observations from a wide range of systems down to a simple power law, using intuitive concepts.

Scaling analysis has also been applied to electrolytic systems to explain the under-screening phenomenon. Lee et al. observed the emergence of a notable scaling relationship between the screening length and Debye length when the Debye length becomes comparable to the ionic diameter in size, which generalises across a wide range of electrolytic systems [229]. The existence of such a scaling suggests that the origin of under-screening lies in the nature
of electrostatic interactions rather than the chemical structure (including shape and charge distribution) of each ion [244]. The scaling is shown in Figure 3.1 and suggests at high concentrations, there may be a change in the type of inter-ion correlations. The observed power law was explained using the idea that in concentrated systems, ions are strongly correlated, and solvent molecules can be considered to act as charge carriers analogously to Shottky defects in an ionic crystal [229]. Experiments using EIS support that neutral solvent molecules added to ionic liquid solutions can act as charge carriers [245]. Others have instead re-scaled the parameters in Eq. 3.1 by deriving an “effective concentration” [226, 246] or “effective” ionic charge [247, 248]. In the latter case, the effective surface charge density of ions is reduced by the presence of diffuse neighbouring counter-ions. The dressed ion theory simultaneously renormalises the surface charge density and the dielectric function, and predicts the increase in screening length with concentration (at high concentrations), going some way to addressing under-screening [247, 248].

3.2.4 Ion clustering

Another explanation of under-screening states that most ions are bound in effectively neutral ion pairs that can be treated as equivalent to solvent molecules, with few “dissociated” ions free to screen charge [226]. Although the ion pairing is intuitive and physically appealing, and has been applied to qualitatively explain experimental observations [249], its construction is artificial [250], and there is no universally accepted definition of an ion pair. Ion pairs are often defined using an arbitrary cut-off distance, such as the first minimum of the pair distribution function [251]. However, physically speaking, there is no clear distinction between two oppositely charged ions being “paired” and simply interacting under a Coulomb potential. In addition, there is uncertainty about how the proportion of ion pairs should be calculated. Bjerrum computed this by simply calculating the fraction of ions that have counter-ions within the cut-off distance [251], whilst Lee reasoned that the proportion of ion pairs should instead be calculated by considering the excess counter-ion density within the cut-off distance relative to the bulk density [250]. The concept of ion pairing to explain under-screening has been met with relative scepticism elsewhere [252–254].

As we will explore further in Chapter 4, there is also a dynamic aspect to ion pairing - ion pairs have a finite lifetime and will dissociate, becoming free ions and eventually pair up with another ion. NMR measurements showed that ion pairs in ionic liquids have a short lifetime, comparable to the diffusion timescale [255], and significantly shorter than the timescale of conductivity measurements [256, 257]. Nevertheless, Kjellander showed that even transient
ion aggregation can change the effective dielectric constant in ionic liquids and result in longer screening lengths [248].

Although in this chapter we will focus on statics and the instantaneous local environment, in Chapter 4 we will delve into the relationship between local environments such as ion pairs and dynamic properties such as conductivity.

### 3.3 Inference of local structure distribution

A key question that would shed light on the structure of the concentrated electrolyte is whether all ions can be considered to share the same ionic environment. If they do, this would suggest that the solution is homogeneous. If they do not, this would naturally lead to the question of what these distinct environments physically correspond to. For example, the ion pair hypothesis proposes the existence of two ionic environments, corresponding to “paired” and “free” states. Thus determining the number of environments could help to resolve the ion pair debate.

#### 3.3.1 Representation of local structure

As described in Chapter 2, the vectorised representation of local environment should capture the physics of interest. Good descriptors are unique, continuous, and invariant with respect to symmetries such as translation invariance [42].

The SOAP representation, which has been applied to fit potential energy surfaces [43] and in molecular property prediction [44], meets these criteria. Here, to determine the local environment of some central particle of type $A$, we consider all neighbouring ions and the central ion to be represented by a Gaussian distribution. Then we can independently consider the contribution of each particle species to forming the local environment, with the contribution from particle type $B$ to the local environment of central particle $a$ being

$$
\rho_a^{(B)}(\mathbf{r}) = \sum_{b \in B, |\mathbf{r}_{ab}| < r_C} \exp \left( -\frac{|\mathbf{r}_{ab} - \mathbf{r}|^2}{2\sigma^2} \right),
$$

(3.6)

where $\mathbf{r}_{ab}$ is the displacement from the central atom to neighbouring atom $b$, $\sigma^2$ is some pre-specified parameter describing the width of the Gaussian, and we only consider the contribution from neighbouring particles closer than some cut-off distance $r_C$. This function is rewritten in terms of a set of orthogonal radial basis functions and spherical harmonic
functions with corresponding coefficients, which are then used to form a vector representation, as outlined in more detail in Chapter 4.

Despite considerable success in the aforementioned applications, the SOAP representation is not without flaws: it is high-dimensional, sparse and difficult to “reverse” (given a representation, it is hard to identify the corresponding environment) [258], thus rendering results difficult to interpret physically.

We instead opt to use a simpler smoothed pair distribution function (PDF), which enables us to physically interpret which local environments are statistically significant:

\[
g_{Ba}(r) = \frac{V}{N_B \sqrt{2\pi} \sigma} \sum_{b \in B} \delta(|r_{ab}| - r) \exp\left(-\frac{(|r_{ab}| - r)^2}{2\sigma^2}\right)
\] (3.7)

where \( r = |r| \), \( V \) is the system volume, \( N_B \) is the number of type \( B \) ions, and each neighbouring ion \( b \) is represented by a normal distribution \( N \) with mean and standard deviation equal to the distance \( |r_{ab}| \) between ions \( a \) and \( b \), and the radius \( \sigma \) of ion \( b \) respectively. This smoothed PDF is vectorised using histogram binning, each bin corresponding to a dimension in feature space.

We note the existence of a relationship between the smoothed PDF and the more commonly used radial distribution function (RDF), \( g_{AB}(r) \). The RDF is the ratio of the average number density of ions of type \( A \) at a distance \( r \) from a given central ion of type \( B \), to the average number density at a distance \( r \) from the central ion in an ideal gas at the same overall density [259]. A variation of the RDF from unity implies a correlation between molecules that has arisen from the inter-molecular interactions between them [260]. The individual RDF for the \( a \)th type \( A \) ion is

\[
g_{Ba}(r) = \frac{V}{N_B} \left( \sum_{b \in B} \delta(|r_{ab}| - r) \right),
\] (3.8)

which is equivalent to the smoothed PDF, defined in Equation 3.7, in the limit that the particle radius \( \sigma \) becomes zero and \( r_C \) becomes infinite. The RDF \( g_{AB}(r) \) is then:

\[
g_{AB}(r) = \frac{1}{N_A} \sum_{a=1}^{N_A} g_{Ba}(r).
\] (3.9)
3.3.2 Grouping environments using Bayesian inference

Once the environments of \( N \) different ions have been computed to form the dataset \( X = \{ x_i \}_{i=1}^N \), we now seek to infer the number of statistically significant groups to which these datapoints belong. Within each group the difference in environments are much smaller than the differences between groups.

It is supposed that data is generated from the sum of \( K \) independent Gaussian distributions over feature space, with each distribution characterising a distinct environment. Then the probability of a datapoint \( x_i \) is

\[
p(x_i | K, \theta_K) = \sum_{k=1}^{K} \pi_k N(x_i | \mu_k, \Sigma_k) \tag{3.10}
\]

where \( \theta_K = \{ \pi_k, \mu_k, \Sigma_k \}_{k=1}^{K} \) is the set of parameters of the \( K \)-environment model; \( \pi_k \) defines the fraction of ions inhabiting the \( k \)th environment, and \( \mu_k \) and \( \Sigma_k \) define the mean of the \( k \)th environment (physically, the local environment of the typical ion in that group) and the variance of environments within that group respectively.

The Bayesian Gaussian mixture model

We consider that the model parameters \( \theta_K = \{ \pi_k, \mu_k, \Sigma_k \}_{k=1}^{K} \) are random variables, whose posterior distribution is to be determined. We use a Bayesian Gaussian mixture model, which is described by the joint distribution

\[
p(X, Z, \pi, \mu, \Lambda) = p(X|Z, \mu, \Lambda) p(Z|\pi) p(\pi) p(\mu|\Lambda) p(\Lambda) \tag{3.11}
\]

where

\[
p(X|Z, \mu, \Lambda) = \prod_{n=1}^{N} \prod_{k=1}^{K} N(x_n | \mu_k, \Lambda_k^{-1})^{z_{nk}} \tag{3.12}
\]

\[
p(Z|\pi) = \prod_{n=1}^{N} \prod_{k=1}^{K} \pi_k^{z_{nk}} \tag{3.13}
\]

\[
p(\pi) = \text{Dir}(\pi|\alpha_0) \tag{3.14}
\]

\[
p(\mu|\Lambda) p(\Lambda) = \prod_{k=1}^{K} N(\mu_k | m_0, (\Lambda_k \beta_0)^{-1}) W(\Lambda_k | W_0, v_0). \tag{3.15}
\]

Here \( X = \{ x_1, ..., x_N \} \) is the observed data, \( \mu = \{ \mu_i \}_{i=1}^{K} \), \( \Lambda = \{ \Lambda_i \}_{i=1}^{K} \) and \( \pi = \{ \pi_i \}_{i=1}^{K} \) are the means, precisions and mixing coefficients of the \( K \) (independent) Gaussian components, and
3.3 Inference of local structure distribution

\( Z = \{ z_1, ..., z_N \} \) denotes the latent variables mapping data points to each component. Note that the precision, \( \Lambda \), is the inverse of the covariance, \( \Sigma \).

**Choice of prior hyperparameters**

In our model, the only manual selection demanded is that of the hyperparameters \( \{ \alpha_0, m_0, \beta_0, W_0, \nu_0 \} \) in the prior distribution over model parameters, defined in (3.14) and (3.15). We select uninformative hyperparameters (those that lead to a broad distribution over model parameters): \( \alpha_0 = 1.0, \beta_0 = 1.0 \times 10^{-11}, W_0 = I, m_0 = 0 \) and \( \nu_0 = d \), where \( d \) is the dimensionality of \( x \). We check for coherence of the resulting prior via validation on well understood physical systems as described below.

**3.3.3 Approximate inference**

We want to find an approximation to the marginal likelihood \( p(X|K) \) of a \( K \)-environment model, and the posterior over model parameters, \( p(\theta_K|X,K) \). The optimal number of distributions, \( K^* \), is that which has the maximal marginal likelihood. \( K^* \) will be interpreted physically as the number of statistically distinct environments in the system.

Calculating the marginal likelihood demands integration over all parameters of the model of interest. Yet, in practice, this integral is usually intractable. Much work in Bayesian machine learning is focused on developing approximate inference methods that circumvent the challenge of computing exact integrals.

These techniques are generally demarcated as Markov Chain Monte Carlo (MCMC) and variational inference methods. MCMC methods are computationally expensive, scale badly with large amounts of data, and it is hard to assess their convergence, but they are mathematically guaranteed to converge exactly in the limit of infinite data [261]. In contrast, variational approaches are cheaper computationally and scale well with large quantities of data. However, the approximation typically will not converge to the true distribution in the infinite data limit [262].

**Variational inference**

Variational inference methods [262] introduce a variational distribution \( q_\phi(\theta) \) that upon optimisation of the variational parameters \( \phi \) will be used as an approximation to some true distribution \( p(\theta) \). The power of this family of techniques lies in their ability to simultaneously approximate the posterior distribution over model parameters and also the marginal likelihood of the model.
The general approach to variational inference is as follows. Suppose that we seek to determine both the marginal likelihood \( p(X|M) \) of some model \( M \), and also to determine the posterior over model parameters \( \theta \) given the observed data, \( p(\theta|X,M) \). These two quantities are related by Bayes’ theorem

\[
p(\theta|X,M) = \frac{p(X,\theta|M)}{p(X|M)}.
\] (3.16)

We now introduce the variational distribution \( q_\phi(\theta) \), which will be used as an approximation to \( p(\theta|X,M) \). Rearranging (3.16) and inserting the factor \( \frac{1}{q_\phi(\theta)} \) gives

\[
p(X|M) = \frac{p(X,\theta|M)}{q_\phi(\theta)} \frac{q_\phi(\theta)}{p(\theta|X,M)}.
\] (3.17)

Taking the logarithm of both sides, multiplying by \( q_\phi(\theta) \) and integrating over \( \theta \), we obtain the central relation

\[
\log p(X|M) = \mathcal{L}_{\text{ELBO}} + \text{KL}[q_\phi(\theta)||p(\theta|X,M)]
\] (3.18)

where the first term is denoted the evidence lower bound (ELBO)

\[
\mathcal{L}_{\text{ELBO}} = \mathbb{E}_{q_\phi(\theta)} \left[ \log \frac{p(X,\theta|M)}{q_\phi(\theta)} \right]
= \int q_\phi(\theta) \log \frac{p(X,\theta|M)}{q_\phi(\theta)} d\theta,
\] (3.19)

and the second term

\[
\text{KL}[q_\phi(\theta)||p(\theta|X,M)] = \int q_\phi(\theta) \log \frac{q_\phi(\theta)}{p(\theta|X,M)} d\theta
\] (3.21)

is the Kullback–Leibler (KL) divergence between \( q_\phi(\theta) \) and \( p(\theta|X,M) \) [263]. Crucially, the KL divergence between two distributions is always non-negative, with equality if and only if \( q_\phi(\theta) \equiv p(\theta|X,M) \) [264]. By minimising the KL divergence (or equivalently, by maximising \( \mathcal{L}_{\text{ELBO}} \)) with respect to variational parameters \( \phi \), we achieve two goals. Firstly, we can use the optimal variational parameters \( \phi^\ast \) to form our approximation to \( p(\theta|X,M) \), using \( q^\ast(\theta) = q_{\phi^\ast}(\theta) \). Secondly, we will obtain a lower bound and approximation to the marginal likelihood via the maximised \( \mathcal{L}_{\text{ELBO}} \). We see that variational inference turns an intractable integration problem into a tractable optimisation problem which can be solved using machine learning techniques such as stochastic gradient descent.
3.3.4 Bayesian hypothesis testing

We will use the Bayes factor, a central metric in Bayesian hypothesis testing [265], to assess the evidence supporting a $K'$-environment model as against a $K$-environment model:

$$BF(K'|K) = \frac{p(X|K')}{p(X|K)}.$$ (3.22)

The Bayes factor provides a quantitative measure of the evidence in favour of an alternative hypothesis defined by a model with $K'$ environments, as against a null hypothesis defined by model with $K$ environments. Various scales exist for assessing the significance of a measured Bayes factor. Generally, the greater the Bayes factor, the stronger the evidence in favour of the alternative hypothesis as against the null hypothesis [265, 266].

3.4 Data generation

3.4.1 Modelling the concentrated electrolyte

The simplest model of the electrolyte is the restricted primitive model (RPM). Here, ions are modelled as neutral hard spheres of the same size, with opposite electric charges at their centres. This is an example of an implicit solvent model, with the presence of polarisable solvent molecules accounted for via inclusion of a uniform dielectric continuum with specified relative permittivity $\epsilon$. In reality, this model does not account for local interactions that ions have with the finitely sized polar solvent molecules. This motivates the family of molecular solvent models which explicitly include solvent molecules, typically by inclusion of their 3D coordinates and size, but with the possibility of also accounting for the presence of dipoles and higher order multipoles. There is a trade off between the level of detail and computational cost.

A compromise is to use the solvent primitive model (SPM), variously referred to as the 3 component model [267] and more recently the semi primitive model [268] and hard sphere ion-solvent mixture model [241], which extends the RPM by including additional, neutral hard spheres (usually set to be the same size as the ions for simplicity), to model the finite size of solvent molecules. This model has been used extensively to study electrolytes under a multitude of conditions, including in the bulk [268, 241] and at charged and uncharged surfaces [269, 270]; others verified its relatively good agreement with experimental results [271]. More recently the SPM was used to investigate under-screening in concentrated electrolytes [241].
3.4.2 Molecular dynamics simulations

Toy systems

The ESPResSO package [272] was used to perform MD simulations of two toy systems, to validate the method. The first system (simulated by A. Härtel and F. Coupette) comprises 100% hard spheres of size 0.3 nm and the second system (simulated by myself) comprises hard spheres of size 0.3 nm and dumbbells (two neutral hard spheres of size 0.3 nm bonded by a strong harmonic potential) in a 1:1 ratio. The same total concentration of 3.0 M is used for both simulations with the temperature fixed at 300K. Hard sphere interactions are modelled using a Weeks-Chandler-Andersen (WCA) potential [273, 274] (a purely repulsive truncated and shifted Lennard-Jones potential with pre-factor $10^4 k_B T$ and cut-off distance at $a$), with dumbbells modelled using additional harmonic bonds of equilibrium separation 0.4 nm and pre-factor $15 k_B T/\text{nm}^2$. Smoothed PDFs are calculated for distances [0.15 nm, 1.2 nm] using a bin size of 0.15 nm and normalised with linear scaling.

Bulk monovalent electrolytes

Again, ESPResSO was used (by A. Härtel and F. Coupette) to simulate both the SPM and RPM. Cations, anions (and solvent molecules for the SPM) are modelled as hard spheres with charges $+e, -e, 0$, all of size $a = 0.4$ nm. Simulations are performed at constant temperature $T = 300K$ and a range of concentrations $c$ and relative permittivities $\varepsilon$: $(c, \varepsilon) \in [0.5 \text{ M}, 6.0 \text{ M}] \times \{20, 40, 60, 80\}$. Hard particle interactions are modelled using a WCA potential and electrostatic interactions modelled using the P3M method [272, 275]. Smoothed PDFs $g_{++}$ and $g_{--}$ are calculated for distances [0.2 nm, 1.0 nm] using a bin size of 0.2 nm and normalised with linear scaling. Only the anionic environments are studied due to charge reversal symmetry.

The technique was also applied to data (provided by the authors of [232]) from all-atom simulations of lithium bis(trifluoromethane)sulfonimide (LiTFSI) in a mixture of organic solvents dimethoxyethane (DME) and dioxolane (DOL), at $c = 1.0 \text{ M}, 2.0 \text{ M}$ and $5.0 \text{ M}$. Charge reversal symmetry can no longer be assumed here, so we separately determine the number of environments inhabited by the Li$^+$ cation and by the central N in the TFSI$^-$ anion.
3.5 Results and discussion

3.5.1 Validation on toy systems

A common critique of the Bayesian approach is that the posterior distribution over model parameters depends not only on the (objective) observed data but also on the subjective prior that is selected by the practitioner. We circumvent this problem by using a prior consistent with prior knowledge of physics. Specifically, we use a broad, uninformative prior, as defined in Section 3.3.2, to prevent exclusion of plausible parameters before observing the data, and then confirm that this leads to the correct posterior in well-understood systems.

Here, I consider two such systems: firstly, one comprising only neutral hard spheres, and secondly, a system comprising 50% neutral hard spheres and 50% dumbbells as described in Section 3.4.2.

In agreement with intuition, the most probable number of environments, $K^*$, is inferred to be one for the system comprising only neutral hard spheres, but two for the system comprising neutral hard spheres and dumbbells in a 1:1 ratio. This is clearly observed in Figure 3.2a.

We now study the differences in these distinct environments. Rather than studying the posterior over model parameters themselves, it is more intuitive to study the unsmoothed PDF, averaged over all particles classified as inhabiting each environment. These are shown for the two systems in Figures 3.2b and 3.2c. For the first system, the recovered mean corresponds trivially to the true mean PDF of the system. For the second system, the recovered environments correspond to “bonded” and “unbonded” environments, with the correct proportion of ions classified as each.1

3.5.2 Bulk monovalent electrolytes

Solvent primitive model

Having corroborated the ability of the model to infer the correct number of environments in simple systems, we now apply the same technique to probe the structure of bulk monovalent electrolytes, modelled using the SPM. Figure 3.3a illustrates how the evidence supporting a two-environment model, as against a one-environment model, varies with concentration $c$ and relative permittivity $\epsilon$. At intermediate $c \in [1.0\text{M}, 2.5\text{M}]$ a two-environment model has the largest marginal likelihood for all $\epsilon$, whilst at higher $c$ the model is no longer able to educe the presence of multiple statistically distinct environments.

---

1Note that the recovered PDFs do not correspond exactly to those of the dumbbells and hard spheres, but the majority of dumbbells are classified as “bonded” and the majority of hard spheres are classified as “unbonded”. 

Fig. 3.2 The method is validated on two systems: one comprising only hard spheres, and one comprising hard spheres and dumbbells in a 1:1 ratio. (a) The optimal number of distinct environments, $K^*$, is that which maximises the marginal likelihood $p(X|K)$; $K^* = 1$ and 2 for the first and second system respectively. (b/c) Unsmoothed PDFs for the identified environment(s), for (b) the hard spheres system, and (c) the 1:1 hard spheres / dumbbells system. Real space plots are provided, with orange and blue spheres corresponding to hard spheres and dumbbells respectively.

Scrutiny of the two environments inferred at intermediate concentrations reveals that surprisingly, the difference between environments arises in like charge correlations, as shown in Figure 3.3b. This is antipodal to the differences in unlike charge correlations implied by the ion-pairing hypothesis. The environments are physically distinguished as aggregated and non-aggregated; in the first case, several like and unlike charges exist in close proximity (less than two ion diameters from its centre), whereas in the second case, there is at most a single unlike charge in the local vicinity. As $c$ and $\epsilon$ are increased, the same differences are identified, but the proportion of ions classified as aggregated increases monotonically as shown in Figure 3.4a. This relationship is justified by the reduced electrostatic repulsion
3.5 Results and discussion

Fig. 3.3 Inference in the Solvent Primitive Model. (a) At intermediate concentrations $c \in [1.0 \text{ M}, 2.5 \text{ M}]$, the most probable number of environments, $K^*$, is 2; at higher concentrations $K^* = 1$. The stronger the evidence supporting a two-environment model (as against a one-environment model), the redder the shading ($\bullet$: $BF(2|1) > 0$). Conversely the stronger the evidence supporting a one-environment model, the bluer the shading ($\blacktriangle$: $BF(2|1) < 0$). (b) The two distinct environments are demarcated as aggregated and non-aggregated. Here, unsmoothed PDFs, averaged over all ions classified as inhabiting each environment, are shown for the $c = 1.0 \text{ M}, \epsilon = 80$ system. Left and right figures show like and unlike charge PDFs respectively.
between like charges at larger $\epsilon$, and the reduced ability to maintain large distances between like charges at higher concentrations.

**Fig. 3.4** The fraction of ions classified as *aggregated* increases both with concentration $c$, and relative permittivity $\epsilon$, for both (a) SPM and (b) RPM simulation data.

**Restricted primitive model**

We now investigate the simpler RPM. Accordantly, as shown in Figures 3.5a and 3.5b, at intermediate concentrations a two-environment model is most probable, with differences arising in like charge correlations. These environments become indistinguishable from noise at $c \sim 4.0$ M. The main features are qualitatively similar to those recovered for the SPM. Figure 3.4b shows that the proportion of *aggregated* ions again increases with $c$ and $\epsilon$.

**All-atom simulations**

Finally, we study data from all-atom simulations of LiTFSI-DME/DOL at $c = 1.0$ M, 2.0 M and 5.0 M. Our method reveals that at 1.0 M a three-environment model is most probable for both cations and anions. At 2.0 M, a two-environment model is most probable for cations whilst a three-environment model is most probable for anions. At 5.0 M, a two-environment model is most probable for both cations and anions. Studying the three environments identified at intermediate concentrations reveals similar distinguishing features as for the SPM, with the same *aggregated* and *non-aggregated* environments being identified alongside an intermediary *weakly aggregated* environment. This can be seen in Figure 3.6.
3.6 Conclusion

In summary, Bayesian inference has been used to identify the number of statistically distinct local ionic environments in bulk monovalent electrolytes, simulated based on three models of differing levels of detail. Interestingly, results suggest the presence of multiple environments at intermediate concentrations, whose differences originate in like charge correlations, rather than unlike charge pairing. Qualitatively similar differences in environments are observed across all simulation models.

Perhaps most importantly, our results suggest that meaningful physical insights can be elucidated in electrochemical systems by studying the statistical differences between local environments as opposed to the more widely used statistical averages. We believe this is a novel way to characterise previously hidden order in electrolytic systems. In the next chapter, we will build on this insight, and investigate how local environments can be mapped to ion transport properties using machine learning.

Fig. 3.5 Inference in the Restricted Primitive Model. (a) For intermediate concentrations, $K^* = 2$; at higher concentrations $K^* = 1$. Data missing for $c = 2.0 \text{ M}, \epsilon = 40$. (b) Unsmoothed PDFs for the $c = 1.0 \text{ M}, \epsilon = 80$ system. Left and right figures show like and unlike charge correlations respectively.
Fig. 3.6 Three distinct environments are identified for TFSI$^-$ anions in 1.0 M LiTFSI-DME/DOL: aggregated, weakly aggregated and non-aggregated. Here the corresponding unsmoothed PDFs, averaged over all anions classified as inhabiting each environment are illustrated. Left and right figures show like and unlike charge correlations respectively.
Chapter 4

Inferring global dynamics from local structure in liquid electrolytes

4.1 Introduction

The ion transport properties of electrolytes directly influence the performance of electrochemical energy storage systems [67, 276]. It is important for electrolytes to exhibit high ion conductivity, \( \kappa \), which is defined from Ohm’s law as the ratio of the ionic flux \( J \) to the applied electric field \( E \), in the absence of any concentration gradients [277, 278]:

\[
J = \kappa E. \tag{4.1}
\]

In liquid electrolytes, Ohm’s law is only valid for small external fields [279, 280]. At significant fields \( \kappa \) is not constant, but is a function of the applied field. In this thesis, we will probe the linear response regime (\( E \rightarrow 0 \)), where the conductivity for each electrolyte system is a constant.

The ion conductivity determines the rate at which ions can move through the system and thus the maximum charging and discharging rate. Low ion conductivities can also negatively impact the Ohmic resistance of the cell and lead to reduced Coulombic efficiency. In addition, in lithium-ion batteries, it is desirable for the lithium cations to be the most (or ideally, only) mobile species, since they are the only species responsible for energy storage and current flow. This can be quantified using the cation transference number \( t_+ \), which is defined as the fraction of the total ionic conductivity that originates from movement of the cations. Full-cell simulations show that at high cycling rates, increasing the transference number (even when...
the conductivity is reduced in parallel by up to an order of magnitude) leads to higher energy
density and higher peak power density due to the reduction in concentration gradients and
over-potentials caused by anion motion [281]. 1

Consequently, a lot of research into improved electrolytes has focused on increasing both ion
conductivity and cation transference number. It was initially considered that a good design
rule for increasing transference number was to use a large, bulky anion [282], or to attach
the anion to a polymer backbone to form a polymer electrolyte, as it was considered that the
mobility of the anion would be negligible [281]. In that case, the cation transference number
would approach unity. However, the calculation that the mobility of anions in polymer
electrolytes would be almost zero relied on use of the Nernst-Einstein approximation, which
assumes the electrolyte is an ideal solution of non-interacting ions. Clearly this approximation
is not valid in polymer electrolytes where there are significant inter-ion interactions and
correlations in ion motion. Recent work has showed that when inter-ion interactions are
accounted for, the transference number of polymer electrolytes is much lower than predicted
by the Nernst-Einstein approximation, bringing into question the utility of these materials in
designing next-generation batteries [283]. In some cases, the cation transference number has
even been observed to be negative [284–287], which is thought to be due to cations being
dragged in the “wrong” direction by much larger anions. Unexpectedly low ion conductivities
have also been observed in non-dilute systems [288, 289].

The previous chapter explored the effect that inter-ion interactions have upon the static
screening properties of concentrated electrolytes. It is also clear that the dynamic properties
of electrolytes are also significantly impacted by strong ion-ion interactions. A key question
is whether the dynamics of ion transport can be predicted by the local static structure alone,
and if so what are the key structural motifs that determine transport.

In this chapter, we show that machine learning can successfully decompose global conductivity
into the spatio-temporal average of local, instantaneous ionic contributions, and relate this
“local molar conductivity” field to the local ionic environment. Our machine learning model
accurately predicts the molar conductivity of electrolyte systems that were not part of the
training set, suggesting that the dynamics of ion transport is predictable from local static
structure.

1Movement of other species in solution, such as anions, creates concentration gradients and overpotentials.
Overpotentials cause lithium plating to commence at the electrodes at lower charging rates and states of charge,
which eventually results in loss of lithium inventory, because lithium has been plated on the electrode rather than
intercalated into the electrode. If lithium metal dendrites grow sufficiently long to reach the separator, internal
short circuits can occur, which pose a safety hazard as they can cause thermal runaway and fire. Overpotentials
also negatively impact discharging, as the concentration of lithium cations in the cathode becomes depleted and
can reach zero if the discharge rate is high enough, resulting in “infinite” Ohmic resistance.
4.2 Theories of ion transport

Through analysing this machine-learned local conductivity field, we observe that fluctuations in local conductivity at high concentration are negatively correlated with total molar conductivity. Surprisingly, these fluctuations arise due to a long tail distribution of low conductivity ions, rather than distinct ion pairs, and are spatially correlated through both like- and unlike-charge interactions.

More broadly, this approach shows how machine learning can extend our understanding of complex soft matter systems, by learning a function that attributes global collective properties to local, atomistic contributions.

This work was carried out with input from collaborators Dr Kara Fong and Prof. Kristin Persson of the University of California, Berkeley as well as my supervisor Alpha Lee. Kara conducted all of the MD simulations, and all three of my collaborators provided invaluable insights throughout. The work resulted in the following arXiv pre-print which is currently under review for publication:


The data used to generate these results is freely available at the public repository https://doi.org/10.5281/zenodo.6957888. The code written to obtain these results is freely available at https://github.com/PenelopeJones/conductivity.

4.2 Theories of ion transport

4.2.1 Nernst-Einstein relations

In ideal dilute solutions, the ionic conductivity is well described using the Nernst-Einstein relation [290, 291], which states that the diffusive flux of ions equals the electrophoretic flux arising due to an external electric field. Motion of ions is assumed to be completely uncorrelated. The relation directly connects ion conductivity $\kappa$ to the self-diffusion coefficients of the substituent ions:

$$\kappa = \frac{1}{k_B T} \sum_i z_i^2 N_i D_i,$$

where $z_i$, $N_i$ and $D_i$ are the ionic charge, concentration and self-diffusion co-efficient of species $i$, respectively.
4.2.2 Stefan-Maxwell equations

In non-dilute systems, where inter-ion interactions become significant, ion transport is most commonly described using the Stefan-Maxwell equations, which were originally developed to describe multi-component diffusion in ideal gases [292]. These equations relate the average thermodynamic driving force on a species $i$ to the average frictional force between that species and all other species in the solution. The assumption is made that the frictional force between two particles is proportional to the difference in average velocities between the two species:

$$c_i \nabla \bar{\mu}_i = \sum_{j \neq i} K_{ij} (\bar{v}_j - \bar{v}_i). \quad (4.3)$$

Here, $c_i$, $\bar{\mu}_i$, and $\bar{v}_i$ are the concentration, average electrochemical potential and average velocity of species $i$, and $K_{ij}$ are the Stefan-Maxwell transport co-efficients characterising the friction between species $i$ and $j$ [293]. In spite of the widespread use of the Stefan-Maxwell equations for describing ion transport, this framework cannot be applied directly to MD simulations [294]. The Stefan-Maxwell co-efficients are also challenging to interpret physically, and the measured co-efficients of some polymer electrolytes even appear to diverge at some concentrations [295].

4.2.3 Onsager formalism

A less common but perhaps more intuitive interpretation of ion transport was developed by Onsager (Figure 4.1A) [278, 296–298]. In this framework, the flux $J_i$ of ion species $i$ is a linear combination of the average thermodynamic driving forces $X_j$ acting on each species in the solution:

$$J_i = \sum_j L^{ij} X_j \quad (4.4)$$

The Onsager transport co-efficients $L^{ij}$ can be combined to compute experimentally measurable properties. For examples, the ion conductivity $\kappa$ and transference number $t_+$ have been derived as [293]:

$$\kappa = F^2 \sum_i \sum_j L^{ij} z_i z_j, \quad (4.5)$$

where $F$ is Faraday’s constant, and

$$t_i = \frac{z_i J_i}{\sum_j z_j J_j} = \frac{\sum_j z_i z_j L^{ij}}{\sum_k \sum_l z_k z_l L^{kl}}. \quad (4.6)$$
In this way, the Onsager coefficients allow us to relate the average microscopic correlations in ion motion to macroscopic transport properties, and thus to gain insights into which microscopic correlations positively or negatively impact conductivity. Additionally, the Onsager co-efficients can be computed directly from MD simulations using Green-Kubo relations [294, 278, 296]:

\[
L_{ij} = \frac{1}{6k_BT V} \lim_{t \to \infty} \frac{d}{dt} \left\langle \sum_{\alpha} [r_{\alpha i}^a(t) - r_{\alpha i}^a(0)] \cdot \sum_{\beta} [r_{\beta j}^\beta(t) - r_{\beta j}^\beta(0)] \right\rangle,
\]

where the indices \(i\) and \(j\) refer to each type of species (cation, anion, and solvent), the indices \(\alpha\) and \(\beta\) refer to individual particles, \(V\) is the system volume and \(r_{\alpha i}^\alpha\) is the position of particle \(\alpha\) (of type \(i\)) relative to the center-of-mass position of the entire system.

The diagonal terms of \(L_{ij}\) can be decomposed into a “self” and “distinct” term. The self term describes ideal, uncorrelated particle motion and is directly related to the self-diffusion coefficients of a given species via

\[
L_{ii}^{\text{self}} = \frac{D_i c_i}{k_B T}.
\]

This is computed using

\[
L_{ii}^{\text{self}} = \frac{1}{6k_BT V} \lim_{t \to \infty} \frac{d}{dt} \sum_{\alpha} \left\langle [r_{\alpha i}^a(t) - r_{\alpha i}^a(0)]^2 \right\rangle.
\]

The distinct term, as defined by

\[
L_{ii}^{\text{distinct}} = L_{ii}^{ii} - L_{ii}^{\text{self}},
\]

captures the extent of correlation in the motion of ions of the same species \(i\), and may be positive or negative [293].

Notwithstanding the insights that Onsager transport coefficients can offer, they are global system quantities which lack spatial resolution. For example, the \(L^{+−}\) transport coefficient capturing cation-anion correlations is computed based on the velocity correlation functions of every pairwise combination of cation and anion, regardless of their separation in physical space. Thus, while knowledge of \(L^{+−}\) gives information on the overall importance of cation-anion correlations to transport in the system, it does not give insight as to which short- or long-ranged structural features of the electrolyte contribute to these correlations. This lack of clear connection between structural properties and transport presents substantial challenges in understanding the molecular origins of conductivity and ultimately designing electrolytes with optimal transport properties [299].
A further challenge with physical interpretation of Onsager transport coefficients is that they are not all independent quantities [293]. For an $n$-component system (including solvent molecules) there are only $n(n-1)/2$ independent quantities, meaning that in the extreme case of an ionic liquid where there are only two components, there is only one independent parameter.

We note there exists a body of literature on analytical derivations of conductivity using the Debye-Hückel-Onsager formalism, beginning with seminal work by Fuoss and Onsager [300, 301] which built on the mean-field theories of Debye and Hückel [234]. More recent papers extended the framework to salt solutions at finite concentrations using fluctuating hydrodynamics [302–304]. These derivations are calculated using perturbations from infinitely dilute concentrations. In addition, some phenomenological approaches forgo the need to derive analytical relationships from first principles, instead fitting polynomials to the observed experimental data [305–307]. This may be suitable in some chemical engineering scenarios for an interpolative prediction of conductivity in electrolyte systems, but does not deliver insights into the microscopic origins of conductivity. For the remainder of this work, we will focus on machine learning insights from simulations, which allows us to probe the molecular origins of conductivity in electrolytes across a wide range of concentrations, in a unified computational framework.

### 4.2.4 Ion clustering

A common way to intuitively relate local structure and global dynamics in electrolytes uses the concept of ion pairing and clustering [308, 285, 309, 310]. This builds upon Arrhenius’s work, conducted over a century ago, which used conductivity to provide evidence for the existence of ion association in dilute electrolytes [311]. As outlined in Chapter 3, the idea is that ions that are paired, or clustered into distinct aggregates, will contribute differently to the overall conductivity of the system than if they were free, and a reduction in conductivity can be explained by an increase in the number of neutral ion pairs. The ion pair picture can be extended by the “cluster Nernst-Einstein” approach [285] (Figure 4.1B), which considers each ionic aggregate as a distinct charge carrier whose net charge and self-diffusion coefficient are used in the Nernst-Einstein equation to predict the conductivity. The self-diffusion coefficients are considered parameters that can be learned by fitting the cluster Nernst-Einstein equation to the experimental data. In effect, whilst the ion pairing model assumes the local structure distribution consists of two delta-functions, the “cluster Nernst-Einstein” approach assumes the distribution can be approximated as a multi-model distribution of delta functions with each mode corresponding to aggregates with a fixed size and net charge. The underlying
4.2 Theories of ion transport

A. Onsager formalism

Conductivity is a linear combination of Onsager coefficients. Each transport coefficient quantifies the extent of correlation between two ion species, averaged across all pairs of ions.

\[ \kappa \propto k_1 + \ldots + k_i + \ldots + k_N \]

\[ \kappa \propto k_{\text{self}} + k_{\text{distinct}} + k_{\text{self}} + k_{\text{distinct}} - 2L^+ \]

B. Cluster Nernst-Einstein

Conductivity is a sum of contributions from free ions and ions belonging to charged clusters. Ions belonging to neutral clusters do not contribute to ion conduction.

\[ \kappa \propto N_{\text{free}}D_{\text{free}} + N_{\text{pair}}D_{\text{pair}} + \ldots + \sum_{C_{2, C_{1}=1}} \sum_{C_{2, C_{1}=1}} C_{2, C_{1}}^2 D_{C_{2, C_{1}}} \]

C. Local conductivity field

Conductivity is the sum of atomistic contributions from each ion. Local conductivity is dependent on the ion's local static structure.

\[ k_i = f(x_i) \]

\[ \kappa \propto k_1 + \ldots + k_i + \ldots + k_N \]

---

Fig. 4.1 Schematic of our approach. We compare our approach to the Onsager formalism [294] and the cluster Nernst-Einstein methodology [285]. The Onsager schematic has been adapted from [294].

assumption in both cases is the general form of the distribution of local structures, and a mapping from local structure to conductivity is found by fitting the parameters of this assumed functional form.

4.2.5 Remaining enigmas in ion transport

The ion pairing approach has demonstrated success in explaining various properties. However, recent work demonstrated that the static picture of ion pairing (defined using a distance criterion alone) may be insufficient to explain observed transport properties in many non-dilute electrolytes [296]. Studies on polymer electrolytes [312] and polyelectrolyte solutions [283, 294], for example, have found that the fraction of ions in pairs or aggregates can be anti-correlated with the extent of correlation in ions’ motion, as quantified by the Onsager transport coefficients. Whilst Onsager transport coefficients can demonstrate discrepancies between predictions of ion pairing theories and experimental observations, it is challenging to directly relate Onsager coefficients to partial pairing or aggregations because they are global rather than local properties.
These findings raise two key questions: First, can the dynamic behaviour of concentrated electrolytes be predicted from static, short-ranged ionic structure alone? If so, what are the ionic environments that contribute to high or low conductivity?

### 4.3 Local conductivity field

#### 4.3.1 Local conductivity hypothesis

In this work, we will show that machine learning on MD simulation data successfully decomposes global conductivity into a spatio-temporal average of local, instantaneous ionic contributions, and relate this “local molar conductivity” field to the local short-ranged ionic environment (Figure 4.1C).

We posit there exists some mapping from the local ionic environment $\mathbf{x}_i(t)$ of ion $i$ at time $t$, to instantaneous local molar conductivity $k_i(t)$, such that $k_i(t) = f_\theta(\mathbf{x}_i(t))$, where $\theta$ is a vector of parameters that is learnt from the simulation data. The instantaneous molar conductivity of each species is the average of the local molar conductivities, i.e.

$$
\Lambda_\pm(t) = \frac{1}{N_\pm} \sum_{i=1}^{N_\pm} k_{i\pm}(t),
$$

where $N_+$ and $N_-$ are the number of cations and anions in the system. The global molar conductivity, $\Lambda$, is the average over time, and across ion species, such that

$$
\Lambda = \frac{1}{2} (\Lambda_+ + \Lambda_-) = \frac{1}{2T} \sum_{t=1}^{T} (\Lambda_+(t) + \Lambda_-(t)),
$$

where $T$ is the number of temporal snapshots.

In order to ensure that the structural environments present in each snapshot are independent from the others, the sampling interval of the MD trajectories is chosen to be longer than the average ion pair lifetime in the system.

The molar conductivity $\Lambda$ is then

$$
\Lambda = \frac{1}{NT} \sum_{t=1}^{T} \sum_{i=1}^{N} k_i(t),
$$

where $N = N_+ + N_-$ is the total number of ions in the system.
Note that the existence of a function $k_i(t)$ is our key hypothesis, which remains to be tested. To test whether $k_i(t)$ exists, we use a machine learning approach. We learn the function parameters $\theta$ by minimising the weighted loss function:

$$
\mathcal{L}(\theta) = \sum_{s=1}^{S} \left( \frac{\Lambda(s) - \frac{1}{NT} \sum_{t=1}^{T} \sum_{i=1}^{N} f_\theta(x_i^{(s)}(t))}{\Delta(s)} \right)^2,
$$

where $\Lambda(s)$ and $\Delta(s)$ are the molar conductivity and variance in molar conductivity of system $s$, respectively. Note that for each system, at each time $t$ there are $N$ measured local ionic environments $\{x_i(t)\}_{i=1}^{N}$ such that the total number of measured local environments (and corresponding local molar conductivities) per system is $NT$.

If $\mathcal{L}(\theta)$ can be minimised, and the resulting $k_i(t)$ can accurately predict the molar conductivity of unseen electrolyte systems, then we have some confidence in the validity of the concept of local conductivity.

### 4.3.2 Machine learning model

In practice, we approximately the function $f_\theta(x_i(t))$ by training an ensemble of 25 neural networks each with two hidden layers of dimensionality 100. We split the data using a random 90%/10% train-test split and then split the training set into five parts. We use five-fold cross validation, and train five neural networks per train/validation random split, each with a different initialisation seed. The network parameters $\theta$ are optimised using the Adam optimiser [313] for up to 1000 epochs at a learning rate of 0.0005. We adopt the early stopping technique to limit the risk of overfitting, by stopping training when the RMSE on the validation dataset is minimised.

### 4.3.3 Representation of local structure

In principle, $x_i(t)$ can be any representation of the ionic environments. To test specifically whether short-ranged local structure predicts conductivity, we implement the Smooth Overlap of Atomic Positions (SOAP) framework [314], using the DScribe package [315], to form a rotationally and translationally invariant vectorised representation of each ion’s local environment. As outlined in Chapter 3, in the SOAP framework we consider all neighbouring particles and the central particle to be described by a Gaussian distribution. Each particle species makes a contribution to the SOAP representation, with the contribution from type $Z$...
particles to the local environment of central particle $a$ being

$$
\rho^{(Z)}_a (r) = \sum_{z \in Z \atop |r_{az}| < r_C} \exp \left( -\frac{|r_{az} - r|^2}{2\sigma^2} \right), \quad (4.15)
$$

where $r_{az}$ is the displacement from the central particle to neighbouring particle $z$, $\sigma$ is the particle diameter, and we only consider the contribution from neighbouring particles closer than a cut-off distance $r_C = 5.0\sigma$. This function is then rewritten as orthonormal spherical Gaussian type radial basis functions

$$
g_{nl}(r) = \sum_{n'=1}^{n_{\text{max}}} \beta_{n'n'l} r^l \exp(-\alpha_{n'l} r^2), \quad (4.16)
$$
as well as a set of orthonormal spherical harmonic functions

$$
Y_{lm}(\theta, \phi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P^m_l(\cos \theta) \exp(i m \phi), \quad (4.17)
$$
such that

$$
\rho^{(Z)}(r) = \sum_{nlm} c_{nlm}^Z g_{nl}(r) Y_{lm}(\theta, \phi). \quad (4.18)
$$

Here, $\beta_{n'n'l}$ and $\alpha_{n'l}$ are pre-determined weights, $P^m_l(\cos \theta)$ are the associated Legendre functions and $c_{nlm}^Z$ are computed coefficients determined by the local environment. The final vector representation is formed from the concatenation of elements of the partial power spectrum,

$$
p_{nn'l'}^{ZZ'} = \pi \sqrt{\frac{8}{2l+1}} \sum_m c_{nlm}^Z (c_{n'l'm}^{Z'})^*, \quad (4.19)
$$

where we set $n_{\text{max}} = 6$ and $l_{\text{max}} = 5$. For this work, we do not explicitly include solvent interactions in the local environment representation.

### 4.4 Data generation

#### 4.4.1 Molecular dynamics simulations

All simulations for this study were carried out by Kara Fong. A coarse-grained MD simulation model was used to simulate bulk electrolyte systems with a range of concentrations and Bjerrum lengths ($l_B$). All simulations were performed using the HOOMD-blue package.
In total, 108 systems were simulated with twelve concentrations ranging from 0.0005 \( \sigma^{-3} \) to 0.05 \( \sigma^{-3} \) and nine Bjerrum lengths in the range 2.5 \( \sigma \) to 10.0 \( \sigma \). Each simulation consisted of cations, anions, and solvent, all of which are modelled as beads of diameter \( \sigma \) (the Lennard-Jones unit of distance) and unit mass. If the size of each bead is mapped to the size of a water molecule (2.75 Å), the concentration range of 0.0005 \( \sigma^{-3} \) to 0.05 \( \sigma^{-3} \) approximately corresponds to 0.04 M to 4 M in real units. All particles interact via a truncated, shifted Lennard-Jones (LJ) potential:

\[
U_{\text{LJ}}(r) = \begin{cases} 
4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r_{\text{cut}}} \right)^6 - \frac{1}{2} \left( \frac{\sigma}{r_{\text{cut}}} \right)^{12} + \frac{1}{2} \left( \frac{\sigma}{r_{\text{cut}}} \right)^6 & r \leq r_{\text{cut}} \\
0 & r > r_{\text{cut}} 
\end{cases},
\]

(4.20)

where \( \varepsilon \) is the LJ unit of energy and the cutoff distance \( r_{\text{cut}} \) is chosen to be \( 2^{1/6} \sigma \). Additionally, cations and anions interact via a Coulomb potential,

\[
U_{\text{Coulomb}}(r) = k_B T \frac{l_B z_i z_j}{r},
\]

(4.21)

where \( k_B T \) is the thermal energy and \( z_i \) is the charge of species \( i \) (set to +1 for cations and −1 for anions). Long-ranged Coulombic interactions were computed using the PPPM method [317].

Simulation cells were prepared by randomly packing all particles into a cubic simulation box using PACKMOL [318] at a density of 0.8 \( \sigma^{-3} \). A standard simulation consisted of 40,000 total particles, with the relative quantities of ions and solvent varied to adjust the salt concentration. Six independent replicates were prepared for each concentration/Bjerrum length combination, one of which included 80,000 total particles to verify that the simulation results were not influenced by finite size effects. The as-prepared systems were initially equilibrated using the Fast Inertial Relaxation Engine minimisation algorithm [319]. Simulations were run with a time step of 0.005 \( \tau \) (the LJ unit of time) for a total of \( 10^7 \) steps. The temperature of each simulation was maintained at \( k_B T / \varepsilon = 1 \) using a Nosé-Hoover thermostat.

The transport properties are estimated via Equations (4.7) and (4.9), and it is ensured that the terms in angular brackets exhibit at least a decade of linearity, i.e., the systems are safely in the diffusive regime. Error bars for \( \kappa \) and \( L_{ij} \) are given as the standard deviation of six independent simulations.
4.5 Results and discussion

4.5.1 Local structure predicts ionic conductivity of electrolytes

We begin by testing whether a model which is trained on simulation data from a very simple electrolyte can accurately predict the behaviour of held out test systems from the same class of electrolytes, but different concentrations and Bjerrum lengths. As described in Section 4.4.1, the model herein consists of charged and neutral Lennard-Jones particles to represent the ions and solvent respectively.

Figure 4.2 shows that the model accurately predicts molar conductivity of each unseen electrolyte system, attaining $R^2 = 0.96$. This is at the upper bound of attainable accuracy of $R^2 = 0.96 \pm 0.02$ which is constrained by the uncertainty in the molar conductivity values estimated using Green-Kubo relations. We note that the model only incorporates short ranged interactions between ions (up to $5.0\sigma$). Therefore, these results appear to suggest that molar conductivity of electrolytes can be predicted given local static structure alone, although electrostatic forces themselves are long ranged. However the relevant local structure is not necessarily ion pairs.

We next seek to determine the extent to which this model is physically meaningful, by testing whether it can generalise to a different class of electrolytes without further retraining. We achieve this by simulating an additional sixteen electrolytic systems, but now some fraction of ions are permanently bonded to an unlike charge via a harmonic bond potential, to form permanent ion pairs. These permanent pairs contribute to dielectric screening and provide polar solvation to neighbouring ions. Because neutral ion pairs do not contribute to overall
system conductivity, we do not compute a local conductivity for ions in these pairs. Crucially however, the local environments of each of the non-harmonically bonded ions accounts for the presence of the ion pairs in its own local environment representation. We look at systems with low ($0.0005\sigma^{-3} / 2.5\sigma$), medium ($0.01\sigma^{-3} / 4.0\sigma$) / ($0.025\sigma^{-3}, 6.0\sigma$) and high ($0.05\sigma^{-3} / 10.0\sigma$) concentrations and Bjerrum lengths, and for each system we consider the case where 10%, 20%, 30% and 40% of the ions are permanently bonded to an unlike charge.

![Graph showing true molar conductivity and predicted molar conductivity for different concentrations and Bjerrum lengths.](image)

**Fig. 4.3 Testing for external validity.** The model can predict the molar conductivity of systems which now contain a proportion of permanently bonded ion pairs. The model was not trained using data from any such system and so is “extrapolating” outside of the training domain.

Figure 4.3 shows that the model, trained only on non-polar solvent, retains a high accuracy when extrapolating into this new class of systems in which new physics are present (i.e. the existence of harmonic potentials causing permanent ion pairs/dipoles in the system). This suggests that the model is generalisable to qualitatively different electrolyte systems. A strength of the model is that we effectively transform an extrapolation problem into an interpolation problem since local environments that are detected in the systems with no permanent ion pairs also exist (to differing degrees) in the systems with permanent ion pairs.

### 4.5.2 Heterogeneity in local conductivity

Having shown that local structure can predict dynamics, we now seek to distil a mechanistic understanding of ion transport using this machine-learnt concept of localised molar conductivity. We begin by analysing the distribution of local molar conductivities and how this changes as the concentration and Bjerrum length increase. Figure 4.4A shows that at low concentrations the distribution of local conductivities is bi-modal, with the majority of
Fig. 4.4 Local molar conductivity distribution. A. At low concentrations \((0.0005\sigma^{-3})\) the local conductivity distribution is bi-modal. B. As the concentration increases (to \(0.01\sigma^{-3}\)), these modes gradually become less distinct. C. At high concentrations \((0.05\sigma^{-3})\), the modes can no longer be distinguished.

particles contributing positively to overall ion conduction whilst a minority of environments inhibit ion conduction and have a negative local conductivity. For a fixed concentration, the proportion of ions negatively contributing to conductivity increases as the Bjerrum length increases. Ions negatively contributing to molar conductivity tend to be closer to an unlike charge – at the lowest concentration of \(0.0005\sigma^{-3}\) and Bjerrum length 2.5, 22.6% of ions with unlike charge located within the first solvation shell (at a distance less than \(1.6\sigma\)) are predicted to have a negative conductivity, whilst just 0.07% of ions farther than \(1.6\sigma\) from any unlike charge are predicted to contribute negatively to molar conductivity.

On the surface, this might suggest the ion pair picture, defined using inter-ionic distance, explains ionic conductivity. However, as the concentration increases (Figures 4.4B and 4.4C), the distribution becomes uni-modal, albeit with a heavy tail skewing towards ionic environments that inhibit conductivity. The lack of a bi-modal distribution suggests that looking at discrete ion pairs does not provide the full picture, and is in agreement with prior findings that at high concentrations there are not multiple statistically distinct types of ionic environment [231]. This is further supported by the much more comparable fractions of “clustered” and “unpaired” ions that contribute negatively to molar conductivity – at a concentration of \(0.05\sigma^{-3}\) and Bjerrum length of 10.0\(\sigma\), 28.0% of ions with unlike charge located within the first solvation shell (at a distance less than \(1.6\sigma\)) are predicted to have a negative conductivity, whilst 21.6% of ions farther than \(1.6\sigma\) from any unlike charge are predicted to contribute negatively to molar conductivity.

The existence of a heavy tail in the conductivity distribution motivates us to explore the variance of the local conductivity as an organising principle. Figure 4.5 shows that low molar conductivity is correlated with high variance in local conductivity. In other words, slow ion transport appears to be associated with heterogeneity in local conductivity. Surprisingly,
4.5 Results and discussion

Despite there being a bi-modal distribution at low concentrations and a uni-modal distribution at high concentrations, the variance of the local conductivity distribution is greater at higher concentrations.

![Diagram](image)

**Fig. 4.5 Heterogeneity in local molar conductivity.** The standard deviation of the localised molar conductivity distribution is negatively correlated with the collective molar conductivity.

### 4.5.3 Local conductivity is spatially correlated

We next analyse the spatial correlations in local conductivity, and decompose this correlation into like-charge and unlike-charge contributions. We define the spatial correlation function $C(r)$ between species $A$ and $B$ as:

$$C(r) = \frac{\sum_{t=1}^{T} \sum_{i=1}^{N_A} \sum_{j \in \{r_{ij}(t)-r < \delta/2\}} \Delta k_i^{(A)}(t) \Delta k_j^{(B)}(t)}{\sum_{t=1}^{T} \sum_{i=1}^{N_A} \sum_{j \in \{r_{ij}(t)-r < \delta/2\}} 1},$$

(4.22)

where $T$ is the number of snapshots, $N_A$ is the number of ions of type $A$, $r_{ij}(t)$ is the distance between particles with conductivities $k_i^{(A)}(t)$ and $k_j^{(B)}(t)$ at snapshot $t$, and $\Delta k_i^{(A)}(t) = k_i^{(A)}(t) - \bar{k}^{(A)}(t)$ where $\bar{k}^{(A)}(t)$ is the average conductivity of ions of type $A$ at snapshot $t$. $\delta$ is the size of the histogram bin and set to $0.2\sigma$. The denominator measures the number of occurrences when type $A$ ions and type $B$ ions are separated by a distance in the range $\{r - \delta/2, r + \delta/2\}$. This enables us to ask: if two particles of types $A$ and $B$ are observed to be at a distance $r$ from each other, how correlated are their local conductivities on average?
Fig. 4.6 The local conductivities of neighbouring like and unlike charges are positively spatially correlated. Figures A, B and C show the like and unlike charge spatial correlation functions for concentrations $0.0005\sigma^{-3}$, $0.01\sigma^{-3}$ and $0.05\sigma^{-3}$, and Bjerrum lengths $2.5\sigma$, $6.0\sigma$ and $10.0\sigma$, respectively. The magnitude of correlations decreases with inter-particle distance, and can be fitted to an exponential decay function to extract two correlation lengthscales. Figures D and E show how the like and unlike charge correlation lengthscales changes with concentration, respectively.

Figure 4.6 shows that the local conductivities of neighbouring like and unlike charges are positively spatially correlated, with the correlations decaying as a function of inter-particle distance. This suggests that conductivity can be spatially localised to some extent. At low concentrations (Figure 4.6A) the dominant spatial correlations are at short distances between unlike charges, which can be attributed to the formation of neutral ion pairs. However as the concentration and Bjerrum length increase (Figure 4.6B), the magnitude of like charge correlations increases relative to unlike charge correlations, such that at the highest concentrations (Figure 4.6C), the like charge local conductivity correlations are almost as large as the unlike charge correlations.

The lengthscales of the correlation can be quantified by fitting to an exponential decay function. We observe that the spatial correlation lengthscale increases as concentration increases, for both neighbouring like charges (Figure 4.6D) and unlike charges (Figure 4.6E). As such, there appears to be a change in transport mechanism from short range ordering at very low concentrations to longer range collective motion at higher concentrations.
4.5.4 Relating local conductivity to global dynamic properties

Our analysis thus far provides spatial resolution to conductivity in electrolytes. However, a question is whether our machine-learnt notion of local instantaneous conductivity can be related to dynamic quantities in non-equilibrium statistical physics. Such a relation will provide further evidence that the local conductivity represents a physically meaningful way to interpret electrolyte transport. As such, we analyse how the local conductivity field is related to the Onsager coefficients for each system. The Onsager formalism [298, 297] can help to bridge the gap between molecular level and macroscopic scale analysis of ion transport [296, 278], with each Onsager coefficient characterising the extent to which motion of two species is correlated on average. We focus here on two Onsager coefficients, firstly, $L_{++}^{\text{self}}$, which captures ideal uncorrelated motion of ions as defined in Eq. 4.8, and secondly $L_{+-}$, which captures the correlation between all anions and cations.

![Figure 4.7](image)

**Fig. 4.7 Relation between the local molar conductivity field and ideal, uncorrelated motion.**

The fraction of ions whose local molar conductivity is negative is related to the amount of ideal, uncorrelated motion (as quantified by $L_{++}^{\text{self}}$).

Figure 4.7 shows the correlation between $L_{++}^{\text{self}}/c$ and the percentage of ions with negative local conductivity. We observe that for a given concentration, as the proportion of ions with negative local conductivity decreases, $L_{++}^{\text{self}}/c$ (and hence $D_+$) increases. This makes intuitive sense as we would generally expect ions with inhibited motion to contribute less positively to molar conductivity. Additionally, in Figure 4.8 we observe a strong positive correlation between the proportion of ions with negative local conductivity and $L_{+-}$. This positive correlation is in line with the fact that positive $L_{+-}^{++}$ values decrease overall ionic conductivity. The intuitive connection between $L_{+-}$ and the local molar conductivity stands in contrast
with the relationship between $L^{+−}$ and the static picture of ion pairing: in previous works, it has been observed that at high concentrations ion motion is less correlated (corresponding to a reduction in $L^{+−}$), despite an increase in the proportion of ions that are paired [312]. This observation that the fraction of ion pairs is not correlated with the ionicity suggested that ion pairing cannot explain the extent of cation-anion correlations that determine transport properties at non-dilute concentrations, and that ion pair dynamics are much more correlated with cation-anion correlations than statics [296]. However, the local conductivity, computed using local statics alone, appears to capture just as much physics as using a dynamic picture of ion pairing.

![Graph showing the relation between local molar conductivity field and correlated cation-anion motion](image)

**Fig. 4.8 Relation between the local molar conductivity field and correlated cation-anion motion.** The fraction of ions whose local molar conductivity is negative is positively correlated with the magnitude of cation-anion correlations (as quantified by $L^{+−}/c$). This is in line with the fact that strong cation-anion correlations negatively impact a system’s conductivity [296].

### 4.6 Conclusion

In this chapter we have demonstrated that it is possible to predict the molar conductivity of a simple electrolyte model, from short-ranged static structure alone, using machine learning. Our model generalises without retraining to a different class of electrolytes with dipolar screening, suggests that it is at least to some extent physically meaningful.

A by-product of our model is a framework that delivers insights into the individual atomistic contribution that each ion, instantaneously experiencing a particular local environment, makes to macroscopic conductivity. This allows us to explore the microscopic determinants of conductivity. We find that at low concentrations, there are two statistically distinct modes of
conduction, with the majority of ions contributing positively to ion conduction whilst a small minority inhibit conduction. These modes are found to be related to conventionally defined “free” and “paired” states. In contrast, at high concentrations, the distribution of local molar conductivities broadens and becomes uni-modal, suggesting that it is not statistically sound to model concentrated electrolytes as comprising well defined clusters of ions. In addition, we observe that systems with low variance in local molar conductivity exhibit higher total molar conductivity in general, and local molar conductivity is spatially correlated through both like and unlike-charge correlations.

More broadly, this approach demonstrates how machine learning can act as a “computational microscope” by attributing collective properties to individual atomistic contributions. By offering us the chance to see the electrolyte in a new light, machine learning can act as an intuition pump, elucidating insights that can help us to develop improved theories of electrochemical systems.
Chapter 5

Forecasting lithium-ion battery performance under uneven usage

5.1 Introduction

Electrification of the transportation industry is now taking place at an increasingly rapid pace, enabling significant strides towards a carbon neutral future. Fundamental to this transition has been the lithium-ion battery, which powers the majority of electric vehicles on the road today. Notwithstanding the environmental benefits of this transition, reliance on the lithium-ion battery poses significant challenges, with consumer concerns including range anxiety, fear of battery failure and charging time. Easing these concerns demands the ability to accurately forecast battery performance, and specifically when usage conditions are variable.

The key challenge is the heterogeneity of the battery. Each user uses their car differently, and even across a single battery pack not all cells are necessarily charged or discharged with identical current [320–322]. These differences mean that each cell’s internal state, including the extent of lithium plating or electrode cracking, can vary significantly both at an intra-pack and inter-pack level [323, 324].

To quantify the extent of degradation within cells, and to identify cells that have reached their end of life (EOL) [136, 137], the scalar State of Health (SOH) metric is typically adopted [138–143]. The problem with this approach is that batteries with the same numerical SOH do not necessarily exhibit identical levels of each degradation process (for example, lithium plating or electrode cracking), yet the impact of future cell usage on the cell’s future performance and degradation pathway depends significantly on the type of degradation that
has already occurred [325–327]. Accurate forecasting of battery performance, both in the immediate [146–148, 141, 149] and longer term [150–152] demands a non-invasive approach to acquire information about the cell state at a microscopic level.

As outlined in Chapter 2, battery health forecasting can be subdivided into empirical, physics-based (PBM), equivalent circuit models (ECM) and machine-learning models, with some models being a hybrid of these. Empirical approaches have been used to model long term capacity fade with power laws but assume fixed operation over battery life and do not account for intrinsic differences in cell state at start of life. These approaches assume that all cells of the same chemistry will fade in the same way if operated in the same way, which is not observed in practice [153]. In PBMs, the battery is either modelled mechanistically using first principles analysis of internal physical and electrochemical processes, whilst ECMs model the cell as a circuit comprising resistors and capacitors that are representative of the underlying electrochemical processes [209, 180]. Both ECMs and PBMs need to be re-fitted for each individual cell and suffer from non-identifiability – several sets of model parameters could explain the observed data equally well, but would make drastically different predictions on test cells or on the same cell later in its life [328].

In contrast, purely data-driven approaches to forecasting use raw data as input to a machine learning algorithm to forecast long term capacity fade, resistance increase and remaining useful life [184, 329]. Feature-based data-driven approaches have applied machine learning on features extracted from the charging/discharging curve [151], EIS spectrum [150], current interruption [175], or acoustic time-of-flight analysis [147, 176] to predict discharge capacity [148], remaining useful life [151], and abrupt capacity decays [152, 155]. Analysis beyond charge/discharge curves, such as EIS, current interruption, and acoustic time-of-flight analysis, can provide a fuller description of battery state. For example, EIS captures the response of the cell over a broad frequency range, with different frequencies correlating to distinct physical, chemical and mechanical changes in the active material [177–180]. These data-driven methods typically utilise data generated in the laboratory setting, where cells are charged and discharged in the same way over the entirety of their lifetimes, thus the impact of variable cell usage on future performance can be ignored (see Figure 5.1). However, extrapolating the models developed for laboratory setting to field data or other realistic usage profiles such as the Worldwide Harmonized Light Vehicles Test Cycles (WLTC) [163, 330, 143], where cells are cycled in vastly different ways over their lifetimes, has proved a major challenge [137].

In this work, we seek to identify whether there exists a sufficiently informative marker of cell health that can be used to forecast short term and longer term future performance, amid uneven historical and future cell usage. Figure 5.1 provides an illustration of our approach,
Feature-based methodologies for degradation prediction have focused on constant charging protocols (the blue/red curve denotes the charge/discharge phase), using features from capacity-voltage curves as input [151, 157]. This necessitates knowledge of historic charging data. Our approach considers variable charging protocols (the shaded blue/red region denotes the range of currents that the charge/discharge protocols are drawn from), which is more comparable to the electric vehicle setting. Further, we employ the electrochemical impedance spectrum measured just before charging as input, without any knowledge of historic data, and predict the impact of different future usage protocols on the discharge capacity.

and how it differs from previous approaches. We find that upon acquisition of an EIS spectrum just before charging, both next cycle and longer term cell capacity can be predicted with a test error of less than 10%. When testing on cells subjected to similar cycling conditions to those used to train the model, our model achieves comparable accuracy to state-of-the-art forecasting models (8.2% test error versus 8.8% test error), except that our model enables forecasting with no access to any historical data, whereas previous state-of-the-art models require historical data from the cell’s cycling trajectory. In addition, when extrapolating to different operating temperatures, our model significantly outperforms the state-of-the-art model, achieving a 57% reduction in test error (from 34.2% to 14.6%).

Fig. 5.1 Schematic comparison of the proposed approach to previous research works. The figure illustrates the comparison between previous feature-based approaches and our approach. Previous methods rely on constant charging protocols and require historical data to predict future discharge capacity. Our approach considers variable charging protocols and uses the electrochemical impedance spectrum measured just before charging to predict future discharge capacity without any historical data. This allows for forecasting the impact of different future usage protocols on the discharge capacity.
Our model is data-efficient, requiring just eight cells to attain a test error of less than 10%, and robust with respect to cell manufacturer, average usage pattern and operating temperature. Additionally, our approach is robust to dataset shift, attaining a test error of less than 7% on a dataset with a different distribution of cycling patterns to the training set. This is important for deployment in the field where driving patterns may be different from those used to train the model. Further, our work fills a gap in publicly available data by contributing a large corpus of cycling data on cells under dynamic working conditions [331]. Our work focuses on a set of idealised usage distributions rather than realistic driving profile in order to demonstrate the extent of generalisability of the model. Our work departs from the NASA randomised usage dataset [332], which randomly cycles cells for 50 cycles before measuring the next cycle discharge capacity after charging via a “reference” protocol. Although several models for forecasting degradation under randomised conditions have been built based on this data [142, 148, 333], the effect of a single protocol on next cycle discharge capacity cannot be disentangled, and there is a need for a reference charge / discharge protocol every few cycles which does not concord with typical field usage.

This work was carried out with collaborators Prof. Ulrich Stimming of the University of Newcastle and my supervisor Dr Alpha Lee, both of whom provided much appreciated feedback. Our results were published in Nature Communications:

Penelope K. Jones, Ulrich Stimming, and Alpha A. Lee, “Impedance-based forecasting of lithium-ion battery performance amid uneven usage”, Nat Commun 13, 4806, https://doi.org/10.1038/s41467-022-32422-w (2022) [334].

The data generated in this study are provided in the Zenobo database at https://doi.org/10.5281/zenodo.6645536. The code required to reproduce this manuscript is available at https://github.com/PenelopeJones/battery-forecasting.

### 5.2 Battery forecasting model

#### 5.2.1 General framework

We posit that at any time \( t \), any macroscopic property \( P_{t+\tau} \) of a battery as measured at some future time, \( t + \tau \), is a function of both the battery’s present internal state, \( s_t \), and the usage conditions that the battery will be subjected to over the future time interval, \( a_{t+\tau} \). Our goal is to learn the mapping \( P_{t+\tau} = f_\theta(s_t, a_{t+\tau}) \). In order to do so, we require a suitable representation of the battery’s present state, a representation of the future action as well as sufficient data to infer the parameters \( \theta \) of the function.
In this work, we focus on forecasting the future discharge capacity of the battery, but in principle this framework could be applicable to other relevant macroscopic properties of the battery including internal resistance, maximum power, discharge energy or internal temperature rise.

**5.2.2 Generation of battery cycling data**

For this study we generate two separate datasets corresponding to commercial LiR coin cells purchased from two different manufacturers, Powerstream and RS Pro. This allows us to test whether our approach is robust with respect to cell manufacturer. In total, we cycle 88 commercial LiR coin cells in a temperature regulated laboratory at $23 \pm 2^\circ C$. A Biologic BCS-805 potentiostat is used for cycling, and photographs of the experimental setup are provided in Figure 5.2.

![Battery cycling set-up](image)

**Fig. 5.2 Battery cycling set-up.** a. Coin cells are connected to a Biologic BCS-805 potentiostat. Cells are cycled in a temperature controlled lab room when cycled at $23^\circ C$ and in a temperature controlled heating chamber when cycled at $35^\circ C$. b. Coin cell holders are provided by Biologic.

Across all datasets, cells are subjected to a sequence of randomly selected charge and discharge currents for 110-120 full charge/discharge cycles. Cycling commences when the cell is in
the fully discharged state, and each cycle comprises the following steps: (a) resting for 20 minutes at the open circuit voltage, (b) acquisition of the galvanostatic EIS spectrum in the fully discharged state, (c) two stage Constant Current (CC) charging, (d) resting for 20 minutes at the open circuit voltage, (e) acquisition of the galvanostatic EIS spectrum in the fully charged state, (f) one stage CC discharging. The galvanostatic EIS spectrum is always measured by collecting impedance measurements at 57 frequencies uniformly distributed in the log domain in the range $0.02\text{Hz-}20\text{kHz}$ using a sinusoidal current with amplitude of 5mA. Cells are cycled in a temperature-controlled lab room at $23 \pm 2 \, ^\circ\text{C}$.

![Fig. 5.3 Applied charge-discharge protocol.](image)

We generate battery cycling data by subjecting cells to a sequence of random charge and discharge currents. We apply two stages of Constant Current (CC) charging for up to 15 minutes each, with currents drawn from the ranges 70mA-140mA (2C-4C) and 35mA-105mA (1C-3C) respectively (the blue shaded region). If the safety threshold voltage of 4.3V is reached before the time limit, then charging is stopped. During discharging, a single constant discharge current, randomly selected in the range 35mA-140mA (1C-4C), is applied (the red shaded region), until the voltage drops to 3.0V.

The first dataset corresponds to 40 Powerstream LiR 2032 coin cells (nominal capacity 1C = 35mAh). We subject 24 cells to a sequence of randomly selected charge and discharge currents at $23 \pm 2^\circ\text{C}$ for 110-120 full charge/discharge cycles. Each cycle consists of an initial diagnosis of battery state, involving acquisition of the galvanostatic EIS spectrum, followed by usage, involving a charging and discharging stage. Charging consists of a two stage CC protocol; currents are randomly selected in the ranges 70mA-140mA (2C-4C) and 35mA-105mA (1C-3C) in stages 1 and 2 respectively. A time limit of 15 minutes is set for each charging stage such that the total charging time is constrained to be 30 minutes or less. Charging will stop before the 30 minute time limit if the safety threshold voltage of 4.3V is reached. During discharging, a single constant discharge current, randomly selected in the range 35mA-140mA (1C-4C), is applied, until the voltage drops to 3.0V. To test the model’s
robustness to domain shift, we additionally cycle an additional 16 cells (also manufactured by Powerstream and of nominal capacity 35 mAh) under the same conditions as above, except now fixing the discharge current for all cells and cycles at 52.5mA (1.5C) instead of randomly changing the discharge current at each cycle. The space of protocols considered is illustrated in Figure 5.3 and an example of the capacity trajectories of three cells is provided in Figure 5.4 for illustration of the difference from typical monotonic capacity fade experiments.

![Fig. 5.4 Examples of capacity fade trajectories. Example of the applied random charge and discharge currents applied to three sample Powerstream cells and the corresponding measured discharge capacity at each cycle. It is seen that the measured discharge capacity does not change in a monotonic way from cycle to cycle because the usage is changing as well as the internal battery state.](image)

Having used the first dataset to confirm the approach can successfully forecast discharge capacity several cycles ahead, we later significantly expand our analysis to explore the model’s robustness to cell manufacturer, changes to usage pattern and operating temperature. To achieve this, we cycle an additional 48 cells from a second manufacturer, RS Pro (nominal capacity 40mAh), under a much wider range of usage patterns.

In this case, each cell is again subjected to 100 cycles of two stage CC charging, and one stage CC discharging, with the three rates randomly selected at the start of each cycle. However,
we now make the problem more challenging by having a different distribution of currents for each cell, to replicate the scenario in which different battery users have different average usage patterns to each other, but still exhibit random cycle-to-cycle behaviour. Of these cells, sixteen are also cycled at a higher operating temperature of $35 \pm 2^\circ C$, in a temperature-controlled heating chamber. The full set of operating conditions that each cell is subjected to is detailed in Table 5.1.

### 5.2.3 Representation of battery state

#### Representation in the absence of historical data

Many state-of-the-art approaches to SOH estimation require the long term collection of historical battery cycling data. However, there are circumstances in which historical data may not be available. We propose that in these circumstances, electrochemical impedance spectroscopy offers a non-invasive technique for acquiring information about the battery’s internal state that captures several degradation modes as well as state of charge and internal temperature.

We can form the battery state vector $s_n$ from the EIS spectrum by concatenating the real ($Z_{re}$) and imaginary ($Z_{im}$) components of the galvanostatic EIS spectrum measured in the fully discharged state at the start of the cycle at 57 frequencies, $\omega_1, ..., \omega_{57}$, in the range 0.02Hz-20kHz; $s_n = [Z_{re}(\omega_1), Z_{im}(\omega_1), ..., Z_{re}(\omega_{57}), Z_{im}(\omega_{57})]$. 

<table>
<thead>
<tr>
<th>Cell IDs</th>
<th>No. of cells</th>
<th>Manufacturer</th>
<th>Stage 1 C-rates</th>
<th>Stage 2 C-rates</th>
<th>Discharge rates</th>
<th>Temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PJ097-PJ112; PJ145-PJ152</td>
<td>24</td>
<td>Powerstream</td>
<td>2C-4C</td>
<td>1C-3C</td>
<td>1C-4C</td>
<td>23±2</td>
</tr>
<tr>
<td>PJ121-PJ136</td>
<td>16</td>
<td>Powerstream</td>
<td>2C-4C</td>
<td>1C-3C</td>
<td>1.5C</td>
<td>23±2</td>
</tr>
<tr>
<td>PJ247-PJ251; PJ264-PJ267</td>
<td>8</td>
<td>RS Pro</td>
<td>2C-4C</td>
<td>1C-3C</td>
<td>1C-4C</td>
<td>23±2</td>
</tr>
<tr>
<td>PJ252-PJ255; PJ268-PJ271</td>
<td>8</td>
<td>RS Pro</td>
<td>2C-3C</td>
<td>2C-3C</td>
<td>2C-3C</td>
<td>23±2</td>
</tr>
<tr>
<td>PJ256-PJ259; PJ272-PJ275</td>
<td>8</td>
<td>RS Pro</td>
<td>3C-4C</td>
<td>1C-2C</td>
<td>2.5C-4C</td>
<td>23±2</td>
</tr>
<tr>
<td>PJ260-PJ263; PJ276-PJ279</td>
<td>8</td>
<td>RS Pro</td>
<td>1.5C-2.5C</td>
<td>1.5C-2.5C</td>
<td>1C-2.5C</td>
<td>23±2</td>
</tr>
<tr>
<td>PJ296-PJ311</td>
<td>16</td>
<td>RS Pro</td>
<td>1C-4C</td>
<td>1C-3C</td>
<td>1C-4C</td>
<td>35±1</td>
</tr>
</tbody>
</table>

Table 5.1 Operating conditions. Overview of the operating conditions that the cells cycled were subjected to.
An alternative battery state representation can be acquired from the EIS spectrum by fitting a set of parameters to the spectrum and using these parameters as the representation. A typical set of parameters arises by fitting an ECM, as outlined in Chapter 2. These parameters are often considered to be physically interpretable, although in reality the battery is not really a circuit.

We will assess whether incorporation of these physical interpretations, in the form of ECMs, improves predictions. We use the widely used Randles (ECM-R) circuit model [210], shown in Figure 2.1a and comprising a series resistance, connected with a resistance in parallel with a capacitance and a Warburg impedance element. We also implement a more complex Extended Randles (ECM-ER) circuit, shown in Figure 2.1b, which adds an additional resistor-capacitor parallel combination in series to the Randles circuit. The ECM is fitted to the spectrum and we use the extracted parameters as the state representation instead of raw EIS data.

Forming a state representation using the ECM parameters (extracted from the EIS spectrum) has an associated computational cost and can be considered a form of dimensionality reduction of the raw EIS data. An additional problem faced by ECMs in general is non-uniqueness, in that multiple different combinations of ECM parameters can generally explain a particular EIS spectrum equally well [328].

**Representation using historical data**

We additionally compare the representation of battery state using EIS to that which could be formed if the entire set of historical cycling data is available. We benchmark the EIS-based state against other approaches utilised in prior literature, including the state-of-the-art feature based method [151, 157]. We consider whether there are additional features to the EIS spectrum that can serve to augment battery state. Simple measures that have been used to forecast or estimate battery SOH include using the previous cycle discharge capacity, or the capacity throughput since cycling commenced. More advanced approaches include extracting features of the historical capacity voltage discharge curves, as shown in Figure 5.1. The state-of-the-art approach to extracting such features was implemented by Severson et al. [151] and inspired the approaches to feature extraction used recently by Attia et al. and Paulson et al. [173, 157]. We benchmark how our EIS-based approach performs relative to those state-of-the-art features.

We consider the following features in our benchmark:

- Previous cycle discharge capacity $Q_{n-1}$. 
• Capacity throughput (CT) since cycling commenced, as defined by the sum of cell charge and discharge capacities from cycles 0 to \( n - 1 \).

• SOH, as defined by \( Q_{n-1}/Q_0 \).

• State-of-the-art capacity-voltage discharge curve features (CVF): Following Severson et al. [151], we form a state representation at the start of cycle \( n \) by extracting features from the capacity-voltage discharge curve after cycle \( n - 1 \). We fit each curve to a spline function, linearly interpolating to measure capacity at 1000 evenly spaced voltages from \( V_{\text{min}} \) to \( V_{\text{max}} \). This 1000-dimensional capacity vector \( Q_{n-1} \) is normalised by subtracting the equivalent vector from cycle 0, \( Q_0 \). The following features are then used as inputs: \( V_{\text{max}}, V_{\text{min}}, \log(\text{var}(Q_{n-1} - Q_0)), \log(\text{IQR}(Q_{n-1} - Q_0)) \). Additionally, we fit the capacity to a sigmoid \( Q(\tilde{V}) = \frac{p_0}{1.0 + \exp(p_1(\tilde{V} - p_2))} \) where \( \tilde{V} \) is the normalised voltage and use the parameters \( p_0, p_1, p_2 \) as features.

In contrast to EIS features, formation of a state representation using these features demands access to historical current-voltage data, over at least the entirety of the previous discharge and for some features, over the entire cell lifetime. However, these features benefit from the advantage of not requiring equipment to measure the EIS spectrum, which comes with an associated financial and temporal cost.

5.2.4 Representation of future action

For the task of predicting next cycle discharge capacity, the action vector \( a_n \) is formed from the concatenation of the \( n \)th cycle charge and discharge currents. When predicting discharge capacity several cycles, \( j \), ahead of time, the future protocol is now formed from all charging and discharging currents that will be applied between cycle \( n \) and cycle \( n + j \).

5.2.5 Machine learning model

All problems in this study are framed as regression tasks. We train a probabilistic machine learning model to learn the mapping \( Q_j = f(s_n, a_{n..j}) \), with uncertainty estimates, where \( s_n \) is the battery state at the start of the \( n \)th cycle, \( a_n \) is the set of future cycling protocols applied over cycles \( n \) to \( j \), and \( Q_j \) is the discharge capacity at the end of the \( j \)th cycle.

For the machine learning model, we use an ensemble of 10 XGBoost models [335], each with 500 estimators and a maximum depth of 100. The mean and standard deviation of the predictions made by each model in the ensemble are used to quantify the predicted output and the predictive uncertainty. To test model performance we use the median \( R^2 \) score and median
percentage error. To obtain test metrics from a dataset comprising \( N \) cells, we randomly leave two test cells out, train on the remaining \( N - 2 \) cells and repeat this process \( N/2 \) times, leaving different cells out each time.

5.3 Results and discussion

5.3.1 Capacity forecasting using EIS

We first consider the setting in which we want to predict the next cycle discharge capacity, for a cell whose usage history (including for example, cycle or calendar age, or historical capacity-voltage data) is completely unknown, if we apply a particular charging and discharging profile. We frame the problem as a regression task, and train a probabilistic machine learning model to learn the mapping \( Q_n = f(s_n, a_n) \), with uncertainty estimates, where \( s_n \) is the battery state at the start of the \( n \)th cycle, \( a_n \) is the future action (the \( n \)th cycle charge/discharge protocol), and \( Q_n \) is the discharge capacity measured at the end of the cycle. The battery state vector \( s_n \) is formed from the concatenation of the real (\( Z_{\text{re}} \)) and imaginary (\( Z_{\text{im}} \)) components of the impedance measured at 57 frequencies, \( \omega_1, \ldots, \omega_{57} \), in the range 0.02Hz-20kHz; \( s_n = [Z_{\text{re}}(\omega_1), Z_{\text{im}}(\omega_1), \ldots, Z_{\text{re}}(\omega_{57}), Z_{\text{im}}(\omega_{57})] \). The action vector is formed from the concatenation of the \( n \)th cycle charge and discharge currents. Finally, we begin by testing whether the approach works for cells from the same manufacturer, Powerstream, and cycled at the same temperatures (25°C), but with varying charging and discharging rates. The cells correspond to the first row of Table 5.1.

![Fig. 5.5 Predicting next cycle discharge capacity. a. Given knowledge of the state (the battery’s internal state, as characterised by the EIS spectrum) and the action (the next cycle charge/discharge protocol), our model predicts the next cycle discharge capacity with an error of 8.2%. Both state and action are needed to accurately forecast performance; using b. state or c. action alone is insufficient.](image-url)
Multi-step forecasting. Our model can also forecast longer term battery performance, as quantified by a. % test error, and b. $R^2$ value. Given the EIS spectrum and knowledge of the next protocols that will be applied to the cell, the discharge capacity is predicted with a test error of less than 10% up to 32 cycles in advance.

Figure 5.5 illustrates the accuracy of our model. Using both state and action as input, the next cycle discharge capacity is predicted with an average error of 8.2%. Importantly, both state and action (Figure 5.5a) are found to be necessary to predict future cell performance: if state (Figure 5.5b) or action (Figure 5.5c) alone are used as inputs, the test error approximately doubles to 20.7% and 15.4% respectively. This demonstrates the importance of both the cell’s internal health and the externally selected usage in determining realised cell performance.

For applications such as optimised charging and repurposing triaging, it is important that a model of battery life trajectory can forecast not only the immediate next cycle discharge capacity, but also capacity several cycles into the future [336, 337]. With this in mind, we next investigate how the predictive accuracy of the model changes as we push the model to predict capacity further into the future. In each case, the input comprises the concatenation of the state representation at the start of the $n$th cycle, $s_n$, with the “action” vector $a_{n...n+j}$ comprising all charging and discharging currents that will be applied between cycle $n$ and cycle $n + j$.

Figure 5.6 shows how $R^2$ changes with $j$. As expected, the accuracy of the model generally decreases as the forecasting interval increases. However, the model still attains $R^2 = 0.75$ when projecting 40 cycles into the future.

5.3.2 Data efficiency and robustness to domain shift

We next test the robustness of our method by investigating data efficiency and model generalisability. To test data efficiency, we measure how performance changes as the number
5.3 Results and discussion

**Fig. 5.7 Data efficiency.** The model performance, as quantified by **a.** % test error and **b.** $R^2$, improves as the number of cells used to train increases. The model is data-efficient, achieving a test error of less than 10% with just eight cells in the training set.

of cells used to train the model increases. As seen in Figure 5.7, there is a marked reduction in test error from 23.8% to 8.2% as the number of cells is increased from two to 22. Nevertheless, the model is demonstrably data-efficient, with just eight cells needed to obtain a test error of less than 10%.

**Fig. 5.8 Robustness to domain shift.** **a.** The distribution of discharge capacity is different for cells cycled under variable discharge rates (blue) compared to a fixed discharge rate (red); the overlap region of the two distributions appears darker in colour. **b.** Our model, trained on the variable discharge rate cells, accurately predicts the discharge capacities of cells cycled under a fixed discharge rate. The colour of the plotted points denotes predicted uncertainty (see colour bar). **c.** The model “knows what it does not know”: when we restrict the test data used to calculate the RMSE by including only the predictions that the model is most confident about (i.e. with lowest predictive uncertainty), the RMSE reduces.
An important test of model generalisability is to study model accuracy when the domain distribution changes, i.e., when the model is being deployed in settings that are different to the training data [142]. This is important for deployment in the field as the approach needs to be robust to driving patterns that might be different to the training data [138]. We test model robustness by cycling an additional 16 cells from the same manufacturer, but now adjusting the cycling protocol by fixing the discharge current to 1.5C for each cell throughout its life. We use a model trained using only cells that were subjected to random discharge currents over their lifetime, to predict next-cycle discharge capacity of cells subjected to fixed discharging. To illustrate the difference in training and test datasets, the distribution of discharge capacities is shown for each in Figure 5.8a.

The predictive accuracy of the model on the fixed discharge dataset is illustrated in Figure 5.8b. Promisingly, the model attains a test error of just 6.3% on this domain-shifted dataset, which corresponds to $R^2 = 0.76$.

Our model also outputs predictive uncertainty, which indicates how certain the model is about the quality of its predictions. It is especially important in the domain-shifted setting that the model “knows what it does not know” and estimates high predictive uncertainty about data points that it is likely to obtain a high error on. We can test the model’s ability to estimate its uncertainty by observing how the average test error changes as the number of data points is reduced to include only the data points that the model is most confident about. If a model can successfully estimate its level of certainty, the average test error should reduce as the proportion of data is reduced to include only the most confidently predicted points. Figure 5.8c shows a 32% reduction in root-mean-squared error (RMSE) as the proportion of data is reduced from 100% to the most confident 25%, demonstrating that our model has learnt which predictions it should be confident about.

### 5.3.3 Comparison of state representations

Having demonstrated the ability of the EIS spectrum to capture battery state, we now benchmark this representation of battery health against other approaches utilised in the literature, including the state-of-the-art feature-based method [151, 157], and consider whether there are additional features to the EIS spectrum that can serve to augment battery state.

Table 5.2 shows how the state representation impacts test error and model goodness of fit. In all cases, the model is trained to predict the next cycle discharge capacity, given the next cycle protocol and the chosen state representation. Interrogating the relative importance of
5.3 Results and discussion

<table>
<thead>
<tr>
<th>Input</th>
<th>$R^2$</th>
<th>Test error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocol only</td>
<td>0.32</td>
<td>15.4</td>
</tr>
<tr>
<td>EIS only</td>
<td>0.05</td>
<td>20.7</td>
</tr>
<tr>
<td>EIS + Protocol</td>
<td>0.83</td>
<td>8.2</td>
</tr>
<tr>
<td>ECM-R + Protocol</td>
<td>0.69</td>
<td>10.7</td>
</tr>
<tr>
<td>ECM-ER + Protocol</td>
<td>0.80</td>
<td>8.4</td>
</tr>
<tr>
<td>SOH + Protocol</td>
<td>0.61</td>
<td>12.4</td>
</tr>
<tr>
<td>CVF + Protocol</td>
<td>0.75</td>
<td>8.8</td>
</tr>
<tr>
<td>CT + Protocol</td>
<td>0.52</td>
<td>13.3</td>
</tr>
<tr>
<td>$Q_{n-1}$ + Protocol</td>
<td>0.56</td>
<td>12.1</td>
</tr>
<tr>
<td>EIS + CVF + Protocol</td>
<td>0.88</td>
<td>6.7</td>
</tr>
<tr>
<td>$EIS + CVF + CT + Q_{n-1}$ + Protocol</td>
<td><strong>0.91</strong></td>
<td><strong>6.2</strong></td>
</tr>
</tbody>
</table>

Table 5.2 Comparison of state representations. We consider whether augmenting the EIS-based state representation with additional features can enhance model performance. The State of Health (SOH), as defined by the ratio between the previous discharge capacity and the initial discharge capacity, does not fully capture the battery’s current health; using this scalar state representation instead of the multidimensional EIS representation increases the test error by 51%. The most informative representation of battery state is obtained by adding previous capacity-voltage discharge curve features (CVF), capacity throughput (CT), and previous discharge capacity $Q_{n-1}$.

features, we first consider the baseline of using EIS only (without including the protocol) and using the protocol only (without including EIS). Perhaps unsurprisingly, battery degradation is a function of both the current state and future charge/discharge protocol. As such, using both EIS and the protocol significantly outperforms using EIS only or using the protocol only.

We then explore the impact of physics-based representation of the EIS spectrum, using the Randles (ECM-R) and extended Randles (ECM-ER) equivalent circuit models. Comparing EIS + Protocol with ECM-R + Protocol and ECM-ER + Protocol reveals that these physics-based models lose information, and using a machine learning approach to directly learn from raw data might be advantageous.

We next consider the different approaches that have been reported in the literature, $Q_{n-1}$, SOH, CT, and CVF, with CVF being the state-of-the-art in the battery informatics literature. In all cases, EIS + Protocol outperforms those other features with Protocol, although CVF is competitive.

Interestingly, information from capacity-voltage curve data (CVF) is complementary to EIS - combining EIS with these features leads to a significant increase in accuracy ($EIS + CVF +$...
Forecasting lithium-ion battery performance under uneven usage

Protocol). This is perhaps unsurprising, as EIS probes the impedance of the single “static”
cell discharged state (with high information content per instant state), whilst capacity-voltage
curves probe how the cell state evolves continuously over the path from charged to discharged
(with low information content per instant state).

Finally, the best model performance is attained by combining all of the above features to form
the state representation. In this case the average test error is just 6.2%.

5.3.4 Robustness to different cell manufacturers

We now extend our analysis to explore how robust our approach is to changing the cell
manufacturer, adjusting the operating temperature and adjusting the average use pattern.
We repeat our experiment on a new batch of 32 commercial LiR coin cells (of nominal
capacity 1C = 40mAh) from RS Pro, a different manufacturer, except we now make the
problem significantly more challenging by subjecting different subgroups of cells to one of
four different usage distributions. These usage distributions are shown in Table 5.1.

<table>
<thead>
<tr>
<th>Input</th>
<th>Random train/test split</th>
<th>Stratified train/test split</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>Test error (%)</td>
</tr>
<tr>
<td>EIS + Protocol</td>
<td>0.78</td>
<td>15.2</td>
</tr>
<tr>
<td>CVF + Protocol</td>
<td>0.69</td>
<td>16.5</td>
</tr>
<tr>
<td>EIS + CVF + Protocol</td>
<td>0.84</td>
<td>12.9</td>
</tr>
</tbody>
</table>

Table 5.3 Robustness of approach to cell manufacturer. We make qualitatively similar
observations when we test our approach on cells manufactured by RS Pro rather than
Powerstream), with EIS found to be a slightly better state representation than state-of-
the-art capacity / voltage features (CVF). The best results are obtained when the two
representations are combined. We test how the model performs when we split the training
and testing sets randomly, and when we instead stratify the training and testing sets such
that the model is tested on cells with a different usage distribution to the cells it was
trained on.

We measure the accuracy of the model in two ways: firstly, we consider the case where the
model is exposed to cells that have been subjected to the same distribution of protocols as
the test set (random splitting), and second, the more challenging case where the model is
only trained on the cells which are subjected to three of the cycling protocol distributions and
tested on the remaining eight cells subjected to a different cycling protocol. This is a much
harder task as the average usage on the test cells is very different to the average usage on the
training cells - it is a test of whether the model can extrapolate to different average use not just different cycle-to-cycle use.

<table>
<thead>
<tr>
<th>Input</th>
<th>(R^2)</th>
<th>Test error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocol only</td>
<td>0.43</td>
<td>21.7</td>
</tr>
<tr>
<td>EIS + Protocol</td>
<td>0.78</td>
<td>15.2</td>
</tr>
<tr>
<td>ECM-R + Protocol</td>
<td>0.68</td>
<td>17.7</td>
</tr>
<tr>
<td>ECM-ER + Protocol</td>
<td>0.65</td>
<td>17.9</td>
</tr>
<tr>
<td>EIS + CVF + Protocol</td>
<td>0.84</td>
<td>12.9</td>
</tr>
<tr>
<td>ECM-R + CVF + Protocol</td>
<td>0.82</td>
<td>13.7</td>
</tr>
<tr>
<td>ECM-ER + CVF + Protocol</td>
<td>0.84</td>
<td>14.4</td>
</tr>
<tr>
<td>CVF + Protocol</td>
<td>0.69</td>
<td>16.5</td>
</tr>
<tr>
<td>(Q_{n-1}) + Protocol</td>
<td>0.58</td>
<td>18.0</td>
</tr>
<tr>
<td>ECM-R + CVF + CT + (Q_{n-1}) + Protocol</td>
<td>0.83</td>
<td>14.5</td>
</tr>
<tr>
<td>ECM-ER + CVF + CT + (Q_{n-1}) + Protocol</td>
<td>0.87</td>
<td>14.0</td>
</tr>
<tr>
<td>EIS + CVF + CT + (Q_{n-1}) + Protocol</td>
<td>0.84</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Table 5.4 Robustness of approach to cell manufacturer (random train/test split). We test how well our approach generalises to alternative chemistries by cycling 32 additional cells (manufactured by RS Pro). Each cell is subjected to random charging and discharging, according to four possible distributions of protocols (see Table 5.1). Here we assess how the model performs under 16-split validation, where two cells are randomly held out in each split, not necessarily from the same subcategory. We assess how the model performance change when the features used to form the state representation are varied.

The results for different state representations is shown in Table 5.3 for both the case where the train/test split is random, and where the split is stratified into different usage patterns. Extended comparisons of different state representations using random split and stratified split are provided in Tables 5.4 and 5.5 respectively. Comparable observations are made for cells purchased from the second manufacturer: namely, the most accurate predictions are made when the state representation is formed using features of the EIS spectrum alongside those formed from the discharge curve (CVF). As expected, the model performs significantly better when it has been trained on data from some cells that have been exposed to a similar distribution of cycling patterns as those that the model is tested on. However, the model remains performant in the stratified split scenario, and in this setting the test error reduces by
Forecasting lithium-ion battery performance under uneven usage

30% when the state representation is formed using the EIS spectrum alongside the features of the discharge curve, instead of solely using features of the discharge curve. These additional results further demonstrate that if available, both the EIS spectrum and discharge curve can act as informative markers of the battery’s internal state, but that they are complementary to each other.

<table>
<thead>
<tr>
<th>Input</th>
<th>$R^2$</th>
<th>Test error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocol only</td>
<td>0.21</td>
<td>28.9</td>
</tr>
<tr>
<td>EIS + Protocol</td>
<td>0.59</td>
<td>21.1</td>
</tr>
<tr>
<td>ECM-R + Protocol</td>
<td>0.46</td>
<td>23.7</td>
</tr>
<tr>
<td>ECM-ER + Protocol</td>
<td>0.61</td>
<td>23.5</td>
</tr>
<tr>
<td>EIS + CVF + Protocol</td>
<td>0.68</td>
<td>19.5</td>
</tr>
<tr>
<td>ECM-R + CVF + Protocol</td>
<td>0.70</td>
<td>20.4</td>
</tr>
<tr>
<td>ECM-ER + CVF + Protocol</td>
<td>0.67</td>
<td>21.4</td>
</tr>
<tr>
<td>CVF + Protocol</td>
<td>0.38</td>
<td>27.7</td>
</tr>
<tr>
<td>$Q_{n-1}$ + Protocol</td>
<td>0.20</td>
<td>28.2</td>
</tr>
<tr>
<td>ECM-R + CVF + CT + $Q_{n-1}$ + Protocol</td>
<td>0.67</td>
<td>20.5</td>
</tr>
<tr>
<td>ECM-ER + CVF + CT + $Q_{n-1}$ + Protocol</td>
<td>0.68</td>
<td>21.5</td>
</tr>
<tr>
<td>EIS + CVF + CT + $Q_{n-1}$ + Protocol</td>
<td>0.67</td>
<td>19.9</td>
</tr>
</tbody>
</table>

Table 5.5 Robustness to cell manufacturer (stratified train/test split). We test how well our approach generalises to alternative manufacturers by cycling 32 additional cells (manufactured by RS Pro, nominal capacity 40 mAh). Each cell is subjected to random charging and discharging, according to four possible distributions of protocols (see Table 5.1). Here we assess how the model performs under 4-split validation, with stratified splitting: for each split 8 cells with one cycling distribution are held out. We assess how the model performance change when the features used to form the state representation are varied.

We next verify that the model is robust with respect to changing external operating temperature. We cycle an additional 16 cells at 35°C and test the model trained on data from cells cycled at room temperature. Table 5.6 shows that our model can extrapolate to cells operated at these higher temperatures, but that the EIS spectrum plays a particularly important role in characterising the battery state when the cell is not operated at the same temperature. The model obtains a test error of 34.2% when only the discharge curve features are used to characterise state, which reduces to 14.0% when both the EIS spectrum and discharge
### Table 5.6 Robustness to operating temperature

Accuracy of the model trained on 32 cells (manufactured by RS Pro) cycled at 23°C and tested on 16 cells from the same manufacturer but cycled at 35°C. Here we compare the model accuracy when different representations are used to characterise the battery’s internal state. An extended comparison of different state representations is provided in Table 5.7.

<table>
<thead>
<tr>
<th>Input</th>
<th>$R^2$</th>
<th>Test error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EIS + Protocol</td>
<td>0.76</td>
<td>14.6</td>
</tr>
<tr>
<td>CVF + Protocol</td>
<td>0.20</td>
<td>34.2</td>
</tr>
<tr>
<td>EIS + CVF + Protocol</td>
<td>0.80</td>
<td>14.0</td>
</tr>
</tbody>
</table>

curve features are used. This further demonstrates the additional information that EIS signals contain relative to charging-discharging curves, and supports the hypothesis that EIS implicitly tracks temperature \([338]\).

### 5.4 Conclusion

In this chapter, we have showed that the electrochemical impedance spectrum accurately characterises the internal state of a cell, and a machine learning model can be trained to accurately forecast both immediate and longer term cell performance with predictive uncertainty, even amid uneven and unknown historical cell usage. Our model achieves comparable accuracy (8.2% test error) to the state-of-the-art forecasting approach (8.8% test error) when testing on cells subjected to the same distribution of operating conditions as the cells used to train the model. However, as outlined in Figure 5.1, the state-of-the-art approach demands access to historical cycling data whereas our model enables forecasting with no historical data. Additionally, our model significantly outperforms the state-of-the-art model when extrapolating to a higher operating temperature, with a 57% reduction in test error (from 34.2% to 14.6%).

Our method is data-efficient, achieving a next-cycle test error of 9.9% with training data from just eight cells, and is robust to shifts in dataset distributions. Additionally, we find that there is scope to boost model performance by 25% if historical cycling data is available; such data can be used to derive features that augment the cell state representation. We demonstrate that our approach can be utilised across different cell chemistries, and the model is robust to different operating temperatures.

Our approach differentiates from the prior art in two important ways: First, we employ an information-rich electrical signal – EIS – which captures the response of the cell across
different timescales without any knowledge of the cycling history. This is in contrast to most existing methods which employ features from the charging-discharging curve – a significantly more coarse-grained signal – as input to machine learning models. Our results suggest significant improvements in battery management systems abound by incorporating circuitries that measure electrochemical impedance, albeit at a financial and temporal cost.

Second, we focus on uneven cycling, where the charging and discharging rates vary from cycle to cycle. This departs from previous studies on machine learning for battery degradation which focused on constant charge/discharge conditions, which are typical in battery testing. Our results problematise the concept of a single scalar State of Health, as the state of the battery is dependent on the extent of the myriad different degradation mechanisms, which in turn depends on the sequence of historic charge/discharge protocols. Rather, we suggest that a cell can be described by a multidimensional state vector, captured using informative high-dimensional measurements like EIS, and a machine learning approach can be used to predict future capacities given the state vector and future charge/discharge protocols. Furthermore, although here we only consider forecasting starting from an initially discharged state, we hypothesise that it should be possible in future work to forecast discharge capacity starting from any state of charge based on the EIS measurement, since EIS spectrum implicitly tracks state of charge [339–341].

We note that the general framework that we have laid out for predicting future battery performance given current cell state and future actions has scope to be applied in a broad range of battery diagnostic and control settings. For example, predicting the effect of a proposed charging protocol on next cycle discharge capacity as well as long term degradation is important for optimising rapid charging applications [157], where a balance must be achieved between charging time and rate of cell degradation [342]. Our work can additionally be extended to consider more complicated dynamic usage protocols, such as WLTC.
Table 5.7 Robustness to operating temperature. Accuracy of the model trained on 32 cells (manufactured by RS Pro) cycled at 23°C and tested on 16 cells (also manufactured by RS Pro) cycled at 35°C. Here we compare the model accuracy when different representations are used to characterise the battery’s internal state.

<table>
<thead>
<tr>
<th>Input</th>
<th>( R^2 )</th>
<th>Test error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocol only</td>
<td>0.10</td>
<td>36.0</td>
</tr>
<tr>
<td>EIS + Protocol</td>
<td>0.76</td>
<td>14.6</td>
</tr>
<tr>
<td>ECM-R + Protocol</td>
<td>0.66</td>
<td>17.1</td>
</tr>
<tr>
<td>ECM-ER + Protocol</td>
<td>0.69</td>
<td>16.4</td>
</tr>
<tr>
<td>EIS + CVF + Protocol</td>
<td>0.80</td>
<td>14.0</td>
</tr>
<tr>
<td>ECM-R + CVF + Protocol</td>
<td>0.70</td>
<td>17.1</td>
</tr>
<tr>
<td>ECM-ER + CVF + Protocol</td>
<td>0.71</td>
<td>17.1</td>
</tr>
<tr>
<td>CVF + Protocol</td>
<td>0.20</td>
<td>34.2</td>
</tr>
<tr>
<td>( Q_{n-1} ) + Protocol</td>
<td>0.27</td>
<td>31.8</td>
</tr>
<tr>
<td>ECM-R + CVF + CT + ( Q_{n-1} ) + Protocol</td>
<td>0.69</td>
<td>17.6</td>
</tr>
<tr>
<td>ECM-ER + CVF + CT + ( Q_{n-1} ) + Protocol</td>
<td>0.66</td>
<td>18.6</td>
</tr>
<tr>
<td>EIS + CVF + CT + ( Q_{n-1} ) + Protocol</td>
<td>0.82</td>
<td>13.2</td>
</tr>
</tbody>
</table>
Chapter 6

Conclusions

This thesis has presented frameworks for understanding and forecasting the performance of electrochemical energy systems using both “bottom-up” and “top-down” machine learning approaches. I summarise the main contributions below and reflect on the ways in which these frameworks could be applied in the future.

6.1 Contributions

A framework to learn the local structure distribution in electrolytes.

Electrolytes play a fundamental role in the performance of electrochemical systems, but at high concentrations they exhibit curious behaviour such as underscreening of electrostatic forces by orders of magnitude. The concept of ion pairing is often invoked to explain this puzzle, which states that ions can either be “free” or paired with a counter-ion. This model implicitly assumes the distribution of local structural motifs is a bi-modal distribution of two delta functions in “local structure space”, with one distribution corresponding to the free state and the other, the paired state. However, the definition of ion pairs is usually qualitative, using concepts such as a distance cutoff. The amount of ion pairs depend on the cutoff used, thus it is challenge to provide quantitative predictions.

In Chapter 3 we generalised the concept of ion pairing, presenting a framework from which we can identify the most probable local structure distribution within an electrolyte, and thus compare the validity of theories which assume different local structure distributions. We used Bayesian unsupervised learning to identify the number of statistically significant types of structural motifs within the electrolyte as well as the differences between these types of
motifs. Our results suggest that differences in local environments in non-dilute systems arise from differences in like-charge correlations rather than unlike charge correlations. This draws into question the validity of the ion pair hypothesis for such systems.

A framework to infer global transport properties from the local structure distribution in electrolytes.

In Chapter 4, we then built upon ideas presented in the work above and posited that each ion in an electrolyte makes an instantaneous contribution to the observed conductivity that is determined entirely by its local static structure. This is a hypothesis that builds upon and generalises the ideas presented by the ion pair hypothesis and the cluster Nernst-Einstein approach.

We used machine learning to approximate the function that maps from local environment to instantaneous contribution to conductivity. When we use this learned function to try to predict the molar conductivity of systems that were not used to train the model, the accuracy of the model remains high, supporting the hypothesis that global molar conductivity can be predicted from local structure alone.

A side-product of this model is that we have effectively built a “computational microscope” that spatio-temporally decomposes global properties of soft matter systems (such as conductivity) into individual atomistic contributions. The framework offers new insights into the most relevant structural motifs for enhanced or degraded conductivity. Our results suggest that homogeneity in local structure is important for designing high conductivity systems.

A general framework for predicting the future performance of lithium-ion batteries under variable use.

A battery’s performance trajectory depends both on the materials from which it is built, and the way it is operated over its life. Because no battery is operated in exactly the same way, each battery follows a unique degradation trajectory which is challenging to forecast.

In Chapter 5, we have presented a general framework for predicting the future performance of a given battery under uneven use conditions. The framework requires acquisition of an informative representation of the battery’s current internal state as well as its expected future use. We have demonstrated that EIS provides a highly informative non-invasive method to acquire this state representation, which eschews the need for historic electrochemical data. We also show that in contexts where EIS is not available, historic data can be leveraged to
obtain a representation that is almost as informative as EIS, and that the two signals of battery health can be complementary to each other.

6.2 Open questions

Electrolyte discovery

Armed with a mapping from local structure distribution to macroscopic properties in liquid electrolytes, we can discover which local structural motifs are positively correlated with desirable properties. This can offer insights into how to design liquid electrolytes with optimised performance.

In order to apply this model, it will be important to probe the generalisability of the model under systems with different inter-particle interactions. Considering alternative representations of local structure will also be an important area for future research. One question that could be explored here is “How local is local?”, i.e. should there be a boundary beyond which interactions need not be considered? The answer to this question is likely to vary across different electrolyte compositions. It would also be useful to explore the relative importance of features in the local representation of environment and identify the most simple representation of local structure that is predictive of global properties. Comparing the performance of models which takes the radial distribution function as input versus incorporating angular distribution will shed light on the geometric shape of ion aggregates that impact equilibrium structure and ion transport. Another pertinent question is how much more complicated the structural motifs need to be, than a simple discrete assignment of each ion to an aggregate of defined size, as suggested by the “cluster Nernst-Einstein” model. Finally, it would be interesting to explore the impact of relaxation time of structural motifs and whether they exist for long enough for us to consider them “real”.

Battery health diagnostics, prognostics and optimal control

In this work we have developed a framework for forecasting battery performance under different operating conditions. This framework could be applied in several industrial settings. Battery materials developers must test batteries for months or years to understand how their batteries will perform over the long term. Having the ability to forecast how batteries will degrade under different use conditions based on early cycling data would accelerate the development cycle significantly. In addition, once the battery is in operation, we can now predict the impact of a particular usage protocol on both short and long term performance. We can integrate this model into optimal control or reinforcement learning algorithms to identify
optimal charging protocols that minimise the charging time whilst preventing long term battery degradation, and which adapt the charging protocol depending on the current state of the battery. Finally, degraded batteries do not always come with associated historical data and so it is challenging to predict how those batteries will perform in second life applications. We provide an approach that uses EIS to obtain the internal battery state without any need for historical data. Such an approach could be applied in repurposing or triaging batteries for second life applications.

In this work we used EIS and historical current-voltage-time data to acquire a representation of the battery state. There is scope to explore additional sources of information, such as in operando EIS [343], acoustic measurements [147, 176] or materials information that could enrich the state representation. We could overcome the need for expensive EIS equipment by developing multi-frequency pulse signals, such as intermittent current interruption [175], to acquire similarly informative state representations. Additionally, although in this work we focused on predicting the performance of lithium-ion coin cells, there is evidence that EIS can detect the presence of faulty cells at a module level [344]. This suggests that our approach should scale up beyond the cell level.

Whilst in this work we focused on forecasting the future discharge capacity of the battery, there are several relevant performance metrics for battery performance including energy density, power density and internal resistance. It would be possible to train similar models to forecast such properties and to build a multi-task learning model that can learn how to predict all of these properties simultaneously. It should also be possible to predict other relevant health metrics such as the probability of sudden death or catastrophic failure. The ability to train machine learning models to predict such metrics relies on the existence of data (which may come from post-mortem analysis, observation of sudden death during ageing tests, or observation of fires) in which sudden death has been observed so that it is possible to identify which are the early warning signals that are correlated with sudden death.

The chemistry and format of batteries is continuously evolving and so there may not always be a great quantity of historical training data for the exact battery chemistry of interest. However, there may be lots of battery data for chemistries that are similar, though not identical. A significant advance in the field of battery prognostics would be achieved by a transfer learning model that can leverage data from one battery chemistry to predict how another will perform. There has been some progress in this direction in the case where usage is fixed [173]. The next step is to generalise this to uneven usage.
References


[136] Research and development of high-power and high-energy electrochemical storage devices. 4 2014.


