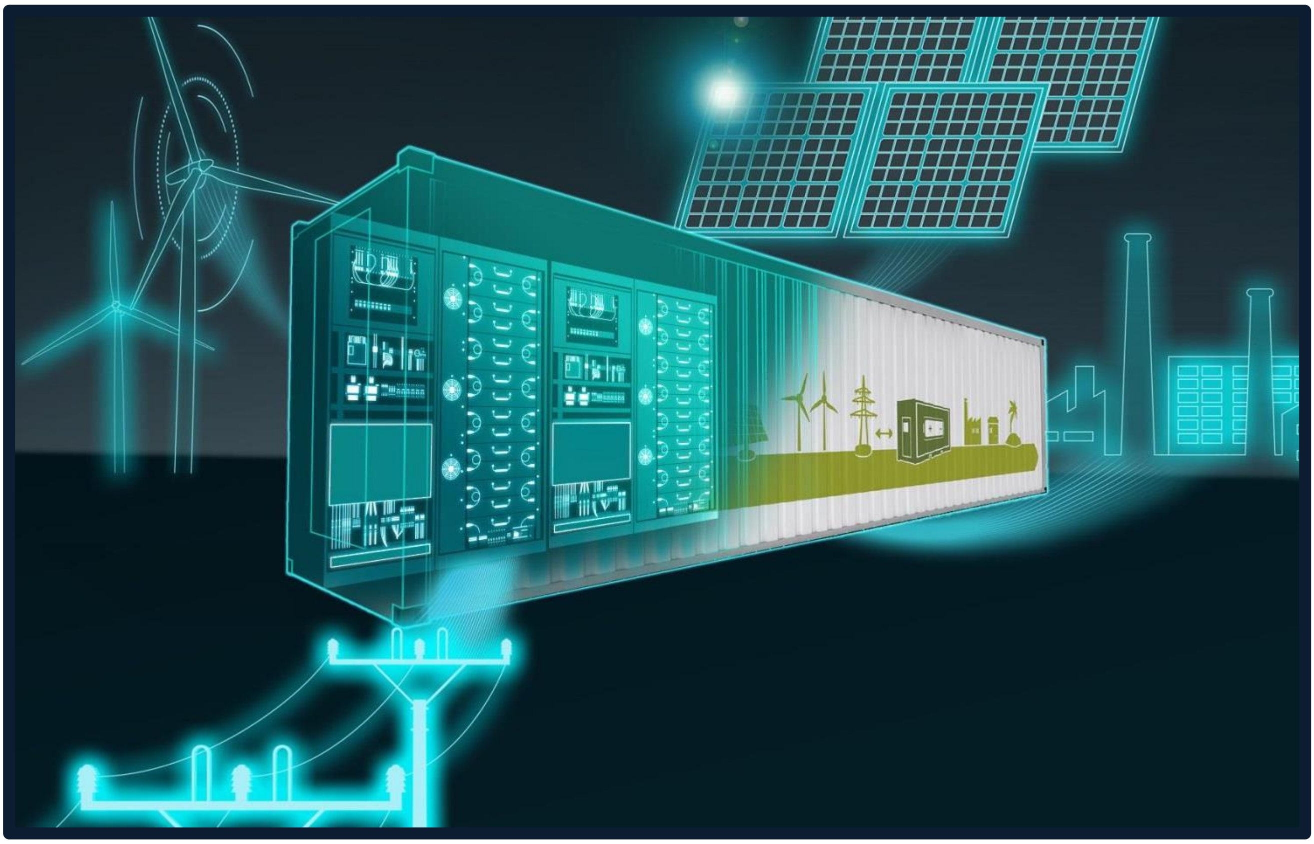
EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling



Degradation of Lithium-ion Batteries

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1. Introduction

Background

Lithium-ion batteries are a ubiquitous technology. Their high energy density, small memory effect, and low self-discharge have made them the power source of choice for portable electronics and electric vehicles. Siemens utilise lithium-ion batteries in grid-scale energy storage systems. These systems charge when the supply of electricity exceeds demand (i.e. when the price is low) and discharge when the demand for electricity is high (i.e. when the price is high). This reduces both national energy losses at off-peak times and the strain on energy suppliers at peak times. With the move towards renewable energy sources, which produce energy at highly fluctuating rates, grid-scale battery storage solutions are becoming increasingly important for the functioning of the national grid.

Understanding degradation is essential to accurately cost the usage of large-scale battery systems.

To properly manage large-scale battery systems, it is essential to accurately cost usage through a thorough understanding of degradation. Large scale battery systems consist of many modules each comprising of numerous individual cells. Each cell degrades as a result of a few key mechanisms: formation of a solid-electrolyte interphase (SEI), loss of active material due to electrode particle fracture, and delamination. The degradation of each individual cell then contributes to the degradation of the system as a whole.

Lithium-ion Cells

A lithium-ion cell forms the fundamental electrochemical unit of a lithium-ion battery. It consists of two current collectors, a positive electrode, a negative electrode, a porous separator, and an electrolyte as shown in Figure 1. Each electrode consists of particles of active material (graphite in the negative electrode, lithium iron phosphate in the positive electrode) embedded in a porous polymer binder.

A lithium-ion cell is a fundamental electrochemical unit, consisting of two current collectors, a positive and negative electrode, a porous separator, and an electrolyte.

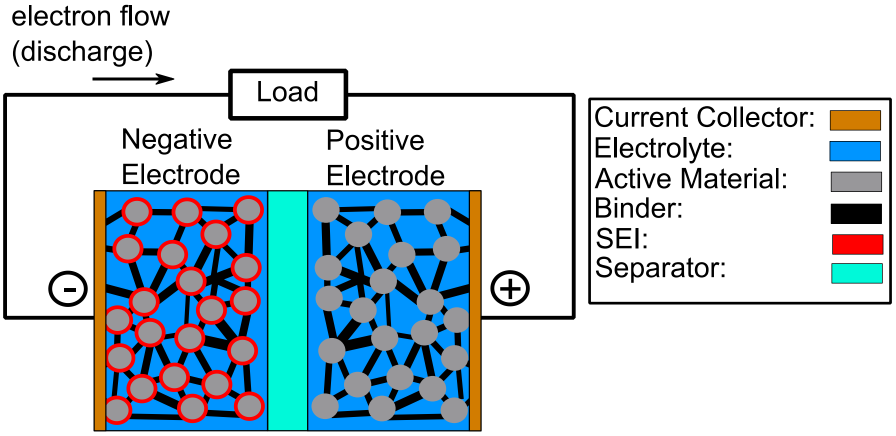

Figure 1: Schematic of a lithium-ion cell. The location of the solid-electrolyte interphase (SEI) is also indicated in this schematic.

When a lithium-ion cell is discharged by connecting an external wire to the negative and positive current collectors, lithium intercalated in the active material of the negative electrode travels to the surface of the active material where a chemical reaction occurs. This reaction converts intercalated lithium into lithium ions free to travel through the electrolyte and electrons free to travel through the negative electrode. The lithium ions are thermodynamically attracted to the positive electrode and therefore travel there through the electrolyte. Meanwhile, the electrons are driven through the external wire to the positive electrode. At the surface of the active material in the positive electrode, the electron and lithium ion recombine through another chemical reaction to become lithium intercalated in the active material in the positive electrode. During charge, the same process occurs in reverse, driven by an applied voltage.

Glossary of terms

- Active material: The material in the electrode within which lithium can be intercalated is known as the Active Material (made from graphite in the negative electrode, and from lithium iron phosphate in the positive electrode).
- Binder: The binder is a porous polymer matrix which 'binds' the active material together and conducts electrons. This ensures electrical contact between the active material and current collector is maintained.
- Current collector: Current collectors (made from copper foil at the negative electrode and aluminium foil at the positive electrode) are electrically conducting layers that external wires are connected to.
- Delamination: The process in which a section of the surface of the active material becomes detached from the binder is known as delamination.
- Elastic Material: An elastic material is one in which the stress is linearly proportional to the strain (e.g. Hooke's law for a spring).
- Electrode: Electrodes are electrically conducting materials that are in contact with both an electrolyte and a current collector. An electrode consists of active material and a binder.
- Electrolyte: A solution that is ionically conducting is known as an electrolyte
- Intercalation: Intercalation is the name given to the process in which an ion is inserted into a layered material such as graphite.
- Method of multiple scales: This is a mathematical technique that is used to create a homogenised macroscale model from a given microstructure.
- Strain: Strain is the relative change in shape or size of an object due to externally applied forces.
- Stress: The force per unit area acting on a body is known as the stress.
- Viscoelastic material: A material which acts like a solid in some situations and a fluid in others (e.g. silly putty) is known as a viscoelastic material.

Degradation Mechanisms

Degradation is a catch all term used to describe a number of effects observed over the lifetime of a cell that render it less valuable (e.g. capacity fade, power fade). It is generally agreed that the chemical mechanism with the largest contribution to degradation is the formation of the solid-electrolyte interphase (SEI). The mechanical mechanisms that are of greatest importance are fracture of the SEI and active material particles, and delamination.

Solid-Electrolyte Interphase (SEI)

Alongside the intercalation reactions, parasitic "side reactions" that consume lithium occur within lithium-ion cells. Occurring primarily at the negative electrode (graphite), the result is the formation of a solid-electrolyte interphase (SEI). Fortunately, lithium ions can travel through the SEI and therefore its presence does not prevent the cell from functioning. However, SEI formation consumes lithium and therefore is a source of capacity loss. Furthermore, its presence increases internal resistance, which results in power fade of the cell. A schematic of the chemical reactions occurring at the negative electrode during charging is displayed in Figure 2.

An SEI forms due to parasitic side reactions. Its presence results in capacity and power fade of the cell

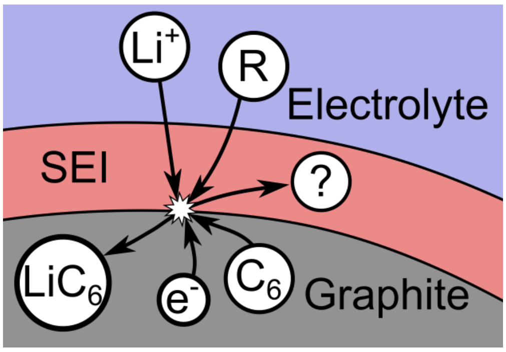

Figure 2: Schematic of the chemical reactions occurring at the negative electrode during charge. Lithium-ions (Li^+) and various reacting species (R) travel from the electrolyte, through the SEI to the surface of the active material where a chemical reaction occurs with graphite (C_6) and electrons (e^-) contained within the active material. The chemical reaction produces intercalated lithium (LiC_6) alongside a wide variety of side products which comprise the SEI.

Initially, SEI formation is fast but, as the thickness of the SEI increases, it slows. The SEI is harder for lithium ions and the various reactant species to travel through than electrolyte. Therefore, thicker SEI reduces the amount of chemical species available at the chemical reaction site hence slows SEI formation. Furthermore, the rate at which chemical reactions occur is dependent on the voltage across the active material and the electrolyte. The SEI increases resistance and therefore reduces this voltage; this also slows the rate of SEI formation.

SEI and Electrode Particle Fracture

As lithium is intercalated, the active material particles swell which can result in fracture of the particle leading to loss of active material. Furthermore, this swelling induces stresses on the SEI surrounding the particle, leading to fracture of the SEI. This can result in a fresh surface upon which new SEI can form, hence accelerating degradation. This is illustrated in Figure 3.

The active material particles swell when lithium becomes intercalated. This induces stresses within the particle and on the SEI, which can cause fracture.

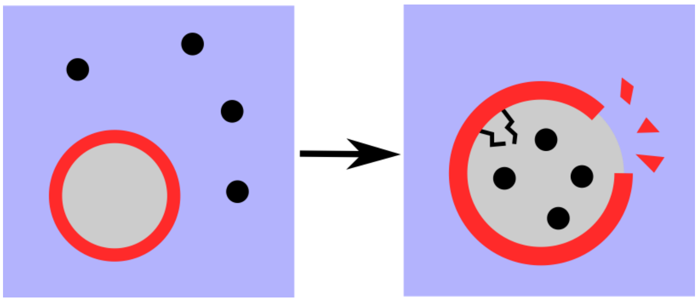

Figure 3: Effects of particle deformation. When lithium (black) is intercalated in the graphite particle (grey) the particle swells causing fracture of the particle and the SEI (red).

Delamination

The active material can detach from the binder as a result of absorption of electrolyte by the binder or particle deformation as a result of lithium intercalation.

The main purpose of the binder is to provide a path between the active material and current collector along which electrons can travel. However, the faces of the active material can detach from the binder; we call this delamination. There are two main causes of this effect: stresses induced by the absorption of the electrolyte by the binder during manufacture, and stresses induced by particle deformation as a result of lithium intercalation. Because, delamination reduces the number of paths along which electrons can travel between the active material and current collector, an increase in cell resistance and therefore power fade is observed. This also results in higher current densities, which produce higher temperatures that accelerate degradation and can lead to thermal runaway. Furthermore, delamination results in a fresh surface upon which SEI can form.

Aim

Due to the complicated nature of degradation in lithium-ion batteries, our aim is to provide a comprehensive review of the mathematical literature and propose appropriate extensions. To this end, we provide an overview of previous mathematical models for a lithium-ion cell, SEI formation, particle deformation, and delamination.

2. Mathematical Models

Newman Model

The standard model for a lithium-ion battery is called the Newman Model [1]. To derive this model, we neglect the effects of particle deformations, the current collectors, the binder, and the porous separator. Therefore, we consider a lithium-ion cell consisting of only active material and electrolyte. The electrolyte is considered to be moderately concentrated, that is, that the concentration of ions is large enough so that interaction forces between ions are important but small enough so that the total concentration of the electrolyte is approximately the concentration of the solvent. The transport of lithium ions is then found by balancing the drag force from interactions between molecules and the force directed down gradients in energy. Transport of intercalated lithium in the active material is modelled by assuming lithium is transported down gradients in concentration of lithium. On the boundary between the active material and the electrolyte, the two regions are coupled together through a phenomenological model known as the Butler-Volmer relation, which represents the intercalation reactions.

Without further assumptions, this microscale formulation is extremely computationally expensive because the geometry involves many active material particles. This complexity is removed by assuming a periodic arrangement of active material particles on the microscale and employing the *method of multiple scales* to develop a macroscopic model of the cell, which is the Newman Model.

Solid—Electrolyte Interphase (SEI)

To model SEI formation assume linear decay of species in SEI and account for resistance of SEI in Butler-Volmer relation

In this section, we outline a model for SEI formation similar to that developed in [2]. We assume that the concentration of each species (lithium-ions and reactant species) in the SEI decays linearly with distance from the electrolyte and that, at the surface of the active material, both species are consumed by a chemical reaction. With these assumptions, the concentration of each species at the surface of the active material is determined in terms of the chemical reaction and the concentration of that species in the electrolyte. To model the chemical reaction that forms the SEI, we formulate another Butler-Volmer relation, similar to that used for the intercalation reactions. The decrease in voltage across the active material and the electrolyte due to the resistance of the SEI is accounted for in this relation. We can now determine the change in thickness of the SEI.

So far, our model is only valid for a single particle. To describe a full cell and couple this model with the Newman model, we must again employ the method of multiple scales. The same numerical techniques can then be applied to solve this modified Newman model. The SEI model in [2] has been shown to predict impedance rise and capacity loss in many cases. However, the model struggles to predict certain types of capacity loss behaviour which suggests other degradation mechanisms must also be studied.

An electrode particle is treated as linear elastic material. Stress must be accounted for in the transport of intercalated lithium and in the Butler-Volmer relation

Active Material Deformation

We outline here the approach taken in [3] to extend the Newman model to account for particle deformations. Here, the active material is treated as a linear elastic material by making the assumption of small strains. The transport of lithium intercalated in the active material is affected by the distribution of stress in the particle. Therefore, an additional stress term is included in the model for transport of intercalated lithium. Furthermore, the chemical reaction rate is stress dependent so an additional stress term is also added to Butler-Volmer relation.

The method of multiple scales is then applied to this modified model. However, with these extensions a microscale model also must be solved alongside the macroscopic model. This is computationally expensive and this motivates taking the limit of fast diffusion in the active material particles and small stress assisted diffusion. As a result, the computation time is drastically reduced.

The binder is treated as a viscoelastic material with an extra term to account for swelling due to electrolyte absorption

Binder Deformation

We outline here the approach taken in [4] to model the deformation of the binder. The binder is assumed to be a porous *viscoelastic* material. Therefore, a model known as the standard linear model of viscoelasticity is used to describe the binder. The binder swells by around 50% of its volume when it absorbs electrolyte. This is accounted for by including a swelling term in the model. Since the active material particle is much harder than the binder, it is considered to be rigid in response to stresses from the binder. When the electrode particle swells due to lithium intercalation, the resulting deformation is forced upon the binder. To account for this in the model, the location of the active material boundary is prescribed at each point in time.

This model for the binder can be solved independently of the Newman model, assuming a prescribed function describes the swelling of the electrode particle. This model predicts stresses that could produce the experimentally observed delamination.

3. Discussion, Conclusion & Recommendations

We have developed an overview of lithium-ion batteries, the key degradation mechanisms and approaches for developing mathematical models. The key degradation mechanisms were identified as SEI formation, fracture of the SEI and active material particles, and delamination. For each process, the mathematical literature was reviewed and modelling approaches studied. This has provided us with an understanding of the models for each degradation mechanism.

The next step is to implement an efficient numerical solver for the Newman model. Once this has been done, we will carry out an indepth study of each of the three key degradation mechanisms identified and new mathematical models developed. Each mechanism will be introduced independently into the Newman model so that its effects can be understood in the context of the usage of a lithium-ion cell. Once each modified Newman model has been solved, we will couple the degradation mechanisms and study, in particular, the effect of particle deformation and delamination on SEI fracture and formation. This will lead to the creation of a coupled modified Newman model that accounts for all the key degradation mechanisms. After studying the degradation mechanisms in the context of the Newman model, which is one-dimensional, we will develop a more sophisticated three-dimensional model of a lithium-ion cell which takes account of the cell geometry and importantly, thermal effects. The degradation mechanisms will then be introduced to this thermal three-dimensional model with the goal of studying degradation in as realistic a setting as possible. Our ultimate goal is to accurately predict degradation in a lithium-ion cell by modelling the key degradation mechanisms, exploiting the mathematical structure of the equations, and employing numerical techniques for fast, efficient solution.

4. Potential Impact

Our work provides a basis to develop sophisticated degradation models. These models are essential for making informed strategic business decisions for large battery systems.

As part of a wider programme, we will develop models for degradation of a single lithium-ion cell. In another project within this programme, these cell models will be used to predict degradation of large battery systems with a particular focus on applications to grid-scale storage systems and electric buses. The marginal cost of making a trade on the energy market, or transporting passengers in an electric bus is determined by degradation of the battery system. Therefore, a quantitative description of degradation is essential for making informed strategic business decisions.

There are also wider societal benefits of this project. Grid-scale battery storage systems allow energy generated at off-peak times, which would otherwise be lost, to be consumed when it is in demand. Therefore, proper management of these systems is vital to minimise energy losses. Energy generation from renewables is typically significantly more volatile than that for traditional sources. Therefore, these battery systems provide the infrastructure necessary to reduce reliance on fossil fuels by switching to renewable energy sources.

Dr Tim Hughes, Head of Research Projects/Principal Scientist Energy Storage at Siemens, commented: *"Siemens's strategy is to be a world leader in electricity distribution and management. To help in achieving this strategy Siemens are establishing a Data Applications and Analytics Centre for Battery Intelligence. Such battery intelligence leverages existing Siemens battery and battery management system activities to enhance those offerings and create new data based value propositions which currently aren't available. One of the key aims of the Centre will be to develop a greater understanding of battery degradation. This understanding will enhance Siemens battery business – from planning and sizing of battery facilities, through optimised operations, to service and maintenance provision. This represents an opportunity to provide new/improved services to the customer based on a much enhanced understanding of battery degradation, coupled with the connectivity and historical data opportunities associated with Mindsphere (Siemens's industrial cloud platform). Within this context understanding the degradation processes within a battery is key to understanding the lifecycle costs and associated risks for a wide variety of applications ranging from ancillary services for grid applications to fleet optimisation for electric buses. The current mini-project has been focussed on providing a firm foundation for degradation modelling which will form the basis of a cohort of students at Oxford looking at combining detailed electrochemical modelling, systematic experimental programs and big data analytics in order to develop a tool chain for lifecycle management."*

References

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