

EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling



Long-term degradation of lithium-ion batteries

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1 Introduction

Background information

With the shift to vehicle electrification and renewable energy sources, lithium-ion batteries are emerging as one of the most important technologies of the 21st century. Siemens utilise lithium-ion batteries in grid-scale energy storage systems, which correct for offsets in electricity supply and demand. This in turn makes intermittent energy sources such as solar and wind viable.

To properly manage such large-scale battery systems, it is essential to understand cell *degradation*. A quantitative description of degradation would allow for accurate forecasting of the value of the battery system. This would then facilitate the formation of strategies for optimal usage of the system.

Lithium-ion pouch cells

A common format of a lithium-ion battery is the pouch cell format, displayed in Figure 1. The interior of the cell consists of two electrically conducting porous electrodes separated by an electrically insulating porous separator. Each electrode consists of *active material* particles, presented as circles in Figure 1, and a *binder* material, which is not shown in Figure 1. Within the pores of the *electrode* and *separators*, an liquid *electrolyte* is present. The two electrodes are sandwiched between two electrically conducting *current collectors* which have tabs at the top to allow for an easy connection to an external circuit.

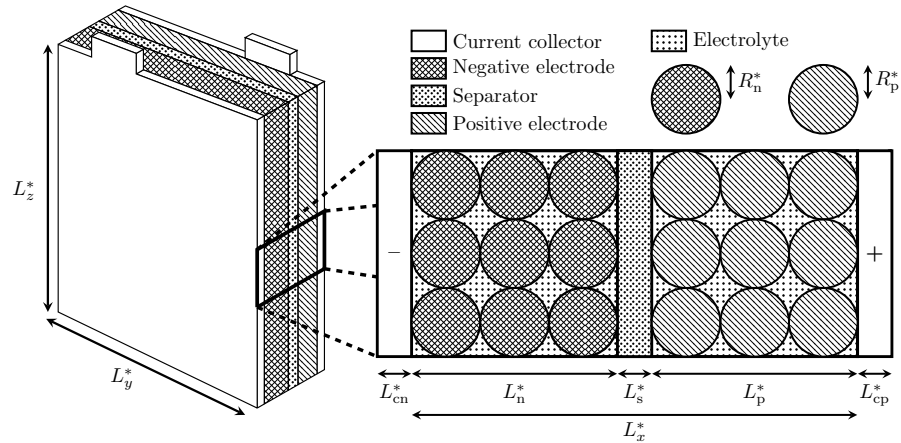


Figure 1 – Schematic of a lithium-ion pouch cell.

When a lithium-ion cell is discharged by connecting the two tabs to an external circuit, lithium *intercalated* in the active material of the negative electrode travels to the surface of the active material where an electrochemical reaction occurs. This reaction converts intercalated lithium into lithium ions contained in the electrolyte and electrons contained in the negative electrode. The lithium-ions then travel through the electrolyte to the surface of the positive active material particles where they recombine with an electron to form lithium intercalated in the positive active material. During charge, the process occurs in reverse, driven by an applied voltage.

Solid–Electrolyte Interphase (SEI) Growth

SEI growth is one of the dominate degradation mechanisms occurring within lithium-ion batteries. The SEI is a layer that forms on the surface of the negative active material particles as a result of the occurrence of parasitic side reactions. In Figure 5, we present a schematic of the structure of the SEI and the side reaction which creates new SEI. The SEI consists of two layers, a dense inner layer and a porous outer layer. In the creation of SEI, electrons within the negative electrode travel through the dense inner layer whilst lithium

ions and *solvent* molecules from the electrolyte travel through the pores of the outer SEI. These three species then combine through an electrochemical reaction at the surface of the inner and outer SEI to form fresh SEI. Since the growth of SEI consumes lithium ions, cyclable lithium is lost from the battery which results in capacity fade. In the presence of SEI, lithium ions can still intercalate into the negative active material. However, since they now have to travel through the inner SEI, there is an increased resistance to this process. This results in increased internal resistances within the cell which make the cell less efficient.

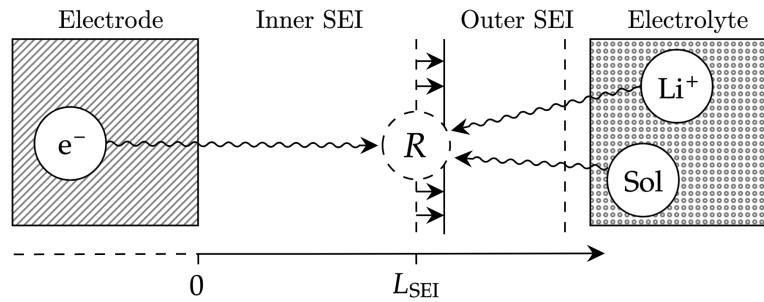


Figure 2 – Schematic of the SEI. The site of the SEI growth reaction is indicated by R , and the species involved in this reaction are indicated. Here, Sol refers to solvent molecules.

Glossary of terms

- **Degradation:** The deterioration of the cell usually in the form of capacity fade or reduced efficiency caused by rising internal resistances.
- **Active material:** The material in the electrode within which lithium can be intercalated is known as the active material.
- **Binder material:** The binder is a porous polymer matrix that “binds” the active material together and conducts electrons. This ensures electrical contact between the active material and current collector is maintained.
- **Current collector:** A sheet of aluminium or copper foil that provides a pathway from the tabs and external circuit to the electrodes.
- **Electrode:** An electrically conducting material consisting of active material and binder.
- **Electrolyte:** An ionically conducting material consisting of positively and negatively charged ionic species within a neutral solvent.
- **Intercalation:** The process in which an atom is inserted into a layered material such as graphite.
- **Asymptotic Methods:** A set of mathematical methods for describing the behaviour of a system in a particular limit (e.g. as a parameter tends to zero). These methods can be used to gain good approximate solutions when certain parameters are either large or small.
- **State of Charge (SoC):** How charged the cell is. If SoC is 1 then cell is fully charged. If SoC is 0 then cell is fully discharged.

Project aims

The degradation of lithium-ion batteries is highly complex with many little understood mechanisms occurring simultaneously. To fully understand the effects of these mechanisms, they must be incorporated into a model of a full lithium-ion pouch cell. Since degradation occurs over many cycles and over very long time periods, it is essential

to first develop mathematical models of pouch cells which can simulate long-term effects in an efficient manner. Once this framework is in place, in-depth analysis of the individual degradation mechanisms should be performed and the resulting models incorporated into the efficient full cell models. Here, we shall focus on one of key degradation mechanisms, the growth of the SEI. Therefore, the two key aims of this project are

- Develop efficient mathematical models of a full lithium-ion pouch cell
- Develop a mathematical model of SEI growth

2 Efficient models of a Lithium-ion pouch cell

Mathematical modelling

We develop a full three-dimensional mathematical model of a lithium-ion pouch cell as follows. To model the flow of electrons in the current collectors and electrodes, we enforce conservation of charge and employ Ohm's law. In the active material particles, we consider conservation of mass and assume lithium is transported down gradients in lithium. In the electrolyte, we enforce conservation of mass for both the positive and negative ionic species. The electrochemical reactions are modelled using the phenomenological Butler–Volmer relations. Finally, we account for thermal effects by employing an energy conservation equation and accounting for Ohmic and reaction heat sources.

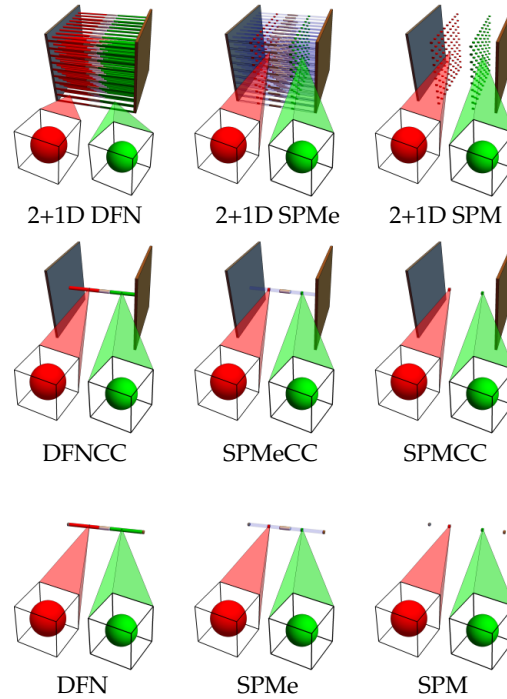


Figure 3 – Pictorial representation of derived suite of reduced-order models of a lithium-ion pouch cell.

This model is very detailed and too computationally expensive for the study of long-term degradation. We therefore adopt *asymptotic methods* to systematically simplify this model. There are two key parameters that we take advantage of to simplify the model. The first is the *aspect ratio* of the cell, that is the cell is much taller and wider than it is thick (in the through-cell direction). The second parameter is the ratio of the typical timescale for diffusion in the electrolyte to the typical discharge time. Typically the discharge timescale is around an hour whereas the electrolyte diffusion timescale is only around a minute. By considering different combinations of asymptotic limits of these two parameter, we develop the suite of reduced-order models of a lithium-ion pouch cell presented in Figure 3.

Figure 3 can be understood as follows. In the top left, we present the most complex reduced model that is derived from an asymptotic limit in the aspect ratio. Instead of a full three-dimensional cell model, this model consists of two-dimensional models for the current collectors coupled to a detailed one-dimensional through-cell model at every point. By proceeding downward in Figure 3, we take further advantage of the aspect ratio. In the bottom left, the current collectors behave uniformly and the model is reduced to a single one-dimensional through-cell model. In the middle row on the left, an “in-between” model is developed which accounts for some of the higher dimensional effects but maintains much of the simplicity of the one-dimensional model. Proceeding from left to right, simplifications are made by taking advantage of the ratio of the electrolyte diffusion and discharge timescales. In the top right, all the active material particles behave in the same way and so only one representative particle must be solved for in each electrode. At the top of the middle column, and ‘in-between’ model is developed that accounts for some of the more complex effects in the through-cell direction but maintains much of the computational simplicity of the model in the top right. The other models are then different combinations of these two sets of simplifications.

Results

We first compared the predictions of key output variables that our asymptotically reduced models make with those of ad-hoc reduced models of similar complexity from literature. The results for the SPMe model (middle column, bottom row of Figure 3) are presented in Figure 4. We found that our models outperform those in the literature in terms of accuracy and are equivalent in terms of computational time across all operating currents. Following these results, we identified the terms in the ad-hoc models that gave rise to greater errors.

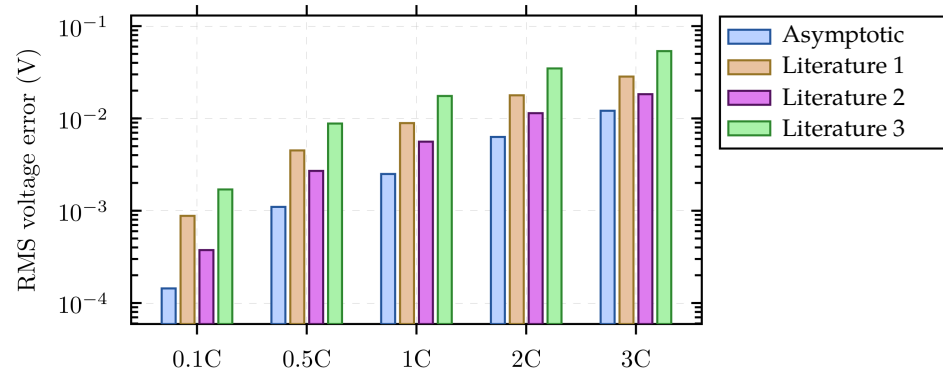


Figure 4 – Voltage errors of asymptotic SPMe and similar models from the literature at different currents. Here, C is this C-rate which is the current that fully discharges the battery in one hour.

We also conducted a full numerical comparison of each of the models in Figure 3 and condensed these results into a single table. A simplified version of this table is presented in Table 1. This table presents the solve speed, memory requirements, and the accuracy of its prediction of key internal cell variables such as the electric potentials, lithium concentrations, cell temperature, and cell voltage. This table allows one to select a model of appropriate fidelity for a particular application. In particular, we identify the SPMeCC as a fast model, with low memory requirements, and a moderate performance at recovering the key cell variables required as inputs in studies of degradation. Therefore, the SPMeCC is a good model to adopt for studying degradation of lithium-ion batteries.

Comments

- Developed a detailed model of a lithium-ion pouch cell
- Employed asymptotic methods to derive a suite of reduced order models from this detailed model

Model	Solve time	Memory	$I = 1\text{ C}$			Voltage		
			Potential	Concentration	Temperature	$I < 1\text{ C}$	$1\text{ C} < I < 4\text{ C}$	$I > 4\text{ C}$
2+1D DFN	●	●	●	●	●	●	●	●
2+1D SPM _e	●	●	●	●	●	●	●	●
2+1D SPM	●	●	●	●	●	●	●	●
DFNCC	●	●	●	●	●	●	●	●
SPMeCC	●	●	●	●	●	●	●	●
SPMCC	●	●	●	●	●	●	●	●
DFN	●	●	●	●	●	●	●	●
SPMe	●	●	●	●	●	●	●	●
SPM	●	●	●	●	●	●	●	●

Table 1 – Simplified table comparing the models in Figure 3. Green is used to indicate faster/low memory/more accurate models and red to indicate slower/high memory/less accurate models. Orange indicates moderately performing models.

- Provided a full numerical comparison and recommendation of appropriate fidelity model for studying degradation.

3 Mathematical Modelling of the SEI

Mathematical Analysis

Within the inner SEI we considered the transport of species: lithium-ions and electrons. For each species, we enforced conservation of mass and took each species to be driven down gradients in concentration and also to be driven by gradients in the electric potentials because the species are both electrically charged. We then employed the phenomenological Butler–Volmer relations to model the reactions occurring on the interface between the active material and inner SEI as well as the reactions occurring on the interface between the inner SEI and outer SEI.

This model is too detailed to be incorporated into a model of a full lithium-ion cell and also contains a large number of unknown parameters. To simplify this model, we again employed asymptotic methods. In this case, we considered a limit in which the timescale for diffusion of electrons through the SEI was long relative to the timescales of the reactions involving electrons. We also took the limit in which the timescale of lithium intercalation reaction at the active material–inner SEI interface was long compared to the timescale for diffusion of lithium-ions through the inner SEI and the timescale of the reaction at the inner SEI–outer SEI interface. We compared this simplified model with the full model and found excellent agreement between the two for appropriate parameter values.

Results

We took our simplified SEI model and compared it with experimental capacity fade data. In the experiment lithium-ion cells were stored at different *States-of-charge* (SoC) and temperatures. The capacity of the cells were then checked after 1.9 months, 3.8 months, 6.5 months, and 9.5 month. Firstly, at lower SoC, we expect that additional degradations cause capacity fade in the lithium-ion cell. However, for SoC greater than 0.2, we observe excellent agreement between our model and the experimental data. In particular, our model captures well the temperature, SoC, and temporal dependence of capacity fade.

After validating our SEI model against experimental data, we incorporated into the SPM, the simplest of the full cell models in Figure 3. We studied then used this model to study SEI growth under dynamic loads. From this study, we developed a map of ‘safe’ and ‘dangerous’ operating conditions for degradation. This map is presented in Figure 6. We observe that degradation occurs most at high SoCs and during charging of a cell and least at low SoCs and during a discharge.

Comments

- Developed detailed model of SEI and used asymptotic methods to simplify this model.

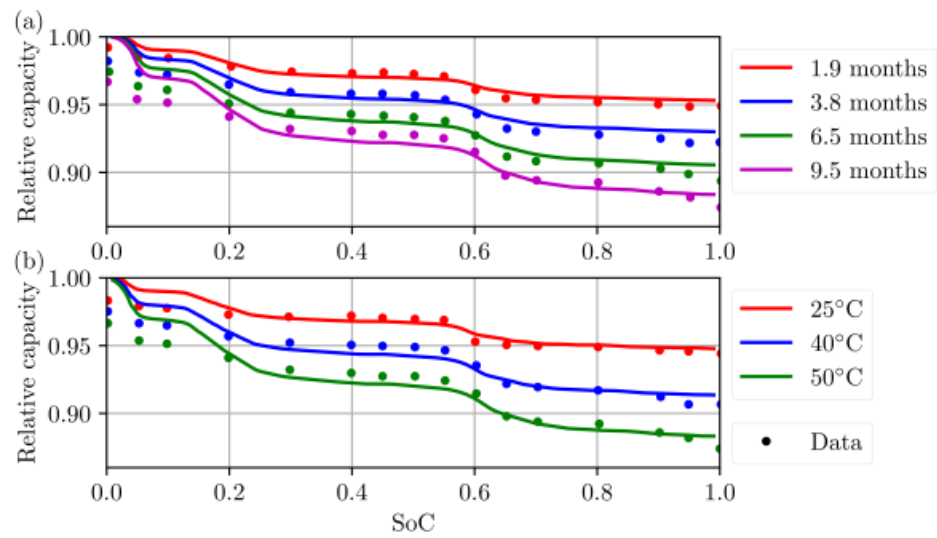


Figure 5 – Comparison of SEI model with experimental capacity fade data. Two parameters in our SEI model were treated as adjustable parameters: (a) time dependence at 50 °C; (b) temperature dependence after 9.5 months.

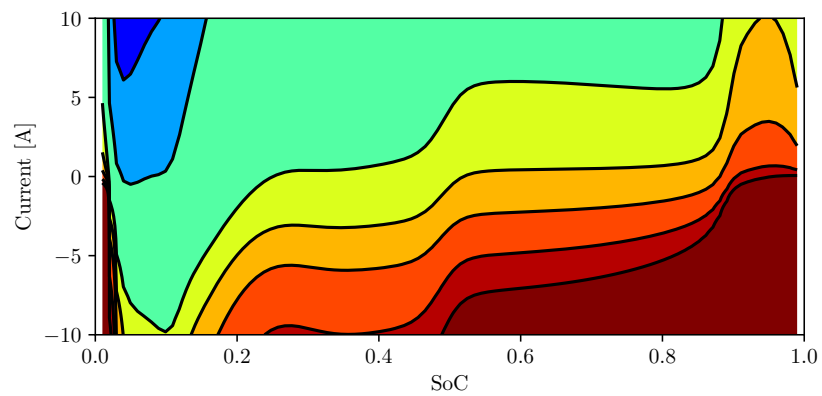


Figure 6 – Map of 'safe' and 'dangerous' operating conditions for degradation. Red indicates high degradation, and blue indicates low degradation. A positive current corresponds to discharging the cell.

- Found excellent agreement between SEI model and experimental capacity fade data.
- Incorporated SEI model into a model of a full lithium-ion cell and determined 'safe' and 'dangerous' operating conditions for degradation.



4 Discussion, conclusions & recommendations

We have tackled the problem of degradation in lithium-ion batteries by addressing two key challenges:

- Develop efficient mathematical models of full lithium-ion cells.
- Develop an accurate model of SEI growth.

For the first challenge, we developed a detailed mathematical model of a full lithium-ion pouch cell and then used asymptotic methods to develop a suite of simplified models. We found that our models outperformed those of similar complexity in the literature. We also performed a full numerical comparison of all of these models and found that the SPMcCC is a good choice of model for studying degradation.

For the second challenge, we developed a detailed model of SEI growth and then employed asymptotic methods to develop a simplified model that agreed well with the detailed model. We then compared this simple model with experimental capacity fade data and found excellent agreement. After validating this model, we then incorporated into a full model of a lithium-ion cell and developed a map of operating conditions and their relative rates of degradation. We found that the highest rates of degradation occur during charging and a low SoCs.

5 Potential Impact

All of the models developed during this project have been implemented within an open-source easy-to-use battery modelling package called PyBaMM (Python Battery Mathematical Modelling). Coupled with the model comparisons in Table 1, this provides an excellent resource for other battery researchers and Siemens to employ. Further, the models have all been implemented in a modular fashion so that additional degradation mechanisms can be easily incorporated into the framework removing duplicate work across institutions and accelerating battery modelling research in general. Siemens are planning to interface PyBaMM with internal software to take advantage of the modular framework and efficient mathematical models developed during this project.

[Insert name], [Job title + company] said: *"Sator Arepo tenet opera rotas. Sator Arepo tenet opera rotas. Sator Arepo tenet opera rotas. Sator Arepo tenet opera rotas. Sator Arepo tenet opera rotas."*