



SHC PROJECT SUMMARY REPORT

Modelling and experimental study of power-optimized lithium-ion batteries

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Summary

The energy storage is a major issue in the future development and adaptation of electric and hybrid electric vehicle technology. Vehicle manufacturers are faced with a large number of difficult questions when they are about to select battery technologies and implement them in the powertrain. These questions require knowledge that to a large extent is merely at an early stage of development. A key point is understanding the relationship between externally observable, macroscopic behaviour in terms of current, voltage and temperature, and design and materials properties on the lower levels.

In this project we have been developing and using mathematical modelling tools to study Li-ion batteries from a physical chemistry- and chemical engineering- perspective, in order to bring the knowledge and methods in this field forward, and to help answering real-world problems. The activities in the project have been addressing issues like energy efficiency, analysis of rate limitations, safety concerns and ageing, as well as characterization of new component materials. The activities have also included collaboration with a number of other PhD student within SHC and within or own research group. The main outcomes of the project are development of improved methods and concepts, and training of a highly qualified electrochemical engineer, in a strategically important area of science and technology.

The project started 2008 and ended 2013.

Background

In this project we have been developing and using modelling tools to study Li-ion batteries from a physical chemistry- and chemical engineering- perspective, thus creating a link between the different scales that are all important, ranging from the molecular level and all the way up to the macroscopic world that we see with our eyes. The motivation for such tools is that they are necessary for understanding the relationship between **externally observable, macroscopic behaviour** in terms of **current, voltage and temperature**, and **design and materials properties** on the lower levels. This is useful for example for:

- Performance prediction
- Evaluation of components, in development of materials, cells and battery modules
- Management of devices (cells and battery modules)
- Understanding of normal performance as well as ageing and safety issues

The interactions outlined above are quite complex. There is no easy way to quantitatively link the properties of one single component material to performance figures of an entire battery cell, let alone a battery module. The tools needed to do this are so called physico-chemically based mathematical models. The framework for models of this kind were developed for Li-ion batteries around 20 years ago and are based on the concepts of physical electrochemistry and chemical engineering, such as thermodynamics, kinetics and chemical reactor design. This framework is widely accepted in the scientific community, but lack of experimentally underpinned models and data for component materials and sub-processes has stopped it from being used as a really powerful tool in engineering and applied research.

In our resaearch group we have been working since the late 1990's with investigations of the most important subprocess in Li-ion batteries in order to fill this knowledge gap. At the time this project started we had experimentally verified sub-models and data that could be used to construct cell models and see to what extent they agreed with experimental observation, and to what extent they could be used to approach real-world problems. Fulfilling this potential formed the overall aim of this PhD project within SHC.

General project description

A new PhD student, Tommy Zavalis, was recruited for the project in January 2008. With the background outlined above in mind the project set out to create a cell model for a real power-optimized battery cell, and to compare the simulation results with experimental data. The activity was able to benefit from cooperation with a more senior PhD student, who was specializing in electrolyte mass transport characterization. The following work in the project consisted of application of this base model to a couple of applied problems:

1. Model simulations were used to analyze energy efficiency and voltage losses during HEV operation of this particular battery cell. An entirely new concept for such analysis and easy-to-understand presentation was developed.
2. The model was expanded to two dimension and non-isothermal conditions. An investigation of thermal and electrochemical behaviour during a couple of different short-circuit scenarios was carried out.
3. Tommy cooperated with two other PhD students in the group, who investigated ageing in Li-ion batteries for HEVs. He developed a model for the response in electrochemical impedance spectroscopy (EIS) measurements on individual electrodes that had been harvested from a battery cell and placed in a cell with a reference electrode. By studying the electrochemical behaviour of electrodes both at beginning of life and after ageing it was possible to identify the causes for performance degradation.
4. Cooperation with a fellow PhD student who was working with materials for structural batteries, i.e. batteries with mechanical-load-bearing capabilities. Tommy

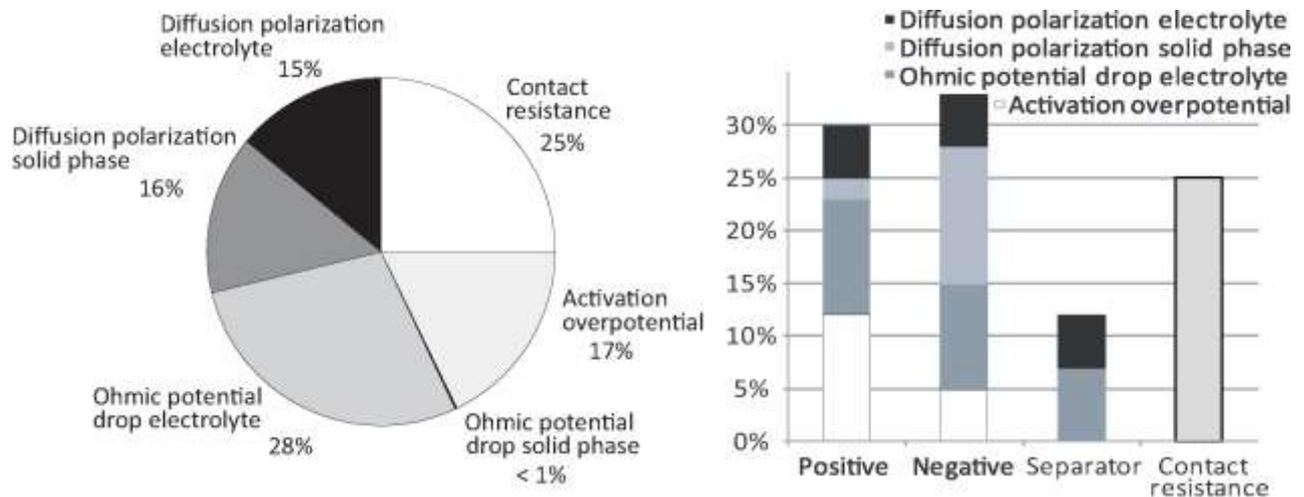
used the model for EIS, mentioned above, for investigation of the rate-limiting processes during intercalation of lithium in carbon fibers, which would be the negative material in such batteries.

5. A study of the properties of a flame retardant electrolyte additive was carried out in cooperation with the two PhD students at Uppsala University and Chalmers, who worked in the same thematic area of energy storage. Together they applied a fairly broad range of experimental characterization techniques and methods to investigate the effects of this additive.

Achieved results

All the activities mentioned above generated new and valuable results. In addition, the activities led to development of new and original methods of study. A brief account of the results of each of the activities is given below.

1. Model simulations of a power-optimized battery cell in load cycles that represent typical usage in HEVs were able to reproduce experimental data in terms of voltage-time profiles to a very high degree, without resorting to parameter fitting without physical justification. The results were therefore deemed to also give a good approximation of the internal variables that are not externally measurable, such as spatial distribution of reaction rates, concentrations of chemical species and electric potential. This data was then used to investigate the location and nature of the energy losses inside the cell during, for example, a load cycle lasting 120 seconds and spanning a 5 % swing in state of charge. A typical outcome is shown in the two figures below, but the results will vary depending on the load profile and the state of charge of the cell. Mass transport in the electrolyte was shown to be a crucial feature to improve, especially if the battery is expected to undergo high-current loads for long periods of time. This approach was entirely new, and it is gradually being adopted by the scientific community.



2. Safety concerns when a battery is short-circuited were investigated for three types of short-circuit scenarios, namely an external short, a nail penetrating through the cell and an internal short in the electrolyte separator. All scenarios raised the temperature at the hottest point within the cell to where exothermic side reactions are expected to initiate (around 120°C) in around 10 seconds. The heat-generating current was in all cases mainly limited by the rate of electrolyte mass transport. The differences, however small, were related to the placement of the short circuit. Especially when the current collectors were not directly connected (the third scenario), an increased

electronic resistance was observed which lowered both the generated current and heat.

3. The aging of a battery cell was investigated by model analysis of electrodes harvested for fresh and aged cells. A methodology was developed where a frequency-dependent model was fitted to measurement data by tuning parameters associated to electrode degradation. By studying how different parameters had changed compared to the fresh cell it was possible to identify the reason for the performance degradation. For the particular case of these cells and these conditions it was found that for cycled cells, electrolyte decomposition products inhibiting the mass transport and particle cracking in the positive electrode increased the impedance.
4. A similar model was set up for investigation of the lithium intercalation processes in a single PAN-based carbon fibers. Somewhat surprisingly it was found that these fibers have in themselves very good electrochemical performance. Thus it was concluded that the energy losses and rate limitations that had been seen in earlier measurement on entire bundles of fibers could be attributed to transport of lithium ions in the electrolyte penetrating the bundle rather than the electrochemical performance of the individual fibers. This understanding is very valuable for the continued development of structural batteries, that are potentially interesting for application in vehicle technology.
5. A study of the impact of the flame retardant additive triphenyl phosphate (TPP) on the performance of graphite/LiFePO₄ cells was carried out in cooperation with two other PhD students within SHC. The study was concluded after Tommy finished his thesis, and therefore his responsibilities were partly taken over by another student in our group, who also works within SHC. Overall, it was found that TPP is not a suitable flame retardant for high-power battery cells since it leads to lower energy efficiency and power capability. By combining the different experimental techniques and approaches of the three research groups we were able to elucidate the causes for this poor performance.

Contribution to hybrid vehicle technology

The method development in the project is one of the most important contributions to hybrid vehicle technology. This outcome should be helpful for design and analysis of energy storage, from component up to system level. This can spread in the scientific community, and we believe that a lot of it can mature into engineering tools and concepts that finds use also outside academia. The method development that was realized in the activities has also been very beneficial for the work of in our research group, where several of the younger PhD students can build on these achievements. A concrete example is the SHC project T3:5 "Thermal aspects of lithium-ion batteries in vehicle applications" with PhD student Henrik Lundgren where the ongoing work on combined thermal-electrochemical modelling of battery modules in cooperation with Scania builds directly on this project, in particular activities 1 and 2.

Training of qualified people is an equally important contribution; in the case of this project it's a graduated PhD, who is now working for a Swedish simulation software company (Comsol AB), as an applications specialist for modelling of electrochemical systems such as batteries and fuel cells.

Apart from method development, the direct scientific results are taken up by the research community and to some extent by R&D in the vehicle industry.

Tommy Zavalis has presented his work through talks at international conferences such as The International Society of Electrochemistry annual meeting in Prague 2012 and on a national level at The Swedish Energy Agency's Energirelaterad fordonsforskning in Örebro 2011, and at workshops organized by SHC.

Uniqueness and news value

It is our opinion that all the activities gave quite unique and new contributions in terms of methodology and results. This is of course hard to measure in an objective manner. Bibliometric data in terms of citations by other gives a metric on the impact the work in the scientific community. Only the first paper has been out long enough to see a trend, and in that particular case it is looking quite good, as can be seen by for example using the Google Scholar service.

Timing and finance

The project started in January 2008 and ended when Tommy Zavalis defended his PhD thesis in June 2013. Tommy has worked around 90% of full time within the project.

The total project budget was SEK 4.5 million, all of which was funded by SHC.

Executors and collaboration

The project has mainly been carried out by PhD student Tommy Zavalis. He presented and defended his PhD thesis, entitled Mathematical Models for Investigation of Performance, Safety and Aging in Lithium-ion Batteries, in June 2013. Tommy Zavalis now works for Comsol AB in Stockholm.

Göran Lindbergh and Mårten Behm were advisors in the PhD project.

As outlined above the Tommy has collaborated with a number of people both within our research group and within the SHC thematic area Energy Storage. More specifically, in sub-project 1 – Andreas Nyman (KTH), sub-project 3 – Maria Hellqvist Kjell and Matilda Klett (KTH), sub-project 4 – Maria Hellqvist Kjell, and finally in sub-project 5 – Susanne Wilken (Chalmers), Katarzyna Ciosek Högström (Uppsala University) and Henrik Lundgren (KTH).

Papers and publications

1. Analysis of the Polarization in a Li-ion Battery Cell by Numerical Simulations, Andreas Nyman, Tommy Zavalis, Ragna Elger, Mårten Behm, Göran Lindbergh, *Journal of The Electrochemical Society*, **157** (2010) A1236-A1246.
2. Investigation of Short-Circuit Scenarios in a Lithium-Ion Battery Cell, Tommy Zavalis, Mårten Behm, Göran Lindbergh, *Journal of The Electrochemical Society*, **159** (2012) A848-A859.
3. Aging in Lithium-Ion Batteries: Model and Experimental Investigation of Harvested LiFePO₄ and Mesoporous Carbon Microbead Electrodes, Tommy Georgios Zavalis, Matilda Klett, Maria H. Kjell, Mårten Behm, Rakel Wreland Lindström, Göran Lindbergh, *Electrochimica Acta*, **10** (2013) 335-348.
4. haracterization of lithium-ion intercalation processes of PAN-based carbon fibers in a microelectrode system, Tommy Georgios Zavalis, Maria H. Kjell, Mårten Behm, Göran Lindbergh, *Journal of The Electrochemical Society*, **160** (2013) A1473-A1481.
5. Impact of the flame retardant additive triphenyl phosphate (TPP) on the performance of graphite/LiFePO₄ cells in high power applications, Katarzyna Ciosek Högström, Henrik Lundgren, Susanne Wilken, Tommy Zavalis, Mårten Behm, Kristina Edström, Per Jacobsson, Patrik Johansson, Göran Lindbergh, *Journal of Power Sources*, **256** (2014) 430-439.