Thermal Aspects and Electrolyte Mass Transport of Li-ion Batteries

T3:5 Thermal Aspects of Lithium-Ion Batteries in Vehicle Applications

Henrik Lundgren
Mårten Behm
Göran Lindbergh
Applied Electrochemistry, Department of Chemical Engineering and Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology

Swedish Hybrid Vehicle Centre
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Summary

Lithium-ion batteries are a key technology for the electrification of vehicles. The performance, safety, and ageing of lithium-ion batteries are highly affected by temperature. In high-power applications, such as hybrid electric vehicles, the electrolyte, a component of a battery, has been found to limit the performance. This project is performed at KTH, started in April 2010 and finished in June 2015 and has been studying temperature and electrolyte related aspects in lithium-ion batteries. More specifically, one part of the project has been studying the mass-transport phenomena of present and future lithium-ion battery electrolytes and how they depend on temperature. Another sub-project evaluated a flame-retardant electrolyte additive in high-power applications, for which it was found to be unsuitable. Lastly, one sub-project has together with Scania been studying a large-format commercial battery cell with a thermal management system in plug-in hybrid electric vehicle applications using both experiments and modelling. Different thermal management strategies were evaluated with the model but were found to only have a minor impact on the temperature of the active components within the battery. The last project contributed greatly to hybrid vehicle technology development as it answered real questions that development engineers had, such as “How hot will the battery get?” and “Would it be better if we cooled this surface instead of that?”. In total, three papers have been published in international journals, with two more on the way. Collaborations within the project include KTH, Uppsala University, Chalmers, and Scania.

Background

Lithium-ion batteries are an integral technology to the electrification of vehicles, as it is the means by which electrical energy is stored. Temperature is one of the most important parameters for the performance, safety, and aging of lithium-ion batteries and has been linked to all main barriers for widespread commercial success of electric vehicles. Furthermore, the electrolyte has been found to limit the high-power performance, highlighting its relative importance in lithium-ion batteries.

General project description

The aim of this project has been to increase the understanding and highlight the importance of the electrolyte and of temperature effects in lithium-ion batteries. Furthermore the importance of accurate materials characterizations in general, and of electrolyte mass transport characterizations specifically, is highlighted. The thesis will give a few examples of characterizations of electrolyte systems with very different mass transport properties, and show how the different electrolytes influence the performance of a commercial large-format battery in a plug-in hybrid electric vehicle application. Additionally, a way of benchmarking electrolytes including all limitations in mass transport is explored and illustrated for several different systems.

Engineering tools in terms of determination of mass transport properties, very valuable for electrochemical models, have been determined for two systems: $LiPF_6$ in EC:DEC and superconcentrated solutions of LiTFSI in acetonitrile. Additionally, the temperature dependency of the mass transport properties of $LiPF_6$ in EC:DEC has been explored. The method used for both studies combines mathematical modelling with three different experiments to obtain the mass transport properties. In addition to the mass transport properties, physical properties such as density and viscosity are also determined.

In a collaboration with Uppsala University and Chalmers University of Technology the flame retardant TPP was evaluated for hybrid electric vehicle applications using several experimental techniques, combining our respective strengths.

Another engineering tool aimed at providing a benchmarking parameter with more information than what is currently used (ionic conductivity), termed electrolyte mass transport resistivity (EMTR) is explored and illustrated for several systems, to show the potential benefits it provides.

A large-format commercial battery intended for use in a heavy-duty hybrid vehicle by Scania CV has been studied using both experiments and modelling. The setup includes a thermal management system, as the cell was connected to a heat sink, and was studied using a very demanding plug-in hybrid electric vehicle load cycle.

Achieved results

The mass transport properties of both $LiPF_6$ in EC:DEC and LiTFSI in Acetonitrile successfully determined and were found to be strong functions of concentration. Furthermore, the behaviour of the two electrolytes were found to be very different. Most notably, the lithium-ion transport number (i.e. the amount of charge being transferred by the lithium ion) is very high for the superconcentrated electrolyte and increasing with concentration, with the opposite being true for other liquid lithium-ion battery electrolytes. The mass transport properties of LiPF6 in EC:DEC were found to vary strongly with temperature. At 10 °C, the electrolyte is close to crystallization, especially at very high and very low concentration, which causes a sharp drop in performance.

The flame retardant electrolyte additive TPP was studied using several experimental techniques. Weighing in both the effects on the electrolyte flammability and electrochemical performance, it is found to be unsuitable for high-power applications, such as hybrid electric vehicles.

The benchmarking method EMTR has been successfully illustrated for several types of electrolytes, including organic liquids, ionic liquids, superconcentrated electrolytes, solid polymers, gelled polymers and organic-liquid based electrolytes containing additives. The different systems are found to have very different behaviour and the additional information provided by the method proved to be very valuable compared to only using ionic conductivity

A large-format commercial battery connected to a thermal management system was successfully characterized using both experiments and modelling. The model is found to fit the experiments well. Large temperature gradients are found to be developed during the plug-in hybrid electric vehicle load cycle used, which will lead to uneven ageing. Different thermal management systems are evaluated using the model but are found to have minor effects on the temperature of the jellyroll (i.e. the active materials where the electrochemical reactions take place).

Contribution to hybrid vehicle technology

The mass transport characterizations contribute to hybrid vehicle technology by providing input to models, which can be used to optimize a certain battery cell, module or pack thermal or electrochemical design.

The evaluation of the additive provided very direct suggestions to the battery manufacturers of hybrid vehicle batteries, as it was found that it was not suitable for the demanding load cycles used in hybrid and plug-in hybrid electric vehicles.

The collaboration project with Scania and their large-format battery contributed to hybrid vehicle technology in a more direct way, as it answered engineering questions relevant to their product design, e.g. how do we cool our battery most efficiently? How hot will the battery get and how large temperature gradients will develop given a specific usage scenario? Would it improve the thermal management systems performance if we changed the surface that is being cooled? This project is an important step to the successful integration of lithium-ion batteries in hybrid vehicles, one of the key targets defined in the SHC programme, and has been a forum for knowledge transfer and collaboration between the academy (KTH) and the industry (Scania).

Uniqueness and news value

The characterizations of $LiPF_6$ in EC:DEC and LiTFSI in acetonitrile are very unique, as characterizations of that sort are very rare. The former was one of the first studies to look at the temperature dependency of the mass transport properties, and the latter the first full characterization of a superconcentrated electrolyte.

The characterization of the flame-retardant additive TPP was the first study to look at flame-redardant additives in the context of high-power applications, such as hybrid electric vehicles, and brought several interesting new insights.

The benchmarking studies presented a new methodology, able to quickly determine the capabilities of any kind of electrolyte, relevant beyond the field lithium-ion batteries, as it is applicable to any electrochemical system.

Timing and finance

- April 2010 – Start of PhD studies
- January 2014 – First published paper in *J. Power Sources*
- January 2015 – Second paper published in *J. Electrochemical Society*
- April 2015 – Third paper published in *J. Electrochemical Society*

- April 2015 – Fourth paper submitted to *J. Electrochemical Society*
- May 2015 – Fifth paper submitted to *Electrochimica Acta*
- June 11th 2015 – Dissertation

The total project budget is SEK 5.2 million, 4.5 of which is funded by SHC.

Executors and collaboration

The flame-retardant additive study was a collaboration between Applied Electrochemistry at KTH (Henrik Lundgren, Tommy Zavalis, Mårten Behm, Göran Lindbergh), Condensed matter physics at Chalmers (Susanne Wilken, Patrik Johansson, Per Jacobsson), and Department of Chemistry – Ångström at Uppsala University (Katarzyna Ciosek Högström, Kristina Edström). In total 4 PhD students funded by SHC worked on the project, plus their respective supervisors.

For the full characterizations of $LiPF_6$ in EC:DEC and LiTFSI the majority of the work was done at Applied Electrochemistry at KTH, with help from Condensed Matter Physics at Chalmers with density and viscosity measurements (Susanne Wilken and Johan Scheers).

The study of the commercial battery was a collaboration between Applied Electrochemistry at KTH and Scania CV. The modelling part was done at KTH (Henrik Lundgren, Henrik Ekström, Mårten Behm, Göran Lindbergh) and the experiments at Scania (Pontus Svens, Carl Tengstedt, Johan Lindström).

The benchmarking study was solely made at Applied Electrochemistry at KTH (Henrik Lundgren, Mårten Behm, Göran Lindbergh).

Dissemination of Results

Swedish conferences:

"Implementation of a flame retardant in a Hybrid Electric Vehicle battery", Chalmers Energy Conference, 2013, Poster

"Electrochemical Characterization of Lithium-Ion Battery Electrolytes", NordBatt, November 2014, Poster

Poster at KTH Energy dialogue 2012 and 2014, Presentation at the KTH Chemistry summer party 2014, presentation of research to new chemistry students autumn 2013, Poster at KTH Chemistry school day 2011.

International conferences:

"Battery research activities in Sweden – from materials to vehicles", *Advanced Automotive Battery Conference*, Pasadena, USA, Spring 2011, Poster and Conference paper

"Temperature dependency of transport properties of $LiPF_6$ in EC:DEC", 220th *Meeting of the Electrochemical Society*, Boston, USA, Autumn 2011, Oral presentation

"Temperature dependency of transport properties of $LiPF_6$ in EC:DEC", *Advanced Automotive Battery Conference*, Orlando, USA, Spring 2012, Poster and Conference paper

"Benchmarking of Li-TFSI doped ionic liquids using normalised potential gradient", Ionic Liquids for Electrochemical Devices, Rome, Italy, Summer 2012, Poster

"Benchmarking of lithium-ion battery electrolytes using normalised potential gradient", Internatioal Meeting on Lithium Batteries, Jeju, South Korea, Summer 2012, Poster

“Electrochemical Characterization of Lithium-Ion Battery Electrolytes”, Gordon Research Seminar & Gordon Research Conference, Ventura, USA, Spring 2014, Poster

“Thermal Modeling of a Large-Format Battery During PHEV Cycling”, Lithium Battery Power & Battery Safety, Washington DC, USA, Autumn 2014

SHC seminars:

“Mass Transport Characterisation of Lithium-Ion Battery Electrolytes”, *SHC day 2012*, Poster

“Towards safer electrolytes - Advanced flame retardant additives”, *SHC Cross-thematic meeting*, Katrineholm, 2013, Oral presentation

“Temperature Dependency of Electrolyte Mass-Transport Properties for Lithium-ion Batteries”, *SHC Day 2014*, Poster

“Thermal Modeling of Large-Format Prismatic Lithium-Ion Battery in PHEV Application”, *SHC Cross-thematic meeting*, Hallsberg, 2015, Oral presentation

Unpublished manuscripts:

Henrik Lundgren, Mårten Behm and Göran Lindbergh, “Electrolyte Mass-Transport Benchmarking of Four Types of Lithium-Ion Battery Electrolytes: Organic liquids, Ionic Liquids, Gelled Polymers, and Solid Polymers”, *Submitted to Electrochimica Acta*

~~Henrik Lundgren, Pontus Svens, Henrik Ekström, Carl Tengstedt, Johan Lindström, Mårten Behm and Göran Lindbergh, “Thermal Management of Large-Format Prismatic Lithium-Ion Battery in PHEV Application”, *Submitted to the Journal of the Electrochemical Society*~~

Papers and publications

K.C. Högström, H. Lundgren, S. Wilken, T.G. Zavalis, M. Behm, K. Edström, P. Jacobsson, P. Johansson and G. Lindbergh., “Impact of the flame retardant additive triphenyl phosphate (TPP) on the performance of graphite/$LiFePO_4$ cells in high power applications”, *Journal of Power Sources* 256, 430-439 (**2014**)

H. Lundgren, M. Behm and G. Lindbergh., “Electrochemical Characterization and Temperature Dependency of Mass-Transport Properties of $LiPF_6$ in EC:DEC”, *Journal of the Electrochemical Society* 162 (3), A413-A420 (**2015**)

H. Lundgren, J. Scheers, M. Behm and G. Lindbergh., “Characterization of the Mass-Transport Phenomena in a Superconcentrated LiTFSI:Acetonitrile Electrolyte”, *Journal of the Electrochemical Society* 162 (7), A1334-A1340 (**2015**)

Henrik Lundgren, Pontus Svens, Henrik Ekström, Carl Tengstedt, Johan Lindström, Mårten Behm and Göran Lindbergh, “Thermal Management of Large-Format Prismatic Lithium-Ion Battery in PHEV Application”, *Journal of the Electrochemical Society* 163 (2), A309-A317 (**2016**)

H. Lundgren, “Thermal Aspects and Electrolyte Mass Transport in Lithium-ion Batteries”, Doctoral thesis (**2015**)

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Swedish Electric & Hybrid Vehicle Centre
Chalmers University of Technology
Hörsalsvägen 11, level 5
SE-412 96 Göteborg

Phone: +46 (0) 31 772 10 00
www.hybridfordonscentrum.se