SHC PROJECT SUMMARY REPORT

Designed, controlled and safer lithium-ion cells – Electrode materials

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Summary

The stability of electrode/electrolyte interfaces in Li-ion batteries is crucial to the performance, lifetime and safety of the entire battery system. It is hence important to control these interfaces for batteries to be used in vehicles. In this work, interface processes have been studied in $LiFePO_4$/graphite Li-ion battery cells that also have been tested by other partners within SHC.

The first part has focused on improving photoelectron spectroscopy (PES) methodology for making post mortem battery analyses. A combination of synchrotron and in-house PES has facilitated non-destructive interface depth profiling from the outermost surfaces into the electrode bulk. A better understanding of the chemistry taking place at the anode and cathode interfaces has been achieved and been used for the study of commercial cells cycled for three years. This work has been collaboration between AB Volvo, Scania, Chalmers, KTH and UU.

Two electrolyte additives have also been studied: a film-forming additive propargyl methanesulfonate (PMS) in collaboration with Chalmers and a flame-retardant triphenyl phosphate (TPP) in collaboration with Chalmers and KTH. A detailed study was made at ambient and elevated temperature (21 and 60 °C) of interface aging for anodes and cathodes cycled with and without the PMS additive. The commonly used TPP flame-retardant was shown to be unsuitable for high-power applications. Low TPP concentrations had only a minor impact on electrolyte flammability, while larger amounts led to a significant increase in cell polarization. All these results were obtained in K. Ciosek's PhD work defended in spring 2014.

Background

Understanding the processes taking place at the interface between the electrode and the electrolyte is of vital importance for the development of safer and more reliable Li-ion batteries. The interface processes have a huge impact on the cyclability, rate capability and thermal stability of the whole Li-ion battery. In fact, these processes are one of the major sources of Li-ion battery aging. To understand and control interfaces is hence a foundation for batteries to be used in vehicles.

Interface processes are not completely understood. Partially, it is due to the complexity of the multi component film formed at the electrode/electrolyte interfaces in the

battery. The thin film formed (in the order of 20 nm) has to be measured and analysed with caution, partly due to a limited amount of techniques that can be used for studying these films and partly due to the chemical sensitivity of the films.

The aim of the research has been two-fold: fundamental research in order to understand, develop and improve a technology for more detailed and consistent studies of the processes taking place at interfaces and applied research where potentially useful materials were studied in Li-ion batteries with this improved technology. A more extended goal of this work was to improve the understanding of aging processes at interfaces in Li-ion batteries as a function of cycling and to study the influence of electrolyte additives. Electrolyte additives are one of the most efficient ways to improve battery performance. They are utilized in commercial Li-ion batteries however their impact on the Li-ion battery is, not always completely clear.

General project description

This work is focused on how the interface processes involving the electrodes and the electrolyte in $LiFePO_4$/graphite full cells develop during Li-ion battery cycling under different conditions. The electrode materials were selected as baseline chemistry within the Swedish Hybrid Vehicle Centre. The important motivation for the chosen electrode materials is that they are non-toxic, have good safety characteristics and are composed of abundant/inexpensive elements, making them a good choice for automotive applications.

The first part of this project was dedicated to the development and improvement of a photoelectron spectroscopy (PES) method for studying electrode/electrolyte interfaces. Since these are very sensitive chemical systems, extra attention was given towards understanding the parameters influencing post-mortem analysis of Li-ion battery interfaces and improving the measurement procedure.

A powerful technique for non-destructive depth profiling was used in order to study electrode/electrolyte interfaces in $LiFePO_4$/graphite full cells. A combination of synchrotron and in-house photoelectron spectroscopy has enabled unique depth profiling from the outermost surfaces into the electrode bulk. This technique was also used to study long-term cycled and stored commercial batteries based on the same chemistry in collaboration within SHC

In the next part of this work the propargyl methanesulfonate (PMS) film-forming additive and triphenyl phosphate (TPP) flame retardant were studied.

Achieved results

The first part was focused on detailed and consistent studies of the processes taking place at interfaces. Combining synchrotron and in-house photoelectron spectroscopy enabled performing a unique non-destructive depth profiling through the electrode/electrolyte interfaces into the bulk materials. It gave better understanding of the complex composition of the interface layer as a means to better understand the cell system [1,2] and how a short exposure of water affected the interface and thus the function of the battery in a negative way [3].A study was carried out comparing the chemistries when cycling at elevated temperature [4]. As a comparison also commercial cells that have been cycled either with a hybrid vehicle test cycle or with constant current for three years were compared with a battery that had been stored the same length of time. A clear picture of inhomogeneities due to cell design and electrolyte drying emerged. The interface results in this study were part of a larger broader study in collaboration with AB Volvo, Scania, Chalmers and KTH [5].

The second part of the project was focused on studying electrolyte additives to improve the understanding of aging processes in Li-ion batteries as a function of cycling. The PMS film-forming additive was shown to improve capacity retention at ambient and

elevated temperature. The higher stability of the interface formed with PMS is probably a main reason for the better capacity retention of the battery due to a lower loss of cycleable lithium [5,6]. A part of this work [5] was carried out in collaboration with Chalmers.

The commonly used flame retardant triphenyl phosphate (TPP) was studied in the context of high power demanding applications. Low impact on electrolyte flammability for low concentrations and significant losses in energy efficiency for high concentrations, led to conclusion that TPP is not a suitable additive for high power applications [7]. This was collaboration between the three PhD students from Chalmers, KTH and UU within theme 3.

Although the additives studied here may not be the final solution for improved lifetime and safety of commercial batteries, increased understanding has been achieved of the degradation mechanisms in Li-ion cells. A better understanding of interface processes is of vital importance for the future development of safer and more reliable Li-ion batteries.

All the results have been summarised in the thesis of Katarzyna Ciosek and defended in March 2014 [8].

Contribution to hybrid vehicle technology

Knowledge about parameters that influence aging and lifetime of a lithium-ion battery is important for the automotive industry. The battery is an expensive component and there are many different cell chemistries to select among. A knowledge within the industry to ask the right questions to battery manufacturers and even influence the manufacturers in certain directions (better power optimization, better additives for enhanced safety etc.) is important. Hopefully this project has added to this knowledge.

Uniqueness and news value

A new technique for non-destructive depth profiling, was achieved by combining synchrotron and in-house photoelectron spectroscopy. It enabled performing a unique depth characterization through the electrode/electrolyte interfaces into the bulk material, which give a better understanding of the chemistry taking place at the anode and cathode interfaces.

Better knowledge about aging of commercial batteries has been obtained.

A very detailed interface aging study at ambient and elevated temperature (21 and 60 °C) for anodes and cathodes cycled with and without the PMS additive showed how the surface layer changes during cycling.

The flame retardant triphenyl phosphate (TPP) study in the context of high power demanding applications showed that an additive which performs well at low cycling rates may be not suitable for high power applications.

Timing and finance

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Describe when the various activities have been be undertaken, important milestones etc.

The total project budget is SEK 6 million, 3.6 million SEK of which is funded by SHC for the period 2010-2014.

Executors and collaboration

Katarzyna Ciosek Högström – planning, experimental work, data analysis, writing and finalizing the manuscripts.

Sara Malmgren –collaboration on method development and depth profile study-

Maria Hahlin - collaboration on method development and depth profile study-

Håkan Rensmo -supervision

Kristina Edström –supervision

Henrik Eriksson – engineering

In SHC: Patrik Johansson, Per Jacobsson and Susanne Wilken Chalmers (PMS additive, TPP project) and Tommy Zavalis, Henrik Lundgren, Mårten Behm and Göran Lindbergh, KTH (TPP project).

Collaboration in the sister project "Lithium cluster" with Jens Groth AB Volvo, Helena Berg Libergreen, Rakel Wreland, Matilda Klett, Mårten Behm and Göran Lindbergh KTH, Pontus Svens Scania.

Collaboraiton in a FFI sister project: Maria Kjell, Mårten Behm, Göran Lindbergh KTH.

Papers and publications

1) K. Ciosek, S. Killiches, T. Zavalis, M. Behm, P. Johansson, K. Edström, P. Jacobsson, G. Lindbergh

Energy storage activities in the Swedish Hybrid Vehicle Centre

World Electric Vehicle Journal 3 (2009) 1-5

2) S. Malmgren, K. Ciosek, M. Hahlin, T. Gustafsson, M. Gorgoi, H. Rensmo, K. Edström

Comparing anode and cathode electrode/electrolyte interface composition and morphology using soft and hard X-ray photoelectron Spectroscopy

Electrochimica Acta 97(2013) 23–32

3) K. Ciosek Högström, S. Malmgren, M. Hahlin, M. Gorgoi, L. Nyholm, H. Rensmo, K. Edström

The buried carbon/solid electrolyte interphase in Li-ion batteries studied by hard X-ray photoelectron spectroscopy.

Under revision in Electrochimica Acta

4) S. Malmgren, K. Ciosek, R. Lindblad, S. Plogmaker, J. Kühn, H. Rensmo, K. Edström, M. Hahlin

Consequences of air exposure on the lithiated graphite SEI

Electrochimica Acta 105 (2013) 83–91.

5) M. H. Kjell, S. Malmgren, K. Ciosek, M. Behm, K. Edström, G. Lindbergh

Comparing aging of MCMB graphite/LiFePO4 cells at 22 °C and 55 °C. Electrochemical and photoelectron spectroscopy studies

Journal of Power Sources 243 (2013) 290-298

6) M. Klett, R. Eriksson, J. Groot, P. Svens, K. Ciosek Högström, R. Wreland Lindström, Helena Berg, T. Gustafson, G. Lindbergh, K. Edström

Non-uniform aging of cycled commercial $LiFePO_4$//graphite cylindrical cells revealed by post mortem analysis

Journal of Power Sources 257 (2014) 126-137

7) K. Ciosek Högström, S. Malmgren, M. Hahlin, H. Rensmo, F. Thébault, P. Johansson, K. Edström

The influence of PMS-additive on the electrode/electrolyte interfaces in LiFePO4/graphite Li-ion batteries,

Journal of Physical Chemistry C 117 (2013) 23476–23486

8) K. Ciosek Högström, H. Lundgren, S. Wilken, T. Zavalis, M. Behm, K. Edström, P. Jacobsson, P. Johansson, G. Lindbergh

Impact of the flame retardant additive triphenyl phosphate (TPP) on the performance of graphite/LiFePO4 cells in high power applications

Journal of Power Sources 256 (2014) 430-439

9) K. Ciosek Högström, M. Hahlin, S. Malmgren, M. Gorgoi, H. Rensmo, K. Edström

Aging of electrode/electrolyte interfaces in LiFePO4/graphite cells cycled with and without PMS additive

Accepted by Journal of Physical Chemistry C

10) K. Ciosek Högström, "The Complex Nature of the Electrode/Electrolyte Interfaces in Li-ion Batteries: Towards Understanding the Role of Electrolytes and Additives Using Photoelectron Spectroscopy".

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