SHC PROJECT SUMMARY REPORT

T3:1 Battery properties: designed, controlled and safer lithium ion cells - Electrolyte additives

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Summary

Despite the LIB commercial success, their electrolytes suffer from poor chemical and thermal stability, why elevated temperatures cause a decrease in battery performance. These phenomena are thus crucial to understand for a better use of the battery in HEV application.

The aim of this project was both detailed studies of degradation and verifications of mitigation strategies. Various routes to electrolyte decomposition, incl. novel NMR and combined ab initio/TGA-FTIR strategies, have been explored; elevated temperatures, impurities, and electrochemical redox stability at the electrolyte/electrode interfaces were suggested as main parameters affecting electrolyte functionality. Mitigation strategies included the application of additives or a change in chemistry toward intrinsically more stable components. For each component careful optimization and trade-offs with performance decline were evaluated.

The project (4.5 MSEK) was performed at Chalmers as a PhD project for Dr. Susanne Wilken 2008-04-01 – 2014-12-31 (3 maternity leaves) and collaborators were AB Volvo, Uppsala University, and KTH.

Background

Although lithium-ion batteries (LIBs) are primarily used in small scale applications today, the expansion into large-scale stationary and electric (hybrid) vehicle applications is well underway. The implementation of LIBs into these new fields is however not as fast and efficient as we would like due to concerns/issues of safety, cycle life, capacity, operational temperature range, materials availability, and cost.

The focus of this project was motivated by the consequences of, in the simplest case, connecting a few hundred LIBs from portable electronics in series to give the required higher voltage and energy for e.g. vehicle applications. In that case, failures, possibly tolerable at the small scale level, become unacceptable simply due to the amount of material involved, and technical obstacles may also render a battery exchange impractical.

The aim was not to point out the unsuitability of the current LIB technology, but to stress the need for a deeper understanding of the known short-comings of the state-of-the-art and to contribute to the efforts scrutinizing the underlying physico-chemical reactions in detail.

General project description

LIB safety is largely related to the electrolyte and its interactions with other battery components. Therefore, the scope of this project was to examine various failure mechanisms of standard LIB electrolytes, especially at elevated temperatures where the decrease in battery performance and release of toxic gases are attributed to electrolyte decomposition and increased film formation on both electrodes.

Initially a book-chapter review of the current knowledge on possible additives and decomposition processes and products of standard LIB electrolytes was performed.

Hereafter, a few detection methods were selected, and more elaborately developed when needed, for a detailed study of electrolyte decomposition and identification of the resulting products. Special emphasis was given to the experimental setup and conditions, and the impact of standard quantum mechanical computations for the interpretation of experimental data.

Various mitigation strategies to counteract the identified failure mechanisms have been investigated including the use of tailored additives or changes of chemistry – with due respect paid to the balance of safety vs. energy and power capabilities of the resulting cells.

Achieved results

Both the studies of the fundamental degradation mechanisms of LIB battery electrolytes and the more applied mitigation strategy studies and examinations of commercial cells have either already been published in peer-reviewed journals of high scientific repute and the most appropriate to the field (see Papers and publications) or exists as manuscripts. Several invited oral presentations at international conferences like SSI, ECS, IMLB *etc.* have been made on the basis of the results.

Results in brief:

- A partially new mechanism of electrolyte degradation has been suggested based on time-resolved NMR-data – opening new possibilities for mitigation

- The role of salt concentration in the electrolyte was studied and higher concentrations than standard found beneficial for safety
- Various ionic liquids used as additives probed and differentiated in terms of safety enhancing capability and performance sustainment.
- A new computational-experimental joint method to study electrolyte degradation created gaseous products was developed.

Contribution to hybrid vehicle technology

All additional knowledge on how the battery (electrolyte) degrades and how to mitigate this are crucial in order to make the best balance between the usage of battery vs. ICE – very crucial for an HEV – vs the durability/life-length of the battery. This is true not the least via understanding properly the impact of for example temperature (externally) and additives (internally) as controllable or not factors. Accelerated degradation has been applied.

Uniqueness and news value

There is no other group in Sweden than the Chalmers group focussing on battery electrolytes for modern batteries. Here the safety properties of LIB electrolytes and how to mitigate them were in focus, but also development of new formulations.

The project also has been instrumental in exploring and developing new techniques to enable further analysis of electrolyte properties under degrading conditions – incl. how to accelerate degradation.

On a European scale we have, partly by the contribution of the SHC project, moved to the very front of battery research groups – seen not the least by involvement in no less than 8 H2020 applications during 2014 – whereof 2+ successful.

Timing and finance

The project was performed 2008-04-01 – 2014-12-31.

The total cash project budget was SEK 4.5 million, 100% of which was funded by SHC.

In addition there was an in kind contribution from Chalmers for co-workers, project leading, and supervision – which adds *ca.* SEK 1.8 million.

Executors and collaboration

The project was in its entirety performed at Chalmers as a single PhD project for Susanne Wilken 2008-04-01 – 2014-12-31 (this time includes 3 maternity leaves) and involved also extensive collaboration within SHC Theme 3 with AB Volvo, Uppsala University, and KTH – especially the projects T3:2 and T3:3.

Susanne and the project have also benefitted from collaboration and hence resulting co-publications with several other researchers (paid from other resources like VR, STINT, ALISTORE) at Applied Physics, Chalmers; Dr. Marcel Treskow, Dr. Johan Scheers, Dr. Erlendur Jònsson, MSc. Shizhao Xiong,

Papers and publications

Note: Only papers/publications published in or submitted to peer-reviewed journals directly resulting from the project are included in this list:

I. Infrared spectroscopy of instantaneous decomposition products of $LiPF_6$-based lithium battery electrolytes
Susanne Wilken, Patrik Johansson and Per Jacobsson
Solid State Ionics 225 (2012) 608–610

II. Initial stages of thermal decomposition of $LiPF_6$-based lithium ion battery electrolytes by detailed Raman and NMR spectroscopy
Susanne Wilken, Marcel Treskow, Johan Scheers, Patrik Johansson and Per Jacobsson
RSC Advances 3 (2013) 16359-16364

III. Additives in organic electrolytes for lithium batteries
Susanne Wilken, Patrik Johansson, Per Jacobsson,
in: Bruno Scrosati, K. M. Abraham, Walter Van Schalkwijk and Jusef Hassoun (Eds.)
Lithium Batteries: Advanced Technologies and Applications, John Wiley & Sons (2013) 39-70

IV. Energy Storage Activities in the Swedish Hybrid Vehicle Centre
Katarzyna Ciosek, Susanne Killiches, Tommy G. Zavalis, Mårten Behm, Patrik Johansson, Kristina Edström, Per Jacobsson and Göran Lindbergh
World Electric Vehicle Journal 3 (2009) 2850-2854

V. Impact of the flame retardant additive triphenyl phosphate (TPP) on the performance of graphite/$LiFePO_4$ cells in high power applications
Katarzyna Ciosek Högström, Henrik Lundgren, Susanne Wilken, Tommy G. Zavalis, Mårten Behm, Kristina Edström, Per Jacobsson, Patrik Johansson and Göran Lindbergh
Journal of Power Sources 256 (2014) 430-439

VI. Ionic liquids in lithium battery electrolytes: composition versus safety and physical properties
Susanne Wilken, Shizhao Xiong, Johan Scheers, Per Jacobsson and Patrik Johansson
Journal of Power Sources, in Press, doi:10.1016/j.jpowsour.2014.11.071

VII. Thermal decomposition of ionic liquid based lithium-ion battery electrolytes – a combined *ab initio* and experimental study
Erlendur Jónsson, Susanne Wilken and Patrik Johansson
Submitted

VIII. Raman spectroscopy on aged electrolytes from commercial graphite/$LiFePO_4$ cylindrical cells
Susanne Wilken, Jens Groot and Patrik Johansson
Submitted