The Influence of Fast Charging on Li-ion Battery Ageing

T3:9c Ageing and Li-ion battery cell testing – in relation to materials properties

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Summary

The project has addressed the challenges related to fast charging of Li-ion batteries for vehicles and how fast charging will influence battery ageing via analysis of materials changes at the very detailed level. New knowledge has come about from attacking the jointly formulated research questions academia and industry within SHC on how fast charging of batteries influence battery cell behaviour and on the novel cell chemistries foreseen as the nearest future batteries. In this subproject at Chalmers the focus was the proper development of advanced tests of systems during operation, *in situ*, that ultimately can lead to better tools for monitoring commercial batteries, but also lay the foundation for the batteries of the future. A commercial test cell has been implemented for our *in situ* set-up, using charge and discharge rates relevant for industry and using materials from a partner university (UU). Hereby we can now monitor changes in the anode material as a function of charging conditions in a time-resolved manner. In house developed cells for special studies have also been developed within the project. The project was performed mainly by the especially recruited experimental postdoc Dr. Anke Dierckx, running 100% for a full year, and assisted by studies by Dr. Erlendur Jónsson to a minor extent. Total project cost 2014-04-01--2015-06-30 was 1.250.000 SEK.

Background

Fast charging of Li-ion batteries for EV or PHEV will require battery chemistries that allow fast transport of lithium-ions in the anode, cathode and electrolyte materials. Fast charging of power optimized batteries for heavy vehicles is not the same as fast charging of energy optimized batteries for EVs. Despite this and the knowledge of a "path dependence", of the reactions of a battery connecting with how it is used (voltage cut-offs, temperature, etc.), the effort will be general as there are a number of questions we still need to address to understand how long-term use of fast charging will influence battery ageing.

The bottleneck for fast charging of a battery cell is the negative electrode due to plating of lithium on the electrode surface. This plating stops all further reactions in the battery. The limitation for how fast the battery can be cycled without any plating to take place is still unclear. It is known that current density, cut-off voltage, and temperature are influencing the process. Therefore not only the negative electrode is important, but also the lithium transport in the electrolyte. We have therefore defined the following specific goals.

Specific goals to evaluate:

- How will fast charging at a vehicle level influence the battery cell ageing and in what way?
- What are the most suitable materials for handling fast charging and how will new and existing materials (especially materials for the negative electrode) be influenced by long-term use of fast charging?
- Can fast charging and its influence on battery ageing be modeled and predicted?

Since there is still little known on how fast charging influences the ageing at battery pack and cell level this project will lead to new insights that will be important the limitations for fast charging. The consortium of complementary competences is unique, also at an international level, will competences ranging from field tests of batteries in vehicles, to modelling of ageing mechanisms to an atomic level understanding of how the processes can lead to battery failure but also to new materials with better properties.

General project description

The overall fast charging/ageing project was divided into several sub-projects which together will lead to better fast charging protocols and understanding of ageing mechanisms related to the fast charging. The subprojects all had the same considerations such as time, cost of materials, cell design, temperature, selection of test protocols, etc., as the foundation for the work.

The six sub-projects identified, where for all it is important keep the demands imposed by the intended application in mind we focused on energy optimized cells (power optimized systems are studied in the lithium cluster supported by STEM), but with fast charging as the main parameter.

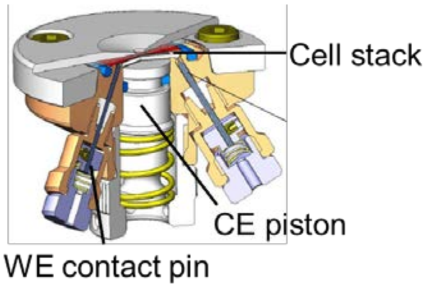
Our sub-project targeted how a battery cell works during fast charging at a molecular level by *in situ* spectro-electrochemistry. The important challenges from the short-list mainly targeted are the electrolyte decomposition, directly measureable in situ by e.g. Raman spectroscopy, and the negative electrode material staging and possible decomposition – the latter easily measureable if the reaction products dissolve into the electrolyte or attach at the surface..

Achieved results

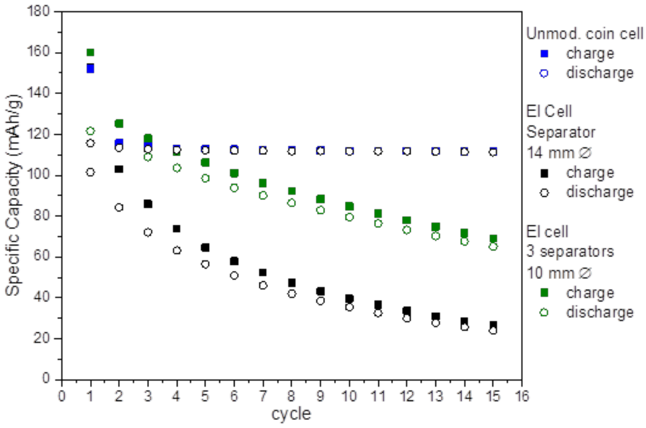
A common our set-up has been created to study fast charging at a molecular level by in situ spectro-electrochemistry targeting i) electrolyte/electrode changes and decomposition and later on also ii) concentration gradients in the electrolyte. For this we use confocal Raman spectroscopy and materials as listed:

- $LiFePO_4$/graphite (within 10% balance) (made at UU)
- 1 M $LiPF_6$ in EC:DMC (1:1 v/v) in 2% wt. VC
- Separator: Polyethylene (approximately 20 µm thick), glass fiber separator (for modified coin cells)

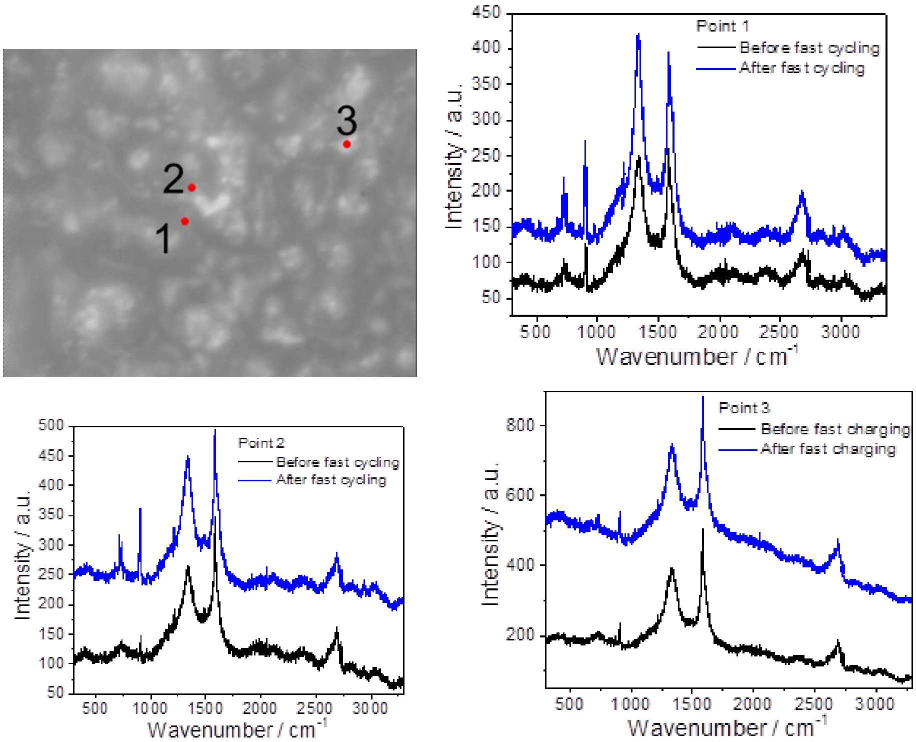
The modified coin cells (above) have been our own development for cheap and multiple analysis – but still has the problem of many failing cells – electrochemically.



As a second line of development we bought a commercial cell (above) to enable faster comparative studies – but this allows a reduced number of cells/conditions to be run.

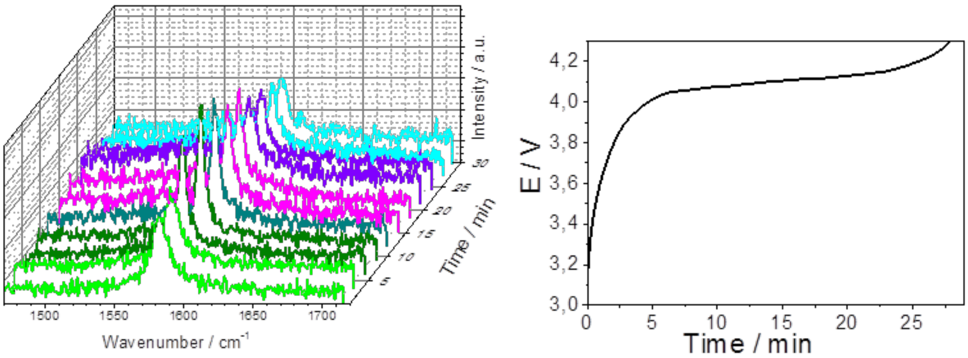


Some typical cycling performance is shown above. Interestingly our own set-up with modified coin cells performs better. However, for the acquisition of spectra the latter gives much better data and reproducibility (below shown for 3 unique grains of the negative electrode).



The typical spectra above focused on the first task: Can we see any unique degradation products on the surface when we are using a 4C-rate? Given that Raman *can* detect species at the ppm-level – the absence of any new features is indicative (and promising).

We have now a large collection of spectra by which we can see also the graphite D/G bands as references for further studies – here an example shown as a function of the voltage during charging at 2C (below).



Contribution to hybrid vehicle technology

The development of proper analysis tools examining the consequences of fast charging is a rather unique task/accomplishment. Very few academic groups have this competence we now have acquired. For the electric and hybrid vehicle technology and industry the new detailed knowledge can, after extension, hopefully be implemented into charging patterns etc. to save life-length for the energy storage.

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Uniqueness and news value

As stated above analysis tools for examining the consequences of fast charging are rather uncommon. Very few academic groups have this competence and when we move to improved and novel materials these tools become even more valuable. The news value of the results themselves is yet to be properly analysed.

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Timing and finance

The project has been performed in stages of agreeing on the exact chemistries and conditions, the design of several cells and purchasing a commercial more standard cell, and finally extensive measurement tasks in order to map the instrumental possibilities and the phenomena combined. The major accomplishments are the final set-up that enables us to record the staging of the graphite properly and to do the analysis for separate anode grains of active material. The latter can be made into a more statistical approach in the future. The total project budget was SEK 1.25 million, 1.25 (100%) of which funded by SHC.

Executors and collaboration

The project was performed mainly by the especially recruited experimental postdoc Dr. Anke Dierckx, running 100% for a full year, and assisted by studies by Dr. Erlendur Jónsson to a minor extent. The project used materials from UU extensively.

Dissemination of Results

The project was reported as part of the final of phase II of SHC in June 2015 at Lindholmen Science Park. Anke is currently hired in a close-by project and will therefore be able to finalize and summarize the main results of the project into an academic publication.

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