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Energy Storage Activities in the Swedish Hybrid Vehicle Centre

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Abstract

Significant efforts are put worldwide on developing new concepts for vehicle propulsion with the hybrid electric vehicle (HEV) being a prominent example. Hybrid technology is clearly a strategic future activity for automotive industries and in response to the rapid development in the area; the Swedish Hybrid Vehicle Centre (SHC) was formed in 2007 to join forces between Swedish industry and academia in the field. The centre emphasizes a holistic view to meet the environmental and societal needs with new technological solutions. The research within SHC is currently divided into three different themes whereof we here describe the Energy Storage theme with emphasis on the activities carried out at the involved universities in the current main project areas: Cell Properties, Electrode Materials and Electrolyte Additives. Examples are given on how these projects attacks the problems at hand separately, but also how we create synergy effects between the projects. As an example cell modelling is performed given a specific chemistry and cycling scheme, the same parameters are used for electrochemical experiments which provide macroscopic data that are connected with molecular level actions in the electrodes, the electrolyte, and the interfaces. All this is done using our base-line chemistry and a subsequent route is to investigate the role of different additives to overcome the limitations that are observed.

Keywords: HEV, energy storage, lithium battery, safety.

1 Introduction

As a result of societal needs, cost reduction for the end-user, and tighter regulations on emissions, the automotive industry has been challenged during the last few years to lower CO_2-emissions and to decrease the fuel consumption of their vehicles. Significant efforts are currently made to develop new concepts for vehicle propulsion with the hybrid electric vehicle (HEV) being a prominent example. In 2007 the Swedish Hybrid Vehicle Centre (SHC) was formed to join forces between Swedish industry and academia in this field, as a virtual distributed centre [1].

The research within SHC is currently divided into three different *themes* considered equally crucial for HEVs: System studies and tools, Electric machines and drives, and Energy storage.

1.1 Energy storage

Storage of electric energy is a central function in an HEV. Both the choice of energy storage and its management are crucial for the performance of the vehicle and the lifetime of the energy storage system. A specific goal of the Energy Storage

theme is to build knowledge to enable maximum use of the energy storage system in an HEV without violating safety or the specified lifetime. The main activities are focused on experimental studies of systems under well-controlled conditions in laboratory scale at the involved universities, but also include development of experimental techniques and mathematical models – to create a deeper understanding of cell components and their interplay. New and future concepts and materials will also be in focus, to serve as a knowledge bank for interpretation of results from lifetime studies of coming generations of commercial batteries.

1.2 Lithium-ion batteries

It is expected that Li-ion batteries gradually will take over in HEVs and therefore the centre completely focuses on this technology. A very important factor, for the up-scaling of this technology to make it to the market, is to show that it is safe and reliable in terms of given specifications. Hence, there is a need for both strategic choices on materials and also on the methods used to evaluate the performance. This fits well into a scientific approach on how we can analyse and evaluate different choices of materials for a better performance with maintained or enhanced stability. The Energy Storage theme is a network of three university groups – each with complementary excellences in the field of rechargeable batteries in general and Li-ion batteries and battery materials in particular. Each group hosts a sub-project, outlined in more detail below, and as a start the groups have chosen a base-line battery chemistry consisting of $LiFePO_4$ as the positive electrode material, a graphite negative electrode, and a 1M $LiPF_6$ EC/DEC 2:1 electrolyte.

2 Research projects

Below the three university projects within the Energy Storage theme are described and some preliminary results within each are outlined in more detail.

2.1 Cell Properties (KTH)

In order to be able to use and develop batteries for energy storage in HEVs profound knowledge is needed regarding how the chemical properties of component materials together with the cell design and modes determine the electrochemical behaviour of the battery cell. Mathematical models that incorporate these battery features will be powerful tools for predicting battery performance at different operating conditions. Thus, a crucial step in developing models will be experimental work involving validation and determination of electrolyte and electrode parameters.

As an illustrative example a battery cell model based on the experimental parameters of a different electrolyte (1.2 M $LiFP_6$ in EC:EMC 3:7) [2] and another positive electrode material ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) [3] has been constructed. The model was validated against an experimental cell with the same chemistry. Figure 1 shows the battery's electrochemical behaviour during a power-assisted galvanostatic hybrid cycle according to EUCAR.

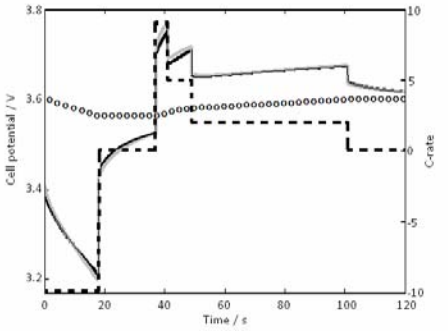

Figure1: Potential curves: ( ) simulated cell potential, (-) experimental cell potential and (o) simulated equilibrium cell potential. (- -) C-rate (EUCAR).

The deviation of the cell potential curves from the equilibrium cell potential curve is a result of a number of sources of polarisation in the battery. These are dependent on the chemistry of the components in the battery system. Here the validated model makes further investigation possible, and may be used to gain more understanding of the underlying processes.

The next goal is to construct a similar model with the base-line chemistry. It will be proceeded by the three SHC areas conducting extensive characterization of electrochemical and transport properties of the electrodes and the electrolyte in question. The final aim is to set up a mathematical tool which also incorporates the effects additives in the electrolyte have on the battery performance during hybrid operation.

2.2 Electrode Materials (UU)

The stability of the electrode materials in a battery context is one basic key for a long-life battery.

$LiFePO_4$ is today seen as one of the few cheap and environmentally benign materials for the positive electrode in an up-scaled lithium battery for HEV or Plug-in HEV. Despite many studies of the mechanism for lithium transport during charge and discharge in the material, important details still remain to understand. Some of the important questions are: How will the material respond during a longer driving-cycle in a vehicle? Is the bulk electrode material sensitive to long-term charge- and discharge of the battery or is it the electrode/electrolyte interface that is the bottle neck for a long life of the system? Is there an optimal combination of electrolyte composition and electrode materials for a safe battery?

The same questions are also relevant for the material on the negative side of the battery. Graphite is used today, but efforts are taken to move to metals that can host larger amounts of lithium and can give the battery and thus the vehicle a faster re-charging [4].

One important aspect of our research is to develop new experimental tools for accelerated testing of electrode materials. This must be done in a battery context as close to a commercial relevant situation as possible, but still be able to give the insights that only model studies allow. Therefore, the tools developed will be linked to how a commercial cell or a battery pack can be tested in a vehicle and how we can miniaturise this concept to a laboratory cell.

The standardised HEV driving cycles such as EUCAR, Freedom Car, IEC, etc., are not ideal for accelerated testing at the materials level. For materials harsher methods are urgently needed and therefore developed within this project. The developed scheme allows for studies of: cycle depth, ΔSOC, temperature, voltage range and cycling properties.

In Figure 2 one simple experimental result is shown; a cell consisting of the base-line chemistry has been discharged to 50% SOC and then micro-cycled with 20% of the capacity 200 times at 1C and then interrupted by some in-depth cycles at C/10. This procedure is then repeated.

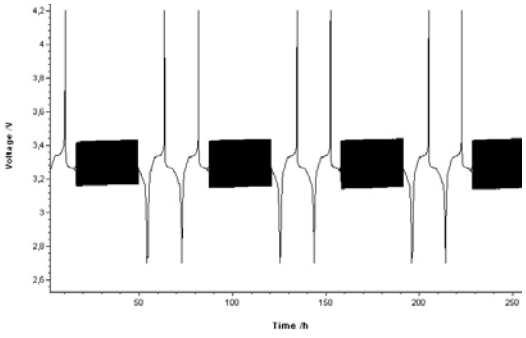

Figure2: A cell consisting of $LiFePO_4$ *vs.* graphite and 1M $LiPF_6$ in EC/DEC. The in-depth cycles are at C/10 and between them are 200 "micro-cycles", each consisting of 20% of the total capacity at a speed of 1C. This is done at room temperature.

The results show that the cell is stable during the conditions of the experiment. There is, however, a tendency for more of the cell-content to be used to keep the capacity to 20%. This is even more pronounced when the battery is scaled-up to a 1Ah cell. Figure 3 shows the micro-cycling to drift to more and more of the cell-content to be used to keep the required 20% of the capacity.

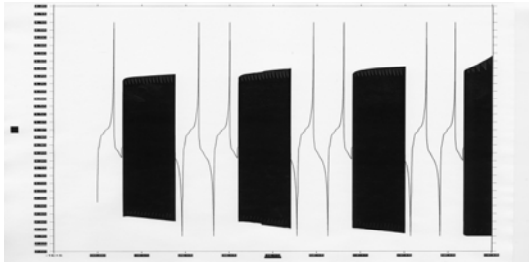

Figure3: A 1Ah cell with the same electrode and electrolytes, cycled under the same conditions as in Figure2.

Our base-line experiments are performed without any special additives in the electrolyte (see 2.3). It is expected that the chemical reactions at the electrode/electrolyte interfaces influence the cycling stability, safety and life-time [5-7] and that different additives stabilising the surface chemistry will improve the situation. Important experimental tools will, therefore, be to characterise the interfaces of cells that have been tested at different situations and with different additives.

2.3 Electrolyte additives

The demand for Li-ion batteries with high energy density has grown and simultaneously there is an urgent need for new advanced electrolytes that can withstand and sustain this useful electrochemistry

[8-9]. While a complete optimization relevant to the physical and electrochemical behaviour of the whole battery system is the long term goal, we here apply molecular level studies to reveal the actions of different electrolyte additives in a model system (based on the common base-line battery chemistry). The properties, and for these tailored additives in focus, are *e.g.* overcharge protection, reduction of flammability and improved low and high temperature reductive stability. Typically, adding as little as 5 wt% of an additive affect the overall battery performance drastically, not always beneficially depending on usage conditions, and thus the additives must be tested in different scenarios. In order to effectively use additives to suppress or enhance certain properties, a molecular level understanding of their functionality is needed.

Hence we study different additives in the base electrolyte system (1M LiPF6 EC/DEC 2:1) using calorimetric and spectroscopic methods such as TGA, DSC, Raman and IR spectroscopy. In addition, computational quantum chemistry methods are used to further explain the underlying reaction mechanisms and to assist in the interpretation of the vibrational spectra (IR and Raman).

Here we exemplify our approach with our current study of an additive used for flammability reduction [10]. Figure 4 shows the Raman spectrum at room temperature of the base electrolyte system + 5% triphenyl phosphate (TPPa).

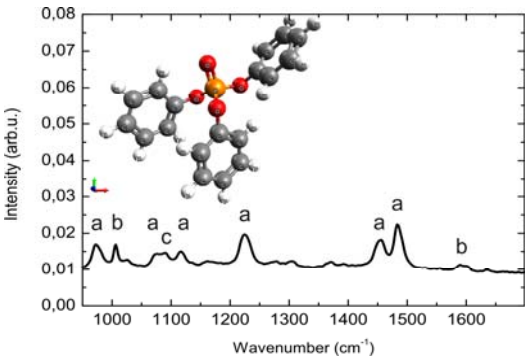

Figure4: A Raman spectrum of a 1M $LiPF_6$ EC:DEC + 5% TPPa battery electrolyte. Peaks denominated *a*, *b* and *c* are with assistance from computed spectra and the spectra of the pure components assigned to EC:DEC, TPPa and PF_6^-, respectively. The TPPa molecular model is resulting from a density functional theory (DFT) calculation (B3LYP/6-311+G*).

The effect of the additive and the molecular mode of operation can easily be monitored following the respective vibrational bands *e.g.* with temperature. These data are typically combined with computed enthalpies of reaction and measured calorimetric data to complete the picture of the overall role of such an additive within the base electrolyte.

In order to also study the role of the electrolyte additives with respect to the chemical reactions at the electrode/electrolyte interfaces we will combine our work with the modelling at KTH and electrode studies in Uppsala with an *in situ* spectro-electrochemical cell and with ex situ studies of battery cycled electrolytes.

3 Summary

The combined efforts made within the Energy Storage theme of SHC are indeed diverse, but still based on our lithium-ion battery base-line chemistry and with a common goal of safer batteries and more efficient usage. The latter also connects the Energy Storage theme with the SHC system aspects.

Acknowledgments

All work presented has been performed within the Energy Storage theme of the Swedish Hybrid Vehicle Centre (SHC).

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