Nordic Battery Conference 2017

1-3 November, 2017, Kokkola, Finland

Book of Abstracts

Nordic Battery Conference 2017

1-3 November, 2017, Kokkola, Finland

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Nordic Battery Conference 2017

1-3 November, 2017, Kokkola, Finland

We are excited to announce the third Nordic battery conference, which will be hosted by the University of Oulu 1-3 November 2017 (www.chydenius.fi/nordbatt2017). Conference venue is located in the city of Kokkola, which is known as the big cluster of inorganic chemistry in Northern Europe.

The conference presents an opportunity to review the recent advances in battery science, from materials development to cell electrochemistry, and battery utilization for a range of different applications. It will provide a local Nordic platform for leading scientists and industrial representatives to communicate novel ideas and new findings, to inspire scientific breakthroughs and technological solutions for energy storage applications. Conference is arranged as a part of Kokkola Material Week (www.materialweek.fi).

You are warmly welcome in Kokkola!

On behalf of the scientific and organizing committee,
Ulla Lassi, professor
Chair of scientific and organizing committee

Nordic Battery Conference 2017

1-3 November, 2017, Kokkola, Finland

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Nordic Battery Conference 2017

1-3 November, 2017, Kokkola, Finland

Program

1 November, Wednesday

Registration open 12-

14.00-14.30 Coffee

14.30-14.45 Conference opening: Professor Ulla Lassi and Stina Mattila, Mayor of Kokkola City

Chair: Dr. Justin Salminen, Boliden

14.45-15.30 Key Note lecture: Prof. Josh Thomas, Uppsala University, Sweden: From DFT to proof-of-concept Li- and Na-ion battery prototypes

15.30-15.55 Researcher Antti Porvali, Aalto University: Waste NiMH battery processing

15.55-16.20 Prof. Jorma Jokiniemi, University of Eastern Finland: Multi-Layer Graphene-Carbon Nanoflower Composite Synthetized by Aerosol Based Methods for Electrochemical Application

Break

Chair: Prof. Daniel Brandell, Uppsala University

16.45-17.10 Dr. Catherine Bounsaythip, EIT Raw Materials: How to bring your material innovation project to the future battery market

17.10-17.35 Dr. Mari Juel, Sintef, Norway: Cycling of zinc-air batteries in alkaline electrolyte

17.35-18.00 Dr. Pertti Kauranen, Aalto University: Raw Materials for Li-ion and Redox Flow Batteries

18.30- Conference get together--- sponsored by Keliber

2 November, Thursday

Registration open 8-

Chair: Prof. Ulla Lassi, University of Oulu

8.30-9.15 Key Note lecture Prof. Dr. Noshin Omar, Brussels: European Battery Material Needs for Automotive Applications

9.15-9.40 Dr. Mario Valvo, Uppsala university: Towards more environmentally friendly iron-based Li-ion batteries

9.40-10.05 Researcher Kristian Kvamme, University of Oslo: LIPO cathode barriers by ALD using phosphite precursors

Coffee break

Chair: Professor Ann Mari Svensson, NTNU

10.35-11.00 Dr. Samuli Räsänen, Freeport Cobalt: Mine to Batteries – The Importance of Cobalt Precipitation

11.00-11.25 Dr Jari Liimatainen, Picodeon Oy Ltd: Use of ultrashort pulsed laser deposition for engineering Li-ion battery materials solutions

11.25-11.50 Research scientist Samppa Jenu, VTT: Lithium-ion battery diagnostics: State of health estimation

Lunch

Chair: Dr. Jonathan Højberg, Danish Battery Society

13.00-13.25 Researcher Juho Välikangas, Kokkola University Consortium Chydenius: Electrochemical performance of Si/NCM cells

13.25-13.50 Dr. Justin Salminen, Boliden: Boliden Kokkola – Forerunner in responsible metals production

13.50-14.15 Ass. professor Juan Maria Garcia Lastra, Technical University of Denmark: Next-generation batteries: Helping to design new battery materials through new computational tools

Coffee break and posters

Chair: Prof. Vesa-Pekka Lehto, University of Eastern Finland

14.50-15.15 Ass. prof. Reza Younesi, Uppsala university: A Cheap and Sustainable Cathode Material for Sodium Ion Batteries

15.15-15.40 Senior research scientist Preben Vie, Institute for Energy Technology, Norway: Safety and ageing of a commercial Li-ion battery

15.40-16.05 Ass. prof. Tanja Kallio, Aalto university: Towards more stable $LiCoO_2$: over-lithiation and doping

16.05-16.30 Dr. Jonathan Højberg, Haldor Topsoe A/S, Denmark: Development of high voltage $Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$

16.30-18 Flash poster session

19.00- Conference dinner at Villa Elba sponsored by Freeport Cobalt

3 November, Friday

Chair: Ass. prof. Tanja Kallio, Aalto university

8.30-9.15 Key Note lecture Professor Kristina Edström, Uppsala university: The SEI revisited – What do we know about interfaces and interphases?

9.15-9.40 Ass. prof. Anders Bentien, Aarhus University, Denmark: Presentation on redox-flow batteries

9.40-10.05 Researcher Timo Ikonen, University of Eastern Finland: Applying porous silicon in Li-ion batteries

Coffee break

Chair: Professor Torbjörn Gustafsson, Uppsala university

10.35-11.00 R&D Manager Pekka Tanskanen, Keliber Oy: Extraction of lithium from hard rock ore – Case Study Keliber

11.00-11.25 COO Paolo Cerruti, NorthVolt

11.25-11.50 Prof. Daniel Brandell, University of Uppsala: How water-soluble binders control the surface chemistry in lithium-ion battery anodes

Conference end session, next Nordbatt conference in Denmark 2019 (Dr. Jonathan Højberg, Danish Battery Society)

Lunch

Nordic Battery Conference 2017

1-3 November, 2017, Kokkola, Finland

ABSTRACTS

FROM DFT TO PROOF-OF-CONCEPT Li- and Na-ION BATTERY PROTOTYPES

Josh Thomas[1,2]

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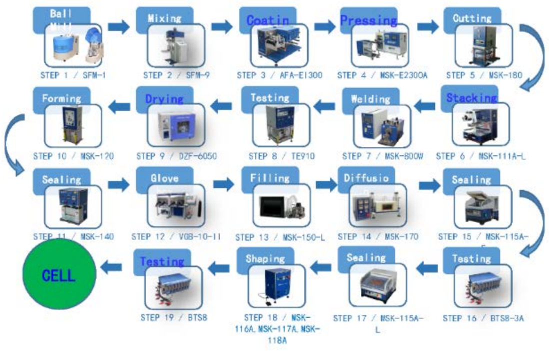
Introduction: Lithium-ion batteries (LIBs) have been on the commercial scene for quite some time now, making their first appearance in Japanese (Sony) mobile-phones in 1990 - more than a quarter of a century ago! Moreover, the basic technology has changed little during that time, and is today in a phase of consolidation. The slow but inevitable market penetration of intrinsically cheaper sodium-ion batteries (SIBs) is the only major innovation we see looming on the near horizon. This would suggest that the time is now ripe for LIB-/SIB-related basic research to move to addressing more closely the technological challenges associated with industrial production. Although this would not diminish the special attraction of battery research, it could mean nevertheless that a greater part of our research should address more applied battery materials issues, where the added challenges associated with *upscaling* become especially demanding. This will be the main focus of my talk – after opening with my personal view of LIB history, as reflected in some of the battery research carried out over the years at Uppsala University.

The need for a "proof-of-concept" battery pilot-line: The successful development of any new LIB or SIB concept will necessarily involve an upscaling phase, where we must proceed from the mg- or g-scale of laboratory research to the kg-scale of a production facility. This process can itself eliminate many innovational materials already at the synthesis stage - but, when "larger quantities" can be obtained, the road lies open for much exciting new research. Virtually every aspect of lab-scale cells must be readdressed from a production perspective: typically; materials supply, environmental footprint, safety, cost, processability, *etc.* We have therefore created in Uppsala a spin-off company (LiFeSiZE AB) to focus specifically on these production-related aspects. Our activities span rheological optimization of the coating-slurry, large-scale electrode coating (using a state-of-the-art 6m-long coater/dryer line), whole-cell battery-prototype fabrication and battery testing/evaluation; *see below*. Some guidelines will be provided to assist prospective users of our facility: generally speaking, 50-100g of electrode material can result in a "one shot" batch; while >1kg will allow slurry optimization and multiple battery batches for comparative analysis. This pilot facility has been financed totally by *The Swedish Energy Agency* (*Energimyndigheten).*



Waste NiMH Battery Processing

A. Porvali[1], B. P. Wilson[1] and M. Lundström[1*]

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Battery recycling is of increasing importance in our modern societies, which increasingly rely on mobile electricity being available on-demand. To that end, different kind of batteries with varying chemistries have been invented in the past 40 years. Nickel metal hydride batteries (NiMH) are a battery type used in various different applications [1]. Their use is not increasing at a rate akin to lithium ion batteries, but they still remain in use and circulation, especially in task-specific applications, e.g. Honda uses them in their hybrid electrical vehicles (HEV) [2]. This type of batteries contain extensive range of valuable metals in significant quantities. The concentration of metal values can be presented in a decreasing order: nickel >> REE > cobalt = zinc. REEs and cobalt have been classified as critical raw materials by EU [3], with REEs having been classified as having highest supply risk of all considered elements. Nickel from NiMH can be recycled in Finland, however as REE recovery is not practiced in Finland the development and understanding of REE recovery processes from waste materials is important.

Industrially crushed batteries were mechanically and chemically treated in order to investigate the dissolution of major elements in to the solution. Sulfuric acid solutions were used as it is known to be efficient in dissolution of pure active powders [4]. Base metals can be readily leached from the battery waste. The industrially crushed NiMH battery waste was shown to provide and inherent ability for REE precipitation. In general, *ca.* 20 – 30 wt.% leach residues remained after leaching. Rare earth precipitates were recovered by modifying the solution with, e.g., sodium hydroxide and high purity (>95%) mixed REE precipitate was achieved. In the future, advanced hydrometallurgical recovery methods will be applied in order to efficiently recover and separate remaining metal values in the solution.

There are several studies using pure reagents and restricted solution compositions, however, the experimental work on real industrial waste is necessary in order to further the knowledge of applicability of proposed laboratory processes in real industrial processes.

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Materials for the EU: Available at: http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=COM:2017:0490:FIN. Accessed 10/5, 2017.

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MULTI-LAYER GRAPHENE-CARBON NANOFLOWER COMPOSITE SYNTHETIZED BY AEROSOL BASED METHODS FOR ELECTROCHEMICAL APPLICATIONS

J. Jokiniemi[1], T. Karhunen[1], A. Meščeriakovas[1], U. Lassi[2], J. Välikangas[2], M. Miettinen[1], A. Lähde[1]
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Different carbon nanomaterials have been synthesized eagerly during the past years because they may result in more efficient materials for energy applications, such as supercapacitors or lithium-ion batteries. The aerosol based synthesis of a multi-layer graphene-carbon nanoflower composite (MLG/CNF) is previously reported (Miettinen et al., 2014). The starting material was synthetized from hexamethyldisilane (HMDS) by the atmospheric pressure chemical vapor synthesis (APCVS). The resulting Si-C material was then annealed at high temperature induction furnace to obtain multi-layer graphene-carbon nanoflower composite (Figure 1). Here the structure and electrochemical performance of the composite was studied.

The structure of the MLG/CNF composite was studied with an aberration corrected high-resolution transmission electron microscope (TEM, JEOL JEM-2200FS). The analyses were performed at electron acceleration voltage of 80 kV. Selected area diffraction analysis (SAED) was performed from the MLG sheets. For the electrochemical testing as prepared powder was sieved (> 45 μm) to remove residual SiC crystals and electrodes were prepared using conventional method. Electrochemical performance of the MGL/CNF composite was tested in Li-ion button cells against graphite reference.

SAED analysis showed that graphene layers were rotated to each other. The most common rotation angle in the MLG sheets was 30 ± 2°, but also other rotation angles were detected (Miettinen et al., 2015). Due to rotational faults the interlayer distance in the sheets was increased ~12 % compared with graphite. The CNFs contained nanosize cavities. The wrinkled network of the MLG sheets and the CNFs may increase, e.g., lithium-ion insertion capacity of the composite. The electrochemical performance of the MLG/CNF composite was better than graphite reference.

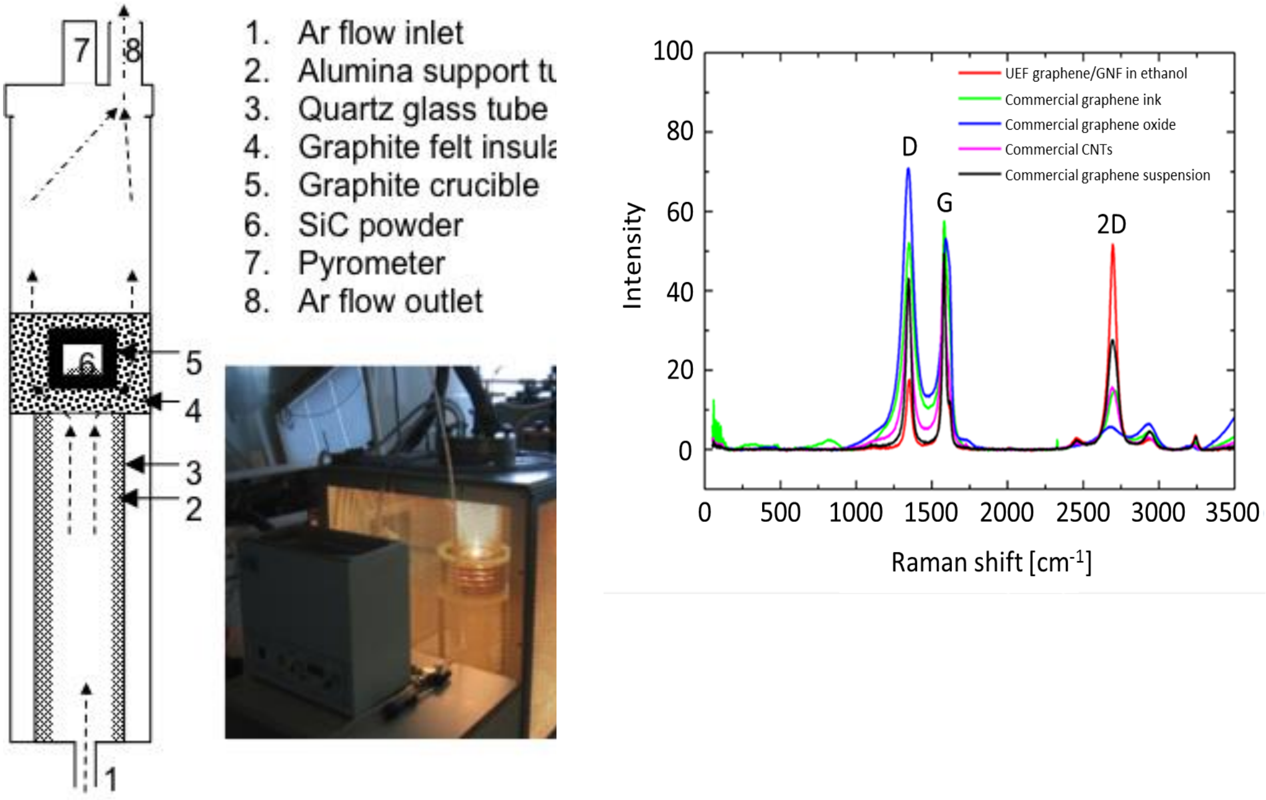

Figure 1. Induction annealing set-up and Raman spectra of the synthetized MLG/CNF composite

Acknowlegments

The authors thank the Fortum Foundation (grant 12-072), the Foundation for Research of Natural Resources in Finland (grant 64488), and the strategic funding of University of Eastern Finland (grant 931057) and Academy of Finland (grant 308062) for supporting the research presented here.

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CYCLING OF ZINC-AIR BATTERIES IN ALKALINE ELECTROLYTE

Mari Juel[1], K. Jayasayee[1], S. Meli-Hanetho[1], J.R. Tolchard[1], E. Sheridan[1], B. Abrashev[2], K. Petrov[2], L.C. Colmenares[3], A.R. Mainar[3], S. Labonnote-Weber[4], A. Kube[5]

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Introduction

In the framework of the EU funded project ZAS (*Zinc-Air Secondary batteries based on innovative nanotechnology for efficient energy storage*); we aim at improving the cycle life performance of secondary Zinc-air batteries using low cost nanostructured materials and production methods. However, the goal is challenging due to the degradation of electrodes during cycling, which results in a rapid reduction in (storage) capacity. Furthermore, in order to improve the overall reversibility of the Zinc-air battery it is necessary to understand the current limitations, requirements and challenges for each cell component (*viz*. anode, electrolyte, and cathode) and their interaction. Through close interaction between computer simulations and experimental testing, the ZAS project will select and develop electrodes and electrolytes to achieve its targets.

Experimental

In the project, a 25 cm^2 horizontal test fixture (developed at IEES, Bulgaria) has been used for cyclability tests in a KOH based electrolyte. The cell components such as the electrodes, current collector and base layer materials as well as the positioning of different types of separators has been optimized through a systematic approach for finding failure mechanisms.

Results and discussion

Post-mortem analysis of the cell components, by. XRD and SEM-EDS, identified problems related to dissolution and migration of unwanted species in the cell. By modifying the cell and test conditions it was possible to increase the discharge/charge cycles of the cell from a few cycles to about 100 discharge/charge cycles with a capacity retention of more than 80% when cycled at a reasonable current density of 4 mA/cm^2, about 0.2C with 20% DoD.

Conclusions

Through optimization of the different cell components of a 25 cm^2 Zinc-air battery cell 100 discharge/charge cycles have been achieved with a capacity retention of more than 80% when cycled at a reasonable current density of 4 mA/cm^2, about 0.2C with 20% DoD.

Acknowledgments

This work is part of the ongoing EU funded H2020 project ZAS* (GA# 646186*)*.

RAW MATERIALS FOR LI-ION AND REDOX FLOW BATTERIES

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Introduction

Fast, even exponential growth of electric vehicle (EV) market has been forecasted, and rapid expansion of lithium-ion battery production capacity is underway. However, there are some concerns about availability of raw materials, especially lithium and cobalt to support this rapid electrification of the road transport. We have compared the availability of these raw materials to market forecasts by EV and lithium battery industries, and addressed the possibilities of mitigating the supply risks by recycling or choice of cathode chemistries with reduced or zero cobalt content. Finally, we have addressed the resource availability for redox flow batteries to supplement Li-ion batteries in the stationary market.

Market forecasts and availability of critical metals

A demand forecast for critical raw materials for Li-ion batteries was carried out in the Strategic Research Board funded project Closing the Loop of High Value-Added Materials (CloseLoop) in early 2017 [1]. Lithium, cobalt and natural graphite were included in this study, which extended to the year 2025. This previous study is compared with more resent market and production forecasts by automotive, battery and mining industries. EV forecasts up to 2040 are accounted for. Finally, the availability of critical metals for redox flow batteries is briefly discussed.

Recycling

The state-of-the art pyrometallurgical Li-battery recycling process by Umicore and more recent work at Aalto University on hydrometallurgical lithium and cobalt recovery from mixed and crushed Li-battery waste are reported [2].

Results and discussion

The study shows that global lithium reserves are sufficient to support the EV industry and other Li-battery applications. However, major investments are needed for new production capacity, and the mining industry appears to be coping with the challenge. Availability of cobalt is more critical. The main reserves are in Congo (DRC) where abuses of human rights have been reported. Decreasing cobalt content in EV and consumer electronics batteries should be attempted and recycling improved. Co-free chemistries should be used for stationary applications.

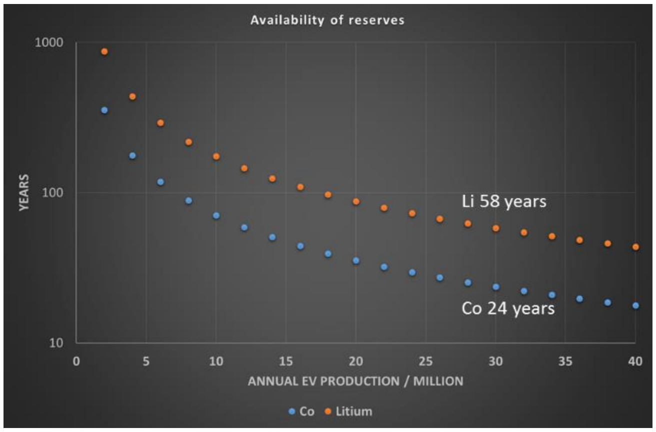

Figure 1. Availability of Li and Co reserves for EV production. 8 kg Li (42 kg LCE) and 10 kg Co assumed for an average EV.

It is not economical to recycle lithium today. In the Umicore process, cobalt is recovered but Li is lost in the slag. In our hydrometallurgical process both metals can be recovered from a real life battery waste but further developments are needed to optimize the whole recycling process.

Vanadium production in China, the main producer with > 50% market share, should be doubled to support the plans by local Vanadium Redox Flow Battery (VRFB) producers. More sustainable redox battery chemistries based on iron, zinc and cooper would be preferred.

Acknowledgments

This work has been supported by the Strategic Research Council at the Academy of Finland, project CloseLoop (grant number 303452).

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Towards more environmentally friendly iron-based Li-ion batteries

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Key words: Iron oxide; Pseudocapacitance; Fluorine-free electrolyte; $LiFePO_4$; Sodium alginate.

Introduction

Despite their tremendous growth as power source in portable electronics, Li-ion batteries (LIBs) suffer from a series of crucial issues, which are relevant for large-scale applications such as electric vehicles and electrical grid storage. Their components and manufacture are expensive (e.g. $LiCoO_2$, graphite), cause polluting gas emissions and employ toxic or hazardous materials (e.g. Co, F-rich compounds, solvents), which are also difficult to recycle, thereby posing a severe threat to the environment. This adds up to typical concerns regarding their safety during heavy-duty operation (e.g. fast charge/discharge). Switching to Na-ion batteries could be appealing to reduce costs and tricky dependence from Li ores, yet LIBs are unrivalled in terms of overall performances and cycle lives. Hence, progresses towards more sustainable LIBs should be sought mainly through a careful choice of the active materials and in making their assembly easier, quicker and greener.

Here, a dedicated design for safer and more environmentally friendly LIBs relying on abundant iron-based positive and negative electrodes [1] has been targeted with the aim of removing all fluorinated components (i.e. PVdF binder, $LiPF_6$ salt) that are costly and harmful. In fact, $LiPF_6$ degradation due to contact with moisture traces causes a progressive generation of highly corrosive HF species [2] that are detrimental for both cell cycling and overall LIB safety.

This investigation takes as point of departure an earlier report on $Fe_2O_3/LiFePO_4$ cells with fluorinated binder and electrolyte [3] and another study on advanced $ZnFe_2O_4/LiFePO_4$ batteries with Na-CMC as renewable binder for both cathode and anode in presence of $LiPF_6$ [4].

A fluorine-free LiBOB [5] electrolyte and a water-soluble Na-alginate functional binder [6] for both our negative (iron oxide) and positive ($LiFePO_4$) electrodes were utilized here with the idea to concurrently address costs, performances and environmental footprint of these cells. Moreover, an unconventional strategy was applied to tackle typical drawbacks (i.e. poor energy efficiency per cycle and limited Coulombic efficiency) due to conversion reactions of transition metal oxides [7]. A procedure of extensive pre-lithiation was carried out for nanostructured iron oxide to achieve a larger interfacial area through the formation of an active nanocomposite, with the intention of boosting not only the pseudocapacitance of this system (i.e. via its preliminary conversion into Fe/Li_2O), but also the output voltage of the resulting electrode in a full cell with $LiFePO_4$.

Experimental

Synthesis of iron oxide, preparation of positive and negative electrodes, applied electrochemical procedures, as well as details on pre-lithiation processes are described in our previous study [1].

Results and discussion

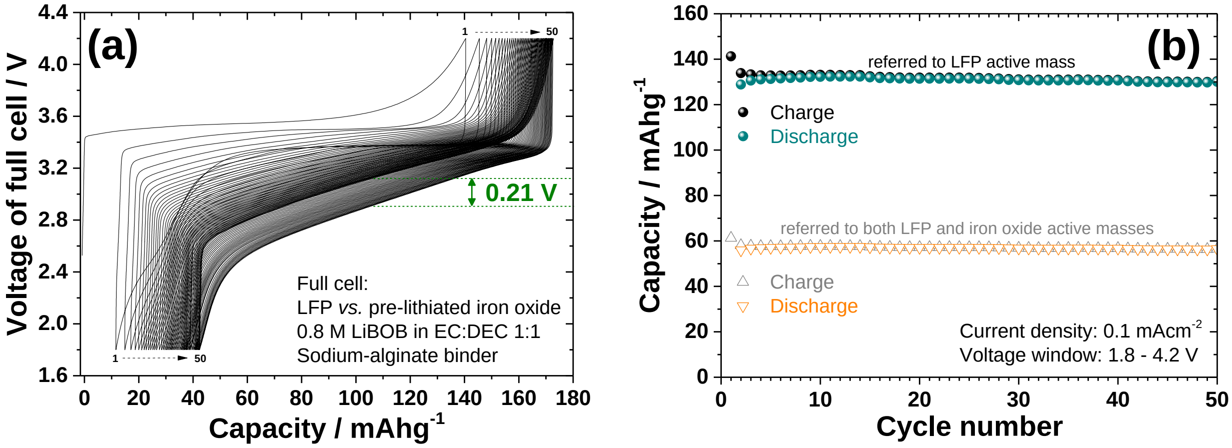

Figure 1. (a) Galvanostatic charge/discharge profiles of a full cell having Na alginate-based coatings with $LiFePO_4$ cathode, pre-lithiated iron oxide anode and LiBOB electrolyte. (b) Cycle performance of the same cell cycled with a current density of 0.1 $mAcm^{-2}$. Note the evolution of the sloping curves and their limited hysteresis during cycling.

The use of pseudocapacitance via extensive formation of Fe/Li_2O phase boundaries through preliminary lithiation and conversion of nanostructured iron oxide (i.e. before its assembly in full cells with $LiFePO_4$) resulted here in an increase the average output voltage of the whole cell, while limiting energy inefficiencies (Fig. 1a). The overall behavior of the cell combines characteristic Faradaic features arising from the insertion reactions of $LiFePO_4$ with those of supercapacitors, thanks to the remarkable pseudocapacitance displayed by the Fe/Li_2O nanocomposite anode.

Conclusions

This choice of electrode/electrolyte materials enabled fast charge/discharge with a good capacity retention, which was better than the one of analogous full cells with $LiPF_6$ upon long-term cycling.

Acknowledgements

The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS) is gratefully acknowledged for funding via the personal grant no. 245-2014-668.

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LIPO CATHODE BARRIES BY ALD USING PHOSPHITE PRECURSORS

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Introduction

Lithium phosphate (Li_3PO_4) is a promising material as solid state electrolyte. In this work a new route for synthesis of phosphorous based materials using Atomic layer deposition (ALD) is demonstrated. The established phosphate precursor for ALD use has been replaced by the more volatile phosphite precursors for synthesis of LiPO and AlPO materials. Furthermore, the LiPO product has been tested as a barrier material onto $LiFePO_4$ cathodes to improve kinetics and cycling performance. We have shown that there is indeed an improvement at low barrier thicknesses **Figure *1***. Adding barrier layers in the interphase between the cathode and electrolyte can be seen as a step on towards development and implementation of commercially viable solid state electrolytes. Deposition of barriers for battery materials by ALD is not a new field [1]. Films of; $AlPO_4$, $FePO_4$ [2], Al_2O_3 [3, 4], TiO_2 [5], Li_3PO_4 [5] and LiPON [6] have all been reported. Our novel approach is application of phosphorous precursors in the +III oxidation state, such as trimethyl phosphite (Me_3PO_3) and triethyl phosphite (Et_3PO_3). These precursors can replace trimethyl phosphate (Me_3PO_4) in established deposition routes for aluminium phosphate ($AlPO_4$) [7] and lithium phosphate (Li_3PO_4) [8, 9] by ALD. Furthermore, the resulting Li_xPO_3 product can form a barrier layer where certain thicknesses will give a positive contribution to kinetics, capacity retention and cycling performance.

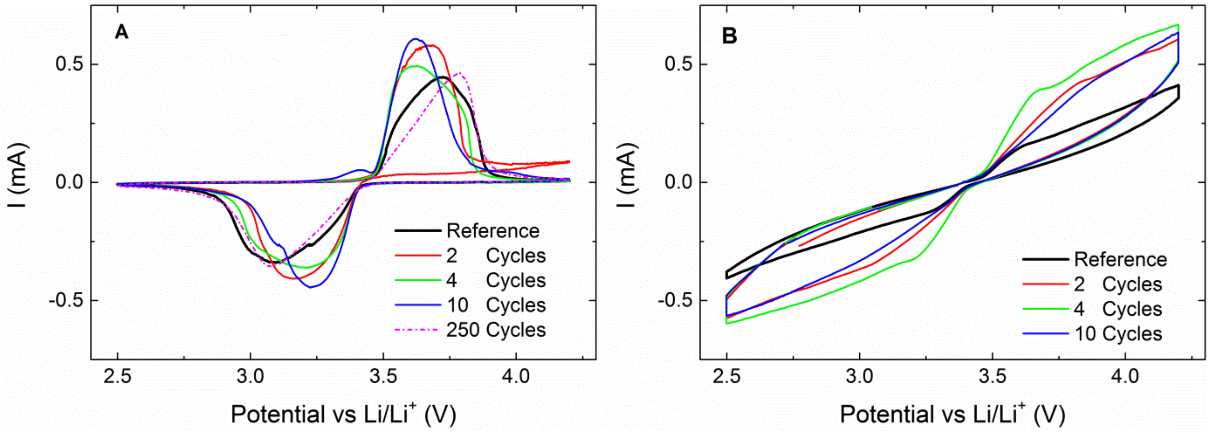

Figure 1: Cyclic voltammetry measurements of LiPO deposited as a barrier material onto a $LiFePO_4$ cathode with different thicknesses. The sweep rate is set to 0.02 mV/s (A) and 0.1mV/s (B) in the voltage range 2.5 V to 4.2V.

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Use of ultrashort pulsed laser deposition for engineering Li-ion battery materials solutions

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Introduction

Silicon based anode materials and microcomposites are attractive candidates for reaching increased anode energy density on Li-ion batteries. Their energy density can be up to 10 times more than that of graphite which is the current anode solution in commercial batteries. One of the weaknesses of silicon based solutions are the huge volume changes during lithiation and de-lithiation processes which result in stress accumulation, microcracking, rupture of SEI layer around Si particles, and loss of contacts to current collector and within the anode material itself. One extensively studied way of improving performance of Si as anode material is the use of nanostructured Si in the form of nanoparticles, nanotubes, nanowires, or as microcomposites. These can accommodate the volume changes without microcracking and loss of contacts. However, nanostructured Si with large surface area is vulnerable to detrimental surface reactions including extensive SEI layer formation or oxidation. Both of these phenomena cause loss of capacity due to loss of lithium into SEI layers or reaction with SiO_2.

Optimizing Si microstructure, including particle size and open surface area, is critical for reaching good mechanical stability and reducing the tendency for SEI and SiO_2 formation. Furthermore, microcomposite materials can be used to improve stress relaxation properties, promote electric conductivity, and protect Si from extensive surface reactions. These approaches make it possible to overcome the traditional weaknesses associated with Si anodes.

Pulsed laser deposition is a versatile technology for processing of materials. Picodeon Ltd Oy is utilizing ultrashort pulsed laser deposition to generate Si-based anode layers with various tailored structures and compositions. This paper presents structures and electrochemical performance of these Si and Si-microcomposites.

Experimental

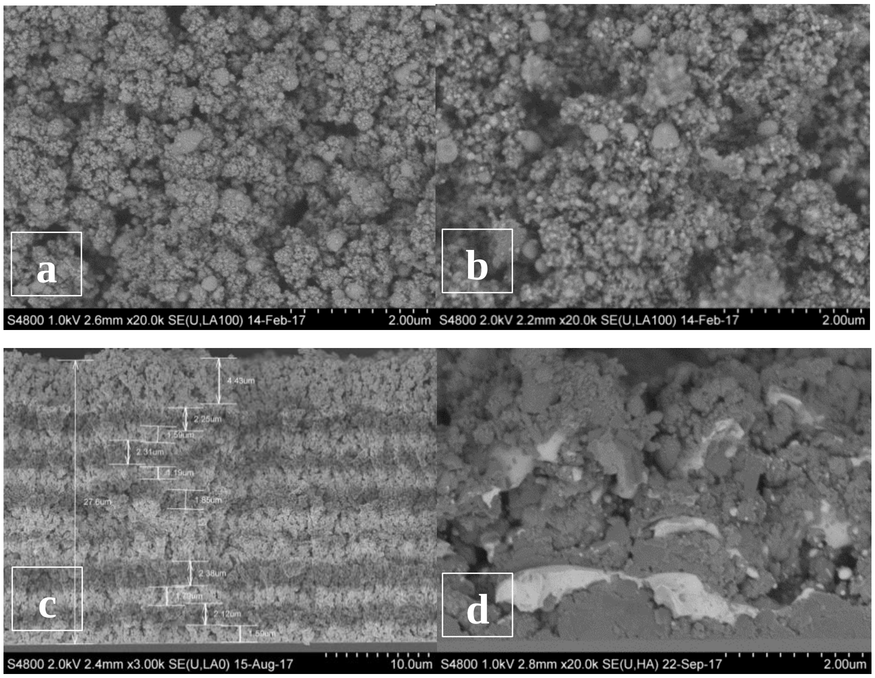

Figure 1. Microstructures of experimental Si containing anode layers. (a) 100% Si, (b) 50% Si-50% C, (c) 50%Si-50%Cu, (d) 85% Si-15%Sn.

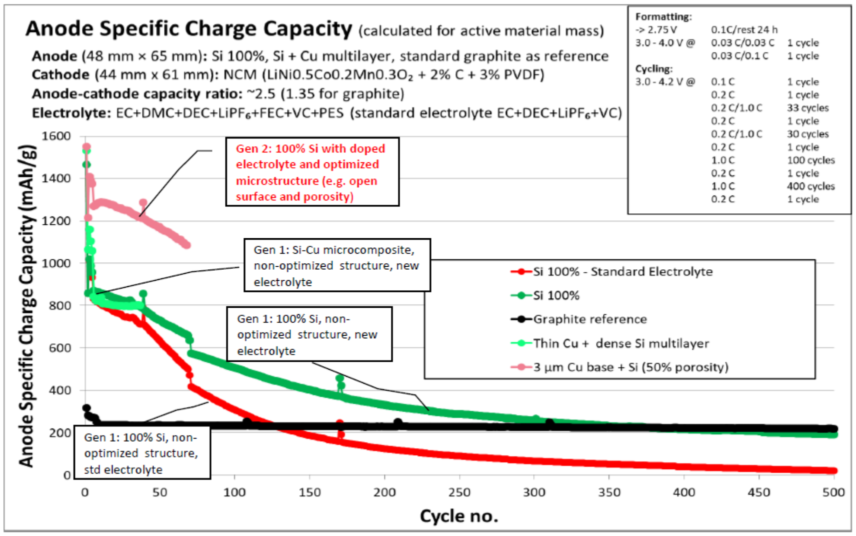

Figure 2. Cycling data for selected experimental Si anode materials.

LITHIUM-ION BATTERY DIAGNOSTICS: STATE OF HEALTH ESTIMATION

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Introduction

VTT participates in an EU-funded H2020 project called INVADE, which focuses on research on the field of smartgrids and storage. In INVADE, five pilot sites are built across Europe, where lithium-ion batteries are integrated in local smartgrids with renewable energy sources, electric vehicles, households and commercial buildings. One of VTT's tasks is to develop methods for estimating the state of health of the utilized batteries based on diagnostics data stored on a cloud-based platform.

Battery state of health estimation

Battery state of health (SOH) describes the present condition of the battery compared to a fresh battery. Battery SOH can be determined according to many factors of which battery energy capability and power capability are the most common. These are indicated by battery capacity fade and impedance increase, respectively. Estimating the SOH accurately is challenging as lithium-ion batteries are complex electrochemical systems with only few directly measurable parameters: voltage, current and temperature. Most straightforward methods are based on direct measurements from the cell. However, they are in general limited in accuracy or unsuitable for online SOH estimation in real applications. A survey on common SOH estimation methods, from model-based methods to methods exploiting machine learning techniques, is presented.

Example method: incremental capacity analysis

Incremental capacity analysis (ICA) is used as a case example of SOH estimation methods. In ICA, the battery charged capacity (Q) versus the terminal voltage (V) is differentiated to form an incremental capacity curve (dQ/dV). In the incremental capacity curve, there are characteristic peaks depending on the battery chemistry. A clear change in the shape of the peaks can be detected as the cell ages. Results obtained from the ICA method implemented on lifetime test data from 12 LFP cells measured at VTT are presented.

Acknowledgments

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Electrochemical testing methods for Si-NCM cells

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Introduction

Secondary battery materials are in great demand of research and new high energy density materials are required for higher quality of batteries[1]. Silicon based anode is one of the most promising anode material for Li-ion batteries, because it has high theoretical capacity (4200 mAh/g, lithiated to $Li_{4.4}Si$) and low operating voltage (~0.3V versus Li/Li^+) [2,3]

Experimental

Different type of electrolytes and testing parameters used to achieve better electrochemical results for silicon anodes. Differences between half-cell and full-cell tests studied to understand behaviour of silicon as an anode material. Full-cell tests were prepared with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode and balanced to have different specific capacity for the silicon anode.

Results and discussion

Results show that electrochemical testing parameter and materials used in testing have great influence on the electrochemical performance of silicon anode materials. Especially additives in electrolyte seems to have great influence on the properties of silicon based anode material. Results also clarify problems with half-cell and full-cell tests. Sample preparation is more complicated and higher accuracy is required from characterization equipment.

Conclusions

Testing parameters and electrolytes can improve properties of Si-NCM cells.

Silicon based anode material is a good candidate for the next generation Li-ion battery.

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Next-generation batteries: Helping to design new battery materials through new computational tools

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Transport phenomena in the cathode materials of batteries, both ionic and electronic, play a key role in the overall performance of the device. An intense modeling activity of different aspects of these transport phenomena has taken place during the last two decades, which covers different time and length scales. In this talk we will focus on modeling at the atomic scale of ionic and electronic transport in the cathode materials of lithium-ion batteries and aprotic metal-air batteries.

The ionic transport of intercalated lithium in different transition metal oxides has been extensively modeled in the literature by combining density functional theory (DFT) and the nudged elastic band (NEB) method to obtain the activation barriers for lithium diffusion within these materials.[1] Lately the method is starting to be applied also to the ionic transport between coating materials (e.g. graphite) and the cathode and also at the interfaces that are created between different phases of the same cathode material[2]. During the talk we will present some examples of lithium transport through these interfaces.

The electronic transport in lithium-ion batteries typically occurs through a polaronic hopping mechanism, which is conventionally modeled using DFT and NEB as in the case of the ionic transport. This way of modeling the electronic transport is valid in the purely adiabatic limit, omitting all the non-adiabatic features of the charge transfer. Here we will briefly introduce our recent developments in the implementation of a DFT-based Marcus theory model which is able to capture the non-adiabatic effects.

In contrast with lithium-ion batteries a conversion process takes place in metal-air batteries. In this conversion process an oxide is formed at the cathode through the reaction between atmospheric oxygen and alkali or alkali-earth ions. We will talk about modelling the formation of these oxides and its relation with the overpotentials observed in these batteries[3].

Finally we will address the electronic transport at metal-air battery cathodes, which can take place through polaronic hopping[4] as in the case of lithium-ion batteries, but also can occur through electron tunneling[5]. We will discuss which of the two processes is dominant depending on the different conditions of the charge/discharge process.

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A Cheap and Sustainable Cathode Material for Sodium Ion Batteries

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Growing concerns over raw material price fluctuations for lithium-ion batteries have led to renewed interest in other ion systems, such as sodium-ion batteries. R-$Na_{1.92}Fe[Fe(CN)_6]$, otherwise known as Prussian White, represents the most realistic attempt so far at producing a truly sustainable positive electrode material for sodium-ion batteries. Unlike other cathode materials, Prussian White is nickel- and cobalt-free. In fact, when incorporated into a sodium-ion battery the full cell will only contain cheap sustainable and environmentally friendly metals, specifically iron and aluminium. Thus, with a theoretical capacity of 170 mAh g^{-1} and an average voltage output of 3.2 V Prussian White is a competitive cathode choice to bring sodium-ion batteries to mass market.

At Altris –a spin-off company from Uppsala University– a cheap, ambient condition synthesis has been developed and is being scaled up to produce kilogram quantities of Prussian White. The two-step synthesis process produces high quality Prussian White via Prussian Blue (Figure 1) and involves the use of abundant and non-toxic reaction precursors. Simultaneously to material synthesis scale up, commercial scale sodium batteries containing Prussian White as the cathode material are being constructed in collaboration with LiFeSiZE. Prototype cells are expected to be delivered in next year.

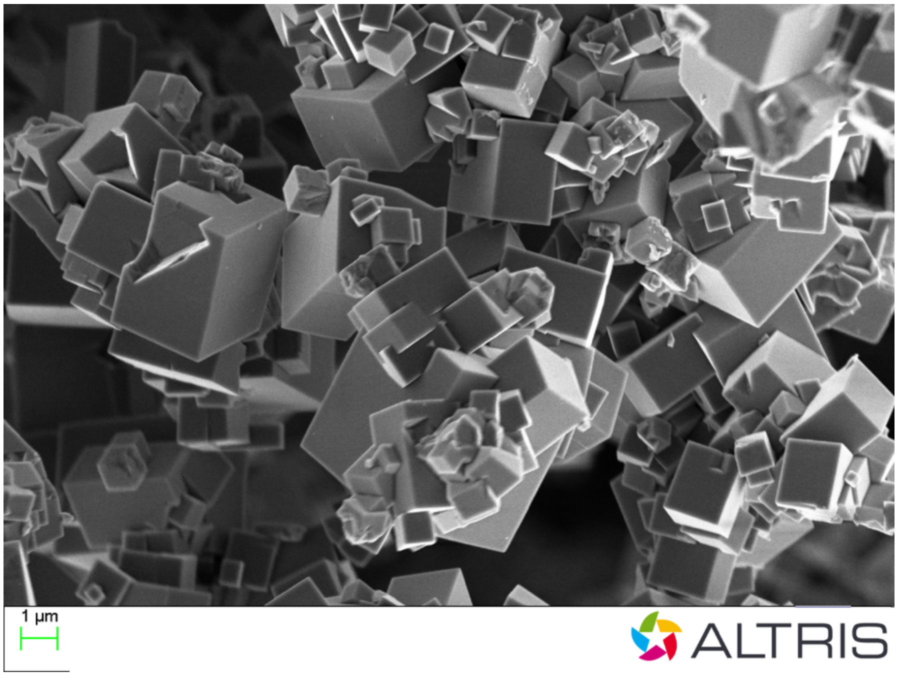

Figure 1. SEM image of Prussian Blue intermediate

Safety and ageing of a commercial Li-ion battery

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Introduction

The electrification and hybridization of ships with Li-ion batteries has gained momentum becoming an important new business area for several industries in Norway. The largest battery system for a ship currently built stores several MWh of electric energy. The consequences of a fire in such a system can be catastrophic. Knowledge of a Li-ion battery's life and "State of Health" is vital for the economy and safety of larger energy storage systems for marine application.

The degradation and ageing of Li-ion batteries will in many cases contribute to reduced thermal stability which potentially affects the safety performance of the batteries. The fact that aging of lithium-ion cells leads to a reduced capacity and cell life, is extensively covered in the literature by several research groups [1-3]. The safety effects of ageing are far less studied, with only a handful of empirical studies published [4-8].

This study presents ageing data on a commercial 6 Ah Li-ion cell with a NCA – graphite chemistry. The thermal stability of cells which have been aged with different ageing mechanisms was characterized with an Accelerated Rate Calorimeter (ARC).

Experimental

The commercial 6 Ah Li-ion cell was cycled at 5, 25 and 45 °C from 0 to 100 % State-of-charge with 2 different combinations of charge and discharge rates; 1C/1C and 1.5C/3C. The remaining capacity at 25 °C and 1C and C/10 discharge rates were recorded every 100-300 cycles. The thermal stability was recorded for new cells and for aged cells with remaining capacities lower than 85% that was cycled at the different cycling conditions.

Results and discussion

A typical cycle life where both 5 °C and 45 °C cycling have a lower cycle life than 25 °C is observed in Figure 1. The ageing mechanisms are however different and will affect the thermal stability of the aged cell. These results will be presented and discussed in-depth through the recorded ARC data.

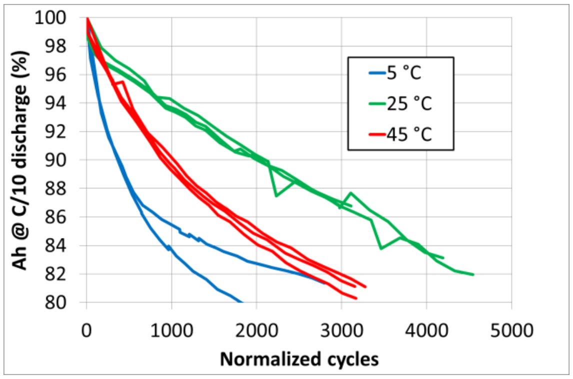

Figure 1. The remaining capacity of the 6 Ah Li-ion cell cycled at 5, 25 and 45 °C from 0 to 100 % SoC and 1C/1C charge and discharge rate.

Conclusions

A 6 Ah Li-ion cell with a NCA – graphite chemistry was aged through cycling at different temperatures and current rates. The thermal stability of the aged cells was recorded and showed a large deviation with respect to ageing mechanism relative to uncycled cells.

Acknowledgments

The authors acknowledge the Research Council of Norway (project no. 228739) for funding through the project ”Life and Safety for Li-ion batteries in Maritime conditions (SafeLiLife)”.

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Towards more stable $LiCoO_2$: over-lithiation and doping

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Key words: lithium cobalt oxide, over-lithiation, doping

Since the commercialization of lithium ion batteries in 1991, $LiCoO_2$ has been used as a positive electrode material. Even now, a few decades later, it is still the most used materials in lithium ion batteries targeted for portable applications because it exhibits high operating voltage, low self-discharge rate and high reversibility. For consumer applications, long cycle life is a critical property of a power source. Hence, we have compared here [1] two different strategies, namely over-lithiation and doping, to increase the stability of $LiCoO_2$. In literature [2-4], both the methods have been reported earlier but results are difficult to compare because of different materials and synthesis methods. Hence, we have used here the same Co_3O_4 precursor for synthetizing the afore-mentioned materials *via* a conventional solid-state process.

The structural properties of the over-lithiated and the stoichiometrically lithiated samples are similar but the dobly doped sample differs from the other two: Though the particle size is similar for all three $LiCoO_2$ materials, the doped lithium cobalt oxide had slightly smaller crystallite size. This difference is reflected in electrochemical behaviour. In rate capability measurements, the doped material had clearly superior rate capability properties compared to the other two materials. The doping was also discovered to enhance the cycle life properties of lithium cobalt oxide. However, not only the doping, but also the Li/Co ratio affected the cycle life of lithium cobalt oxide. In cycle life measurements, the stoichiometrical $LiCoO_2$ material appeared to be more stable than the over-lithiated $LiCoO_2$ material. The doped $LiCoO_2$ material, which had a similar Li/Co ratio to the stoichiometrically lithiated material, had the longest cycle life.

As a summary, while the doping does enhance the rate capability and the cycle life properties of lithium cobalt oxide, the Li/Co ratio has clear effect on them as well. The observed differences in rate capability are attributed to charge transfer impedances and diffusion of lithium in the $LiCoO_2$ material, induced by changes in the structure. Moreover, solubility of the doped material is clearly retarded compared the other two, which may contribute to the longer cycle life.

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DEVELOPMENT OF HIGH VOLTAGE $Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$

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Introduction

$Li_{1.0}Ni_{0.5}Mn_{1.5}O_4$ (LNMO) high voltage spinel is a very promising next generation battery cathode material. Among the most interesting features are the high operating voltage and the absence of cobalt, which enable an energy dense and cheap battery. The challenges are mainly related to the surface reactions involving electrolyte degradation and dissolution of nickel and manganese. Strategies to limit these unwanted degradation reactions often involve surface treatments and doping.

This presentation will present untreated LNMO material with superior electrochemical properties and give insides from key methods that has been used in the development.

Experimental

The LNMO precursor is made by co-precipitation to obtain spherical particles with a controllable particle size distribution. The precursor is calcined with our proprietary calcination program that increases the density of the spherical particles and reduces the surface area to below 0.2 m^2/g. The material has a high phase purity, high power capability, low degradation and low dissolution rate of manganese and nickel.

Materials are screened physically by XRD and SEM and electrochemically in half cell coin cells at 55C. The performance is later confirmed in full cells.

Much work has been put into building a reliable test system designed for testing the cathode material. The electrochemical half cell is based on lithium disc anode (EQ-Lib-LiC25, MTI), 1 M $LiPF_6$ in EC:DMC electrolyte (E001, Solvionic) in coin cells (Hohsen) and cathode electrodes with 84 wt% active material, 35% porosity and a loading of 0.7 mAh/cm^2. Dissolution of Mn and Ni is a standard post mortem analysis.

Results and discussion

Figure 1 shows voltage curve and cycling data from a test of untreated LNMO. The capacity is almost 140 mAh/g, the degradation rate in accelerated cycling test at 55 C is only 5% per 100 cycles.

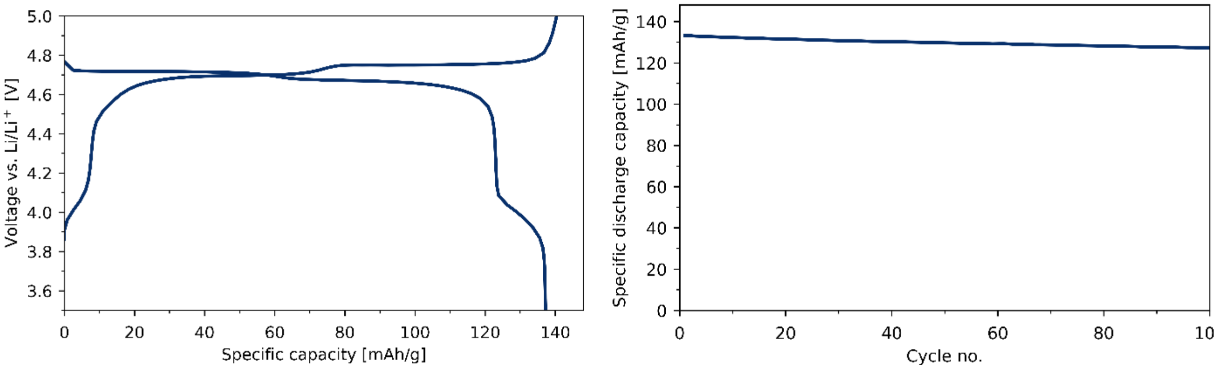

Figure 1. Left: Typical half cell charge/discharge curve of the LNMO active material at 0.2C/0.2C. Right: Discharge capacity of the LNMO in half cell screening test at 55 C and a 0.5C/1C charge/discharge rate.

Figure 2 shows *jn operando* XRD measurement of LNMO half cell during electrochemical cycling. One purpose with this method is to follow the changes in lattice parameter as the LNMO is lithiated and delithiated. This is used to describe how much the material is stressed during cycling.

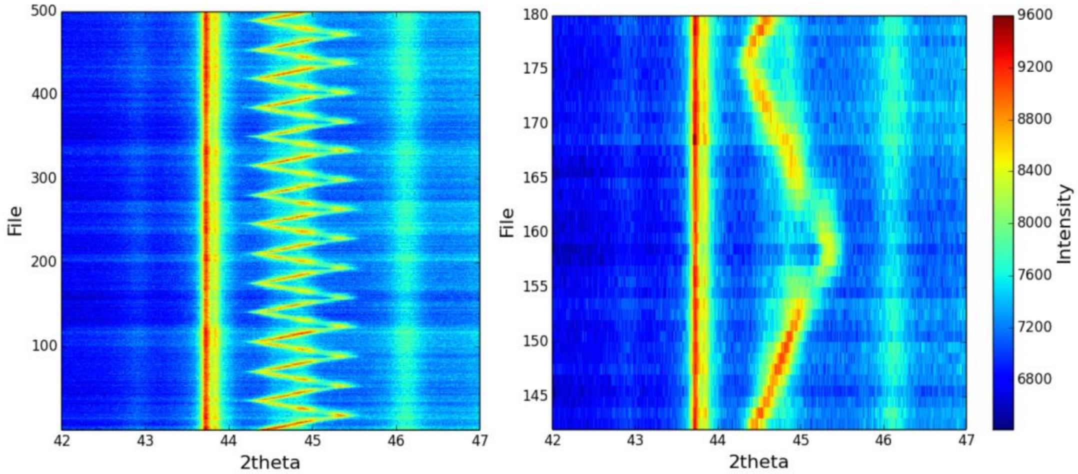

Figure 2. *In operando* XRD measurement of LNMO half cell during electrochemical cycling.

Conclusions

It has been possible to synthesize a material that show superior performance without a dedicated surface treatment. In the development, it has been very important to have a very reliable test system and utilization of many different techniques.

THE SEI REVISITED – WHAT DO WE KNOW ABOUT INTERFACES AND INTERPHASES?

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Introduction

The Solid Electrolyte Interphase (SEI) and other interfaces in lithium- and sodium ion batteries are despite of many scientific studies still attracting a lot of interest. This presentation aims at reviewing why interfaces in batteries are so crucial for the function, thermal stability, lifetime and ageing of a battery.

Characterizing interfaces in batteries is both simple and difficult. It is simple in the sense that it is easy to take a battery apart and then use different techniques to study the composition and morphology of interfaces of electrodes and separators post mortem. It is, however, difficult to study in situ how an interface forms and evolves during battery operation.

The SEI on negative electrodes can be described as a mixture of inorganic and organic compounds where the inorganic compounds are formed closer to the electrode surface. The layer is a consequence of the low potential – close of that of lithium – where for lithium-ion batteries the reduction of the thermodynamically instable organic solvent (below 0.8V vs. Li^+/Li) is taking place. There are even descriptions of the SEI consisting of an inner, more dense inorganic layer, where electrons can tunnel through until a certain thickness of the layer has been obtained where the SEI becomes electronically insulating but where ions can penetrate. How the different SEI-compounds interplay to form a well-functioning layer is not yet clear.

Experimental

The results shown are mainly based on electrochemical cycling combined with photoelectron spectroscopy (PES) results; both in house and synchrotron based. PES has been performed both at the Helmholtz Zentrum Bessy, Germany, and at Diamond UK. The advantage with synchrotron radiation is the possibility to tune the incoming photon energy to reach into a surface at different depths.

Results and discussion

The result and discussion will be based on a number of thesis produced at Uppsala University with the aim to answer the following questions:

Will the electrolyte salt influence the interfaces formed in batteries? Yes. Examples will be given for both lithium and sodium batteries.

Will the electrode material influence the SEI composition? Not very much but to some extent.

Is particle size and morphology important for SEI formation?

What is a good SEI former? Is it better to have an additive in the electrolyte forming the SEI or can the binder be just as good?

How thick is the SEI? What does the buried interface between the SEI and the electrode look like?

How is the conditions for a stable interface on a positive electrode? How can metal-ion dissolution be prevented?

There are results trying to answer all these questions which will be discussed in the presentation.

Conclusions

Interfaces in batteries are complex. They are formed electrochemically or chemically. A well-functioning interface protect from unwanted side reactions. New methods are needed to understand the true formation in situ and to better describe the function of interfaces.

Acknowlegments

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Grid storage and perspectives for new battery chemistries

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Introduction of renewable and intermittent photovoltaic and wind electricity sources in the utility grid will increase the demand for stationary electrical energy storage technologies. In such applications high energy density has less importance, while a low cost has highest priority. This can be quantified by the levelized-cost-of-electricity-storage (LCES)[1,2] and is given by $\mathrm{LCES}[\$\ \mathrm{kWh}^{-1}\mathrm{cycle}^{-1}] = \mathrm{CC}[\$\ \mathrm{kWh}^{-1}]/(N \cdot \eta)$, where LCES expresses the cost of storage and discharge of one kWh. CC are the capital costs per kWh, *N* the number of cycles during lifetime and η is the cycle efficiency. The US Department of Energy set a long-term goal of CC below \$150 kWh^{-1} and LCES below ¢5 kWh^{-1} cycle^{-1} as a breakthrough for batteries in grid-storage applications.[3] This is currently not met by any of the state-of-the-art batteries like Li-ion or NiMH batteries. However, the main driver for battery development for the past decades has been for mobile applications (electric vehicles and consumer electronics) where large energy density has highest priority. For stationary power applications energy density is less important while cost, lifetime and safety is paramount. This has created a driver for R&D in new (aqueous) battery chemistries where these goals are meet.

In this presentation I will give short introduction to the emerging incentives for local and large scale storage of electricity in the power grid. This will be followed by a more detailed cost analysis of vanadium flow batteries, that are currently considered as a potential cost-effective solution for grid storage. The presentation will be concluded by some recent research and results in new aqueous semi-organic based batteries (both flow and solid state batteries).

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Applying porous silicon in Li-ion batteries

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Silicon (Si) is an alluring anode material for Li-ion batteries because of its easy availability and high theoretical capacity. Our aim is to solve the problems related to volumetric expansion and low conductivity of Si by using mesoporous silicon (PSi) in the micrometer-sized particles and combine them with carbon nanotubes (CNTs) as the conductive additive, respectively. Starting from the determination of the optimal size range for the PSi particles in Li-ion anodes (Figure 1), the effect of surface modifications and doping degree [1], we have continued to study the effects of CNTs as small-scale additives to PSi anode material.

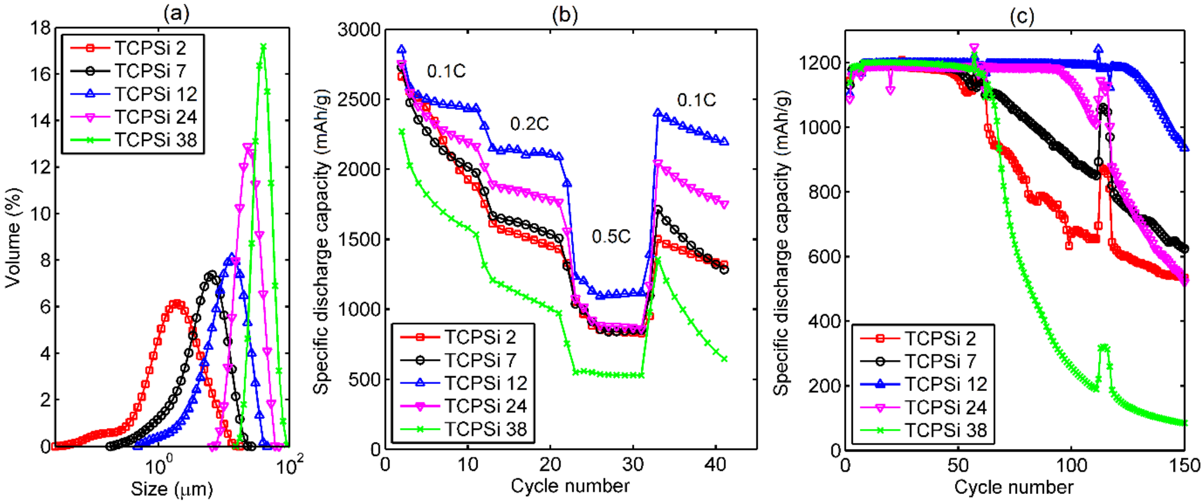

Figure 1. PSi particle size distributions and corresponding electrochemical cycling results for different sizes. (**a**) Particle size distributions for the TCPSi samples. (**b**) Galvanostatic rate capability results for the TCPSi samples. Mass loading of silicon was 1.1 mg/cm^2. (**c**) Galvanostatic capacity results with a limited capacity of 1200 mAh/g. Cycling was done periodically: 5 × 0.1 C + 50 × 0.2 C while 1 C equals to 4200 mA/g. Mass loading of silicon was 0.8 mg/cm^2. The results are adapted from [1].

CNTs are not only used as a conductive additive but they should also contribute to the mechanical stability of the PSi-CNT hybrid. The idea is to conjugate the PSi and CNTs together with carbodiimide crosslinker. To this end, different ways of functionalization of PSi and CNTs will be discussed.

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EXTRACTION OF LITHIUM FROM HARD ROCK ORE – CASE STUDY KELIBER

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Continuously increasing utilization of lithium-ion battery powered applications like electrical and hybrid vehicles, mobile electronics and home and grid batteries will require soaring in global primary lithium production. Currently lithium is extracted from salt lake brines and hard rock mineral concentrates. Spodumene ($LiAlSi_2O_6$) is the most important hard rock mineral used in lithium extraction. Recycling of lithium is still negligible compared to the primary production.

Keliber Oy is a Finnish SME planning to start lithium carbonate production from company's own spodumene pegmatite ores. The company holds several well studied lithium ores in the extensive (over 500 km^2) lithium province of Central Ostrobothnia, Finland. Keliber plans to start lithium ore mining and lithium chemicals production in early 2020. The target is to produce annually 9000 tonnes of battery-grade lithium carbonate for the strongly increasing lithium-ion battery chemicals markets.

With Outotec the company has developed a novel process for lithium extraction and high-quality lithium carbonate production. The production starts with common mining and beneficiation processes for producing spodumene concentrate. Prior the lithium extraction stage spodumene concentrate is heat treated at about 1000 °C temperature enabling natural α-spodumene transformation to lithium leachable β-spodumene. Lithium is leached with the sustainable pressure leaching process, bi-carbonated, separated from solid analcime residue, purified and crystallized as high purity lithium carbonate

Key words: Lithium, extraction, spodumene.

HOW WATER-SOLUBLE BINDERS CONTROL THE SURFACE CHEMISTRY IN LITHIUM-ION BATTERY ANODES

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Introduction

The key for a long battery cycle life is the formation of a stable solid-electrolyte interphase (SEI) on the surface of the negative electrode. This layer typically forms on the first cycle due to decomposition reactions at the electrode-electrolyte interface. More control over the surface layer can be gained when the layer is generated *prior* to the battery operation. Such a layer can be tailored more easily and can reduce loss of lithium inventory considerably. In this context, water-soluble electrode binders, e.g. sodium carboxymethyl cellulose (CMC-Na) and poly(acrylic acid) (PAA), have proven themselves exceptionally useful. Since the binder is a standard component in composite electrodes anyway, its integration into the electrode fabrication process is easily accomplished.

In this work, parameters that govern binder distribution in electrode coatings, control the stability and electrochemical performance of the electrode and that determine the composition of the surface layer are investigated. Several commonly used electrode materials (graphite, silicon and lithium titanate) are applied in order to study the impact of the binder on the electrode morphology and the different electrode-electrolyte interfaces. The results are correlated with the electrochemical performance and with the SEI composition studied by in-house and synchrotron-based photoelectron spectroscopy (PES).

Results and discussion

The results demonstrate that the poor swellability of the water-soluble binders leads to a protection of the active material when the surface coverage is high and the binder well distributed. This can generate functionality of sensitive anode materials, such as graphite, also in aggressive solvent environments such as propylene carbonate (Fig. 1) [1]. This, in turn, can render graphite electrodes useful in novel battery chemistries such as graphite-sulfur [2]. For anode materials which undergo large volume changes during cycling, for example Si, the SEI layer formation increases substantially, rendering the binder properties increasingly important for the surface chemistry of the electrodes [3]. As the binder content is decreased, complete surface coverage is more difficult to achieve. Thereby, the benefits provided by CMC-Na and PAA at the electrode surface are compromised and the performance differs less distinctly from electrodes fabricated with the conventional PVdF binder. Composites of alloying and conversion materials, on the other hand, typically employ binders in larger amounts. Despite the frequently noted resiliency to volume expansion, which is also a positive side-effect of the poor swellability of the binder in the electrolyte, the protection of the surface and the formation of a more stable interphase is the major cause for the improved electrochemical behaviour, compared to electrodes employing PVdF binders.

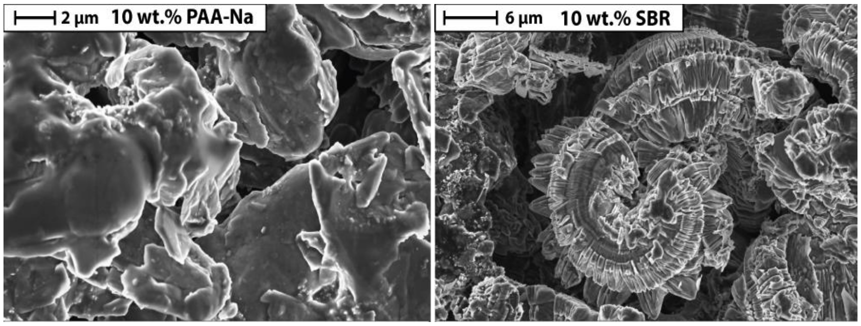

Figure 1. Cycled graphite electrodes in PC-based electrolytes. The different binders applied display distinctive differences in graphite exfoliation.

Binder content [4] and binder type [5] have shown crucial for the SEI layer formed on the anodes, being either graphite, $Li_4Ti_5O_{12}$ or Si. Moreover, binder type and content also display fundamental differences in the rheological properties during battery fabrication [6], which has a clear impact on the possibility of processing electrodes at a larger (industrial) scale.

Conclusions

Since the polymer is located directly at the interface between electrode and electrolyte, a poorly permeable surface layer can greatly reduce the amount of co-intercalation. Owing to their poor solubility in the electrolyte, PAA-Na and CMC-Na binders can provide an intrinsic surface layer. In contrast, fluorinated binders interact strongly with the electrolyte solvent and thus swell. Among the investigated binder systems, the established CMC-Na:SBR provided the overall best reproducibility and retention when investigated at a larger scale.

Acknowlegments

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