NORDBATT 1

UPPSALA
UNIVERSITET

NORDIC BATTERY CONFERENCE

December 4-5, 2013
Uppsala, SWEDEN

STandUP for ENERGY

SWEDISH HYBRID VEHICLE CENTRE shc

Höganäs

gammadata

Venue: Siegbahnsalen,
Ångström Laboratory

Welcome to NordBatt 1!

Welcome to the first Battery Conference in the Nordic Countries: NordBatt 1! This conference presents an opportunity to review the most 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 advances for energy storage solutions of the future.

The NordBatt meeting will be a multidisciplinary forum with participants from primarily the Nordic countries Sweden, Norway, Denmark, Finland and Iceland together with some internationally well-distinguished battery scientists. The focus of the meeting is primarily on Li-ion battery chemistry and future battery cell concepts, and will encompass anode, cathode and electrolyte materials, as well as cell and battery development. The need for improved batteries for electric vehicles will be particularly addressed.

Uppsala University, the oldest university of the Nordic countries, is proud to be hosting the first NordBatt meeting. We welcome you all to Uppsala, and hope you will be able to enjoy meeting colleagues and make new collaborations here in December. You are most welcome.

Kristina Edström
Organizing committee chair

Programme

December 4, 2013

11.00–13.00	**Registration**
12.00–13.00	**Lunch**
13.00–13.15	Welcome address by Prof. Kristina Edström Uppsala University
	Plenary lecture **Chair: Prof. Kristina Edström, UU**
13.15–14.00	Li-ion batteries and beyond: where we are and what next *D. Guyomard, (IMN), Université de Nantes, France, Plenary speaker*
	Oral session **Chair: Prof. Ulla Lassi, University of Oulu**
14.00–14.20	COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDY OF THE ROLE OF CO2 POISONING ON THE ELECTRONIC CONDUCTION AND OVERPOTENTIALS IN LI-AIR BATTERIES *Tejs Vegge, DTU, Denmark (Inv.)*
14.20–14.40	NEXT GENERATION BATTERIES – NEW MATERIALS MAKE ALL THE DIFFERENCE *Patrik Johansson, Chalmers, Sweden (Inv.)*
14.40–15.00	THE CARBON-ELECTROLYTE INTERFACE IN LI-ION BATTERY ANODES AND CATHODES FOR VARIOUS ELECTROCLYTE COMPOSITIONS *Ann Mari Svensson, NTNU, Norway (Inv.)*
15.00–15.30	**Coffee**
	Oral session **Chair: Prof. Tejs Vegge, DTU**
15.30–15.50	BATTERY CHEMISTRY RESEARCH ACTIVITIES AT THE RESEARCH GROUP OF APPLIED CHEMISTRY *Ulla Lassi, University of Oulu and Kokkola (Inv.)*
15.50–16.10	ENVIRONMENTALLY-FRIENDLY PREPARATION AND RECYCLING OF WATER-SOLUBLE ORGANIC Li-ION BATTERY ELECTRODE MATERIALS *Stéven Renault, UU, Sweden (Inv.)*
16.10–16.30	Li-ion battery materials made by atomic layer deposition *Ola Nilsen, Oslo University (Inv.)*
16.30–16.45	SINGLE-STEP GAS-PHASE SYNTHESIS OF Li4Ti5O12 FOR LI-ION BATTERIES *Jorma Jokiniemi, Univ. Eastern Finland and VTT, Finland*
16.45–17.00	OPTIMIZING Li4Ti5O12 ELECTRODES FOR LOW TEMPERATURE LITHIUM-ION BATTERIES *Tanja Kallio, Aalto University, Finland*
17.00–17.20	The strategy for battery research at IFE, Norway *Martin Kirkengen, IFE, Norway*
17.20–17.30	**Short break**
	Plenary lecture **Chair: Prof. Kristina Edström, UU**
17.30–18.15	Perspectives on Energy Storage: From Flywheels to Batteries *Daniel Abraham, Argonne National Laboratory, US, Plenary speaker*
18.15–21.00	**Poster session and dinner**

Programme

December 5, 2013

	Plenary lecture **Chair: Elna Holmberg, Director of SHC**
8.30–9.15	Invited SHC lecture: CASE STUDIES USING BATTERY DIAGNOSTIC TOOLBOX *Bor Yann Liaw, Univ. Honolulu, Hawaii, US, Plenary speaker*
	Oral session **Chair: Prof. Patrik Johansson, Chalmers**
9.15–9.45	LI-ION BATTERY CELLS IN HEAVY DUTY HYBRID APPLICATIONS *Johan Lindström, Scania (Inv.)*
9.45–10.05	Battery challenges at Volvo Cars *Theresa Granérus, Volvo Cars (Inv.)*
10.05–10.30	AGEING FACTORS AND CYCLELIFE TEST RESULT FOR POWER-OPTIMISED LITHIUM-IRON PHOSPHATE CELLS *Jens Groot, Chalmers and AB Volvo (Inv.)*
10.30–11.00	**Coffee**
	Oral session **Chair: Prof. Fride Vullum-Bruer, NTNU**
11.00–11.20	APPLIED BATTERY RESEARCH FOR HEAVY DUTY ELECTRIC COMMERCIAL VEHICLES *Ville Erkkilä, VTT, Finland*
11.20–11.40	EXPERIMENTAL AND MODELING INVESTIGATIONS OF ELECTRODE DEGRADATION IN BATTERY AGING STUDIES FOR VEHICLE APPLICATIONS *Matilda Klett, KTH, Sweden*
11.40–12.00	FAILURE MECHANISMS IN COMMERCIAL LI-ION BATTERIES *Annika Ahlberg-Tidblad, Etteplan (Inv.)*
12.00–12.20	The Lithium-Air Battery: How Difficult Is to Make It Rechargeable? *Reza Younesi, DTU, Denmark*
12.20–12.40	IMPEDANCE PERSPECTIVES ON LI-AIR BATTERY OVERPOTENTIALS *Jonatan Højberg, DTU and Haldor Topsøe*
12.40–13.00	CARBON FIBRES IN STRUCTURAL LITHIUM-ION BATTERIES – TAKING ADVANTAGE OF MULTIFUNCTIONAL PROPERTIES *Göran Lindbergh, KTH, Sweden (Inv.)*
13.00–14.00	**Lunch and poster session**
	Plenary lecture and oral session **Chair: Prof. Göran Lindbergh, KTH**
14.00–14.45	ADVENTURES IN POLYMORPHISM: LI2FESIO4 AND BEYOND *Robert Armstrong, St Andrews, UK, Plenary speaker*
14.45–15.05	SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED Li2Fe1+xSiO4/C COMPOSITES *Fride Vullum-Bruer, NTNU, Norway (Inv.)*
15.05–15.25	NOVEL SOLID POLYMER ELECTROLYTES FOR LARGE AND SMALL LITHIUM-BATTERY APPLICATIONS *Daniel Brandell, UU, Sweden*
15.25–15.45	(WHERE) HAS UPPSALA'S BATTERY RESEARCH MADE A DIFFERENCE? *Josh Thomas, UU and LiFeSiZe, Sweden (Inv.)*
15.45–16.00	Summary of the conference – what to do next?
16.00–16.30	**Coffee**

Plenary speakers

LI-ION BATTERIES AND BEYOND: WHERE WE ARE AND WHAT NEXT

D. Guyomard, B. Lestriez, N. Dupré, J. Gaubicher, P. Moreau, F. Boucher, M. Cerbelaud, J. Le Bideau, G. Ouvrard

Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, France. Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France.
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The first part of the talk gives an overview highlighting main application fields of Li-based batteries and batteries beyond, state-of-the-art positive and negative electrode materials, and general research directions needed to improve performance.

The second part illustrates recent developments in our Lab at IMN on advanced electrode and electrolyte materials for next-generation energy storage systems. Our recent activity deals with the following interconnected topics: development of new materials, comprehension of reaction mechanism, characterization and modification of electrode/electrolyte interface, and design of high power and long cycle life electrodes and of safe electrolytes for next-generation batteries. Increasing the power delivered by electrodes is a challenge for some applications. We analyse which parameters limit the power of a thick composite electrode, and we describe a novel concept to boost both energy and power of batteries. The longevity of the batteries depends on the side reactions at the interfaces that must be minimized. MAS NMR, coupled with TEM/EELS and XPS, is developed to quantitatively characterize interface species on electrode materials and their evolution upon battery aging and cycling. We describe recent results on the cycle life improvement of Si electrodes. Comprehension of the end-of-life mechanism and of the origin of irreversibility through the use of multi-technique characterisation, allowed us to propose some key directions for performance optimization. Safety problems of lithium ion batteries need intrinsic solutions. The concept of all-solid-state lithium batteries using an ionic liquid confined in a mesoporous solid is described, it should enable the production of safer Li-ion batteries.

Plenary speaker
December 4, 17.30–18.15

Perspectives on Energy Storage: From Flywheels to Batteries

Daniel P. Abraham

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The development of energy storage technologies is vital to the economic health of nations. These technologies are needed because the demand for energy is seldom constant over time. Excess energy available during periods of low demand can be used to charge an energy storage device, which can then supply the energy during periods of high demand. Portable energy storage devices, especially batteries, are important for consumer electronic applications, such as cell phones and laptop computers. Batteries and supercapacitors are also critical enabling technologies for the development of fuel-efficient vehicles, such as hybrid electric vehicles, plug-in hybrid electric vehicles, and electric vehicles. Electricity storage technologies, such as pumped hydroelectric, flywheel and battery systems, are essential to improving the efficiency and reliability of electric utilities. These systems can be used to follow changing loads during peak period consumer demand, stabilize voltage & frequency, improve power quality, and store energy from renewable sources (wind, solar) that generate energy intermittently. This discussion will provide an overview of energy storage technologies that run the gamut from large-scale pumped hydroelectric systems, medium-scale flywheel systems, to relatively small-scale battery systems. Our current research on lithium-ion batteries, and our perspectives on developments beyond lithium-ion, will be highlighted in this presentation.

CASE STUDIES USING BATTERY DIAGNOSTIC TOOLBOX

Bor Yann Liaw, Matthieu Dubarry, Arnaud Devie

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Battery diagnosis can significantly increase the quality of information from the assessment and evaluation of cell performance and provide temporal quantification on cell degradation. Proper diagnostics can generate significant improvements on reliability and safety of a battery system and its functionality. To understand battery degradation behavior of different battery chemistries in a clear context of cause-and-consequence clearly identified remains very challenging today. Postmortem analyses of a spent cell might reveal the cause of degradation and failure of a battery, but they are not useful to provide temporal resolution for practical battery monitoring, protection, and diagnosis during operation. Without useful diagnostic information, prognosis could lose fidelity in representing the actual situation in cell degradation. In reality, an effective battery diagnosis tool needs two major elements: a reliable method to determine the state of the battery and a high fidelity model to simulate and analyze the complicated but crucial voltage variations as a function of cell operating parameters.

A reliable model and simulation method has been developed and presented by us recently [1] that allows emulating a variety of “what if” scenarios to simulate the corresponding charge discharge behavior under various operating and aging conditions. The model employs three simple, well-known, and quantifiable degradation modes: loss of lithium inventory (LLI), loss of active materials (LAM) and reaction kinetics degradation (RKD), which is often detected by impedance changes in the cell. To simulate possible degradation mechanism that comprises various degrees of contribution from each mode, this model and simulation is capable of providing a realistic estimate of degradation symptoms that can be validated with experimental data.

This work presents two case studies of the aging behavior of (1) two types of commercial GCI || LFP cells with high energy (HE) and higher power (HP) designs, and (2) a comparison of a LTO || NMC cell chemistry that was cycle aged with and without overcharging event. In the first case, the capacity variations as a function of cycle number at four rates, C/25, C/5, C/2 and 1C, at 25°C in cycle aging experiments with the HE and HP cell were analyzed to explain some peculiar aging behavior in the HE cell, which displays a sensitive rate-dependent capacity variation with aging that was not observed in the HP cell. The impact of cell design on aging behavior is thus illustrated. In the second case, the overcharging event on the cell degradation was analyzed to show the impact of the event on cell aging.

References:
[1] M. Dubarry, C. Truchot, B.Y. Liaw. J. Power Sources 219 (2012) 204-216.

Plenary speaker
December 5, 14.00–14.45

ADVENTURES IN POLYMORPHISM: LI_2FESIO_4 AND BEYOND

A. Robert Armstrong

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Lithium transition metal silicates, Li_2MSiO_4 (M=Fe, Mn, Co)[1], have attracted a lot of interest as positive electrodes for Li-ion batteries due to their potentially high theoretical capacities and to their rich crystal chemistry. Polymorphs of these tetrahedral structures can be classified into low (β) and high (γ) temperature forms which differ in the ordering/distribution of cations within tetrahedral sites of an hcp based packing of oxygen. β forms exhibit only corner sharing and γ polymorphs both corner and edge sharing.

Li_2FeSiO_4 samples prepared at different temperatures show the existence of at least 3 different polymorphs. Material prepared hydrothermally at 200 °C exhibits an ordered β_{II} structure. Annealing at 700 °C produces a well-ordered γ_s polymorph in space group $P2_1/n$ [2]. Annealing at 900 °C, with subsequent quenching, yields a third γ_{II} polymorph, space group *Pmnb* [3]. The transitions between these polymorphs as a function of temperature will be discussed along with the effect on the electrochemistry. All polymorphs undergo a structural change on cycling to a fourth polymorph, the inverse β_{II} form [4].

Polymorphism in other Li_2MSiO_4 materials will also be discussed along with the structural flexibility exhibited in this system. This enables a number of substitutions whose effect on structure and electrochemical properties will be described.

1a) A. Nytén, A. Abouimrane, M. Armand, T. Gustafsson and J.O. Thomas, Electrochem. Comm., 7, (2005) 156; b) M. S. Islam, R. Dominko, C. Masquelier, C. Sirisopanaporn, A. R. Armstrong and P. G. Bruce, J. Mater. Chem., 21 (2011) 9811.
2 S. I. Nishimura, S. Hayase, R. Kanno, M. Yashima, N. Nakayama, A. Yamada, *J. Am. Chem. Soc.*, 130 (2008) 13212.
3 C. Sirisopanaporn, A. Boulineau, D. Hanzel, R. Dominko, B. Budic, A. R. Armstrong, P. G. Bruce, C. Masquelier, *Inorg. Chem.*, 49 (2010) 7446.
4 A.R. Armstrong, N. Kuganathan, M.S. Islam and P.G. Bruce, *J. Amer. Chem. Soc.*, 133 (2011) 13031.

Oral presentations

Invited speaker [O1]
December 4, 14.00–14.20

COMBINED COMPUTATIONAL AND EXPERIMENTAL STUDY OF THE ROLE OF CO2 POISONING ON THE ELECTRONIC CONDUCTION AND OVERPOTENTIALS IN LI-AIR BATTERIES

T. Vegge, J.M. Garcia-Lastra, J. Højberg, R. Younesi, Y.S. Mekonnen, J.S.G. Myrdal, K.B. Knudsen, P. Norby

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Li-air batteries hold the potential to surpass the energy density of the Li-ion technology by up to an order of magnitude [1], but Li-air batteries face significant challenges in terms of high overpotentials [2], low current densities [3], degradation and poisoning, e.g., by CO_2 [4]. A detailed atomic level understanding of the fundamental mechanisms governing the electronic conduction, electrode-electrolyte interface reactions and degradation is needed to resolve these challenges.

Here, we present a combined Density Functional Theory (DFT) and Differential Electrochemical Mass Spectroscopy (DEMS) investigation of the interaction of CO_2 with Li_2O_2 formed at the cathode during discharge of aprotic Li-air batteries (see Figure 1a).

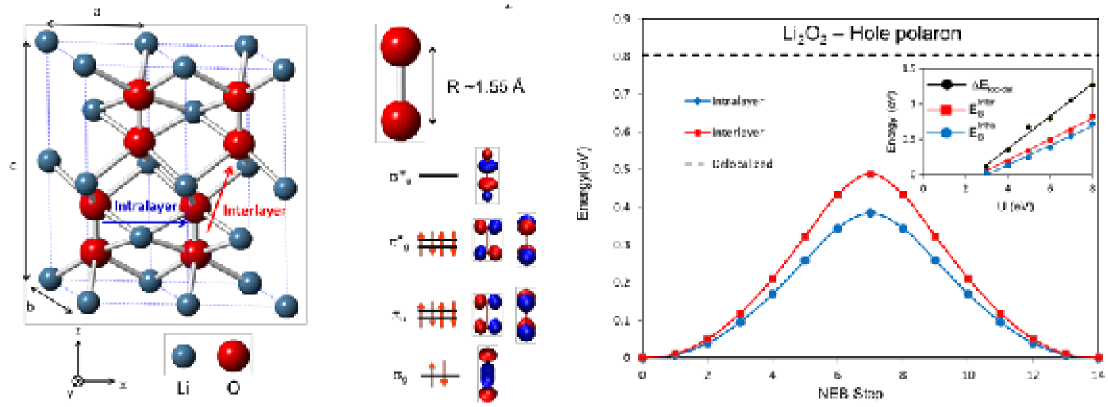

Figure 1: A) The unit cell of Li_2O_2 *repeated twice along the [100] direction. The intralayer (red arrow) and interlayer (blue arrow) paths for the polaron hoping are also shown. Structure and frontier orbitals of the* O_2^{2-} *peroxide ion. [5]. B) Calculated total energy along the intra- (blue circles) and interlayer (red squares) hoping paths in a 4x4x2* Li_2O_2 *supercell using U=6 eV for a hole polaron. Energies of the delocalized states are also shown [5].*

The Li_2O_2 growth mechanisms and overpotentials are investigated computationally with and without CO_2 at different nucleation sites such as steps, kinks and terraces on the (1-100) Li_2O_2 surface. CO_2 is found to bind weakly at steps and kinks on the Li_2O_2 surface, forming a type of lithium coordinated carbonate species (Li_nCO_3); effectively reducing the discharge potential. Trace amounts of CO_2 can also affect the morphological growth directions of Li_2O_2, due to blocking of nucleation centers.

The charge/discharge processes are found to be limited by poor electronic conduction through the insulating Li_2O_2 deposits [5] and the formation Li_2CO_3 resulting from, e.g., CO_2 poisoning may worsen this problem [4].

We also present DFT+U calculations, which determine the formation and transport of hole and electron polarons in Li_2O_2 and Li_2CO_3 (figure 1b). For both materials, we find that the formation of polarons (both hole and electron) is stabilized with respect to the delocalized states for all physically relevant values of U. We find a much higher mobility for hole polarons than for the electron polarons, and we show that the poor charge transport in Li_2CO_3 compared to Li_2O_2.

A combination of computational and experimental results will be presented in this presentation.

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[1] G. Girishkumar, B. McCloskey, A. C. Luntz, S. Swanson, and W. Wilcke, *J. Phys. Chem. Lett.* 2010, **1**, 2193–2203

[2] J. S. Hummelshøj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K. S. Thygesen, A. C. Luntz, K. W. Jacobsen, and J. K. Nørskov, *J. Chem. Phys.* 2010, **132**, 071101

[3] J. Chen, J. S. Hummelshøj, J. S. G. Mýrdal, J. K Nørskov, K. Thygesen and T. Vegge, *Catalysis Today* 2011, **165**, 2-9

[4] S.R. Gowda, A. Brunet, G. M. Wallraff, B. D. McCloskey, *J. Phys. Chem. Lett.* 2013, **4**, 276-279

[5] J. M. Garcia-Lastra, J. S. G. Mýrdal, K. S. Thygesen and T. Vegge, *J. Phys. Chem. C* 2013, **117**, 5568-5577

NEXT GENERATION BATTERIES –
NEW MATERIALS MAKE ALL THE DIFFERENCE

Johan Scheers, Maciej Marczewski, Susanne Wilken, Erlendur Jónsson, Damien Monti, Andrea Boschin, Manfred Kerner, Martin Bergman, Per Jacobsson, and Patrik Johansson

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While the current state-of-the art for electrochemical energy storage in the personal mobility sector is the omnipresent Li-ion battery (LIB), this technology has severe limitations in capacity, life-length, cost, and not the least safety. These obstacles hinder not only extended usage in the already conquered market niches (mobile phones, laptops *etc*), but also prevents the expansion urged for *e.g.* storage for load-leveling of renewable energy, making the electromobility revolution come true by EVs and HEVs, advancing the powering of medical implants *etc.*

Depending on the final application these obstacles can be addressed in different ways – but a common factor is that by advancing the materials used we can move forth both to better LIB's as well as new battery concepts. This presentation will cover some material advances made for the current LIB technology, with special focus on the electrolytes used, but furthermore also the prospects and development of next generation battery concepts like Na-ion, Li-sulphur, Li-air, organic, structural *etc.*

An equally important perspective is how we at Chalmers together with our collaborators cover the full chain of battery (materials) research; from screening materials by predictive quantum mechanical calculations to delicate synthesis efforts, via proper physico-chemical characterization incl. specific safety aspects, to the assembly and testing of research-size batteries including implementation of standardized cycling protocols, and finally ageing and post mortem studies – all these steps are crucially needed for a rational development of new battery materials and concepts based on a fundamental understanding.

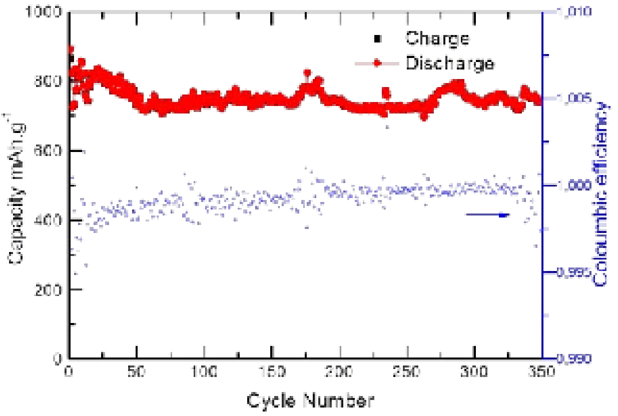

Figure: Cycling data for a Li-sulphur cell developed within the FP7- EUROLIS project – an example of the promise of the next generation batteries.

Invited speaker [O3]
December 4, 14.40–15.00

THE CARBON-ELECTROLYTE INTERFACE IN LI-ION BATTERY ANODES AND CATHODES FOR VARIOUS ELECTROCLYTE COMPOSITIONS

Ann Mari Svensson, Carl Erik Lie Foss, Fride Vullum-Bruer, Ahmet Oguz Tezel, Ingrid Roten Mattson and Benedicte Eikeland Nilssen

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Carbon materials are important constituents in Li-ion batteries, with graphite as the standard choice of anode material, and carbon black, acetylene black or very fine graphite as conductive additive in both anode and cathode. Since the graphite anode operates outside the electrochemical stability window of common electrolytes, the performance relies on the formation of a stable surface film resulting from the reduction of electrolyte, the so-called SEI (solid-electrolyte-interface) layer. In addition to capacity, rate capability and cycling stability, operation in a wide temperature range is of great practical importance; as is also the thermal stability. Electrolyte stability is a challenge for the next generation high-voltage cathodes, causing severe stresses also on the carbon conductive additive. For both anode and cathode, optimization of the carbon-electrolyte interface, with careful selection of electrolyte composition (including various additives) and carbon is a prerequisite for good performance.

The work to be presented here includes the electrochemical performance of graphite anodes in various electrolytes, with emphasis of the performance at reduced temperature, see Figure 1. Thermal stability was investigated by differential scanning calorimetry (DSC). Furthermore, electrochemical characterization has been utilized for the investigation of the stability of various carbon conductive additives for high-voltage cathodes. Experiments have been conducted with standard compositions of cyclic (EC and PC) and linear electrolytes (DEC, DMC, EMC), and with additions of a so-called anion receptor, THFIPB [1].

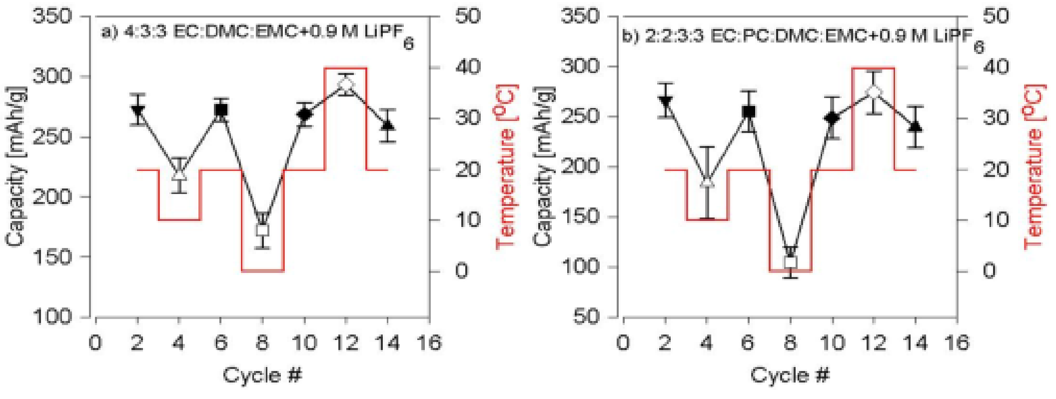

Figure 1. Comparison of capacity of a graphite anode (SLP30 from TIMCAL) cycled at C/8 rate at various temperatures for a) electrolyte composed of 0.9 M LiPF6 dissolved in 4:3:3 EC:DMC:EMC and b) electrolyte composed of 0.9 M LiPF6 dissolved in 2:2:3:3 EC:PC:DMC:EMC.

References

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Invited speaker [O4]
December 4, 15.30–15.50

BATTERY CHEMISTRY RESEARCH ACTIVITIES AT THE RESEARCH GROUP OF APPLIED CHEMISTRY

Ulla Lassi[1,2], Juho Välikangas[2], Tao Hu[1]

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Battery research activities at our laboratory have focused on the preparation and characterization of electrode materials for lithium ion batteries. Research has been carried out in collaboration with research groups of Aalto University and University of Eastern Finland as well as many companies. Several cathode materials, such as $LiCoO_2$ (LCO)[1], $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM)[1], modified $LiFePO_4$ (LFP)[2,3], and LFP-CNT composite[4] have been studied. Anode research has focused on the synthesis and characterization of pure and doped $Li_4Ti_5O_{12}$ (LTO)[5].

Main methods for the preparation of cathode and anode materials have been hydrothermal synthesis and/or high-temperature processing. Several characterization methods have been applied to study surface and bulk properties of battery chemicals. Recently, new laboratory facilities with humidity controlled dry room enabled testing of electrochemical properties of lithium ion battery cells. Currently, both coin cells and pouch cells are prepared and tested. Especially, the effects of slurry properties on the electrochemical performance are studied[1].

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Invited speaker [O5]
December 4, 15.50–16.10

ENVIRONMENTALLY-FRIENDLY PREPARATION AND RECYCLING OF WATER-SOLUBLE ORGANIC Li-ION BATTERY ELECTRODE MATERIALS

Stéven Renault, Alina Mihali, Torbjörn Gustafsson, Kristina Edström and Daniel Brandell

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The growing large-scale production of LIBs makes their environmental impact and recycling a problem that must be addressed. During the last years, organic electrodes have emerged as promising alternatives to conventional inorganic LIB electrode materials due to that they are potentially cheap, environmentally friendly, abundant and recyclable, if derived from biomass *via* ecofriendly processes with minimum energy consumption (Scheme 1). Specifically, molecules containing carbonyl groups have attracted attention due to their redox-active nature and abundance in natural-based compounds. Structures such as quinones, imidates, anhydrides or lithium carboxylates have been successfully used in prototype rechargeable LIBs.

Our goal is to develop an efficient organic electrode material using a minimal quantity of energy and limited produced waste during synthesis, optimization of the electrochemical performances and recycling of the active material from spent batteries. To realize this, we have restricted ourselves to the usage of water and ethanol only, two of the most environmentally friendly solvents.

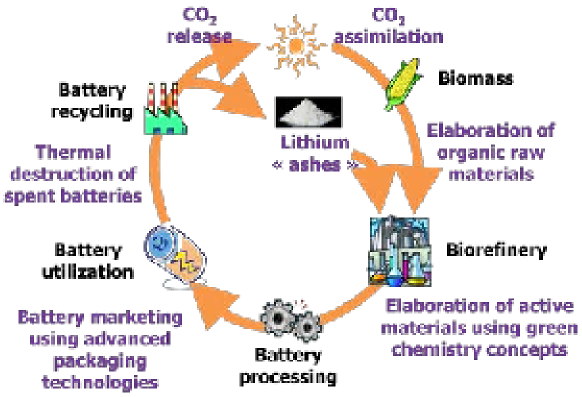
Given the inherent solubility of conjugated dilithium dicarboxylates in water, dilithium *trans-trans* benzene diacrylate has here been selected as a model compound. Dilithium dicarboxylates are insoluble in ethanol or carbonate type solvents which make them good candidates for application as Li-ion battery electrode material.

The low conductivity of the selected material and its poor electrochemical performance can be greatly improved using two simple techniques:

- *in situ* carbon-coating during synthesis while the model compound is in the liquid state enhances the surface contacts between the organic material and the conductive additive after drying.
- freeze-drying for removal of water through sublimation improves the surface area of the resulting material.

The consequence of these techniques on the galvanostatic cycling of dilithium *trans-trans* benzene diacrylate will be shown.

Extraction and recycling of this material has also been investigated using simple filtration/drying sequences from spent batteries and a single thermal decomposition to lithium carbonate. The extracted lithium is then introduced in a new synthesis for the preparation of fresh electrode material, and cycled in a battery. A complete life cycle of the electrode material has therefore been achieved.



Scheme 1 Idealized life cycle of an organic electrode issued from renewable materials

Li-ion battery materials made by atomic layer deposition

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The Atomic Layer Deposition technique is especially suitable for formation of conformal coating of pinhole free films on surfaces with complex geometrical shapes, an architecture most commonly adopted for micro battery designs. Realization of all solid state Li-ion microbatteries should therefore be close at hand, however, no fully functional all solid state ALD-type battery is yet demonstrated. Deposition of Li-containing materials by the ALD technique has shown to be challenging both from a practical and analytical point of view, but progress is being made. The field has advanced significantly within the last few years and electroactive materials suitable as cathode, electrolyte and anode have been demonstrated. The present contribution will give an overview of ALD-type deposition of functional battery materials with the aim of developing all-solid-state batteries.

Oral presentation [O7]

December 4, 16.30–16.45

SINGLE-STEP GAS-PHASE SYNTHESIS OF $Li_4Ti_5O_{12}$ FOR LI-ION BATTERIES

Tommi Karhunen[1,*], Tiina Torvela[1], Juho Välikangas[2], Siru Tuomaala[3],
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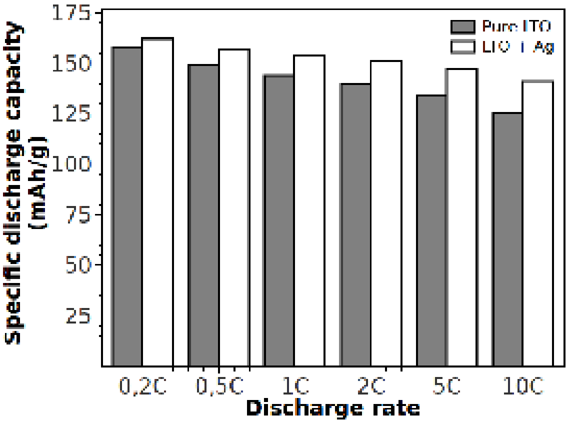
Lithium titanium oxide ($Li_4Ti_5O_{12}$, LTO) is recognized as a promising material for the negative electrode of Li-ion batteries as it is cheap and safe, and has an excellent cycle life. However, the major drawback of LTO is its low electronic conductivity. To overcome this problem the particle size can be reduced to the nanoscale increasing the specific surface area, and decreasing the diffusion lengths within particles and the local current density. For LTO an optimum size of about 17 nm has been reported. However, the current method of solid-state chemical reaction typically produces LTO particles with a diameter of the order of 1 µm. Another solution is to use metal dopants (e.g. Ag). Currently the doping is typically carried out in a separate process which increases the complexity and costs of the production.

Here, pure and doped LTO nanoparticles are prepared in the gas phase with flame spray pyrolysis (FSP). It is a fast, dry, and single-stage process that enables the preparation of materials with high-purity. The precursor solution used for the studies contained lithium acetyl acetonate and titanium isopropoxide in organic solvent. The silver doping was performed by adding silver 2-ethyl hexanoic acid directly into the precursor solution. Finally, a vertical flow aerosol reactor was used to increase the high-temperature residence time and thus the crystallinity of the particles.

The resulting particles were found to be high-purity (99%), single crystalline nanoparticles with a primary particle size down to 10 nm. A uniform dopant distribution was observed in the doped LTO nanoparticles. The silver dopant nucleated independently and deposited on the surface of the LTO particles. The doping was found to improve the specific capacity of the LTO on average by 3% (at 0.2C) to 12% (at 10C) in a Li-ion half cell.



This work was supported in part by the Finnish Funding Agency for Technology and Innovation (40051/09), the strategic funding of the University of Eastern Finland (Namber) and by the Fortum foundation (10-136, 12-072).

OPTIMIZING $Li_4Ti_5O_{12}$ ELECTRODES FOR LOW TEMPERATURE LIHIUM ION BATTERIES

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Graphite negative electrode is known to suffer from loss of capacity or even a safety hazard when charged at sub-zero temperatures. So for outdoor applications, such as power tools and vehicle applications, materials allowing charging at sub-zero temperatures are needed. Lithium titanate ($Li_4Ti_5O_{12}$) can be used as an alternative negative electrode material because its relatively high redox potential (1.55 V vs. $Li|Li^+$) prevents plating of metallic lithium, allowing sub-zero charging. Moreover, as a zero-strain material lithium titanate has potentially long cycle life.

In this study, lithium titanate has been synthetized in a pilot scale process using the same starting material so that the last process steps have been different. Primary particle size of the obtained material is similar before the last process steps. During the more expensive wet process these $Li_4Ti_5O_{12}$ particles suffer damages resulting in truncated particles with a high specific surface area in comparison to dry process. Also tap density of the wet processed material is higher than that of the one obtained from dry processed.

Effect of electrode processing parameters, such as carbon content and thickness of the electrode layer, on the performance of the lithium titanate negative electrode is investigated using half cell measurements. Capacities are found to be similar at room temperature and low charging/discharging currents. With increasing charging/discharging currents, profiles depend on the $Li_4Ti_5O_{12}$ material so that flatter profiles are obtained for the dry processed one with smaller agglomerate size.

The wet processed material is observed to achieve higher capacities at low temperature, and therefore, its cycling behaviour at sub-zero temperatures was studied further in $Li_4Ti_5O_{12}|LiFePO4$ full cells. Several successive charging/discharging cycles at sub-zero temperatures are shown not to affect the $Li_4Ti_5O_{12}$ electrode structure or performance.

The strategy for battery research at IFE, Norway.

Martin Kirkengen,

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IFE is an independent research institute working in the field of energy research. We depend on contract research with industry, with or without support from the national research counsil. This means we are dependent on having a national industrial customer base to justify having activity. The battery supply chain contains many different industry types. While there is no significant battery cell manufacturing in Norway, other elements of the value chain could be good niches for Norway, both upstream and downstream in the value chain, and form the basis of our strategy.

In particular, raw materials for electrode production represent a niche where Norwegian industry has relevant competences. In Li-ion batteries, silicon has been identified as an anode material with great potential, but also with great challenges. One potential market is therefore to provide silicon which has been prepared to be easy to include in batteries. The Norwegian silicon industry has extensive knowledge within silicon production technologies. IFE is aiming to complement this with battery knowledge, so that the industry can provide products with added value, and thus extend their share of the value chain. This is the foundation of the SiNode project with Elkem and our project with Graphene Batteries, working on combining silicon with graphene in order to make the electrode more stable. IFE also has it's own silicon production technology which is currently being adapted to provide high-value silicon, in a project financed by the research counsil. [as presented in a separate abstract.] A separate PhD study is also performed on this material, utilizing the thin film production facilities at the Solar department of IFE.

In the other end of the value chain, margins can be made in the intelligent use of batteries. IFE has recently initiated a project where we aim to make the Norwegian maritime industry more competent battery users. In ships, the payback time for batteries can be in the range of 2-5 years depending on application. But still, the risks are significant. Battery safety is essential when operating a hybrid energy system off shore, with energy amounts far exceeding what we are used to seeing in automobiles, and lifetime matters for investments of millions of NOKs.

In order to achieve high quality research a broad spectrum of competences is needed. IFE does not have a customer base to justify maintaining all these competences. We therefore depend on collaborations with interested partners if we are to achieve international relevance. In such collaborations, we would aim to provide the silicon, with all our competence in silicon specific questions and techniques. This we would like to complement with others specializing in carbon, electrolytes, binders etc. By communicating clear strategic intentions, it is our hope that partners can enter collaborations based on greater trust, and that we can maybe even achieve collaboration outside of projects. An overview of IFEs equipment and lab facilities will be presented, as an invitation for collaboration. This will include comments on the use of the neutron sources of IFEs nuclear reactor as a battery characterization tool.

LI-ION BATTERY CELLS IN HEAVY DUTY HYBRID APPLICATIONS

,Johan Lindström

Scania

Battery challenges at Volvo Cars

Theresa Granerus

The Li-ion battery technology is the number one enabler of electric drive systems. At the same time mastering the new battery technology is the number one challenge on the way to reliable performance and solid profitability for VCC's electrification strategy. Which are the biggest technical challenges for battery systems? What is the life time of these batteries? What is VCC planning to do to overcome the challenges with high cost, system complexity, battery life time, battery safety and complex supply chains?

AGEING FACTORS AND CYCLELIFE TEST RESULT FOR POWER-OPTIMISED LITHIUM-IRON PHOSPHATE CELLS

Jens Groot

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Li-ion batteries have successfully been used as energy storage system for a wide variety of HEVs, PHEVs and EVs. While the performance has increased significantly and the cost has started to decrease, the cyclelife is still not satisfactory, especially not for heavy-duty applications with challenging requirements on reliability and up-time.

Although the ageing mechanisms are complex and non-linear, most studies have identified current rate, temperature and state-of-charge range as the most important ageing factors. However, heavy-duty xEVs are used in a very wide range of operating conditions where temperature, current rate and dynamic load profile characteristics vary over time, between different markets and over time. That is, a specific application such as a PHEV city-bus may be operated very differently depending on customer requirements. Consequently, it is difficult to find a general optimization of energy storage size or to predict the battery ageing rate. Nevertheless, a deeper understanding of ageing factors and their co-dependence may enable a better forecast of cyclelife, thus ensuring better reliability and performance.

The present work includes extensive laboratory testing of commercial $LiFePO_4$//graphite cells followed by an assessment of the ageing using differential voltage analysis, incremental capacity analysis and modeling of ageing using data from half-cell tests. A number of different load profiles have been designed to address ageing at different charge/discharge current rates, state-of-charge ranges, load cycle dynamics as well as temperature. Test results indicate that increased temperature and current rate not always lead to a decrease in cyclelife; batteries subjected to more demanding operating conditions in terms of temperature or current rate may actually show a prolonged cyclelife in some cases. Generally, the main ageing mechanism appears to be loss of cyclable Lithium followed by loss of active negative electrode material.

Oral presentation [O13]
December 5, 11.00–11.20

APPLIED BATTERY RESEARCH FOR HEAVY DUTY ELECTRIC COMMERCIAL VEHICLES

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The focus of the activities of the VTT Technical Research Centre of Finland on electrochemical energy storages is on applied research for heavy duty Electric Commercial Vehicles (ECVs) and their systems. ECVs are here understood to cover heavy road transport such as buses and trucks, and mobile machinery. An extensive experimental testing together with modelling, technology reviews, and broad network of partners is aimed towards solving the problems associated with energy storages.

At the moment, extensive range of lithium-ion cells is being tested to create a comprehensive battery database. In the first stage of testing, characterization and performance tests are conducted in different environmental conditions. Based on the first stage of testing, average cells are selected for further testing. Second stage of testing includes calendar and lifetime testing with cycles and temperatures representing heavy duty use cases. With this database a battery lifetime prediction tool is to be created. First results from the VTT battery database are presented, including performance comparisons between battery cell chemistries, comparisons between cell and module level performance, and battery pack level test results. Performance and selection criteria of batteries for different applications, vehicles and mobile machinery are discussed.

EXPERIMENTAL AND MODELING INVESTIGATIONS OF ELECTRODE DEGRADATION IN BATTERY AGING STUDIES FOR VEHICLE APPLICATIONS

Matilda Klett, Tommy Zavalis, Pontus Svens, Mårten Behm, Rakel Wreland Lindström, Göran Lindbergh

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Battery aging is an important issue due to the high demands of performance and durability of Li-ion batteries for vehicle applications and large efforts are therefore put into the investigation of processes leading to capacity and power fade. Depending on the aging conditions, the degradation can be the combined effect of several different processes occurring in different parts of the cell. Post-mortem analysis of separate electrodes by impedance spectroscopy can be an effective tool in analyzing degradation in terms of electrode properties that directly relate to performance.

The evaluation of the electrode degradation is based on half-cell EIS measurements of harvested electrodes and the comparison of electrode properties at pristine and aged states as evaluated by a physics-based model. The model describes processes and electrode properties that can be physically related to, and is therefore useful for learning about the experimental system. However, physics-based models deal with the issue of requiring a high number of parameters for evaluation. The applicability of the model as a quantitative or qualitative tool is hence to a large extent based on the available information of the electrode properties in the pristine state.

We have studied the effect of different aging conditions on harvested electrodes from lab-scale and commercial cylindrical graphite/$LiFePO_4$ cells. To investigate the effect of cycling and temperature, electrodes from lab-scale cells aged either by a synthetic hybrid vehicle cycle or by storage, both at 22 and 55 °C were collected[1,2]. EIS analysis showed that 22 °C cycling resulted in morphological degradation of the $LiFePO_4$ electrode, while causing increased contact resistances in the composite electrode at higher temperature. For graphite, cycling caused material loss and there were indications of film growth and porosity decrease. However, when going from well-controlled model systems (represented by lab-scale pouch cells) to commercial cells (2.3 Ah), spatial distributions of graphite degradation was found, attesting current density/temperature variations in the cell during use. In the most degraded graphite samples, deposition of a surface film concentrated to the outer layer of the composite electrode was indicated to locally inhibit the electrolyte ion transport.

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Invited speaker [O15]
December 5, 11.40–12.00

FAILURE MECHANISMS IN COMMERCIAL LI-ION BATTERIES

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Following a decade of successful use in small scale portable electronics, Li-ion batteries are currently becoming the technology of choice in power sources for more demanding applications, like electric drive and energy storage for smart grids. These applications typically require relatively large batteries with voltages ranging from 10's to several 100 V and capacities from 10's to several 1000's of Ah.

Safety remains a major concern. The energy content inside a battery cell primarily stems from two sources: the electrochemical energy stored in the electrodes and the chemical energy that can be released from the system if all combustible constituents react with air. The electrochemical energy alone can raise the Li-ion cell temperature up to 700°C, but the total chemical energy may be up to 10 times greater

Battery performance and safety are affected by internal processes, such as material degradation and by external factors, like ambient conditions and mechanic stress. Safety failures due to external triggers, like over-charge, over-discharge, over-temperature, mechanical stress and external short-circuits, have been extensively studied by the industry. Standardized tests have been designed to evaluate cell and battery tolerance to abusive conditions. For Li-ion cells, safety incidents leading to massive recalls have occurred in the field for batteries operating under normal conditions, without obvious abusive situations. These batteries have typically passed industry standard safety tests and failures often occur after significant time of usage. The failures are generally attributed to internal short circuits. The most common explanation for initiation and development of internal short circuits is the presence of foreign particles in or on the cathode. However, it cannot be excluded that thermal runaway may also be derived from physical and chemical changes inside the cell associated with ageing processes, which is the focus of this investigation.

The Lithium-Air Battery: How Difficult Is to Make It Rechargeable?

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The rechargeable Li-air (Li-O_2) battery has attracted attention in recent years due to its high theoretical energy density. However, several obstacles including the instability of electrolyte solvents and salts, poor rate capability, lithium dendrite formation, safety issues, etc have hampered the development of the Li-air battery.[1]

I) Degradation of electrolyte solvents and salts

During cycling of Li-air cells in non-aqueous electrolytes, the oxygen reduction and oxygen evolution reactions (ORR and OER) take place in the cathode during the discharge and charge, respectively. Lithium superoxide and lithium peroxide (LiO_2 and Li_2O_2) as the intermediate and final discharge reaction products form in the cell. However, it has been shown that ORR and OER result in decomposition of aprotic carbonate and ether based electrolytes. Also, ORR and OER decompose most common Li salts like $LiPF_6$, $LiBF_4$, LiTFSI, $LiClO_4$, and LiBOB.[2]

Furthermore, Li_2O_2 as the final discharge product is very reactive, and therefore, it can degrade electrolyte solvents and salts. It has been revealed that carbonate, ether, and dimethyl sulfoxide solvents as well as common Li salts such as $LiPF_6$, $LiClO_4$ and $LiBF_4$ decompose in contact with Li_2O_2, and consequently, form degradation products on the surface of Li_2O_2.[2,3]

II) Issues regarding utilization of Li metal

A proper electrolyte needs to be compatible with lithium metal anode in the Li-air battery. Owing to its very negative potential, lithium metal decomposes aprotic electrolytes as soon as its surface is exposed to electrolyte. As a consequent, a solid electrolyte interphase (SEI) can be formed on the surface on Li metal. This electrode/electrolyte interphase should be stable during cell cycling to protect electrolyte from further decomposition. However, it has been shown that the SEI on Li anode in the presence of oxygen evolves.[2]

Thus, poor performance of SEI on Li anode results in i) dendrite formation, and ii) low columbic efficiency. Therefore, these challenges regarding the utilization of Li metal anode should be investigated carefully. The dendrite formation can ultimately cause an internal short circuit, which produces local heating, often leading to fire. This issue could be hindered by different approaches like using solid membrane, improving cell design, etc. The columbic efficiency of Li plating/stripping on Li anode is significantly influenced by electrolyte solvents and salts as well as by electrolyte additives. The columbic efficiency of Li anode should be improved by using tuning electrolyte chemistry for designing a functional Li anode.

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Oral presentation [O17]
December 5, 12.20–12.40

IMPEDANCE PERSPECTIVES ON LI-AIR BATTERY OVERPOTENTIALS

Jonathan Højberg[1,2], Bryan D. McCloskey[3], Alan C. Luntz[3,4], Johan Hjelm[1], Keld Johansen[2], Poul Norby[1], Tejs Vegge[1]

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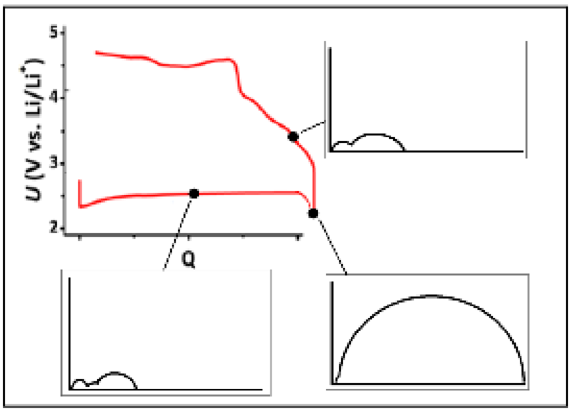

Lithium-air batteries have attracted much attention in recent years because of a potentially high specific energy density and experiments with flat electrodes show that the intrinsic electrochemistry of Lithium-air batteries has a very low overpotential[1]. In real batteries with a porous electrode, the observed overpotentials are, however, significantly larger[2]. The origin of the overpotentials at especially sudden death and during charge has been heavily debated in the literature. Among others, arguments proposed are based on modeling[1], DEMS measurements[2], in-situ TEM[3], and conductivity measurements using a redox-mediator combined with ex-situ characterization methods like FTIR and Raman[4].

In this presentation, a series of electrochemical impedance spectra measured at different states of charge and current densities will be used to analyze three states of the Lithium-air battery electrochemistry; The discharge plateau, sudden death and the initial stage of the charging process.
By combining the measurements with previous results presented by Bryan D. McCloskey and Alan C. Luntz et al. (ref. 1, 2 and 5 among others), the internal resistance in the battery is related to the measured overpotential. This relation is essential to understand the reactions inside the battery.

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Invited speaker [O18]
December 5, 12.40–13.00

CARBON FIBRES IN STRUCTURAL LITHIUM-ION BATTERIES – TAKING ADVANTAGE OF MULTIFUNCTIONAL PROPERTIES

Göran Lindbergh[1], **Maria H. Kjell**[1], **Eric Jacques**[2], **Mårten Behm**[1], **Dan Zenkert**[2]

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Structural batteries, i.e. structural polymer composite materials with intrinsic electrochemical energy storing capability are desired for their potential to both reduce weight and provide the energy needs for mobile phones, laptops or even future electric vehicles. The concept is to employ carbon fibres for mechanical performance and as electrodes in a structural battery, and to use a lithium ion conductive solid polymer electrolyte matrix for mechanical load transfer between fibres and for lithium-ion transport and electronic insulation between electrodes. Carbon fibres are attractive for this type of multifunctional use as graphitized carbon is commonly used both in high performance reinforcements and electrodes, the latter for their ability to store Li ions. The approach, however, is new and faces significant scientific challenges.

Our work shows that carbon fibres can perform on par with ordinary graphite-based commercial electrode materials.[1] The ability for commercially available PAN-based fibres to intercalate lithium is close to that of the theoretical maximum for pure graphite, i.e. as good as state-of-the-art lithium ion (non-structural) battery electrodes. Furthermore, the carbon fibres show excellent mass transport and kinetic properties compared to other carbon-based negative electrode materials. A strong state-of-charge dependence is shown for most electrochemical properties, including the electronic conductivity.[2] The fibres retain their stiffness after lithium intercalation, but lose some strength, although the decrease is small and will have limited practical effect. The strength is regained after discharge and there seems to be a relation between state-of-charge (lithium content) and strength. Repeated electrochemical charging and discharging of the fibres show that cycling does not degrade their tensile properties.[3] Similarly, mechanical load does not affect the electrochemical capacity or rate of charge. Carbon fibres expand longitudinally when charged which seems to explain the drop in strength. Radial fibre expansion up to 10% during charging has also been observed.[4] Recent results also show a newly found pieze-electrochemical effect in carbon fibres which may enable further multi-functionality.[5]

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Invited speaker [O19]
December 5, 14.45–15.05

SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED Li_2Fe_{1+x} SiO_4/C COMPOSITES

Fride Vullum-Bruer[1], **Haitao Zhou**[2], **Fengliu Lou**[2], **Per Erik Vullum**[3], **Mari-Ann Einarsrud**[1] **and De Chen**[2]

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Polyanion materials such as Li_2MSiO_4 (M = Fe, Mn, Co, Ni) have attracted a great deal of interest as cathode material for lithium ion batteries due to its high theoretical capacity (333 $mAhg^{-1}$), low costs, high thermal stability, increased safety, and environmental friendliness [1]. Unfortunately, these materials, like many other promising cathode materials reported in literature, suffer from poor electronic and ionic conductivities [2]. Strategies to enhance the charge transfer include nanostructuring and introduction of a conductive layer such as carbon. Also, it is quite challenging to produce a completely phase pure material. However, the present work has shown that a reduction of the secondary phases can be achieved by introducing additional Fe to produce a hyperstoichiometric $Li_2Fe_{1+x}SiO_4$/C composite.

The work that will be presented here includes sol-gel synthesis of nanostructured $Li_2Fe_{1+x}SiO_4$/C composites, where the synthesis parameters are carefully optimized in order to control pore sizes and pore size distribution as this appears to be a determining factor as to whether the Li-electrolyte complexes are allowed access to the available surface area. Also, results showing the improved electrochemical properties achieved by combining this synthesis route with adding excess Fe will be presented. In addition, sol-gel synthesis has been combined with aligned carbon nanotubes on a substrate in order to produce a 3D cathode/current collector structure without the use of binders and toxic solvents normally employed in the production of cathodes (Fig. 1 below).

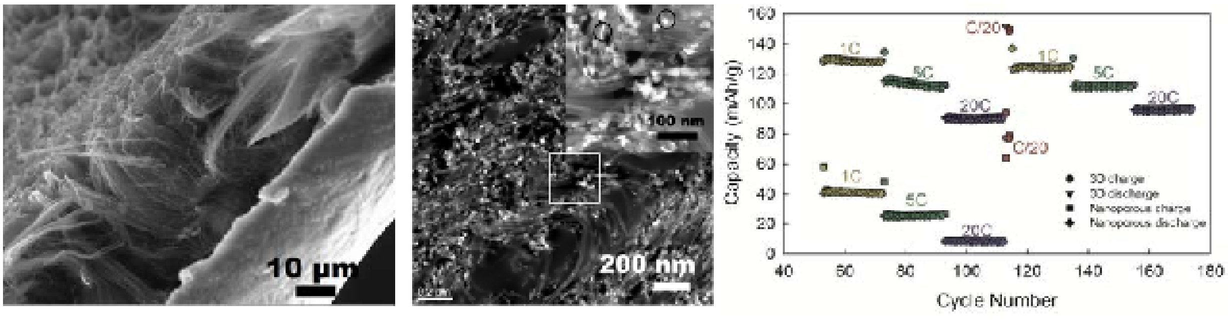

Figure 1: Cross section of a CNT/Li_2FeSiO_4 electrode (left), magnified TEM image showing the nanoparticles on the CNTs (middle), and capacity vs cycle plot comparing the nanoporous and the 3D cathodes (right) [3].

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NOVEL SOLID POLYMER ELECTROLYTES FOR LARGE AND SMALL LI-BATTERY APPLICATIONS

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Solid Polymer Electrolytes (SPEs) for Li-batteries has in recent years experienced somewhat of a renaissance. Since their discovery in the 1970s, this class of material has been targeted for a number of different energy relevant applications due to the mechanical flexibility, their overall stability and their chemical inertness, which is highly beneficial as compared to their liquid counterparts. These materials could for example work well in systems utilizing the Li-metal electrode. However, their intrinsic room temperature ionic conductivity is too low for most applications, for example portable electronics. Improving the room-temperature ion conductivity of SPEs for lithium-ion polymer batteries (LIPB) has therefore been a research target for decades. The possible solutions include adding plasticizers or nano-particles, and polymer modifications such as side-chains or co-polymers to promote material flexibility and suppress crystallinity. Nevertheless, the ionic conductivities of SPEs are generally too low for most applications, and commercial devices use gels or liquids carbonates in combination with an inert separator. However, these suffer from side-reactions which limit the thermodynamic stability of the system and constitute a safety issue.

The recent increasing interest in SPEs has several origins. One example is the development of very small 3-dimensional microbatteries (3DMBs) [1], which generally requires solid state electrolytes. Here, the combined flexibility and mechanical strength of the polymer can be highly advantageous. Another example is batteries where room-temperature operation is less of a necessity, and where elevated temperature operation can be advantageous, which can be realized in some battery vehicle applications. At temperatures >60 °C, SPEs generally have acceptable conductivities, but are still not associated with the rapid ageing experienced in liquid electrolyte systems.

This presentation will address some critical issues regarding SPE development. It will be discussed how monomer functionalization can contribute to improved contacts at the electrode/electrolyte interface, which will improve battery performance [2], and how electropolymerization can be used to tailor ultra-thin SPE coatings onto 3DMB electrodes. Furthermore, advantages of exploring novel polymer host systems, alternative to the conventional polyethers, will be addressed by the example of poly(trimethylene carbonate) (PTMC) [3]. Finally, the hygroscopic properties of conventional SPEs and their influence on the Solid Electrolyte Interphace (SEI) layer formation will be explored by results from X-ray Photoelectron Spectroscopy (XPS).

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Invited speaker [O21]
December 5, 15.25–15.45

(WHERE) HAS UPPSALA'S BATTERY RESEARCH MADE A DIFFERENCE?

Josh THOMAS

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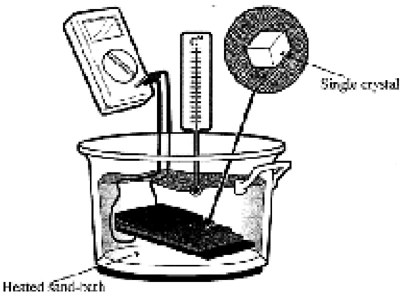

"Modern" battery research began in Uppsala in the late 1970s and was flavoured strongly by the dominant discipline of its founders: crystallography. The first 10 years thus involved "structural studies of relevant battery materials". Our very first activity (*ca.* 1976) had notably Nordic connections – as part of the notorious Anglo-Danish Advanced Battery Project – involving Harwell(UK) and ERL, Odense(DK). The major focus was the Na/S-battery, and our contribution involved structural and MD studies of the (even today) fascinating β/β''-alumina family of materials. At some point in the early 1980s, our research focus then shifted almost overnight with the promise of the Li-polymer battery, facilitated by the advent of "polymer electrolytes". The pivotal point in our research came with our development of the "coffee-bag" cell for *in situ* XRD studies of structural changes occurring on Li insertion into electrode materials [Gustafsson *et al. Electrochim. Acta:* 37 (1992) 1639]. Our work contributed to the development of today's "rocking-chair" Li-ion battery – and crystallographers had become solid-state electrochemists! A piece of work which well illustrates this transition is Bergström *et al., SSI*: 110 (1998) 179 – see figure, where a "coffee-bag" cell immersed in a heated sand-bath under cycling was successively removed for *in situ* XPD analysis in transmission mode. However, the cell also contained small single-crystals (of V_6O_{13}) embedded in the cathode. These could be removed at successive stages in the lithiation process for accurate single-crystal XRD studies. A fascinating picture emerged of sequential superlattice cell formation during Li insertion; even the changes in V oxidation-state could be pinpointed in the structure. A flow of similarly exciting studies has been steadily maintained over the years: anode Li-insertion processes, XPS/PES analyses of the SEI-layer, development of new electrode materials and battery concepts (3D-MBs!) – often accompanied by definitive MD- and DFT-based theoretical calculations to help us understand the in-cell behaviour of Li-ion battery materials. My talk will try to exemplify as many of these studies as time allows. I will also endeavour to indicate where I feel our work can perhaps have made a more lasting contribution.

Poster presentations

Poster presentation [P1]

SCREENING LIFE CYCLE ASSESSMENT OF LITHIUM AIR BATTERIES WITHIN THE STABLE PROJECT

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The EU research project STABLE (STable high-capacity lithium-Air Batteries with Long cycle life for Electric cars) aims to develop lithium-air batteries for electric vehicles. The project focuses on innovations of battery anode, cathode, electrolyte materials and technologies, as well as assembly of battery cells, cost and environmental impact. In the first phase of the project a preliminary streamlined life cycle assessment (LCA) has been carried out to provide input to the cell development. The LCA was complemented by risk assessments of the main materials and chemical substances new to the involved laboratories. In addition, a literature survey was conducted in order to identify key issues relevant to LCA of lithium based batteries.

The scope of the preliminary screening LCA was narrowed down to the manufacturing of the main materials in the initial cell design, i.e. only the first phases of the life cycle of a battery cell. The environmental impact categories used were: climate change, a toxicity score (Usetox) and a weighted single score indicator (ReCiPe). The preliminary LCA, the risk assessments and the literature survey highlight the following to be of extra importance for the next phase of the assessments:

- The lithium metal, the electrolyte and a PVDF binder, carry around ten times more environmental impact per unit of weight than any of the other materials in the lithium-air cell.
- A comparison with lithium-ion cells indicate similar carbon footprint per unit of weight.
- Risk assessments serve primarily to raise awareness and mitigate risks but are also useful for collecting data and knowledge about the materials and chemicals used.
- To enable comparability between battery studies it is important (and not difficult) to report environmental impact both per unit of weight and per unit of energy.
- Assessment of new technologies still at laboratory scale involves a lot of uncertainty that needs to be addressed.
- Most researchers lean towards concluding that the lithium resource is “sufficient”; however, for a technological transition, time and flow rate constraints could be more difficult to handle than available quantities in the ground.
- LCA impact assessment methods are currently not covering lithium resource use nor lithium-ion toxicity.

Poster presentation [P2]

INVESTIGATIONS OF HIGH T_+ POLYMER ELECTROLYTES BY MOLECULAR DYNAMICS SIMULATIONS

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Improving the room-temperature ion conductivity of solid polymer electrolytes (SPE) for lithium-ion polymer batteries (LIPB) has been a research target for decades. The possible solutions include adding plasticizers or nano-particles, and polymer modifications such as side-chains or co-polymers to promote material flexibility and suppress crystallinity. Nevertheless, the ionic conductivities of SPEs are generally too low for most applications, and commercial devices use gels or liquids carbonates in combination with an inert separator. However, these suffer from side-reactions which limit the thermodynamic stability of the system and constitute a safety issue.

In a common LIPB, the polymer plays both the roles of the electrolyte and the separator between electrodes. The polymer should then be flexible, yet strong enough to ensure proper electrode separation. The charge carriers are mostly introduced into the polymer matrix in the form of a dissolved lithium salt. The polymer matrix should act as a solvent in respect of the lithium salt.

One of the major problems is that the Li-ion conductivity is low at the room temperature, thereby limiting battery power. An associated drawback is that the charge transport is dominated by the anions; t_+ is often 0.1-0.2, at best. For an effective Li-ion battery, both t_+ and the ionic mobility should be as high as possible. On the other hand, many of the applications where Li-batteries could play an important role in the future energy system – not least vehicles – could envision a larger operating temperature, where polymers could constitute an alternative.

In a recent study [1], Armand and co-workers have synthesized an SPE with t_+ close to 1. By covalently bonding the anion to a polymer backbone, it is immobilized and the cation transference number thereby significantly raised. By blending this ionic polymer, lithium poly(4-styrenesulfonyl (trifluoromethylsulfonyl) imide) (PSTFSI), with conventional poly(ethylene oxide), the mechanical properties of the electrolyte membrane is improved and the dissolution of Li ions enhanced.

The present work [2] discusses classical Molecular Dynamics (MD) simulations of this polymer electrolyte system. The simulations are carried out to study the conduction mechanisms of the Li-ions, and the role of PSTFSI in Li-ion transport. It is observed that the Li-ion mobility is highly dependent on the PEO mobility, which is then connected to the nano-scale phase separation of the two polymeric systems. This nano-scale structure is difficult to determine experimentally, but can be analyzed with the aid of computer simulations. Furthermore, the temperature dependence of the effects and processes mentioned above are studied to investigate the use of the SPE in elevated temperature (80 °C) applications.

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CHARACTERIZATION OF NaX (X=TFSI, FSI) - PEO BASED SOLID POLYMER ELECTROLYTES FOR Na^+ BATTERY APPLICATION

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At present sodium ion batteries represent a possibly cheaper alternative to lithium ion batteries. Indeed sodium is more abundant than lithium and still shows similar chemical and electrochemical properties. The sodium-ion battery electrolyte research is diverse; organic solvents, polymers, and ionic liquids as matrices are all being used[1,2]. Ion conducting solid polymer electrolytes (SPEs) avoids the use of organic liquids and thereby enables fabrication of flexible, safe and compact solid-state structures. The ionic conductivities of sodium and lithium SPEs based on poly (ethylene oxide), PEO, are comparable[3,4], however, both having low conductivity values: 10^{-5}-10^{-6} Scm^{-1} at room temperature.

The main part of the research performed so far on Na^+ conducting SPEs was carried out during the 1980-90's[3,5]. Here we focus on PEO SPEs with NaTFSI or NaFSI as the sources of Na^+ and with O: Na^+ ratios (n) of 20, 9, and 6. Characterization has been carried out using dielectric spectroscopy, differential scanning calorimetry (DSC), Raman and ATR-IR spectroscopy, in order to evaluate possible differences due to employing different anions and/or different O:Na ratios. The highest ionic conductivity at 20 °C ($5 \cdot 10^{-6}$ Scm^{-1}) is obtained for $NaTFSIPEO_9$. The conductivity increases up to $3 \cdot 10^{-4}$ Scm^{-1} at 70 °C.

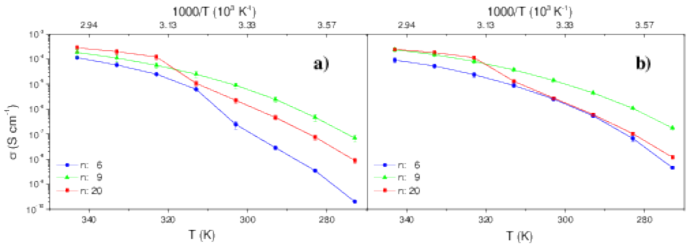

Figure 1. Ionic conductivities of a) $NaFSI\text{-}PEO_n$ and b) $NaTFSI\text{-}PEO_n$ polymer electrolytes in the range 273-343 K.

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Formation of solid electrolyte interphase in solid polymer electrolyte based lithium ion batteries: an XPS study

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The importance of the solid electrode/electrolyte interface (SEI) layer chemistry is well known for conventional carbonate-based liquid electrolyte Li-ion battery systems, and much research has therefore been directed towards understanding its structure and kinetics. However, less attention has so far been devoted to the investigation of the electrode/electrolyte interface chemistry in solid polymer electrolyte lithium-ion batteries. There are a number of questions which are yet unanswered: Is the SEI layer formation similar also in these solid polymer electrolyte systems? What is its composition? Can degradation processes of the battery components be found also on these interfaces?

This work focuses on PEO-based solid polymer electrolytes. Results from different PEO-based electrolytes cycled in graphite "half-cells" will be presented. Since the water content in the polymer electrolyte will greatly affect the electrochemical performance, the effect of water in interfacial chemistry is also interesting and has been studied in this work. Photoelectron Spectroscopy (PES) is an extremely surface sensitive technique and able to determine the local chemical and physical environment. As such, PES is a suitable technique to understand the interface chemistry, and the main focus of this work.

The results obtained for the polymer systems are significantly different as compared to conventional liquid electrolyte systems, in which most of the electrode/electrolyte interface compounds are solvent reduction products. Degradations of LiTFSI salt as well as of PEO, which are otherwise considered to be inert, were observed in the investigations. The S2p spectra shown in Fig. 1 demonstrate salt decomposition on the graphite surface; the sulfur-containing product is supposedly $Li_2S_2O_4$ [1].

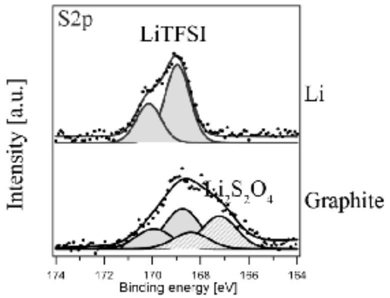

Fig. 1. S2p spectra for Li (top) and graphite electrode (bottom) cycled in a graphite "half-cell" using a solid polymer electrolyte.

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Poster presentation [P5]

ELECTROPOLYMERIZED SOLID POLYMER ELECTROLYTES FOR THREE-DIMENSIONAL MICROBATTERIES

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Solid polymer electrolytes (SPEs) have been considered to be a cost-effective and safe alternative as a replacement for conventional liquid/gel electrolytes in Li-ion batteries. Although the low room temperature conductivity of most SPEs pose limitations, it has been demonstrated that the poor ionic conduction in SPE can be compensated by minimizing the electrolyte thickness in three-dimensional microbattery (3DMB) applications, thus reducing the Li^+ diffusion path length [1]. Both high energy and power densities could be realized in the 3DMB by proper utilization of the electrode surfaces in all three dimensions. To achieve this goal, a conformal and pinhole-free solid electrolyte with a thickness on the micro- and nano-scale would be required during the assembly of whole-cell 3D batteries.

This work presents results of our studies on the integration of electrodeposited SPEs onto Cu_2O coated 3D Cu-nanopillars. Through cathodic electroninitiated polymerization of vinyl monomers – such as poly(propylene glycol) diacrylate and a novel bifunctional poly(oxypropylene) triamine-based monomer [2] – conformal and thin SPE layers consisting of cross-linked polypropylene glycol diacrylate doped with LiTFSI were deposited on the 3D surfaces. Both SEM and XPS characterization results confirmed the presence of a conformal polymer electrolyte after self-limiting electropolymerization. Electrochemical impedance results also indicated that the thin polymer electrolytes obtained may have useful ionic conductivities, e.g. 10^{-5}-10^{-6} S cm^{-1}, at room temperature.

Acknowledgements

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Poster presentation [P6]

SEI FORMATION USING LITDI ELECTROLYTE ON SILICON ELECTRODES

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Silicon is an interesting new negative electrode material in lithium ion batteries (LIB) since it offers high Li-storing capacities. Utilizing Si as a negative electrode material has been proven difficult due to large volume changes during cycling. Although progress has been achieved, cycle life and cycling efficiency is still not sufficient for use in practical LIB. Limiting factors are due to surface interactions between active material and electrolyte forming a solid electrolyte interphase (SEI) layer [1]. It is important to investigate other electrolytes and salts that offer alternative chemistries to passivate the surface and to avoid formation of unwanted byproducts. Several Li-conducting salts have been investigated but the list of topical salts is short and new alternatives are sought for. A recently introduced salt showing promising properties is lithium 4,5-dicyano-2-(trifluoromethyl)imidazolide (LiTDI) [2-3].

In this work, the compatibility of LiTDI as the salt for Si-based composite electrodes was investigated during the first lithiation and de-lithiation. Photoelectron spectroscopy with different photon energies was used to get a more complete understanding of reactions and mechanisms at the surface level and the SEI formation, as well as the reactions and mechanisms in the bulk of the active material. Results show that the SEI is growing continuously until full lithiation and the SEI layer becomes relatively thick. The SEI is mainly composed of decomposition products from electrolyte solvents but also partial LiTDI decomposition was observed. After de-lithiation, evidence of Si that remains in a lithiated state and also possibly a new Si-containing phase was identified. A shift of the SiO_2 peak to lower binding energies during lithiation indicates that also this phase is active during lithiation. Possible mechanisms behind this will be discussed further.

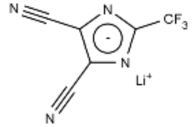

Fig. 1, the LiTDI molecule.

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Poster presentation [P7]

REVIEW OF BATTERY MANAGEMENT SYSTEMS FOR LI-ION BATTERIES

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Consequences of electrical or thermal abuse on some types of Li-Ion batteries (LIBs) may only range from higher degradation rates to permanent damage. On the other hand, some other types of LIBs are especially prone to thermal runaway: venting with flames or explosion. It is the function of a Battery Management System (BMS) to ensure that each cell of a battery pack is charged and discharged properly, operating always inside a safe area limited by certain currents, voltages and temperatures.

An advanced BMS does not only ensure safe operation, also optimizes the energy usage of the energy inside the battery according to internal and external conditions, controls charging process while minimizing energy losses and charging time and provides an accurate estimation or prediction of battery internal states such Impedance, State-of-Charge (SoC), State-of-Health (SoH), State-of-Function (SoF) or Remaining Useful Life (RUL).

Nevertheless, since batteries are non-ideal electrochemical systems and limited sensing and actuation is possible, this is not a trivial task. Voltage, current and cell surface temperatures are the only measurable variables and are related to the internal states through highly non-linear functions. Additionally, the lack of standards or specific references makes more difficult the assessment of battery states as SoH or SoF.

This presentation aims to provide an overview of the state-of-the-art of BMSs for LIBs, covering the entire range of functions that can be included, such as measuring, protection, balancing, external communications, logging, telemetry and analysis or state evaluation. These functions are summarized in Fig. 1.

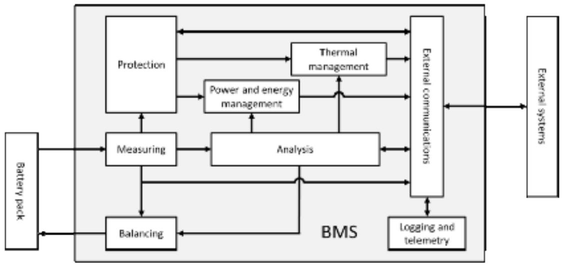

Fig. 1. Overview of management functions of a BMS.

Furthermore, in order to facilitate analysis, BMSs will be classified according to their functionality, applicability, technology, topology and design.

Last but not least, new challenges (e.g. feasibility of laboratory methodologies on real-life environments) and future solutions (e.g. integration of cloud based management of battery information) will be presented and discussed as well, considering possible differences in BMSs hardware and software for present and future LIB technologies.

Poster presentation [P8]

SYNTHESIS OF GRAPHENE NANOSTRUCTURES FOR LITHIUM-ION BATTERIES

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Poor lithium-ion diffusion into the graphene layers due to small interlayer distance limits the intercalation kinetics of the commercial carbon-based lithium-ion batteries (Yoo et al., 2011). An expansion of the interlayer distance e.g. via incorporating fullerene molecules or carbon nanotubes into graphene nanosheet material has been shown to enhance lithium storage capacity (Yoo et al., 2008). We have recently produced layered graphene sheets and new carbon nanostructures, i.e. carbon nanoflowers (CNF) (Fig. 1) using aerosol assisted synthesis (AAS) method. In this two-stage process spherical, preceramic SiC particles with diameter below 100 nm are first produced via atmospheric pressure chemical vapor synthesis (APCVS) from an organometallic precursor hexamethyldisilane (HMDS) (Miettinen et al., 2011). These particles are then annealed at high temperature (2600 °C) in argon atmosphere using an inductively heated furnace. Sublimation of silicon from the precursor SiC particles that contain an excess of carbon enables the formation of the graphene layers and the CNFs. Based on transmission electron microscopy (TEM) analysis the interlayer distance in the produced graphene sheets and the CNFs is 0.36-0.38 nm which is larger than in graphite (0.335 nm). The applicability of this new carbon nanomaterial in batteries is currently under investigation.

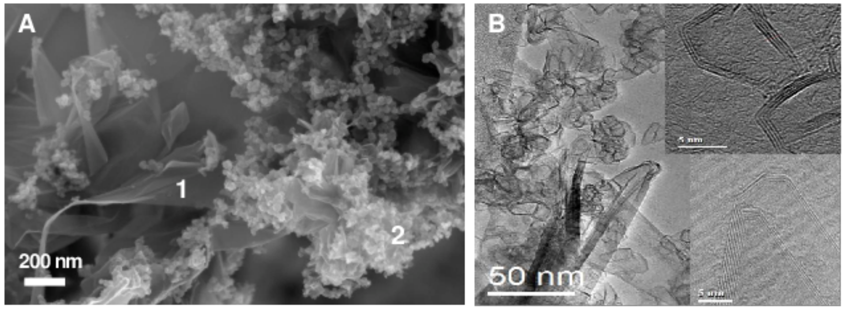

Fig. 1 a) SEM and b) TEM images of the produced graphene nanostructures. Graphene layers and carbon nanoflowers are indicated in the SEM image with the numbers 1 and 2, respectively

Miettinen, M. et al. (2011) J Nanoparticle Res **13**:4631-4645
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Poster presentation [P9]

A STATE-OF-HEALTH ESTIMATION METHOD FOR LITHIUM-ION BATTERIES IN ELECTRIC VEHICLES

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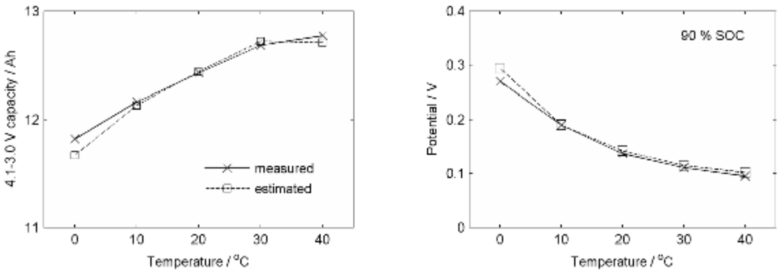
Capacity and resistance are state-of-health (SOH) indicators that are essential to monitor during the application of batteries on board electric vehicles. For the SOH determination in laboratory environment, standard battery performance tests are established and well-functioning. Since standard battery performance tests are not available on-board a vehicle, we suggest a method where those standard tests are applied virtually to a support vector machine (SVM)-based battery model, which is based on variables available during ordinary electric vehicle (EV) operation.

The previously field-tested method [1] is set into a controlled laboratory environment in order to conveniently compare estimation results to experimental standard performance tests [2]. Automotive lithium-ion battery cells are exposed to a testing profile consisting of conventional capacity and resistance tests as well as EV simulation tests based on a current profile from a Volvo C30 Electric. From the collected EV simulation data, SVM models, which link voltage to current, state-of-charge (SOC), and temperature, are created. In a second step, virtual standard performance tests are applied to the data-driven battery models to estimate the SOH indicators.

The figure below illustrates that this SOH estimation method provides accurate estimations of the partial capacity (4.1-3.0 capacity from C/3 discharge) and the direct resistance (instantaneous potential drop during 2C discharge pulse) over a temperature and SOC range (only 90 % SOC shown here; 70, 50 and 30 % data also available) typical for EV operating conditions. The proposed method is moreover found to be suitable for on-board application in respect of processing power and memory restrictions.



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Poster presentation [P10]

Polypyrrole@nanocellulose Composites for Binder- and Carbon-free, High Active Mass, Paper-based Sustainable Energy Storage Devices

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To meet the requirements of the next-generation electronic industry, there is a strong need for the development of lightweight, flexible, inexpensive and environmentally-friendly high-performance supercapacitor and battery electrodes [1]. Contemporary functional electrodes for supercapacitors and batteries generally contain carbon black and polymeric binders to increase the electrical conductivity and to obtain better physical contact between the active materials and the current collector. As these additive materials do not contribute significantly to the electrochemical charge storage capacity, the development of free-standing, high active mass electrodes is becoming one of the key challenges.

Conducting polymers, such as polypyrrole (PPy) and polyaniline are particularly interesting electrode materials in this quest since these polymers exhibit fast redox switching, high conductivity, mechanical flexibility, and low weight [2]. Recent work has also demonstrated that nanocellulose fibers can serve as a promising substrate material for conducting polymer based electrodes due to its high abundance in nature and its well-established industrial use [3]. We have thus shown that electrodes composed of PPy coated nanocellulose composite combine high conductivity with good mechanical properties and that this be can used to obtain free-standing, additive-free high-performance supercapacitors electrodes [4].

The present communication will focus on the results of our recent research on the possibility of using polypyrrole coated nanocellulose fibers in the manufacturing of free-standing, high active mass paper electrodes for sustainable energy-storage devices. It will be shown that this type of devices exhibit high cell capacitances at high current densities during thousands of cycles in aqueous solutions and that this approach holds great promise for the fabrication of high performance electrodes for advanced energy-storage devices.

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Poster presentation [P11]

OPTIMIZING THE PERFORMANCE OF ORGANIC LI-BATTERY ELECTRODE MATERIALS

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Organic electrodes represent a promising alternative as new electrode materials for Li-ion batteries (LiBs). Among the different existing categories, especially conjugated carbonyl materials have gained interest due to their abundance, cheapness and recyclability. However, they are associated with three major drawbacks which prevent their commercial usage: solubility in liquid electrolytes, poor volumetric density and poor conductivity [1,2].

Recently, dilithium trans-trans benzenediacrylate ($BDALi_2$) performances have been improved by a simple method such as in situ carbon-coating in the liquid state [3], but the large particle size obtained after drying restricts the performance at elevated current rates. Combining the benefits of in situ carbon-coating with a high surface area, would therefore be beneficial. Here freeze-drying has shown to be a useful method for reducing the size of water-soluble particles and to be compatible with in-situ carbon-coating [4].

A series of aqueous solutions have been prepared with different concentrations of $BDALi_2$: 2, 5, 6, and 7 wt%. The samples were submitted to a freeze-drying process, where after electrodes were prepared by mixing the resulting powders with carbon SP (33 wt%).

Galvanostatic cycling performed between 0.9 and 3 V at a rate of 1 Li^+ per 10 h in 1 M LiTFSI/DMC electrolyte, showed that the best observed performance is seen for the 6 wt% material. An improvement in particle size can also be observed. The combination of freeze drying with in-situ carbon coating was expected to give even better results but, this was not the case, which might be explained by a high cell resistance resulting from a poorly connected carbon matrix in the electrode.

By increasing the carbon SP content to 50 % of the total weight (using a sample of 6 wt% of dispersed $BDALi_2$ in solution and there after freeze-dried), a clear improvement could be made, indicating that this problem can be overcome. Galvanostatic cycling at a comparatively high C-rate showed promising results which cannot be explained merely by the additional amount of carbon additive: good capacities and moderate capacity fading are achieved when cycled at C/2 and 2C.

A simple and potentially cost-effective method for optimizing the electrode formulation of water-soluble organic electrode material for LiBs will thus here be presented, using a combination of in situ carbon coating and freeze-drying.

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Poster presentation [P12]

CONDUCTING REDOX POLYMERS – NEW CANDIDATES FOR ORGANIC ELECTRODE MATERIALS

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Conducting redox polymers composed of polypyrrole with covalently attached hydroquinone groups have been studied.[1] This is a rare type of polymers in that they are both conducting and redox polymers. At low potentials, the polymers behave as conducting polymers and exhibit capacitive charging similar to that of unsubstituted polypyrrole. At higher potentials, the hydroquinone units are oxidized, with the behavior of a redox polymer. In the present study, the redox activity of the pending groups was found to have a large influence on the doping of the polypyrrole backbone. This effect has, to the best of our knowledge, never been observed previously. Electrochemical and in situ spectroscopic methods were used to investigate this phenomenon. EQCM experiments also provided insight into the redox reactions of the backbone and pending groups, and the interplay between them. Conducting redox polymers might find use as electrode materials in organic charge storage devices. Small organic compounds, i.a. quinones, that have previously been suggested for this purpose often suffer from slow kinetics due to high resistances, and low cyclability due to dissolution.[2] Immobilization of the redox active units on a conducting polymer decreases both the resistance and the solubility, while maintaining a high specific capacity. The two-electron redox reaction of the quinone units in these polymers yields a theoretical capacity of approximately 300 mAh/g.

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ELECTRODEPOSITION OF VANADIUM OXIDE ON NANOSTRUCTURED ALUMINIUM SUBSTRATES

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Fabrication of 3-D microbatteries requires techniques that allow the manufacturing of 3-D current collectors coated with thin layers of active materials and suitable electrolytes, e.g. polymer or solid state electrolytes [1, 2]. Electrodeposition has emerged as a particularly promising tool for this type of fabrications, enabling easy and cost-effective preparation of 3-D microbattery components [1]. Although, extensive work has been performed regarding the synthesis of nanostructured anode materials [3], there is a need for corresponding development of 3-D cathodes. Cathode materials mainly include intercalation compounds such as: oxides, phosphates and sulphides, which require well defined lattice planes to enable reversible lithium ion transport within the structures [1, 4]. Electrodeposition of cathode materials is therefore generally more challenging than its anode counterpart, particularly as the low temperature synthesis technique limits the possibility to deposit highly crystalline materials. Vanadium oxide is an interesting microbattery cathode candidate based on its multiple valence states, the possibility to electrodeposit the material as well as its relative high abundance in nature [5].

This study is focused on the use of electrodeposition to coat aluminium nanorods with V_2O_5 thereby fabricating an inexpensive and versatile 3D-cathode. The intrinsic hurdles to attain stable V_2O_5 coatings without compromising the underlying Al structures are described and the crucial points addressed during the synthesis process are discussed, as well as the novel strategy implemented to facilitate V_2O_5 electrodeposition on nanostructured Al current collectors.

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Synthesis and electrochemical behaviour of tin films on gold

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Tin films on gold have been prepared via electrodeposition from tin citrate solutions. These films, as well as the nanometer thin tin oxide layer formed on these films in contact with air, have been characterized using XRD, XPS, SEM and electrochemical techniques.

Cyclic voltammetry was employed to gain an improved understanding of the electrochemical reactions taking place when cycling the tin films against a lithium counter electrode. Although the reduction of tin oxide to tin is generally considered to be irreversible in lithium ion batteries, our experimental data suggests the presence of a certain degree of reversibility for the tin oxide conversion reaction when cycling in potential intervals above 0.9 V where interferences from the alloying reaction between tin and lithium are avoided.

The reaction products formed upon the cycling were investigated using XPS and the results suggest that a tin fluoride is responsible for the reversible behaviour seen when the alloying reaction is avoided.

Poster presentation [P15]

FIRST PRINCIPLE INVESTIGATION OF $NaFe_{0.5}Co_{0.5}O_2$: A NEW CATHOD MATERIAL.

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The research interest in Na ion batteries has increased considerably in the past years. It is due to possible application as alternative to lithium ion batteries in large energy storage systems such as electrical cars [1-3]. Sodium based batteries reduces production cost (in comparison with lithium batteries) as well as avoid geopolitical limit of lithium sources. Recently, layered NaFe0.5Co0.5O2 shows to have a large reversible capacity and excellent rate-capability, which are clearly better than those of the well known NaCoO2 achieves on the basis of NaFeO2-derived sodium insertion materials [4]. The main idea of this work is to apply the framework of the density functional theory as implemented in Vienna ab initio simulation package (VASP) to have insights into the phase stability, electrochemical properties and electronic structure of NaFe0.5Co0.5O2 cathode material. We have predicted lattice constants and atomic fractional coordinates for each case (the "desodiated" limit and "sodiated" limit). Furthermore, relevant battery-related properties such as average voltage, energy density and specific energy have been derived.

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Poster presentation [P16]

TiO_2 NANOPARTICLES FOR LI-ION BATTERIES

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TiO_2 nanoparticles has been considered a very promising alternative to commercial graphite and $Li_4Ti_5O_{12}$ as anode material in Li-ion batteries.[1] TiO_2 exists in several crystal structures of which anatase, rutile and TiO_2(B) are the most promising for Li-ion batteries. The theoretical capacity of TiO_2 in various polymorphs is 335 mAh/g compared with 372 mAh/g for graphite and 175 mAh/g for $Li_4Ti_5O_{12}$. In order to achieve a capacity close to the theoretical value for TiO_2, nanostructuring of the particles is essential. The potential for Li-insertion/extraction in TiO_2 is in the range of 1.0-2.5 V vs. $Li\text{-}Li^+$, whereas the working potential of graphite is below 0.2 V. While the higher working potential results in lower energy density, it also implies that undesired reactions with the electrolyte is avoided, and thus may give increased safety, stability and cycle and shelf life. Furthermore, TiO_2 exhibits good low-temperature properties[2] and the good rate performance of TiO_2 nanoparticles may give superior power density compared with graphite. Depending on the synthesis and processing the price of TiO_2 and graphite may be comparable, and therefore TiO_2 could soon find its way into commercial Li-ion batteries.

In this work TiO_2 anatase and rutile nanoparticles are synthesized by facile, scalable, low-temperature and hydrothermal methods. The structural properties, including particle size, morphology, crystallinity and specific surface area are investigated by Rietveld refinement of Powder X-ray Diffractograms (PXRD), Transmission Electron Microscopy (TEM) and the Brunauer-Emmett-Teller method (BET). The structural properties are related to the electrochemical Li-insertion/extraction at various currents in half-cells, with Li as counter electrode.

Furthermore, in-operando X-ray diffraction is performed on half-cells while charging/discharging.

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Poster presentation [P17]

BICONTINUOUS CARBON ELECTRODES FOR 3D MICROBATTERIES

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The rapid growth in microbattery research is stimulated by the need for miniature power sources for use in autonomous sensing, wireless communications, medical implants and so forth. Currently either thin film or thick film microbatteries are in common use. However, 2D electrode geometries suffer from severe limitations and are unable to meet the demands for both high power and high energy densities. Hence, a shift to 3D configuration has been identified as a feasible solution to alleviate the drawbacks of the 2D approach. With this end in view, a variety of 3D electrode designs and fabrication techniques are being explored.[1–3]

Of all the techniques studied so far, synthesis of electrode structures via templates is the most commonly applied. Electrodeposition of nano-pillars through porous alumina[4] and synthesis of bicontinuous and interconnected electrode structures making use of self-organized polymer nanoparticles are shining examples in this regard. Three dimensional ordered macroporous (3-DOM) electrodes have been synthesized mainly using polystyrene and polymethyl methacrylate nanospheres and are widely investigated for microbattery applications.[5] Other methods include sol-gel synthesis of aerogels and template synthesis of carbon foams from high internal phase emulsion (HIPE) polymer precursors[6]. Porous and interconnected electrodes based on carbon foams, 3-DOM structures and aerogels offer the combined benefits of large specific surface area, high porosity and buffering against volume change during cycling.[3] Whereas they provide plenty of room for depositing the active materials, the electrolyte and the current collector(s), they are unfortunately associated with low volumetric energy densities and high ohmic losses. Success with porous electrode designs, therefore, hinges on the ability to prepare materials with optimum porosity, less tortuous channels and acceptable conductivity[5].

In this work, we demonstrate the use of emulsion-templated porous polymers as precursors for the manufacturing of bicontinuous carbon structures (foams).[7] The obtained carbon foams are coated with polyaniline by electrodeposition and $LiFePO_4$ using the Pechini sol-gel method.[8] Several techniques are used to fully characterize the carbon foams and the composites prior to electrochemical testing.

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Poster presentation [P18]

ADVANCED OXIDE POWDERS BY SPRAY PYROLYSIS

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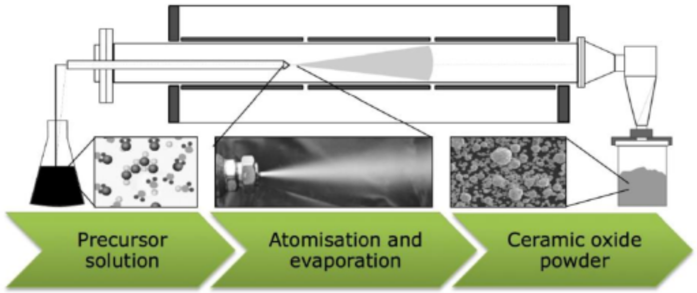
Powder quality is the key for obtaining components of high performance. Characteristics such as particle size, particle size distribution, surface area, homogeneity, and purity influences both sintering behaviour and functional properties of the final material. Spray pyrolysis is a wet-chemistry route to produce complex oxides in the sub-micron range with excellent properties. A water-based precursor, mixed in stoichiometric ratios, is atomised by a nozzle and sprayed into a rotating furnace in which the liquid evaporates forming hollow spheres consisting of metal oxides. Furthermore, the as-prepared powders are thermally treated to completely decompose and the particles are broken down during milling.

Ceramic Powder Technology AS (CerPoTech) is a spin-off company founded at the department of Materials Science and Engineering at NTNU. CerPoTech specializes in development and manufacturing of advanced oxides for various applications, such as solid oxide fuel cells, ceramic membranes, batteries, piezo- and thermoelectrics. Since the start-up in 2007 the company has been partner in four EU-projects (FP-7) and has over 50 different materials in the portfolio. During 2013 the company moved into new facilities outside the campus and expanded its production capacity and ability to deliver large batches.



Poster presentation [P19]

Ternary and quaternary electrolyte mixtures of glyme solvents for improved cycle stability of the lithium sulfur system

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Increasing attention in lithium battery research is paid to post lithium ion batteries as a result of the limited capacity of Li-Ion batteries. The lithium sulfur system is known for more than four decades and exhibits a theoretical capacity of 1,672 mAh g^{-1} and gravimetric energy density of 2,600 Wh kg^{-1}. The abundance of sulfur as waste product during oil refinery makes this active material inexpensive compared to many currently used transition metal oxide intercalation compounds, such as lithium cobalt oxide. Moreover the toxicity of the reaction products and cell components are considered to be low[1].

However, sulfur and its reduction product Li_2S are both electronically insulating and insoluble in the electrolyte. The low average cell voltage of only 2.2 V necessitates the use of lithium metal anodes to maximize energy density at this end. Anode surface expansion as a result of stripping and plaiting of lithium during discharge consumes electrolyte components continuously. Additionally, the so-called polysulfide redox shuttle, an internal discharge mechanism, leads to poor capacity retention, self discharge and substantial loss of active mass upon cycling[2].

The development of highly porous carbons as component in composite cathode formulations, in order to confine reaction intermediates soluble in the electrolyte ($Li_2S_{x>3}$) in the host structure and prevent the diffusion into the bulk electrolyte[3], triggered the publication of numerous studies exploring this approach. One needs to bear in mind, that the solubility of these intermediates are crucial for the kinetics of the cell reaction[4].

PEGDME-500 was previously identified by our group to improve initial discharge capacity due to higher solubility of low-order polysulfides, which retards cathode passivation[5,6]. In this follow-up study we modified the established electrolyte mixture comprising of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) with relatively small amounts (< 15 vol.%) of higher molecular glymes. After an considerable drop in capacity on the first initial cycles the capacity retention is significantly improved when compared with the frequently reported DOL:DME solvent mixture. Since DME was reported to form parasitic reduction products in contact with lithium it is our goal to explore the possibility to use the improved dissolution power of these ternary and quaternary solvent mixtures to reduce the DME content. Combination of these solvents with electrolyte additives might eventually yield an optimized electrolyte system with smaller losses of active material, good wettability / penetration of the cathode matrix and suitable film forming / interface stabilizing properties on the anode side.

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Poster presentation [P20]

A high-throughput production method for powdered silicon for high-capacity anode material for Li-ion batteries

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The use of silicon as part of the anode in Lithium ion batteries enhances the possible storage capacity greatly. While the graphite anode used in standard Li-ion batteries has a theoretical capacity of about 400mAh/g, the theoretical capacity for Si is about 4000mAh/g. This is due to the fact that graphite can accept one Li per six C-atoms, while Si can incorporate 4.2 Li per Si atom. To take out the potential of silicon anodes, specific properties of the silicon are needed. In particular, the expansion associated with full charging of the Si is large, leading to cracking of particles and very detrimental surface effects. The methods explored in order to circumvent these problems have been slow and too expensive for commercial use, using lithography, incorporation of silicon in carbon nanotubes or similar methods.

This presentation shows results from using a silane-based free-space reactor in order to produce silicon particles with a suitable microstructure for use in Li-ion battery anodes. The silane gas is decomposed in a controlled environment with a temperature of 500-600 °C. The current pilot has demonstrated production of up to 200 g/hour in an easily up-scalable lab reactor. Particles of diameter from 100 nm and up to 500 nm has been produced with a relatively small size distribution.

The presentation entails an explanation of the principles of the production method and an analysis of the microstructure and crystallinity of the produced particles. Results from initial testing of the material in half cells of Li-ion batteries will also be presented.

Figure 1. An example of the produced silicon powder material.

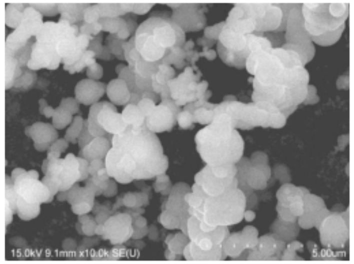

Figure 2. SEM image of the microstructure of the silicon particles.

ALL FLUORINE-FREE ELECTROLYTES FOR LI-ION BATTERIES

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Electrolytes based on $LiPF_6$ and carbonate solvents are the almost exclusive choice for small-sized Li-ion cells. However, the poor thermal stability of $LiPF_6$ and low flashpoints of linear carbonate solvents are intrinsic safety disadvantages that limit the upper temperature of operation to T<60°C and hinder application of these electrolytes in large-sized batteries. The toxicity and bio-accumulation of fluorine decomposition products vented at cell failure are additional safety problems associated with these standard electrolytes [1]. The problems can be addressed by the development of more thermally stable materials and by avoiding the use of fluorine containing salts altogether.

The development of salts and solvents with nitrile functionality are being pursued as interesting alternatives to electrolytes with standard compositions [2,3]. In this work we present physical and electrochemical properties of a series of novel electrolytes based on lithium salts with nitrile groups [LiN_5C_4 (LiDCTA) and $LiB(CN)_4$]. These salts are dissolved in liquid polyethers [$CH_3O(CH_2CH_2O)_nCH_3$ (PEGDME)] and soaked in electrospun polyacrylonitrile separators [$(CH_2CH\text{-}(CN))_m$ (PAN)].

Thermal properties, ion conductivity, oxidation stability, and cycling data of the electrolytes in $Li/LiFePO_4$ cells – at ambient and elevated temperatures – are reported. The role of the anion and solvent are addressed by a comparison with reference electrolytes incorporating the standard $LiPF_6$ or LiTFSI salts, and with propylene carbonate (PC) as an alternative to PEGDME. We also discuss changes in the physical properties of the electrolytes by using binary or ternary solvent mixtures, with adiponitrile as the main component, in place of PEGDME.

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LITHIUM-AIR BATTERIES: BATTERY MANAGEMENT AND SAFETY

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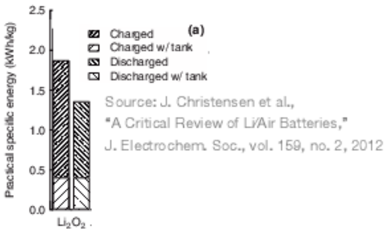
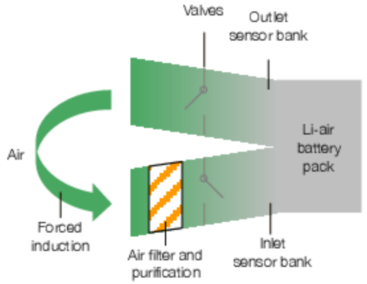


Source: J. Christensen et al., "A Critical Review of Li/Air Batteries," J. Electrochem. Soc., vol. 159, no. 2, 2012

As the lithium-air technology advances, the use of these new batteries becomes a topic of its own. Multiple researchers emphasize the relation between lithium-air batteries and electrical vehicles due to the increased specific capacity. The notion of a new battery technology that allows for more than double the driving range is very enticing, but as with all energy, the release must be accomplished in a controlled manner.

To enable safe energy release and maximize battery performance it is necessary to utilize a battery management system (BMS). BMSs commonly has three key functionalities: protection, performance, and interface. Each of these functionalities are tuned toward the governed battery technology and therefore an extensive understanding of both the applications and battery technology is essential.



The lithium-air technology is still in the early stages of development and it is therefore necessary to make assumptions on the design of a future lithium-air battery pack. From a system level perspective the main differences between lithium-air and lithium-ion batteries is the porous cathode that requires oxygen for the Li_2O_2 formation. Since pure oxygen is difficult to store efficiently onboard a vehicle - as compressed oxygen is hazardous if the vehicle should be involved in an accident - the oxygen must come from the atmospheric air. The air is assumed to require some form of purification and the pressure and amount of oxygen must be monitored and, if possible, managed.

The safety of lithium-air batteries is vital if the technology is to be used in electric vehicles, but it is known from other lithium battery studies that the metallic lithium anode can cause lithium dendrite formation that could lead to internal short circuits and hazardous thermal run-aways. Lithium-air batteries are also affected by overcharge, high currents, and thermal operating windows. Thus many of the functionalities from battery management systems for lithium-ion batteries can be used to mitigate the safety risks of lithium-air batteries. On-board electrochemical impedance spectroscopy which may be used to enhance the BMSs ability to predict safety critical events and even enhance battery parameter estimations by using real-time impedance data and dynamic battery modelling.

Physics-Based Battery Life Prediction Models

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The lifetime of lithium-ion batteries is still challenging to predict and originates in the complex impact battery design and operating conditions have on degradation. The fact that the operating conditions a battery experiences in some applications are innumerable adds on to the complexity and also makes experimental lifetime determination difficult. Physics-based modeling with well-characterized degradation mechanisms can provide the opportunity to make realistic predictions for numerous types of conditions and at the same time identify the cause of the degradation.

Experimental methods are currently being developed as means to extract model parameters describing degradation for certain battery cell chemistries. The methods are based on high precision measurements together with strategic cycling scenarios (1). For instance, low current cycling using high precision equipment can detect the loss in cyclable lithium, which is manifested in the coulombic efficiency being below 100% (figure 1). The utilized physics-based models account for porous electrode theory, concentrated solution, and intercalation in active electrode materials (2). Emphasis is on capturing local variations, since observations in recent post-mortem studies of battery cells showed lifetime to be influenced by degradation related to mass transport in the electrolyte-filled pores (3). A simulation example is displayed in figure 2, where 1C discharge-charge cycles have been modeled. The model includes some degradation in the negative electrode due to growth of a lithium-consuming SEI layer accompanied with increased SEI layer resistance (4) and decreased porosity (5). The discharge curves (Fig. 2a) predict increased polarization and capacity fade, with reduced porosity (Fig. 2b) being one important contributor.

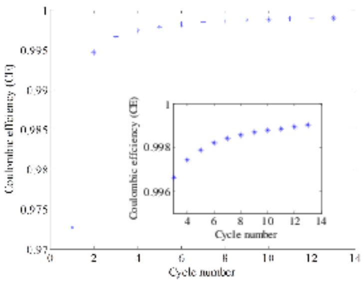

Fig. 1. Measured coulombic efficiency for C/20 charge-discharge cycling between 0-100% SOC in a commercial KIC-PHET (graphite/$LiFePO_4$) cell.

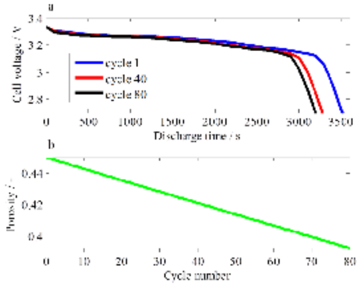

Fig. 2. a) Discharge curves (at what rate?) and b) change of negative electrode porosity (near separator) with cycle number in graphite/$LiFePO_4$ cell.

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IN-SITU SYNCHROTRON PXRD STUDY OF SPINEL $LiMn_2O_4$ NANOCRYSTAL FORMATION

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Many solvothermal reactions have a great potential for environmentally friendly and easily scalable way for producing nanocrystalline materials on an industrial scale. Here we study hydrothermal formation of spinel $LiMn_2O_4$ which is a well-known cathode material for Li-ion batteries. The $LiMn_2O_4$ nanoparticles are formed by reducing $KMnO_4$ in an aqueous solution containing Li-ions. The reducing agent is an alcohol (here ethanol) and the reaction takes place under high pressure and temperature. The $LiMn_2O_4$ nanocrystals are unstable towards further reduction to Mn_3O_4 nanocrystals. Proposed reaction route for this system is shown in equations (1) and (2).

$$(1)\quad 4LiOH_{(aq)} + 8KMnO_{4(aq)} + 7CH_3CH_2OH_{(l)} \overset{\Delta}{\rightarrow} 4LiMn_2O_{4(s)} + 8KOH_{(aq)} + 7CH_3COOH_{(l)} + 5H_2O_{(l)}$$

$$(2)\quad 12LiMn_2O_{4(s)} + 5CH_3CH_2OH_{(l)} + H_2O_{(l)} \overset{\Delta}{\rightarrow} 8Mn_3O_{4(s)} + 12LiOH_{(aq)} + 5CH_3COOH_{(l)}$$

Our group has developed an experimental technique for in-situ measurements of solvothermal reactions under sub- and supercritical conditions [Becker et al, J. Appl. Crystallogr. (2010) 43]. The technique uses synchrotron X-ray radiation to measure time resolved powder x-ray diffraction patterns while the reaction is happening thereby giving real time information on crystalline phase formation, particle sizes and other structural properties for the reaction being studied. The in-situ setup can also be used for studying solvothermal reaction using other types of measurements, such as SAXS and total scattering.

In-situ measurements at different reaction temperatures have been conducted to see how the formation rate and particle growth is affected by temperature while the precursor concentration is kept constant. The precursor solution is an aqueous solution with Li:Mn:EtOH molar ratio of approximately 1:2:7 and the reactions conditions are constant temperature at 220°C, 260°C, 300°C, 350°C and 400°C at 250 bar.

First results show the formation of the $LiMn_2O_4$ and Mn_3O_4 phases, the growth of the nanocrystals of each phase and evolution of structural properties (such as unit cell constants) as a function of reaction time. Further analysis will involve estimation of reaction rate constants and reaction mechanism using and Johnson-Mehl-Avrami kinetic theory. Activation energies for each of the reactions can be calculated using Arrhenius equation. These information give us better fundamental understanding of the hydrothermal reaction system.

EFFECT OF ANION RECEPTOR ON Li-ION BATTERY PERFORMANCE IN $LiPF_6$ AND LiF CONTAINING ELECTROLYTES

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In response to the need for high energy density batteries, dual carbon cells are promising systems. In such cells, carbonaceous materials serve as both anode and cathode active materials that intercalate Li^+ and PF_6^- or (F^-) ions respectively. The major shortcoming associated with the use of LiF as the salt is its limited solubility in organic electrolytes (1). Anion complexing agents (i.e. Trishexafluoroisopropyle-Borate, THFIPB) are employed as the modifying additives to promote LiF dissolution (2). Therefore its compatibility with the anode and cathode chemistries should be addressed.

This work relates to the effect of THFIPB on Li^+ intercalation into SLP50 (TIMREX, TIMCAL) in both 1M $LiPF_6$ and 1M LiF in EC:DEC(1:1 wt.%). Cell performances at different temperatures and (dis)charge rates are discussed. SEI chemistry and Li^+ desolvation process are discussed in terms of electrochemical impedance of anode materials.

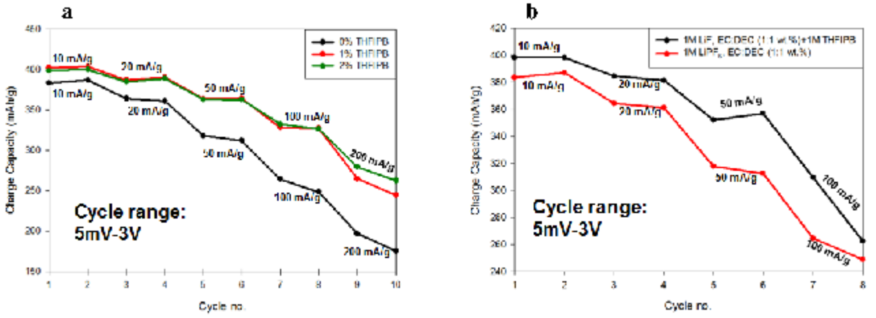

Figure 1. **a)** Charge capacity of SLP50 in 1M $LiPF_6$ with and without THFIPB. **b)** Comparison of the charge capacity of SLP50 in 1M $LiPF_6$ and 1M LiF. Solvent mixture for all the experiments was EC:DEC (1:1wt.%).

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USING COLLLIDAL PROCESSING FOR CONTROL AND DESIGN OF PORE STRUCTURES IN ELECTRODE LAYERS

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The pore structure of the electrode layers is important for the performance and aging of batteries with liquid electrolytes. Ions are transported by the electrolyte to and from the electrode surface. Small pores with open porosity create a large area for ion reactions, but a drawback of small pores, and the high tortuosity often associated with small pores, is a higher resistance to ion transport trough the electrolyte. The transport through the electrolyte is limited by resistance that is controlled by the width and the length of the transport path. Many small pores will tend to create high resistance pathways. Volume changes during charging and discharging and external mechanical loads such as vibrations will tend to damage the pore structure and this put demands on the structural integrity of the pores. Fracture mechanics considerations favours a narrow pore size distribution compared to a wider size distribution.

Using colloidal processing, such as tape casting or slot die, it is possible to design the pore structure and control the pore size. Deposition of thin layers using particle suspensions or pastes followed by drying is influenced by colloidal forces. The smaller the particles the lager influence of the attractive van der Waals attraction between particles. Strong flocculation of particles will tend to create structures with a wider pore sized distribution. Flocculation can be controlled by adding dispersants. The stability and behaviour of suspension during deposition can be characterized using rheological techniques. The different stages of the deposition process takes place at different shear rates. Flow through a slot die or under a doctor blade takes place at high shear while the levelling and compaction of layer take place at very low shear rate.

The strength of a deposited layer is influenced by added binders but also by powder packing. The compressibility of a flocculated deposited powder layer is larger than a layer deposited from a dispersed suspension. This will influence behaviour during calendering of the layer. The binder can be used to influence the deposition process and the pore structure of the deposited layer. In water based processing it is possible to use latex based binders that have much lower viscosity than soluble polymeric binders. One example of pore structure control is using of anionic latex binders that exhibit phase separation during drying. These binders tend to create drying channels that form pores perpendicular to the deposited layer.

Poster presentation [P27]

FROM ADDITIVES TO CO-SOLVENTS: IONIC LIQUIDS FOR SAFER LITHIUM-ION BATTERY ELECTROLYTES

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$LiPF_6$ based liquid electrolytes are widely used in lithium-ion batteries despite their well-known problematic thermal and chemical behaviour. Reliable safety is crucial for the potential upgrading of the technology to large-scale applications. To address this issue, ionic liquids (ILs) have received attention for their low vapour pressure, electrochemical stability, thermal stability and high conductivity and have been investigated as possible co-solvents in liquid electrolytes. Mixtures of carbonate and IL based solvents lowering the total vapour pressure and content of flammable gases have been proposed to drastically improve the cell safety [1-3]. At the same time, the performance of the cell should not be unreasonably affected, but increased viscosity and compatibility problems with current collectors are currently obstacles. Here, we monitor the flammability behaviour of the electrolyte 1M $LiPF_6$ EC:DEC (1:1 wt %) upon addition of two ILs, EMImTFSI or $EMImPF_6$, using flashpoint tests, measurements of vapour pressures, and the self-extinguishing times (SETs). In addition, the macroscopic properties density and viscosity are determined for each electrolyte and finally, the molecular level changes are detected using Raman spectroscopy.
For EMImTFSI, we find a decrease in flammability with an increase in flashpoint of 20 °C for 30 mol% IL. On the other hand, adding $EMImPF_6$ does almost not change the flammability behaviour of the electrolyte. On the molecular level we find drastically altered interactions between the solvent molecules and the salt ions responsible.

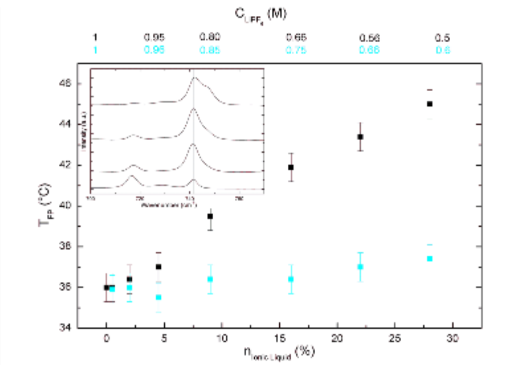

Figure: Dependence of electrolyte flashpoint as a function of IL content; 1M $LiPF_6$ EC/DEC + black: EMImTFSI; blue: $EMImPF_6$, insert: Raman spectra of electrolytes with increasing EMImTFSI content.

Acknowledgements: The flashpoint tests, vapour pressure and density/viscosity measurements were performed at ZSW, Ulm, Germany. The support from ZSW is gratefully acknowledged.

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Poster presentation [P28]

LONG-TERM STABILITY OF POLYCARBONATE-BASED SOLID POLYMER ELECTROLYTES: 1-YEAR ANNIVERSARY OF THE FIRST PTMC LI-ION CELL

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Through their widespread use, lithium-ion batteries have become well-known not only for being a convenient means of high-density energy storage but also, through a series of high-profile accidents, a potentially unstable safety hazard. A major source of these problems is the liquid electrolyte, consisting of a mixture of flammable organic solvents, and containment of the electrolyte is a key issue in the design and manufacture of safe Li-ion batteries. [1, 2]
The use of solid polymer electrolytes would reduce or eliminate several of the safety issues of liquid electrolytes. Although indeed combustible, polymers are much less flammable than liquid organic solvents. A mechanically stable solid state electrolyte would also be able to act as an electrode separator. Since no liquid needs to be contained, this allows for more flexibility in cell design, allowing for, e.g., 3D-microbattery architectures. [3] Solid polymer electrolytes have also shown to suppress the formation of lithium dendrites, thus permitting the use of lithium metal as an anode material. [4]
We have investigated the use of poly(trimethylene carbonate) – PTMC – as a solid polymer electrolyte. While earlier studies have confirmed that this polymer is a decent conductor of Li ions, [5] we recently assembled the first half-cells using PTMC-based electrolytes to investigate the cycling behavior. [6] Interestingly, such cells initially show a continuous increase in capacity on storage to eventually reach a plateau at the full practical capacity, which is retained for an extended period of time during active cycling. Results from long-term cycle stability testing indicate that such Li | SPE | LFP half-cells can cycle with retained capacity at a temperature of 60 °C for close to a full year. The high capacity and stability of these cells, together with the flexibility of aliphatic polycarbonate chemistry, highlight the potential to further develop these polycarbonate-based electrolytes for use in efficient 2D and 3D batteries.

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CONVERSION REACTIONS IN TRANSITION METAL OXIDES: AN OLD CONCEPT TO BE BRUSHED UP FOR EMERGING BATTERY APPLICATIONS?

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Conversion reactions in transition metal compounds have been investigated intensively for possible use in Li-ion batteries since their early discovery[1,2]. However, major issues have so far hindered their usage in commercial cells, due to a number of different reasons[3]. In particular, conversion reactions in transition metal oxides (TMOs) remain a highly debated field and the intriguing in situ formation of metal/Li_2O phase boundaries upon lithiation points at the importance of accessing distinctive electrochemical storage properties via the generation of extended interfaces and related size effects[4-6]. Moreover, the possibility of adopting inexpensive and non-toxic compounds such as iron oxides or, for example, copper oxides, which could be easily integrated onto Cu substrates, make this type of reactions particularly appealing. Proper design of current collectors[7], accurate binder choice[8] and advanced assembly of nanocomposite TMO electrodes[9] can sensibly alleviate most of the shortcomings[3] associated with their conversion mechanism. In this respect, the critical points of TMOs are still represented by their large voltage hysteresis upon discharge/charge and their operational potential, which is not optimal for anodes. However, these factors may not necessarily represent crucial limitations in complementary battery technologies having primary requirements different from those of contemporary commercial Li-ion cells, which rely on insertion materials. In this work, two examples of systems that could beneficiate from the use of nanostructured Fe_2O_3 and Cu_2O will be considered: i) Na-ion batteries, where low costs and environmental footprint, together with high durability and specific capacities are mandatory[10] and ii) 3D Li-ion microbatteries[11], where enhanced surface areas and interface contact of thin films with complex substrate architectures are needed to maximize both power and energy densities per footprint area, as well as the ultimate cycle performance of these electrodes in miniaturized devices.

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SYNTHESIS OF LiFePO4 USING INDUSTRIAL BY-PRODUCTS AS PRECURSORS

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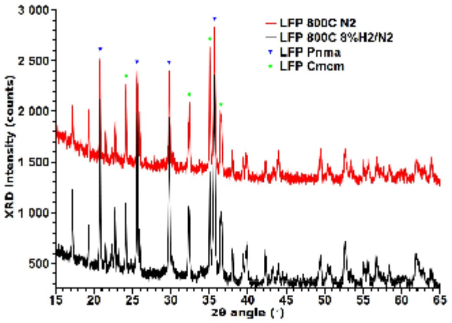
One of the main obstacles in the wide scale adoption of Li-ion batteries is their high cost. This can be overcome, firstly, by increasing the operational life time of the batteries. $LiFePO_4$ is a very promising electrode material for achieving this. In proper combination with an conductive additive it can be used to make Li-ion batteries that can undergo at least 1000 charge/discharge cycles without significant degradation in performance. Furthermore, $LiFePO_4$ and its precursors are environmentally friendly.

Secondly, the cost of the precursor materials can be reduced by utilising alternative sources, such as industrial by-products. At least iron and phosphorus are available in the industrial waste streams. Utilising these streams will also reduce the environmental impact of the production.

Lastly, the synthesis process itself can be optimised. Gas-phase processes are highly material and energy efficient routes for synthesis of nanoparticles with controlled composition and particle size. With the proper selection of the process environment the waste streams can also be easily utilised in these processes.

In this paper we present a gas-phase method for the synthesis of $LiFePO_4$ nanoparticles utilising industrial waste stream of $FeSO_4{\cdot}7H_2O$. The precursors were dissolved in water and atomized using an ultrasonic nebuliser. The produced droplets were then carried to the heated zone of the reactor. Experiments were carried out at temperatures between 200 and 800°C in atmospheres with varying reduction potentials. The aerosol exiting the heated zone was rapidly cooled with a large volume of dilution gas (air or N_2) at ambient temperature.

With increasing temperature the particles became more solid with increasing fraction of $LiFePO_4$. Increasing the reducing potential of the synthesis atmosphere increases the ratio of the Pnma-to-Cmcm polymorphs of $LiFePO_4$. The effects of temperature, precursor composition and process atmosphere on the product composition will be presented.



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INCREASED STABILITY OF LITHIUM IRON PHOSPHATE TOWARDS HUMIDITY BY IRON SITE SUBSTITUTION

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Lithium iron phosphate has been investigated as a prominent positive electrode material for Li-ion batteries because of its nontoxicity, environmental friendliness, inexpensive elements, and safe three dimensional structure. As a hygroscopic material, $LiFePO_4/C$ reacts with air humidity resulting in unwanted side products weakening the electrochemical performance. Recently it was observed that partial substitution of iron with manganese stabilizes $LiFePO_4/C$ towards humidity making water absorption/desorption process reversible (Räsänen et al. Solid State Ionics **211** (2012) 65). In this work, the absorption/desorption behavior and stability of $LiFe_{1-x}M_xPO_4/C$ (M = Mn, Co, Zn) under humid atmosphere are studied using an in situ thermogravimetric humidity device. This work is significant when evaluating the effect of storage conditions on $LiFePO_4/C$ and surveys a possibility to avoid the harmful phenomena weakening the electrochemical performance.

The materials were synthesized via solid state synthesis by mixing stoichiometric amounts of high-purity Li_2CO_3, $NH_4H_2PO_4$, $FeC_2O_4 \cdot 2H_2O$, and $MnCO_3$, $CoC_2O_4 \cdot 2H_2O$ or $ZnC_2O_4 \cdot 2H_2O$. The carbon coating was made using saccharose and the content was 3 w-% according to elemental analysis. The water absorption/desorption behavior was studied using a four-step program in in situ thermogravimetric humidity device. The program was repeated several times: (i) the sample is heated to 130°C and isothermally heated at this temperature to desorp all water absorbed. After desorption, (ii) the sample is cooled to 30°C and stabilized for a while after which (iii) the humid atmosphere is switched on, and again, (iv), dry air is switched on. Steps (i) to (iv) take 11 hours.

Samples of $LiFe_{1-x}M_xPO_4/C$ were phase-pure based on the XRD analyses except for a small lithium deficiency in some samples. Lattice parameters changed monotonously along the substitution level confirming successful transition metal to iron substitution. The specific surface areas were determined by BET method and they are 20-25 m^2/g. The particle size of $LiFe_{1-x}M_xPO_4/C$ was 7 μm and < 7 μm, when x = 0 and x > 0, respectively. SEM images supported the particle size distribution and indicated no morphological differences between the samples.

Based on the results achieved with thermogravimetric humidity device, the reversibility of the water absorption/desorption behavior is discussed in terms of the transition metal substitution level.

CHARACTERIZATION OF LITHIUM PHOSPHOROUS OXYNITRIDE (LiPON) THIN FILMS FOR LITHIUM ION BATTERIES

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The increasing demand on microelectronic components has made the development of compact, all-solid-state thin film batteries highly interesting. Lithium phosphorous oxynitride[1] (LiPON) is an amorphous Li^+ conductor that has a very high electrochemical stability of up to 5.5 V. This makes it a strong candidate as electrolyte in compact, flexible and high-power-density batteries needed for various miniaturized electronic devices, such as sensors, circuit boards, medical implants, etc. LiPON are prepared by RF magnetron sputtering of a Li_3PO_4 target in N_2 atmosphere and the properties of the LiPON thin films are highly dependent on the sputtering parameters. It is well known that the Li^+ conductivity is dependent on the structural disorder induces by the nitrogen incorporation in the Li_3PO_4 network, but despite extensive research this dependence is not yet well understood. The objective of this work is to identify the type and concentration of the reactive species formed during sputtering using detailed plasma diagnostics. The influence of RF power and N_2 pressure on reactive species formed in the plasma is investigated in direct correlation with morphology and electrochemical properties of the LiPON thin films. It was found that using a RF power of 100 W and a pressure of 5 mTorr gives the best results, i.e. a flat dense film with the highest Li^+ conductivity ($2.2 \cdot 10^{-6}$ Scm^{-1}). An increase in the N_2 pressure results in the growth of "volcano-shaped" structures with a lower conductivity (see fig. 1), while an increase in RF power results in cracks and rough thin film morphologies. Mass spectrometry revealed that a high degree of nitrogen decomposition is an important factor for achieving high-quality LiPON thin films.

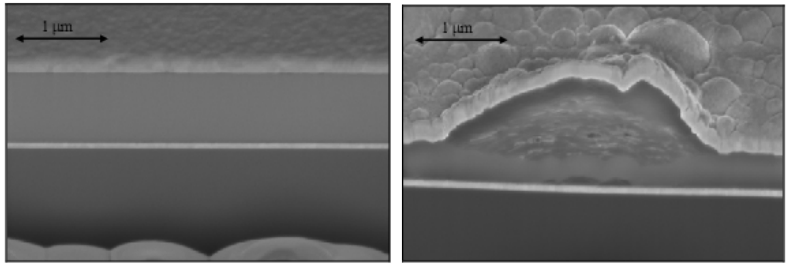

Figure 1: FIB-SEM cross-sectional micrographs of Ag/LiPON/Au structures on Si wafers. The LiPON films are deposited with 100 W and a N_2 pressure of (left) 5 mTorr and (right) 50 mTorr.

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CONDUCTIVITY STUDIES OF Li_2O_2 ON AU SURFACES WITH OUTER-SPHERE REDOX COUPLES IN DIMETHOXYETHANE

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The net electrochemical reaction in non-aqueous Li-O_2 batteries on discharge is $2Li^+ + O_2 \rightarrow Li_2O_2$ and from this a high theoretical specific energy of 3505 Wh/kg can be estimated[1]. This has attracted a great deal of attention during the past years, but despite this; specific discharge capacities are still substantially lower than the theoretical value[2-3].

This limited discharge capacity is mainly a consequence of the deposition of Li_2O_2 on the cathode - a high band gap discharge product of 4.9 eV[4]. Since Li_2O_2 is insoluble in non-aqueous solvents it builds up on the cathode surface as the cell is discharged, causing electrical passivation. It is therefore of great interest to determine a critical thickness and the conductivity of the electrodeposited Li_2O_2 layers.

A 3-electode cell was used to study the deposition and the conductivity through Li_2O_2 on Au electrodes. The electrolyte consisted of 1 M LiTFSI and DME (dimethoxyethane) with 2 mM of an outer-sphere redox couple. Ferrocene, Cobaltocene, and decamethylcobaltocene will be used as redox couples and make it possible to study the conductivity of Li_2O_2, in oxygen free electrolyte, at different state of charge, and at different potentials. In the experiments, the Li_2O_2 deposition was stopped at various stages of discharge and subsequently the conductivity was probed by monitoring the charge transfer resistance of the redox couple using Electrochemical Impedance Spectroscopy (EIS).

The charge transfer resistance measured using EIS reflects the exchange current density, and by studying how this is influenced by the passivating layer it is possible to determine a critical thickness of the deposited Li_2O_2 and also allows determination of the layer conductivity. The results will be compared with a previous study by Viswanathan et al (V. Viswanathan et al., The Journal of Chemical Physics, 135, 214704 (2011) on the conductivity of Li_2O_2 layers deposited on glassy carbon electrodes.

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DETERMINING THE AGEING MECHANISM IN $Li_4Ti_5O_{12}|LiMn_2O_4$ BATTERY CELLS WITH XRD AND XPS

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This study examines parts of the kinetics and performance in Li-battery cells using lithium titanate anodes and lithium manganese oxide cathodes. Lithium titanate ($Li_4Ti_5O_{12}$) is a candidate for battery applications in automotive vehicles due to its long lifetime and its suggested zero-strain ability. The zero-strain ability, meaning no volume changes in the material during cycling, would allow for the high charge/discharge rates required in high load hybrid electric vehicles. Two approaches of analysis have been performed. In situ XRD-analysis was used to verify the zero-strain ability of lithium titanate and XPS studies were used to analyze the surface chemistry of lithium titanate after cycling. It is known that lithium titanate/lithium manganese oxide battery cells suffer from abnormal gas evolution and power degradation, and it is therefore of interest to find ways to prevent this. To be able to find methods of preventing the performance degradation deeper understanding of the kinetics are needed, since the mechanism behind this is not fully understood. The results acquired so far strengthen the understanding of lithium titanate as a zero-strain material. Furthermore, it is seen that the performance degradation possibly can be avoided or postponed by ALD deposition of aluminium oxide on the surface of the lithium manganese oxide electrode.

Poster presentation [P35]

ENTROPY CHANGE IN LITHIUM IRON PHOSPHATE, LITHIUM MANGANESE IRON PHOSPHATE, LITHIUM TITANATE AND GRAPHITE ELECTRODE MATERIALS

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Knowing the thermal behavior characteristics of an individual lithium-ion cell is very important for the design of proper cooling system for large battery packs. The total heat generation of a lithium-ion cell can be divided into irreversible and reversible contributions. The irreversible part results from voltage losses and is always associated with heat production whereas the reversible part is a function of entropy change and can be either absorbed or produced heat. At low currents the reversible heat generation rate dominates, and depending on its sign and magnitude, the cell either absorbs or produces heat. Entropy change reflects the ordering of lithium-ions in the electrode material lattices: positive entropy change implies increasing disorder as charge is passed through while negative is a sign of ordering.

The entropy change of different lithium-ion cell electrode materials was studied as a function of state of charge. The entropy change was determined potentiometrically by recording the open circuit voltage at different temperatures. $LiFePO_4$, $LiMn_{0.67}Fe_{0.33}PO_4$, $Li_4Ti_5O_{12}$ and artificial graphite materials were studied in half-cells against metallic lithium.

$LiFePO_4$ and $Li_4Ti_5O_{12}$ both show an almost constant entropy change, typical for a two-phase reaction. The entropy change in graphite material follows the different lithium intercalation stages. In $LiMn_{0.67}Fe_{0.33}PO_4$, the redox reaction is divided into two regions corresponding to Fe^{3+}/Fe^{2+} and Mn^{3+}/Mn^{2+} redox couples. The entropy change behavior follows these regions: Fe region has a sloping profile whereas Mn region shows a more constant entropy change, typical of a two-phase reaction. The Fe region behavior is clearly different from pure $LiFePO_4$. This is suggested to be due to the changed mechanism of the Fe^{3+}/Fe^{2+} redox reaction, which has been demonstrated to proceed completely as a single-phase solid-solution reaction in $LiMn_yFe_{1-y}PO_4$ when $y > 0.6$.

The cell's entropy change is a sum of the contributions from positive and negative electrodes. To avoid variations in heat generation, a minimum net entropy change for the cell reaction would be optimal. The entropy change of different positive and negative electrode combinations was calculated from the half-cell results. LFP/LTO combination was found to have the smallest net entropy change.

One calorimetric experiment was done on a commercial LFP/graphite cell to show the entropy change effects on the cell thermal behavior in practice. At low discharge currents, the cell actually absorbed heat and cooled down inside a certain SOC-range because of the positive net entropy change of the cell reaction.

Poster presentation [P36]

FUNCTIONAL, WATER-SOLUBLE BINDERS FOR IMPROVED CAPACITY, RATE CAPABILITY AND STABILITY OF LITHIUM-SULFUR BATTERIES

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The demand for ever-higher energy density in portable electrical storage is increasingly motivating research in systems beyond lithium-ion. Of these, the lithium-sulfur (Li-S) couple, with a theoretical energy density of 2,600 Wh kg^{-1}, is particularly promising, with the possibility of fully-assembled battery packs boasting an energy density two to three times larger than that of current lithium-ion[1,2]. Naturally, then, this system today attracts considerable interest from the automotive and aerospace industries.

However, the commercial realisation of this exciting technology has been hampered – for decades – by short cycle life and a high degree of self-discharge, attributable to the well-documented inefficiency of the lithium metal anode and the so-called polysulfide redox shuttle. Furthermore, the combination of poor electronic and ionic conductivity of the charge and discharge products with poor electrochemical reversibility limit sulfur utilization and make this a system of relatively low rate capability compared to lithium-ion.

The mechanism of this system involves a considerable number of reactions of intermediate polysulfide compounds in solution. As such, the choice of electrolyte chemistry is of considerable importance in this system. What is often overlooked, however, is that the cathode binder – ordinarily a minor component included to ensure mechanical stability – may influence the chemistry of intermediates through the inclusion of functional groups.

In this work, we have identified that binders comprised of mixtures of poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP) significantly improve the capacity, rate capability and stability of Li-S cells compared to conventional alternatives, e.g., poly(vinylidene fluoride) (PVdF)[3]. An overview of the electrolyte chemistry of the system will be presented, as well as a study on the influence of the binder on the electrochemistry of simplified lithium-sulfur cells.

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SUSTAINABLE BATTERIES BASED ON CONDUCTING POLYMERS WITH HIGH CAPACITY PENDING GROUPS

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Organic matter based battery materials have attracted large interest due to their inherent ability to provide an environmentally benign alternative to inorganic batteries because organic materials can be produced from renewable resources via eco-efficient processes.[1] The development of organic battery materials rely on several key factors that need to be resolved, the most important being dissolution of active material, limited conductivity, degradation and slow redox kinetics.

Conducting polymers are insoluble in most electrolytes, they are electronically conducting and show fast redox conversion and thus they provide a key to solve problems with dissolution and poor conductivities without compromising redox conversion rate capabilities. The intrinsic capacity to store charge in conducting polymers is however inferior to current battery materials.[2] By attaching high capacity redox component to the conducting polymer backbone the capacity can be dramatically improved. Polypyrrole, for instance, shows specific capacities of around 100mAh/g.[3] With the attachment of quinone to polypyrrole the resulting capacity is 300mAh/g.[4]

The concept relies on a conducting polymer backbone for conduction while the pending group serves as capacity carrying functionality. In their neutral state common conducting polymers such as polyacetylene, polythiophene and polypyrrole are semiconductors with band gaps well above kT and conductivity are achieved by oxidative or reductive introduction of mobile charge carriers. In order to benefit from polymer backbone conductivity the pending group redox conversion must occur at a potential where the polymer backbone is charged and energy matching between the polymer backbone and the pending group is crucial (figure 1).

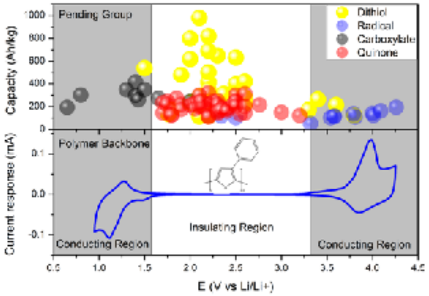

Figure 1: Illustration of the polymer-pendant energy matching requirements exemplified by Poly(3-phenyl-3,5-thiophene) and known organic redox groups divided into four categories.

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The Li$^+$ intercalation in $Ni_{0.5}TiOPO_4$ anode material investigated using HAXPES and XAS

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Li-ion batteries in comparison to many other battery technologies possess a high energy density making them highly attractive as energy storage system. Today they are e.g. used in portable electronics such as mobile telephones and laptops, and the development of electric vehicles is a strong driving force for development of better performing batteries. New electrode materials are constantly being synthesized and $Ni_{0.5}TiOPO_4$ is one of them.

$Ni_{0.5}TiOPO_4$ belongs to the metal titanium oxyphosphate family, and other metals that has been used is e.g. Fe, Mn, Mg, and Co[1]. When $Ni_{0.5}TiOPO_4$ is cycled it is able to intercalate 3 Li$^+$ per unit cell during the first discharge. During the charge only 2 Li$^+$ is deintercalated, implicating that one Li$^+$ per unit cell is irreversibly lost during the first discharge [2]. The intercalation mechanism, involving intercalation of 1 more Li$^+$ than theoretically expected, is still not fully explained.

We will present data from synchrotron based hard x-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and X-ray diffraction measurements on $Ni_{0.5}TiOPO_4$ cycled versus lithium. The changes in composition of the surface and the oxidation states of the material components at the different intercalation steps during the first one and a half cycle are presented.

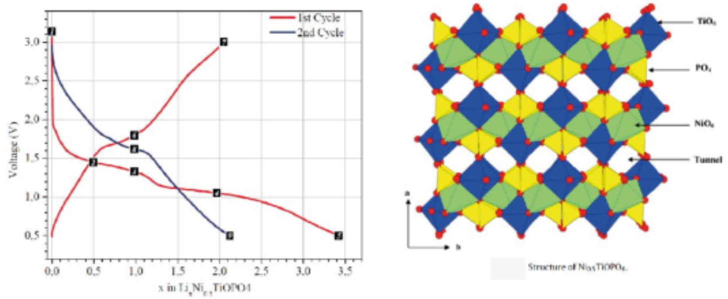

Figure. (Left) Points for measurements from the galvanostatic Discharge/Charge voltage profile of $Ni_{0.5}TiOPO_4/C$.

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NEW SODIUM-ION BATTERY ELECTROLYTES BASED ON IONIC LIQUIDS

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Batteries are expected to be masterpieces for future large-scale energy storage, but the emergence of ecological and financial concerns has forced us to think about complementary battery technologies to the today outstanding lithium-ion batteries (LIBs). The sodium-ion battery (SIB) is one concept worth studying - especially for large-scale applications due to the abundance of sodium as an element, the overall low cost anticipated, and the similarities with LIBs, which should ease a technology change. SIB electrolytes can be based on polymers, organic solvents, or ionic liquids (ILs), all doped with the appropriate sodium salt. Here data will be presented on several properties of IL-based sodium electrolytes obtained by dielectric spectroscopy, differential scanning calorimetry, Raman spectroscopy, viscometry, densitometry, and DFT modeling [1]. Moreover, the results are compared with similar lithium-ion systems. The electrolytes exhibit excellent conductivities, up to 5.5 mScm^{-1} at room temperature, and useful thermal windows of ±150°C – within which all Na-salt doped samples are totally amorphous.

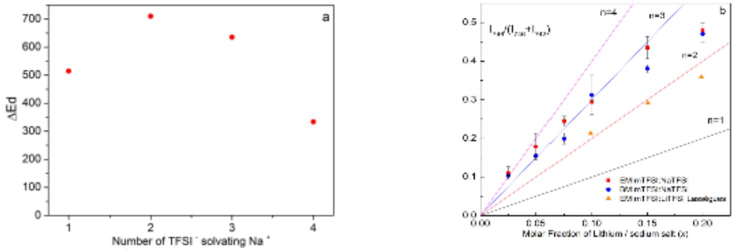

Figure 1. Resulting maximum Na$^+$ binding energy as a function of the solvation number (a), integrated Raman intensities of the 746 cm^{-1} band (748 for Li-systems) normalized by adding the 742 cm^{-1} component as a function of x for EMITFSI:NaTFSI (squares), BMITFSI:NaTFSI (circles), and EMITFSI:LiTFSI (triangles), at room temperature. Solid lines are guides to the eye corresponding to n=1,2,3,4 (b)

In more detail, the Raman data coupled with DFT calculations (Fig. 1a) and density measurements allow us to characterize the sodium-ion charge carriers; numbers and solvation. While we know that TFSI based lithium salt doped IL-based electrolytes essentially form the $[Li(TFSI)_2]^-$ complex for a wide concentration range [2], (indicated by a strong Raman band at ~748 cm^{-1}), our corresponding sodium salt (i.e. NaTFSI) doped systems dominantly form $[Na(TFSI)_3]^{2-}$ complexes (band at ~746 cm^{-1}), as the data points predominantly are close to the n=3 line (Fig. 1b). The DFT calculations point to either the $[Na(TFSI)_2]^-$ or the $[Na(TFSI)_3]^{2-}$ complex to be the preferred complexes. The latter observation has implications both to the total and useful conductivity – to be further elaborated upon.

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ORIGIN OF CAPACITY FADING IN Li_2MnSiO_4 CATHODE MATERIAL

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Among the possible candidates as cathode materials for large scale lithium secondary batteries, transition metal silicates is one group of materials that need to be studied in depth, due to its high theoretical capacity, above 300 mAh/g, and superior abuse tolerance. Li_2MnSiO_4 is one of the potentially promising candidates since it has high theoretical capacity (333 mAh/g) and high operating voltage. However, it shows poor electrochemical performance after 1st charging, while the isostructural material Li_2FeSiO_4 shows better capacity retention with lower energy density than Li_2MnSiO_4 [1].

This fading in capacity has not been fully understood. Most of previous studies has tentatively ascribed this fading to both the poor electronic properties of the material and the likely structural collapse [2,3]. Systematic studies using combined well-defined in situ techniques are crucial to obtain in-depth understanding of the structural origin of this fading upon cycling. Here synchrotron X-ray diffraction, X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) are combined to detail the structural changes during the first charge/discharge cycle for Li_2MnSiO_4 cathode material.

XAS and RIXS was used to provide valuable information on the oxidation state and the local structural environment of a specified atom (Mn) like bond distance, Jahn-Teller distortion associated with Mn^{3+} and Mn dissolution, etc. In situ XRD was used to establish the phase transition or loss of crystallinity of Li_2MnSiO_4 at the end of first charge.

The most observation provide by these techniques is that a valance change of Mn from +3 to +4 is associated with a loss of the long range order of the crystal structure and that during the first part of the charging process the extraction of lithium ions is not accompanied by a change in the electronic structure of the expected redox active Mn atom but rather by a change of the electronic structure of the Si–O network.

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Poster presentation [P41]

$Li_4Ti_5O_{12}$ ELECTRODES IN COIN CELLS AND COMMERCIAL BATTERIES

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Operation temperature range of traditional graphite based Li-ion batteries is limited to +60…-30°C, and moreover they are known to suffer from a loss of capacity or even a safety hazard when charged at sub-zero temperatures. Lithium titanate ($Li_4Ti_5O_{12}$) can be used as an alternative anode material to the problematic graphite. It has the advantage of high charge and discharge currents and it is more resistant to abusive conditions. In addition, due to a rather high lithium insertion potential (1.55 V vs. $Li|Li^+$), no solid electrolyte interphase (SEI) formation or lithium plating can occur on the surface of $Li_4Ti_5O_{12}$ even when charged at sub-zero temperatures.

In this study, the properties of $Li_4Ti_5O_{12}$ electrodes were investigated in coin cells with lithium or $LiFePO_4$ counter electrodes and the results were compared to a commercial 60 Ah Li-ion cell with $LiNiMnCoO_2/Li_4Ti_5O_{12}$ chemistry. The effect of the $Li_4Ti_5O_{12}$ particle size and shape on the rate capability and low temperature performance was studied in the half cells and the effect of low temperatures was studied in the full cells and the commercial cell.

It was found that the obtained capacities for $Li_4Ti_5O_{12}$ half cells with different active material particle size were similar at room temperature and low charging/discharging currents. However, the shape of the charging and discharging profiles depends on the $Li_4Ti_5O_{12}$ particle size; flat charge/discharge profiles are measured for $Li_4Ti_5O_{12}$ with larger primary particle size and low surface area whereas more curved charge/discharge profiles with shorter plateau are obtained for $Li_4Ti_5O_{12}$ with small primary particle size and high surface area. When high charging/discharging currents or low temperatures (-20 °C) are used, the performance of $Li_4Ti_5O_{12}$ with small particle size exceeds that of $Li_4Ti_5O_{12}$ with larger particle size.

$Li_4Ti_5O_{12}$ with the smaller primary particle size was also tested in $LiFePO_4/Li_4Ti_5O_{12}$ full cells at low temperatures (+22°C…-30 °C). The reversible low temperature capacity decrease of the coin cells was studied and the results were compared to those of the commercial batteries.

Poster presentation [P42]

THREE DIMENSIONAL ALUMINIUM RODS: FROM CURRENT COLLECTORS TO ELECTRODES

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Lithium-ion batteries cannot keep up the pace of microelectronic industry. Devices such as sensors and actuators are continuously decreasing in size and traditional thin films Li-ion batteries do not have enough energy density per footprint area to offer on-board power for these devices. One possible solution would then be to employ three dimensional (3D) battery configurations, such as interdigitated rods of anodes and cathodes separated by a solid electrolyte.

Aluminium is used as current collector for the positive electrodes in commercial Li-ion batteries. In the present work, galvanostatic deposition was used for the manufacturing of free standing 3D arrays of aluminium rods on aluminium substrates, by electrodeposition in the pores of commercial membranes. It will be shown that the use of a short potentiostatic nucleation pulse leads to homogeneous deposition of aluminium rods, while the use of pulsed current techniques results in a narrower distribution of rods heights compared to when using a constant current approach.

Aluminium could potentially be used as a negative electrode for Li-ion batteries, as it alloys with lithium at a potential close to that for lithium deposition. The use of aluminium in Li-ion batteries is, however, hampered by rapid capacity fading and there is at present no consensus in the literature regarding the origin of this effect. The two main explanations offered for this cycling behaviour are volume changes during cycling and lithium trapping in the electrode. To study this further, aluminium rod electrodes with native as well as 30 nm and 60 nm thick aluminium oxide layers have been cycled against metallic lithium in Li-ion pouch cells. It was found that the capacity retention was poor when the electrodes were cycled between 0.1 and 3 V vs. Li^+/Li and that no improvement in the cycling behaviour was found for the aluminium electrodes having a thicker Al_2O_3 layer than the native one. The cycling behaviour of the aluminium electrodes was, however, significantly improved when the oxidation cut-off voltage was changed from 3 V to 1 V vs. Li^+/Li, indicating that the volume expansion effects were negligible and that the loss of capacity instead was coupled to the diffusion of lithium in the aluminium electrode.

CYCLING STABILITY OF FLEXIBLE POSITIVE ELECTRODES FOR LI-ION BATTERIES USING NANO-FIBRILLATED CELLULOSE AS A BINDER

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Li-ion batteries are the most important power source in the application of portable electronics. Flexible Li-ion batteries attract increasing interest and could be very useful in bendable and wearable electronic devices. Nano-fibrillated cellulose (NFC), a renewable material, is a promising candidate as a binder material for flexible Li-ion batteries with good mechanical properties. They can be produced using water-based paper making process, avoiding the use of toxic solvents. Recent work has shown capacity fading during repeated cycling of the paper based Li-ion batteries and the traces of moisture in the NFC may be the cause for this degradation[i,ii]. In the present work, the cycling stability of flexible positive electrodes (Fig. 1) for Li-ion batteries using NFC as a binder is investigated and discussed as function of time to dry the electrodes. The results show that the cells with longer drying time of the positive electrode obtains a better cycling performance at C/10, as well as a higher coulombic efficiency.

Fig. 1 A flexible positive electrode

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Electropolymerization onto carbon fibers – a route towards structural batteries?

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The concept of structural batteries circles around a multi-functional material that can both carry a mechanical load, as well as storing electrical energy. By introducing a structural battery into an e.g. electrical vehicle (EV) design, large weight savings can potentially be made since a free-standing battery no longer is needed. This will, of course lower the energy consumption of the car allowing for a greater range of the EV.

The multi-functionality adds further restrains on the structure as compared to the mono-functional structural composite and batteries. The structural battery must at the same time be mechanically stiff and conduct lithium ions adequately. Unfortunately, these two properties are in inverse relation in which the ionical conductivity is too low in reasonably stiff polymer systems. One way around this problem is to make a very thin electrolyte surrounding each individual carbon fiber. The approach chosen to achieve such coatings is electropolymerization. By using this procedure in a monomer/salt/solvent electrolyte, an applied potential will start an initiation reaction at the carbon fiber interface, followed by polymer propagation thus forming a polymeric coating (fig. 1).

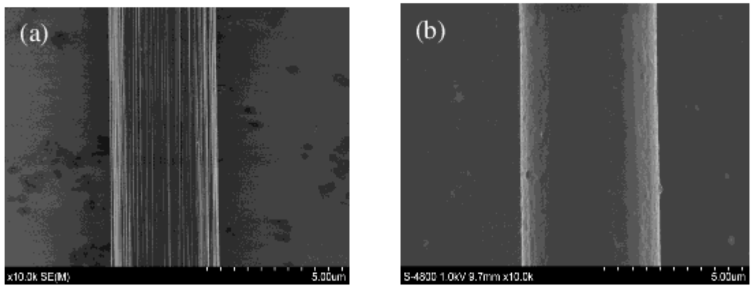

Figure 1 – (a) Unmodified carbon fiber as compared to a (b) electrocoated carbon fiber.

The work to be presented at NordBatt1 is focused on how to control the final polymeric coating on the carbon fibers. Mainly, the effect of the electrolyte formulation on the final coating properties will be studied.

Poster presentation [P45]

UNDERSTANDING AND CONTROLLING THE SURFACE CHEMISTRY OF POLYOL SYNTHESIZED $LiFeSO_4F$ FOR AN ENHANCED CATHODE FUNCTIONALITY

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Recently, the tavorite polymorph of $LiFeSO_4F$ has attracted considerable attention within the lithium battery community stimulated by the high potential for the Fe^{2+}/Fe^{3+} redox couple (3.6 V vs. Li/Li^+), competitive specific capacity (151 mAh/g), beneficial structure for fast lithium ion transport, and low temperature synthesis[1]. It is thus considered as an attractive contender to $LiFePO_4$ as a next-generation cathode material. Since its discovery, various synthesis routes for producing tavorite $LiFeSO_4F$ have been explored, including ionothermal[1], solvothermal[2], polymer assisted[3], and solid-state methods[4]. Reviewing the literature, one can conclude that the electrochemical performance presented for this material has been notably varied. This inconsistency is difficult to understand given the excellent purity, crystallinity, and similar sample morphologies achieved by all methods.

In this contribution, we examine the role of the surface chemistry on the electrochemical performance of tavorite $LiFeSO_4F$. We demonstrate that particularly restricted performance may be obtained for materials synthesized using tetraethylene glycol (TEG) as reaction media, which can be largely attributed to residual solvent traces remaining on the surface of pristine powders, inhibit the electrochemical reactions. Moreover, we show that the cycling performance of $LiFeSO_4F$ can be significantly improved by removing the TEG residues and applying a conducting polymer coating, which decreases the contact resistance between the electrode components and creates a highly percolating network for electron transport throughout the composite material. This surface modified material displays a well defined voltage plateau with sharp and distinct charge and discharge end points, as expected from a two-phase lithium insertion compound.

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Poster presentation [P46]

POROUS SILICON AS ANODE MATERIAL FOR LI-ION BATTERIES – STRUCTURE AND PERFORMANCE

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Silicon has proven to have a great potential as anode material in lithium-ion batteries due to its high theoretical electrochemical capacity. However, silicon anodes deteriorate quickly during cyclic charging and discharging, rendering them useless in only a few cycles. This has been attributed to the stresses induced by the large volume change of the material during cycling. By using finely structured silicon, these stresses can be effectively reduced, in what is aptly called dimensional stabilization. Numerous attempts have been made to exploit this effect, *e.g.* by using nanoparticles, nanorods and nanowires, with a varying degree of success. This study is an investigation into the use of porous silicon for anodes with reduced level of stress. The work consists of two main phases; the formation and characterization of porous silicon, and the testing of the resulting porous structures in electrochemical cells. In addition, an investigation into the use of prelithiated silicon as base material for composite electrodes has been conducted.

Porous silicon was obtained by electrochemical etching of n- and p-type silicon wafers in hydrofluoric acid (HF) at different current densities and for different durations. The resulting material was analyzed by SEM to characterize its morphology and pore size. One n-type and one p-type structure were selected for electrochemical testing, involving cyclic charge and discharge in half cells with lithium metal as a counter electrode. The chosen samples were tested both as etched and with a carbon coating made by a pyrolization procedure with polyacrylonitrile (PAN) as precursor. In a different part of the work, composite electrodes were made from an alloy consisting of the intermetallic phase $Li_{17}Si_{13}$, carbon black and PAN. These were tested using the same conditions as the porous electrodes – however, the electrochemical testing of the prelithiated composite electrodes revealed that reversible capacity was very limited, possible due to contamination of the base material during its handling after synthesis, despite the extensive preventive measures that were taken.

AGING OF ELECTRODE/ELECTROLYTE INTERFACES IN $LiFePO_4$/GRAPHITE CELLS

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The electrode/electrolyte interface has a huge impact on Li-ion battery safety, lifetime, low and high temperature performance and power capability. Furthermore, changes in the solid electrolyte interphase (SEI) on graphite as the negative electrode are considered as one of the major sources for a too rapid aging of a Li-ion battery[1]. One of the most effective ways of influencing the composition and properties of the SEI and improving battery performance is use of film-forming electrolyte additives, such as propargyl methanesulfonate (PMS)[2].

Here, changes in the electrode/electrolyte interfaces in $LiFePO_4$/graphite cells are studied with hard X-ray Photoelectron Spectroscopy (HAXPES). Cells cycled in a standard organic electrolyte with $LiPF_6$ salt are compared to the ones cycled with addition of PMS. For both systems the evolution of electrode/electrolyte interfaces are studied during prolonged cycling (Figure 1) and the changes are discussed for both, positive and negative electrodes. A similar study is performed for cells cycled at 60 °C in order to determine differences in aging processes at elevated temperature.

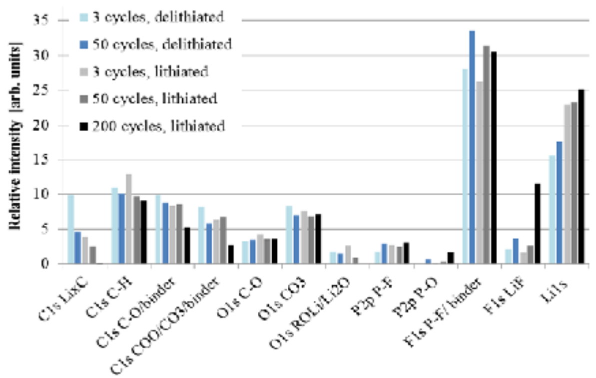

Fig. 1 Relative intensities of detected components for graphite electrode cycled in a standard organic electrolyte with $LiPF_6$ salt.

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STRUCTURAL STUDY OF THE CONTROLLED HYDROTHERMAL SYNTHESIS OF $LiMn_2O_4$ AND $Li_xMn_yO_2$

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$LiMn_2O_4$, which crystallizes in the spinel structure, is of great interest as a cathode material for Li-ion batteries due to the high natural abundance of manganese, low toxicity, fast ionic diffusion and excellent battery capabilities. The structure is closely related to that of $Li_xMn_yO_2$, a layered structure, which can also be described as a defective spinel structure.
Here, we show that both $LiMn_2O_4$ and $Li_xMn_yO_2$ nanoparticles can be synthesized from a simple, low-temperature hydrothermal synthesis. By tuning a single synthesis parameter (Li-concentration) each of the 2 structures or mixtures hereof can be obtained. The products have been characterized by X-ray powder diffraction both in-house and at SPring-8.

Rietveld refinement was carried out on the high-resolution data from the synchrotron source and detailed structural models for both the spinel and the layered phase were obtained, with focus on the size of the nanoparticles. Using a two-phase model, the Rietveld refinements showed a bimodal size distribution for the $LiMn_2O_4$, which, to our knowledge, has previously only been determined using SEM. Using the structural Rieveld models for $Li_xMn_yO_2$ and $LiMn_2O_4$, a comparison of the two structures was made, by refinement of the structural models of one phase using diffraction data from the other. It was shown that the $LiMn_2O_4$ phase can be described nearly as well using the layered model compared to the spinel.

Poster presentation [P49]

$Li_2FeP_2O_7$: AN IRON BASED CATHODE MATERIAL FOR HIGH TEMPERATURE AND HIGH POWER Li-ION BATTERIES

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To meet the growing demand for Li-ion batteries, inexpensive cathode materials made from abundant natural resources are required. Today's cathode materials are to a large extent based on cobalt, which is considered a strategic metal[1], thus both expensive and not very abundant. Iron based cathode materials provide possible alternatives to cobalt based ones.

With the intention to investigate a number of existing and novel iron based materials regarding their electrochemical properties as cathodes, initial studies of $Li_2FeP_2O_7$[2] have been conducted in this work. The reason for the initial focus on $Li_2FeP_2O_7$ is its thermal stability[3] and potentially fast Li-ion transport. The advantageous thermal properties make it a candidate for high-temperature Li-ion batteries. Fast Li-ion transport is beneficial in applications where high power is demanded, such as in hybrid electric vehicles.

In comparison to the current state-of-the art iron based cathode material $LiFePO_4$[4], $Li_2FeP_2O_7$ offers a slightly higher potential but lower gravimetric capacity when considering extraction of one Li-ion per formula unit. But $Li_2FeP_2O_7$ offers a quasi two-dimensional diffusion pathway for Li-ions, in contrast to the one-dimensional diffusion in $LiFePO_4$. Two-dimensional Li-ion diffusion is beneficial for fast Li-ion transport in the material and enables high electrochemical capacity even without nanosizing. Materials with one-dimensional lithium diffusion, such as $LiFePO_4$, are also more sensitive to structural defects upon cycling, which could block the Li-ion diffusion in a large part of the material.

In this contribution, characterization of $Li_2FeP_2O_7$ with X-ray diffraction, Mössbauer spectroscopy and scanning electron microscopy will be presented together with galvanostatic cycling data of the material vs. lithium foil in half cells.

Acknowledgements
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Poster presentation [P50]

INVESTIGATING THE POSITIVE ELECTRODE REACTION IN Li-O_2 BATTERIES

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The Li-O_2 battery has been attracting a lot of attention during the last years due to its high theoretical energy density making it very promising for vehicle applications. The literature reports of systems exhibiting reversibility over 100 cycles (Peng et al., Science, 2012, vol. 337, 563-566). However, there are problems associated with Li-O_2 batteries, such as electrolyte decomposition, low cycle life, high overpotentials and lack of reaction mechanism understanding. Cyclic voltammetry (CV) is a useful method when it comes to examining electrode kinetics and reaction reversibility. By utilizing a carbon fiber ultramicroelectrode as working electrode an experimental setup with well-defined geometry and good mass transport properties is obtained. Cyclic voltammograms of Li-O_2 cells exhibit overpotential for both reduction and oxidation. However, comparing the CVs with cycling experiments, the oxidation overpotential is much higher for cycling experiments suggesting a passivation of the electrode surface during long discharge making the reduction product harder to oxidize. The results from the combination of ultramicroelectrodes and CV displays features not observed in porous electrodes adding knowledge to the complex reaction mechanism of Li-O_2 batteries.

A PAIR DISTRIBUTION FUNCTION ANALYSIS OF NON-STOICHIOMETRIC $Li_xFe_ySiO_4$ USING HIGH ENERGY SYNCHROTRON X-RAY RADIATION

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The local order of non-stoichiometric lithium iron silicate (LFS) is investigated by pair distribution function (PDF) analysis [1] using high energy synchrotron X-ray radiation. LFS is a cathode material for Li-ion batteries which has received quite a lot of attention as a promising cheaper and non-toxic alternative to more conventional Co-based cathode chemistries. Belonging to the family of orthosilicates, all iron and silicon cations are coordinated by oxygen in corner-sharing tetrahedra, allowing for intercalation of Li ions in the structure. However, much like many other cathode materials based on the oxidation and reduction of the Fe^{2+}/Fe^{3+} couple in Li-ion batteries, LFS is prone to local distortions and defects such as the Li/Fe antisite defect, leading to altered electrochemical properties.

LFS has the theoretical possibility of extracting and inserting 2 Li per formula unit (Li_2FeSiO_4), but has in practice been limited to only 1 Li/fu. By taking advantage of the Li/Fe mixing, one can control the stoichiometry of the compound. Thereby it might be possible to achieve a >1-electron reaction, for instance by facilitating the diffusion of Li-ions if more vacancies are introduced due to Li/Fe mixing. Here, some samples of $Li_xFe_ySiO_4$ are studied using a total scattering approach (Bragg peaks and diffuse scattering) in an effort to gain a deeper understanding of the local order in these materials.

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THE INFLUENCE OF THE SEPARATOR AND ELECTRODE THICKNESS ON THE CELL RESISTANCE FOR ENERGY STORAGE DEVICES BASED ON POLYPYRROLE-CELLULOSE COMPOSITES

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There is currently a strong need for the development of inexpensive, flexible, light-weight and environmentally friendly energy storage devices [1]. As a result of this, research is carried out to develop versatile and flexible electrode materials as a complement to the materials used in contemporary batteries and supercapacitors. Electronically conducting polymers have received significant interest as it is well-known that these materials can be used to manufacture all-polymer-based batteries and supercapacitors [2]. The performance of the energy storage devices is ultimately limited by the resistance of the cell [3]. One step to improve the performance of these devices is therefore to consider the resistance contributions when optimizing the operational conditions and cell design.

We have previously shown [4,5] that a flexible and porous cellulose and polypyrrole composite, obtained by chemical polymerization of pyrrole on a cellulose substrate, can be used as paper-based electrode material for environmentally friendly charge storage devices. The resulting PPy-cellulose composite is highly porous and the cellulose fibers are coated with a thin layer of polypyrrole. Energy storage devices utilizing this PPy-cellulose composite as electrode material and aqueous electrolytes exhibit good cycling stability even at high charge and discharge rate [4, 5].

In the present work, we investigate the influence of the electrode and separator thickness on the cell resistance of symmetric cellulose-polypyrrole-based energy storage devices. The influence of the porosity of the separator, and the contact resistances between the current collectors and the composite on the cell resistance will be discussed, as well as the possibilities of designing inexpensive all-organic energy storage devises with promising performance regarding cycling stability and rate capability.

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ELECTROCHEMICAL CHARACTERIZATION OF LITHIUM-ION BATTERY ELECTROLYTES

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Mass-transport in the electrolyte is one of the major limiting factors for power density and energy efficiency in lithium-ion batteries. With the introduction of high power applications, such as hybrid electric vehicles, these properties are becoming increasingly important. Mass-transport characterizations of electrolytes are therefore important for benchmarking of different electrolytes, to find optimum compositions and for accurate modeling of battery cells.

Depending on the needs, the characterization can be of different levels of complexity, but still include all needed components. In the lower end of complexity is a method developed at our group called electrolyte mass-transport resistivity, used as a quick way to benchmark the losses during steady state, including both the effect of ohmic losses and losses related to concentration gradients. The results cannot, however, be used as input to models.

A more complex type of characterization, able to extract salt diffusion coefficient and cation transport number at single concentration, is based on in Situ ^{7}Li NMR imaging. It provides a direct measure of the lithium-ion concentration gradients during operation, which can then be fitted to a model to extract the mass-transport properties. To fully characterize an electrolyte, a method combining galvanostatic polarizations and concentration cells is used. It is able to extract the same properties as the NMR-based method, but also thermodynamic factors and Maxwell-Stefan diffusivities, and also their concentration dependence.

Full characterizations of the transport properties of the electrolyte have rarely been published, mainly due to lack of well-established methods. Most studies have been limited to a single temperature (most commonly 25°C), but since temperature is the single most important parameter for the lifetime of the battery and also closely related to both performance and safety, there is clearly a need to extend such studies to see how they depend on temperature. This work presents a study of the mass-transport of lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, w/w), a common electrolyte for lithium-ion battery systems, at three different temperatures: 10°C, 25°C and 40°C. The characterization method combines experimental work, modeling and numerical optimization methods to obtain the mass-transport properties.

PREPARATION AND OPTIMIZATION OF COIN CELL AND POUCH CELL FOR LI-ION BATTERY MATERIAL RESEARCH

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In battery material research several variables in sample preparation has to be taken account for reliable and repeatable characterization of electrochemical properties. Electrochemical characterization for battery materials with a new laboratory facilities were recently started at Kokkola University Consortium Chydenius. As beginners in this field we quickly observed a noticeable gap in the literature concerning practical parts of sample preparation. Humidity controlled dry room allowed us to study carefully the effects of the slurry preparation and the electrode preparation for the electrochemical performance of the samples in coin and pouch-type cells

In this research two cathode materials $LiCoO_2$ and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ were used for the cells. In order to achieve the best and most reliable testing results, the preparing parameters including slurry composition, slurry viscosity, casting thickness, casting speed and drying conditions were optimized. Anode material for the pouch cells was graphite and different types of separators were tested. Slurry and electrode coating for the parallel cells have been optimized to minimize variation in electrochemical testing

Results indicate that the casting thickness has influence on the electrochemical performance of the materials. The casting speed and viscosity of slurry have influence on the uniformity of the electrode thickness.

Poster presentation [P55]

INFLUENCE OF CO_2 POISONING ON OVERPOTENTIALS AND DISCHARGE CAPACITY IN NON-AQUEOUS Li-AIR BATTERIES

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ABSTRACT

In this letter, the effects of lithium carbonate species originating from reactions between CO_2 and Li_2O_2 or LiO_2 at the cathode of non-aqueous Li-air batteries were studied by density functional theory (DFT) and galvanostatic charge-discharge measurements. The adsorption energy of CO_2 at various nucleation sites such as step and terrace of valley and step of ridge on a stepped $(1\bar{1}00)$ Li_2O_2 surface was determined. The results show that, CO_2 binds most strongly at the step valley sites. Selective poisoning of a pure Li_2O_2 step surface by a molecule of CO_2 significantly alters the morphology of the surface due to carbonate like species formation. Nudged elastic band (NEB) calculations show that once CO_2 is adsorbed on a surface, it is unlikely to diffuse from step to terrace or vice versa. Moreover, its impact on Li_2O_2 growth mechanism, capacity and discharge/charge overpotentials is discussed. The recharging process is strongly influenced by CO_2 contamination, and exhibits significantly increased charging overpotential, which is observed already with 1 % CO2 in the cathode gas and intensified with increasing CO_2 concentration. Furthermore, a large capacity loss is seen at 50 % CO_2.

Poster presentation [P56]

PXRD STUDIES ON SODIUM ION BATTERY AT OPERANDO

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Lithium ion batteries have been successfully commercialized in the last two decades,[1-2] the availability of Li is now a serious concern in large-scale hybrid electrical vehicles and energy storage devices. Since sodium is much more abundant than Li, and Na has similar electropositive nature to Li, Na ion battery is considered to be a promising choice for these fields.[3-4] Among all different Na-based cathode materials, layered Na material is one of the most interesting types. The layered Na cathode materials have similar structure with its analogous Li materials; however, their electrochemical behavior might differ remarkably. Whilst some Li-based layered compounds (i.e., $LiMnO_2$[5], $LiFeO_2$[7], and $LiCrO_2$[9]) exhibit no reversible capacity or very fast capacity fading due to various reasons, their counterpart, Na-based compounds (i.e., $NaMnO_2$[6], $NaFeO_2$[8], and $NaCrO_2$[10]) show attractive electrochemical performance. Hence, it is of great interests to investigate the mechanisms behind the phenomenon, especially for those with abundant transition metals ($NaFeO_2$)[8]. The Powder X-ray diffraction (PXRD) is an ideal tool for investigate the crystallographic properties of the electrode materials, which enable us to correlate the structure changes of the materials to their performances when employed it during battery operation.

In this work, we have synthesized a layered O3-type cathode $Na_{0.84}Fe_{0.56}Mn_{0.44}O_2$ by means of co-precipitation and solid state method. The effect of applied voltage on capacity and cycle stability of the material has been studied. The structure change of the material during Na insertion and extraction is investigated by operando PXRD. Detail results will be shown in the poster.

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Poster presentation [P57]

DESIGN OF POLYMER-BASED NEGATIVE ELECTRODES FOR SUSTAINABLE ORGANIC BATTERIES

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Organic batteries based on conducting polymers, such as polypyrrole, polythiophene, polyaniline, have been widely studied. These devices show fast electron transport properties high recyclability and flexibility when polymers serve as anode and/or cathode materials. Conjugated polymers based on pyridines are well known as electron-transport polymer in light-emitting diodes and due to the π-deficient properties of pyridine, this type of conjugated polymers can serve as anode materials. Also, thiophene based conducting polymers shows reversible n-doping properties at low potentials. In order to increase the charge capacity of the conducting polymer, high capacity pending groups can be bound to the polymer. Since polymer conduction is only efficient at potentials where the polymer is charged the reduction potential for the pending group must be energy matched with the reduction onset of the conducting polymer. In order to enable judicious choices of polymer-pendant combinations a computational screening protocol has been developed and verified against electrochemical experiments.

The electrochemical properties of the functionalized polymers in solution have been investigated through density functional theory. The calculations were carried out within the framework of the hybrid functional B3LYP and using thermodynamics cycles for the assessment of the redox properties. The self-consistent reaction field method has been employed to account for the solvation effects. The redox potential of the pristine polymers displays good agreement with the experimental findings. The correlation between the electronic structure and electrochemistry as a function of the number of monomers, were also investigated. Furthermore, a number of possible substituents were investigated with the aim of identifying suitable functionalized polymers for the application as negative electrodes.

Poster presentation [P58]

CYCLE AND CALENDAR LIFE FOR COMMERCIAL NMC LITHIUM-ION CELLS

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The lifetime and durability of secondary batteries are vital for the competitiveness and profitability of electric vehicles and other larger energy storage applications. In this study the cycle and calendar life of Li-ion pouch cells was evaluated through long-term accelerated testing. For cycle life, Li-ion cells from the same batch were evaluated at various temperatures and charge and discharge rates. The calendar life was scrutinized at various temperatures and at different state of charge. All experiments were thoroughly controlled and statistically planned. The cells were characterized, based on continuous monitoring of capacity and energy content. In addition, periodic capacity and impedance data was recorded for all cells at the same temperature (25 °C) and discharge rate (1C). The data recording is still on-going (> 2 years) and the latest results will be presented.

The results show a distinct negative effect on both cycle and calendar life of increased temperature. For cycle life testing at 25 °C, 1C/1C and 0 to 100% depth of discharge, the remaining capacity was 70% after 5000 normalized cycles. At 32, 42 and 55 °C, the corresponding normalized cycles were 3500, 2000 and 500 respectively. A similar behavior was observed for the calendar life testing. After 2 years of storage at 80% state of charge the remaining capacities were 88, 81, 70 and 30% after storage at respectively 25, 32, 42 and 55 °C. It was also observed a negative effect of storage at higher state of charge. The recorded degradation data was fitted to an Arrhenius type model.

This work was supported by Research Council of Norway (http://www.forskningsradet.no) and ZEM AS (http://www.zemenergy.com).

ELECTROCHEMICALLY-INDUCED STRUCTURAL TRANSITIONS IN INTERCALATION MATERIALS

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The electrochemically induced rearrangement of Transition Metal (TM) cations in Li-ion intercalation compounds is not uncommon and best depicted by the conversion of layered lithium manganese oxide to spinel. Unlike the Mn-spinel, which remains highly redox-active, the layered $LiNiO_2$ structure suffers deterioration in electrochemical performance when Ni-ions are present in Li-layer.

More recently, a diverse family of polyanionic compounds has emerged with potential for improvement over the conventional TM-oxide electrode materials. While some of these, such as TM-phosphates, remain structurally stable, other such as TM-silicates Li_2MSiO_4 exhibit a substantial structural rearrangement upon electrochemical cycling. While this rearrangement renders Mn-counterpart nearly inert, it does not deteriorate the performance of Li_2FeSiO_4. Despite the fact that for Li_2FeSiO_4 this transformation involves an extensive mixing of Li- and Fe-sites during the first cycles, as found by in situ diffraction studies [1]. In general, for any new electrode material it would be very desirable to be able to predict and explain their propensity towards structural rearrangements together with the accompanying effect on the electrochemical performance.

Here we show how DFT calculations can be used to explain the mechanism and the consequences of the electrochemically induced structural phase transitions with Li_2FeSiO_4 as an example system. It is shown that full reversal of Li/Fe site occupations is energetically favoured on delithiation for all three electrochemically active Li_2FeSiO_4 polymorphs [2]. The common layered topology in the arrangement of SiO_4 and FeO_4 tetrahedra in these polymorphs transforms into a 3D-framework. Calculations show here that such a change in structure leads to a lowering of electrochemical insertion potential from ~3.1 to ~2.8 V, in good agreement with experimental data. Similar activation barriers and the dimensionality calculated for Li-ion diffusion in layered and 3D-framework Li_2FeSiO_4 essentially explain the invariably good electrochemical performance before and after the cation rearrangement [3]. Other experimental observables such as X-ray diffracton patterns have been readily simulated from the calculated structure models. Such intimate comparison of simulated data with the experimental counterpart proved to be particularily useful in discriminating the structural and topological details of the layer to 3D-framework transformation in Li_2FeSiO_4.

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IMPROVED PERFORMANCES OF NANO-SILICON BASED ELECTRODES USING LiFSI AS ELECTROLYTE SALT- A PES STUDY

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Silicon is a very promising negative electrode material for the next generation of lithium-ion batteries, as an alternative to carbonaceous electrodes used today. The interest of researchers for this material comes from its high theoretical capacity (ten times higher than graphite). However, several problems still need to be addressed: finding binders that can handle the large volume expansion experienced during cycling; understand the degradation reactions occurring during cycling; understand how to control the Solid Electrolyte Interphase (SEI) on the silicon; etc.

In our earlier work, interfacial mechanisms occurring upon the first electrochemical cycle of Si-based electrodes cycled with the classical salt $LiPF_6$ were investigated [1].

The mechanisms of Li insertion (Li_xSi formation) have been illustrated as well as the formation of a new irreversible compound, Li_4SiO_4, at the outermost surface of the particles. Upon long cycling, the formation of SiO_xF_y was shown at the extreme surface of the particles by reaction of SiO_2 with HF contributing to battery capacity fading [2].

In this work we focus on the interfacial chemistry of silicon electrodes occurring during cycling with another salt: lithium bis(fluorosulfonyl)imide $LiN(SO_2F)_2$ (LiFSI) and compared the results with the one obtained with $LiPF_6$.

When LiFSI is used, the performances of the battery are significantly improved. This electrochemical result can be correlated to the absence of fluorination of the particles surface upon long cycling. LiFSI is indeed much less sensitive to moisture than $LiPF_6$, and thus the fluorination of the surface by HF is negligible.Some degradation of LiFSI will be shown by PES and supported by calculations[3]. Our results are based on a careful depth profiling characterisation of the surface by X-ray Photoelectron spectroscopy combining both soft and hard X-rays from two different synchrotron facilities, as well as by the use of in-house XPS (Al $K\alpha$=1486.6 eV).

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BINDER-FREE NANOTUBE ELECTRODES FOR HIGH ENERGY AND POWER DENSITY 3D LI-ION MICROBATTERIES

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Over the past decades, thin-film Li-ion microbatteries with thicknesses up to 100 µm have become the dominant power sources for a wide variety of miniature electronic devices and implantable medical devices. Nevertheless, due to the increasing power requirements of the latter devices and emerging technologies, the next generation of Li-ion microbatteries is expected to provide even higher energy and power densities on a small footprint area (e.g., <1 cm^2). To date, the most promising way to maximize the energy and power densities of a microbattery is to build 3D microbatteries, in which the battery components are incorporated into a 3D micro- or nanoarchitecture.[1] Due to the limited packing size as well as high safety issues, the microbattery electrodes generally lack binders and conductive additives. So far, the studies have been mainly dedicated to the development of binder-free 3D micro- and nanostructured electrodes rather than full 3D-microbatteries, since the attainment of 3D electrodes with both high areal capacities and rate capabilities, in addition to long term cycling stability, still is not straightforward.

In the present work, we demonstrate that by using highly ordered anatase TiO_2 nanotube electrodes, an areal capacity of 0.24 mAh cm^{-2} (i.e., 96 mAh g^{-1}) at a charge /discharge current density of 2.5 mA cm^{-2} (i.e., 5C rate), and 0.46 mAh cm^{-2} (i.e. 184 mAh g^{-1}) at 0.05 mA cm^{-2}, can be achieved. The present nanotube electrodes, which have been cycled for 500 cycles with only a 6% loss of capacity, exhibited higher energy and power densities, as well as an excellent cycling stability, compared to earlier reported 3D Li-ion microbattery electrodes.

The influence of the parameters such as, the ordering, geometry and crystallinity of the nanotubes, on the microbattery performance was investigated, as shown in Figure 1. It is also demonstrated that the rate capability of the nanotube electrode depends mainly on the rate of the structural rearrangements associated with the lithiation/delithiation reaction and that the intercalation / deintercalation reaction rather than the high surface area of nanotubes is the main contributor of the high areal capacity. The areal capacity can be increased by increasing the tube wall thickness or the length, up to 0.6 mAh cm^{-2} for 100 cycles.

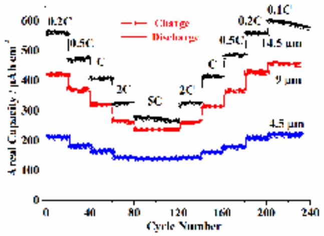

Figure 1. Rate capabilities of TiO_2 nanotube electrodes with lengths of 14.5, 9 and 4.5 µm

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SYNTHESIS AND CHARACTERIZATION OF A NEW LAYERED CATHODE MATERIAL FOR SODIUM ION BATTERIES

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Owing to the high abundance of sodium and its low cost comparing to lithium, sodium ion batteries have recentlyattracted a lot of interest as candidates for stationary and mobile energy storage device.

Herein, we present a new Na^+ ion intercalation material $Na(Co,Mn,Ni)O_2$(with space group $P6_3/mmc$) synthesized by sol-gel route in air followed by a heat treatment of 800°C for 12h. The experimental and calculated XRD of the prepared phase are represented in the figure bellow (figure1). This material offers a specific capacity of 110 mAh/g in the 2-4.2 V window, with good capacity retention and coulombic efficiency exceeding 99.2%. Figure 2 shows the first 5 cycles of the material at a current rate of C/20.

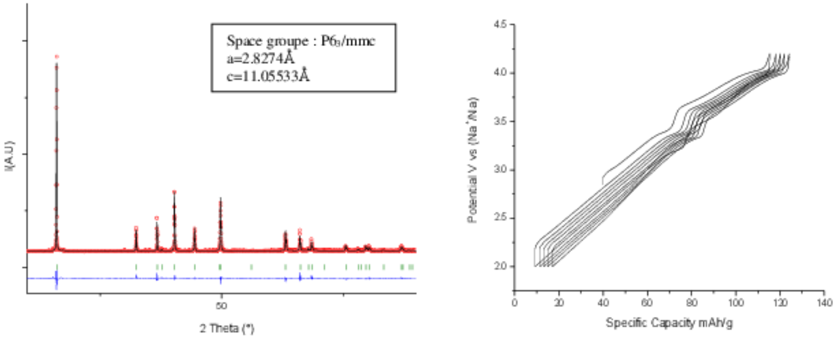

Figure1: Observed and calculated XRD profiles: (Red) observed, (black) calculated and (blue) difference plot; bar: reflections. Figure2: Potential versus capacity of the 5 first cycles at a current rate of C/20.

Poster presentation [P63]

ATOMIC LAYER DEPOSITION OF AL_2O_3 ON $LiFePO_4$ COMPOSITE ELECTRODES

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Lithium iron phosphate (LFP) is one of the most promising positive electrode materials. Inherently, it should be stable in the commonly used $LiPF_6$ based electrolytes, but even trace amounts of water produce hydrogen fluoride, which will have a degrading effect on the electrode performance. One approach to negate the electrode-electrolyte side reactions is to form a protective oxide coating on the particle or electrode surface. Atomic layer deposition (ALD) is a particularly useful technique for manufacturing such coatings as it is known to produce conformal coatings even on porous substrates with atomic scale control of film thickness. Additionally, the low process temperatures allow the deposition directly on pre-manufactured composite electrodes.

In this work, the effect of aluminum oxide coating on the rate capability and capacity retention of LFP electrodes was investigated. The aluminum oxide was applied directly on the composite electrodes using ALD with trimethyl aluminum (TMA) and H_2O as precursors. For the rate capability and capacity retention measurements, 2032-type coin cells were assembled with lithium metal as negative electrode. Cyclic voltammetry and electrochemical impedance measurements were performed using a three electrode cell with Li metal as reference electrode.

It was observed that an aluminum oxide coating of suitable thickness markedly increases the rate capability of LFP especially with higher current rates. Similarly, a reduction of polarization due to the coating was seen in the charge-discharge profiles with a more pronounced difference at higher current rates. The effect was also seen in the cyclic voltammetry measurements. From the electrochemical impedance spectroscopy it was interpreted that the charge transfer resistance of the coated electrode was 60 percent lower compared to pristine LFP electrode. In addition, the high frequency semicircle associated with the electrode-electrolyte interfacial resistance was only observed with the pristine LFP electrode. Thus it is interpreted that the aluminum oxide coating prevents the degrading reaction between LFP and the electrolyte.

Poster presentation [P64]

POST-MORTEM CHARACTERIZATION OF CYCLED COMMERCIAL LIFEPO₄//GRAPHITE CYLINDRICAL CELLS

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A better understanding of how battery usage relates to its lifetime is essential for the implementation of HEV battery systems in heavy duty, trucks and busses. In this poster we present results from a post-mortem analysis of cycle-aged commercial $LiFePO_4$//Graphite 2.3 Ah cylindrical Li-ion batteries. A similar study on calendar aged batteries at different state-of-charge (SOC) and temperatures was recently published [1] but corresponding studies of cycled commercial cells [2] have not yet been reported. Here, a battery cycled with a synthetic hybrid electric vehicle cycle (HEVC) within a narrow SOC-range and a battery cycled in constant current mode (CCC) close to 100% SOC-range are investigated and compared. After full-cell electrochemical characterization the batteries were disassembled and electrode samples from different regions were investigated by a wide range of methods including Electrochemical Impedance Spectroscopy (EIS) and capacity measurements as well as Scanning Electrode Microscopy (SEM)/Energy Dispersive X-ray (EDX), X-ray and hard X-ray photoelectron spectroscopy (XPS/HAXPES) and X-Ray Diffraction (XRD) using synchrotron facilities. The post-mortem analysis showed that the negative graphite electrodes were unevenly degraded dependent on the location in the jellyroll, whereas the positive $LiFePO_4$ electrodes appeared unaffected. For the cell cycled at constant current, showing the largest capacity loss, the major part of the central area of the negative electrode surface was covered by a thick P- and F-rich SEI film, whereas the areas close to the battery skin were much less degraded. The high impedance measured in the thick film areas, was shown to consequence in low utilization of the corresponding region of the positive electrode that was showing a lower lithiation degree. Also the hybrid-cycled cell was shown to be degraded non-uniformly over the negative electrode surface. However, the central parts of this cell were, despite the apparent Li-plating, in better shape than the outer parts. The SEI was comparably thinner and the electrochemical performance good. Accordingly, the corresponding positive electrode could be used to almost its full potential. The different and uneven aging is proposed to be a consequence of variations in current and temperature distribution in the electrodes of the cylindrical cells.

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Poster presentation [P65]

NANOSTRUCTURED MATERIALS FOR HIGH RATE-PERFORMANCE LI$^+$ BATTERY ANODES BASED ON TETRAVALENT TITANIUM COMPOUNDS

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Ti is rock-forming abundant element that makes up 0.45 % of the earth's upper continental crust. Among the Ti^{4+} (the most stable oxidation state of Ti) compounds which dominate the titanium chemistry, TiO_2 with its various polymorphs; and lithium titanium oxide ($Li_4Ti_5O_{12}$, LTO) exhibit interesting Li+ storage properties for power-oriented applications: In spite of their relative low theoretical capacities (168 mA h g^{-1} for anatase TiO_2 and 175 mA h g^{-1} for LTO), lithiation occurs at a relatively "safe" potential of 1.5 V (versus Li/Li$^+$) and above. Besides, the Li$^+$ intercalation/de-intercalation reactions in either anatase TiO_2 or LTO incur very small volume changes and hence good cycle stability is theoretically possible. However, the tetravalent Ti in TiO_2 or LTO contains empty 3d states, which characterize these Ti-based compounds electrical insulating properties. The nanoengineering modifications of anatase TiO_2 were firstly attempted to address slow electrode kinetics caused by such innate conductivity issues. A series of TiO_2 microspheres with different morphologies and microstructures were prepared and their electrochemical performance was compared to evaluate the importance of overall morphology (particle geometry, surface roughness) and microstructure (crystallite size, porosity). The results indicated that microspheres consisting of anatase nanocrystallites and a uniform distribution of mesopores could provide simultaneous improvement in the transport of Li$^+$ and electrons in the material. Another as-prepared carbon/LTO composite shows how to incorporate several design concepts in a single structure: substitutional fluoride doping to introduce Ti^{3+} in the LTO lattice to improve solid-state electronic conductivity, compact structure with nanocrystalline subunits to improve the solid-state electron/Li$^+$ diffusion, hollow interior within the structure to facilitate electrolyte percolation, and a nanocarbon coating to decrease the interparticle electrical resistance. The best-performing LTO anode highlights the importance of rationally combing these strategies for the greatest complement of functional features.