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# **ABSTRACTS – POSTER PRESENTATIONS**

# ELECTROCHEMICAL STABILITY AND SPECIATION OF A MAGNESOCENE / THF ELECTROLYTE

## Rainer Schwarz<sup>1</sup>, Piotr Jankowski<sup>2,3</sup>, Patrik Johansson<sup>2</sup>, Anna Randon-Vitanova<sup>4</sup>, Reza Younesi<sup>5</sup>, and <u>Mario Wachtler<sup>1,5,\*</sup></u>

<sup>1</sup>ZSW – Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, 89081 Ulm, Germany

<sup>2</sup> Chalmers University of Technology, Department of Physics, 41296 Göteborg, Sweden

<sup>3</sup> Warsaw University of Technology, Faculty of Chemistry, 00-664 Warsaw, Poland

<sup>4</sup> Honda R&D Europe (Deutschland) GmbH, 63073 Offenbach, Germany

<sup>5</sup> Uppsala University, Department of Chemistry – Ångström Laboratory, 75120 Uppsala, Sweden

\* mario.wachtler@kemi.uu.se

Magnesium batteries are currently attracting a lot of interest as potential post Li-ion battery technology. One of the critical issues is to find a suitable electrolyte. Classical electrolytes based on simple salts, such as  $Mg(ClO_4)_2$  or  $Mg(TFSI)_2$  (TFSI = bis(trifluoromethylsulfonyl)imide), result in a strong passivation of the Mg metal anode, which prevents reversible plating and stripping of Mg. With very few exemptions the typical Mg electrolyte is composed of metal chloride complexes or reactive chlorine-containing metal-organic compounds [1], and the contained chloride can cause problems with corrosion for several of the cell components.

Recently, we have introduced bis(cyclopentadienyl)magnesium (magnesocene, MgCp<sub>2</sub>) in tetrahydrofuran (THF) as a new chlorine-free electrolyte for low-voltage Mg batteries [2]. Unlike ferrocene, magnesocene behaves as a weak electrolyte and shows some minor dissociation in electron-donating solvents, thus exhibiting low conductivities in the order of  $10^{-5}$  S/cm [3,4]: MgCp<sub>2</sub>  $\leftrightarrow$  MgCp<sup>+</sup> + Cp<sup>-</sup>; MgCp<sub>2</sub> + Cp<sup>-</sup>  $\leftrightarrow$  MgCp<sub>3</sub><sup>-</sup>; MgCp<sub>2</sub> + MgCp<sup>+</sup>  $\leftrightarrow$  Mg2Cp<sub>3</sub><sup>+</sup>

Despite the low conductivity, high Mg plating / stripping current densities can be observed (Figure 1), which are comparable to those of other Mg electrolytes, such as Mg(BH<sub>4</sub>)<sub>2</sub> / THF [2]. The plating / stripping process shows high reversibility for many cycles, which suggests that the Mg metal anode is not overly passivated in the MgCp<sub>2</sub>-based electrolyte. X-ray photoelectron spectroscopy (XPS) characterization of the surface of the cycled Mg electrode does not reveal any significant amounts of decomposition products or passivation films (Figure 2), and indicates that the electrolyte is rather stable at the working potential of the Mg metal electrode. The anodic stability has been investigated by linear sweep voltammetry, and values of approx. 1.5, 1.7, and 1.8 V vs.  $Mg^{2+}/Mg^0$  have been observed on Pt, Cu, and stainless steel, respectively (Figure 3).

The experimental findings are corroborated by density functional theory (DFT) calculations performed for various hypothetical Mg-Cp-THF species, using implicit (C-PCM) THF solvation. The cathodic stability of these species is well below 0 V vs.  $Mg^{2+}/Mg^0$ , indicating that they should not be reduced at the potentials of the Mg plating / stripping reactions. The overall anodic stability of the electrolyte is limited by the Cp<sup>-</sup> species, which is oxidized at 1.86 V vs.  $Mg^{2+}/Mg^0$ . The DFT calculations, furthermore, show  $MgCp_2THF_2$  to be the most stable neutral species, wherein one Cp moiety is  $\eta^5$ -coordinated, the other one is  $\eta^1$ -coordinated, and the THF molecules are coordinated via their oxygen atoms (Figure 4). The structure previously resolved for solid MgCp\_2THF<sub>2</sub> crystals by X-ray diffraction [5] is thus preserved in THF solution.

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- 1. J. Muldoon, C.B. Bucur, A.G. Oliver, T. Sugimoto, M. Matsui, H.S. Kim, G.D. Allred, J. Zajicek, and Y. Kotani (2012) *Energy Environ. Sci.* 5: 5941-5950.
- 2. R. Schwarz, M. Pejic, P. Fischer, M. Marinaro, L. Jörissen, and M. Wachtler (2016) *Angew. Chem. Int. Ed.*, 55: 14958-14962.
- 3. W. Strohmeier, H. Landsfeld, and F. Cernert (1962) Z. Elektrochem. 66: 823-827.
- 4. W. Strohmeier, F. Seifert, and H. Landsfeld (1962) Z. Elektrochem. 66: 312-316.
- 5. A. Jaenschke, J. Paap, and U. Behrens (2003) Organometallics 22: 1167-1169.







Figure 3. Anodic stability of 0.5 M MgCp<sub>2</sub> / THF on Cu, Pt, and stainless steel, measured by linear sweep voltammetry at a scan rate of 0.1 mV/s.



Figure 4. Structure of MgCp<sub>2</sub>THF<sub>2</sub>, as obtained by the DFT calculations (M06- $2X/6-311++G^{**}$ , C-PCM = THF).

Figure 2. XP spectra (Mg 2p, O 1s, and C 1s) of pristine Mg metal and of Mg electrodeposited onto Cu from 0.5 M MgCp<sub>2</sub> / THF.

# Amorphous Silicon Nitride Thin Film Anodes for Li-ion Batteries

## Asbjørn Ulvestad<sup>1, 3</sup>, <u>Marte Orderud Skare<sup>2</sup></u>, Jan Petter Mæhlen<sup>1</sup>, Hanne F. Andersen<sup>1</sup>, Thomas J. Preston<sup>2</sup>, Hallgeir Klette<sup>2</sup>, Øystein Prytz<sup>3</sup> and Martin Kirkengen<sup>1,3</sup>

<sup>1</sup>Institute for Energy Technology, Department of Energy Systems, Post box 40, NO-2027 Kjeller, Norway <sup>2</sup>Institute for Energy Technology, Department of Solar Energy, Post box 40, NO-2027 Kjeller, Norway <sup>3</sup>University of Oslo, Department of Physics, Post box 1072 Blindern, NO-0316 Oslo, Norway E-mail address of corresponding author: Marte.Orderud.Skare@ife.no

Silicon has a great potential as anode material for lithium ion batteries due to its high theoretical capacity, however; there are several obstacles that need to be overcome in order to make it a commercially viable option. Two of the main issues stem from the fact that silicon undergoes a large volume change during lithiation and delithiation (1). This makes forming a stable solid electrolyte interphase (SEI) difficult, resulting in a continuous loss of electrolyte and lithium as SEI is formed and broken each cycle. Uneven expansion and contraction causes the silicon to fracture, both exposing new surface on which more SEI might form, as well as electrically disconnecting material from the electrode, rendering it inactive.

One method to reduce these effects has been to use so-called *in-situ* convertible oxides, like tin oxide and silicon sub-oxide. In this work we investigate the use of amorphous silicon nitride as an alternative convertible alloy anode material. Silicon nitride is believed to form lithiated silicon and lithium nitride or one of several lithium silicon nitride ternary phases during initial lithiation (2, 3). The silicon can be reversibly lithiated, while the remaining "matrix" is inactive under normal cycling conditions. The resulting material is therefore believed to combine the high lithium storage capacity of silicon with the high lithium ion conductivity and structural stabilization of inactive lithium containing nitrides. In a sufficiently fine structure, we hypothesize the silicon would be able to expand and contract with little to no fracturing owing to dimensional stabilization, short diffusion distances, and fast lithium transport in the matrix, resulting in a high cycling stability.

We have investigated this theory using a thin film electrode system. For this purpose, a-SiN<sub>x</sub>:H thin films were deposited on copper foil substrates using plasma enhanced chemical vapor deposition (PECVD) with silane (SiH<sub>4</sub>) and ammonia (NH<sub>3</sub>) as precursors. By comparing films with different stoichiometry, obtained by changing the flow ratio of the precursor gases in the plasma, the effect of nitrogen content on the materials lithiation capacity, Coulombic efficiency, and cycling stability was explored. In this work ellipsometry and transmission electron microscopy (TEM) were used to determine the thickness, composition, structure and quality of the pristine films. Electrochemical tests were conducted in 2032 coin cells, with a lithium metal counter electrode, using a commercial electrolyte with 5% FEC and 1% VC, and cycling was conducted between 50 mV and 1 V.

Figure 1 shows the charge capacity of three 40 nm thick SiN<sub>0.89</sub> thin film electrodes which were primed at C/6 for 6 cycles and cycled at 1C for 2400 cycles compared to a 41 nm pure silicon thin film cycled under the same conditions. The  $SiN_{0.89}$  electrodes had an average starting charge capacity of more than  $1238 \pm 24$  mAh/g, and experienced a slight increase in capacity during approximately the first 200 cycles, reaching  $1286 \pm 37$  mAh/g before leveling out. After finishing

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2400 cycles, the cells still retained an average capacity of  $1227 \pm 21 \text{ mAh/g}$ . While the pure silicon reference had a far higher starting capacity, at 3197 mAh/g, it retained only 20.0 % after 2400 cycles, compared to 99.1 % for the SiN<sub>x</sub> electrodes. Based on these results, preliminary experiments using more commercially relevant SiN<sub>x</sub> particle based electrodes have been performed. In these experiments, electrodes were made by tape casting of an aqueous slurry containing 60 wt. % SiN<sub>x</sub> produced by a method developed in-house at IFE, mixed with 10 wt. % graphite, 15 wt. % carbon black and wt. 15 % CMC binder, onto dendritic copper foil. Electrochemical testing was conducted in the same manner as the thin film electrodes, but with a rate of C/10 for the continuous cycling. Initial results from this work can be seen in Figure 2, which shows that the particle based electrodes show the same trends as were seen for the thin film electrodes. Stoichiometric crystalline silicon nitride, on the other hand, was found to exhibit negligible reversible capacity, underlining the importance of understanding the material characteristics to fully utilize its potential.



**Figure 1:** Charge capacity during cycling over 2400 cycles of three 41 nm  $SiN_{0.89}$  thin film electrodes and a 42 nm pure silicon thin film reference electrode.

**Figure 2:** Charge capacity during cycling of a  $SiN_x$  powder based electrode compared to two reference electrodes, based on silicon powder and crystalline  $Si_3N_4$  powder.

- 1. Kasavajjula U, Wang C, Appleby AJ. Nano-and bulk-silicon-based insertion anodes for lithium-ion secondary cells. Journal of Power Sources. 2007;163(2):1003-39.
- 2. Ahn D, Kim C, Lee J-G, Park B. The effect of nitrogen on the cycling performance in thinfilm Si1–xNx anode. Journal of Solid State Chemistry. 2008;181(9):2139-42.
- 3. Suzuki N, Cervera RB, Ohnishi T, Takada K. Silicon nitride thin film electrode for lithiumion batteries. Journal of Power Sources. 2013.

# IN SITU MÖSSBAUER STUDIES OF THE ELECTROCHEMISTRY IN SYMMETRIC CELLS

# Anti Liivat

Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-75121, Uppsala, Sweden.

Key words: Li-ion batteries, positive electrode, Li<sub>2</sub>FeSiO<sub>4</sub>, *in situ* Mössbauer spectroscopy, Fe<sup>4+</sup>

## Introduction

A novel form of in situ Mössbauer spectroscopy (MS) is developed to monitor the oxidation state of the Fe-ions in symmetric cells such as  $LiFeSiO_4 \parallel LiFeSiO_4 [1,2]$ . Here we use this technique to map the poorly resolvable Mössbauer spectra from the expected  $Fe^{3+}/Fe^{4+}$  redox couple in the working electrode onto the highly resolvable  $Fe^{2+}/Fe^{3+}$  spectra from the counter electrode. Comparison of such data from half-delithiated  $Li(1)Fe^{3+}SiO_4 \parallel Li(1)Fe^{3+}SiO_4$  and almost lithium-free "Li(0)Fe<sup>4+</sup>SiO<sub>4</sub>  $\parallel$  Li(0)Fe<sup>4+</sup>SiO<sub>4</sub>" symmetric cells is demonstrated – to distinguish the electrode reactions from the those involving the electrolyte.  $Li_2FeSiO_4$  has been chosen as a potential candidate for the so-called "two-electron" reactions promising doubling the capacity.

# Experimental

 $3\text{cm}^2$  disk electrodes of Li<sub>2</sub>FeSiO<sub>4</sub>/C composite with loading ~2mg/cm<sup>2</sup> were used in half- or symmetric cells (here, the electrodes were taken from cycled half.cells) in a pouch configuration suitable for MS in transmission mode. More details can be found in [1].

# **Results and discussion**



**Figure 1** a) A symmetric cell  $Li(1)FeSiO_4 \parallel Li-ref. \parallel Li(1)FeSiO_4$  working- (red) and counter (black) electrode potentials vs the amount of charge (x) are shown under charging to progressively higher voltage cut-offs (M0-M3);

Mössbauer spectra for for the working electrode (b) and for the whole cell (c) show poorly resolvable  $Fe^{4+}$  in working electrode, but clearly distinguishable emergence of  $Fe^{2+}$  (arrow) in counter electrode under the charge.

Fig. 1 shows the benefits for using a symmetric Li(1)FeSiO<sub>4</sub> || Li(1)FeSiO<sub>4</sub> cell design, in which the obscure "Fe<sup>3+</sup>/Fe<sup>4+</sup>" redox activity in the one working electrode (Fig 1b) is implicitly coupled to the readily quantifiable Fe<sup>3+</sup>/Fe<sup>2+</sup> redox activity in the other (Fig1c). Step-wise charging curves and their corresponding *in situ* MS spectra are shown in Fig. 1a for the symmetric cell at electrode potentials 4.4V, 4.6V and 4.8V vs Li<sup>+</sup>/Li. The high-velocity non-overlapping branch of the Fe<sup>2+</sup> doublet (at around v≈2 mm/s) is very sensitive to changes in the Fe oxidation states in the symmetric cell (Fig. 1c), and can therefore serve as an ideal fingerprint of bulk electrode reactions.

# Conclusions

*In situ* MS studies of  $Li_{2-x}FeSiO_4$  suggest that charging above 4V can be monitored more definitively using symmetric cells. However, electrolyte decomposition also contributes to relithiation of the Li(1)FeSiO<sub>4</sub> counter electrodes in the symmetric cells. Generally, the resolution of the *in situ* Mössbauer data can be substantially improved for any system working beyond Fe<sup>2+</sup>/Fe<sup>3+</sup> redox activity.

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- 1. A. Liivat, J.O. Thomas, J. Guo and Y. Yang (2017) Electrochim. Acta, 223, 109-114.
- 2. A. Nytén, A. Abouimrane, M. Armand, T. Gustafsson and J.O. Thomas (2005) Electrochem. Commun., **7**, 156-160.

# Variations in optimal salt content depending on polycaprolactonepolycarbonate composition in polymer electrolytes

## Christofer Sångeland, Jonas Mindemark, Reza Younesi, and Daniel Brandell

Uppsala University, Department of Chemistry – Structural Chemistry Lägerhyddsvägen 1, 751 21 Uppsala, Sweden christofer.sangeland@kemi.uu.se

Recent events concerning batteries in handheld devices have brought attention to the inherent flaw in commercial Lithium Ion Batteries – the flammable nature of the liquid electrolyte<sup>1</sup>. The liquid electrolyte facilitates the transport of ions between the electrodes and is an essential part of the battery. One strategy to solve the safety concerns is to replace the liquid electrolyte with a stable solid state electrolyte, such as the PECL-PTMC copolymer with LiTFSI salt developed by Mindemark *et al.*<sup>2</sup>. Other advantages of polymer electrolytes also include reduced cell design complexity, large scale process-ability in comparison to ceramic electrolytes, and mechanical tuneability therefore making them attractive alternatives despite lower conductivity at ambient temperature. The increasing use of batteries in our daily lives also forecasts an impending shortage and subsequent price surge of lithium. This warrants a shift towards more sustainable battery chemistries such as sodium. Sodium shares many electrochemical properties with lithium, but unlike lithium it is abundant and evenly geographically distributed<sup>3</sup>. In addition, the slightly different atomic properties of the Na<sup>+</sup> ion may prove favourable in terms of electrolyte performance. Majority of research has so far been heavily focused on ether-based polymer electrolytes operating at elevated temperatures thus leaving room for development. In this work, different compositions of PeCL-PTMC ranging from 70-30 to 100-0 mol % with different salt concentrations ranging from 5 to 35 wt. % NaFSI were synthesized and then characterized.

Electrochemical Impedance Spectroscopy (EIS) and Differential Scanning Calorimetry (DSC) were employed to characterize the polymers. Room temperature conductivity values derived from EIS measurements were on-par with the lithium-ion equivalent<sup>2</sup>. Furthermore, the optimal salt concentration varies depending on the PCL-PTMC composition (see figure 1). The relationship between conductivity and salt concentration at room temperature for the 90-10 system (see figure 1) shares some resemblance to the PEO polymer systems studied by Gray<sup>4</sup> and Sequeira *et al.*<sup>5</sup>. At elevated temperatures this behaviour becomes less evident for all systems as the PCL component becomes mechanically fluid-like and exhibits conductivity bordering to liquid electrolytes.. DSC measurements reveal that the glass transition temperature ( $T_g$ ) increases with increasing salt content. The ability to tune the optimal conductivity for the PCL-PTMC polymer system is promising, especially since it allows for high ambient temperature conductivity at low salt concentrations.



**Figure 1:** *Left* Salt concentration and Na<sup>+</sup>-conductivity dependence at room temperature (black) and 90°C (red). *Right* Salt concentration and  $T_g$  dependence.

- 1. Kalhoff. J, Eshetu. GG, Bresser. D, Passerini. S. ChemSusChem. 8(2015) 2154-2175N.
- 2. Mindemark. J, Sun. B, Törmä. E, Brandell. D. J.Power Sources. 298(2015) 166 170
- 3. Ponrouch. A, Monti. D, Boschin. A, Steen. B, Johansson. P, Palacin. MR. J. Mater. Chem. A. 3(2015) 22-42.
- 4. Fiona M. Gray. Polymer electrolytes; Chemistry, R. S. of, Ed.; Royal Society of Chemistry, 1997.
- 5. Sequeira, C.; Santos, D. Polymer Electrolytes Fundamentals and Applications; Sequeira, C.; Santos, D., Eds.; Woodhead Publishing Ltd: Great Abington, UK, 2010.

# IMPROVED CYCLABILITY OF Li METAL ELECTRODES FOR Li-O<sub>2</sub> BATTERIES WITH ADDITION OF LiNO<sub>3</sub>

# <u>Heidi Thuv</u><sup>1</sup>, Matthias Augustin<sup>1</sup>, Per Erik Vullum<sup>2</sup>, Fride Vullum-Bruer<sup>1</sup>, Ann Mari Svensson<sup>1</sup>

<sup>1</sup>Norwegian University of Science and Technology, Materials Science and Engineering, NO-7491 Trondheim, Norway <sup>2</sup> SINTEF Materials and Chemistry, Trondheim, Norway heidi.thuv@ntnu.no

## Introduction

Lithium is the desired material for the negative electrode in Li-O<sub>2</sub> batteries due to its high specific capacity and low electrochemical potential.[1] The main challenge with rechargeable metallic Li electrodes are poor cycling behaviour due to dendritic/mossy deposits and low current efficiency caused by side reactions.[2] These problems are intimately linked with the properties of the solid electrolyte interphase (SEI) which forms spontaneously on the Li surface in combination with the electrolyte, and kinetically hinders further Li corrosion. Thus, tailoring the electrolyte composition, and hence the composition and properties of the SEI can improve the performance of Li electrodes.[3, 4].

In this study, tetraethylene glycol dimethyl ether (TEGDME) and dimethylsulfoxide (DMSO) were investigated as solvents. LiTFSI and LiFSI has been proposed as compatible salts for these solvents in  $\text{Li-O}_2$  batteries. LiNO<sub>3</sub> is another promising candidate for Li metal batteries, and this salt is expected to give a more stable SEI and thus allows for the use of more reactive solvents like DMSO. [5]

# Experimental

Plating/stripping experiments were conducted in Cu/Li cells with different electrolytes.

# **Results and discussion**

Electrochemical plating and stripping of Li in Li/Cu cells were conducted in electrolytes containing the salts LiTFSI, LiFSI and LiNO<sub>3</sub> in combination with DMSO and/or TEGDME solvents, and compared to a conventional Li-ion battery carbonate electrolyte (1 M LiPF<sub>6</sub> in EC:DMC). Addition of LiNO<sub>3</sub> significantly improved the current efficiency (CE) of the Li/Cu cells with the TEGDME and DMSO based electrolytes compared to cells with only LiTFSI or LiFSI salt. Although the performance of Li metal in DMSO is improved, LiNO<sub>3</sub> does not provide sufficient passivation as this solvent reacts too vigorously with Li. Fig. 1 shows the CE of three TEGDME-based electrolytes compared to a cell with a carbonate electrolyte. The cell with only LiTFSI in TEGDME obtains a CE of only 3 % (yellow), whereas the combination of LiNO<sub>3</sub> and LiTFSI (0.5 M of each) in the same solvent, results in a CE of 97 % in the first cycles (blue). By using LiNO<sub>3</sub> as the main salt (1 M), the same high CE is reached, but the cell suddenly short circuits after only 66 cycles (red). The TEGDME based electrolytes with LiTFSI and LiNO<sub>3</sub> provides a higher and more stable initial CE than the cell with carbonate electrolyte, whereas the

latter can cycle for more cycles before failure. Electrical impedance spectroscopy (EIS) over several days has revealed that a TEGDME-LiTFSI-LiNO<sub>3</sub> electrolyte leads to a higher interfacial resistance on the Li metal than in the EC-DMC-LiPF<sub>6</sub> electrolyte, and that the interfacial resistance of Li in the TEGDME-based electrolyte also increases more with time. This can also explain the shorter cycle life of the TEGDME-based cells, as the increased resistance may favour dendrite formation. The effect of sputtered, thin films of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> on the Cu-foil was also investigated, and found to improve the coulombic efficiency for the first 50 cycles, but leading to a more rapid failure of the cells.



Figure 1. Current efficiency for Cu-electrodes in TEG-DME solvents with various salts

# Conclusions

The addition of LiNO<sub>3</sub> to LiTFSI and LiFSI containing electrolytes considerably improved the cyclability of metallic Li electrodes.

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- 1. Xu, W., et al., *Lithium metal anodes for rechargeable batteries*. Energy & Environmental Science, 2014. **7**(2): p. 513-537.
- 2. Aurbach, D., et al., A short review of failure mechanisms of lithium metal and lithiated graphite anodes in liquid electrolyte solutions. Solid State Ionics, 2002. **148**(3-4): p. 405-416.
- 3. Aurbach, D., *Review of selected electrode–solution interactions which determine the performance of Li and Li ion batteries.* Journal of Power Sources, 2000. **89**(2): p. 206-218.
- 4. Xu, K., *Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries*. Chemical Reviews, 2004. **104**(10): p. 4303-4418.
- 5. Uddin, J., et al., *Lithium nitrate as regenerable SEI stabilizing agent for rechargeable Li/O<sub>2</sub> batteries.* Journal of Physical Chemistry Letters, 2013. **4**(21): p. 3760-3765.

# Nanoplasmonics for online monitoring of lithium-ion batteries

## Jonas Hedman<sup>1</sup>, Julia morat<sup>1</sup>, David Johansson<sup>2</sup>, Elin Langhammer<sup>2</sup>, Fredrik Björefors<sup>1</sup>

<sup>1</sup>Uppsala University, Department of Chemistry - Ångström Laboratory, Box 538, SE-75121, Uppsala, Sweden Corresponding author: <u>jonas.hedman@kemi.uu.se</u> <sup>2</sup>Insplorion AB, Medicinaregatan 8A, SE-41390, Göteborg, Sweden

As the transportation industry moves towards increasing use of electrical vehicles, new improved and efficient battery systems need to be developed. The complete transition to electrical vehicles is for example inhibited by poor capacity and inadequate techniques for monitoring and understanding harmful chemical processes taking place in the battery systems. Today, information about the batteries state of charge and state of health is mainly evaluated by the temperature, current and voltage from the battery. Although readily obtained, these parameters are often insufficient tools since they do not give detailed information of what is happening in the battery during cycling.

The fabrication of nanoscale metallic structures which interact with light has lately received increasing attention in different fields of science such as photonic circuitry, metamaterials and biomedicine [1, 2]. Metallic nanostructures support optical charge carrier resonance, referred to as localized surface plasmon resonance (LSPR) [3]. Sensors based on the LSPR phenomenon are generally manufactured on a chip with noble metal nanoparticles (such as Au or Ag) deposited on a substrate such as glass. This type of sensor often requires large and expensive optical equipment and is better suited for lab environment [4]. The implementation of an optical fibre sensor based on LSPR could therefore potentially be used in batteries as a direct, on-board in-situ technique for measuring the state of charge and state of health as well as other parameters related to battery health and operation. This might help to protect the battery pack in case of unexpected failure or if set limits are exceeded leading to harmful use of the batteries. It also offers the possibility to analyse cells separately which could lead to a more efficient use of the batteries if one cell needs replacement instead of the whole battery pack.

Moreover, optical fibre based LSPR sensors have several advantages compared to other sensors based on the same phenomenon such as remote sensing capability, non-invasive nature, simplified optical design and ease of use, and great compatibility with all material types [4].

The research presented in this contribution will be focused on understanding and developing new tools for diagnostics in lithium batteries and to understand the electrochemical processes that takes place in novel materials used for energy storage. The main focus will be on what type of information that can be obtained from lithium ion batteries using nanoplasmonics as a diagnostic tool.

Nanoplasmonic sensors for batteries are presently being developed in a collaboration between Insplorion AB and Uppsala University. The cells have both been in the form of a glass chip configuration (window cell) as well as optical fibres. Figure 1 shows the LSPR peak shift for a LiFePO<sub>4</sub>-lithium half-cell using indium tin oxide (ITO) coated glass as sensor for the cathode during charge and discharge.



Figure 1. LSPR response for a LiFePO<sub>4</sub>-lithium half-cell with ITO-glass containing gold nanoparticles. Voltage vs.  $Li/Li^+$ .

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- 1. H. Nguyen, F. Sidiroglou, S. F. Collins, T. J. Davis, A. Roberts, G. W. Baxter (2013) *Applied Physics Letters*, 103(19):193116.
- J. Cao, MH. Tu, T. Sun, KTV. Grattan (2013) Sensors and Actuators B: Chemical, 181:611– 9.
- 3. A. Dmitriev, C. Hägglund, S. Chen, H. Fredriksson, T. Pakizeh, M Käll, et. al (2008) *Nano Letters*, 8(11):3893–8.
- 4. J. Cao, EK. Galbraith, T. Sun, KTV. Grattan (2012) IEEE Sensors Journal, 12(7):2355-61.

# Micron sized Si as anode for high capacity LIB

# K. Asheim<sup>1</sup>, H. Kaland<sup>1</sup>, N. P. Wagner<sup>1,2</sup>, H. F. Andersen<sup>3</sup>, J. P. Mæhlen<sup>3</sup>, A. M. Svensson<sup>1</sup>

<sup>1</sup>Norwegian University of Science and Technology, Materials Science and Engineering, NO-7491 Trondheim, Norway <sup>2</sup>SINTEF Materials and Chemistry <sup>3</sup>Institute for Energy Technology, Instituttveien 18, NO-2007 Kjeller, Norway

# Introduction

Silicon is a candidate as high capacity anode material for Li-ion batteries. Silicon has <u>a</u> ten times higher theoretical capacity compared to graphite due to the ability to form a Li rich alloy. In comparison to nano sized Si, the production cost of micron sized Si is lower, and it has a lower specific surface area reducing the amount of solid-electrolyte interphase (SEI) on the electrode. For crystalline Si, to avoid complete lithiation and electrode degradation due to volume expansion, the voltage window can be limited. This limits the lithiation of Si and provides a two-phase material where the amorphous phase is active and the crystalline phase is a stable core, giving longer cycle life [1]. In order to have a slow transition from the crystalline to the amorphous phase, a four-step precycling (or formation cycling) procedure where the lithiation is increased gradually can be applied [2].

# Experimental

Silicon based electrodes are made of 60 wt% Si (Silgrain e-Si 400), supplied by Elkem, with an average particle size of 3  $\mu$ m, 10 wt% graphite (Timcal, KS6L), 15 wt% carbon black (Timcal, C-Nergy C65, CB) and 15 wt% Na-CMC binder. Slurries were cast onto dendritic copper foil. 2016 coin cells were assembled with 1M LiPF<sub>6</sub> in EC:PC:DMC (1:1:3) + 5 wt% FEC and 1 wt% VC as electrolyte, Celgard 2400 as separator and circular Li foil as counter electrode.

Three cycling programs were evaluated; 1) voltage range 0.05 - 1.0 V at 0.1 C with 1-step formation, 2) voltage range 0.05 - 1.0 V at 0.1 C with 4-step formation, 3) voltage range 0.12 - 0.9 V at 0.1 C with 4-step formation. These were selected in order to assess the effect of the initial formation cycling and effect of limiting the voltage range. 1-step formation is defined as four cycles at 0.05 C with voltage range 0.05 - 1.0 V. 4-step formation is defined as lithiation to  $1^{st}$  500 mAh/g(Si),  $2^{nd}$  1000 mAh/g(Si),  $3^{rd}$  1500 mAh/g(Si) and  $4^{th}$  2000 mAh/g(Si) with corresponding delithiation steps to 1.0 V.

Cross sectional analysis of cycled electrodes was performed using Focused Ion Beam (FEI Helios Nano Lab Dual Beam FIB) with an acceleration voltage of 30 kV for the ion source and current of 9.3 nA. Scanning electron micrographs of the cross sections were obtained using SEM (FEI APREO).

#### **Results and discussion**

Long term galvanostatic cycling using the three programs showed that program 3) with limited voltage range gave the best cycling stability (200 cycles above 80% of initial capacity). Cells

running program 2) cycled second longest (158 cycles above 80% of initial capacity), while program 1) gave the poorest cycling with 85 cycles above 80% of initial capacity. Initial capacity being the capacity of the first cycle after the four formation cycles.

Differential capacity plots show that the difference between the formation cycling procedures is mainly the formation of crystalline  $Li_{15}Si_4$ , which is not apparent for the cells initially cycled with the 4-step formation procedure.

SEM images of cross sections made by FIB show the difference between the 1-step and 4-step formation cycling. The electrode subjected to a 1-step formation cycle is more porous and have higher degree of disconnection between particles compared to the electrode subject to the 4-step formation. Hence, for the electrodes subject to the 1-step formation cycle, it seems that the expansion and contraction of the silicon particles have been larger than for the electrodes subject to the 4-step formation procedure.

After long term cycling when the cell fails, a significant drop in capacity is observed, and the electrode material is found to have been completely covered in SEI, as shown by FIB-SEM micrographs. This indicates that at least part of the failure mechanism is electronic disconnection due to the SEI covering every part of the electrode material, probably preventing electron transport. Before the cell reaches the region where it fails, the electrode looks healthy. Even after 100 cycles as shown in a FIB-SEM micrograph of an electrode where the voltage range has been limited.

# Conclusion

Improved stability of Si-based electrodes was demonstrated by applying a 4-step initial formation procedure with gradual increase of capacity over the first four cycles. As expected, limiting the lower cut-off voltage to 120 mV also improved considerably the cycling stability compared to a lower cut-off voltage of 50 mV.

# Acknowlegments

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- M. N. Obrovac, L. J. Krause (2007) Journal of the Electrochemical Society, 154 (2) A103-A108
- 2. B. Philippe, R. Dedryvère, M. Gorgoi, H. Rensmo, D. Gonbeau, K. Edström 2013) *Journal* of the American Chemical Society, 135, 9829-9842

# ALL COPPER REDOX FLOW BATTERY

# P. Kauranen<sup>1</sup>, T. Vainikka<sup>1</sup>, L. Murtomäki<sup>1</sup>, D. Lloyd<sup>2</sup>

<sup>1</sup>Aalto University, Dept. Chemistry and Materials Science, PO Box 16100, FI-00076 Aalto, Finland pertti.kauranen@aalto.fi <sup>2</sup>Broadbit Batteries Ltd, Viikinkaari 4, 00790 Helsinki, Finland

## Introduction

Simple, robust, and potentially low cost redox flow batteries can be designed and constructed using the electrochemistry of copper. CuCl in HCl supporting electrolyte is used both as the anolyte and catholyte. During charge, Cu<sup>+</sup> is reduced to metallic copper in the negative half-cell and oxidized to Cu<sup>2+</sup> in the positive one [1,2]. The benefits of the copper redox flow battery (CuRFB) over the state-of-the-art vanadium redox flow battery (VRFB) are abundant and recyclable raw materials, simple electrolyte synthesis and use of cheap microporous separators to decrease the cost of the battery stack.

## Experimental

A five-cell CuRFB stack with 120 cm<sup>2</sup> active electrode area and rated 25 W was designed and constructed using the materials listed in Table 1 and shown in Figure 1a. The total system comprising the stack, electrolyte tanks and circulation pumps is shown in Figure 1b.

Component	Material
Bipolar electrode	Graphite foil
Anode electrode	Carbon ink
Cathode electrode	Carbon felt
Separator	Microporous PE
Flow frame	ABS
Gasket	Viton

Table 1. CuRFB stack materials.

The system was initiated for 300 h to determine the optimal operating conditions. Then, the system was operated for about 400 hours using 1 M CuCl in 6 M HCl electrolyte at 8 A (67 mA/cm<sup>2</sup>) charge and discharge current in 10 cycle sequences including a charge balancing step to equalize any imbalance between the cells due to shunt currents. Thereafter, the CuCl concentration was increased to 2 M and the current to 10 A (83 mA/cm<sup>2</sup>) and the battery was run

for another 500 hours. The nominal charging time was 1 h in both cases and the electrolyte temperature 50  $^{\circ}$ C.



Figure 1. CuRFB a) Stack design and b) prototype system.

# **Results and discussion**

The battery reached on upper voltage limit at 6.9 Ah charge in the 1 M electrolyte. A full 10 Ah could be charged in the 2 M electrolyte. The discharge performance as well as Faradaic and voltage efficiencies are shown in Figure 2. The total electrochemical efficiency was 67-70 % in both electrolytes.



Figure 2. a) Discharge capacity and b) efficiency of the prototype system.

# Acknowlegments

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- 1. D. Lloyd, E. Magdalena, L. Sanz, L. Murtomäki, K. Kontturi, (2015) *Journal of Power Sources, Vol.* 292 pp. 87-94.
- 2. Patent application PCT/FI2015/050166 / WO2015136158A1.

# FOLLOWING INTERNAL RESISTANCE CHANGES IN BATTERIES WITH A VERSATILE INTERMITTENT CURRENT INTERRUPTION TECHNIQUE

# Matthew J. Lacey<sup>1</sup>

<sup>1</sup> Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, Lägerhyddsvägen 1, 751 21 Uppsala, Sweden matthew.lacey@kemi.uu.se

Determination of the internal resistance of a battery is valuable as an indicator of performance (power capability) and state-of-health. Internal resistance is also dependent on state-of-charge (SoC) for many battery systems and may also be useful in SoC determination methods.

While there are a number of established electrochemical techniques for determining internal resistance, the most commonly employed is electrochemical impedance spectroscopy (EIS), which is a powerful technique allowing for the probing of the various resistive and reactive processes in the battery over a wide timescale. However, practical application of EIS is complicated by the requirement for specialist equipment and particularly specialist interpretation of data, especially if equivalent circuit modelling is desired. This complexity is even more the case if one wishes to follow the change in resistance over long-term testing. In many cases, a simpler method may suffice.

Galvanostatic cycling combined with an intermittent current interruption (ICI) resistance determination method is presented as such method for following resistance changes in batteries over long-term cycling. By comparison with EIS, the method gives a single time-independent value of resistance, is fast, accurate, simple to interpret and can be implemented with most conventional battery testing instruments. The method is also readily applied to three-electrode measurements.

This presentation will give an overview of the technique and some examples of its application, particularly to the analysis of lithium-sulfur batteries but also recent application to three-electrode measurements in Li-ion batteries.



Figure: Cell voltage and internal resistance vs capacity for a single cycle of a lithium-sulfur battery at a slow (C/10) charge/discharge rate. Arrows indicate direction of charge/discharge.

- 1. M. J. Lacey (2017), ChemElectroChem, 4 (8), pp. 1997-2004.
- 2. M. J. Lacey, K. Edström, D. Brandell (2015), Chem. Commun., 51, pp. 16502-16505.

# Mesoporous Si - CNT hybrid material for Li-ion battery anodes

# T. Ikonen<sup>1</sup>, <u>N. Kalidas<sup>1\*</sup></u>, J. Nieminen<sup>2</sup>, K. Lahtinen<sup>2</sup>, T. Kallio<sup>2</sup>, V.-P. Lehto<sup>1</sup>

<sup>1</sup>Department of Applied Physics, University of Eastern Finland, FI-70210 Kuopio, Finland <sup>2</sup>Department of Chemistry, Aalto University, FI-00076 Aalto, Finland \*nathiya.kalidas@uef.fi

# Introduction

Silicon is considered a promising anode material for Li-ion batteries (LIBs) but the applications in practice are limited due to the extensive volumetric expansion/contraction during lithiation/delithiation and limited conductivity as silicon is a semiconductor. The first problem can be solved by using silicon with mesoporous structure so that the pores can accommodate the volumetric expansion. The second problem can be circumvented by adding a small amount of carbon nanotubes (CNT) into the anode to increase the conductivity between the silicon particles. In the present work, different approaches to add CNTs into the anode material with mesoporous silicon microparticles were investigated. The aim was to improve the rate performance of the mesoporous silicon - carbon nanotube hybrid (PSi-CNT) material in LIB anodes.

# Experimental

Thermally carbonized PSi (TCPSi) was prepared by electrochemical etching from silicon wafers and was further milled with a planetary ball mill into micrometer range. After sieving the particles to the size fraction of 10 - 25  $\mu$ m [1], thermal carbonization was made under the gas mixture of acetylene and nitrogen in a tube oven [2]. The surface of TCPSi particles and CNTs were functionalized with amine and carboxylic groups, respectively [3]. Subsequently, silicon and CNTs were mixed in a 96:4 weight ratio based on preliminary studies on the hybrid material. For the conjugation, the carboxylic groups (-COOH) of CNTs were first activated with Nhydroxysuccimide (NHS) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) in ethanol after which TCPSi particles with amine groups (-NH2) were added into the dispersion. Four different ways to combine TCPSi and CNTs were investigated. First, a physical mixture of TCPSi and CNTs was prepared. Second, TCPSi-NH<sub>2</sub> was conjugated with CNT-COOH. Third, TCPSi-NH<sub>2</sub> was conjugated with CNT-COOH and the un-bound -NH<sub>2</sub> groups were changed into -COOH groups with succinic anhydride (SA). Fourth, the conjugation was reversed, i.e., TCPSi-COOH was conjugated with CNT-NH<sub>2</sub>.

The electrodes were prepared by mixing the PSi-CNT hybrid material, binders (CMC and PAA) and carbon black in deionized water. The prepared slurry was cast onto a copper foil and dried. The sheet was cut into electrodes and the 2016 type coin cells were assembled in a glove box under Ar atmosphere. The electrolyte used was 1 M LiPF<sub>6</sub> in 1:1 ratio of EC:DMC. The counter and reference electrode was lithium metal. Galvanostatic cycling was performed between 0.01 and 2 V while the mass loading of Si was 0.9-1.2 mg/cm<sup>2</sup>.

# **Results and discussion**

The results from galvanostatic cycling with different charging/discharging rates can be seen in Figure 1. The reference sample without CNTs (*TCPSi*) performs quite well with the low rates below 1 A/g. Physically mixed sample (*TCPSi-CNT*) performs much better at higher rates delivering a capacity over 1000 mAh/g with the rate above 2 A/g. When TCPSi was functionalized with NH<sub>2</sub> groups and subsequently conjugated with carboxylated CNTs (*TCPSi-CNT conj.*), the performance

was bad even at the lowest charging rate. It seems that the remaining amine groups after the conjugation (the ratio of TCPSi to CNT is 96/4 by weight) are detrimental to the lithiation kinetics. This was verified by reversing the conjugation of TCPSi and CNT (*TCPSi-CNT rev.*). Here, the reversely functionalized sample outperforms the original conjugation method. As the last trial, succinic anhydride was used to remove the free amine groups from the *TCPSi-CNT conj*. sample. The resulting sample (*TCPSI-CNT* + *SA*) is better than the original one but the capacity is still quite low.



**Figure 1.** Rate capability measurements on TCPSi (only silicon), TCPSi-CNT (physically mixed), TCPSi-CNT conj. (amine groups on silicon), TCPSi-CNT rev. (amine groups on CNTs), TCPSi-CNT + SA (succinic anhydride treated). Succinic anhydride treatment stabilises the capacity nicely.

#### Conclusions

Adding a very small amount of CNTs enhanced the rate capability of the silicon anode essentially. The positively charged free amine groups left on TCPSi particles hinder the capacity of the anode. The reversed functional groups work better and can also be beneficial for the Si-binder interaction.

#### References

[1] T. Ikonen, T. Nissinen, E. Pohjalainen, O. Sorsa, T. Kallio, V.-P. Lehto (2017) Scientific Reports, 7:7880.

[2] J. Salonen and V.-P. Lehto (2008) Chemical Engineering Journal, 137(1): 162-172.

[3] W. Xu, J. Riikonen, T. Nissinen, M. Suvanto, K. Rilla, B. Li, Q. Wang, F. Deng, V.-P. Lehto (2012) *Journal of Physical Chemistry C*, 116(42): 22307-22314

# The solid electrolyte interphase formation in Na<sup>+</sup>-based electrolytes

# Le Anh Ma<sup>1</sup>, Reza Younesi<sup>1</sup>

<sup>1</sup>Department of Chemistry-Ångström Laboratory, Uppsala University, SE-75121 Uppsala, Sweden Le.anh.ma@kemi.uu.se

Na-ion batteries (NIBs) have recently gained a lot of research interest due to their environmentally friendliness and cost effectiveness compared to their counterpart Li-ion batteries (LIBs). Due to the generally low electrode potential of common anode materials for NIBs (*i.e.* below 1 V vs. Na<sup>+</sup>/Na which is equal to about -1.7 vs. H<sup>+</sup>/H<sub>2</sub>) electrolyte decomposition at the negative electrode occurs. Therefore, a passivation layer known as the solid electrolyte interphase (SEI) is essential to obtain kinetically stable NIBs. In this respect, investigations on the electrolyte stability and the SEI formation is crucial.<sup>1,2</sup> The SEI layer is formed ideally during the initial discharging/charging cycle and acts like a passivation layer which is ionically conductive and electrolyte is suggested to be more soluble.<sup>3</sup> Thus, fundamental studies on SEI formation and dissolution in different Na<sup>+</sup>-based electrolyte systems become necessity.<sup>4,5</sup>

Here, we studied the SEI formation and its stability in different Na<sup>+</sup>-based electrolyte systems - with comparative experiments of equivalent Li<sup>+</sup>-based electrolytes. By conducting electrochemical techniques such as potentiometry and chronoamperometry tests on conductive substrates, we investigate the electrochemical window and the SEI dissolution after certain discharging/charging cycles. Whereas the Li<sup>+</sup>-based electrolytes maintain a stable SEI over a certain storage or relaxation time, the Na<sup>+</sup>-system shows SEI-dissolution after much shorter storage times. The composition of the SEI -and its changes over relaxation time- in Na<sup>+</sup>-electrolytes are studies using synchrotron-based hard X-ray photoelectron spectroscopy (HAXPES) measurements.

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- 1. M. Dahbi, N. Yabuuchi, K. Kubota, K. Tokiwa (2014) *Phys. Chem. Chem. Phys.*, 16: 15007-15028.
- 2. A. Bhide, J. Hofmann, A. K. Durr, J. Janek, P. Adelhelm (2014) *Phys. Chem. Chem. Phys.*, 16: 1987-1998.
- 3. R. Mogensen, D. Brandell, R. Younesi (2016) ACS Energy Lett. 1: 1173–1178.

- 4. X. B. Cheng, R. Zhang, C. Z. Zhao, F. Wei, J. G. Zhang, Q. Zhang (2016) Adv. Sci., 3, 1500213.
- 5. M. Moshkovich, Y. Gofer, D. Aurbach (2001) *Journal of The Electrochemical Society*, 148 (4): E155-E167.

Mechanical and Electrochemical Pre-lithiation of Silicon Nanoparticles <u>Alise J. Hjellbrekke<sup>1,2</sup></u>, Jan Petter Mæhlen<sup>3</sup>, Trygve T. Mongstad<sup>2</sup>, Samson Y. Lai<sup>4</sup>

<sup>1</sup>Department of Mathematical Sciences and Technology, Norwegian University of Life Sciences (NMBU), NO-1432 Ås, Norway, <u>alise.j.hjellbrekke@nmbu.no</u>

<sup>2</sup>Solar Energy Department, Institutt for Energiteknikk (IFE), NO-2007 Kjeller, Norway
<sup>3</sup>Energy Systems Department, Institutt for Energiteknikk (IFE), NO-2007 Kjeller, Norway
<sup>4</sup>Physics Department, Institutt for Energiteknikk (IFE), NO-2007 Kjeller, Norway, samson.lai@ife.no

Keywords: silicon, anode, lithium-ion battery, pre-lithiation

#### Introduction

Silicon is a widely studied material as the negative electrode of lithium-ion batteries because of its high theoretical capacity (3,572 mAh/g<sub>Si</sub> for Li<sub>15</sub>Si<sub>4</sub>) but suffers from low initial Coulombic efficiency. Pre-lithiation, which is the process of lithiating the silicon nanoparticles before they are assembled into a cell, is considered a solution to low initial Coulombic efficiency. Despite being a costly process, a silicon electrode can be electrochemically lithiated in half cells, disassembled and extracted, and reassembled into new cells with the positive electrodes. Silicon electrodes can also be mechanically pre-lithiated by pressing the electrode into lithium metal foil, effectively shorting a half cell. Compared the electrochemical pre-lithiation (EP), mechanical pre-lithiation (MP) is simpler and more cost-effective but lacks control of the lithium silicide stoichiometry or the degree of pre-lithiation. Mechanical pre-lithiation has been demonstrated to be useful, with caveats, for pre-lithiating nanowires [1]. Other methods of pre-lithiation also exist, such as with Stabilized Lithium Metal Powder (SLMP®), which has been demonstrated with graphite electrodes [2], or lithia-coated lithium silicide [3].

In this work, we compare EP and MP of silicon nanoparticles produced using a silane free space reactor at the Institutt for Energiteknikk (IFE) [4]. We hypothesize that the degree of prelithiation can be controlled by time, using mass and discharge capacity as measuring tools. We also evaluate the electrochemical cycling performance.

#### **Experimental**

Silicon nanoparticles pre-produced in a free space reactor (FSR) at IFE were used as active material on the anodes. An electrode slurry was prepared according to our previously reported methods [4]. The EP cells were assembled as half cells in 2032 coins with lithium metal foil as the counter and reference electrode. EP cells were cycled for one cycle with a rate of C/20 in Arbin, and lithiated at C/20 until reaching a voltage of 0.05 V. The lithiated cells were disassembled in an Ar-filled glove box. The Si anodes were washed with dimethyl carbonate (DMC) to remove any salts or SEI layer formed during cycling, and left overnight to dry. The dried and washed Si anodes were then weighed and reassembled into new coin cells.

The MP process was inspired by Liu et al. [1] who prelithiated Si-based anodes by sandwiching the electrode and a piece of Li-foil mechanically. Inside an Ar glove box, Li foils were scraped until shiny before being directly placed onto the Si anode wetted with 15  $\mu$ l of 1 M LiPF<sub>6</sub> electrolyte (ethylene carbonate/propylene carbonate/dimethyl carbonate (DMC) in a 1:1:3 weight ratio, respectively, with 5 wt % of fluoroethylene carbonate and 1wt % of vinylene carbonate as additives). Glass dishes were used to sandwich the pieces, and pressure was added by putting a small weight on top. After a certain number of minutes passed, the pre-lithiated Si anodes were washed with DMC to remove any salts, and left to dry overnight, before being

assembled into CR2032 half cells. Reference half cells with the same silicon were used for comparison purposes.

#### **Results and discussion**

Figure 1 describes how mechanical pre-lithiation for 3, 9, and 27 minutes affects the first and second cycle discharge capacities and the measured mass of the electrode (samples tested in duplicates). The low 1<sup>st</sup> cycle discharge capacity of the 27 minute pre-lithiation showed nearly complete pre-lithiation and the most mass gain. Note that the mass gain was larger than theoretically predicted by lithiation of only silicon, which could indicate some carbon uptake and/or residual electrolyte or rinsing solution.



Figure 1. (left) First and second cycle discharge capacity and (right) mass provide measures of degree of mechanical pre-lithiation as a function of pre-lithiation time.

#### Conclusions

Our results show that mechanical pre-lithiation can be measured by mass and 1<sup>st</sup> cycle discharge capacity and controlled by the pre-lithiation time. Work in progress is focused on comparing the performance of mechanically pre-lithiated cells with electrochemically pre-lithiated cells and reference silicon, especially with limited capacity cycling.

#### Acknowledgments

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#### References

- 1. Liu, N., et al., *Prelithiated Silicon Nanowires as an Anode for Lithium Ion Batteries*. ACS Nano, 2011. **5**(8): p. 6487-6493.
- 2. Wang, Z., et al., *Application of Stabilized Lithium Metal Powder (SLMP®) in graphite anode – A high efficient prelithiation method for lithium-ion batteries.* Journal of Power Sources, 2014. **260**(Supplement C): p. 57-61.
- 3. Zhao, J., et al., *Dry-air-stable lithium silicide–lithium oxide core–shell nanoparticles as high-capacity prelithiation reagents.* Nature Communications, 2014. **5**: p. 5088.
- 4. Andersen, H.F., et al., *Production of Silicon Particles for High-Capacity Anode Material Yielding Outstanding Production Capacity*. ECS Transactions, 2014. **62**(1): p. 97-105.

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# CLADOPHORA CELLULOSE SEPARATORS FOR LITHIUM-ION BATTERIES

# <u>Ruijun Pan<sup>1</sup></u>, Zhaohui Wang<sup>1</sup>, Jonas Lindh<sup>2</sup>, Maria Strømme<sup>2</sup>, Kristina Edström<sup>1</sup>, Leif Nyholm<sup>1</sup>

<sup>1</sup>Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, SE-751 21, Uppsala, Sweden

Ruijun.Pan@kemi.uu.se

<sup>2</sup>Department of Engineering Sciences, Nanotechnology and Functional Materials, The Ångström Laboratory, Uppsala University, Box 534, SE-751 21, Uppsala, Sweden

Lithium-ion batteries (LIBs) play a dominating role in portable devices[1] and are now gaining increased importance within the large-scale renewable energy storage and electrical vehicle markets[2]. Despite the advances in energy density (gravimetric and volumetric) and price reduction[3], safety issue, due to the use of flammable electrolyte and thermally unstable separators, remains a major problem. While solid electrolytes could provide a solution to the electrolyte problem, their use still remains challenging due to their low ionic conductivity at room temperature and insufficient mechanical robustness[4]. As a result of this, liquid organic electrolytes are still the most common LIB electrolytes, which has increased the interest in the development of thermally stable separators[5]. Another problem with polyolefin separators is their poor electrolyte wettability that prevents easy electrolyte incorporation. In this context, cellulose has emerged as the most studied alternative material to polyolefins owing to its high thermal stability, hydrophilicity, sustainability and inexpensiveness[6].

In the present work, it is demonstrated that Cladophora cellulose (CC) is particularly well-suited for use in LIB separators and that such separators straightforwardly can be fabricated via a facile and up-scalable filtration method[7]. One important advantage of the CC stems from its high crystallinity as this ensures that this type of cellulose contains very little water. The water content of the cellulose is generally a significant problem since this can give rise to large irreversible capacities upon cycling. CC separators with different thicknesses have been studied and their pore structures and performances when used in LIBs are compared. Our work shows that the CC separators are highly porous, thermally stable, inexpensive, electrochemically inert and easily wettable by common LIB electrolyte, indicating that CC separators hold significant promise with respect to application in future battery systems including large-scale applications.

# References

[1] J.-M. Tarascon, M. Armand, Nature, 414 (2001) 359-367.

[2] M.H. Ryou, Y.M. Lee, J.K. Park, J.W. Choi, Adv. Mater., 23 (2011) 3066-3070.

[3] Y. Ma, R. Younesi, R. Pan, C. Liu, J. Zhu, B. Wei, K. Edström, Adv. Funct. Mater., 26 (2016) 6797-6806.

[4] J. Zhang, J. Zhao, L. Yue, Q. Wang, J. Chai, Z. Liu, X. Zhou, H. Li, Y. Guo, G. Cui, L. Chen, Adv. Energy Mater., 5 (2015) 1501082.

[5] P. Arora, Z.J. Zhang, Chem. Rev., 104 (2004) 4419-4462.

[6] A. Mihranyan, J. Appl. Polym. Sci., 119 (2011) 2449-2460.

[7] R. Pan, O. Cheung, Z. Wang, P. Tammela, J. Huo, J. Lindh, K. Edström, M. Strømme, L.

Nyholm, J. Power Sources, 321 (2016) 185-192.

# Cathodic protection of all-solid-state LiS batteries by magnetron sputtering with lithium phosphorous oxynitride

#### Jessica Lefevre, Didier Blanchard, Eugen Stamate

Department of Energy, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark.

#### jelef@dtu.dk

Increasing use of systems based on renewable energy sources has made the battery research an important area. Li-ion batteries are commonly used in electronics devices but require many improvements to obtain longer life-time and higher energy densities. The current use of organic liquids and gels electrolytes limits these improvements because of lithium dendrites formation, reducing the lifetime of the battery and which can possibly be hazardous due to risks of short circuits.

Various alternatives to current state-of-art lithium-ion batteries exist. Among them are lithiumsulfur solid-state batteries; solid electrolytes have higher stability when compared to liquid electrolytes, with no risks of vaporization and leakage while sulfur cathodes have high theoretical energy density. LiBH<sub>4</sub> is a promising material for solid-state batteries as it is lightweight and stable electrochemically at least up to 6 V. While the orthorhombic phase (P*nma*), stable at room temperature has a low ionic conductivity (~10<sup>-5</sup> mS cm<sup>-1</sup> at 30 °C), the hexagonal phase (P63/*nmc*), stable above 110 °C, has a much higher ionic conductivity (~1 mS cm<sup>-1</sup> at 120°) [1]. When LiBH4 is nano-confined into SiO<sub>2</sub> nanoporous scaffolds, the high conductivity is kept at room temperature. We have successfully built and cycled solid-state lithium-sulphur batteries based on nanoconfined LiBH<sub>4</sub>. The first charge-discharge cycle shows capacity larger than the theoretical one based on the reduction of sulfur (see figure 1). This is most likely due to LiBH<sub>4</sub> reacting with the positive electrode and forming a cathode-electrolyte interface (CEI) [2].



**Figure 1.** Cyclic voltammogram of a LiS battery at rate 0.03 C at 55°

**Figure 2.** Cyclic voltammogram of a LiS battery at rate 0.03 C at 55° with a Lipon-coated cathode

To protect the cathode we have deposited a thin film of lithium phosphorous oxynitride (LiPON) by magnetron sputtering (see figure 2).



Figure 3. SEM image of the surface of cathodes covered with LiPON thin films

LiPON has high electrochemical stability window (0 - 5.5V) vs Li and is stable against Li metal. It is an acceptable Li-ion conductor ( $\sim 2 \cdot 10^{-6} \text{ mS cm}^{-1}$ ) and has low electron conductivity ( $\sim 8 \cdot 10^{-14} \text{ S cm}^{-1}$ ) at 25°C, furthermore the films are flexible and do not crack, even during the swelling of the cathode. These qualities make LiPON a suitable material to stabilize the electrolyte /cathodes interface in solid-state batteries [3]. We have cycled solid-state lithium-sulphur batteries with LiPON protected cathodes (see figure 2). The batteries show no increased capacity during first charge-discharge cycle and better capacity retention is observed during cycling compared to a battery with non-coated cathode (see figure 1).

- 1. D. Blanchard, A. Nale, D. Sveinbjörnsson, T. M. Eggenhuisen, M. H. W. Verkuijlen, Suwarno, T. Vegge, A. P. M. Kentgens, P. E. de Jongh, (2015) Nanoconfined LiBH4 as a Fast Lithium Ion Conductor. Adv. Funct. Mater. 25, 184 (2015).
- S. Das, P. Ngene, P. Norby, T. Vegge, P. de Jongh, D. Blanchard (2016) All-Solid-State Lithium Sulfur Battery based on a Nanoconfined LiBH4 electrolyte. Journal of the Electrochemical Society, 163 (9) A2029-A2034 (2016)
- 3. A. Christiansen, E. Stamate, K. Thyden, R. Younesi, P. Holtappels (2014) Plasma properties during magnetron sputtering of lithium phosphorous oxynitride thin films. Journal of Power Sources 273 (2015) 863-872.

# **IN OPERANDO DIFFRACTION STUDIES OF METAL-O2 BATTERIES**

## Torbjörn Gustafsson, Chenjuan Liu, William Brant, Reza Younesi and Jiefang Zhu

Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-751 21, Uppsala, Sweden torbjorn.gustafsson@kemi.uu.se

Non-aqueous metal-air (Li-O<sub>2</sub> and Na-O<sub>2</sub>) batteries have been emerging as one of the most promising high-energy storage systems to meet the requirements for demanding applications due to their high theoretical specific energy. In the present work, characterization techniques are demonstrated for the exploration of metal-O<sub>2</sub> batteries. Prominently, the electrochemical reactions occurring within the Li-O<sub>2</sub> and Na-O<sub>2</sub> batteries upon cycling are studied by *in operando* powder X-ray diffraction (XRD). This can give quantitative information about the formation of crystalline reaction products, as well as particle size and shape information.

A new *in operando* cell with a combined form of coin cell and pouch cell was designed. *In operando* synchrotron radiation powder X-ray diffraction (SR-PXD) was applied to investigate the evolution of Li<sub>2</sub>O<sub>2</sub> inside the Li-O<sub>2</sub> cells. By quantitatively tracking the Li<sub>2</sub>O<sub>2</sub> evolution, a two-step process during growth and oxidation was observed. This newly developed analysis technique was further applied to the Na-O<sub>2</sub> battery system. The formation of NaO<sub>2</sub> and the influence of the electrolyte salt were followed quantitatively *by in operando* SR-PXD. The results indicate that the discharge capacity of Na-O<sub>2</sub> cells containing a weakly solvating ether solvent depends heavily on the choice of the conducting salt anion, which also has impact on the growth of NaO<sub>2</sub> particles.

The stability of the discharge product in Na-O<sub>2</sub> cells was studied. Using both *ex situ* and *in operando* XRD, the influence of sodium anode, solvent, salt and oxygen on the stability of NaO<sub>2</sub> were quantitatively identified. These findings bring some insights into the understanding of conflicting observations of different discharge products in previous studies.

# STEP-by-STEP INVESTIGATIONS OF DEGRADATION PHENOMENA IN SILICON-CARBON COMPOSITE ANODES FROM INDUSTRIAL BATTERY GRADE SILICON

H.F. Andersen<sup>1</sup>, P.E. Vullum<sup>2</sup>, S. Müssig<sup>1</sup>, A. Ulvestad<sup>1</sup>, J. Voje<sup>3</sup>, <u>J.P. Maehlen<sup>1</sup></u>

 <sup>1</sup> Institute for Energy Technology, Kjeller, Norway jepe@ife.no
<sup>2</sup>SINTEF Materials and Chemistry, Trondheim, Norway <u>PerErik.Vullum@sintef.no</u>
<sup>3</sup>Elkem Technology AS, Kristiansand, Norway jorunn.voje@elkem.no

Silicon is a remarkable material - even in lithium ion battery technology it seems to find its utilisation. Silicon can potentially store ten times more lithium than graphitic carbon, the material commonly used as anode material in lithium ion batteries [1].

But, as always, great performance in one parameter comes with great costs in other parameters. The large lithiation capacity of silicon comes with extreme volume changes during lithiation and delithiation, resulting in cyclability becoming a huge challenge: The silicon-based anodes typically encounter massive cracking and degradation during electrochemical cycling, accompanied with a steady growth of SEI and reduction in conductivity, blocking of channels for electrolyte transport and irreversible consumption of Li-ions and electrolyte solvents and additives. Typical mitigation methods involve using nanostructured silicon [2], building of hierarchical structured silicon composites [3], optimisation of binders [4] and adding appropriate SEI forming additives [5]. Silicon as anode material has now grown to a mature field, and many degradation phenomena have been explored in detail, in particular on nanostructured silicon using powerful *in-situ* TEM studies [6].



**Figure 1**: High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image that shows a cross-section of a delithiated Silicon-Carbon composite anode cycled 39 times. The contrast scales with  $Z^2$  (Z = atomic number) and is proportional to the TEM sample thickness (vacuum is dark).

The bright areas, the "fractal blobs" or "dendritic areas", are silicon. These structures are formed due to Si migration and electrochemical sintering during the cycling. They all lay within structures with less dense carbon-containing material (dashed red lines are drawn to indicate on the circumference of these). It seems reasonable to assume that in the lithiated state, the Li-Si fills these areas and that the dashed red lines would correspond to the circumference of lithiated silicon.

The surface area is likely to give poor electric conductance. Ionic conductance can also be reduced, depending on whether the remaining pores are empty or filled with electrolyte. The full theoretical capacity of silicon of 3579 mAh/g is not required for lithium ion batteries in the near future; further improvement beyond more than approximately 1200 mAh/g have negligible impact on the overall cell capacity as the other components in the battery become dominating limiting factors. Thus, composite anodes containing both silicon and a conventional anode material such as graphite, both in considerable fractions, will likely be sufficient to meet the short-term targets for anode materials. However, while degradation mechanisms of pure nano-silicon structures have been studied in detail, similar phenomena specific to composite silicon-carbon electrodes have not. In addition, *in-situ* TEM studies of degradation mechanisms are often limited by the fact that only a single cycle or a small number of cycles are observed. In our work we have performed post-mortem FIB-SEM and TEM studies to investigate degradation occurring over a large number of cycles, examining the effect and interplay between the graphite and the silicon in composite anodes. In this presentation, we will explore different degradation phenomena observed in silicon-carbon composite anodes including:

- Electrode thickening
- Silicon migration
- Electrochemical sintering
- Dendritic surface formation

The composite silicon-carbon anodes are based on industrial battery grade silicon produced at Elkem, one of the world's leading companies for environment-friendly production of metals and materials. The anodes typically consist of nano-sized silicon crystallites, embedded in graphite and conductive carbon additives. The electrochemical performance was tested in half cells where the working electrode was typically made by mixing a silicon-carbon composite powder with an organic binder in an aqueous slurry and coated on a dendritic Cu-foil. Lithium metal was used as the counter electrode. Structural properties and degradation mechanisms were examined by electron microscopy (SEM, FIB-SEM, TEM) and XRD.

# Acknowledgments

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- [1] D. Larcher, S. Beattie, M. Morcrette, K. Edström, J.-C. Jumas, and J.-M. Tarascon, J. *Mater. Chem.*, vol. 17, no. 36, p. 3759, 2007.
- [2] U. Kasavajjula, C. Wang and A. J. Appleby, *J. Power Sources*, 2007,163, 1003; X. Su et al., *Adv. Energy Mater.*, 4 (2014), p. 1300882.
- [3] Liu, N., Z.D. Lu, J. Zhao, M.T. McDowell, H.W. Lee, W.T. Zhao, and Y. Cui, *Nature Nanotechnology*, 2014. 9(3): p. 187-192.
- [4] D. Mazouzi et al. Journal of Power Sources, 280 (2015), pp. 533-549.
- [5] L. Chen, K. Wang, X. Xie, J. Xie . Journal of Power Sources, 174 (2007), pp. 538–543.
- [6] M.T. McDowell et al., Adv. Mater. 2013, 25, 4966

# BATTERY RECYCLING: A Case Study on Metal Recovery from Spent Alkaline and Zn-C Battery

# Burçak Ebin, Martina Petranikova, Britt-Marie Steenari, Christian Ekberg

Nuclear Chemistry and Industrial Material Recycling, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

burcak@chalmers.se

# Abstract

In this study, a pyrolysis process was studied for one-step recycling of zinc (Zn) in the form of fine particles from the spent alkaline and Zn-C batteries. The Zn recovery from battery waste depends on several parameters including pretreatments to the battery waste, process temperature, gas flow rate, residence time, type of reducing agent and feeding amount. Zn recovery amount and properties of the Zn particles, as well as the pyrolysed residue processed by developed pyrolysis method from spent batteries were investigated. The results show that process temperature and reducing agent type are dominant factors affecting the Zn recovery. The recovered metallic Zn particles are in submicron size range, and particular properties are suitable for reused in primary and Zn-air batteries. The residue composes of manganese oxides and the oxidation state of the manganese can be controlled.

Keywords: battery waste, alkaline batteries, zinc, recycling, pyrolysis

# Introduction

Spent batteries are one of the main electronic waste stream and their collections have been increasing all around the world, which makes them suitable to develop sustainable recycling models. Spent primary batteries (alkaline and Zn-C) have been considering as a valuable resource for metallurgical industry due to their high metallic content of such as iron, zinc and manganese. However technological level of recycling processes are not sufficient for the widespread recovery of the spent batteries [1-3].

Currently, pyrometallurgical processes are generally used to reclaim the spent primary batteries as an alloying additive for steel industry. However, such as Zn, which is highly concentrated in the spent batteries, evaporates at the process temperature and usually collected in the steel making dust with other elements, which is difficult to recycle. On the other hand several hydrometallurgical processes were also developed to recover the valuable metals from the spent batteries. The basic steps of the hydrometallurgical approach are leaching of the spent batteries, solvent extraction, and at last electrolysis and/or precipitation. Although, there are some techniques to recover the metals from spent primary batteries, innovative recycling processes should be developed to ensure economical non-ferrous resources, as well as to support sustainable development [2-5].

# Experimental

The industrial mechanically pre-treated (shredding of batteries and magnetic separation of iron cover) alkaline and zinc-carbon battery black mass was supplied by Renova, Sweden. The battery

black mass was pyrolysed at 850 to 950°C for 15 to 60 min durations. The Zn product and residue were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), BET surface area equipment and particles sizer.

# **Results and discussion**

Zn recovery amount increases by elevating temperature and extending duration. Zn recovery reached to 99.8% at 950°C for 60 min duration using  $H_2$  as a reducing agent.



**Figure 1.** (a) Zn recovery amount as a function of temperature, time, and reducing agent type [3,5], and (b) SEM image of recovered Zn particles [4].

The recovered Zn particles has high purity and the average particle sizes range from 500 nm to 900 nm depending on the process temperature, gas flow rate and carrier gas. The pyrolysis residue mainly contains manganese (Mn), and impurities of iron (Fe) and potassium (K). Oxidation state of Mn can be controlled in the developed laboratory process, and MnO,  $Mn_2O_3$  and  $Mn_3O_4$  structures obtained from spent alkaline batteries.

# Conclusions

Zn was recovered from alkaline and Zn-C battery black mass by a pyrolysis process without using additional chemicals. The present results indicate that the suggested pyrolysis system is a promising alternative process for not only efficient Zn recovery from battery waste, but also to reclaim the manganese oxide residue for advanced material applications.

# Acknowledgments

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- 1. T. Buzatu, G. Popescu, I. Birloaga, and S. Saceanu (2013) Waste Management, 33: 699-705.
- 2. M. V. Gallegos, L.R. Falco, M. A. Peluso, J. E.Sambeth and H. J. Thomas (2013) *Waste Management*, 33: 1483-1490.
- 3. B. Ebin, M. Petranikova, B-M. Steenari, C. Ekberg (2016) Waste Management, 51: 157-167.
- 4. B. Ebin, M. Petranikova, B-M. Steenari, C. Ekberg (2016) *Journal of Analytical and Applied Pyrolysis*, 121: 333-341.
- 5. B. Ebin, M. Petranikova, B-M. Steenari, C. Ekberg (2017) Waste Management, 68: 508-517.

# BATTERY RECYCLING: Implementation of Innovative Laboratory Scale Mechanical Treatment, Hydro- and Pyro- Processes in Battery Recycling Technology

# Burçak Ebin, Martina Petranikova, Britt-Marie Steenari, Christian Ekberg

Nuclear Chemistry and Industrial Material Recycling, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

burcak@chalmers.se

# Abstract

Mechanical pretreatment, hydro- and pyro- processes were studied to recover the metals from waster battery stream. Mechanical pretreatment method were investigated not only for the waste preparation to the recycling process, but also enrichment of the waste fractions. Volatile content of the batteries were separated by pyrolysis and insoluble compounds were decomposed for the further processing. Acidic leaching and solvent extraction methods were applied to reclaim the metals in high purity. The results show that mechanical pretreatment enrich the metal fractions depending on particle size of grinded batteries. After pretreatment, high amount of the metallic fraction is recyclable from battery waste by hydro-, pyro- processes and their combinations.

*Keywords:* Battery waste, Li-ion batteries, NiMH batteries, alkaline batteries, mechanical pretreatment, hydrometallurgy, pyro- process.

# Introduction

Batteries are the indispensable part of the daily life, and various battery chemistries are used for different applications, such as alkaline batteries in daily electronic gadgets and remote controls, Zn-C batteries in hearing aids, NiMH batteries in electronic equipment and vehicles, Li-ion batteries phones, tablets, laptop computers and electronical vehicles. The future market analysis estimate that the demand on different battery chemistries will continue increasing. The amount of battery waste gives rise to concern about not only environmental issues, but also their economic value. Thus waste management of the spent batteries, which is covering their collection, classification, recycling and landfilling, is a critical issue for sustainable use of materials [1-6]. Alternative process should be developed to reclaim the metals from battery waste and create a circular economy and material chain for battery technology.

# Experimental

Li-ion car batteries and NiMH vehicle batteries were collected from car companies and battery producers. Li-ion, NiMH, alkaline and Zn-C AAA and AA type batteries were collected from industrial waste collection, separation and landfilling stations in Gothenburg, Sweden. Different processes (mechanical treatment, hydrometallurgy and pyro- processes) were applied to recover the valuable metals from the battery waste. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to elemental analysis of waste and also purity of recovered metal solutions. The waste and products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), BET surface area equipment and particles sizer.

## **Results and discussion**

The battery composition is effected from mechanical pretreatment methods. Samples from disassembled the battery waste by hand and by mechanical pretreatment show different phase compositions, which effects the further process steps. The steps of the developed recycling process for NiMH batteries is given in Figure 1.



Figure 1. Process flow of developed recycling process for NiMH batteries.

# Conclusions

Valuable metals, such as Co, Li, Ni, Mn, Zn and REEs were successfully recycled from battery waste stream. The present results indicate that the developed laboratory scale hydro- and pyro-processes are capable to recover valuable contents of the battery waste with low carbon footprint. However research should continue focusing on recycling of the new battery chemistries to create a circular material flow for battery industry.

# Acknowledgment

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- 1. S. Al-Thyabat, T. Nakamura, E. Shibata, A. Iizuka (2013) Minerals Engineering, 45: 4-17.
- 2. J. Dewalf, G. V. et al. (2010) Resources, Conversation and Recycling, 54: 229-234.
- 3. K. Larsson, C. Ekberg, A. Ødegaard-Jensen (2013) Hydrometallurgy, 133: 168-175.
- 4. C. Ekberg, M. Petranikova (2015) Lithium Process Chemistry, Chapter 7: Lithium Batteries Recycling, Elsevier, 233-267.
- 5. B. Ebin, M. Petranikova, B-M. Steenari, C. Ekberg (2016) Waste Management, 51: 157-167.
- 6. M. Petranikova, B. Ebin, S. Mikhailova, B-M. Steenari, C. Ekberg (2018) *Journal of Cleaner Production*, 170: 1195-1205.

# **Developing Manganese Oxide as Cathode for Aluminum-Ion Battery**

#### **Chunze Yuan**

Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-75121, Uppsala, Sweden chunze.yuan@kemi.uu.se

Aluminum-ion battery (AIB) is a promising alternative to Lithium-ion battery (LIB) since it presents the potential for low cost and high safety by using the earth-abundant and environmentfriendly element of Al as the anode, graphite as cathode, and non-flammable ionic liquid (IL) electrolyte.<sup>1,2</sup> Due to three-electron redox property, the Ai<sup>3+</sup>/Al of AIB anode could offer a high theoretical gravimetric capacity of 2,980 Ah kg<sup>-1</sup>, compared to 3,862 Ah kg<sup>-1</sup> of Li<sup>+</sup>/Li and 1,166 Ah kg<sup>-1</sup> of Na<sup>+</sup>/Na.<sup>3</sup> Although the low-cost, safety and stability (over 5,000 cycles) are much better, the energy density (60~76 Wh kg<sup>-1</sup>) and the efficiency (98~99.7% at a current density of 100 mA g<sup>-1</sup>) of AIB are still lower than those of LIB. Therefore, improvement of cathode materials is needed in order to match high capacity of Al anode and thus improve energy density.

Manganese oxide is a candidate to replace graphite, which can offer AIB with a higher theoretical capacity of 400 mAh g<sup>-1</sup>, energy density of 1,060 Wh kg<sup>-1</sup> and voltage of 2.65 V.<sup>4</sup> The synthesis of Manganese oxide with different crystallographic types and morphologies can be facilely controlled by hydrothermal route, wet chemical method, sol-gel method, pulsed laser deposition, and precursor technique.

Preliminarily, a type of layered structure  $MnO_2$  was synthesized by hydrothermal method. In this method aqueous KMnO<sub>4</sub> solution was acidified by HNO<sub>3</sub> to give pH ~2.5, and then the solution made a hydrothermal reaction in an autoclave under ~170°C. The black MnO<sub>2</sub> was obtained by filtering, washing, and freeze-drying. As shown in Fig. 1, the resulting MnO<sub>2</sub> was successfully used as the cathode in AIB although the capacity (~15 mAh g-1) in the first device was lower than graphite-based AIB. The high overpotential (the difference between charge and discharge voltage plateau) suggests low conductivity of cathode. And the low capacity is also attributed to low crystallinity and dense surface of MnO<sub>2</sub> cathode.

In this project, the cathode will be developed by improving MnO<sub>2</sub> quality in particle size, morphology, lattice structure, purity, crystallinity etc. The conductivity is proposed to improve by adding high conductivity additive such as graphene. The fundamental understanding of intercalation/deintercalation process and its relationship with properties of cathode material, such as the composition, morphology, lattice structure, and crystallinity, will be investigated.



Figure 1. Galvanostatic charge and discharge curves of an Al/MnO<sub>2</sub> cell at a current density of 100 mA g<sup>-1</sup>

- 1. Lin, M. C. et al. An ultrafast rechargeable aluminium-ion battery. Nature 520, 325-328 (2015).
- 2. Wang, D. Y. *et al.* Advanced rechargeable aluminium ion battery with a high-quality natural graphite cathode. *Nature communications* **8**, 14283 (2017).
- 3. Li, Q. F. & Bjerrum, N. J. Aluminum as anode for energy storage and conversion: a review. *J. Power Sources* **110**, 1-10 (2002).
- 4. Brown,G. M., Paranthaman, M. P., Dai, S., Dudney, N. J., Manthiram, A., McIntyre, T. J. & Sun, X. G. US pat., US 2012/0082904A1, (2012)

# Performance of Novel Carbon Coating on Aluminium Current Collectors for Cathode Materials in Lithium-Ion Batteries

# Morten Onsrud<sup>1</sup>, Ahmet Oguz Tezel<sup>2</sup>, Ann Mari Svensson<sup>1</sup>

<sup>1</sup>Department of Materials Science and Engineering, NTNU, 7491 Trondheim, Norway <u>mortenon@ntnu.no</u> <u>annmari.svensson@ntnu.no</u> <sup>2</sup>Graphene Batteries AS, c/o SINTEF, Forskningsveien 1, 0314 Oslo Norway <u>tezel@graphenebatteries.no</u>

Key words: LiFePO<sub>4</sub>, carbon coating, electrochemical impedance spectroscopy

LiFePO<sub>4</sub> (LFP) cathode material is generally regarded as the most favourable candidate to fulfill the safety requirements and production volume demands for electrical transportation in the future. Graphene Batteries has engineered a simple and cost effective method to improve the synergy between LFP and aluminium current collector within the cell by applying a carbon coating on the aluminium surface. The process can be easily implemented in current manufacturing techniques and it is free of any solvents or binder. As a result, rate capability measurements of coated electrodes show better performance at higher rates compared to uncoated electrodes

# Introduction

There is an unquestionable demand for better batteries in the terms of capacity, power and efficiency. The driving forces behind this necessity is multifaceted, but it is mainly driven by environmental concerns related to global climate change, human development factors and energy storage. It is predicted that petroleum-based transportation will be decrease and be substituted by the electrical car. Likewise, the shift toward intermittent renewable energy will not be achievable without some sort of energy storage system and electrochemical devices will undoubtedly play an important role. Improvements in lithium-ion battery (LIB) technology, therefore continues to be relevant. For lithium-ion batteries, cathodes are considered to be one of the crucial bottlenecks for further development.

# Experimental

Aluminium current collectors were coated with carbon, by a laboratory-developed method, before active material was applied by conventional means. Cells were assembled with lithium counter electrode and standard electrolyte. Various techniques was used to evaluated the effect of carbon coating.

#### **Results and discussion**



Figure 1. Performance comparison of coated, uncoated and commercial cells. Charge and current is measured against the volume of the LiFePO<sub>4</sub>-cathode.

#### Conclusions

A comparison of the electrochemical performance of LiFePO<sub>4</sub> (LFP) based cathodes in conjunction with and without in-house carbon coating was carried out. Several test methods have been employed, which exclusively show an improved performance for the cells with coated electrodes. In general, it can be concluded that the coating process leads to a decrease in contact resistance between the cathode material and current collector.

#### Acknowledgments

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# EXPLORING SILICA FROM DIATOM FRUSTULES AS A HIGH PERFORMANCE LOW COST AND ENVIRONMENTALLY FRIENDLY ANODE MATERIAL FOR LITHIUM ION BATTERIES

## Andreas N. Norberg<sup>1</sup>, <u>Henning Kaland<sup>1</sup></u>, Fride Vullum-Bruer<sup>1</sup>, Nils. P. Wagner<sup>1</sup>, Ann Mari Svensson<sup>1</sup>

<sup>1</sup>Norwegian University of Science and Technology, Materials Science and Engineering, NO-7491 Trondheim, Norway

henning.kaland@ntnu.no

## Introduction

SiO<sub>2</sub> materials may possess a high capacity and good cycling stability when used as anode materials for Li-ion batteries. Mostly, porous and/or carbon coated SiO<sub>2</sub> has been used, and a capacity of 1055 mAh/g at a current density of 500 mA/g at 150 cycles has been reported [1]. Furthermore, Lepoivre *et al* [2] demonstrated increased capacity of SiO<sub>2</sub> nanoparticles after application of an electrochemical activation procedure.

In this work we have investigated the potential use of  $SiO_2$  from diatom frustules as anode material for Li-ion batteries. Simple and cost efficient procedures for electrode preparation were applied, including carbon-coating procedures based on starch or sucrose. Furthermore, the electrochemical activation procedure analogous to the one described in Ref. 2 was investigated.

# Experimental

The diatom frustules were cleaned prior to use, and are depicted in SEM micrographs in Fig. 1.





Electrodes were fabricated from pristine and milled materials, and milled materials with a thin carbon coating obtained with corn starch or sucrose as carbon precursor. The slurry was composed of 50 wt% SiO<sub>2</sub>, 35 wt% carbon black (Super C65 Imerys) and 15 wt% Na-alginate binder (medium viscosity Sigma-Aldrich).

## **Results and discussion**

In Fig 2 the capacity of electrodes made from the diatom frustules are compared for the pristine (unmilled), milled, and milled and carbon coated material when cycled at 200 mA/g up to 2 V. The milled materials were subject to an electrochemical hold step of 2 mV for 48 hrs prior to cycling. A steady increase in the capacity is observed for the first 100 cycles for all electrodes, with the pristine, milled material being superior with respect to capacity.



Figure 2. a) Specific discharge capacity of electrodes with pristine, milled and milled and carbon coated diatom frustules in 1M LiPF6 1:1 EC:DEC electrolyte.

# Conclusions

A high gravimetric capacity (up to 723 mAh/g) and excellent cycling stability has been demonstrated for electrodes made from milled diatom frustules.

#### Acknowlegments

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- 1. X. Cao, X. Chuan, R.C. Massé, D. Huang, S. Li G. Cao, J. Mater. Chem A, 3 (2015) 22739
- 2. F. Lepoivre, D. Larcher, J.M. Tarascon, J. Electrochem. Soc., 163 (2016) A2791

# The influence of electrolytes on discharge products in aprotic Li/O<sub>2</sub> batteries

# Matthias Augustin<sup>1</sup>, Per Erik Vullum<sup>2</sup>, Ann Mari Svensson<sup>1</sup>, Fride Vullum-Bruer<sup>1</sup>

<sup>1</sup> Department of Material Science and Engineering, Norwegian University of Science and Technology (NTNU), Høgskoleringen 1, NO-7491 Trondheim, Norway <sup>2</sup> SINTEF Materials and Chemistry, Trondheim, Norway matthias.augustin@ntnu.no

## Introduction

The interest in secondary Li/air batteries has grown rapidly over the past two decades, as they exhibit a practically achieveable specific energy of about 1,700 Wh/kg, which equals that of gasoline and is well beyond those of conventional lithium ion (160 Wh/kg), Ni metal hydride (50 Wh/kg) and Zn/air batteries (350 Wh/kg).<sup>1,2</sup> The large energy density is due to the very lightweight cell components: a lithium metal anode, a porous carbon cathode and gaseous oxygen as active cathode material. During discharge LiO<sub>2</sub> and Li<sub>2</sub>O<sub>2</sub> (as well as Li<sub>2</sub>O) are formed *via* the oxygen reduction reaction (ORR) in the porous carbon matrix. These products are oxidized again upon recharge.

This seemingly simple system, however, has a major drawback: a decomposition of the organic electrolytes during battery cycling. The decomposition products are deposited in the cathode pores, which results in a minimized active electrode surface, decreasing capacities and cell failure upon continued cycling.<sup>3</sup>

For an in-depth investigation of the causes for early battery failures information on the ORR and/or decomposition products deposited in the carbon cathode during is needed. In order to achieve this, galvanostatic cycling and CV measurements were conducted to analyze the electrolyte influence on the cycling behavior. At different states of charge, the surface and inner structure of the cathode were investigated by SEM to obtain information on the nature, the morphology and the distribution of the product deposits in the carbon pores. Here, the potential-and time-dependent development of the product morphology is of special interest, as it gives insight into the electrochemical and/or chemical formation of the desired Li oxides and any decomposition products.

# Experimental

Galvanostatic cycling and CV measurements were performed with a Gamry600 potentiostat employing an ECC-Air test cell (EL-CELL GmbH, Hamburg, Germany) with a constant O<sub>2</sub> gas flow of 10 nL/min. The cycling experiments were done at a constant current of  $i = 75 \text{ mA/g}_{\text{C}}$  in a potential range of 2.4 V – 4.15 V vs. Li/Li<sup>+</sup>. The same potential range was used for CV measurements, which were recorded at different scan rates between 0.1 mV/s and 1 mV/s.

# Results

For the investigation of electrolyte influence on the cycling performance galvanostatic measurements were conducted with (1 M Li<sup>+</sup> ion-containing) mixtures of LiTFSI/DMSO, LiTFSI/TEGDME and (LiNO<sub>3</sub>+LiTFSI)/TEGDME. During the first cycle the LiTFSI/DMSO electrolyte showed a considerably higher initial discharge capacity  $C_{\text{spec,dis1}}$  and a lower discharge

overpotential  $\eta_{dis}$  than LiTFSI/TEGDME electrolyte (see Fig. 1, left). These observations are in good agreement with the CV measurements, where larger ORR onset and peak potentials  $E_{onset,ORR}$  and  $E_{peak,ORR}$  as well as lower initial ORR current densities  $j_{ORR}$  were observed for LiTFSI/TEGDME compared to the DMSO-based electrolyte (see Fig. 1, right).



Figure 1. Galvanostatic cycling (top) and CV (bottom) measurements with 3 different electrolytes.

However, from the second galvanostatic discharge cycle onward, the TEGDME-based electrolyte showed a considerably higher cycling stability compared to LiTFSI/DMSO. An addition of LiNO<sub>3</sub> to the TEGDME-based electrolyte resulted in an increased  $C_{\text{spec,dis1}}$  and a decrease of  $\eta_{\text{dis}}$  (see Fig. 1, left). This is also reflected in an increase of  $j_{\text{ORR}}$  as well as  $E_{\text{onset,ORR}}$  and  $E_{\text{peak,ORR}}$  in the CV (see Fig. 1, right). On the other hand, the higher cycling stability of LiTFSI/TEGDME compared to LiTFSI/DMSO was negatively influenced by an addition of LiNO<sub>3</sub> to the TEGDME-based electrolyte.

# Conclusion

LiTFSI/TEGDME shows considerably better cycling stability than LiTFSI/DMSO, although the latter electrolyte has an advantage in terms of other parameters such as the discharge overpotential and the initial discharge capacity. An addition of LiNO<sub>3</sub> to LiTFSI/TEGDME results in an improvement regarding discharge capacity and overpotential but also a decrease of the cycling stability.

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- 1. P.G. Bruce et al. (2012) Nat. Mater., 11: 19–29.
- 2. X. Yao et al. (2016) Angew. Chem. Int. Ed., 55: 11344–11353.
- 3. D. Sharon et al. (2015) Isr. J. Chem., 55: 508–520.

# Graphite Anode in K-ion Battery: The Solid Electrolyte Interphase probed by Photoelectron Spectroscopy

# M. Carboni<sup>1</sup>, R. Younesi<sup>1</sup>

<sup>1</sup>Uppsala University, Department of Chemistry - Ångström Laboratory, SE-75121 Uppsala, Sweden marco.carboni@kemi.uu.se

Since the birth of lithium-ion batteries (LIBs) in the early 1990s, this technology has been dominating the global market of the energy storage devices. One of the key features for further development of rechargeable batteries lies in the use of cheap, non-toxic and widely available materials. The increased development of devices such as portable electronics, electric vehicles, large-scale storage at power stations etc., has rapidly increased number of lithium batteries used, and therefore, the abundance of lithium reserves is becoming an important concern. In this respect, the scientific research has expanded towards new attractive alternatives such as sodium-ion batteries (NIBs) [2] and potassium-ion batteries (KIBs) [3]. Because of their higher abundancies in the Earth's crust than lithium, sodium and potassium based batteries could lower cost of rechargeable batteries. However, potassium (K) based batteries have shown to be able to provide higher cell-voltage compared to that in sodium-ion batteries. (add refs here)

Anodes consisted of graphite, hard or soft carbon have been reported to be suitable for applications in KIBs [3]. For example, K-ions can be reversibly intercalated into graphite, forming KC<sub>8</sub> with a stage-1 structure and reaching a reversible capacity of 244 mAh  $g^{-1}$  [4].

In this study, we report promising electrochemical performances of commercial graphite anode cycled *vs*. K metal in aprotic electrolytes. The composition of the solid electrolyte interphase (SEI) is here characterized using synchrotron-based photoelectron spectroscopy (PES). Galvanostatic discharge/charge cycles were carried out in half-cell composed of K metal as the negative electrode, KPF<sub>6</sub> dissolved in a mixture of EC:DEC solvent as the electrolyte, and commercial graphite as the positive electrode. Optimizing few parameters like the salt concentration and the applied current density, a specific capacity of 298 mAh g<sup>-1</sup> with a capacity retention of around 75% was achieved after the first discharge. The capacity however decreased to almost 225 mAh g<sup>-1</sup> in the following cycles, which is consistent with the theoretical capacity of KC<sub>8</sub>, forming during the last K ion intercalation stage[5].

In addition, synchrotron based hard x-ray photoelectron spectroscopy (HAXPES) measurements were performed on graphite electrodes after the first discharge and the first charge. The HAXPES spectra elucidate the composition and the stability of the SEI upon a charge/discharge cycle. The fully understanding of the mechanisms of formation/decomposition of interfaces between electrolyte/graphite can present a turning point in the development of a suitable anode for high density KIBs.

#### Acknowledgments

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- 1. J.B. Goodenough and K-S. Park (2013) J. Am. Chem. Soc., 135 (4), 1167-1176.
- 2. J-Y. Hwang, S-T. Myungb and Y-K. Sun (2017) Chem. Soc. Rev., 46 (12), 3529-3614.
- 3. X. Wu, D.P. Leonard and X. Ji (2017) Chem. Mater., 29, 5031-5042.
- 4. S. Komaba, T. Hasegawa, M. Dahbi and K. Kubota (2015) *Electrochem. Commun.*, 60, 172-175.
- 5. Z. Jian, W. Luo and X. Ji (2015) J. Am. Chem. Soc., 2015, 137, 11566-11569.

# LITHIUM INSERTION MATERIALS FOR LITHIUM-ION CAPACITORS

# <u>Taina Rauhala<sup>1,\*</sup></u>, Benedikt Rausch<sup>1,2</sup>, Olli Sorsa<sup>1</sup>, Mohammad Tavakkoli<sup>1</sup>, Jaan Leis<sup>3</sup>, Kai Vuorilehto<sup>1</sup>, Tanja Kallio<sup>1</sup>

<sup>1</sup>Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, P.O. Box 16100, 00076 AALTO, Finland, \*e-mail: taina.rauhala@aalto.fi
<sup>2</sup>University of Innsbruck, Department of Physical Chemistry, Josef-Möller-Haus Innrain 52c, 6020 Innsbruck, Austria
<sup>3</sup>Skeleton Technologies OÜ, Kaare tee 3, Lubja 74010 Harjumaa, Estonia

There is a growing need for energy storage technologies that are able to provide both high power density and high energy density in one device. Recently, lithium-ion capacitors (LICs) have emerged as one alternative to meet this demand [1]. A LIC is an asymmetric cell in which one electrode stores charge through the faradaic lithium-insertion reaction and the other utilizes the formation of the electrical double layer. In this work, we discuss the use of traditional lithium-ion battery negative electrode materials,  $Li_4Ti_5O_{12}$  and graphite, as the negative electrode in LIC cells. In addition, we have prepared a composite of single-walled carbon nanotubes and iron oxide as an alternative material for the negative electrode, which could overcome some of the shortcomings of the traditional materials.

To prepare LIC cells, we have combined  $Li_4Ti_5O_{12}$  and graphite with a high-surface area carbon positive electrode. The cells demonstrated an excellent stability over 1000 charge-discharge cycles, showing an energy retention of at least 97.5 %. Graphite was able to provide LIC cells with a high cell voltage and thus a high specific energy (90 Wh/kg on active material basis) due to its low operating potential of 0.1-0.2 V vs. Li/Li<sup>+</sup>. However, graphite must be pre-lithiated before utilization in LICs to account for the loss of electrochemically active lithium from the electrolyte due to the well-known SEI formation. Pre-lithiation introduces an additional step to the manufacturing process, which is not desirable from the industrial perspective. On the other hand,  $Li_4Ti_5O_{12}$  could be used without pre-lithiation due to its higher operating potential of 1.55 V vs. Li/Li<sup>+</sup>, but the specific energy was significantly lower (30 Wh/kg). [2]

Thus, there is a need for more optimized materials for the negative electrode that could provide a high specific energy without the problem of SEI formation. A negative electrode material with an operating potential in the lower end of the electrochemical stability window of the electrolyte is desirable. Therefore, we have prepared a composite of carbon nanotubes and iron oxide as an alternative material for the negative electrode. The carbon nanotubes have a high surface area combined with good conductivity, whereas the iron oxide undergoes a redox reaction at potentials 0.5–2.0 V vs. Li/Li<sup>+</sup>. Moreover, the carbon nanotubes can be processed into self-standing, binder-free electrodes. Therefore, we can create a composite electrode with high specific energy, high conductivity, high surface area and an operating potential within the stability window of the electrolyte.

#### References

G.G. Amatucci, F. Badway, A. Du Pasquier, T. Zheng, J. Electrochem. Soc. 148 (2001) A930–A939.
T. Rauhala, J. Leis, T. Kallio, K. Vuorilehto, J. Power Sources. 331 (2016) 156–166.

# **Electrochemical Properties of Functionalized Lithium Organic Thin Films**

J. Heiska<sup>1</sup>, M. Nisula<sup>1</sup>, M. Karppinen<sup>1</sup>

<sup>1</sup>Department of Chemistry and Materials Science, Aalto University, FI-00076 Aalto Finland juho.heiska@aalto.fi

#### Introduction

Lithium-ion microbattery is already an established technology, but there is yet a high demand to increase the energy available per area [1]. Organic electrode materials provide us with an interesting alternative to the currently employed inorganic electrode materials as they possess high gravimetric energy and power densities, their structural diversity is immense, they are abundant, and the production is possible from sustainable recourses. In addition, the thin films consisting of inorganic-organic hybrids often appear to be flexible and transparent; both of these properties could be of benefit in some microbattery applications.

One of the major problems of organic electrode materials is their low intrinsic conductivity and therefore large amounts of conductive carbon need to be added when these materials are used in conventional battery cells [2]. However, when the organics are deposited as thin films the diminished dimensions mitigate the conduction problem such that it is possible to take the full advantage of the intrinsic high gravimetric capacity of the organics. Another problem arises from the fact that the organic electrode materials are often prone to dissolve in the conventional liquid electrolytes, which would result in poor cycling stability and fast capacity fade. However, in the thin-film microbatteries the electrolyte is solid, which completely negates the problem with dissolution.

# Experimental

The organic molecules investigated in this study as novel microbattery electrode candidates are analogous to the already known organic negative electrode material lithium terephthalate (Li<sub>2</sub>TP). For the growth of the thin films we employ the strongly emerging atomic/molecular layer deposition (ALD/MLD) technique that is derived from the state-of-the-art and industrially feasible ALD technique for inorganic thin films. We have already demonstrated earlier that ALD/MLD is a viable method for producing high-quality and electrochemically active Li<sub>2</sub>TP thin films [3].

The organic molecules investigated differ by having various functional groups or substituted heteroatoms compared to the terephthalic acid (TPA) precursor used for the deposition of the Li<sub>2</sub>TP films. The investigated organic compounds were 2-aminoterephtalic acid (TPA2A), 2-bromoterephtalic acid (TPABr), 2,5-dihydroxylterephtalic acid (TPA25OH) or 2,5-pyridinecaboxylic acid (PDC25) coupled with the metal precursor LiTHD (THD = 2,2,6,6-tetramethyl-3,5-heptanedione). The resultant Li-organic thin films were characterized using XRR, GIXRD and FTIR. Electrochemical properties of the films were examined with cyclic voltammetry and galvanostatic cycling in a cell with a Li/Li<sup>+</sup> counter electrode.

#### **Results and discussion**

All the films were uniform and in theory the process should work as well for 3D structures increasing the capacity per area even more. Out of the hybrids investigated,  $Li_2TP2A$  and  $Li_2TP25OH$  were found to be crystalline and the rest of them amorphous. The amino group of  $Li_2TP2A$  or the hydroxyl groups of  $Li_2TP25OH$  were not lithiated during the deposition.

In inorganic systems the redox reaction is based on the modified valence state of a metal atom. In organic systems the negative charge is balanced over the whole aromatic system even if the redox active atom is often an oxygen. This opens up the possibility to modify the energy of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO are directly related to the voltage where the delithiation and lithiation occur, respectively. By substituting a carbon atom or by attaching an electron withdrawing or electron donating group to the conjugated section of the molecule the HOMO and LUMO energies are modified. For our Li-organic thin films, the electrochemical measurements revealed that the average discharge voltage was decreased for compounds with the electron donating groups and increased for the electron withdrawing groups, as expected. While the parent Li<sub>2</sub>TP thin films had exhibited a flat reduction potential over numerous cycles [3], the modified Li-organic materials were found to have a flat reduction potential only during the 1<sup>st</sup> cycle and thus the lithiation mechanism was drastically altered by the functionalization.

- 1. M. Roberts, P. Johns, J. Owen, et al. (2011) J. Mater. Chem. 21(27): 9876-9890.
- V. Oltean, B. Philippe, S. Renault, R. Duarte and D. Brandell (2016) *Chem. Mater.* 28(23): 8742-8751.
- 3. M. Nisula and M. Karppinen (2016) Nano Lett. 16(2): 1276-1281.

# The impact of cut-off voltage in tin-phosphide anodes for sodium-ion batteries

# Ronnie Mogensen<sup>1</sup>, Reza Younesi.

<sup>1</sup> Department of Chemistry-Ångström Laboratory, Uppsala University, SE-75121 Uppsala, Sweden. Ronnie.Mogensen@Kemi.uu.se

## Introduction

Tin phosphide (Sn<sub>4</sub>P<sub>3</sub>) is a promising anode material for sodium-ion batteries (NIBs) since it has been shown to provide a quite stable cycling in comparison to most other alloying anodes for NIBs<sup>1</sup>. As tin phosphide undergoes high volume expansion-contraction during dischargingcharging<sup>2</sup>, there is a challenge to create and maintain a functional solid electrolyte interphase (SEI) during the cell cycling. In an attempt to find a practical cycling regime for tin phosphide anodes, we have investigated the impact of cut-off voltage on capacity retention using hard x-ray photoelectron spectroscopy (HAXPES) and electrochemical methods. The study includes the two most popular salts for NIBs -1 M NaPF<sub>6</sub> and 1 M NaFSI- which were dissolved in 1:1 EC:DEC with 10 vol% FEC. Electrochemical methods included both galvanostatic cycling and pause/relaxation tests in order to assess the stability for the SEI for the respective systems at high and low potentials. HAXPES is utilized to investigate the SEI composition in cells cycled to a charge voltage of 1.2 V and 2 V.

#### Experimental

Tin phosphide  $(Sn_4P_3)$  was synthesized by ball milling metallic tin (Aldrich >99%) and red phosphorous (Alfa Aesar 325 mesh 98.9%) in a 4:3 stoichiometric mix.

Tin phosphide anodes were produced by ball milling  $Sn_4P_3$  with Super P carbon (Erachem) and sodium carboxymethylcellulose (NaCMC)(Sigma-Aldrich) binder in an 8:1:1 weight ratio after which the water-based slurry was coated on copper foil.

The two electrolytes investigated consisted of 1 M sodium hexafluorophosphate (NaPF<sub>6</sub>) (Alfa Aesar >99%) and 1 M sodium bis(fluorosulfonyl)imide (NaFSI, Solvionic) both in a separate 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (both BASF) with 10 vol% of fluoroethylene carbonate (FEC, Aldrich 99%). The galvanostatic cycling and pause/relaxation tests was performed with the current density of 50 mA g<sup>-1</sup> using a Digatron Battery Testing System.

#### Results

The galvanostatic cycling results showed that there is increased capacity retention in the cells charged up to 1.2 V as compared to the cells charged to 2 V using the NaPF<sub>6</sub> based electrolyte, while there seems to be no significant difference for the cells with NaFSI based electrolyte. However, the capacity retention is superior in the cells using the NaFSI based electrolyte.

HAXPES results on composition of SEI formed on tin phosphide anodes at different state of charge will be presented in the conference.

In addition to the results from half-cells using sodium counter electrodes, symmetrical cells and full-cells utilizing Prussian blue cathodes will also be included in order to elucidate the contribution of metallic sodium in the cells.



Figure 1. Normalised discharge capacities from galvanostatic cycling of tin phosphide cells containing NaPF<sub>6</sub> (black) and NaFSI (red) using two different cut-off voltages.

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- 1. H. Usui *et al.*, Charge–Discharge Properties of a Sn 4 P 3 Negative Electrode in Ionic Liquid Electrolyte for Na-Ion Batteries. *ACS Energy Lett.* **2**, 1139–1143 (2017).
- 2. Y. Kim *et al.*, Tin phosphide as a promising anode material for Na-ion batteries. *Adv. Mater.* **26**, 4139–4144 (2014).

# AALTO METALLURGY: ENVIRONMENTAL AND CIRCULAR ECONOMY IN BATTERY RECYCLING

#### <u>B. P. Wilson<sup>1\*</sup></u>, A. Porvali<sup>1</sup>, M. Aaltonen<sup>1</sup>, S. Ojanen<sup>2</sup>, E. Eronen<sup>1</sup>, A. Chernyaev<sup>1</sup>, R. Serna<sup>2</sup> and M. Lundström<sup>1</sup>

<sup>1</sup> Hydrometallurgy and Corrosion, Dept. of Chemical and Metallurgical Engineering (CMET), School of Chemical Engineering, Aalto University, P.O. Box 16200, FI-00076 Espoo, Finland <sup>2</sup> Minerals Processing, Dept. of Chemical and Metallurgical Engineering (CMET), School of Chemical Engineering, Aalto University, P.O. Box 16200, FI-00076 Espoo, Finland \*ben.wilson@aalto.fi

Battery consumption is growing at an ever-increasing rate as modern lifestyles rely more and more on equipment that requires mobile electrical storage solutions. Consequently, the requirement for the components that comprise modern battery chemistries are also experiencing unprecedented levels of demand. For example, many of the materials used in contemporary batteries types for applications like mobile phones, laptops and electric vehicles typically contain lithium, cobalt and nickel or combinations thereof e.g. NCA (LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>), NMC (LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub>), LMO (Li<sub>2</sub>Mn<sub>2</sub>O<sub>4</sub>) [1]. NiMH batteries also contain appreciable amounts of Rare Earth Elements (REEs) like cerium, lanthanum, praseodymium and neodymium that have been identified by the European Union as critical raw materials due to their shortage of supply or economic impact [2].

Furthermore, the current recycling rates of these materials is also low – for example,  $\geq 1\%$  for REEs and Li – meaning that at current rates of use, many of these resources could quickly become exhausted. As a consequence, spent battery waste offers a rich source of both critical (Co, REEs) and economically valuable (Li, Ni, Cu) materials, the concentrations of which, are comparable with current ore bodies e.g. Co ~20% w/w *cf*. 0.1 to 0.4% (sedimentary ores, Mt. Isa, Australia) [3]; Li 2.9 – 3.7% w/w *cf*. 0.4% - 4% (Hectorite, Jaderite and Pegmatite minerals, Sonora, Mexico, Jadar, Serbia and North Carolina, USA) [4].

The purpose of Aalto MET's projects has been to investigate new ways for the exploitation of this "*Resource Rich Urban Mine*" in order to maximise the industrial potential of battery waste and as consequence, produce a positive impact on the global environment. Research was performed for all unit processes in metal production from mechanical separation through pyrometallurgical and/or hydrometallurgical treatment. Investigations into innovative methodologies based on the twin principles of circular economy and industrial best practice have resulted in a critical understanding to Finland of how to deal with these types of wastes that encompasses manufacturing processes from crushing/sorting to the generation of prospective feedstock materials for both metal and battery/electronics production.

#### References

[1] N. Nitta, F. Wu, J.T. Lee, G. Yushin, *Li-ion battery materials: present and future. Mater. Today*, 18, **2015**, 252-264.

[2] European Commission, EU Communication: 2017 List of Critical Raw Materials for the EU (COM (2017) 490), 2017, 1-8.

[3] S. Hannis, A. Minks, Cobalt, British Geological Survey, 2009, 1-19.

[4] T. Brown, A. Walters, N. Idoine, G. Gunn, R.A. Shaw, D. Rayner, Lithium, *British Geological Survey*, **2016**, 1-39.

# Comparison of cyclability of over-lithiated and doped lithium cobalt oxide electrode materials for lithium ion batteries

# K. Lahtinen<sup>1</sup>, T. Rauhala<sup>1</sup>, S. Räsänen<sup>2</sup>, T. Kallio<sup>1</sup>

<sup>1</sup>Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, P.O. Box 16100, FI-00076, AALTO, Finland katja.lahtinen@aalto.fi

<sup>2</sup>Freeport Cobalt, B.O. Box 286, FI-67101 Kokkola, Finland

Since the commercialization of lithium ion batteries in 1991, lithium cobalt oxide (LiCoO<sub>2</sub>) has been used as positive electrode material in them. Even now, a few decades later, LiCoO<sub>2</sub> is still one of the most used materials in lithium ion batteries in portable applications as it exhibits high operating voltage, low self-discharge and high reversibility. As the result of three decades of investigation, several improvements have been done. Among these, the voltage ranges in the LiCoO<sub>2</sub> applications have increased. This in turn has introduced new challenges for the material durability. To enhance the cycle life of LiCoO<sub>2</sub>, several procedures have been proposed. However, comparing these procedures is difficult because the preparation methods are not convergent. In this work, we have compared two procedures, doping and over-lithiation, and their effect on the cycle life properties of the LiCoO<sub>2</sub> materials. Both the procedures have already been reported in literature [1-4]. However, in our work the same preparation method and the same  $Co_3O_4$  precursor were used to prepare all the LiCoO<sub>2</sub> materials to ease the comparison. The purpose of this work is to compare the cycle lives of the materials at two different potential ranges.

The LiCoO<sub>2</sub>/graphite full cells cycled in larger voltage range (3.0 V - 4.4 V) have clearly shorter cycle lives than the cells cycled in smaller voltage range (3.0 V - 4.2 V). Of the investigated materials, the doped LiCoO<sub>2</sub> has clearly superior cycling properties compared to the stoichiometric and over-lithiated LiCoO<sub>2</sub> materials. In addition, the relative cycle life differences between the small and the large voltage ranges varied depending on the LCO materials. Especially the cycle lives obtained at the small voltage range are promising compared to cycle lives of commercial applications. The differences between the materials are attributed to charge transfer impedances of the LiCoO<sub>2</sub> materials induced by changes in the structures.

- 1. S. Levasseur, M. Menetrier, E. Suard, and C. Delmas (2000) *Solid State Ionics*, 128(1-4): 11-24.
- 2. N. Imanishi (2001) Solid State Ionics, 140(1-2): 45-53.
- 3. C. N. Zaheena, C. Nithya, R. Thirunakaran, A. Sivashanmugam, and S. Gopukumar (2009) *Electrochimica Acta*, 54(10): 2877-2882.
- 4. J. W. Fergus (2010) Journal of Power Sources, 195: 939-954.

# Sol-gel synthesis and characterization for high voltage cathodes materials LiMnPO<sub>4</sub>

Tao Hu<sup>1</sup>, Daniele Di Lecce<sup>2</sup>, Jusef Hassoun<sup>3</sup>, Ulla Lassi<sup>1</sup>

<sup>1</sup>University of Oulu, Research unit of Sustainable chemistry, FI-90014 Oulu, Finland tao.hu@oulu.fi <sup>2</sup>Sapienza University of Rome, Chemistry Department, P.le Aldo Moro 5, 00185 Roma, Italy

<sup>3</sup>Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via Fossato di Mortara, 17, 44121, Ferrara, Italy

#### Introduction

As one of the phosphor-olivine materials LiMnPO<sub>4</sub> is a potential cathode for lithium-ion battery because of high thermal stability, low cost, environmental sustainable and high theoretical energy density. The LiMnPO<sub>4</sub> material is prepared by sol-gel method and characterized by X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and transmission electron microscopy. The material shows suitable galvanostatic cycling with a working voltage of about 4.1 V that is higher than the 3.5 V value expected from the most common olivine material, i.e. LiFePO<sub>4</sub>, however with a low specific capacity. Hence, electrochemical impedance spectroscopy (EIS) is used to study the lithium deinsertion-insertion within the LiMnPO<sub>4</sub> structure.

#### Experimental

A solution containing lithium dihydrogen phosphate, manganese acetate tetrahydrate and citric acid in the molar ratio 1:1:1 was mixed in a rotary evaporator at 60 °C until a gel was formed (after about 12 h of stirring). The gel was dried overnight in oven at 70 °C, heated under air to 350 °C with a rate of 2 °C min<sup>-1</sup> and held 1 h at 350 °C. The powder obtained was ground in a mortar, heated under air to 550 °C with a rate of 5 °C min<sup>-1</sup>, and held 10 h at 550 °C to obtain the LiMnPO<sub>4</sub> phase. This light gray powder LMP was afterwards carbon coated by pyrolysis procedure. The LMP powder was suspended in a sucrose/water solution (weight ratio LMP:sucrose = 80:20 %); the suspension was dried in a rotary evaporator at 60 °C in order to precipitate a homogeneous sucrose layer over the olivine particles. The powder above obtained was heated under Ar flow to 700 °C with a rate of 5 °C min<sup>-1</sup>, and held 3 h at 700 °C to produce a carbon-LiMnPO<sub>4</sub> composite (black powder LMP@C).

#### **Results and discussion**



Fig. (a) Evolution of the lithium diffusion coefficient ( $D_{Li+}$ ) by changing the state of charge from analysis of the EIS spectra. Top panel: lithium diffusion coefficient; Bottom panel: related position on the voltage profile and schematic representation of the MnPO4/LiMnPO4 ratio. (b-d) Galvanostatic cycling of C-coated LiMnPO4 electrode cycled in lithium half-cell at 70 °C in the 2.5-4.5 V voltage range by using CC procedure; (b) voltage profiles at C/5, C/3, C/2, and 1C rates; (c) voltage profiles and (d) corresponding cycling behavior at C/2 rate (1C=170 mA g<sup>-1</sup>).

We characterized a LiMnPO<sub>4</sub> electrode prepared by sol-gel technique and coated by 3 wt% of carbon. The olivine material revealed aggregates of submicrometrical grains (< 100 nm), and minor structural and morphological changes upon carbon coating. The study in lithium cell suggested a reversible lithium insertion-deinsertion into the olivine, a (de)lithiation degree of about 70 %, and an EIS response including passivation layers, charge transfer process, semi-infinite lithium diffusion into LiMnPO<sub>4</sub>, as well as finite length effects. The results indicated lithium diffusion coefficient slightly varying within the within the  $10^{-14} - 10^{-13}$  cm<sup>2</sup> s<sup>-1</sup> range at several states of charge.