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A hard X-ray photoelectron spectroscopy study on the solid electrolyte interphase of a lithium 4,5-dicyano-2-(trifluoromethyl)imidazolid based electrolyte for Si-electrodes

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Abstract

This report focuses on the relatively new salt, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolid (LiTDI), and its functionality together with a silicon based composite electrode in a half-cell lithium ion battery context. LiTDI is a promising alternative to the commonly used LiPF₆ salt because it does not form HF which can decompose the oxide layer on Si. The formation of a solid electrolyte interphase (SEI) as well as the development of the active Si-particles are investigated during the first electrochemical lithiation and de-lithiation. Characterizations are carried out at different state of charge with scanning electron microscopy

(SEM) as well as hard x-ray photoelectron spectroscopy (HAXPES) at two different photon energies. This enables a depth resolved picture of the reaction processes and gives an idea of the chemical buildup of the SEI. The SEI is formed by solvent and LiTDI decomposition products and its composition is similar to SEI formed by other carbonate based electrolytes. The LiTDI salt or its decomposition products are not in itself reactive towards the active Si-material and no unwanted side reactions occurs with the active Si-particles. Despite some decomposition of the LiTDI salt, it is a promising alternative for electrolytes aimed towards Si-based electrodes.

Keywords: lithium 4,5-dicyano-2-(trifluoromethyl)imidazolid, silicon negative electrode, solid electrolyte interphase, hard x-ray photoelectron spectroscopy

1. Introduction

Batteries using the lithium-ion technology have the highest gravimetric and volumetric capacities among the commercially available rechargeable battery systems. In recent years these advantages have made lithium-ion batteries the dominating power supply technique for portable electronics [1]. Yet the demand for improved performance leads to a race for new battery materials with better functionality at a lower cost.

One group of materials that offer high storage capacities are those which can form alloys with lithium [2]. Silicon is in this perspective the most interesting alternative because it has the highest theoretical storing capacity of 3579 mAh g^{-1} ; almost ten times higher than graphite [3]. Si as a negative electrode material for lithium ion batteries is, on the other hand, connected to limitations due to large volume changes during lithiation and de-lithiation. One mechanism limiting the functionality of composite Si-electrodes originates from the difficulties in achieving a sufficiently stable solid electrolyte interphase (SEI) to prevent continuous decomposition of the

electrolyte [4]. Different approaches have been employed to counter these effects and are reviewed elsewhere [5,6]. Despite all progress that has been achieved for Si-composite electrodes, cycle life and the cycling efficiency are still not sufficient for use in practical lithium-ion batteries.

The ideal SEI layer is often described as a Li ion-conducting but electronically insulating film. This film is usually formed by decomposition products from the electrolyte and it passivates the surface to prevent further electrolyte decomposition. A lot of work has been done to understand the SEI on graphitic negative electrodes while the field of SEI formation on silicon is still a young area with only a rather small number of publications.[4,7-19] Philippe et al. have successfully used different kinds of photoelectron spectroscopy (PES) to analyze the SEI formation on Si-electrodes [7,8,16]. Results suggest that the LiPF_6 salt decomposes to form HF that reacts with the silicon oxide to form new compounds [7,8], possibly detrimental to the cycling of Si. In a follow-up study using the LiFSI salt that does not form HF, the cycling performance was improved [16]. Altogether, these studies show that the choice of salt and the SEI properties are important factors that strongly influence the cycle life of the Si-electrode.

During the history of lithium-ion batteries, several Li-conducting salts have been investigated but the list of less suitable examples is long: LiAsF_6 is one example where byproducts are toxic [20-22], LiClO_4 is explosive [23,24], lithium trifluoromethanesulfonate ($\text{Li}(\text{CF}_3\text{SO}_3)$) and LiTFSI ($\text{Li}[\text{N}(\text{SO}_2\text{CF}_3)_2]$) are not compatible with the aluminum current collectors on the positive electrode [25] and LiBF_4 forms an inferior SEI compared to LiPF_6 [26]. Lithium bis(oxalate)borate (LiBOB) and lithium fluoroalkylphosphate (LiFAP) are considered promising [26] but more alternatives should be investigated with the aim to find a new electrolyte that

forms a sufficient SEI layer and that prevents detrimental side reactions, especially for Si based electrodes. Such a finding would significantly improve the performance of the Si-electrode.

A new salt, lithium 4,5-dicyano-2-(trifluoromethyl)imidazolid (LiTDI) (structural formula in Fig. 1) has recently been presented [27,28]. It is based on the imidazole ring and has all the desired properties in terms of conductivity and transference number required for use in lithium-ion batteries. Investigations have shown that the salt has a higher thermal stability compared to LiPF_6 as well as high electrochemical stability in the voltage range of all commercially available cathode materials. Anodic compatibility was investigated vs. a lithium foil and was found to be stable down to a potential of 0.5V vs. Li^+/Li where the decomposition of the propylene carbonate solvent started. However, only scarce information on actual cycling performance using this salt is available in the literature, although it has been shown to cycle with good performance in a $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ cell vs. lithium at room temperature as well as at 60 °C [29].

In this report, the compatibility of LiTDI as electrolyte salt for Si-based composite electrodes was investigated during the first lithiation and de-lithiation in a lithium-ion battery context. Hard x-ray photoelectron spectroscopy (HAXPES) was used to obtain a depth profile for a more complete understanding of reactions and mechanisms of the SEI formation at the surface as well as in the bulk of the active materials.

Fig. 1. The LiTDI molecule

2. Experimental section

2.1 Electrode Preparation

An electrode slurry was prepared by mixing powders of crystalline silicon (APS ≤ 50 nm, Alfa Aesar), carbon black (CB) (Super P, Erachem Comilog N.V.), sodium carboxymethyl cellulose (CMC) (Typical MW = 700 000 g mol⁻¹, D.S. = 0.90, Sigma-Aldrich) and water:ethanol (Solveco, 99.5%) (70:30 vol%). Weight ratios of the dry components were 80% Si-powder, 12% CB and 8% CMC. The slurry was ball-milled for 1 h in a planetary mill (Retsch PM4 planetary mill) and casted on a 22 μ m thick Cu-foil. The coated Cu-foils were dried at 60 °C over night. Electrodes of 20 mm in diameter were punched out and brought into an argon filled glovebox (H₂O, O₂ <10 ppm) where they were dried in a vacuum oven at 120 °C for at least 6 h. The active Si material loading was approximately 0.6 mg cm⁻².

2.2 Electrochemical and Surface Morphology Analysis

So called half-cells were assembled with the silicon composite electrode, two layers of Solupor® (DSM) separator soaked in electrolyte (0.6 M LiTDI in ethylene carbonate (EC):dimethylcarbonate (DMC), 1:2) and a Li-foil counter electrode and finally sealed in a plastic coated aluminum pouch under vacuum. Half-cells were cycled at a constant current of 150 mA g⁻¹ to different potentials using a Digatron BTS600 galvanostat, and allowed to relax before the PES analysis. The surface morphology was examined at four different stages with a Zeiss Merlin scanning electron microscope (SEM). Electrodes were rinsed in DMC prior to analysis and during transfer to the analysis chamber they were exposed to air for about one minute.

2.3 Photoelectron Spectroscopy

Electrodes for the PES measurement were carefully disassembled in an argon filled glovebox, rinsed with DMC and transferred to the analysis chamber in a special transfer chamber without being exposed to air [30]. The pressure during PES measurements was about 10^{-8} mbar in the analysis chamber. HAXPES measurements were carried out at the HIKE end station at the KMC-1 beamline at the synchrotron facility BESSY II operated by the Helmholtz-Zentrum Berlin. As excitation energies, 2005 eV and 6015 eV were selected and the emitted photoelectrons were analyzed using a Scienta R4000 analyzer. Charge neutralization was used during the measurements. The pure LiTDI salt was investigated with in-house XPS using Al K α radiation and an electron flood gun for charge neutralization. For this measurement, LiTDI salt was dissolved in DMC and a droplet was put on a Si-wafer and the DMC was allowed to evaporate inside a glovebox. The sample was transferred to the analysis chamber without exposure to air. All data analysis was performed with the software Igor Pro 4.07. Calibration of the binding energy was done with respect to the hydrocarbon peak set to 285.0 eV.

3. Results and discussion

3.1 Electrochemical Results

The galvanostatic lithiation and de-lithiation curve of the full first cycle is presented in Fig. 2. Points in the figure indicate the potentials where samples are collected for the HAXPES analysis and also a pristine electrode is analyzed. Sample A is kept at open circuit voltage (OCV) without any lithiation. During the first lithiation, the main SEI formation begins at 0.8 V vs. Li⁺/Li and sample B (collected at 0.7 V) in Fig. 2 represents the early stage of SEI formation. Sample C (0.5 V) in the same figure is collected during SEI formation and sample D (0.13 V) after the main SEI formation. Electrochemical lithiation of nano-crystalline silicon results in a transformation

from a crystalline phase into an amorphous Li-Si alloy [3]. In the galvanostatic cycling curve this is observed as a fairly stable plateau starting at 0.13 V (sample D) going through the halfway lithiated sample E and reaching the end of lithiation at 0.01 V (sample F) vs. Li^+/Li . During de-lithiation, the amorphous structure is retained and in the galvanostatic cycling curve this is observed as a more sloping region [3]. Samples G (0.5 V) and H (0.9 V) during de-lithiation are collected for HAXPES-analysis as well.

The SEI formation using the LiTDI/EC/DMC electrolyte consumes a capacity of roughly 400 mAh g^{-1} until the plateau for the lithiation of Si is reached and starts at 0.13 V (see point D in Fig. 2). Comparing this number to a similar system with LiPF_6 in EC:DEC, the lithiation of Si is reached after approximately 200 mAh g^{-1} [7]. This implies that SEI formation is more extensive in the system with LiTDI/EC/DMC as nearly twice as much capacity is consumed for this process. During the first lithiation, a capacity corresponding to 2700 mAh g^{-1} is reached. During de-lithiation approximately 1500 mAh g^{-1} is recovered meaning that 1200 mAh g^{-1} is irreversibly lost. Roughly 400 mAh g^{-1} can be explained by the initial SEI formation, and in addition to this another 800 mAh g^{-1} would have to be explained by either further SEI formation or by loss of electrical contacts to the active material. In the following section this discussion will be supported by micrographs from the SEM analysis.

Fig. 2. Lithiation and de-lithiation of a composite Si-electrode vs. Li metal using LiTDI in EC:DMC. Dots show where samples were extracted for HAXPES analysis.

3.2 Surface Morphology: SEM

SEM analysis is performed at four different stages in the first cycle to probe the evolution of the surface. Fig. 3a shows the pristine composite electrode structure and in the inset, with lower magnification, a smooth surface is observed with no cracking of the composite film. The larger magnification images in Fig. 3b, c and d reveal that SEI formation continues during lithiation as a thicker layer covers the composite electrode with further cycling and individual particles are more and more difficult to distinguish. The lower magnification images still show a surface without any formations of cracks.

Fig. 3. SEM micrographs of a pristine composite electrode (a), sample D (b), sample F (c) and sample H (d).

3.3 HAXPES Characterization

The benefit of using X-rays with different photon energies to obtain a reasonably non-destructive depth profiling of Si electrodes has previously been proven successful [7,8,16,17]. By using 2 – 7 keV excitation energy (HIKE endstation, KMC-1 beamline, BESSY II synchrotron) a larger fraction of photoelectrons generated in the bulk of the active particles will reach the sample surface and can be detected even as the SEI thickness is increasing. This enables a more detailed picture of the bulk material during electrochemical cycling. Altogether, this provides important information on how the salt interacts with the active Si material.

3.3.1 Binding Energy Variations Associated with SEI Formation or Changes in Chemical Environment

Peak positions are the most valuable information obtained from PES measurements and it is therefore important to be aware of phenomena that may influence these positions in order to

assign each peak to its correct chemical environment. In this study all the measured spectra are calibrated versus the hydrocarbon signal in the C1s spectra. While the peak positions from species in the SEI are maintained at constant binding energies, peaks originating from the bulk electrode, i.e. bulk Si, SiO₂ and CB, experiences a shift during the first lithiation and delithiation. Such peak shifts may derive from several factors e.g. a change in chemical environment [31,32] or the buildup of insulating layers [33-35].

If a Si material is alloyed with Li, the chemical environment for the Si atoms is changed and also the binding energy of the core electron is likely to change. Also other properties such as the work function can be altered. A change in either of these will give rise to a peak shift in the resulting spectrum. As an example, the lithiation of Si single crystals results in a more negative peak shift with higher degree of lithiation [31,32]. For the most lithiated phase, the shift has been found to be slightly below -2 eV for Si2p electrons. Similar peak shifts can also be observed in earlier PES studies on Si electrodes [7-10,16]. Observations of changes in peak position due to state of charge for graphite electrodes has also recently been presented and discussed as a result of changes in chemical environment and/or changes in work function [36].

Another factor that influences the measured binding energy is the formation of an electrically insulating layer on a conductive substrate [33-35] and to the best of our knowledge, this has not been discussed in the context of SEI formation on electrodes. In this paper we will briefly differentiate between peak shifts caused by a change in chemical environment or due to the formation of an SEI.

Fig. 4 shows the shift in peak positions (compared to their original position in the pristine sample) of bulk Si, SiO₂ and CB as deduced from the respective spectra (see Fig. 5 and 6) at

6015 eV excitation energy. During SEI formation (sample A to D) the potential for the electrode is higher than what is generally required to achieve any lithiation reaction of the bulk Si. Therefore we expect no changes in the chemical environment for bulk Si. As a consequence, the observed peak shift for bulk Si from sample A to D should be connected to the SEI formation. Also the SiO₂ and CB experience a similar peak shift and it seems reasonable that the main part of this shift is also due to SEI formation, although some lithiation of CB could occur. In sample D, the slightly larger shift for the SiO₂ could indicate that a lithiation of this phase has already started.

During lithiation, the relative CB peak position for sample D to E only slightly shifts to more negative numbers, either due to lithiation or due to continuous SEI formation. The peak position for bulk Si is shifted approximately -2.2 eV from sample D to F. Although SEI formation continues during lithiation, the major part of the shift of -2.2 eV from sample D to F for the bulk Si is attributed to a change in the chemical environment due to the formation of lithium silicides. The SiO₂ peak is shifted in a similar manner about -1.9 eV, mainly due to the formation of lithium silicates.

During de-lithiation the peak position for CB is only slightly shifted back to higher binding energies while the lithium silicide peak is shifted back by about +1.6 eV. The fact that the de-lithiation shift for bulk Si is smaller than the lithiation shift could indicate that Si-particles are not completely de-lithiated. This would also be a reasonable explanation for the low coulombic efficiency of the first cycle. The lithium silicate peak also only experiences a minor shift to higher binding energies, implying that the lithium silicate formation is less reversible.

Fig. 4. Changes in binding energy for bulk Si, SiO₂ and CB at 6015 eV excitation energy.

3.3.2 Silicon species

Fig. 5 shows the Si1s spectra from the 6015 eV excitation energy measurement. The Si2p spectra are presented in the supporting information (Fig. S3). Binding energies mentioned below are referred to the fitted Si2p_{3/2} peaks and/or Si1s, respectively. As can be seen in Fig. 5 and Fig. S3, two components are present in the Si spectra. In the pristine sample, SiO₂ is indicated with red peaks at a binding energy of 103.5/1844.0 eV and bulk Si is observed at 99.3/1839.0 eV, indicated with gray peaks. With increased excitation energy, the relative amount of bulk Si is increased. This is consistent with an increased probing depth for higher photon energies and confirms that a SiO₂ layer is covering the surface of the particles.

No additional peaks emerge during the first lithiation and de-lithiation. Thus we consider a gradual transformation into lithium silicide (yellow peaks) and lithium silicate (pink peaks) and no side reactions between the salt and the active Si material are observed. The peak shifts for

sample A to D are mainly due to SEI formation. From sample D to H the main reason for peak shifts are lithiation and de-lithiation of bulk Si. The bulk Si signals are broader in sample G, indicating that during de-lithiation, a wider composition of lithium silicides exists.

Fig. 5. Si1s spectra at 6015 eV excitation energy at various state of charge during the first electrochemical cycle.

3.3.3 Carbon Species

The carbon spectra are complex due to the many components i.e. the CMC-binder, the CB in the composite electrode, electrolyte residues and SEI products on the surface that all contribute to the carbon peaks.

Fig. 6 shows the C1s spectra with important features that are possible to distinguish and that reveal valuable details of the SEI composition, its thickness and how it is evolving. It is important to stress that the intensity of these spectra are normalized to the most intense peak. Thus caution should be taken when interpreting peak intensities between two samples since a change in peak intensity between two samples is always a relative change with respect to the most intense photoemission line. Therefore, the intensity variations are not necessarily representative for a change in absolute numbers or concentration of the component within the entire sample. In the following section, peaks are treated one by one starting from the lowest binding energy.

The signal from the CB (black peaks in Fig. 6) in the pristine sample is observed at a binding energy of 283.8 eV (the shift toward lower binding energies has been discussed in a previous section). With the use of higher excitation energy, also the relative amount of CB is increased. This is consistent with a model where other carbon species such as binder, electrolyte residues and adventitious carbons are covering the CB particles. During SEI formation (sample B to D) the relative amount of CB signal is heavily decreased for both photon energies due to the SEI covering the bulk electrode particles. The CB signal continues to decrease during lithiation and is not possible to observe at the end of lithiation. During de-lithiation (samples G and H), the CB signal is again possible to distinguish, possibly due to a decreased SEI thickness.

In the pristine electrode, none of the components in the composite electrode is expected to yield any hydrocarbon signals. All carbons in the CMC molecule are bound to at least one oxygen atom and those carbons will therefore be found at higher binding energies. Adventitious carbon species are, however, more or less always present in PES analysis. Therefore we fixed the binding energy for these species to 285.0 eV and adjusted all other spectra with respect to this binding energy. In Fig. 6, these hydrocarbons are represented by a solid white peak indicated with C-H/C-C. All other samples that have been in contact with electrolyte may have electrolyte residues contributing to this peak as well. The decrease in the hydrocarbon signal with higher excitation energy confirms that hydrocarbons are more frequent near the very surface of the sample.

For the simplicity, peaks around 286 to 290 eV are treated in a more general manner. The spectra at these binding energies are divided into three different peaks that contain information on carbons bound to N, O and possibly F as well. The complexity of the spectra does unfortunately not allow for an unambiguous evaluation and further analysis of the SEI species will have to depend on the spectra of the other elements. However, we will briefly summarize the information that can be extracted from these peaks.

The dark grey peak at approximately 287 eV (labeled -C-N/-C-O) is in the early samples (A-B) mainly attributed to carbons bound to ether-type oxygen in the CMC binder. During and after the SEI formation (sample C and D) this peak is increasing and also slightly shifted to a binding energy of 286.7 eV. This is likely due to carbonate solvent decomposition products containing carbon oxygen bonds. Carbon species from the LiTDI salt are expected at 287.0 eV according to the reference measurement (see Fig. S2) and also residues from decomposed LiTDI could give contributions to this peak. In sample D, after the main SEI formation, this peak is the dominant

part of the C1s spectra. No relative changes in peak ratios are observed between the two photon energies and the concentration of this component is therefore considered similar throughout the SEI.

A peak at roughly 288-289 eV is indicated with a lighter grey color (denoted -O-C-O-) and is originally deriving from carboxylic groups in the CMC binder. Additional species at approximately the same binding energy are formed during SEI formation, likely arising from solvent decomposition. Later in the discussion we will show that the LiTDI molecule is partially decomposing and a possible decomposition product is carbon-fluorine species that also would contribute at roughly this binding energy.

The darker grey peak at 290-291 eV (indicated with -CO₃/-CF_x) is assigned mainly to carbonate species such as alkyl carbonate or Li₂CO₃. Such species are generally found in any SEI using carbonate solvents for lithium ion batteries [37,38]. In the examined SEI we mainly observe carbonate species when SEI formation started. Also hypothetical LiTDI decomposition products, such as CF₂, could potentially add to this peak.

In sample A there is a trace of LiTDI residues in the form of CF₃ at 292.8 eV, highlighted with a blue peak in Fig. 6. The peak position and the relative amount of CF₃ compared to the other components in the carbon spectra are fairly stable and of similar amounts in both photon energies. This is interpreted as that the LiTDI is embedded in the SEI at a fairly constant rate while the SEI is growing. The relative amount of CF₃ compared to previously discussed peaks is fairly low and the inclusion of LiTDI salt into the SEI is considered small.

Fig. 6. C1s spectra at 2005 and at 6015 eV excitation energy at various state of charge during the first electrochemical cycle.

3.3.4 Fluorine species

Fluorine is present in the LiTDI molecule as a CF_3 group (see Fig. 1) and this C-F bond is possible to detect in sample A (OCV – electrode only soaked in electrolyte) in Fig. 7 at a binding energy of 688.0 eV. Also a peak at 686.0 eV is detected, which indicates that some decomposition of the CF_3 group in the LiTDI salt must have occurred already in the contact between the electrolyte and the electrode. Possibly this could produce some CF_x group, for that reason the peak at 688.0 eV is denoted CF_3/CF_x . The specific origin of the peak at 686.0 eV remains unclear but, the higher intensity with higher excitation energy suggests that this compound is more frequent deeper into the sample.

In sample B the formation of LiF is evident due to the peak at 685.0 eV (purple peak in Fig. 7). Since the CF_3 group in LiTDI is the only fluorine source, the formation of LiF can only originate from the decomposition of this group. In sample B to D (during SEI formation), the LiF peak is slightly more intense at 6015 eV excitation energy than the 2005 eV equivalent when compared to the CF_3/CF_x peak. This indicates that LiF is more likely to be found deeper into the SEI than CF_3/CF_x . In samples F to H the relative intensity is less dependent on the excitation energy and therefore we consider the SEI in these samples to be more homogeneous.

To what extent the LiTDI salt decomposes is not trivial to deduce but nonetheless an important matter. From the C1s spectra in Fig. 6 we could evaluate the amount of CF_3 in the overall SEI to be fairly small. These insights together with what is known from the F1s spectra in Fig. 7 make us confident that also the decomposition of LiTDI is fairly small.

Fig. 7. F1s spectra at 2005 and 6015 eV excitation energy at various state of charge during the first electrochemical cycle.

3.3.5 Nitrogen species

Cyano nitrogen and nitrogen in an aromatic environment like the imidazole ring are expected to yield photoelectrons of 399-400 eV [39,40]. According to the reference measurements in the supplementary information (Fig. S2), the nitrogen photoemissions from LiTDI are found at 399.7 eV. These give the main contribution to the nitrogen spectra in Fig. 8 and are found at a slightly

lower binding energy of 399.2 eV. The evaluation of the N1s signals at 2005 eV excitation energy is aggravated due to the overlapping Si Auger. Using 6015 eV excitation energy the nitrogen signal is clearly present from sample A and forward. A peak at slightly higher binding energies (~ 401 eV) is present from sample C and forward, highlighted with a green peak in Fig. 8. The origin of this peak is most likely caused by a new nitrogen chemical environment as a consequence of the decomposition of the LiTDI molecule.

Fig. 8. N1s, spectra at 2005 and 6015 eV excitation energy at various state of charge during the first electrochemical cycle.

3.3.6 Oxygen species

The oxygen detail spectra are presented in supporting information Fig. S5. A major peak at 532.5 eV is present in sample A and this peak is mainly composed by SiO₂ and the oxygen species from the CMC binder. From the C1s spectra in Fig. 6 we know that several carbon-oxygen components are forming during SEI buildup. These new components are the reason for the changes in the O1s spectra from sample A to D. In sample D to H, after the main SEI formation, the oxygen spectra remain fairly constant. These spectra resemble to a great extent the spectra from the formation of MeOCO₂Li and EtOCO₂Li as reported by Derdryvere et al. [38]. Thus we conclude that oxygen containing species in the SEI in this study is composed by these two and similar compounds. Since no pronounced variation in peak shape is observed depending on the used excitation energy, these compounds seem homogenously distributed throughout the SEI layer.

3.3.7 Summary

The HAXPES measurements show that the LiTDI salt decomposes when used as an electrolyte salt in combination with Si composite electrodes cycled versus lithium. This is evident because of LiF formation and also by the small additional high binding energy peak in the nitrogen spectra. The amount of decomposed LiTDI salt is fairly low but the decomposition continues throughout the first cycle. However, there is no evidence of irreversible or unwanted side reactions between the active Si material and the LiTDI salt. Only gradual transformation of the Si particles into lithiated phases is observed in the Si spectra and no other Si containing compounds are observed. The lithium silicate formation is reversible only to a low extent.

The electrolyte formulation used in this study leads to the formation of a thicker SEI compared to a similar system with LiPF_6 or LiFSI based electrolytes [7,16]. This is clear if comparing the relative amount of CB in the spectra after one cycle. The SEI is composed of mainly organic species originating from the carbonate solvents used in the electrolyte together with embedded LiTDI salt and its decomposition products. In this sense the SEI is similar to earlier reports on Si electrodes but also comparable to the SEI on graphite electrodes. Since PES is a surface sensitive analysis technique, and the surface of an electrode is constantly building up during electrochemical cycling, it should be kept in mind that different surfaces are monitored at different stages. Elements that form the SEI, in this case all but Si, will have smaller part of the pristine surface in their resulting spectrum as the SEI grows thicker. Also the measurements of bulk Si and SiO_2 are compromised by the thick SEI, resulting in a low signal to noise ratio.

The observed peak shifts of the bulk Si, SiO_2 and CB are attributed to two different mechanisms: Initially, the shift towards lower binding energy is due to SEI formation but at the later stage the lithiation reaction of the Si-particles causes an actual chemical shift of the bulk Si and SiO_2 signal.

4. Conclusions

An electrolyte with LiTDI has for the first time been used as a Li-conductive salt in silicon composite electrodes in a half-cell lithium ion battery. HAXPES was successfully used to monitor the processes during the buildup of the SEI at both the surface and the bulk of the Si-electrode.

During the SEI formation, peak positions in the spectra for the embedded particles are shifted to lower binding energies. A thicker SEI causes a larger shift and this fact should be kept in mind

when peaks are assigned to certain compounds. During lithiation and de-lithiation peaks are also shifted but, due to a change in chemical environment. Since several factors affect the measured binding energy in PES, it is a challenge to assign each binding energy shift to the correct process. This is, however, a key factor since binding energies are the basis for interpretations derived from PES measurements and it will be addressed in a further study.

We have shown that LiTDI is fairly stable towards the electrode during storage of assembled batteries and that LiTDI is partially decomposing during cycling. However, no detrimental side-reactions are observed in the active Si material. The SEI is built up mainly before the lithiation of Si but, SEI formation continues during the lithiation process. Decomposed carbonate solvents make up a majority of the SEI but also LiTDI and some decomposition products of it are observed. The distribution of these components is homogeneous throughout the SEI. Altogether this means that LiTDI is a promising salt for future lithium ion batteries with Si negative electrodes.

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Supplementary information

A hard X-ray photoelectron spectroscopy study on the solid electrolyte interphase of a lithium 4,5-dicyano-2-(trifluoromethyl)imidazolid based electrolyte for Si-electrodes

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Figure S1. Peak position shift for bulk Si, SiO₂ and CB at 2005 eV excitation energy.

Figure S2. XPS spectra of LiTDI salt.

Figure S3 Si2p spectra at 2005 eV excitation energy.

Figure S4. Survey spectra at excitation energy of 2005 eV. The intensity of the survey spectra is normalized to the most intense carbon peak.

Figure S5. O1s spectra at 2005 and 6015 eV excitation energy at various state of charge during the first electrochemical cycle.