

# Role of 1,3-Dioxolane and LiNO<sub>3</sub> Addition on the Long Term Stability of Nanostructured Silicon/Carbon Anodes for Rechargeable Lithium Batteries

Tony Jaumann,<sup>a,z</sup> Juan Balach,<sup>a</sup> Markus Klose,<sup>a,b</sup> Steffen Oswald,<sup>a</sup> Jürgen Eckert,<sup>a,b,c,d</sup> and Lars Giebeler<sup>a,b</sup>

<sup>a</sup>Leibniz Institute for Solid State and Materials Research (IFW) Dresden e.V., Institute for Complex Materials, D-01171 Dresden, Germany

<sup>b</sup>Technische Universität (TU) Dresden, Institut für Werkstoffwissenschaft, D-01069 Dresden, Germany

In order to utilize silicon as alternative anode for unfavorable lithium metal in lithium – sulfur (Li–S) batteries, a profound understanding of the interfacial characteristics in ether-based electrolytes is required. Herein, the solid electrolyte interface (SEI) of a nanostructured silicon/carbon anode after long-term cycling in an ether-based electrolyte for Li–S batteries is investigated. The role of LiNO<sub>3</sub> and 1,3-dioxolane (DOL) in dimethoxy ethane (DME) solutions as typically used electrolyte components on the electrochemical performance and interfacial characteristics on silicon are evaluated. Because of the high surface area of our nanostructured electrochemical reversibility opening a detailed analysis. We show that the use of DME/DOL solutions under ambient temperature causes higher degradation of electrolyte components compared to carbonate-based electrolytes used for Li–ion batteries (LIB). This behavior of DME/DOL mixtures is associated with different SEI component formation and it is demonstrated that LiNO<sub>3</sub> addition can significantly stabilize the cycle performance of nanostructured silicon/carbon anodes. A careful postmortem analysis and a discussion in context to carbonate-based electrolyte solutions helps to understand the degradation mechanism of silicon-based anodes in rechargeable lithium-based batteries.

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Silicon is a highly attractive anode material for rechargeable Liion batteries (LIB) and post LIB systems owing to its high capacity and comparable discharge potential to lithium metal. Considerable progress has been achieved in recent years to tackle the peculiarities of silicon during de-/lithiation.<sup>1-2</sup> The enormous volume expansion which causes fracture of individual particles and a low reversibility could be addressed by hierarchically designed nano-sized and amorphous silicon structures.<sup>3-6</sup> However, it was shown that among other parameters the electrochemical performance of particularly nanostructured silicon significantly depends on the chosen electrolyte.<sup>7-9</sup> This observation is mainly caused by the characteristics of the interfacial layer strongly related to the surface area of the electrode material which is especially high on nanostructures. The interfacial layer, commonly known as solid-electrolyte-interface (SEI), is a surface film typically formed in the initial cycles by decomposition of electrolyte components. Because of the large volume expansion of silicon during lithiation, the SEI likely cracks and is regenerated causing continuous electrolyte consumption and high degradation. In order to reduce degradation and apply silicon as high-performance anode in rechargeable Li-based batteries, a profound knowledge of the interfacial characteristics is necessary. The SEI on silicon is typically studied in carbonate-based electrolytes since silicon is majorly considered as alternative anode for graphite in LIB.<sup>10-13</sup> However, in recent years silicon proved to be an advanced anode not only in LIB, but also in the next generation lithium – sulfur (Li–S) battery as replacement for lithium metal anodes.<sup>14–18</sup> The Li–S system is a primary candidate to boost the use of green energy in electro mobility,<sup>19-21</sup> but cannot be used in combination with carbonate-based electrolytes due to the incompatibility with soluble polysulfides.<sup>22</sup> Ether-based solutions, typically mixtures of dimethoxy ethane (DME) and 1,3-dioxolane (DOL), turned out to be an ideal electrolyte system for Li-S batteries owing to its compatibility with polysulfides and good dissolution properties for bis(trifluoromethane)sulfonamide lithium (Li-TFSI) as typical conductive salt, but its effect on silicon anodes has been rarely studied

yet. An investigation in this direction is of high interest since the application of lithium metal anodes bear some serious issues. This anode type is known for uncontrollable dendrite formation owing to an instable SEI, which can penetrate the separator causing a short circuit and a thermal runaway.<sup>15</sup> Furthermore, the use of lithium metal leads to a depletion of the electrolyte and a self-reduction of soluble polysulfides, resulting in a low cycle life and hampering the commercial-ization of such batteries.<sup>19,23</sup> The electrolyte additive lithium nitrate (LiNO<sub>3</sub>) is proven as an effective compound to extent cycle life and efficiency of Li-S batteries by positively influencing the interfacial properties on lithium metal.<sup>24–27</sup> It is well accepted in literature that LiNO3 forms a protective layer composed of LixNOy compounds and oxidized polysulfides.<sup>26,28</sup> This protective layer reduces the polysulfide shuttle effect and thus improves the overall Coulombic efficiency. The synergetic effect of LiNO<sub>3</sub> and polysulfides is also found as a major factor to inhibit dendrite formation and to enhance efficiency.<sup>2</sup> LiNO<sub>3</sub> turned out to be an efficient additive not only for Li - S batteries, but also for other lithium metal battery systems, such as Li–O<sub>2</sub>.<sup>7,30</sup> Although LiNO<sub>3</sub> can somewhat protect the lithium metal, but serious issues of hazardous dendrite formation and depletion of electrolyte in Li–S batteries remain.<sup>14–15</sup> In most publications dealing with alternative silicon anodes for Li - S batteries the LiNO3 is kept as additive in the ether-based electrolyte and it seems to enhance the reversibility similar as found for lithium metal foil.<sup>15</sup> However, the role of LiNO<sub>3</sub> as additive on silicon electrodes is rarely investigated. Etacheri et al. tested silicon nanowires (SiNW) in DOL as electrolyte solvent at 60°C, in dependency of LiNO3 addition and found excellent reversibility.<sup>7</sup> It was majorly attributed to the DOL solution which is typically used as co-solvent in electrolytes for Li-S batteries. DOL plays a significant role in secondary lithium batteries since it was shown to stabilize lithium metal anodes due to its polymerization to form polydioxolanes.<sup>31</sup> The influence of the electrolyte liquid DOL together with the additive LiNO<sub>3</sub> on the interfacial characteristics of silicon-based anodes after long-term exposure is still unclear and needs a detailed and fundamental discussion.

Motivated by these questions, we investigated the SEI components on a nanostructured silicon/carbon-based electrode after galvanostatic long-term cycling versus lithium metal in ether-based electrolytes, containing Li-TFSI and LiNO<sub>3</sub> dissolved in mixtures of DME/DOL,

<sup>&</sup>lt;sup>c</sup>Present address: Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, A-8700 Leoben, Austria.

<sup>&</sup>lt;sup>d</sup>Present address: Department Materials Physics, Montanuniversität Leoben, Jahnstraße 12, A-8700 Leoben, Austria.

<sup>&</sup>lt;sup>z</sup>E-mail: t.jaumann@ifw-dresden.de

as used for Li–S batteries. We will show that the LiNO<sub>3</sub> additive not only forms a protective layer on lithium foil, but also on silicon anodes which prevents decomposition of the conductive salt and the dissolution of certain SEI compounds typically observed on the surface of silicon in Li–ion batteries. Furthermore, the role of DOL as co-solvent is studied and evaluated. The interfacial characteristics were analyzed by electrochemical methods, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction experiments (XRD). The results are discussed in context to our recent findings in alkyl carbonates as electrolyte for LIB.<sup>32</sup> The role of organic and inorganic compounds, in particular Li<sub>2</sub>O and LiF, as typical interfacial components on silicon will be highlighted.

#### Experimental

**Preparation of the silicon/carbon nanocomposite.**—The nanostructured silicon/carbon composite was prepared according to a recently published synthesis.<sup>33</sup> We first synthesized a hydrogen silsesquioxane (HSQ) precursor by polycondensation of HSiCl<sub>3</sub> (Sigma-Aldrich) with water in presence of a surfactant (Pluronic P123) under inert gas atmosphere. After drying in vacuum for two days, the HSQ precursor was annealed at 1100°C (heating rate 12.5 K/min) leading to a transformation of a Si@SiO<sub>2</sub> composite with silicon nanocrystallites of 2–5 nm in size determined by TEM and XRD.<sup>33</sup> After annealing, the composite was wrapped into carbon through carbonization of sucrose and finally etched with hydrofluoric acid to remove the silica matrix. The porous silicon-carbon nanocomposite (nc-Si@C) was dried under vacuum overnight.

Electrochemical testing .--- A slurry of 85 wt% silicon nanocomposite, 10 wt% Super P Li (Timcal) and 5 wt% polyacrylic acid (PAA) binder was prepared in ethanol by using a swing mill and sonication. The temperature of the slurry should not exceed room temperature to avoid excessive oxidation of small nc-Si. The electrodes were prepared by blade-coating on copper foil (9 µm thickness) with a slurry thickness of 300 µm. 12 mm copper discs were punched out. The mass loading was  $2.1 \pm 0.2$  mg per electrode with around 31 wt% of total silicon on the electrode. The electrodes were dried at 100°C in vacuum overnight before assembly of Swagelok test cells under argon atmosphere (H<sub>2</sub>O < 1 ppm,  $O_2$  < 0.1 ppm). We used a glass fiber separator (Whatman) and 250 µl of an electrolyte composed of 1 M Li-TFSI (BASF, dried under vacuum at 100°C) in a) DOL/DME (1:1), b) 0.25 M LiNO<sub>3</sub> in DOL/DME (1:1) or c) 0.25 M LiNO<sub>3</sub> in DOL. DOL (Sigma-Aldrich, anhydrous), DME (Sigma-Aldrich, anhydrous) and LiNO<sub>3</sub> (Merck KGaA, >99.99%, dried at 100°C under vacuum) were used without further purification. 1 M LiPF<sub>6</sub> in dimethyl carbonate (DMC)/ethylene carbonate (EC) (1:1) (LP30, Selectilyte, BASF) was used as carbonate-based reference electrolyte and lithium foil (Chempur, 250 µm thickness, 11 mm diameter) as counter electrode. Galvanostatic cycling was carried out between 0.01-1.2 V vs Li/Li+ with a BaSyTec cell test system. All measurements were climatized at 25°C. Electrochemical impedance spectroscopy (EIS) was carried out at 1 V vs Li/Li<sup>+</sup> with an amplitude of 5 mV in the frequency range of 10 mHz - 1 MHz. Specific capacity and current rates were calculated based on the mass of silicon.

Characterization of morphology.—Prior to morphology characterization the Swagelok cells were disassembled in the glove box and the silicon electrodes were washed two times in 2 ml DOL and once in 2 ml DOL with additional 5 min sonication in order to remove interfering electrolyte components. The procedure was described elsewhere.<sup>32</sup> The electrodes were finally dried under vacuum for 1 hour. XRD experiments were performed in transmission geometry with Co K<sub>a1</sub> radiation on an STOE Stadi P diffractometer with curved Ge(111) crystal monochromator and 6°-position sensitive detector. The samples were prepared in the glove box with Kapton tape to avoid exposure to air during scanning. The scan range was  $10 \le 2 \theta \le 90^\circ$  with a step size of  $\Delta 2\theta = 0.01^\circ$ . The program MAUD<sup>34</sup> was used for the Rietveld analysis assuming an isotropic crystallite size distribution. The Popa line broadening model was chosen to determine the size and strain of the crystalline phases. LiF ( $Fm\bar{3}m$ ),<sup>35</sup> Li ( $Im\bar{3}m$ )<sup>36</sup> and LiOH (P4/nmm)<sup>37</sup> were used as structure models. XPS was carried out on a Physical Electronics PHI 5600 CI equipped with Mg Kα radiation (350 W) X-ray source at a pass energy of 29 eV and a step size of 0.1 eV. A transfer chamber (PHI Model 04-110) was used to avoid contact with air and moisture. Binding energies were normalized to LiF F 1s (685.5 eV).<sup>32,38</sup> Elemental concentrations determined from the XP spectra were calculated applying standard single-element sensitivity factors. Spectra were normalized and the core level signals of each chemical compound were fitted with a gaussian function using basic linear background subtraction. The silicon content in the nc-Si@C composite was determined by thermogravimetry after combustion in synthetic air at 900°C (10°C/min heating rate). From the amount of residual silica the silicon-to-carbon ratio was calculated.

## **Results and Discussion**

Electrochemical characterization of the silicon/carbon nanocomposite .- A recently developed silicon/carbon nanocomposite composed of sub 5 nm silicon nanoparticles attached to a porous carbon scaffold was used in our study.<sup>32-33</sup> The pristine electrode and the interfacial characteristics after exposure to carbonate-based electrolytes for LIB (commercial LP30) were characterized in our previous report.<sup>32</sup> In order to evaluate the effect of LiNO<sub>3</sub> and DOL, three different electrolyte solutions all with 1 M Li-TFSI as conductive salt were tested. Two typically applied Li-S electrolytes composed of DOL/DME (1:1 v/v) with and without LiNO3 addition (0.25 M) were examined.<sup>21,27,39</sup> Furthermore, a pure DOL solution with LiNO<sub>3</sub> addition was investigated since high reversibility with SiNW was reported.<sup>7</sup> Fig. 1a displays the galvanostatic cycling performance of the porous silicon nanocomposite vs Li/Li<sup>+</sup> in all three electrolytes. A standard test program of deep discharge cycles  $(0.01 \text{ V vs Li/Li}^+)$  at 2.5 A/g<sub>Si</sub>  $(1.5 \text{ mA/cm}^2)$  was applied to compare the results to our previous study in carbonate-based electrolytes.<sup>32</sup> Additional tests at lower current rates (500 mA/g<sub>Si</sub> 0.34 mA/cm<sup>2</sup>) were conducted to evaluate the effect of internal resistance caused by different ion conductivity of DOL and DME/DOL solutions (Fig. S1). The retained delithiation capacity of the DME/DOL configuration (Fig. 1a) was determined to be approximately 23% after 100 cycles and accounts to merely 7% after 250 cycles. A comparison to ethylene carbonate-based electrolytes (LP30) for LIB reveals significantly lower reversibility with DME/DOL electrolytes (Fig. S1). In our previous study, we found a retained capacity of 66% after 100 cycles and 40% after 250 cycles with commercial LP30 at constant conditions<sup>32</sup> which is significantly related to the ether-based electrolyte. Furthermore, no initial capacity increase is observed herein which bases upon an enhanced Li-Si alloying kinetics in DOL solutions as proposed by Etacheri et al.<sup>7</sup> We suggest that under the influence of ethers a complete lithiation is already realized after the first cycle whereas alkyl carbonates result in a partial lithiation and thus, an increase in capacity due to the step-wise utilization of silicon.

The addition of LiNO<sub>3</sub> into the DME/DOL electrolyte clearly enhances the reversibility, but decreases the initial delithiation capacity of about 23%. In pure DOL solutions with LiNO<sub>3</sub>, the initial delithiation capacity further decreases, but the reversibility is even higher. At lower current rates (Fig. S1) the difference in the initial delithiation capacity becomes smaller indicating different mass and charge transport resistances. In order to evaluate these transfer phenomena such as Li<sup>+</sup> ion migration, electrochemical impedance spectroscopy (EIS) was carried out. Fig. 1b shows the Nyquist plots in dependency of all three different electrolytes after 7 cycles. At high frequencies the electrolyte resistance  $(R_{Ele})$  is evaluated and at medium frequencies a semicircle appears as a result of surface film and charge transfer  $(R_T)$ modeled with a constant phase element (simplified  $R_T \| C$  circuit).<sup>4</sup> At low frequencies solid state diffusion and electrode capacitance appear as leaning line modeled by a Warburg (W) type resistance and capacitor element.<sup>40</sup> Since only the electrolyte changes and all other parameters are constant, the resistance values are comparable. As



Figure 1. a) Galvanostatic cycling of the nanostructured silicon/carbon electrode between  $0.01 V - 1.2 V vs Li/Li^+$  at 2.5 A/g<sub>silicon</sub> (two pre-cycles at 0.5 A/g<sub>Si</sub>), b) electrochemical impedance spectroscopy (EIS) after 7 cycles in dependency of the electrolyte composition, c) the corresponding Coulombic efficiency and d) the dQ/dV plot of the first lithiation.

expected we find lowest electrolyte resistance in the DME/DOL (10  $\Omega$ ) and highest electrolyte resistance in DOL + LiNO<sub>3</sub> mixture (19  $\Omega$ ) attributed to the higher viscosity of DOL compared to DME. LiNO3 addition slightly increases the electrolyte resistance from 10  $\Omega$  to 12  $\Omega$ . These findings agree well with another report.<sup>26</sup> The higher solution resistance is mainly responsible for the initially lower capacity at high current rates owing to a higher internal resistance drop of the potential. Pure DOL solutions cause lowest surface film resistance after 7 cycles concluded from the semicircle. This result correlates with the enhanced reversibility of lithium metal and SiNW anodes in pure DOL solutions owing to the formation of stable and conductive polydioxolane oligomers.<sup>7,31</sup> The addition of LiNO<sub>3</sub> merely affects the surface film resistance after 7 cycles. The SEI formation was evaluated by considering the CE (Fig. 1c) and the differential capacity profile of the first lithiation process (Fig. 1d). The low CE (25%) with LiNO3 addition suggests a high initial electrolyte consumption independent of the solvent mixture (DME/DOL and DOL) which starts at about 1.71 V vs Li/Li<sup>+</sup> (Fig. 1d) followed by a large reduction current at 1.64–1.66 V owing to the decomposition of LiNO3 and complex reactions of diverse intermediates with electrolyte components, respectively.<sup>27</sup> Note that some electrolyte is irreversible consumed by the high surface area of the carbon scaffold in the first cycle, but further irreversible consumption caused by the carbon after the first cycle can be neglected (Fig. S2). The overall reversible capacity of the bare carbon scaffold is 65 mAh/g (Fig. S2). The broad reduction current continues to span over the entire range of the voltage window. In the next 5 cycles the large electrolyte consumption disappears evidenced by a high CE of 97.2% (Fig. 1c). In contrast, the additive-free DME/DOL electrolyte starts with a reduction current at 0.8 V vs Li/Li+ with lower initial electrolyte consumption (CE = 36%). After the first cycle a considerably lower CE is found compared to LiNO3 addition which only reaches values < 95% over 50 cycles in the following. These results suggest

that a protective SEI on silicon is formed by consumption of  $LiNO_3$ in the first cycle. Hence, the  $LiNO_3$  not only reduces the well-known self-reduction of polysulfides on lithium metal, but also stabilizes a silicon-based anode to prevent further electrolyte decomposition.  $LiNO_3$  addition is not only mandatory for the reversibility of sulfur cathodes, but also for nanostructured silicon anodes in rechargeable LiSi-S batteries.

The overall results reveal that the reversibility of pure DOL solutions with LiNO<sub>3</sub> additions is highest as found by Etacheri et al.,<sup>7</sup> though the capacity at room temperature is lowest owing to the poor ionic conductivity. In contrast to Etacheri et al., we found a higher reversibility in carbonate-based than in DOL-based electrolytes. The partially contrary findings may be attributed to the different temperature applied in the experiments. Etacheri et al. tested SiNW at 60°C<sup>7</sup> which positively affects the solubility as well as ionic conductivity of certain SEI components and thus the reversibility.

**Post-mortem investigations of the SEI.**—In order to study the surface chemistry and the structure of the electrode after long-term cycling, the cells were disassembled after 250 cycles at 2.5 A/g<sub>Si</sub>. The cycle number was chosen because only little activity in DOL/DME was observed later on and to provide a reasonable comparison to our previous investigations in carbonate-based electrolytes (LP30).<sup>32</sup> XRD as a technique for bulk characterization was carried out to identify crystalline or nano-crystalline phases in the silicon/carbon nanocomposite since amorphous contents are not visible as discrete reflections due to the absence of a long range order. Based on the patterns displayed in Fig. 2 lithium metal ( $Im\bar{3}m$ ), LiF ( $Fm\bar{3}m$ ) and LiOH (P4/nmm) are detected. Several patterns have been taken over a period of 24 h (Fig. S3) and only negligible change in the present structure is observed suggesting no impact of X-rays or possible air diffusion through the kapton tape. Note that the sample DOL + LiNO<sub>3</sub>



Figure 2. XRD pattern of the nanostructured silicon/carbon anode after 250 galvanostatic cycles vs  $Li/Li^+$  in dependency of  $LiNO_3$  addition (in DME/DOL (1:1)).

is not shown because of no difference compared to DME/DOL + LiNO<sub>3</sub>. Nanocrystalline silicon is not observed owing to an amorphisation process over the period of cycling.<sup>32</sup> The presence of lithium metal is majorly the result of lithium plating and dendrite formation during the periods of 250 cycles at high current rates ( $\sim$ 1.5 mA/cm<sup>2</sup>). LiF originates from decomposition of Li-TFSI salt<sup>26</sup> and the reason for LiOH has not been clarified yet. Probably, it results of electrolyte decomposition and the presence of water traces, but also partial oxidation of the highly reactive lithium dendrites cannot be excluded. Interestingly, no lithium plating is observed in our recent investigations dealing with carbonate-based electrolytes even after 400 cycles at high current rates.<sup>32</sup> The result suggests that etherbased electrolytes promote Li dendrite formation on silicon-based electrolytes.

By Rietveld analyses the content and crystallite sizes of each crystalline phase were determined (Fig. 2 and Table I). The electrode cycled in DME/DOL without LiNO<sub>3</sub> exhibits high amounts of LiF with a crystallite size of approximately 4 nm. The concentration of Li, probably in the form of dendrites, is very low and reaches up to 3 wt% with a crystallite size of 62 nm. The cycled electrode in DME/DOL with LiNO3 contains no crystalline LiF and considerable more lithium metal (13 wt%) of a crystallite size of 23 nm. The results suggest that LiNO3 effectively prevents the decomposition of the conductive salt Li-TFSI at the silicon surface. Interestingly, nanocrystalline LiF of similar morphology has been observed in our recent study dealing with fluoroethylene carbonate (FEC)-containing standard carbonate-based LP30 electrolytes for LIB.32 FEC is well-known to enhance the reversibility of silicon electrodes often attributed to the occurrence of stable LiF layers.41-42 Herein, the pronounced formation of LiF seems to deteriorate the reversibility strengthening our recent assumption that LiF is not necessarily responsible for an enhanced reversibility owing to its electrically and ionically isolating properties.<sup>32,43</sup> However, since the LiF may be also amorphous and

Table II. Surface elemental composition (at.%) after 250 cycles determined by XPS in dependency of the electrolyte configuration.

Sample	Si	С	0	F	Li	S	Ν
Pristine*	11.3	68.1	16.9	3.7	-	-	-
DME/DOL (1:1)	0.4	28.4	22.3	14.2	25.2	6.2	3.4
DME/DOL $(1:1) + LiNO_3$	0.3	34.0	30.3	2.3	30.3	1.0	1.8
$DOL + LiNO_3$	0.3	18.0	37.4	3.4	37.1	1.4	2.0

\*taken from Reference 32.

hence not detectable by diffraction further information is provided by XPS.

Surface-sensitive XPS was performed to investigate the chemical characteristics of the first 3–4 nm of the sample surface and the subsurface region after treatment to gain knowledge about the solid state near part of the SEI. The elemental composition of the electrodes before and after cycling is shown in Table II. The surface of the pristine electrode is composed of approximately 11 at.% silicon. Apart from elemental silicon, considerable amounts of silicon dioxide and silicon sub-oxides as a result of incomplete oxidation are found owing to both the high reactivity and large surface area of 5 nm silicon crystallites.<sup>32</sup>

The cycled electrodes show a very low silicon composition indicating a thick passive surface film on the active material independent of LiNO3 addition. The Si 2p binding energy (Fig. S4) features a peak at about 100.8 eV attributed to LixSiOy as dominant silicon species on the surface independent of the electrolyte configuration.44-45 Negligible concentrations of elemental silicon at about 98.8 eV and SiO<sub>2</sub> at 102.8 eV are observed. The results suggest an interfacial layer on the silicon nanocrystallites with a thickness of at least 3-5 nm or larger for all samples due to the low attenuation length of 3-4 nm at this radiation energy (1253.6 eV). However, an exact determination of the SEI thickness is not reasonable since the washing procedure not only removes electrolyte components, but also upper organic SEI components which are well soluble.<sup>46,32</sup> The C 1s spectra (Fig. 3a) of all three samples show a binding energy maximum at 284.6 eV corresponding to the conductive carbon and to oligomers of reduced DOL such as (CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>O-)<sub>n</sub> and (CH<sub>2</sub>CH<sub>2</sub>O-)<sub>n</sub>.<sup>47</sup> Further, an energy peak at 290 eV appears originating from semi organic salts such as HCO<sub>2</sub>Li (Li formate) as result of DOL decomposition.<sup>31,47</sup> By considering both electrolyte configurations  $DME/DOL + LiNO_3$ and DOL + LiNO<sub>3</sub>, the decomposition of the co-solvent DOL mainly contributes to signal at 290 eV for these semi organic salts. For that reason, the addition of LiNO3 cannot prevent the decomposition of DOL. However, these semi organic salts seem to provide good Li<sup>+</sup> ion conductivity and enhanced reversibility because a low surface film resistance was observed by EIS measurements (Fig. 1b). In the absence of LiNO<sub>3</sub>, an additional binding energy signal is observed at 293 eV corresponding to -CF3 groups of closely related Li-TFSI compounds. The presence of retained conductive salt can be excluded due to the modified washing procedure.<sup>32</sup> The reductive decomposition scheme of Li-TFSI was already proposed by Etacheri et al.<sup>7</sup> and Aurbach et al.<sup>26</sup> Initially, species closely-related to Li-TFSI are most likely formed identified in the C 1s spectrum without LiNO<sub>3</sub> addition:

$$\text{Li}(\text{NSO}_2\text{CF}_3)_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_2\text{NSO}_2\text{CF}_3 + \text{Li}\text{SO}_2\text{CF}_3 \quad [1]$$

Table I. Proportions of crystalline phases in the nanostructured silicon/carbon electrode after 250 cycles vs  $Li/Li^+$  in dependency of  $LiNO_3$  addition (in DME/DOL (1:1)) determined by Rietveld analysis.

	LiF			LiOH	Li		
Sample	wt%	D <sub>Crystallite</sub> (nm)	wt%	D <sub>Crystallite</sub> (nm)	wt%	D <sub>Crystallite</sub> (nm)	
DME/DOL	49	4.4	48	4.3	3	62	
DME/DOL + LiNO <sub>3</sub>	0	-	87	4.2	13	26	

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Figure 3. High resolution XP spectra of a) carbon C 1s, b) fluorine F 1s, c) sulfur S 2p and d) nitrogen N 1s of the nanostructured silicon/carbon electrode cycled 250 times vs  $Li/Li^+$  in dependency of the electrolyte configuration.

Further reduction of these compounds results in inorganic compounds such as Li<sub>3</sub>N, LiF, Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, Li<sub>2</sub>S, Li<sub>x</sub>S<sub>y</sub>O<sub>z</sub>, LiCF<sub>3</sub> and  $Li_xC_2F_y$ . The overall fluorine concentration is almost 7 times higher in the absence of LiNO3 (in DME/DOL) originating from decomposed Li-TFSI as only fluorine source. The F 1s binding energy (Fig. 3b) of the LiNO<sub>3</sub>-free electrolyte displays a large signal at 688.8 eV and 685.5 eV corresponding to related Li-TFSI (such as Li<sub>2</sub>NSO<sub>2</sub>CF<sub>3</sub> species – Eq. 1) and LiF, respectively. In contrast, organic fluorine species at 688.8 eV are merely observed with LiNO3 addition and majorly LiF at 685.5 eV is present which is in accordance to the C 1s spectrum. The concentration of R<sub>2</sub>SO<sub>4</sub> species shown in the S 2p spectrum (Fig. 3c) is higher with LiNO<sub>3</sub> addition than in the absence. This result suggests that related Li-TFSI compounds (such as  $Li_2S_2O_4$ ) are further oxidized to sulfates ( $R_2SO_4$ ) by LiNO<sub>3</sub>. Low binding energy signals at 161 eV and 164 eV are observed in all electrolyte configurations corresponding to minor concentrations of Li2S and -S-S- bridging, synonymous for elemental sulfur, respectively. Li<sub>2</sub>S is commonly observed on lithium metal after cycling in Li-S batteries as a result of polysulfide self-reduction.<sup>26</sup> Herein, the Li<sub>2</sub>S is formed without the presence of polysulfides and implies that also the decomposition of Li-TFSI considerably contaminates the anode.

The N 1s binding energy (Fig. 3d) for both electrolyte formulations containing LiNO<sub>3</sub> displays an energy signal at 396 eV  $\leq \Delta E \leq$  399 eV corresponding to Li-TFSI derivatives such as R-SO<sub>2</sub>-NR<sub>2</sub> species and Li<sub>3</sub>N.<sup>26</sup> An additional binding energy maximum occurs at 404.6 eV only in the presence of LiNO<sub>3</sub> which is assigned to functional nitro groups R-NO<sub>2</sub> (R = organic) or nitrite (NO<sub>2</sub><sup>-</sup>) compounds. No remaining LiNO<sub>3</sub> is found (N 1s  $\approx$  407.5 eV). NO<sub>x</sub> species were already proven to act as protective layer on lithium metal cycled in ethers with LiNO<sub>3</sub>.<sup>28</sup> Etacheri et al.<sup>7</sup> investigated the decomposition of LiNO<sub>3</sub> on SiNW and suggested the formation of Li<sub>x</sub>NO<sub>y</sub> as stabilizing agent. To our opinion, a deposition of LiNO<sub>2</sub> may not occur which is related

to its similar solubility in polar organic solvents compared to LiNO<sub>3</sub>. Furthermore, a reaction of LiNO<sub>3</sub> with DOL was suggested to promote DOL polymerization.<sup>7</sup> We propose that LiNO<sub>3</sub> gets reduced to a NO<sub>2</sub> radical and Li<sub>2</sub>O (Eq. 2) at 1.71 V vs Li/Li<sup>+</sup> which initiates a polymeric reaction with DOL to from organic nitro compounds. The dQ/dV plot (Fig. 1d) reflects this assumption due to a broad reduction current at high electrolyte consumption with low CE. However, a two-electron reaction to form nitrites may also be possible (Eq. 3).

$$NO_3^- + e^- + 2Li^+ \rightarrow NO_2 + Li_2O$$
<sup>[2]</sup>

$$NO_3^- + 2e^- + 2Li^+ \rightarrow NO_2^- + Li_2O$$
 [3]

The protective surface layer formed by LiNO<sub>3</sub> contains low concentrations of completely decomposed Li-TFSI (LiF, Li<sub>3</sub>N and R<sub>2</sub>SO<sub>4</sub>) and RNO<sub>2</sub> functional groups preventing Li-TFSI decomposition. However, as specified before, this layer cannot inhibit the continuous reduction of DOL. The O 1s binding energy (Fig. 4) shows a maximum at 532 eV independent of LiNO3 addition corresponding to carbon-oxygen species from carbonates and decomposed ethers. Furthermore, a signal at 530.5 eV is present corresponding to majorly  $Li_x SiO_y$  and LiOH.<sup>44,48</sup> In the presence of LiNO<sub>3</sub> an additional low energy signal at 529 eV is resolved corresponding to Li<sub>2</sub>O. No Li<sub>2</sub>O is found in the absence of LiNO<sub>3</sub>. Both compounds, Li<sub>x</sub>SiO<sub>y</sub> and Li2O were reported to be initially formed from the reaction of the native  $SiO_x$  layer with electrolyte.<sup>44,49</sup> Herein, the Li<sub>2</sub>O may also be formed by LiNO<sub>3</sub> (Eqs. 2/3) decomposition. To further analyze the presence of Li<sub>2</sub>O, we sputtered the sample for 5 min to remove the top 15-20 nm of the surface since Li<sub>2</sub>O is typically a reaction product on the surface of silicon and should be located beneath the upper SEI.<sup>44</sup> Indeed, considerable high amounts of Li<sub>2</sub>O are detected in the presence of LiNO<sub>3</sub> and only low concentrations in the additive-free



**Figure 4.** O 1s binding energy of the nanostructured silicon/carbon electrode cycled 250 times vs Li/Li<sup>+</sup> in dependency of the electrolyte configuration a) before sputtering and b) after sputtering ( $\sim$ 15 nm surface removal).

electrolyte (Fig. 4b), confirming its predominant localization beneath the upper SEI. It has to be considered that sputtering can induce  $Li_2O$ formation to some extent from decomposition of SEI compounds such as  $Li_2CO_3$ . However, we previously sputtered silicon anodes cycled in carbonate-based electrolyte (LP30) and could not detect notable amounts of  $Li_2O$ .<sup>32,50</sup>

In order to corroborate our theory and to further identify degradation phenomena, we studied the nanostructured silicon/carbon anode at different states of cycling in the additive-free electrolyte. We observe a gradual increase of LiF and related Li-TFSI compounds (Fig. 5a) in the SEI as a result of continuous Li-TFSI decomposition causing low reversibility of the silicon anode. The total concentration of fluorine increases from 4 at.% after 1 cycle to 22 at.% after 250 cycles. The O 1s spectra (Fig. 5b) indicate that initially Li<sub>2</sub>O is formed as a result of SiO<sub>x</sub> reaction with lithium. The surface concentration of Li<sub>2</sub>O is very low since it is majorly located beneath the upper SEI.<sup>45</sup> Upon cycling the concentration of both Li<sub>2</sub>O and Li<sub>x</sub>SiO<sub>y</sub> decreases which may be attributed to dissolution or a growing SEI. No Li<sub>2</sub>O is detected after long-term cycling anymore. In accordance to these results, the silicon concentration decreases upon cycling due to the growing SEI layer. Interestingly, the electrode cycled 250 times with LiNO3 exhibits similar surface characteristics compared to the electrode cycled once in the additive-free electrolyte such as similar elemental composition and low concentration of related Li-TFSI species. This result highlights that the initially formed RNO<sub>2</sub> species can protect the electrode from Li-TFSI decomposition and hence helps to retain its initially formed surface structure.

Discussion in context to carbonate-based electrolytes .- In order to evaluate the role of SEI components on the reversibility, the results herein are discussed in context to our previous results in fluoroethylene carbonate (FEC)-containing carbonate-based LP30 electrolytes<sup>32</sup> obtained under identical conditions. Although the organic SEI compounds in ether- and carbonate-based electrolytes differ, similar inorganic components such as Li<sub>2</sub>O and LiF are observed which are typically final decomposition products of most electrolyte components. FEC is well-known to cause an extremely high reversibility of silicon-based anodes and high concentrations of both Li2O and LiF were found after long term cycling using the FEC additive.<sup>32</sup> However, the role of both compounds on the reversibility is still discussed controversially. In the additive-free ether-based electrolyte high concentrations of LiF of similar morphology compared to the FEC-containing electrolyte were observed along with a low reversibility. This result suggests that LiF is not necessarily beneficial for the reversibility as often proposed<sup>41-42</sup> probably because it is not present as a closed film neither with FEC addition nor with the ether-based electrolyte. It rather suggests that other compounds are responsible for an enhanced reversibility as it seems to be applied to Li2O which was found along with a good reversibility for LiNO3 and FEC addition. Lithium oxides are believed to play a key role for an enhanced reversibility owing to its favorable transport properties for Li<sup>+</sup> ions.<sup>41</sup> We propose that its formation and preservation seems to be essential to obtain a good reversibility. Li2O formation can result from different mechanisms such as initial SiO<sub>x</sub> (native oxide layer on silicon) reaction with electrolyte and LiNO<sub>3</sub> decomposition,<sup>32,44</sup> but it seems to be susceptible for



Figure 5. Evolution of the a) fluorine F 1s, b) oxygen O 1s and c) silicon Si 2p binding energies and the total concentration of each element upon cycling of the nanostructured silicon/carbon electrode vs Li/Li<sup>+</sup> in the additive-free DME/DOL solution.

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Scheme 1. Simplified illustration of the mechanistic SEI formation on the nanostructured silicon/carbon electrode after long-term cycling in 1 M Li-TFSI in DOL/DME in dependency of LiNO<sub>3</sub> addition.

dissolution during cycling. Similar to carbonate-based electrolytes, the dissolution of  $Li_2O$  in ether-based electrolytes may be caused by HF which can originate from the reaction of Li-TFSI derivatives (Eq. 1) with traces of water at the anode surface (Eq. 4). The water traces may originate from the binder PAA which is well-known for extremely high adsorbing capabilities. It was shown that the binder indeed seems to influence the SEI characteristics.<sup>32</sup> HF formation during decomposition of Li-TFSI may explain the formation of large amounts of LiF due to the reaction of HF with Li<sub>2</sub>O and semi organic lithium salts. Through the addition of LiNO<sub>3</sub> a protective surface layer is formed which prevents conductive salt decomposition on the silicon surface and thus the formation of HF. This mechanism may be responsible for the presence of Li<sub>2</sub>O.

$$2\text{LiSO}_2\text{CF}_3 + \text{H}_2\text{O} + 2\text{e}^- + 2\text{Li}^+ \rightarrow \text{HF} + \text{LiOH} + \text{Li}_2\text{S}_2\text{O}_4 + \text{LiC}_2\text{F}_5$$
[4]

After all investigations and discussions the main reason for the degradation of silicon-based anodes in additive-free ether-based electrolytes is found in the decomposition of both the conductive salt Li-TFSI and the ether solvents. LiNO<sub>3</sub> addition prevents the decomposition of Li-TFSI and thus enhances the reversibility. In contrast, the major degradation in carbonate-based LP30 electrolytes is assigned to the decomposition of the alkyl carbonate solvent. Addition of FEC to LP30 prevents also the decomposition of the alkyl carbonates resulting in an exceptional reversibility.<sup>32</sup>

#### Conclusions

The addition of LiNO<sub>3</sub> to DME/DOL electrolyte solutions significantly improves the electrochemical reversibility of the nanostructured silicon/carbon electrode highlighting its importance for LiSi - S batteries. It forms a protective SEI composed of R-NO<sub>2</sub> species (R = presumably organic) as essential stabilizing compound. The protective surface layer inhibits decomposition of the conductive salt Li-TFSI, but seems not to deteriorate the decomposition of DOL via NO<sub>2</sub> radicals to form rather flexible polymeric RNO<sub>2</sub> compounds. The SEI was investigated at different cycling states and it was found that Li<sub>2</sub>O is part of the reaction of electrolyte with SiO<sub>2</sub> and silicon suboxides (SiO<sub>x</sub>). After long-term cycling the Li<sub>2</sub>O was only identified with LiNO<sub>3</sub> addition suggesting that the LiNO<sub>3</sub> either prevents its dissolution or decomposes to Li<sub>2</sub>O. A comparison to previous results

performed with carbonate-based electrolytes reveals that an enhanced reversibility is frequently observed along with Li<sub>2</sub>O in the SEI. Its presence after long-term cycling seems to be a good indicator for an enhanced stability of silicon-based anodes likely due to its beneficial transport properties for Li<sup>+</sup> ions. In contrast, high concentrations of LiF were found along with a low reversibility and the enhanced properties of the SEI with embedded LiF, frequently reported, cannot be confirmed herein. This result suggests that the favorable role of LiF may therewith often be overrated and other compounds or their synergetic effects with LiF seem to stabilize the SEI and the reversibility, respectively. We observe a lower reversibility of ether-based electrolytes than for carbonate-based electrolytes which has to be solved until silicon-based anodes can be applied in rechargeable high-energy LiSi - S batteries. Scheme 1 represents a simplified illustration of the SEI formation considering the findings in this study.

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