Solid Electrolyte Interphase Formation on Silicon and Lithium Titanate Anodes in Lithium-Ion Batteries

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Abstract

To gain new insights into the formation of the solid electrolyte interphase (SEI), as a basis for the safe and efficient use of new anode materials, we studied SEI formation on silicon and lithium titanate (LTO) anodes by electrochemical impedance spectroscopy (EIS) and *ex situ* X-ray photoelectron spectroscopy (XPS) measurements. While EIS measurements performed at equidistant voltage intervals provided insights into the SEI formation process, *ex situ* X-ray photoelectron spectroscopy (XPS) measurements supplied data on the chemical composition of the SEI layer. On silicon anodes we observed that resistance decreases in the second cycle which suggests the formation of a stable SEI with SiO_2, Li_4SiO_4, LiF and different carbonates as its main components. On LTO anodes, however, resistance increases by a factor of two indicating incomplete SEI formation. Here LiF and different carbonates were identified as the SEI's main components.

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1 Introduction

Due to their high energy density, low self-discharge and lack of memory effects lithium-ion batteries (LIB) are under discussion as cache facilities for offsetting the instabilities of an electricity supply increasingly generated by renewable energies. Yet most types of lithium-ion batteries are operated in voltage regions exceeding the stability window of the electrolytes and therefore present a potential safety hazard, which limits the voltage range. Critical degradation mechanisms and further electrolyte break-down can be prevented by the formation of a homogeneous and stable electron-insulating solid electrolyte interphase (SEI) on the anode.

Composition and structure of the SEI formed on the most commonly used anode material graphite have already been studied extensively [1-8]. Recently a variety of alternative anode materials were discussed recently to meet the demand for higher capacities and increased safety [9]. For improving specific capacity promising candidates are alloy materials based on silicon [10,11], tin [12,13], antimony [14] or germanium [15]. Alloy materials, however, suffer from volume expansions of up to 400 vol.% during lithiation, so that the existing SEI cracks. As a result (fresh) blank surfaces emerge, and the SEI is continuously renewed through electrolysis of the electrolyte [16-18]. To optimize alloy anodes and to improve capacity retention and longevity it is essential to better understand the process of SEI. With regard to operating safety, especially titanium oxides (TiO_2, $Li_4Ti_5O_{12}$) are reported to have advantageous properties [19,20], as they are operated at higher voltages. But lithium titanate (LTO) anodes still show severe gassing when getting into contact with the electrolyte, which results in battery swelling and suggests film formation on the anode surface. To reduce gassing of LTO-based batteries, stable SEI layers are said to be effective barrier layers that can suppress further electrolyte decomposition [21].

In this study, we studied the formation of the SEI layers formed on silicon and on LTO anodes after the first cycle; we used X-ray photoelectron spectroscopy (XPS) to determine their chemical composition, and electrochemical impedance spectroscopy (EIS) to analyze the SEI formation process. We also calculated the distribution of relaxation times to gain better insights into the range of electrochemical processes involved. We found that overall resistance of the silicon anodes significantly decreased in the second cycle indicating the formation of a stable SEI. This is in contrast to LTO anodes, where overall resistance increased by a factor of two under similar conditions suggesting that surface layer formation might not have been complete after the first cycle.

2 Experimental

2.1 Cell Preparation and Scanning Electron Microscopy

Commercially available LTO electrode foils (Custom Cells Itzehoe GmbH) with a capacity of 2.0 mAh cm^{-2} were used. They consist of 84 wt.% LTO, 6 wt.% conductive additives and 10 wt.% binder materials, coated on an Al current collector foil. Before use the electrode foil was dried at 110 °C for at least 12 h under vacuum.

For the silicon electrode coating a slurry was prepared by mixing 80 wt.% nanosilicon (crystalline, average particle size $\leq$ 50nm, 98 % purity, laser synthesized from vapor phase, Alfa Aesar), 12 wt.% Super P carbon black (Timcal), and 8 wt.% sodium carboxymethyl cellulose (average M_w 250k, degree of substitution 0.7, Sigma Aldrich) in a closed vial. Five stainless steel balls with a diameter of 10 mm were added for mixing. The powders were dry-mixed by putting the closed vial on a roller bank. After 1 hour deionized water was added as a solvent to reach adequate viscosity for coating and the mixing continued for at least two more hours. The slurry was evenly cast on a copper foil (20 µm thickness, special coating for improved adhesion, Schlenk AG) using the doctor-blade method with a coating gap of 100 µm, and dried at room temperature in air for at least 1 hour. After this first drying process the electrode was further dried at 90°C in vacuum overnight.

The anodes were morphologically characterized by scanning electron microscopy (SEM, Zeiss ULTRA plus with Charge Compensation). The accelerating voltage was 1 kV and secondary electron detection was used.

For electrochemical testing in the two-electrode set-up, Swagelok® type cells were assembled in a glovebox under argon atmosphere with oxygen and water contents of less than 1 ppm. A 1.5 mm thick lithium foil (99.9 %, Sigma Aldrich) served as counter electrode. The separator was a 20 µm thick trilayer separator (Cellgard® 2320). As electrolyte we used a 1 M solution of lithium hexafluorophosphate ($LiPF_6$, battery grade, ≥ 99.99% trace metal basis, Sigma Aldrich) in a mixture of ethylene carbonate (EC) (anhydrous, 99%, Sigma Aldrich) and diethyl carbonate (DEC) (anhydrous, ≥ 99 %, Sigma Aldrich) in a ratio of 3:7 v/v.

For the three-electrode set-up an EL-Cell with a lithium ring reference electrode was used. The counter electrode was also a 1.5 mm thick lithium foil (99.9 %, Sigma Aldrich). The electrodes were separated by three glass fiber separators as well as an additional trilayer separator like in the Swagelok cells were used.

2.2 Electrochemical Impedance Spectroscopy

EIS and cycling performance were investigated 24 h after cell assembly with a Zahner IM6 electrochemical workstation with the corresponding Thales battery software (Thales 3.02, Zahner-Elektrik). Cells were tested inside a climate chamber (Weiss & Vötsch, WK 340) and kept at a constant temperature of 23 °C. Silicon anodes were cycled with a constant current of 180 mA per gram active material, which corresponds to a C/20-rate. Here the voltage range was 0.8 V - 0.04 V vs. Li/Li^+. LTO anodes were cycled with a constant current of 8.75 mA per gram active material, which also corresponds to a C/20-rate. The voltage limits were 2.0 V and 1.3 V vs. Li/Li^+, respectively. A full discharge and charge cycle including EIS measurements lasted approximately 48 h.

EIS measurements were carried out potentiostatically in equidistant voltage intervals of 0.1 V during the first two cycles to monitor initial SEI growth. A relaxation time of 5 minutes was allowed before starting a new EIS measurement. The frequency range was 1 MHz to 10 mHz, with an excitation voltage of 5 mV. The measured impedance spectra were fitted with an electrochemical equivalent circuit (EEC) using the Thales software where a complex linear least square method is implemented. The starting frequencies were derived from the distribution of relaxation times to obtain good initial values.

2.3 Calculation of the Distribution of Relaxation Times

The distribution of relaxation times (DRT) was analyzed on the basis of impedance data to separate electrochemical processes with different time constants, to help detect processes which might otherwise remain unresolved. The numerical scheme followed a Levenberg-Marquardt algorithm and was already described in detail previously [22]. The measured spectra were transformed with the Z-HIT function of the Zahner Software Thales to ensure that no unwanted artifacts occur due to test duration or drifts in the system.

2.4 Characterization by X-Ray Photoelectron Spectroscopy

The elemental composition of the sample surfaces was determined by XPS measurements using monochromatic Al K_α (1486.6 eV) radiation (PHI 5800 MultiTechnique ESCA System, Physical Electronics). A surface spot of 0.8 × 0.8 mm^2 was used for analysis. The measurements were performed at a detection angle of 45°, using pass energies at the analyzer of 93.9 and 29.35 eV for survey and detail spectra, respectively. For a depth profile of elemental concentrations, the top surface layers were removed by successive sputtering (I_{Sp} ~1 µA, U_{Sp} 5 kV) for 2 and When necessary, the samples were neutralized with electrons from a flood gun (current 3 µA) to compensate for charging effects at the surface. For binding energy calibration the C(1s) peak of graphitic carbon was set at 284.5 eV. To avoid surface contamination, the samples were transferred in inert gas atmosphere to the sample load lock of the XPS system.

3 Results and discussion

3.1 Anode Morphology

A qualitative impression of the anode's morphology was obtained from SEM micrographs and EDX-mapping (see Fig. 1 and 2). The silicon anode shows a homogeneous distribution of carbon black and silicon particles. The silicon particles have diameters of up to 50 nm and are round in shape. It has been shown that carbon-coated silicon particles perform well as anode material in lithium-ion batteries [23,24]. During anode preparation no special coating process was applied, still EDX-mapping revealed that silicon particles are evenly covered with carbon black (see Fig. 1(a)). Complete and uniform carbon coverage of the particles was reported to be most effective in suppressing interfacial reactions after the first cycle [21].

Fig. 1: (a) EDX-mapping of the uncycled silicon anode with magnification 1,000 × (red: carbon, green: silicon) (b)-(d) SEM micrographs with magnifications of 3,000 ×, 10,000 × and 30,000 ×, respectively.

Figs. 2 (a)-(d) show micrographs of the uncycled LTO anode with picture magnifications of 1,000 ×, 3,000 ×, 10,000 × and 30,000 ×. The LTO anodes show a less homogeneous distribution of particles and the particles appear somewhat angular. Moreover, with several hundred nanometers in diameter the LTO particles are significantly larger than the silicon particles.

Fig. 2: (a)-(d) SEM micrographs of the uncycled LTO anode with magnifications of 1000 ×, 3000 ×, 10,000 × and 30,000 ×, respectively.

3.2 XPS Characterization

Fig. 3 shows the XPS detail spectra of the cycled silicon anode and after successive sputtering for 2 and another 4 minutes (6 minutes in total).

The Li(1s) spectrum in Fig. 3 (a) shows a single peak at approx. 56.4 eV, which decreases slightly in intensity after the second sputter step. The Si(2p) spectrum (Fig. 3 (b)) shows two pairs of peaks (each consisting of $2p_{3/2}$ and $2p_{1/2}$ components due to the spin-orbit coupling) before sputtering, one at approx. 99.1 eV, the other at approx.103.1 eV ($2p_{3/2}$ peak). The peak at 99.1 eV can be attributed to bulk silicon, the one at 103.1 eV is related to SiO_2 [25]. It is known that a SiO_2 layer (native SiO_2) forms on silicon surfaces when exposed to air, e.g., during electrode fabrication [26]. After two and after six minutes of sputtering a third peak emerges at around 101.1 eV which is attributed to Li_4SiO_4 [27].

Fig. 3: XP detail spectra in the Li(1s), Si(2p), P(2p), C(1s), O(1s) and F(1s) regions on the cycled silicon anode. The spectra were recorded before sputtering (bottom spectrum) and after 2 and 6 minutes of sputtering (middle and top spectra, respectively).

With sputtering the peak intensity for SiO_2 decreases whereas that for elemental silicon increases. The P(2p) spectrum of the unsputtered anode shows two distinct peak couples with $P(2p_{3/2})$ peaks at 134.7 and 137.6 eV. The peak at 137.6 eV is attributed to PF_6^-, the peak at 134.7 eV to P centers where the F ligands are partially or completely exchanged by O [25]. Since the intensity of the peak at 137.6 eV decreases after sputtering, we attribute this decrease to residuals of the conducting salt $LiPF_6$ at the electrode surface. In the C(1s) spectrum four peaks can be distinguished at 284.5 eV, 285.2 eV, 286.8 eV and 290.5 eV. The peak at 284.5 eV is related to graphitic C in the carbon black of the anode and is therefore present in all three spectra. The peak at 285.2 eV is mainly present in the surface spectrum and related to hydrocarbon contaminations at the surface. Next, the peak at 286.8 eV is related to carbon with C-O bonds and decreases with increasing sputtering depth. This peak is thus attributed to the CMC binder and to decomposition products of the carbonate solvents. The last peak at 290.5 eV is attributed to (organic) carbonates and decreases with increasing sputtering depth. For the unsputtered electrode this could be attributed to remainders of the electrolyte solvents (EC, DEC). At higher sputtering depth, however, this peak could also be related to Li_2CO_3 or lithium alkyl carbonates that are forming during the decomposition of ethylene carbonate [28]. The O(1s) spectrum shows only one broad peak at 532.7 eV, which decreases over the time of sputtering and is tentatively attributed to carbonates and their decomposition products and to the SiO_2 surface oxide. In the F(1s) spectrum two peaks appear at 685.6 eV and 687.7 eV. The first one can be related to fluorides such as LiF which are known components of the SEI [29]. The peak at 687.7 eV is most pronounced in the unsputtered anode and assigned to F in the PF_6^- ion in the conducting salt $LiPF_6$. Table 1 gives an overview of the measured peaks and their assignments.

Table 1: Measured peaks and their assignments on the cycled silicon anode

Assignments	Measured binding energy (eV)					
	Li 1s	Si $2p_{3/2}$	P $2p_{3/2}$	C 1s	O 1s	F 1s
	56.4					
Si		99.1				
SiO_4^{4-}		101.1				
SiO_2		103.1			532.7	
$PO_xF_y^{z-}$			134.7			
PF_6^-			137.6			687.7
Carbon black				284.5		
Hydrocarbons				285.2		
C-O				286.8		
Carbonates				290.5	532.7	
F^-						685.6

Fig. 4 shows the XP spectra of the LTO anode before and after sputtering. The maximum of the Li(1s) peak is again situated at 56.4 eV (Fig. 4 (a)), the peak intensity decreases successively with increasing sputter time (the characteristic feature at higher binding energy is the Ti(3s) peak). Fig. 4 (b) shows the P(2p) spectrum where, before sputtering, two peaks can be seen at 137.4 eV and 134.5 eV. Like in the P(2p) spectrum of the cycled silicon anode they are attributed to PF_6^- and its partially or completely oxygenated degradation products, respectively. The peak at 137.4 eV is strongest at the electrode's surface. The attribution to remainders of the conducting salt adsorbed on the electrode surface is supported by the corresponding PF_6^- peak at 687.8 eV present in the F(1s) spectrum, which is also most intense for the unsputtered electrode surface.

Fig. 4: XP detail spectra in the Li(1s)/Ti(3s), P(2p), C(1s), O(1s) and F(1s) regions on the cycled LTO anode. The spectra were recorded before sputtering (bottom curve) and after 2 and 6 minutes of sputtering.

The C(1s) spectrum of the unsputtered LTO anode (Fig. 4 (c)) shows four peaks, at 284.5 eV, 285.2 eV, 286.8 eV and 290.8 eV, respectively. Again, the peak at 284.5 eV is attributed to carbon black used in the anode. The peak at 285.2 eV stems from hydrocarbons and is only present in the topmost layer. Therefore, this peak is most likely to stem from organic electrolyte solvents in general. The peak at 286.8 eV is related to carbon with C-O bonds. This peak, too, has its highest intensity in the unsputtered anode, but contrary to the peak at 285.2 eV, it is still present after sputtering. Thus it could be related to electrolyte components and the binder used. As in the XPS spectra of the silicon anode, the peak at 290.8 eV results from carbonates. It is present in all spectra. The pronounced intensity at the unsputtered surface is attributed to carbonate species in the electrolyte solvents, whereas after sputtering the peaks might as well result from Li_2CO_3 and lithium alkyl carbonates which are formed as reduction products of EC. In the O(1s) spectrum (Fig. 4 (d)), three peaks can be distinguished, at 530.5 eV, 532.3 eV and 533.8 eV. The peak at 530.6 eV is assigned to O^{2-} species in LTO. The peak at 532.3 eV, which decreases with increasing sputtering depth, is again related to carbonates. It is strongest at the topmost layer, yet still present in the lower layers detected after 6 min sputtering. As pointed out for the C(1s) spectrum, the carbonate peak after sputtering may at least in part be attributed to Li_2CO_3 and lithium alkyl carbonates, which are known SEI components [30]. The peak at 533.8 eV in the O 1s spectrum is mainly present at the surface layer and might be related to oxygen atoms in the C-O-C groups of the organic carbonates (or of decomposition products in which this structure motive is still intact). Buchner et al. have shown that the O 1s peak of such a group is located at 534.3 eV after ethylene carbonate adsorption on Cu(111) at 80 K and that it shifts to slightly lower BE after warming to 200 K, which leads to decomposition of the molecule [31]. In the F 1s spectrum finally, two distinct peaks can be identified at 685.6 eV and 687.8 eV. The peak at 687.8 relates to PF_6^- and has its highest intensity at the unsputtered electrode, which decreases over the time of sputtering. It is assigned to the conducting salt $LiPF_6$. The peak at 685.6 eV is present in all three spectra and is related to fluorides such as LiF. Table 2 lists the measured binding energies at the LTO anode and their attributions.

Table 2: Binding energies and their attributions measured on the cycled LTO anode.

Assignments	Measured binding energy (eV)				
	Li 1s	P $2p_{3/2}$	C 1s	O 1s	F 1s
	56.4				
$PO_xF_y^{z-}$		134.5			
PF_6^-		137.4			687.8
Carbon black			284.5		
Hydrocarbons			285.2		
C-O			286.8		
LTO				530.5	
Carbonates			290.8	532.3	
C-O-C groups				533.8	
F^-					685.6

3.3 Electrochemical Impedance Spectroscopy

To further study the formation of the surface layer, impedance spectra of the first and second lithiation process were recorded. As the impedance spectra of the second cycle do not show significant differences to those of later cycles, we only consider the impedance spectra of the first and second cycle [32]. For silicon anodes overall resistance decreases considerably from the first to the second cycle (compare Figs. 5 (a) and (b)). The impedance spectra were fitted with an EEC consisting of an ohmic resistance, three R||CPE elements and a Warburg element, followed by a capacitor. In general it is difficult to derive the number of processes involved from impedance spectra alone. To confirm the number of processes taken into account for the EEC, we calculated the distribution of relaxation times from the measured impedance data (see Figs. 5 (c) and (d)).

Fig. 5: Nyquist plots of the impedance spectra during the first (a) and second (b) lithiation of the silicon anode (off-set on y-axis) and the corresponding distribution of relaxation times in (c) and (d), respectively. (Symbols: measured impedance data; full lines: corresponding fit.) For clarity EEC and the semi-circles of the corresponding processes are depicted (P_1 – P_3).

The ohmic resistance can be derived directly from the impedance spectra and equals the zero crossing at high frequencies. Here it is about 4 Ω. The process at highest frequencies (P_1) relates to the anode charge transfer processes. In the mid-frequency region the processes related to the contact resistance between anode and current collector as well as the resistances caused by surface layers are superimposed (P_2). The semi-circle at lower frequencies (P_3) represents the cathode charge transfer resistance. Finally, limited lithium ion diffusion leads to a strong and almost linear increase of the impedance at low frequencies. In accordance with the EEC three main processes can be identified in the DRT of the first and second lithiation (Fig. 5 (c) and (d)).

For the LTO anode, however, overall resistance increases from first to second lithiation (Fig. 6). The measured impedance data were fitted with the same EEC as the silicon half cells.

Fig. 6: Nyquist plots of the impedance spectra during the first (a) and second (b) lithiation (off-set on y-axis) of the LTO anode and the corresponding distribution of relaxation times in (c) and (d), respectively. (Symbols: measured impedance data; full lines: corresponding fit.)

To explain the differences in the impedance behavior of the LTO and the silicon anode we performed additional measurements in a three-electrode set-up with a Li ring reference electrode. Nyquist representations of the impedance data for the silicon anode are given in Fig. 7 (a) and (b); those for the LTO anode in Fig 7 (c) and (d).

The three-electrode set-up allows to individually and separately observe the processes at the anode side. The measurements show that the Ohmic resistance of the LTO anode increases only slightly (1.5 Ω to 2.5 Ω) from the first to the second lithiation process (Figs. 7 (c) and (d)). The impedance increase in the second lithiation below 1.6 V is related to the phase change of LTO. The main formation of a LTO SEI layer takes place directly when the electrode gets into contact with the alkyl carbonate solvents, resulting in severe gassing and phase transformation of the LTO surface and a layer of SEI surrounding the LTO particles [21]. Still, from literature it is well known that the growth of surface layers does not end after the first cycle, but continues at a reduced growth rate, leading to continuous capacity fading [33,34].

Fig. 7: Nyquist plots of the impedance spectra during the first (a) and second (b) lithiation process of the LTO and the first (c) and second (d) lithiation process (off-set on y-axis) of the silicon anode in a three-electrode set-up with a lithium ring reference electrode.

However, the resistance increase from first to second lithiation by a factor of two for the two-electrode cell is not caused by the formation of the SEI layer on the LTO anode. The impedance spectra of the two-electrode set-up are strongly influenced by the SEI layer forming at the lithium electrode and by the formation of an insulating passivation layer at the aluminum current collector [34]. Schweikert et al. have shown in symmetrical LTO/LTO cells that the interfacial resistance at the LTO/electrolyte interphase is relatively low, so that the resistance of the Li/electrolyte interphase cannot be neglected [35]. Furthermore, it has been shown on symmetrical Li/Li cells that the interfacial impedance on Li metal continues to increase upon prolonged storage [36] as well as with increasing cycle numbers [34]. For the silicon half cell, in contrast, impedance decreases from the first to the second lithiation process. Thus the impedance behavior trend stays the same in the two- and the three-electrode set-up (see Figs. 5 (a),(b) and 7 (c),(d)). It was found by He et al. that the SEI forming on LTO particles is rather thin (ca. 3 nm) [21]. Veith et al. reported a layer thickness of the SEI on silicon anodes of about 20 nm [2]. Therefore, surface layer formation on the lithium electrode has a bigger influence on the overall impedance of LTO anodes than on that of silicon anodes.

To understand the electrochemical behavior of the SEI we evaluated the change in surface resistance R_{Surf}, which correlates with the element P_2 fitted with the EEC (fitting error: ca. 1.5 %). Reactions at the electrode surfaces of the silicon half cell take place during the first cycle, leading to a reduced R_{Surf} in the second cycle (see Fig. 8). During the first lithiation process of the silicon anode, R_{Surf} reaches 263 Ω at the upper cut-off voltage of 0.8 V vs. Li/Li$^+$. resistance stays relatively constant between 0.8 V and 0.1 V vs. Li/Li$^+$ and slightly increases at the lower cut-off voltage, reaching eventually 312 Ω. During the second lithiation process R_{Surf} has distinctly decreased between 0.8 V and 0.2 V vs. Li/Li$^+$ in comparison to the first lithiation, with R_{Surf} reaching a value of around 100 Ω. Below 0.2 V vs. Li/Li$^+$, the resistance increases substantially and reaches a maximum of 282 Ω at 0.04 V vs. Li/Li$^+$.

The cyclic voltammogram of the first silicon lithiation process (Fig. 8) shows a peak between 0.7 V and 0.6 V vs. Li/Li$^+$ that can be attributed to the decomposition of ethylene carbonate which is one of the main reactions leading to SEI formation [38,30]. Another peak can clearly be observed at the lower cut-off voltage of 0.04 V vs. Li/Li$^+$, which corresponds to the formation of higher lithiated compounds [11]. Upon charging, two peaks at 0.36 V and 0.53 V vs. Li/Li$^+$ are to be seen, which are related to the delithiation reaction [39]. During the second lithiation process the peak corresponding to SEI formation is not observed anymore. The peaks representing lithiation and delithiation become more distinct during the second cycle. A similar behavior was reported previously and explained by the fact that the native oxide layer might act as a barrier layer and that further lithiation does not occur unless the native oxide layer is at least partially reduced [40]. This is in line with our findings that also after the first cycle SiO_2 and Li_4SiO_4 can be identified in the XP spectra. The decrease in R_{Surf} between the first and second lithiation process is mainly related to the SEI formation and its influence on Li^+ desolvation [41,42]. R_{Surf} is further reduced by the diminution of the native SiO_2 layer. Furthermore, combined neutron reflectometry, XPS and cyclic voltammetry measurements have shown that the SEI layer on silicon anodes changes its thickness and composition with the charging state. With increasing lithiation the layer thickness of the SEI decreases from 25 nm to 18 nm. At first sight, the increase of R_{Surf} at low voltages is contradictory to these findings. This apparent contradiction can be explained, however, by a severe reduction in the specific conductivity of the SEI in this state. The XPS measurements of Veith et al. furthermore showed that the content of poorly conducting LiF increases with higher lithiation grades [36].

Fig. 8: Cyclic voltammetry curves (green dashed – delithiation, green solid – lithiation) during the first (a) and second (b) cycle of the silicon anode and R_{Surf} (black) during the corresponding lithiation.

For LTO half cells we find an increase of R_{Surf} from the first to the second lithiation process (Fig. 9). During the first cycle R_{Surf} stays constant at a level of 125 Ω between 2.0 V and 1.6 V vs. Li/Li^+. Below 1.6 V vs. Li/Li^+ R_{Surf} rises slightly to a constant value of ca. 200 Ω. During the second lithiation process R_{Surf} stays at a constant level of ca. 260 Ω between 2.0 V and 1.6 V vs. Li/Li^+. Below 1.6 V vs. Li/Li^+ R_{Surf} rises to reach its maximum value of 406 Ω at 1.3 V vs. Li/Li^+. In comparison to the first lithiation R_{Surf} has increased by a factor of more than two. The cyclic voltammograms of the first and the second lithiation process show a peak at the lower cut-off voltage, which can be correlated to the

Fig. 9: Cyclic voltammetry curves (green dashed - delithiation, green solid – lithiation) during the first (a) and second (b) cycle of the LTO anode and R_{Surf} (black) during the corresponding lithiation.

redox reaction of the Ti^{4+}/Ti^{3+} couple in the spinel structure. The peak between 1.7 V and 1.8 V vs. Li/Li^+ during delithiation corresponds to the reverse process.

The three-electrode measurements have shown that the influence of the SEI layer formation at the LTO surface has only a minor influence on R_{Surf}. The main influencing factors determining the behavior of R_{Surf} in this case are the formation of a SEI layer on the lithium counter electrode and additionally the time-dependent formation of a passivation film at the Al current collector [34].

4 Conclusions

We performed SEM, XPS, EIS and DRT analyses for silicon and LTO to study SEI growth in half cells during the first cycle. The combined methods show that a surface layer is formed on both silicon and LTO anodes. However, especially in the case of LTO, surface layer formation on the lithium counter electrode cannot be neglected, as it contributes distinctly to the overall surface resistance R_{Surf}. EIS measurements are often discussed as a non-invasive, easily applicable method to monitor and thus improve battery performance and safety. Yet for the systems examined a three-electrode setup is necessary to differentiate overlapping processes and adequately describe SEI growth.

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