Comparison of Electron Transfer Properties of the SEI on Graphite Composite and Metallic Lithium Electrodes by SECM at OCP

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The passivating properties of solid electrolyte interphases (SEI) at metallic lithium were characterized using the feedback mode of scanning electrochemical microscopy (SECM) and 2,5-di-tert-butyl-1,4-dimethoxybenzene (DBDBM) as redox mediator at OCP. The SEI at Li allows electron transfer toward DBDBM with finite rate. In comparison to charged graphite composite electrodes, the electron transfer rate tends to be smaller at Li. Both, graphite composite and Li electrodes, show a local variation of electron transfer rates and temporal changes within a time span of hours. The long-term changes of SEI passivity at metallic Li are dependent on the solvents in the liquid electrolyte. In addition, significant short-term changes of SEI passivity occur at both electrodes. However, the frequency of such events is smaller for metallic Li compared to graphite. A strong decrease of SEI passivity and a strong increase of fluctuations in the passivating properties are observed when the microelectrode mechanically touches the metallic Li and damages the SEI. The changes of SEI passivity by a mechanical touch are orders of magnitude larger compared to spontaneous changes. A local SEI damage by the microelectrode decreases not only the SEI passivity locally, but also a few hundreds of μm apart.

Li metal is currently an electrode material of interest for rechargeable lithium-air and lithium-sulfur batteries.1,2 It is promising because of its high theoretical specific capacity1 of 3860 mA h g−1 and smallest electrochemical potential of −3.040 V vs. SHE. Li metal reductively decomposes electrolyte molecules upon contact, because the potential of Li exceeds the stability window of the electrolytes.3 The decomposition products form a solid electrolyte interphase (SEI) on top of the metallic Li.4 The properties of the SEI are very important for the performance of the Li negative electrode, because the SEI affects Li dendrite growth.5 The tendency of Li to form dendrites or high surface area lithium during galvanic deposition is one major drawback of Li metal and causes safety concerns regarding this electrode. The second major drawback is the low coulombic efficiency caused by the ongoing lithium corrosion and sensitivity to SEI passivity.6 Thus, SEI passivity is a relevant parameter for practical applications.

Since the SEI properties are significant for battery performance, substantial ex situ, in situ and in operando techniques were applied for SEI investigation in general.7 SEI formation on graphite occurs mainly in the first cycle because of the rather stable graphite host structure.8 In contrast, the SEI on metallic Li is subject to continuous reformation upon cycling. Despite this significant difference, both graphite and Li metal are covered by similar SEIs.9

In this study the SEI passivity is characterized by in situ scanning electrochemical microscopy (SECM)10 using 2,5-di-tert-butyl-1,4-dimethoxybenzene (DBDBM) as a redox mediator. DBDBM was introduced by Dahn et al.11 as overcharge protection agent for lithium ion batteries (LIB) and turned out to be an excellent choice as SECM mediator in organic solvents as well.11 Scanning probe techniques are frequently applied for battery research.12,13 Among them are in situ atomic force microscopy (AFM)14,15 and in situ scanning vibrating electrode technique (SVET)16,17 for the investigation of Li metal. SVET provides information about the local Li+ ion transfer, whereas SECM is capable of selectively probing the local electron transfer rates in the electrolyte environment.

In the last years significant progress was made by using the SECM and related techniques to study LIB electrodes and related processes. Takahashi et al.18 mapped redox activity of LiFePO4 positive electrodes with a resolution of 100 nm using the scanning electrochemical cell microscopy (SECCM). CO2− dissolution and O2 release from LiCoO2 positive electrodes were analyzed in ionic liquids by the sample generation/tip collection mode of SECM.19 Xu et al.20 characterized the Li+ ion transport from LiCoO2 positive electrodes by reductive currents at the probe. Using ferrocene as a redox mediator Zampardi et al. investigated the electron transport at SEI covered TiO2 paste negative electrodes21 and SEI covered glassy carbon model negative electrodes.22 In addition, a combined SECM/AFM setup was developed to study the SEI on glassy carbon model electrodes.23 Bülters et al.11 characterized spatiotemporal changes of the SEI passivity of charged graphite composite negative electrodes.

There are two major reasons for our motivation to study the passivation films on battery electrodes. (i) It is generally assumed that the SEI both on graphite24,25 and metallic Li3,8 is electronically insulating. Thus, the general operation principle of overcharge protection agents is in question,26 because the oxidized species must be reduced at the SEI covered negative electrode. Consequently, one aim is to characterize the electron transfer of redox shuttles at the SEI covered negative electrode, which may be locally different due to heterogeneities in the SEI composition according to the model of Besenhard and Winter.27 (ii) The long-term goal is to understand the reduction of electrolyte components at negative electrodes. Electrolyte reduction is essential for SEI formation, however, if occurring continuously it is detrimental for battery stability and the understanding of its spatiotemporal behavior would guide steps to improve battery performance by improved electrode and/or electrolyte components.

DBDBM is a mediator of choice to study electrolyte reduction because its functional groups are rather similar to typical electrolyte solvents like ethylene carbonate (EC) and diethyl carbonate (DEC) etc. This is in contrast to other commonly used SECM mediators such as ferrocene or ferrocene derivatives.26,28–30

Experimental

Electrodes preparation.— The preparation and characterization of the graphite composite electrodes (Figure 1a) was described in...
Figure 1. Cross sections of investigated electrodes. (a) Porous graphite composite electrode consisting of graphite, carbon black and PVDF. (b) Metallic Li foil. Figure reproduced and modified from Reference 38.

detail elsewhere.11 Briefly, electrodes were prepared with a composition of 81 mass-% graphite, 6 mass-% carbon black and 13 mass-% polyvinylidene fluoride (PVDF). All three solid components were thoroughly mixed in the dry state under dynamic vacuum (<100 mbar, R02Vac intensive mixer, Eirich, Hardheim, Germany) for 3–5 min. N-methylpyrrolidone (AppliChem GmbH, Darmstadt, Germany) was slowly added under continuous stirring and vacuum until a solid mass concentration of 0.44 g/cm³ was reached. Stirring was continued for another 2 min before opening of the vacuum vessel.

Graphite composite electrodes were produced from the slurry by doctor blade coating on a continuous coating machine (Werner Mathis AG, Oberhasli, Switzerland) on a 20 μm thick, electrochemically roughened copper foil (Carl Schlenk AG, Roth, Germany). The solvent was then removed from the wet film (approximately 150 μm initial thickness) in a two-step process by heating using infrared radiation and subsequent hot air drying. Finally, calendaring of the electrodes was carried out at 100 N mm⁻¹ line pressure. Final loading of the electrodes was 8.5 mg cm⁻² with a final thickness of 80 μm (Figure 1a). Layer porosity amounted to 50%.11 The graphite particles had a specified average size of 32 μm. The Ra = 2.5 μm value for quantifying the overall roughness was calculated according to DIN EN ISO 4287:1997.11

Formation of electrodes.— Pouch cells were constructed using the graphite composite as working electrode and a lithium foil (BASF SE, Ludwigshafen, Germany) as counter electrode for electrochemical conditioning in an Ar-filled glove box. The graphite electrodes and Li metal were cut to identical size and stacked with a layer of glass filter (Whatman GF/A, GE Healthcare, Little Chalfont, UK) as separator. The electrolyte was 1 M LiPF₆ in EC:DEC 1:1 (LP40, Merck KGaA, Darmstadt, Germany).

Electrochemical cycling was carried out between 0.01 V to 1.5 V vs. Li/Li⁺ at galvanostatic conditions (corresponding to 0.5 C). In the first half cycle, the graphite electrode was lithiated and its voltage was 0.01 V vs. Li/Li⁺. In the second half cycle, the delithiation took place and was interrupted when the electrode reached 1.5 V vs. Li/Li⁺. For SECM investigations, cycling was finished with a fully lithiated graphite electrode (i.e. after 5.5 cycle), followed by a transfer to an Ar-filled glove box and dissecting immediately prior to SECM investigation. We also investigated samples after 0.5 cycles in the pouch bag cell, without finding pronounced differences in the behavior. During this step, the graphite electrode was always covered by a layer of the liquid electrolyte LP40.

Scanning electrochemical microscopy setup.— The scanning electrochemical microscope (SECM) was operated under the SECMx control software developed in house.32 It used a 3 axes micropositioning system (MS30 precision actuator and PS30 distance measurement system, CU30 controller, mechOnics AG, Munich, Germany) and a bipotentiostat (Compactstat, Ivium Technologies, Eindhoven, The Netherlands). The positioning system was placed under a custom-made plexiglas bell (Figure 2a).33 The bell and the controller for the micropositioning system were placed inside an Ar-filled glove box (Uni-Lab, M. Braun GmbH, Garching, Germany). The cables for the 4 electrodes and the USB cable for the CU30 controller were fed through ports on the back side of the glove box.

The SECM was operated with microelectrodes (MEs) of radius rₘ ≈ 13 μm (Figure 2b), the graphite composite or Li metal electrodes as samples (Figure 1) and a platinum wire and a silver wire as auxiliary and reference electrodes, respectively. MEs were prepared by sealing a Pt wire of 25 μm specified diameter (Goodfellow GmbH, Bad Hauenheim, Germany) into borosilicate glass capillaries (Hilgenberg GmbH, Malsfeld, Germany). The electrodes were grinded using a...
Micro Grinder EG-400 (Narishige, Tokyo, Japan) and polished using rotating wheels with micropolishing cloth with a suspension of 0.05 μm alumina particles to a mirror finish and a RG ratio of ≈5–10. RG is the ratio of the thickness of the insulating glass sheet around the Pt wire and the radius \( r_T \) of the active electrode area.

The cylindrical opening of the SECM cell served as reservoir for 0.4 mL electrolyte solution. The basic electrolyte was LP40 or 1 M LiClO₄ in propylene carbonate (PC, BASF SE, Ludwigshafen, Germany) with 5 mM DBDMB as redox mediator.

Scanning electrochemical microscopy measurements.— The ME was polarized to 4.1 V vs. Li/Li⁺, where DBDMB is oxidized under a diffusion-controlled condition (Figures 2b/2c). The timer was set to zero, when the working solution was filled into the SECM cell. The approach curves of Figure 3 were recorded with a step size of 0.5 μm and a delay of 1.0 s between the translation and the data acquisition giving an average translation rate of 0.25 μm s⁻¹ and a delay of 1.0 s between the translation and the data acquisition. Approach curves of Figure 3 were recorded with a step size of 0.5 μm and a delay of 1.0 s between the translation and the data acquisition giving an average translation rate of 0.25 μm s⁻¹ and a delay of 1.0 s between the translation and the data acquisition. Approach curves of Figure 3 were recorded with a step size of 0.5 μm and a delay of 1.0 s between the translation and the data acquisition giving an average translation rate of 0.25 μm s⁻¹ and a delay of 1.0 s between the translation and the data acquisition.

Approach curves.— Approach curves in normalized coordinates are plotted in Figure 3. The ME current depends strongly on the type of sample and on \( d \). When the ME approaches the uncharged graphite composite electrode (Figure 3, curve 1), the oxidized DBDMB⁺ is reduced at the graphite composite electrode to DBDMB (Figure 3, inset). The reduction of DBDMB⁺ at the graphite composite electrode yields an additional flux of DBDMB at the ME and thus increases \( r_T \) with decreasing distance. Compared to the case of diffusion-controlled reactions at the ME and the sample (Figure 3, curve 6), the electron transfer is significantly slower at graphite composite electrodes.

Table I summarizes all parameters of the SECM image acquisition. The distance between ME and sample electrode \( d \) is given for the horizontal position \((x/\mu m, y/\mu m) = (0, 0)\) of the image.

**Results and Discussion**

The recorded differences can be attributed to SEI formation (Figure 3, curves 2/3) whereas the electron transfer rate significantly compared to uncharged graphite composite electrodes. Curve 2 and 3 indicate the curves with the largest and smallest electron transfer rate out of ca. 30 similar curves indicating that the electron transfer rate might vary locally on charged graphite composite electrodes. The reasons for the local variation in electron transfer rates could be differences in local composition of the graphite composite electrode and local varying properties of the SEI.
The tendency of decreasing average currents with 1ML of Li in EC:DEC (1:1). Thus, the SEI passivity is higher for 1 nm corresponds to only 0.02 of local composition and might account for the local change of electron potential (OCP), the partially strong changes cannot be caused by thickness variations well below a micrometer at the open circuit marker. In summary, the passivity of SEI-covered metallic Li depends on the electronegativity composition (Table II). For 1 M LiClO4 in PC the $k_{\text{eff}}$ range with $3.6 \times 10^{-3}$ – $1.7 \times 10^{-4}$ cm s$^{-1}$ is below the range of $k_{\text{eff}}$ for 1 M LiPF6 in EC:DEC (1:1). Thus, the SEI passivity is higher for 1 M LiClO4 in PC compared to 1 M LiPF6 in EC:DEC (1:1). Figure S1 shows the x range of approach curves in 1 M LiClO4 PC electrolyte solution.

**Long-term stability of SEI passivity in LP40 electrolyte.—** As reported before, the SEI passivity changed locally at some positions over a time span of hours in LP40 electrolyte after the transfer of lithiated graphite electrodes from the pouch bag cells to the SECM over a time span of hours in LP40 electrolyte after the transfer of lithiated graphite electrodes from the pouch bag cells to the SECM and addition of further electrolyte with DBDMB.11 In order to compare the behavior of charged graphite electrodes with metallic Li electrodes, a sequence of images of an identical region on Li was recorded over a time span of 9.8 h at a constant height (Figure 4). Within this sequence from Figure 4a to Figure 4e one observes regions where the current increases relative to the average current of the image frame (marked by upwards oriented arrows). Since swelling is not expected for a metallic electrode and SEI formation may lead only to thickness variations well below a micrometer at the open circuit potential (OCP), the partially strong changes cannot be caused by topographic changes, but must result from local changes of the electron transfer rate. Thus, the upwards oriented arrows in Figure 4 show an increase of the electron transfer rate, i.e. the SEI passivity decreases. At the same time the downwards oriented arrows indicate an increase of SEI passivity on other regions of the same image frame. There are also regions in the image frames, in which no changes are observed over the whole time span (≠ marker). In summary, the passivity of the SEI on Li shows a dynamic behavior on the micrometer scale over a time span of hours after electrolyte addition similar to the already reported behavior of charged graphite composite electrodes in LP40 electrolyte.11

Cohen et al.14 demonstrated by in situ AFM at OCP morphological changes of the surface film on metallic Li within 50 minutes in EC/DEC solution. The morphological changes were as large as 266 nm within an area of 1 μm × 1 μm. This corresponds to changes of local composition and might account for the local change of electron transfer rate. On the other hand the topographic variation of 266 nm corresponds to only 0.02 $r_f$ and therefore it is negligible for the SECM imaging process. Changes of the Li electrode surface resistance determined by electrochemical impedance spectroscopy6 at OCP in EC/DEC over a time span of several days are in line with changes of the electron transfer rate constant. Both charged graphite composite11 and Li metal reveal changes of the SEI passivity over a time span of hours. This might be explained by the similarity of the formed SEI in the same solution.6

The maximum of $i_T$ decreases from 4.0 nA in Figure 4a to 3.5 nA in Figure 4b along with an decrease of the average current in the SECM images. The tendency of decreasing average currents with time (Figure 4) is related to impurities in the electrolyte which adsorb on the Pt surface of the ME probe. Since each image is built up of consecutively measured data points and the relative time difference between the measured locations of one image frame is constant, the continuous decrease of $i_T$ due to impurities does not affect the analysis of relative current changes within one image frame of the sequence shown in Figure 4.

### Table II. Apparent heterogeneous rate constants $k_{\text{eff}}$

| Electrode                      | $k_{\text{eff}}$ cm s$^{-1}$ | 1 M LiPF6 EC-DEC 1:1 (LP40) | 1 M LiClO4 PC |
|--------------------------------|-----------------------------|------------------------|---------------|
| Uncharged graphite composite  | $8.6 \times 10^{-3}$        | -                      | -             |
| Charged graphite composite    | $1.7 \times 10^{-4}$ – $8.4 \times 10^{-4}$ | -                      | -             |
| Metallic Li                   | $3.6 \times 10^{-5}$ – $3.1 \times 10^{-4}$ | $2.2 \times 10^{-6}$ – $3.6 \times 10^{-5}$ | -             |

**Long-term stability of SEI passivity in 1 M LiClO4 PC electrolyte.—** Figure 5 shows an image sequence recorded above a metallic Li foil in 1 M LiClO4 PC solution. The current difference between $y = 0$ and $y = 240$ μm is mainly caused by a height difference. Fits of approach curves at $x = 0/\mu m = 0$ and $x = 240$ μm/μm = 240 μm (arrows in Figure 5a) reveal a height difference of 10 μm, whereas the ME Li foil separation is the smallest at $x = 0/\mu m = 0$ with 12 μm. The distance was decreased between Figures 5a/5b by 6 μm. On one hand, the overall current decreased because of the smaller d (compare Figure 3, curves 3/4) and on the other hand the overall shape remained similar because of the relatively small range of local variation of $k_{\text{eff}}$ (Table II). In contrast to LP40 solution (see above), there is not a significant decay of $i_T$ with $t$ in 1 M LiClO4 PC solution. Consequently, the absolute $i_T$ values can be analyzed in 1 M LiClO4 PC solution.

The Figures 5b–5h are consecutive images recorded at the same d of an identical region. Since the distance was kept constant, no changes are expected from topographic influences. 19.5 h after addition of the electrolyte to the cell $i_T$ increased strongly at a specific region in Figure 5c (square symbol). Afterwards, $i_T$ of this specific region (square symbol) decreased again and in Figure 5f at 22.0 h $i_T$ is again almost identical to $i_T$ in Figure 5b, which were recorded 18.2 h ago. Thus, the original SEI passivity at $x = 240$ μm/μm = 105 μm in Figure 5b is reestablished within 2.5 h after the detection of a significant decrease of SEI passivity in Figure 5c. According to Figures 5a–5f only the region around the square symbol shows long-term changes at OCP without a mechanical touch by the ME.

This observation is shown more quantitatively in Figure 6 where the average current $i_{T,av}(x,y,t)$ between the forward and reverse scan plot is presented for the selected location with the largest current (the square symbol in Figure 5 at $x = 240$ μm/μm = 105 μm). This plot was chosen in order to minimize the effect of short-term fluctuations of SEI passivity. The error bar in Figure 6 is based on a 30 pA noise for each scan. $i_{T,av}$ increases between 1.8 nA (Figure 6, label b) and 2.9 nA (Figure 6, label c) by 57%. Since $i_{T,av}$ increase relatively large, the SEI passivity decreases significantly. Assuming an average $k_{\text{eff}}$ of $1.9 \times 10^{-5}$ cm s$^{-1}$ (Table II) for the position $x = 240$ μm/μm = 105 μm (square symbol) in Figure 6, label b, d amounts to 12 μm for $i_{T,av} = 1.8$ nA. When $i_{T,av}$ increases to 2.9 nA in Figure 6, label c and d is constant, $k_{\text{eff}}$ amounts to 2.3 $\times 10^{-4}$ cm s$^{-1}$. Thus, $k_{\text{eff}}$ for the square symbol in Figure 6, label c increases by a factor of 12 (Table III). Please note that the estimated $k_{\text{eff}} = 2.3 \times 10^{-4}$ cm s$^{-1}$ for Figure 6, label c exceeds the $k_{\text{eff}}$ range for metallic Li in 1 M LiClO4 and is within the range for both metallic Li and charged graphite composite for LP40 electrolyte solution. The ratio between the estimated $k_{\text{eff}}$ for Figure 6, labels c-f and the estimated $k_{\text{eff}}$ for Figure 6, label b decreases from 12 to 1 (Table III). The average time difference between the labels c-f of Figure 6 (i.e. the time difference between the images of Figures 5c–5f) amounts to 0.8 h. Therefore, the ratios of the $k_{\text{eff}}$ values in Table III are halved between 0.8 h of two consecutive images starting from Figure 6, label c.
Figure 4. SECM feedback images on an identical region of a metallic Li foil with 5 mM DBDMB at (a) 6.0 h, (b) 6.7 h, (c) 7.6 h, (d) 9.0 h and (e) 9.8 h after filling LP40 electrolyte solution in the SECM cell; $d \approx 10 \mu m$. Arrows indicate a relative increase or decrease of the local SEI passivity, whereas the relative SEI passivity does not change locally at the $\neq$ sign. Figure reproduced from Reference 38.

Figure 6 shows that $i_{T,av}$ for the position with the square symbol changed slightly after label f at 22.0 h until label h at 127.7 h. The variation of $i_{T,av}$ is within 0.1 nA and thus there are no significant changes. For comparison, the position $x = 100 \mu m/y = 105 \mu m$ was chosen arbitrarily. This position is marked with the circle symbol in Figures 5 and 6 and was located along the same line at the position $x = 240 \mu m/y = 105 \mu m$ (square symbol). The variation of $i_{T,av}$ for this reference position (circle) remains within 0.1 nA over the entire time shown in Figure 6. Considering the noise of 30 pA for each single scan, $i_{T,av}$ was considered as stable.

In comparison, there were significant differences of the detected long-term SEI passivity developments between LP40 and 1 M LiClO$_4$ PC solutions: A larger fraction of the 240 $\times$ 240 $\mu m^2$ image frame showed long-term changes in LP40 compared to 1 M LiClO$_4$ PC electrolyte, where the SEI passivity of most regions did not change significantly. For LP40 electrolyte solutions only unidirectional long-term changes were detected. Repassivation was not observed. In contrast, $i_T$ of the square symbol region in the case of 1 M LiClO$_4$ PC electrolyte solution increased first and decreased later, i.e. the long-term change was bidirectional.

In contrast to EC/DEC solutions, no morphological changes upon storage were detected by in situ AFM in PC solutions. However, the investigated PC solutions contained LiPF$_6$ and LiAsF$_6$ as conducting salt in contrast to LiClO$_4$ used in this study. Therefore, the conditions are not comparable. The fact that no morphological changes were observed for PC solutions could account for the large regions without significant changes of long-term SEI passivity.

Short-term stability of SEI passivity.— Figure 7a shows the forward image of a Li foil with dimensions of 480 $\mu m \times 480 \mu m$. The
Figure 5. SECM feedback images on an identical region of a metallic Li foil with 5 mM DBDMB at (a) 1.9 h, (b) 3.8 h, (c) 19.5 h, (d) 20.5 h, (e) 21.2 h, (f) 22.0 h, (g) 124.3 h and (h) 127.7 h after filling 1 M LiClO₄ PC solution in the SECM cell. The region around the square is after some time c) increasing and then d) decreasing. The region around the triangle in g) is increasing after ME touch at 119.9 h.
measured reactivity was heterogeneous. Since \( i_T \) decreased with decreasing vertical distance to the Li sample (Figure 3), a protruding spot on the Li foil resulted in a smaller \( i_T \) value. Thus, Figure 7a would represent the inverse of topography. However, since also the local electron transfer rate differed (Figure 3), the local \( i_T \) value in Figure 7a is a result of differences in electron transfer rate and in topography. Consequently, it cannot be decided based on Figure 7a alone, if the image shows topographic and/or reactivity features. Figure 7b depicts the reverse image of Figure 7a. Each single line scan of the reverse image was directly recorded after the line scan of the forward image. Consequently, the comparison of forward and reverse images provides the short-term changes in the range from seconds to ca. one minute. In general both Figures are similar, however, Figure 7b shows significant differences compared to Figure 7a at selected positions (indicated by arrows). Figure 7c presents the absolute current difference between the images of Figures 7a and 7b. At most positions the current difference \( \Delta i_T \) remains below 0.1 nA, whereas \( i_T \) amounts to 0.9 nA at positions marked by arrows. Since the working distance is identical in forward and backward images of the same run, the changes of \( \Delta i_T \) are related to changes of the electron transfer rate only. Thus, short-term changes of the SEI passivity occur on Li.

A major observation on SECM feedback images of charged graphite composite electrodes was the occurrence of peaks. A major observation on SECM feedback images of charged graphite composite electrodes was the occurrence of peaks. Figure 8 depicts our interpretation of these peaks. When the reverse line scan of the reverse image was directly recorded after the line scan of the forward image, the local electron transfer rate differed (Figure 3), the local \( i_T \) value in Figure 7a at selected positions (indicated by arrows). Figure 7c presents the absolute current difference between the images of Figures 7a and 7b. At most positions the current difference \( \Delta i_T \) remains below 0.1 nA, whereas \( i_T \) amounts to 0.9 nA at positions marked by arrows. Since the working distance is identical in forward and backward images of the same run, the changes of \( \Delta i_T \) are related to changes of the electron transfer rate only. Thus, short-term changes of the SEI passivity occur on Li.

Table III: Estimated k_{eff} increase at x = 240 μm, dy = 105 μm during imaging in Figure 5.

| Image | Label Figure 6 | k_{eff} / k_{eff}(Figure 5b) | t - t(Figure 5b) / h |
|-------|----------------|-------------------------------|---------------------|
| Figure 5b | b | 1 | 0 |
| Figure 5c | c | 12 | 15.7 |
| Figure 5d | d | 6 | 16.7 |
| Figure 5e | e | 3 | 17.4 |
| Figure 5f | f | 1 | 18.2 |

Figure 6. Average SECM ME currents \( i_{FM} \) of two specified positions extracted from feedback images of a metallic Li foil with 5 mM DBDBM after filling 1 M LiClO_4 PC electrolyte solution in the SECM cell at a constant distance of 6 μm. A single \( i_{FM,av} \) value is the average of both forward and reverse image. The \( i_{FM,av} \) values labeled with b)-h) correspond to the SECM images of Figure 5 and the square and circle symbols indicate the same position as in Figure 5. The error bar indicates a 30 pA noise for each unilateral line scan.

In order to count the peak events, a criteria was defined. A deviation between forward and reverse scan is considered as a significant “event” if \( i_T \) of the forward line scan at a defined position deviates from the current in the reverse scan at the same position by more than 21% of the average image current \( (i_T) \). Figure 9a indicates the 21% threshold by the gray shaded band. Because \( i_T \) of the solid curve exceeds the threshold at x = 210 μm, four events are counted as indicated by black arrows in Figure 9a. In Figure 9b the reverse line scan follows the forward line scan without exceeding the threshold. This situation is found for most line scans within the recorded image frames. The threshold of 21% \( (i_T) \) was chosen in order to overcome experimental imperfections and to count only strong changes of SEI passivity.

Figure 10a shows a 2D histogram plot where the local events on Li are summarized over a sequence of nine forward and nine reverse images using a threshold of 21% \( (i_T) \) in LP40 solution. Each square represents a measurement position and the gray filling of a square indicates the occurrence of an event during the image sequence. Seven positions showed a single event over the whole images sequence. Consequently, significant short-term changes of SEI passivity take place on metallic Li similar to charged graphite composite electrodes. Recording one event on Li did not indicate a probability to find further events in subsequent image frames. This is in contrast to lithiated graphite (vide infra).

For comparison, Figure 10b shows a histogram plot for a charged graphite composite electrode in LP40 electrolyte. Here the number of events is indicated by the darkness of the circle filling. Similar to Li, there are many positions with no event at all. However, in contrast to Li, there are also positions with multiple events (up to three) which are also close to each other, indicating hot spots of strong short-term changes of SEI passivity. Despite the fact that the example in Figure 10b was rather inactive (compared to the sample reported in reference 11), the event density is much larger for the charged graphite composite electrode.

Figure 11a depicts a plot where the events are summarized over a sequence of eight forward and eight reverse images using a threshold of 21% \( (i_T) \) in 1 M LiClO_4 PC electrolyte solution in contrast to the plot for the LP40 electrolyte in Figure 10a. Only three single events are counted and thus the result is similar as for the LP40 electrolyte. Figure 11a is based on the image sequence between 3.8–25.1 h of Figure 5. As demonstrated in the previous chapter, bidirectional long-term changes of SEI passivity took place at SEI covered metallic Li in 1 M LiClO_4 PC electrolyte solution. Since only a few single events
are located within the square symbol region of the long-term change in Figures 5 and 6, the long-term change over at least 2.5 h is not accompanied by significant short-term changes of SEI passivity.

**Impact of mechanical stress on SEI passivity.**—Figure 12a shows a SECM feedback image of a Li foil. \( i_T \) is decreasing in general from left to right, i.e. with increasing \( x \) values, because of a small tilt of the Li foil in \( x \) direction. \( i_T \) of Figure 12a was generally relatively small, because \( d \) is very small (Figure 3, curves 4/5). Assuming an average \( k_{\text{eff}} \) of \( 1.74 \times 10^{-4} \text{ cm s}^{-1} \) (Table II), the maximum \( i_T \) at \( x = 240 \mu\text{m} \) of 1.13 nA (\( I = 0.31 \)) and minimum \( i_T \) at \( x = 0 \) of 0.47 nA (\( I = 0.13 \)) suggest a \( d \) of 1.95 and 0.11 \( \mu\text{m} \), i.e. 2 and 0 \( \mu\text{m} \), according to the theory of Conmut and Lefrou.\(^{34}\) Thus, the tilt is about 2 \( \mu\text{m} \) in \( z \) for a change of 240 \( \mu\text{m} \) in \( x \). The movement of the ME relative to the Li foil in \( z \) direction is indicated by arrow I (Figure 12a). The \( i_T \) values of all linescans in Figure 12a were continuously decreasing with increasing \( x \) because of the tilt, except lines \( y = 0, 15 \) and 30 \( \mu\text{m} \). At \( y = 0 \) there is a significant increase of \( i_T \) after \( x = 180 \mu\text{m} \). Since all other lines are decreasing with \( x \) except \( y = 15 \) and 30 \( \mu\text{m} \) and \( d \) amounts to 0, the strong increase of \( i_T \) is explained by a mechanical touch of the ME at the SEI covered Li surface at these positions.

Figure 12b depicts the reverse image. Similar to the forward image in Figure 12a, \( i_T \) increased with decreasing \( x \) starting at \( x = 240 \mu\text{m} \). However, the increase is much stronger in every line. Especially at the local maxima \( x = 185 \mu\text{m} \) and \( x = 0 \mu\text{m} \) (Figure 12b, arrow VI) and \( y = 185 \mu\text{m} \) (Figure 12b, arrow V) the increase of \( i_T \) amounts to 224\% and 329\% compared to \( i_T \) of the forward image at the same positions (Figure 12a). Since the distance was not changed between forward and reverse image, the strong increase of \( i_T \) reflects a change of electron transfer rate, i.e. a significant decrease of SEI passivity.

Figure 12c shows the current difference, \( \Delta i_T \), between the forward and backward images. The shape of Figure 12c with respect to its main features is similar to the reverse image in Figure 12b. Consequently, strong changes of \( i_T \) are characteristic for the reverse image. According to Figure 12c, most positions provide \( \Delta i_T \geq 0.2 \text{nA} \), except a few at \( x = 240 \mu\text{m} \) and \( x = 0 \). This observation become more evident in Figure 13a where the events are shown using a threshold of 21\% \( i_T \). In Figure 13a 88.84\% of all positions show at least one event. In contrast the results from Figure 10a showed only 7 events over a sequence of 9 images under conditions without mechanical touch between ME and sample. Consequently, only 0.09\% of all positions over the whole sequence provided events. Since \( i_T \) of Figures 12a/12b is relatively small due to the small distance, the threshold was doubled to 42\% \( i_T \) (Figure 13b) in order to decrease sensitivity. Although the event density decreased from 88.84\% in Figure 13a to 21.57\% in Figure 13b, the event density is still larger by a factor of \( 2 \times 10^{3} \) compared to the condition without mechanical touch by the ME. In conclusion, the event density is significantly affected by mechanical stress by the ME.

According to Figures 12c and 13a there are no large \( \Delta i_T \) values or events close to \( x = 0 \) and up to \( x = 25 \mu\text{m} \). This is expected since the ME Li foil separation was estimated to be 2 \( \mu\text{m} \) at \( x = 0 \) and the SEI was not damaged by the ME in this region. The arrows III and IV in Figures 12b/12c and 13a/13b indicate local maxima of \( \Delta i_T \). These maxima are separated from the region with no event at \( x = 0 \) by only a few tenth of \( \mu\text{m} \). Based on the relatively large distance between ME and Li foil at \( x = 0 \) of ca. 2 \( \mu\text{m} \), the unavailability of events close to \( x = 0 \) and the vicinity of the local maxima to \( x = 0 \), it is supposed that the ME did not destroy the SEI at the local maxima of arrows III/IV. Consequently, the damage of the SEI at \( d = 0 \) i.e. \( \approx 200 \mu\text{m} \) affected not only the passivity locally, but also the SEI passivity ca. 150 \( \mu\text{m} \) apart at the positions of arrows III/IV.

Further evidence for the assumption that the ME did not touch the Li foil at \( x = \approx 50 \mu\text{m} \) is provided by Figure 13b: Using a threshold of 42\% \( i_T \), the neighboring events in the regions of arrows III/IV are separated from the region with a high frequency of events between 145 ≤ \( x/\mu\text{m} \) ≤ 225 of arrows V/VI by a large region without events between 60 ≤ \( x/\mu\text{m} \) ≤ 140. Because the threshold 42\% \( i_T \) is relatively large and indicates only significant changes of SEI passivity, the region with a high frequency of events between 145 ≤ \( x/\mu\text{m} \) ≤ 225 is caused by a local contact of the ME to the SEI covered Li foil. Since the large region without events between 60 ≤ \( x/\mu\text{m} \) ≤ 140 is located in an area with relatively large working distance between ME and Li foil, a contact to the Li foil was unlikely compared to the region with a high frequency of events between 145 ≤ \( x/\mu\text{m} \) ≤ 225. Thus, a contact at the arrow III/IV positions in Figures 12b/12c and 13a/13b is not reasonable, since the ME Li foil separation is even larger compared to the region with no events between 60 ≤ \( x/\mu\text{m} \) ≤ 140.

Although there is significant evidence for a touch of the ME to the Li foil at \( x = \approx 200 \mu\text{m} \), a current overflow is not observed in contrast to charged graphite composite electrodes\(^1\) for which there might be the following reasons: (i) The overflow current is caused by a direct contact of the sample and the active area of the ME. However, the active area of Pt is surrounded by an insulating glass sheath, which is
Figure 8. Interpretation of peaks in SECM feedback images. (a) Initially a linescan is recorded. (b) The reverse linescan (2\textsuperscript{nd} scan) shows a strong local increase of $i_T$ (solid curve) compared to the previous linescan (dotted curve). The increase of $i_T$ indicates a partial destruction of the SEI and a significant decrease of passivity. (c) The 3\textsuperscript{rd} linescan along the same line (solid curve) is similar to the 1\textsuperscript{st} one and does not provide the peak of the 2\textsuperscript{nd} scan (dotted curve). Thus, the SEI is reformed. The schematic is not to scale! The vertical extension is greatly enlarged with respect to the working distance and the ME radius is reduced by a factor of 5. Figure reproduced from Reference 38.

between five and ten times larger than the active Pt in diameter. Since the surface of the ME is not likely to be perfectly planar oriented to the Li foil (Figure 13, insets), contact between ME and Li foil is more likely to occur between the insulating glass sheath and the Li foil. (ii) The average roughness of the investigated charged graphite electrodes was 2.5 $\mu$m.\textsuperscript{11} In contrast, the Li foil is smoother and the roughness is less than a few hundred nm.\textsuperscript{14} In addition, the graphite particle arrangement provides higher flexibility to the ME touch and might therefore still touch the active Pt disk at the ME. (iii) Furthermore, a possible tilt of the Li foil will shift the contact positions of the ME to the outer insulating glass sheath. It is questionable why $\Delta i_T$ is significantly smaller between 225 $\leq x/\mu$m $\leq$ 240 compared to the region with a high event frequency between 145 $\leq x/\mu$m $\leq$ 225 (Figures 12c and 13a/13b) because of the rather small electron transfer kinetics (Table II). At a very small distance between ME and Li foil of $L \approx 0$, the dimensionless current $I$ approaches the detection limit, because of contact between the ME and Li foil. After 17 s (Figure 14d) the ME is retracted from the Li foil and the retraction curve is shown in curve 1b of Figure 14a. Curve 1b demonstrates a strong increase of $I$ compared to curve 1a before. For comparison calculated curves for different $\kappa$ values are shown in Figure 14a. $I$ of the retraction curve 1b at $L \approx 0.05$ matches the calculated $I$ for $\kappa = 0.75$ (curve 4). Since curve 1a is characterized by $\kappa = 4.0 \times 10^{-3}$, $\kappa$ increased by a factor of $2 \times 10^2$. Thus, the SEI passivity decreased significantly by the mechanical touch of the ME.

In addition, the overall shape of curve 1b in Figure 14a is very different from the calculated curves and consequently it is impossible to fit the curve to the theory.\textsuperscript{34} The outstanding shape of curve 1b is a further indication of significant short-term changes caused by the mechanical contact before.

After 18 minutes (Figure 14d) an approach curve is again recorded at the same position (Figure 14b, curve 1c). In contrast to curve 1b,

Figure 9. Counting of events. (a) The difference between forward and reverse scan exceeds at $x \approx 210 \mu$m the gray shaded band and events (black small arrows) are counted. (b) The difference is within the gray shaded band and no event is counted. Figure reproduced from Reference 38.
curve 1c was again matching the theory and the resultant $\kappa$ of $1.1 \times 10^{-2}$ was three times larger than the initial $\kappa$ of curve 1a. As a conclusion, the SEI passivity was almost recovered 20 minutes after the mechanical touch by the ME.

Curve 1d in Figure 14c was recorded 1.3 h after curve 1c at the same position (Figure 14d). $x$ of curve 1d amounted to $4.9 \times 10^{-3}$ and was identical to $x$ of the initial curve 1a (Figure 14a) considering the accuracy of the fit. Thus, SEI passivity was fully recovered 2 h after mechanical touch by the ME. During the mechanical touch by the ME, the ME was pushed 1.5 $\mu$m inside the metallic Li foil indicated by the fit and the overflow currents. Consequently, the repassivation of the SEI on metallic Li occurs within some tens to one hundred minutes after a gentle ME touch.

Although the approach curves of Figure 14 suggest a complete repassivation at $x = 0 \mu m/y = 0 \mu m$ 2 h after a mechanical touch by the ME, imaging experiments revealed increased currents within 60 $\mu$m around the position $x = 0 \mu m/y = 0 \mu m$ after 4 h and 7 h (triangle symbol in Figures 5g/5h). This apparent contradiction might be explained by two facts: (i) Because the ME was pushed into the Li foil for a few $\mu$m, permanent topographic changes might occur, which will change $i_T$ because of the distance dependence (Figure 3). The affected area of 60 $\mu$m around the position $x = 0 \mu m/y = 0 \mu m$ is also reasonable, because the ME including the insulating glass sheath provides a radius of a similar size. (ii) A SECMB feedback image of this study provides information for a single position only for a very short time compared to the duration of the entire imaging experiment. Thus, the development of $i_T$ at a single position is unknown in between two subsequent image frames. Since the images in Figures 5g/5h were recorded after the approach curves and strong long-term changes of SEI passivity at OCP took place (Figure 5c), there could be an additional long-term change after the approach curves around $x = 0 \mu m/y = 0 \mu m$ as a consequence of the contact before.

The occurrence of increased currents at positions of mechanical touch by the ME was also observed for graphite composite electrodes. The measurements at graphite composite in LP40 electrolyte showed that the increased currents during repassivation occurred for at least 14.3 h.

As stated above long-term changes of SEI passivity take place after approaching the ME to contact the Li foil (Figures 5g/5h). Figure 11b characterizes the short-term changes of SEI passivity, which occur during the forward and reverse images corresponding to Figures 5g/5h and three additional images between Figures 5g/5h. Figure 11b depicts only one event. Although this event is located within the region where long-term changes took place in Figures 5g/5h (marked by a triangle), it is not repeated. Therefore, Figure 11b does not demonstrate significant short-term changes of SEI passivity similar to Figure 11a without a mechanical touch. In summary, the event density is only increased during the mechanical contact (Figure 13). A few hours after
the contact, the event frequency is comparable to the situation without preceding mechanical contact (Figure 11).

Conclusions

In this study the electron transfer at metallic Li was characterized using the feedback mode of SECM and 2,5-di-tert-butyl-1,4-dimethoxybenzene (DBDMB) as redox mediator. Li foils showed a local variation of electron transfer rate similar to charged graphite composite electrodes. The SEI at Li and graphite are not electronically insulating for DBDMB as redox mediator. Thus, DBDMB is useful to study the electron transfer at Li. The ranges of electron transfer rate constants at charged graphite composite and Li metal overlap, with the average electron transfer rate at Li being slightly smaller than on lithiated graphite. The SEI passivity at Li was higher for 1 M LiClO$_4$ in PC compared to 1 M LiPF$_6$ in EC:DEC (1:1) solution.

We have already reported about the local variation and temporal development of SEI properties on graphite composite electrodes. Several reasons might be responsible for this behavior at composite electrodes: (i) Due to calendaring, mechanical stress is build up within the composite. Releasing the mechanical stress by particle movement may damage the SEI. Electrolyte-binder interactions and electrochemical swelling due to lithiation further increase the stress between the particles of the rough graphite composite electrode. (ii) Inhomogeneous SEI formation on individual particles may be due to different surface structures, functionalization or nucleation phenomena. Release of mechanical stress is avoided in using smooth Li metal electrodes. The inhomogeneous formation of SEI indicates that inhomogeneous SEI formation seems to be an intrinsic property of this interface and does not only depend on preceding mechanical processing (i.e. calendaring, dissecting of cells etc.).

Both metallic Li and graphite composite electrodes showed locations of changing electron transfer rates over a time of several hours of continuous imaging after addition of electrolyte at OCP. Since short-term and long-term changes of the SEI occur even at the metallic Li foils, the changes are rather caused by the SEI itself than by interactions within a composite electrode in a LIB. A 12-fold spontaneous increase of the electron transfer rate was observed in 1 M LiClO$_4$ PC solution. The long-term changes of SEI passivity at metallic Li were dependent on the electrolyte: Unidirectional long-term changes were observed in 1 M LiPF$_6$ EC:DEC (1:1) and bidirectional in 1 M LiClO$_4$ PC solution.

Similar to charged graphite composite electrodes, metallic Li showed significant short-term changes of SEI passivity over a time span of hours. However, the frequency of such events was much lower at Li. Events were not repeated at the same location independent of the solution composition. A strong decrease of SEI passivity and a strong increase of event density were observed when the ME touched the metallic Li foil. The SEI passivity decreased 200-fold 20 s after mechanical touch by the ME in LiClO$_4$ PC solution. Thus, the decrease of SEI passivity after mechanical touch was an order of magnitude larger compared to the spontaneous changes at OCP without ME touch. Repassivation occurred within 2 h after touch in 1 M LiClO$_4$ PC solution.
PC solution. In addition, a local SEI damage by the ME decreased not only the SEI passivity locally, but also a few hundred μm apart.

The use of smooth Li electrodes in this experiment also eliminates the uncertainty connected to the quantitative interpretation of SECM approach curves for rough graphite composite electrodes. Such setups might be ideally suited for in situ studies of the impact of electrolyte additives on the formation potential of SEIs, their passivating properties and stability. A suitable additive is expected to decrease the extent of long-term changes and cause a lower frequency of short-term changes.

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Figure 14. SECM feedback approach curves with 5 mM DBDMB in 1 M LiClO4 PC electrolyte solution. (a-c) (1a-d) Approach to metallic Li; calculated curves for (2) diffusion-controlled regeneration of DBDMB at the sample and for (8) an inert insulating surface; for comparison calculated curves for finite kinetics including (3) \( \kappa = 1 \), (4) \( \kappa = 0.75 \), (5) \( \kappa = 0.5 \), (6) \( \kappa = 0.3 \), (7) \( \kappa = 0.1 \) are shown. Experimental data is shown by the black solid curve and the fitted curves by the dotted curves. The dashed curve indicates overflow currents by the next recorded approach curve point (0.5 μm step size). (d) Time scale of the experiment and assignment of either approach or retraction to the recorded curves in a)-c).
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