Li-ion batteries (LIBs) are currently the most rapidly developing commercial rechargeable batteries. They are mainly used for portable electronics but increasingly find application for electrified vehicles and stationary storage applications because of the high practical energy density, good cyclability and low self-discharge. GRAPHITE is used in most commercial LIBs as the negative electrode material. The “graphite electrode” is a composite consisting of graphite particles, conductive agents, and binder.

The binder preserves mechanical stability of the composite electrode during battery operation including the stabilization of contacts between graphite particles and conductive agents as well as good adhesion of the composite material to the current collector. Consequently, the binder is important for the performance of the LIB electrodes. The binder poly(vinylidene fluoride) (PVDF) is a very stable and prominent example. It is well known that PVDF takes up organic electrolyte due to electrolyte-binder interactions, i.e. both negative and positive composite electrodes containing PVDF do swell. Graphite is used in most commercial LIBs as the negative electrode material. The “graphite electrode” is a composite consisting of graphite particles, conductive agents, and binder.

The physical swelling of uncharged graphite composite electrodes due to electrolyte-binder interactions is investigated by scanning electrochemical microscopy (SECM) using 2,5-di-tert-butyl-1,4-dimethoxybenzene as a redox mediator. A series of approach curves at the same location is conducted in order to quantify in situ and locally the physical swelling. The film thickness change $\Delta t\text{film}$ amounted to 9.1 $\mu$m on average for a 80 $\mu$m thick uncharged graphite composite electrode in LP40 electrolyte between 1.1 and 5.9 h. Curves of $t\text{film}$ vs. $t$ usually reach a saturation within 12 h. The swelling ratio $\chi$ varies from 0.3% to 17.6% for uncharged graphite composite electrodes from the same batch in the same electrolyte. In contrast, the 8 $\mu$m thick polyvinylidene fluoride (PVDF) model sample swelled by $\chi = 99\%$. Approach curves demonstrate that swelling of the PVDF is the main cause for the physical swelling of uncharged graphite composite electrodes. Both PVDF model sample and uncharged graphite composite electrodes show locally different swelling ratios by SECM imaging. Based on these results a swelling model is proposed, where the uncharged graphite composite electrode swells physically on average by at least $\chi = 11\%$ and the local topography is changing during swelling.

In the last years significant progress was made by using the SECM and related techniques to study LIB electrodes and related processes. The research fields can be divided into (i) the investigation of chemical species released or produced at the LIB electrodes and (ii) the analysis of the electron transport at negative electrodes, which are covered by the solid electrolyte interphase (SEI).

Preparation of graphite composite electrodes.— The preparation and characterization of the graphite composite electrodes was described in detail elsewhere. Electrodes were prepared with a composition of 81 mass-% graphite, 6 mass-% carbon black and 13 mass-% poly(vinylidene fluoride) (PVDF). All three solid components were thoroughly mixed in dry state under dynamic vacuum (< 100 mbar, R02Vac intensive mixer, Eirich GmbH & Co KG, 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/cm² was reached. Stirring was continued for another 2 min before opening 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 20 $\mu$m thick, electrochemically roughened copper foil (Carl Schlenk AG, Roth, Germany).
Figure 1. Cross sections of investigated electrodes. (a) Graphite composite electrode consisting of graphite, carbon black and PVDF. (b) Pure PVDF model sample.

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 convection 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/cm² with a final thickness of 80 μm (Figure 1a). The layer porosity amounted to 50%. The graphite particles had a specified average size of 32 μm. The Ra value of 2.5 μm was calculated according to DIN EN ISO 4287:1997 and characterizes the overall roughness. All graphite composite electrodes reported here were prepared within the same batch.

Preparation of the PVDF model sample.— The PVDF model sample was prepared by the same amount of PVDF as for the graphite composite electrode, providing an 8 μm thick layer of pure PVDF (Figure 1b).

Scanning electrochemical microscopy.— The scanning electrochemical microscope (SECM) was running under the SECMx control software developed in house. It used a 3 axes micropositioning system (MS30 precision actuator and PS30 distance measurement system, CU30 controller, mechatronics 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). 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 MEs of radius rT ≈ 13 μm as probe (Figure 2b), either the graphite composite electrode or the PVDF film as sample and a platinum wire auxiliary electrode and a silver wire as reference electrode. MEs were prepared by sealing a Pt wire of 25 μm specified diameter (Goodfellow GmbH, Bad Nauheim, 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 sheath around the Pt wire and the radius rT of the active electrode area.

The cylindrical opening of the SECM cell served as reservoir for 0.4 mL working solution. The electrolyte was 1 M LiPF₆ in either ethylene carbonate (EC):diethyl carbonate (DEC) 1:1 (LP40, BASF SE, Ludwigshafen, Germany) or EC:DEC 3:7 (LP47, BASF SE, Ludwigshafen, Germany). Either 5 mM 2,5-di-tert-butyl-1,4-dimethoxybenzene (DBDMB), or 5 mM 1,2,4,5-tetramethoxybenzene (TMB) or 5 mM tri(p-bromophenyl)amine (TPA) was added as redox mediator to the electrolyte solution.

Scanning electrochemical microscopy measurements.— Before approach curves and images were recorded, the ME was polarized to a potential, where the redox mediator molecule is continuously oxidized (4.1 V vs. Li/Li⁺ for DBDMB, 4.1 V for TPA and 3.9 V for TMB, Figures 2b and 2c). The timer was set to zero, when the SECM working solution was filled into the cell. The approach curves were recorded with a step size of 0.5 μm, a delay of 1.0 s between the translation and the current recording giving an average translation rate of 0.25 μm s⁻¹. Prior to fitting of the approach curves to the analytical approximations by Cornut and Lefrou, the radius of the electroactive area rT and the RG were determined by confocal laser scanning microscopy (CLSM) using a TCS SP2 AOBS (Leica Microsystems GmbH, Wetzlar, Germany). During fitting, the uncertainties of 0.5 μm and 1.5 for rT and RG with respect to the CLSM results were considered (Supporting Information (SI) 2 for further information). Approach curves were fitted by adjusting κ, iT,∞ and do (within...
reasonable range) using a least square approach. $\kappa$ is the normalized first-order rate constant, $i_{T,\infty}$ the diffusion-limited steady-state current in the bulk solution (at quasi-infinite distance to the surface) and $d_0$ is the smallest ME-sample distance of the curve where a valid data point was recorded before the mechanical touch between ME body and sample. The apparent heterogeneous rate constant $k_{eff}$ was calculated by Equation 1 using a diffusion coefficient of $D = 2.15 \times 10^{-6}$ cm$^2$ s$^{-1}$ for DBDMB in LP40 and $D = 2.57 \times 10^{-6}$ cm$^2$ s$^{-1}$ for DBDMB in LP47 electrolyte solution. The diffusion coefficient was determined from the steady-state diffusion limited current of the ME $i_{T,\infty}$ (SI-1). The distances between ME and sample electrode during imaging are given for the position $x/\mu m$, $y/\mu m = 0, 0$ of the image.

$$\kappa = \frac{k_{eff}i_T}{D} \quad [1]$$

**Results and Discussion**

**Choice of redox mediator.**— We aim for following in situ the physical swelling of graphite composite electrodes by repeatedly recording approach curves over identical locations. The choice of the redox mediator is essential for such long-term SECM experiments, because the current response of the ME depends on many factors: (i) the ability of the oxidized redox mediator species to take up electrons from the sample of interest; (ii) the stability of both oxidized and reduced species; (iii) compatibility of the redox mediator with the active material of the ME. The effect of the mediator choice for SECM feedback images is illustrated in Figure 3 by SECM feedback images recorded from an identical region before and after a mediator exchange. Initially the solution contained 5 mM DBDMB and the feedback image shows locally different ME currents $i_T$ (Figures 3a–3c). They are caused by the combination of locally different topography (roughness $R_s = 2.5 \mu m$) and locally different electron transfer rates (Figure 4, curves 1a vs. 1b, see below) due to variations in local distribution of graphite, carbon black and PVDF at the surface of the composite. Within 2.5 h the overall shape of the feedback image of the identical region is retained using DBDMB as redox mediator (Figures 3a–3c). After exchange of the working solution to 5 mM TMB + LP 40, the obtained feedback image (Figure 3d) remains similar to the previous image in Figure 3c. Thus, neglecting the small local change in topography (as will be discussed below), the local electron transfer rates are supposed to be identical. Considering the structural analogy of DBDMB and TMB (Figure 3), this is also expected since both molecules provide a similar steric hindrance and similar interactions of the functional groups with the graphite composite electrode. There is no significant change between the two sequential images using TMB (Figures 3d and 3e). After exchange of TMB to TPA as mediator, the obtained reactivity image was less clearly resolved (Figure 3f). The origin of the blurred appearance of the reactivity image might be the difference in steric hindrance and interactions of the functional groups with the graphite composite electrode. There is no significant change between the two sequential images using TMB (Figures 3d and 3e). After exchange of TMB to TPA as mediator, the obtained reactivity image was less clearly resolved (Figure 3f). The origin of the blurred appearance of the reactivity image might be the difference in steric hindrance and interactions of the functional groups with the graphite composite electrode. There is no significant change between the two sequential images using TMB (Figures 3d and 3e). After exchange of TMB to TPA as mediator, the obtained reactivity image was less clearly resolved (Figure 3f).
Approach curves on graphite composite and PVDF model film.—

SECM approach curves are a recording of the ME current \( i_I \) as a function of decreasing working distance \( d \). The ME current \( i_I \) is caused by the continuous oxidation of DBDMB (Figure 2c) and depends strongly on the type of sample and \( d \). When the ME approached the uncharged graphite composite electrode (Figure 4, curves 1a and 1b), the oxidized DBDMB\(^+\) was reduced at the graphite composite electrode to DBDMB,\(^+\) which caused an additional flux of DBDMB to graphite composite electrodes (i.e. before formation of a solid SEI-covered metallic Li electrode,16 thus, the electron transfer rate at the PVDF model sample was within the range of the electron transfer rate constants of graphite composite electrodes, which decreases the electron transfer rate (see below).

The approach curve to the pure PVDF model sample (Figure 4, curve 3) exhibits a \( k_{\text{eff}} \) of 5.8 \( \times 10^{-3} \) cm s\(^{-1} \), which is smaller by a factor of 10\(^{-2} \) compared to the average \( k_{\text{eff}} \) of graphite composite electrodes. However, the approach curve on PVDF is distinct from the curve to an insulating surface (Figure 4, curve 4), where there is no back reaction at all. Consequently, DBDMB\(^+\) diffused through the 8 \( \mu \)m thick PVDF layer and was reduced at the Cu current collector with a rate slower than the binder of the graphite composite electrodes, which decreases the electron transfer rate. The local and in situ nature of this procedure represents the main advantage of this methodology to study the physical swelling. In addition, both physical and electrochemical swelling can be investigated separately. An intrinsic disadvantage is the fact that swelling already starts with electrolyte addition (Figure 5b). Since the approach of the ME to the sample after addition of electrolyte requires time and other experimental manipulations are necessary, the time \( t_1 \) of the first thickness determination cannot be smaller than ca. 0.5 h. Thus, swelling data are not assessable for \( t < 0.5 \) h.

Swelling behavior of graphite composite electrodes.— Figure 6a shows a typical development of \( \delta_{\text{lim}} \) with time after addition of LP40 electrolyte to graphite composite electrodes. The curve represents a saturation behavior. For other locations (6–9 and 11–13) on different samples of the same batch a similar saturation behavior was found (Figure 6c). Yoo et al.\(^3\) measured the weight difference due to solvent uptake of graphite composite electrodes using PVDF in EC:ethyl methyl carbonate (EMC) solutions. They concluded that solvent diffusion is saturated after 1 day at room temperature and before one day at 50 °C. Based on Figures 6a and 6c the saturation occurs even below

| Figure 4. SECM feedback approach curves with 5 mM DBDMB and 1 M LiPF\(_6\) in EC:DEC 1:1 electrolyte. (1) Approach to pristine graphite composite electrodes; (2) for comparison the calculated curve for diffusion-controlled regeneration of DBDMB at the sample; (3) approach to a pure PVDF model sample on a Cu back contact; (4) and for comparison the calculated curve for an inert insulating surface. |
| Figure 5. Concept for the characterization of the swelling behavior of a graphite composite electrode by approach curve fits. (a) Initial thickness of a graphite composite electrode is given by \( z_0 \). (b) When electrolyte is added to the cell, the swelling starts immediately. (c) After \( t_1 \) the relative thickness \( z_1 \) is determined by fit of the measured approach curve (d) for the first time. (e) After \( t_2 \) the relative thickness \( z_2 \) is again determined by a fit of an experimental approach curve. The difference \( \delta_{\text{lim}} = z_2 - z_1 \) is the film thickness change. (f) After a repetitive approach curve fit, the film thickness change is given by \( \delta_{\text{lim}} = z_3 - z_1 \). |
In line with the typical data set in Figure 6a, most investigations on graphite composite electrodes suggest a significant increase of $\delta_{\text{film}}$ (Figure 6c, measurement locations 5–9, 11–13), i.e. the electrodes swell even without Li-ion intercalation. The largest swelling amounted to 15.9 $\mu$m or 19.8% of the total film thickness (Figure 6c, measurement location 12). The swelling ratio $\chi$ is defined by $\chi = \delta_{\text{film}}/d_{\text{film}}$, where $d_{\text{film}}$ is the absolute initial film thickness. However, there were also positions with no significant change of $\delta_{\text{film}}$ (Figure 6b, measurement locations 1–3) because the change of $\delta_{\text{film}}$ was within the uncertainty margin of $\pm 1 \mu$m.

In order to demonstrate the potential of the method to differentiate between physical and electrochemical swelling, a short lithiation pulse was applied for 120 s at a constant potential of 0 V vs. Li/Li$^+$. A charging state of 2.9% is estimated from the measured current and the mass of the graphite material after the pulse (SI-3). The thickness change amounts to $\delta_{\text{film}} = 3.8 \mu$m. Thus, volume expansion due to lithiation can be clearly observed, although the same horizontal position did not show any significant physical swelling before. A complete investigation of volume expansion due to Li-ion intercalation requires further instrumental developments. A lithium counter electrode must be included into the open SECM cell and a method must be devised to account for the change of interfacial kinetics accompanying the formation of the SEI. Since $k_{\text{eff}}$ did not change significantly after the lithiation pulse (Figure 6b), a stable and pronounced SEI was not established, because in this case $k_{\text{eff}}$ would be orders of magnitude smaller. Furthermore, small $k_{\text{eff}}$ values due to SEI formation after an extended lithiation pulse do not alter the results of the swelling ratios, because $\delta_{\text{film}}$ can be determined for both large and small $k_{\text{eff}}$ values by the approach curve fits.

**Statistical analysis of the swell behavior.**— The histogram in Figure 7a shows the distribution of swelling ratios $\chi$ for different measurement locations in LP40 between 1.1 $\pm$ 0.5 h and 5.9 $\pm$ 0.5 h. $\chi$ varies locally between 0.3% and 17.6%. Thus, the variations of local swelling within the same LP40 electrolyte and the same batch of graphite composite electrode are very large. When the data from the last measurements at 7.2 $\pm$ 1.8 h is included in the analysis, the variation of the swell ratios is even larger (Figure 7b, 0.3% to 19.8%).

Table I summarizes all averaged $\chi$ values determined by in situ approach curves. $\chi$ amounts to 11.4% when the time interval is considered between 1.1 $\pm$ 0.5 h and 5.9 $\pm$ 0.5 h (Table I). Thus, on average graphite composite electrodes swelled significantly upon electrolyte contact (Figure 6c). When the analyzed time interval is extended to 7.2 $\pm$ 1.8 h, the swelling becomes more significant ($\chi = 12.5\%$). Thus, the average physical swelling ratio of $\chi \geq 11\%$ is larger as the reported electrochemical swell rate of 10% for Li-ion intercalation in graphite composite electrodes.

Chang et al. determined ex situ and globally $\chi$ of graphite composite electrodes after 24 h contact to 1 M LiPF$_6$ EC:dimethyl carbonate (DMC) (1:1) electrolyte. Depending on the preparation process, $\chi$ varied between 9 and 23%. This result is consistent with our data of graphite composite electrodes (Table I) considering the difference in soaking time, preparation procedure, methodology, electrode components and composition. Zhang and Tang used a micrometer to determine $\chi$ ex situ and globally for artificial graphite electrodes after electrolyte contact. $\chi$ amounted to maximal 3.0% within 6 h, whereas $\chi$ did not increase significantly with time. Thus, the curve of $\chi$ vs. $t$ did not show a saturation behavior in contrast to the commonly observed saturation curve in Figure 6a. $\chi$ decreased almost continuously after 6 h to $-3.2\%$, i.e. the artificial graphite electrode shrunk. This global ex situ observation of the thickness changes of artificial graphite electrodes contradicts our local in situ observations at graphite composite electrodes, where $\chi$ rather increases after 6 h (Table I). Zhang and Tang attributed the shrinking to the aging of polymer chains because of continuous structural weakening due to the electrolyte-polymer interactions. Please note that the graphite composite electrodes in our SECM setup are uncovered and not pressed against a glass sample, where neither mediator regeneration nor swelling occur, showed that the uncertainty of height determinations is smaller than $\pm 0.4 \mu$m (SI-4).
The impact of PVDF on swelling.— Since the impact of PVDF on swelling is well documented in literature, the swelling of the PVDF model sample was investigated using the feedback mode of SECM. Figure 8 shows SECM images of an identical region between PVDF model sample was investigated using the feedback mode of SECM. Figure 8 shows SECM images of an identical region between negative and a positive electrode (Figure 2a), i.e. the graphite composite electrodes might easily expand in the direction of the electrolyte solution.

| Electrode       | Electrolyte | $t_{\text{start}}$ / h | $t_{\text{end}}$ / h | $\delta_{\text{lim}}$ / μm | $\chi$ / % | # data |
|-----------------|-------------|------------------------|----------------------|---------------------------|------------|--------|
| Graphite composite | LP40       | 1.1 ± 0.5              | 5.9 ± 0.5            | 9.1                       | 11.4       | 9      |
| Graphite composite | LP40       | 1.1 ± 0.5              | 7.2 ± 1.8            | 10.0                      | 12.5       | 9      |
| PVDF model      | LP40        | 1.1                    | 6.6                  | 7.9                        | 98.9       | 1      |

Such a behavior is known from work on PVDF films in a different context. Figures 8d and 8e show extracted line scans from Figures 8a–8c. As already discussed above, $\chi$ strongly decays with $t$ over the entire line scans because of significant swelling of the PVDF model sample. The decay of $\chi$ at $(x/\mu$m, $y/\mu$m) = (240, 0) between 1.7 h and 2.4 h (Figure 8d) is four times larger in comparison to the position (240, 225) (Figure 8e). Since $\chi = 1.93 \text{nA}$ for $x = 240 \mu$m is similar for the line scans at $y = 0 \mu$m and at $y = 225 \mu$m at 1.7 h, the different decay of $\chi$ must have been caused by a locally different swelling ratio of the PVDF layer. Assuming an average $k_{\text{eff}}$ of $5.3 \times 10^{-5}$ cm s$^{-1}$ for the PVDF model sample (SI, Figure S4), the ME-PVDF sample separation amounts to $d = 6.1 \mu$m at $x = 240 \mu$m for $t = 1.7$ h in both line scans (Figures 8d and 8e). At $(x/\mu$m, $y/\mu$m) = (240, 225) $d$ decreases by 0.7 μm at $t = 2.4$ h, whereas $d$ decreases by 2.1 μm at the same time in the case of (240, 0). Consequently, the local swelling ratio between 1.7 h and 2.4 h at $x = 240 \mu$m is three-fold larger for $y = 0 \mu$m compared to $y = 225 \mu$m. An increase of $\delta_{\text{lim}} = 2.1 \mu$m for the PVDF model sample within 0.7 h is relatively large compared to graphite composite electrodes considering the total PVDF layer thickness of only 8 μm. A similar tendency is observed in approach curves to the PVDF model sample, where a swelling by 7.9 μm ($\chi = 99\%$) is found between $t_{\text{start}} = 1.1$ h and $t_{\text{end}} = 6.6$ h (Table I). In other words, the PVDF model sample swelled by almost its own initial thickness of 8 μm. Thus, $\chi$ is ca. nine-fold larger for the PVDF model sample compared to graphite composite electrodes of the same PVDF mass loading within a comparable time window and in the same electrolyte (Table I). Since $\delta_{\text{lim}} = 7.9 \mu$m of the PVDF model sample was only slightly smaller than $\delta_{\text{lim}} = 9.1 \mu$m for the graphite composite electrode for a similar time window (Table I), the swelling of the graphite composite electrodes can be ascribed mainly to the swelling of PVDF binder within the composite. The heterogeneous swelling of the PVDF model sample can be explained by a locally different rate of electrolyte uptake.

Figure 7. Histograms of swell ratios of graphite composite electrodes at different samples. All first approach curves started at 1.1 ± 0.5 h and the last measurements were conducted at (a) 5.9 ± 0.5 h and (b) 7.2 ± 1.8 h after filling 5 mM DBDMB and 1 M LiPF$_6$ EC:DEC 1:1 electrolyte solution in the SECM cell.

Figure 8. SECM feedback images of an identical region of a PVDF model sample at (a) 1.7 h, (b) 2.4 h and (c) 3.1 h after filling 5 mM DBDMB and 1 M LiPF$_6$ EC:DEC 1:1 electrolyte solution in the SECM cell at $d = 2 \mu$m at the horizontal location $(x, y) = (0, 0)$ at 1.1 h. The line scans at (d) $y = 0 \mu$m and (e) $y = 225 \mu$m were extracted from the SECM feedback images of a–c.
Figure 9. (a) SECM feedback image of an uncharged graphite composite electrode at OCP at 4.4 h after filling 5 mM DBDBM and 1 M LiPF6 EC:DEC 1:1 electrolyte solution in the SECM cell at $d \approx 11 \mu m$. The blunt ends of the arrows indicate the location of the marked positions. Development of $i_T$ with $t$ of the positions (b) III ($x/\mu m, y/\mu m) = (75, 240)$, IV (165, 210) and V (235, 210) as well as (c) VI (10, 30) and VII (125, 0) relative to the average $i_T$ of the positions I (85, 105) and II (95, 60) with maximum currents ($i_{T,\text{max}}$). Further images in Figure S7.

Imaging of graphite composite electrodes.— Figure 9a shows an SECM image above an uncharged graphite composite electrode with 5 mM DBDBM in LP40 electrolyte at OCP. As expected, $i_T$ was heterogeneous over the entire image because of local variations in topography (see above) and local differences in the electron transfer rate (Figure 4).

Figure 10. Schematic illustration of the observed swelling behavior at graphite composite electrodes. (a) Before electrolyte contact, graphite composite electrodes exhibited an average roughness of $R_a = 2.5 \mu m$. (b) After electrolyte-binder interactions, the graphite composite electrode is swollen overall. The film thickness change is locally different. In the sketch the vertical scale is greatly enhanced to visualize the effect.

The high current regions in Figure 9a marked by the circles at the positions I ($x/\mu m, y/\mu m) = (85, 105)$ and II (96, 60) serve as reference values for the analysis of the image. The locations III (75, 240), IV (165, 210) and V (235, 210) marked by downwards oriented arrows in Figure 9a exhibit a relative decrease of $i_T$ with respect to the average $i_T$ of the high current regions ($i_{T,\text{max}}$) between 4.4 h and 9.1 h (Figures 9b, S7). In the same image frame there are also locations VI (10, 30) and VII (125, 0), where $i_T$ continuously increases relative to the average $i_T$ of the encircled regions (Figure 9b). A change of $i_T$ is either caused by (i) topographic changes or (ii) changes of the electron transfer rate. Since there was no evidence for a significant change of the electron transfer rate during approach curve experiments to uncharged graphite composite electrodes (Figures 6a–6c), the change of $i_T$ was mainly caused by topographic changes. Because $i_T$ increased and decreased locally at the same time relative to the encircled positions, the swelling ratio is locally heterogeneous. Thus, the PVDF model sample (Figures 8d and 8e) and the graphite composite electrode (Figure 9) show a heterogeneous distribution of swelling ratios. The heterogeneous swelling ratio of graphite composite electrodes is explained by the locally heterogeneous swelling ratio of the PVDF binder.

As stated elsewhere,16 $i_T$ at the ME decreases continuously in LP40 electrolyte solution because of impurities which cover the Pt surface of the ME probe. Since each image is build up of consecutively measured locations and the relative time difference between the measured locations within one image frame remains constant, the decrease of $i_T$ due to impurities does not affect the analysis of relative current changes within one image frame of the sequence.

Proposed model for the swelling of graphite composite electrodes.— Figure 10 summarizes our swelling model of graphite composite electrodes based on the results presented in this article. The graphite composite electrodes provide an average roughness of $R_a = 2.5 \mu m$ before electrolyte contact (Figure 10a) and swell by at least $\chi = 11\%$ (Table I) over the entire surface due to electrolyte-binder
interactions (Figure 8) as demonstrated by height data extracted from approach curves (Figure 6). In addition, the swelling ratio of graphite composite electrodes is locally heterogeneous (Figure 9) because the swelling ratio of the pure binder is locally heterogeneous (Figures 8d and 8e). Thus, the topography of the graphite composite electrode changes locally after swelling (compare \( \Delta z_1 \) and \( \Delta z_2 \) in Figures 10a and 10b).

Conclusions

2,5-di-tert-butyl-1,4,5-dimethoxybenzene (DBMDB) has been used successfully as a redox mediator to study the electron transport at uncharged graphite composite electrodes whereas tri(p-bromophenyl)amine (TPA) is not effective. The electron transfer rate at uncharged graphite composite electrodes is heterogeneously distributed as demonstrated by approach curves at different locations. At uncharged graphite composite electrodes \( k_{\text{eff}} \) varies between 3.0 \( \times 10^{-3} \) and 8.6 \( \times 10^{-3} \) \( \text{cm s}^{-1} \) and is therefore significantly larger than at charged graphite composite and metallic lithium electrodes that form a passivating solid electrolyte interphase.16 By approach curves to a PVDF model sample it is shown that DBMDB diffuses through a 8 \( \mu \text{m} \) thick PVDF layer and reacts at the Cu current collector, although the electron transfer rate constant was rather low (\( k_{\text{eff}} = 5.3 \times 10^{-3} \text{ cm s}^{-1} \)).

Height determinations from consecutive approach curves at the same location are suitable for local in situ quantification of the physical swelling of uncharged graphite composite electrodes. The average \( \delta_{\text{lim}} \) amounts to 9.1 \( \mu \text{m} \) for a 80 \( \mu \text{m} \) thick graphite composite electrode in LP40 electrolyte between 1.1 \( \text{cm s}^{-1} \). This value varies from 0.3% to 17.6% at different locations for graphite composite electrodes from the same batch in the same electrolyte. Consequently, a few locations do not swell significantly. In contrast, the 8 \( \mu \text{m} \) thick PVDF model sample swells by 7.9 \( \mu \text{m} \) \( (\chi = 99\%) \), i.e. by its own initial thickness. Because \( \delta_{\text{lim}} \) of the PVDF model sample is almost as large as \( \delta_{\text{lim}} \) of the much thicker graphite composite electrodes, the physical swelling of the composite electrode is mainly due to the swelling of the PVDF binder.

Both PVDF model sample and uncharged graphite composite electrodes show locally different swell ratios by SECM imaging. Based on these results a swelling model is proposed, where the uncharged graphite composite electrode swells physically on average by at least \( \chi = 11\% \) and the local topography is changing during swelling due to locally heterogeneous swelling ratios.

The embedding of electrochemical swelling into our swelling model is a topic of ongoing research. In addition, the swelling of composite electrodes with different compositions will be addressed as well as the impact of the electrolyte composition on physical swelling. Moreover, the swelling of different binder systems as for instance carboxymethylcellulose (CMC)/styrene-butadiene rubber (SBR), which is gaining increased significance for graphite composite electrodes, can be quantified. However, the swelling of CMC/SBR in carbonate electrolytes is at least 20 times smaller compared to PVDF. Thus, the swelling ratios of CMC/SBR in organic electrolytes might be below the detection limit of the presented methodology.

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