

Development of an *in situ* Mediator Dosing Concept for Scanning Electrochemical Microscopy in Lithium-Ion Battery Research

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In scanning electrochemical microscopy (SECM), the addition of a redox active species plays an essential role. Those deliberately added mediators may alter results in SECM studies. In investigations of lithium-ion battery (LIB) materials, especially of the positive electrode, the oxidation potentials of commonly used mediator substances such as ferrocene are located within the operation potential of the electrode. Thus, they possibly interfere with the regular charge/discharge processes. *In situ* studies are therefore in need of approaches reducing or eliminating the use of mediators. Within this publication, a novel mediator dosing (MD) concept is introduced. A capillary

was closely positioned at the tip of the scanning probe. By gravity flow, stable flow rates of mediator solution of up to $32.4 \pm 0.6 \mu\text{L h}^{-1}$ were achieved. These low amounts were found to be sufficient to form a ferrocene zone at the probe tip enabling feedback mode SECM measurements with comparable quality to measurements directly in ferrocene solution. Proof of concept experiments were conducted by investigation of a thin-film electrode with a micro-structured surface. Furthermore, the MD concept was applied in imaging experiments of a commercially available LIB graphite electrode.

Introduction

In recent years, lithium-ion batteries (LIBs) gained more and more importance due to their countless applications, for example electromobility and energy storage.^[1–3] This type of secondary cell generally consists of two electrodes, positive and negative, a separating, porous membrane, and electrolyte.^[4]

Much effort was and still is dedicated to further optimization of those basic components regarding battery life, operation safety, and energy density.^[5] Commercial LIBs mainly utilize state-of-the-art materials capable of intercalating lithium ions during charge/discharge cycles. The most widely applied material as negative electrode is graphite due to low cost, low toxicity, and long cycle life.^[2,6] A common material for the positive electrode is LiCoO_2 , but the demand for higher energy densities has driven the development of materials operating at higher potentials such as lithium nickel manganese cobalt oxides (NMC).^[3]

The operation of a LIB includes repeated insertion of lithium into the host materials and redissolution. Therefore, LIBs are also called “rocking-chair batteries”.^[7] The potentials reached during those cycles may exceed the electrochemical stability

window of the electrolyte, resulting in its degradation and the formation of interphases between electrode and electrolyte.^[1] In the case of the negative electrode, the newly formed interphase is called solid electrolyte interphase (SEI).^[8] It inhibits further degradation of the electrolyte and is therefore a prerequisite for safe and stable operation of a LIB. For positive electrodes, the formation of an interphase and its nature is still controversial and a hot topic in LIB research.^[9] Sophisticated analytical techniques are needed to drive further improvements in LIBs. Scanning probe microscopies (SPMs) are a family of microscopic techniques which can be applied in LIB research *in situ* and even *in operando*.^[10,11]

Amongst others, scanning electrochemical microscopy (SECM)^[12] is part of that group. An ultra-microelectrode (UME), often a platinum disk, is used as probe. By application of a suitable potential, a usually deliberately added redox-active substance, the so-called mediator, is either oxidized or reduced. The resulting tip current delivers information about the electrochemical activity as well as the topography of a substrate's surface.^[13] In the scope of LIBs, an extensive number of studies were conducted including SECM as characterisation technique.^[14] Topics range from SEI formation on different electrode materials,^[15,16] swelling of composite electrodes,^[11] hyphenation of SPMs,^[17,18] to, more rarely, the study of positive electrode materials.^[19] Most works consider possible interfering effects^[20] due to the deliberately added mediator in some way or another. In the study of Zampardi et al.^[18] on the SEI formation on glassy carbon, the formation protocol is conducted in pure electrolyte without added mediator, followed by an exchange of solutions to mediator-containing electrolyte. The same approach of an electrolyte change between procedures was used in several other LIB investigations with SECM.^[15,21] As careful as this exchange may take place, changes

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in the surface properties can't be fully ruled out. Another approach is to operate the investigated battery electrode in solution with the mediator already present during cycling. This method was applied in the studies of Zeng et al.^[22] in their investigation of temporal changes of the SEI after various numbers of charge/discharge cycles. Similarly, the mediator was also present during the formation protocols in other publications.^[16,17,23] Although the redox potentials of commonly used mediators ferrocene (Fc)^[16–18,22,24] and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene^[11,15,24] lie outside of the regular operating potentials of negative electrodes, their influence on the complex formation processes of the SEI should not be neglected as they can potentially alter SEI properties.^[25] For investigations of positive electrode materials, the interference of mediators is more severe, as supported by Zampardi et al.^[19] in their study of the positive electrode/electrolyte interface in LIBs.

In the scope of this contribution, an alternative approach to minimize mediator interferences is introduced. By highly localized dosage of mediator solution at the SECM probe tip, the overall mediator concentration in the battery cell is drastically reduced. The gravity flow of mediator solution in the proposed setup is controlled by adjusting a height difference between inlet and outlet solvent levels of a dosing capillary. Proof of concept measurements with a micro-structured thin-film electrode as model substrate were conducted. As a possible application, feedback mode SECM images of a commercial LIB graphite electrode were recorded under MD conditions and compared to images recorded directly in mediator-containing electrolyte.

Results and Discussion

The novel approach on feedback mode SECM with minimized mediator usage was designed with several requirements in mind. First, the data quality should be as close to regular SECM measurements in mediator solution as possible. Second, the amount of deliberately added mediator should be kept at a minimum. Third, the overall setup should be as simple as possible, i.e. no complicated probe fabrication. Those requirements were met by utilization of a dosing capillary mounted together with a regular SECM probe in a previously described dual-probe holder.^[17]

Similar approaches utilizing the dosage of solutions in the context of SPM measurements could be found in literature. Two recent examples should be mentioned here. Asserghine et al.^[26] employed a micro-sized pipette installed in the probe positioning system of a SECM device to dose defined volumina of an oxygen-containing solution. In their approach comparable to the microjet electrode^[27] and pioneering works by Engstrom^[28] the solution is dosed by the pipette and the signal collection is achieved by the substrate, which was termed as pumped-micropipette delivery/substrate collection mode (Pumped-MD/SC) of SECM. This novel variation of the MD/SC mode of SECM^[29] was then used in the investigation of the oxygen reduction reaction during the corrosion of a model system of

copper-rich aluminium alloys. The second approach which is related to the MD concept was used in the study of the SEI formation conducted by Muñoz-Torrero et al.^[30] In their research a redox-mediated scanning droplet cell^[31] was used to deliver a series of different solutions in a fixed position on the sample surface. This setup enabled the SEI formation with no mediator present followed by investigation of the passivation properties using Fc.

Determination of Gravity-driven Flow Rates at Various Height Differences

Gravity flow in the context of capillary-based setups was introduced by Matysik et al.^[32] in 1993. In their original works the adjustment of the height difference between the liquid levels in inlet and outlet reservoirs resulted in well-defined introduction of sample solution into a fused-silica capillary. This capillary flow injection analysis (CFIA) system was then applied in the determination of trace metals in tear samples. The obtained gravity flow was found to be highly reproducible and stable for extended time periods. To determine the amount of mediator introduced into the bulk solution by the MD approach, chronoamperometric experiments with varying height differences were performed. Measurements were conducted in triplicates for each height difference. An exemplary *i*-*t* curve is shown in Figure 1A. After a certain time, the mediator solution inside the dosing capillary reaches the outlet end and subsequently the platinum macro electrode, resulting in an increasing current signal from the oxidation of Fc. The average times until the oxidation signals were detected are summarized in Table 1. By application of a height difference of 5 cm, in average, a time interval of 12.9 ± 0.2 min passed until the Fc solution reached the macro electrode. Doubling the height difference to 10 cm resulted in a decrease of the time interval to an average of 7.2 ± 0.1 min. At the maximum height difference of 15 cm achievable in the design of the MD concept, an average signal time of 5.1 ± 0.1 min was determined. With the help of equation 1, the flow rates could be calculated.

$$\text{flow rate} = \frac{V_{\text{capillary}}}{t_{\text{Fc signal}}} = \frac{\pi \cdot r_{\text{capillary}}^2 \cdot l_{\text{capillary}}}{t_{\text{Fc signal}}} \quad (1)$$

Table 1. Measured Fc signal times (average of three individual measurements each) in the mediator dosing setup in chronoamperometric experiments at the respective height differences (Δ height). Determined flow rates and resulting dynamic concentration changes in the electrolyte solution based on a volume of 5 mL in the electrochemical cell.

	Δ height = 5 cm	Δ height = 10 cm	Δ height = 15 cm
time _{Fc signal} /min	12.9 ± 0.2	7.2 ± 0.1	5.1 ± 0.1
flow rate/ μL h ⁻¹	12.8 ± 0.2	22.9 ± 0.3	32.4 ± 0.6
Δ conc. _{Fc} / μM h ⁻¹	3.8 ± 0.1	6.9 ± 0.1	9.7 ± 0.2

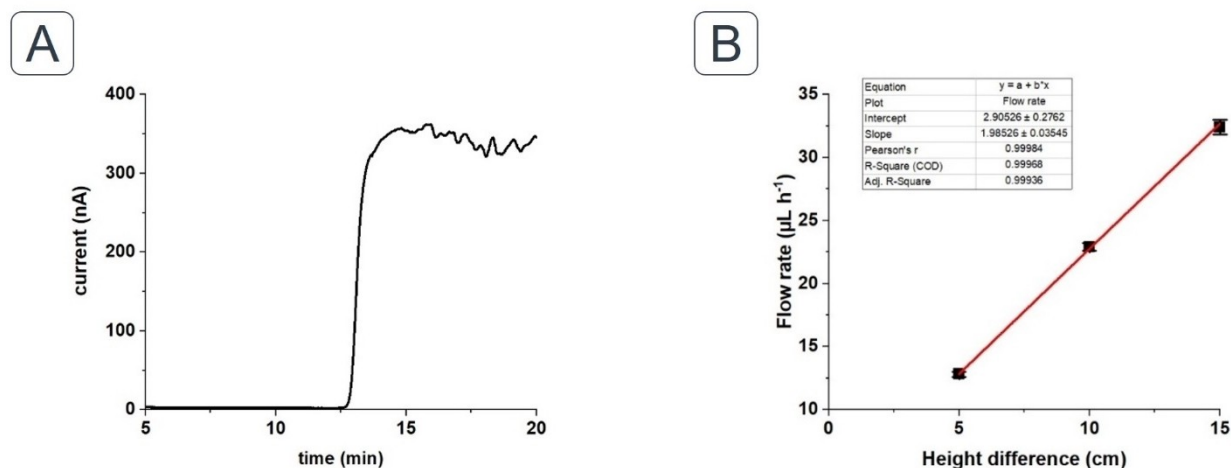


Figure 1. Determination of flow rates resulting from a height difference between inlet and outlet of the dosing capillary. A) Exemplary amperometric *i-t* curve recorded with a height difference of 5 cm. B) Dependency of the flow rate on the applied height difference. The outlet of the dosing capillary (OD = 360 μm , ID = 100 μm , length = 35 cm) was positioned closely to the surface of a platinum macro electrode which was used as working electrode. Experiments were conducted in 0.1 M LiPF₆ solution (EC:EMC 30/70), three measurements per height difference. Working electrode potential was 3.574 V vs. Li/1 M Li⁺.

with $V_{\text{capillary}}$: volume of dosing capillary; $t_{\text{Fc signal}}$: time interval until oxidation signal of Fc was detected; $r_{\text{capillary}}$: inner radius of the capillary; $l_{\text{capillary}}$: total length of the dosing capillary.

Flow rates were determined to be in the range of 12.8 ± 0.2 (Δ height = 5 cm) up to $32.4 \pm 0.6 \mu\text{L h}^{-1}$ (Δ height = 15 cm). Mathematical fitting of the applied height differences with the corresponding flow rates revealed a linear dependence as shown in the graph in Fig. 1B. By considering the volume of the bulk solution in the electrochemical cell ($V_{\text{cell}} = 5 \text{ mL}$) a more practical parameter was calculated, the temporal change of Fc concentration. Operating the MD setup at a height difference of 15 cm would result in a change of the Fc concentration in the bulk solution of $9.7 \mu\text{M h}^{-1}$. At a typical measurement session of 6 hours only approximately 200 μL of mediator solution are introduced into the electrochemical cell, less than 4% of the volume of the bulk solution. Since the mediator dosage could be stopped at any time, for example during the charge/discharge of a battery electrode, real values of introduced mediator would be lower. The dosage could be easily stopped by repositioning the capillary inlet out of the mediator solution. Overall, the gravity-driven dosage of mediator solution by applying a height difference between the solvent levels in the inlet and outlet reservoirs (Δ height) of a capillary was found to deliver smooth and stable flow rates and resulted in a minimized introduction of mediator solution into SECM experiments. The comparatively low flow rates couldn't be reproduced in measurements where the dosing was achieved via a syringe pump. Furthermore, the pulsating action of the syringe pump had a distorting effect on SECM images. Therefore, further experiments were solely conducted with the gravity-driven approach. A height difference of 15 cm was chosen, since it showed a good compromise between amount of introduced mediator and achievable SECM data quality.

Proof of Concept Measurements with a Micrux Thin-Film Electrode as Model Substrate

After clarifying the flow rates and deciding on a suitable height difference in the mediator dosing setup, measurements with a model substrate were conducted to showcase the performance of the approach. A thin-film electrode with an interdigitated electrode structure (Micrux IDRA1) was chosen for that purpose. First, a series of probe approach curves (PACs) towards conductive and non-conductive parts of the sample surface was performed in order to evaluate the reproducibility and the accordance with theoretical fits for negative^[33] and positive^[34] feedback PACs. In Figure 2A, five consecutive PACs under MD conditions over a non-conductive part of the model substrate's surface are shown together with the theoretical, negative feedback PAC calculated according to Cornut et al.^[33] The mathematical approximation was obtained for an R_g value of 5.1. Experimental PACs were found to be highly reproducible with minor distance variations of up to 200 nm. A systematic deviation from the theoretical feedback model for negative feedback was found for normalized distances smaller than four. This phenomenon can be explained by the proximity of the dosing capillary to the SECM probe. The practically applicable value for R_g is therefore greater than with a simple probe. Figure 2B depicts five sequential PACs recorded with the MD setup towards a conductive part of the substrate surface. The mathematic approximation for a purely positive feedback PAC was generated according to Amphlett et al.^[34] for an R_g value of 5.1. Again, PACs exhibited high reproducibility under MD conditions with deviations up to 500 nm. Experimental data is described very well by the theoretical fit.

After appropriate levelling of the model substrate by a series of PACs and line scans, imaging experiments were started at the highlighted area of the model substrate shown in Figure 3A. The recorded SECM image in Fc solution can be found in Figure 3B. Details of the interdigitated electrode

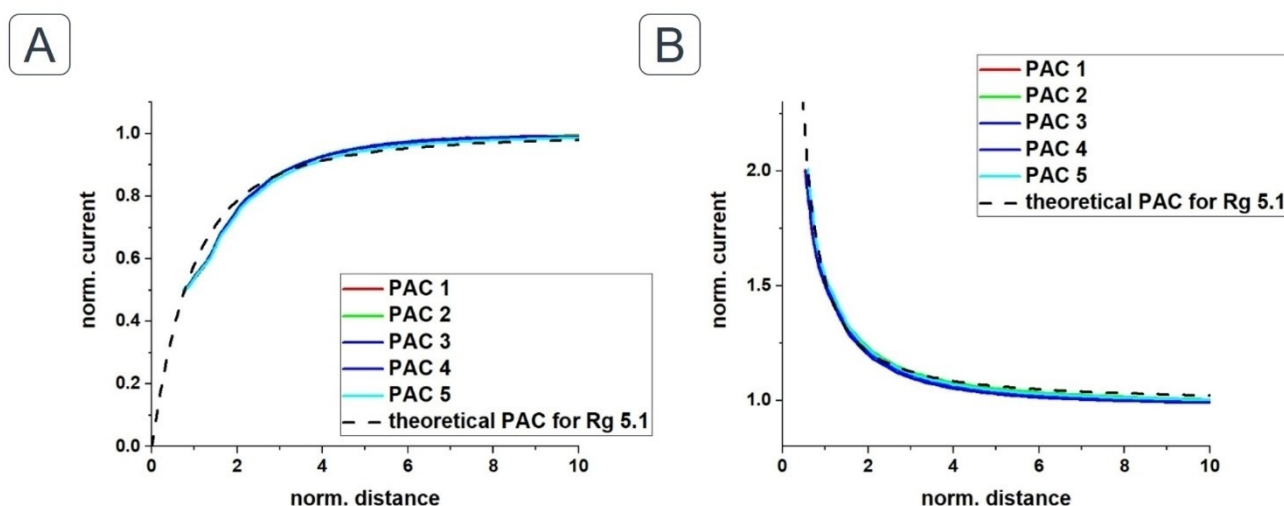


Figure 2. Consecutive PACs towards the surface of a Micrux thin-film electrode used as a model substrate. A) Five PACs towards a non-conductive part of the thin-film electrode surface. B) Five PACs towards a conductive part of the thin film electrode. Measurements were recorded in 0.1 M TBAPF₆ solution (EC:DMC 30/70). Fc solution (1.5 mM in 0.1 M TBAPF₆, EC:DMC 30/70) was dosed via a fused-silica capillary (OD = 360 μ m, ID = 75 μ m, length = 35 cm) by application of a height difference of 15 cm. SECM probe was a platinum UME ($r = 6.25$ μ m, $R_g = 5$). Probe potential was 3.424 V, quiet time of 15 s, maximum approach speed was 2.5 μ m s⁻¹.

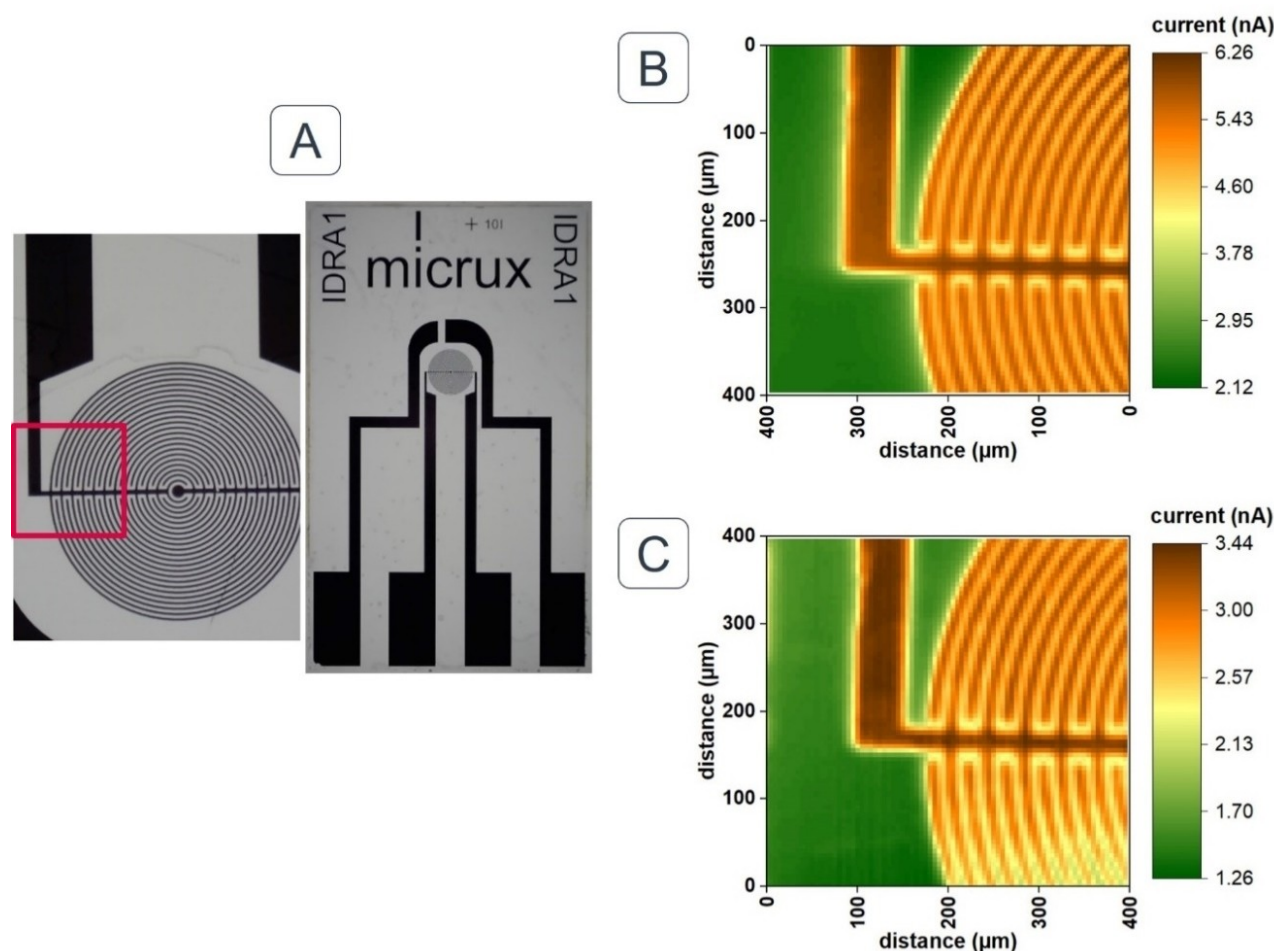


Figure 3. Model substrate experiments with a Micrux thin-film electrode. A) Microscopic images of a Micrux chip with interdigitated electrode area (10 μ m bands with 10 μ m spacing). The area imaged in SECM measurements is highlighted in red. B) SECM image recorded in 1.5 mM Fc in 0.1 M LiPF₆ solution (EC:DMC 30/70). C) SECM image recorded in 0.1 M LiPF₆ solution (EC:DMC 30/70). Fc solution (1.5 mM in 0.1 M LiPF₆, EC:DMC 30/70) was dosed via a fused-silica capillary (OD = 360 μ m, ID = 100 μ m, length = 35 cm) by application of a height difference of 15 cm. SECM probe was a platinum UME ($r = 6.25$ μ m, $R_g = 5$). Probe potential was 3.574 V, quiet time of 15 s, movement speed was 100 μ m s⁻¹.

structure of the thin-film electrode were well resolved, the electrode bands with a width of 10 μm and a distance between two bands of 10 μm were well visible. The identical area was then imaged by application of the MD setup in electrolyte containing no Fc. Again, the distinct features of the model substrate could be resolved with high quality, conductive and non-conductive parts could be easily differentiated and the gaps between the electrode bands were finely resolved. Overall, the image quality was found to be on par with the image generated in Fc solution. Measured currents were lower in the MD approach, but the contrast given by the ratio of highest and lowest current was identical.

Investigation of a Customcells LIB Graphite Electrode

Proof of concept studies with a model substrate revealed comparable data quality generated under MD conditions. Further studies were then conducted with a typical battery electrode material to put emphasis on the applicability of the newly developed MD approach. As such, a commercially available LIB graphite electrode from Customcells was chosen. Samples were investigated as received with no further treatment of the surface. Initially, the surface of the graphite electrode was characterised by means of optical microscopy and scanning ion conductance microscopy (SICM), which is

another SPM able to map a sample's topography at micro- and nanoscale in a non-contact measurement.^[35] In Figure 4A and B, a microscopic image and a false colour image of the sample are shown. The particles had typical sizes at the micrometre scale. Surface roughness parameters were measured according to ISO 25178^[36] from four randomly chosen areas with a size of 216 \times 289 μm each. A core surface roughness S_k of 2.3 μm and a maximum height of 9 μm were determined for the sample. The SICM image shown in Figure 4C is coherent with the findings from optical microscopy and furthermore reveals a slight curvature of graphite samples. In the investigated area of 500 \times 500 μm , a plateau could be found in the middle of the image, which was also found in a series of similar measurements conducted on the same batch of electrode samples.

Eventually, the graphite electrode was investigated by means of feedback mode SECM. After the careful adjustment of dosing capillary and SECM probe, the sample was levelled by a series of PACs and line scans in electrolyte containing no mediator and local dosing of Fc. Subsequently, a SECM image was recorded over a suitable spot of the sample. The image recorded under MD conditions is shown in Figure 5B. Overall, positive feedback was observed in the investigated area with the exemption of a non-conductive spot at the coordinates (x370/y450). Other local variations of the measurement signal can be explained by the distinct surface topography of the sample, as described before by the results from optical micro-

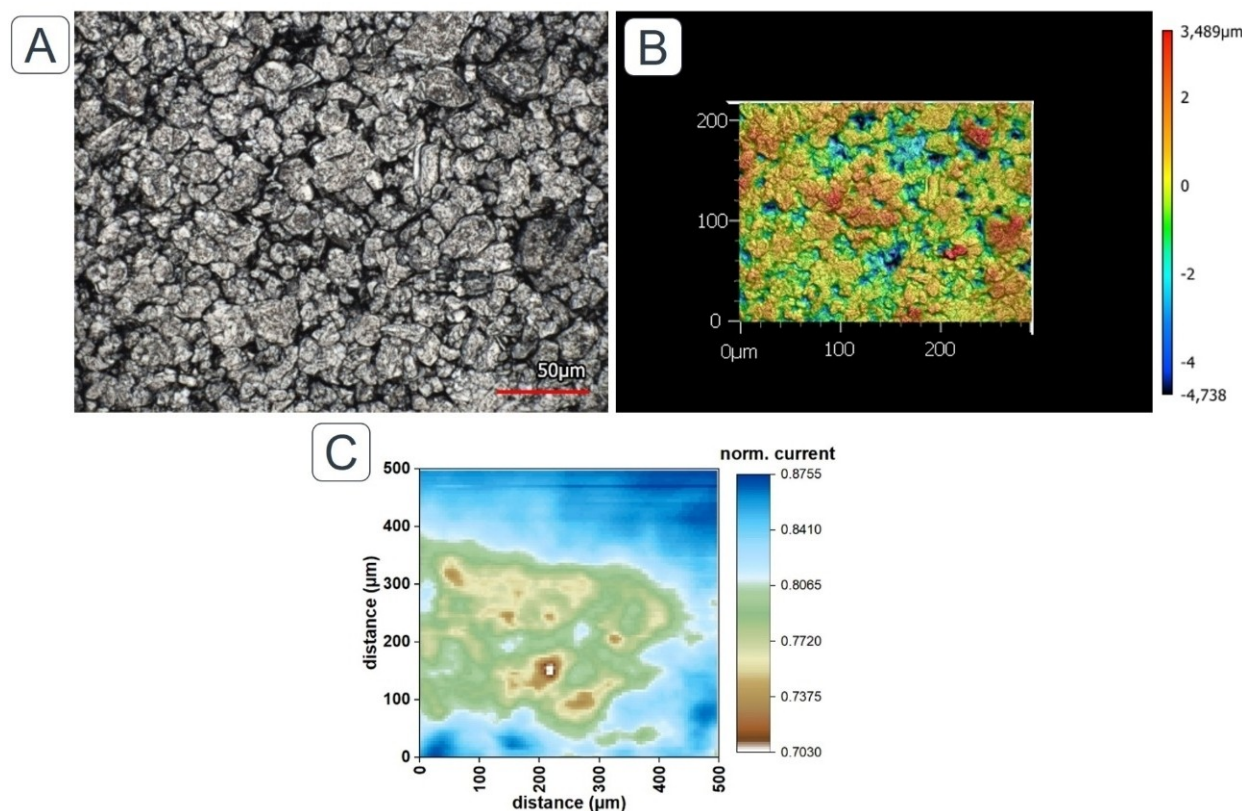


Figure 4. Customcells graphite electrode for LIBs which was used for investigation with the mediator dosing setup. A) Microscopic image of the graphite electrode surface showing particle size. B) False colour image highlighting the graphite surface roughness. C) SICM image highlighting the topography of the graphite sample. Image was recorded in 0.1 M LiPF_6 solution (EC:EMC 30/70). Probe potential was 3.374 V, quiet time of 15 s, movement speed was 100 $\mu\text{m s}^{-1}$.

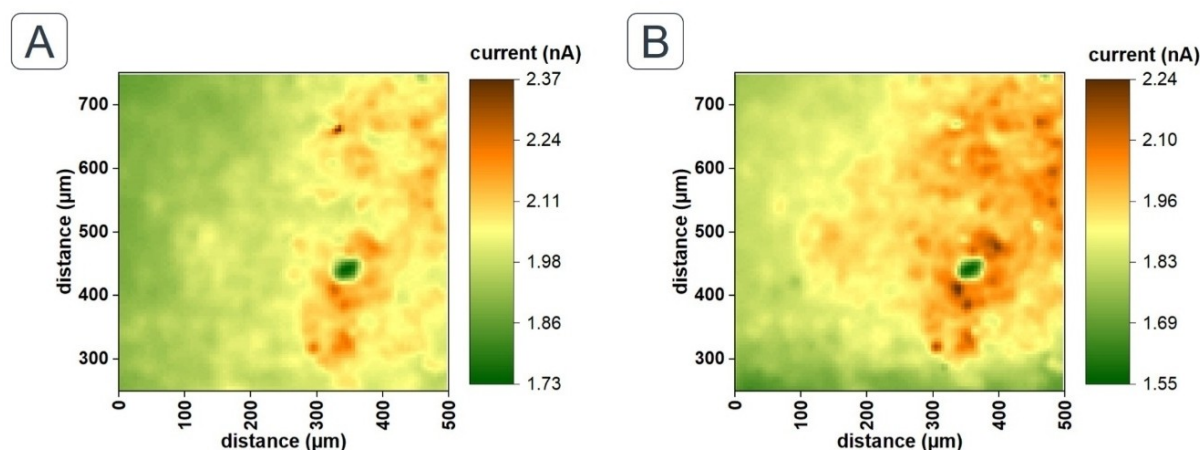


Figure 5. SECM images of a Customcells graphite electrode. A) SECM image recorded in 1.5 mM Fc in 0.1 M LiPF₆ solution (EC:EMC 30/70). B) SECM image of the graphite electrode recorded in 0.1 M LiPF₆ solution (EC:EMC 30/70). Mediator solution (1.5 mM Fc, 0.1 M LiPF₆, EC:EMC 30/70) was dosed via a fused-silica capillary (OD = 360 μm, ID = 100 μm, length = 35 cm) by application of a height difference of 15 cm. SECM probe was a platinum UME (r = 6.25 μm, R_g = 7). Probe potential was 3.574 V, quiet time of 15 s, movement speed was 100 μm s⁻¹.

scopy and SICM. Homogeneous distribution of electrochemical activity is generally assumed for pristine graphite electrodes in literature.^[15,22] Following the completion of the SECM image, the solution in the electrochemical cell was exchanged with electrolyte containing 1.5 mM Fc (0.1 M LiPF₆ in EC:EMC 30/70). Subsequently, a SECM image of the identical area at the same starting height was recorded. Distinct surface features, as the non-conductive spot (x370/y450) verified that the position was not changed during the exchange of solutions. Slight differences in the image details could be found. These changes can be explained by the study of Bülter et al.^[11] who investigated the swelling of graphite composite electrodes in contact with electrolyte. It was found that immense physical swelling of binding agents could occur resulting in a volume expansion of the whole graphite electrode. Furthermore, the process of the solvent swap between measurements could have had a distorting effect. In total, surface details were resolved in excellent image quality by the MD approach while significantly reducing the introduction of mediator into the system.

Conclusions

In this publication, a novel concept on localized dosing of mediator solution in the context of feedback mode SECM was introduced for applications in LIB research. A dosing capillary was used to deliver small amounts of mediator solution driven by application of a height difference between capillary inlet and outlet. The capillary outlet could be positioned precisely near the tip of a regular SECM probe by installation in a custom-made dual-probe holder which was previously utilized in the hyphenation of SECM and SICM.^[17]

First experiments were performed to determine the flow rates of mediator solution at various height differences. Chronoamperometric measurements revealed flow rates in the range of 12.8 up to 32.4 μL h⁻¹ resulting from height differences

of 5, 10, or 15 cm. Within that range a maximum of mediator concentration change of 9.7 μM h⁻¹ was determined considering the electrolyte volume in the electrochemical cell (V_{cell} = 5 mL). Afterwards, the performance of the newly developed concept was tested with a thin-film electrode as model substrate. Negative and positive feedback PACs towards the surface of the sample revealed remarkable reproducibility as well as good accordance with theoretical approximations for both cases of feedback. The distance deviations between PACs of a set were found to be below 500 nm. Furthermore, the micro-structured electrode area of the model substrate could be finely resolved under MD conditions with image quality comparable to measurements conducted directly in mediator solution. To further test the applicability of the MD approach in feedback mode SECM experiments, a real-world sample was investigated. The LIB graphite composite electrode could be imaged well, again, with quality on par with regular SECM measurements. Surface details resulting from the graphite particles were well visible.

The introduced MD concept was found to meet all the initial requirements, namely minimized mediator use, comparable data quality, and avoidance of complicated probe designs. Possible applications could be *in situ* studies of interphase formation on negative and positive LIB electrodes, while reducing mediator interference during charge/discharge processes to a minimum. Another advantage even for *in operando* setups is the possibility to stop mediator dosage at any given time for example during battery cycling. Furthermore, the setup is not limited to LIB applications. It could be applied in SECM studies of sensitive samples where the usage of typical redox mediators may alter the results, for example in studies of biological cells.

Experimental Section

Chemicals and Materials

The following chemicals were purchased from Sigma-Aldrich (St. Louis, USA): dimethyl carbonate (DMC, anhydrous, $\geq 99\%$), ethyl methyl carbonate (EMC, 99%), ethylene carbonate (EC, anhydrous, 99%), ferrocene (Fc, 98%), ferrocenium hexafluorophosphate (FcPF_6 , 97%), lithium hexafluorophosphate (LiPF_6 , battery grade, $\geq 99.99\%$), and tetrabutylammonium hexafluorophosphate (TBAPF_6 , $\geq 99\%$). Platinum wires with radii of 6.25 μm (99.99%) and 0.5 mm (99.99%) were purchased from Advent Research Materials (Oxford, UK). Platinum wire with a radius of 0.25 mm (99.99%) was purchased from Goodfellow (Huntingdon, UK). Graphite electrodes for LIBs (Product ID 11124) were acquired from Customcells (Itzehoe, Germany). Thin-film electrodes (Type IDRA1) were purchased from Micrux Technologies (Gijón, Spain). Fused-silica capillaries with an outer diameter of 360 μm and inner diameters of 75 and 100 μm were supplied by Polymicro Technologies (Phoenix, USA). Soda-lime glass tubes with an inner diameter of 1.1 mm were purchased from Technische Glaswerke Ilmenau (Ilmenau, Germany). Lapping film sheets with particle sizes ranging from 0.3 to 30 μm were purchased from Precision Surfaces International (Houston, USA). Two-component adhesive (Epoxy resin L + Hardener S) were acquired from R&G Faserverbundwerkstoffe (Waldenbuch, Germany).

SICM probes were filled with a mixture containing 1.5 mM Fc, 1.5 mM FcPF_6 , and 0.1 M LiPF_6 dissolved in EC:EMC 30/70. Fc/Fc^+ based reference electrodes^[37] were prepared with 1.5 mM Fc, 1.5 mM FcPF_6 , and 0.1 M LiPF_6 dissolved in either EC:EMC 30/70 or EC:DMC 30/70. DMC was used to rinse and clean SPM probes and the electrochemical cell.

SPM Probe and Dosing Capillary Fabrication

SPM probes were prepared from soda-lime glass, which was pulled to pipettes with opening diameters of approximately 100 μm in a butane flame. In the case of a SECM probe, a platinum wire (radius of 6.25 μm) soldered to a piece of jumper wire was carefully inserted into a glass pipette until it was protruding circa 1 mm from the tip. Afterwards the platinum wire was sealed in the glass tip and subsequently exposed again by polishing in a custom-made polishing device. Resulting SECM probes had a mirror-finish disk electrode and R_g values of ca. 5–7. SICM probes were manufactured according to the previously published instructions.^[17] A glass capillary with a tip opening diameter in the range of 10–30 μm was filled with electrolyte solution, and a platinum wire (radius of 0.25 mm) was inserted.

Fused-silica capillaries with inner diameters of 75 or 100 μm were used as dosing capillaries. A piece with a length of 35 cm was cut from the base material with a ceramic cutter. Afterwards, approximately 0.5 cm of the polyimide coating was removed from both sides. Tips were polished with the polishing device and lapping film sheets with particle sizes of 30 μm (first step, coarse polishing) and 1 μm (second step, fine polishing) to a clean, flat finish. Subsequently, a glass hull enabling the installation in the dual-probe holder was glued to the capillary.

A more detailed description of the SPM probe and dosing capillary fabrication steps is supplied in the supporting information, section SI-1.

Experimental Setup

All experiments, sample preparation steps and parts of the SPM probe and dosing capillary fabrication were carried out in an Argon-filled glovebox. Within the glovebox, the electrochemical setup and the positioning motor unit were placed on a dampening mat located inside a laboratory-constructed Faraday cage.

A commercial SECM 920 C system from CH Instruments (Austin, USA) was used in combination with electrochemical cells made from polytetrafluoroethylene. The working electrode channel was either connected to the SPM probe in SECM experiments or to a platinum macro-electrode in the flow rate determination. The auxiliary electrode was a platinum wire. A Fc/Fc^+ based reference electrode, briefly a platinum wire immersed in Fc/Fc^+ containing electrolyte, was utilized in most measurements. All potentials within this publication are recalculated to a $\text{Li}/1 \text{ M Li}^+$ reference system based on the open circuit potential of the Fc/Fc^+ reference of +3.274 V vs. $\text{Li}/1 \text{ M Li}^+$.

The dosing of mediator solution was enabled by usage of a laboratory-constructed dual-probe holder.^[17] It is possible to mount two probes at once, where one probe is installed in upright position while the second one is tilted by a 15°-angle. In Figure 6, the mediator dosing setup is illustrated. A capillary is used to locally dose a 1.5 mM Fc solution in close proximity to the SECM probe tip. The capillary was pre-flushed with Fc solution by application of a pressure pulse via the septum of the inlet vial while the assembly was positioned far away from the substrate. A height difference between inlet and outlet (Δ height) results in a defined, gravity-driven flow of the solution forming a Fc zone near the platinum disk electrode. Tips of SECM probe and dosing capillary were carefully aligned under a digital microscope camera. The scan direction for the high frequency axis during imaging experiments is shown in Figure 6B, the pipette was ahead of the SECM probe.

Two different substrates were utilized in the evaluation of the mediator dosing concept. A thin-film electrode with an interdigitated electrode structure was used as model substrate. The structure consisted of a circular arrangement of electrode bands with a width and distance of 10 μm , each. Furthermore, SECM experiments were conducted on a commercially available LIB graphite electrode as realistic substrate. Additionally, the electrode material was characterised with a VK-X 3000 3D laser scanning microscope from Keyence (Neu-Isenburg, Germany). The experimental setup is described in more detail in the supporting information, section SI-2.

Experimental Procedures

Initially, the flow rates of mediator solution resulting from Δ height of 5, 10, and 15 cm between inlet and outlet of the dosing capillary were determined. Therefore, a platinum disk electrode with an electrode diameter of 3 mm was mounted in the bottom of the electrochemical cell and the cell was filled with 5 mL of 0.1 M LiPF_6 solution (EC:EMC 30/70). Then, a mediator dosing assembly (SECM probe + dosing capillary) was approached under mediator flow (Δ height = 15 cm) towards the surface by measuring a PAC. Parameters were: probe potential = 3.574 V vs. $\text{Li}/1 \text{ M Li}^+$, quiet time = 15 s, maximum approach speed = 10 $\mu\text{m s}^{-1}$, feedback target = 200%. The auxiliary electrode was a platinum wire, the reference was a Fc/Fc^+ based reference electrode. After approaching the surface, the working electrode connection was switched from the SECM probe to the bottom-mounted platinum electrode. Two inlet vials were inserted in the adjustable height stand, one filled with mediator solution (Vial 1, 1.5 mM Fc in 0.1 M LiPF_6 EC:EMC 30/70) and one filled with pure electrolyte (Vial 2, 0.1 M LiPF_6 in EC:EMC 30/70).

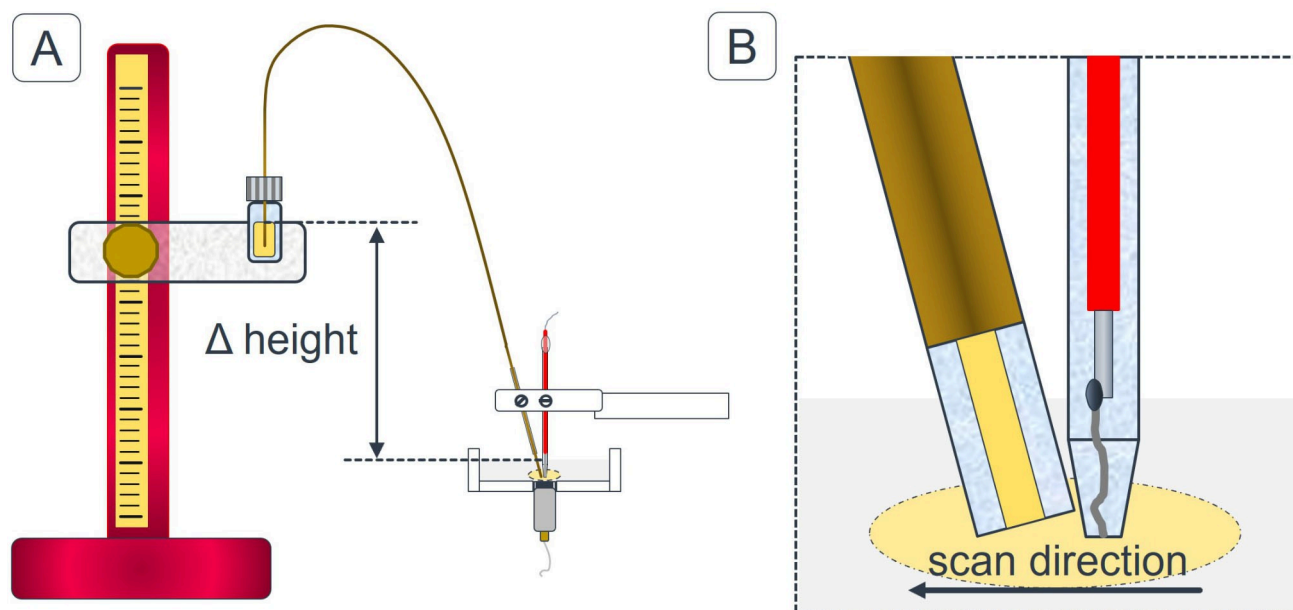


Figure 6. Schemes of mediator dosing setup and highlighted view of the capillary-probe tip assembly. A) The inlet vial filled with ferrocene solution is mounted at an adjustable height difference (Δ height) to the outlet of the dosing capillary resulting in a gravity-driven flow of the mediator solution. B) Dosing capillary and SECM probe are closely aligned at their tips. A ferrocene zone is formed in close proximity to the platinum disk electrode.

The height difference was adjusted to 5 cm, the inlet side of the capillary was positioned in vial 2, and an *i-t* curve was started (electrode potential = 3.574 V vs. Li/1 M Li⁺). After 30 s, the capillary inlet was moved into vial 1 resulting in the flow of mediator solution towards the platinum electrode. The time until the oxidation signal of Fc could be detected was used together with the capillary dimensions to calculate the corresponding flow rate. For each Δ height, the experiment was conducted three times.

To showcase the performance of the mediator dosing setup, a thin-film electrode with an interdigitated electrode structure (Micrux type IDRA1) was investigated. The substrate was mounted in the electrochemical cell, which was subsequently filled with 5 mL of a 1.5 mM Fc solution (0.1 M LiPF₆ or 0.1 M TBAPF₆ in EC:DMC). Then, a dosing capillary and a SECM probe were installed and aligned in the dual-probe holder under inspection with a digital microscope camera. Levelling of the substrate was achieved by a series of PACs at three different positions surrounding the area of interest. A reference image in Fc solution was recorded after which the solution in the electrochemical cell was exchanged with pure electrolyte. A vial was filled with 1.5 mM of Fc solution and installed together with the capillary inlet at a corresponding Δ height of 15 cm. The reproducibility under mediator dosing conditions was then evaluated by five consecutive PACs towards the glass surface of the thin-film electrode (negative feedback) and another set of five PACs towards the conductive platinum electrode surface (positive feedback). Furthermore, to compare the image quality received in Fc bulk solution with the mediator dosing setup, SECM images of the same electrode structure were recorded under both experimental conditions. PACs were recorded in 0.1 M TBAPF₆ (EC:DMC 30/70), probe potential was 3.424 V vs. Li/1 M Li⁺, maximum approach speed was 2.5 $\mu\text{m s}^{-1}$, and a quiet time of 15 s before current recording was chosen. The probe movement is slowed down close to reaching the feedback target. In the measurement set of negative feedback PACs, at a norm. distance of 1 (feedback current of approx. 54%), the average movement speed was 0.36 $\mu\text{m s}^{-1}$. Further away, at a norm. distance of 1.5 (feedback current of approx. 65%), the average speed was 1.26 $\mu\text{m s}^{-1}$. The auxiliary electrode was a platinum wire, and an Ag/AgCl wire was

used as quasi-reference. The SECM images were obtained with a platinum wire as auxiliary electrode, and a Fc/Fc⁺ based reference electrode. Probe potential was 3.574 V vs. Li/1 M Li⁺, scan speed of 100 $\mu\text{m s}^{-1}$, pixel size of 5 μm , and the quiet time was 15 s. Mediator dosing images were recorded in 0.1 M LiPF₆ (EC:DMC 30/70).

Eventually, a commercially available LIB graphite electrode (Customcells product ID 11124) was evaluated comparing imaging in Fc solution and under mediator dosing conditions. After mounting the substrate and filling the electrochemical cell with 5 mL of electrolyte solution (0.1 M LiPF₆ in EC:EMC 30/70), the sample was levelled by a series of PACs at three different positions on the surface. Next, a SECM image was recorded by application of the mediator dosing setup, followed by exchanging the measurement solution with Fc containing electrolyte (1.5 mM Fc in 0.1 M LiPF₆ in EC:EMC 30/70). Subsequently, a SECM image of the same area was generated. Mediator dosing was achieved by applying a Δ height of 15 cm between inlet and outlet reservoirs connected with a fused-silica capillary with an inner diameter of 100 μm and a length of 35 cm. The experimental parameters were identical in both cases. Auxiliary electrode was a platinum wire, and a Fc/Fc⁺ based reference electrode was utilized. A probe potential of 3.574 V vs. Li/1 M Li⁺ was applied, probe movement speed was 100 $\mu\text{m s}^{-1}$, pixel size was 5 μm , and a quiet time of 15 s was used before current recording. The SECM probe was a platinum UME (radius = 6.25 μm) with a R_g value of 7.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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