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Simultaneous Scanning Ion Conductance and Electrochemical Microscopy in Lithium-Ion Battery Research

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Deeper understanding of processes involved in operation of lithium-ion batteries (LIBs) is necessary to further optimize them for future applications. Extensive research was conducted on the formation of a solid electrolyte interphase (SEI) on negative battery electrodes, still leaving several questions unanswered. Scanning probe microscopies (SPMs) enable *in situ* and *operando* investigations and have the potential to explain some phenomena. Scanning electrochemical microscopy (SECM) and scanning ion conductance microscopy (SICM) could be employed in LIB studies. A novel SICM method based on the redox couple ferrocene/ferrocenium is introduced for applications in carbonate solvents widely used in LIBs. Proof of concept measurements were conducted with a micro milled copper circuit board as model substrate. Furthermore, the proposed SICM approach was hyphenated with feedback mode SECM resulting in the simultaneous mapping of morphology and electrochemical activity. A flexible dual-probe arrangement was developed enabling usage of both SPM techniques at the same time, and furthermore, an easy replacement of both individual probes if needed. The setup was applied in the characterisation of commercial graphite electrodes for LIBs before and after conducting a pre-charging protocol. Changes in electrochemical activity and topography of the graphite electrode were resolved in simultaneously generated SECM/SICM recordings.

Introduction

Lithium-ion batteries (LIBs) are among the most important energy storage devices of our time.[1,2] Their main applications are portable electronic devices and electric vehicles.[3] Typically, a LIB consists of negative electrode, positive electrode, and a separator in between plus the organic electrolyte solution. Because of safety issues related to bare lithium, host materials capable of lithium-ion intercalation are normally used. During charge and discharge processes, lithium-ions are shuttled between these host electrodes, which led to the description of LIBs as "rocking chair" batteries.[4] While charging, the potential of the negative electrode, often graphite in commercial cells, exceeds the electrochemical stability window of the electrolyte. This generally results in the formation of a so-called solid electrolyte interphase (SEI), which mainly consists of insoluble degradation products.[5] The intrinsic properties of the SEI are detrimental for safe and long-term stable operation of batteries. Ideally, it prevents further degradation of the electrolyte solution, while still enabling diffusion of Li^+. Furthermore, the formation of the SEI is responsible for the initial, irreversible capacity loss of a LIB due to changing the intercalation capacity of the negative electrode. Extensive research has been dedicated to the investigation of SEI formation and corresponding properties, because of its importance regarding long-term cycling stability and battery safety.[6–11] Although LIBs improved immensely since their commercialisation, there is still a lot of potential for improvement of LIB technology, e.g., novel electrode materials, full understanding of processes involved in operation, and replacement of hazardous liquid electrolytes.[1] To further drive innovations in these fields, there is a growing demand for powerful analytical techniques capable of *in situ* or even *in operando* investigations.

Several scanning probe microscopies (SPMs) are well suited for this task. One of the more prominent SPM applied for investigations in LIB research is scanning electrochemical microscopy (SECM).[12] In this contactless technique, a nano- or micro sized electrode is scanned across the surface of interest. By application of an appropriate potential, a diffusion-limited current is measured resulting from the oxidation/reduction of a redox-active substance, the mediator. In the scope of LIB related research, two commonly used mediators are ferrocene[10,11,13] and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene.[6,13] Since its introduction in the late 1980s, SECM excelled in diverse applications, ranging from biological samples,[14] kinetic characterisation of novel materials[15] to lately studies of battery electrode materials and processes.[6,10] A drawback of stand-alone SECM approaches lies in the interpretation of recorded data. This is because the current signal is not only dependent on the electrochemical activity, but also on the morphology of the investigated substrate. Over the past decade, various solutions were introduced to overcome this limitation. Measuring shear force on a vibrating SECM probe,[16] application of an alternating current (AC-SECM),[17] or hybridisation with the atomic force microscope[7,9,18] are only a short selection of possibilities which should be mentioned. Not all of them were yet successfully

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implemented in battery research due to the intrinsic challenges of the subject.

An alternative approach to separate morphological from electrochemical activity information in SECM studies is the hyphenation with a complementary SPM technique called scanning ion conductance microscopy (SICM). This SPM was introduced in 1989 by Hansma *et al.*[19] and became a well-established non-contact method in a variety of research fields ever since. The principle of SICM is typically applied in aqueous solutions. A silver-silver chloride wire is placed in a glass capillary filled with a chloride containing solution. In this approach, a second silver-silver chloride wire is placed in the bulk solution and an ionic current between the two wires could be measured by application of a potential bias.[20] During operation, the current decreases as soon as the tip of the capillary is approaching a surface, i.e. the orifice will be partly blocked. Scanning the probe across the surface enables the generation of highly resolved topographical information about the substrate. In the context of LIB research, to the best knowledge of the authors, few contributions from 2011,[21] 2014,[22] and 2023[23] including SICM experiments could be found. Lipson *et al.* [21,22] used a lithiated tin wire within an electrolyte-filled capillary in the investigation of lithiation processes on tin thin films and MnO substrates. Takahashi *et al.*[23] evaluated the correlation of ion-concentration profile and surface topography changes on graphite electrodes with a SICM approach based on a lithium-coated copper electrode inside of the capillary. The simultaneous operation of SICM together with SECM was already accomplished in aqueous media,[24] but not yet in non-aqueous, carbonate-based solvents widely used in LIBs. Despite its attractiveness in mapping topographical information and ion-flux, SICM is still under-represented in this field of research.[2,21–23]

Within this contribution, a simple-to-use SICM method for applications in the context of LIBs is introduced. The method is based on the ferrocene-ferrocenium (Fc/Fc^+) redox couple, which was found to enable a stable SICM signal and could also be used as a redox couple-based reference electrode in carbonate solvents. It's open circuit potential vs. a Li/1 M Li^+ reference electrode was determined at +3.274 V. Furthermore, the proposed SICM method was coupled with feedback mode SECM to simultaneously generate topographic information as well as spatially resolved electrochemical activity characterisation of substrates. The application of our dual-probe SECM/SICM approach was demonstrated in the characterisation of LIB graphite electrodes before and after treatment with a pre-charging protocol.

Results and Discussion

Development of a novel SICM method for applications in LIB electrolytes

The goal of this publication is to design a novel SICM method based on using the Fc/Fc^+ couple as a reference system for two main reasons. Firstly, the combination of a platinum wire with the Fc/Fc^+ redox couple was already used as a reference electrode in experiments in propylene carbonate[25] and similar approaches on platinum-based reference systems for non-aqueous solvents were already published.[26] Secondly, the mediator of choice for the SECM investigation was Fc, because of its recently reported superior signal stability in organic carbonate-based electrolytes.[9,10,13] Chronoamperometry was conducted at fixed potentials of 3.174, 3.374, and 3.474 V vs. Li/1 M Li^+ in preliminary studies to evaluate the signal stability of the proposed SICM approach. Results suggested that the measured current generated from the SICM probe is sufficiently stable in the tested potential range. Highest signal stability in the chronoamperometric experiments was achieved by application of a potential difference of 3.374 V vs. Li/1 M Li^+. The signal decrease with a probe potential of 3.374 V was less than 4% for a period of 15 min compared to 4.5% at 3.174 V, and 6.3% at 3.474 V. Thus, this potential bias was chosen for further experiments.

Afterwards, the reproducibility of the SICM method was tested. For that purpose, five consecutive probe approach curves (PACs) with a current target of 85% of bulk current towards the same position on a model substrate were conducted. As such, a copper circuit board with micro milled channels was used. In Figure 1, the results are shown as normalized current, given by the ratio of the tip current at the respective position divided by bulk current. To start, the SICM probe tip was positioned at a distance of approximately 110 μm above the sample surface. It was found that the course as well as the ending point of the approach curves was highly reproducible with only minor deviations of less than 100 nm in the total travel distance.

Final steps in the SICM method development were imaging experiments mapping the topography of the model substrate. The channels in the copper circuit board were micro milled and they had a width of 200 μm, as shown in Figure 2A. After approaching the SICM probe to a distance of 5 μm, correlating

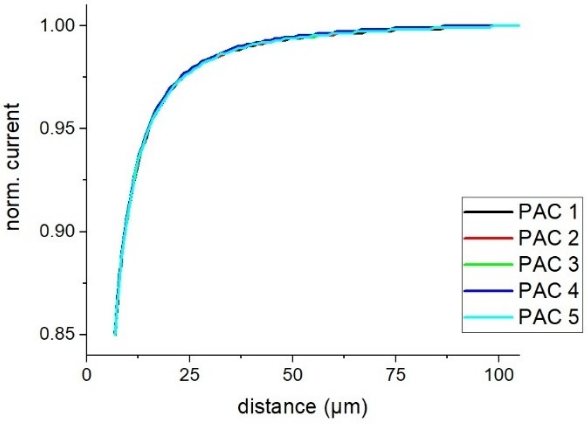

Figure 1. Signal reproducibility of the SICM method shown by five consecutive probe approach curves towards the surface of the model substrate. Measurements recorded in 1.5 mM Fc in 0.1 M $LiPF_6$ solution (EC:EMC 30/70). The probe consisted of a Pt wire inserted into a glass capillary (opening diameter 30 μm, total tip diameter 90 μm) filled with 1.5 mM Fc/Fc^+ solution. PAC parameters: Probe potential was 3.374 V vs. Li/1 M Li^+, quiet time of 15 s, maximum approach speed was 10 $\mu m\,s^{-1}$.

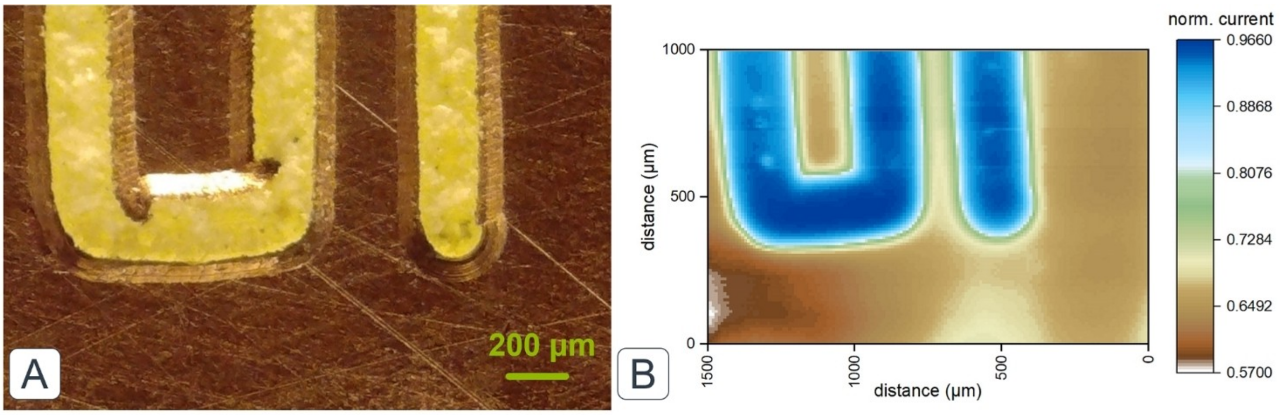

Figure 2. Model substrate used in the development of the SICM method. A) Micrograph of the model substrate. A copper circuit board with micro milled channels (width = 200 µm) was used. B) SICM image of the circuit board measured in 1.5 mM Fc in 0.1 M $LiPF_6$ solution (EC:EMC 30/70). The probe was a Pt wire inserted into a glass capillary (opening diameter 30 µm, total tip diameter 150 µm) filled with 1.5 mM Fc/Fc^+ solution. Probe potential was 0.1 V, quiet time of 15 s, height corresponding to70% of bulk current, movement speed was 200 $\mu m\,s^{-1}$.

to a signal of 70% of bulk current, a topographical map was recorded (Figure 2B). Above the channels the distance from probe tip to substrate was greater resulting in higher currents (blue) than above the copper surface (brown). Even small details in the channels (X 1200/Y 600) were visible in the SICM image, and the channels could be clearly resolved in the current map. The signal changes were attributed to blockage of the SICM probe's orifice above the copper surface, or the almost unobstructed capillary opening above the micro milled channels. Thus, the applicability of the proposed SICM method in carbonate-based solvents was shown.

Simultaneous SECM/SICM Characterisation of a LIB Graphite Electrode

With more complex investigations in mind, e.g. SEI formation and characterisation, stand-alone SICM measurements are suited to track morphological changes of the electrode material. The formation of an SEI is generally linked with changes in the electrochemical activity. Therefore, the possibility to map the topographical as well as the electrochemical changes of the surface is highly attractive. In the next step, the proposed SICM method was combined with feedback mode SECM to generate complementary information on the substrate characteristics. Successively measuring with both methods is possible but more reliable information would be achieved by simultaneous measurements. This is due to the fact that exchanging probes would inevitably lead to a small misplacement of the probe tip resulting in measuring at a different position on the sample surface. Thus, only a hybrid approach with simultaneous usage of both SPM techniques is adequate.

The most important part for the approach towards hybrid SECM/SICM with two individual probes was to design a satisfactory probe holder. It should be resistant against the used carbonate-based solvent, the positioning of both probe tips should be as close as possible, and the signal response of both techniques should not be changed significantly because of the probe arrangement. The in-house built holding system, which is shown in more detail in the Experimental section, was found to be sufficient regarding those requirements. A tilted position of one of the two probes at a 15 degree angle was determined to be the sweet spot in lowest possible change of signal response and close positioning of both probe tips. In preliminary experiments, the influence of a tilted position on the behaviour of the probe was determined. PACs and imaging in feedback mode SECM revealed poor performance of a flatly polished probe mounted in the tilted position. Therefore, the SECM probe was also polished at a 15 degree angle resulting in a parallel orientation towards the sample surface. This adjustment theoretically amounts to an increase of the electrode's surface area of 3.5%, and a slight distortion of the tip shape. The resulting performance decrease was acceptable.

Prior to measuring surface characteristics of the sample, the arrangement of SICM and SECM probes was carefully adjusted and controlled with the help of a digital microscope camera. The performance of both SPM was then tested with PACs, and eventually, the adjustment was repeated. Further experiments were started only after the behaviour of both probes during PACs was sufficient. For SECM, a probe potential of 3.574 V was chosen based on cyclic voltammetry and the redox potential of the used mediator Fc, which was determined at 3.274 V vs. Li/1 M Li^+ in the applied experimental setup. In SICM, a potential bias of 3.374 V vs. Li/1 M Li^+ was applied based on the signal stability measurements described in the previous section.

The sample material of choice for showcasing the strengths of the non-aqueous SICM method in hyphenation with feedback mode SECM were typical graphite electrodes for LIBs. Samples were characterised as received, with no additional surface treatment. Prior to SECM/SICM measurements, microscopic images were taken of a part of the graphite electrode and the surface roughness was determined. A representative microscopic image and a false colour image are shown in Figure 3. Particles were found to have sizes in the micrometre range. The surface area roughness was determined from four randomly selected regions on the sample, with an area of

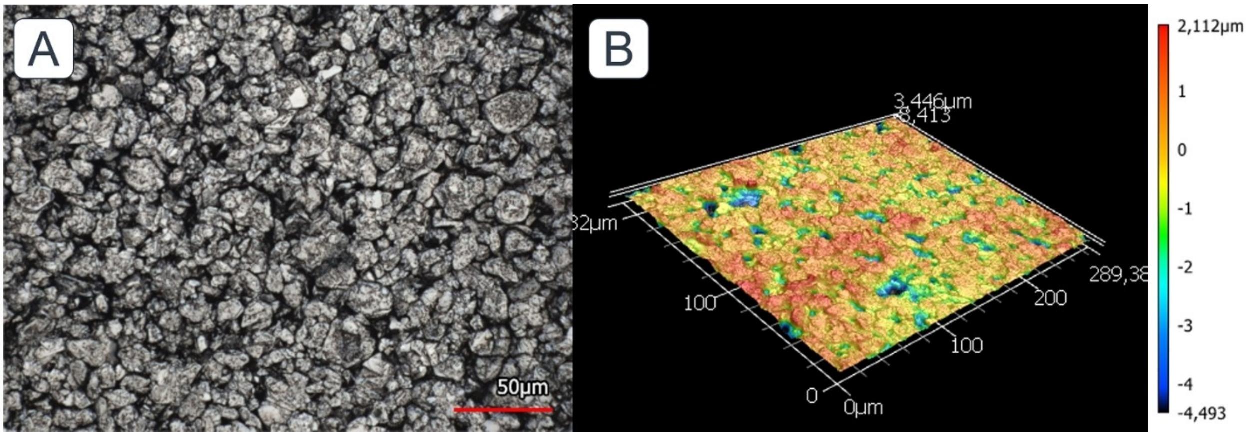

Figure 3. Graphite electrode for LIBs which was used for investigation with the dual-probe setup. A) Micrograph of the graphite electrode surface. B) False colour image highlighting the graphite surface roughness.

216×289 µm each. The core roughness depth Sk according to ISO 25178[27] was measured at 2.3 µm, and the maximum height Sz was 9 µm in the investigated areas.

Following the careful adjustment of SECM and SICM probe in the positioning unit of the SECM setup, a PAC was started to approach the graphite surface. An example of such a PAC is shown in Figure 4A, which was recorded at the position (X 0/Y 0) of later imaging experiments. On one hand, the current signal of the SECM probe increased with less distance to the surface, indicating positive feedback of the uncovered graphite electrode. The SICM signal, on the other hand, decreased with the probe assembly getting closer to the substrate, because of the increasing blocking of the tip orifice. Several preliminary PACs and images were recorded until a suitable, representative imaging area was found. Subsequently, the SECM/SICM imaging experiment was started. To be able to show the identical area mapped with both SPM techniques, it was a necessity to scan a larger area of 500 x 1000 µm. From those larger matrices, corresponding areas for SECM and SICM were extracted. The areas were selected based on the measured distance between the active tip elements from optical microscopy, and by the comparison of surface details. Matching current maps from SECM and SICM signals before pre-charging of the graphite electrode are shown in Figure 5A and 5B. From the SECM image (Figure 5A), a rather homogeneous distribution of electrochemical activity was observed with small variations depicting particles of the electrode material. Furthermore, a slight signal increase was measured in the middle right part of the imaged area, which could either mean higher electrochemical activity or a reduced distance between tip and sample surface. It was explained by the findings in the SICM current map (Figure 5B), where a matching signal decrease, i.e., an elevation of the surface, was recorded in the identical area. Signal variations resulting from electrode particles in both SPM modes matched well with the size determination from laser scanning microscopy results. In literature, it is generally assumed that the

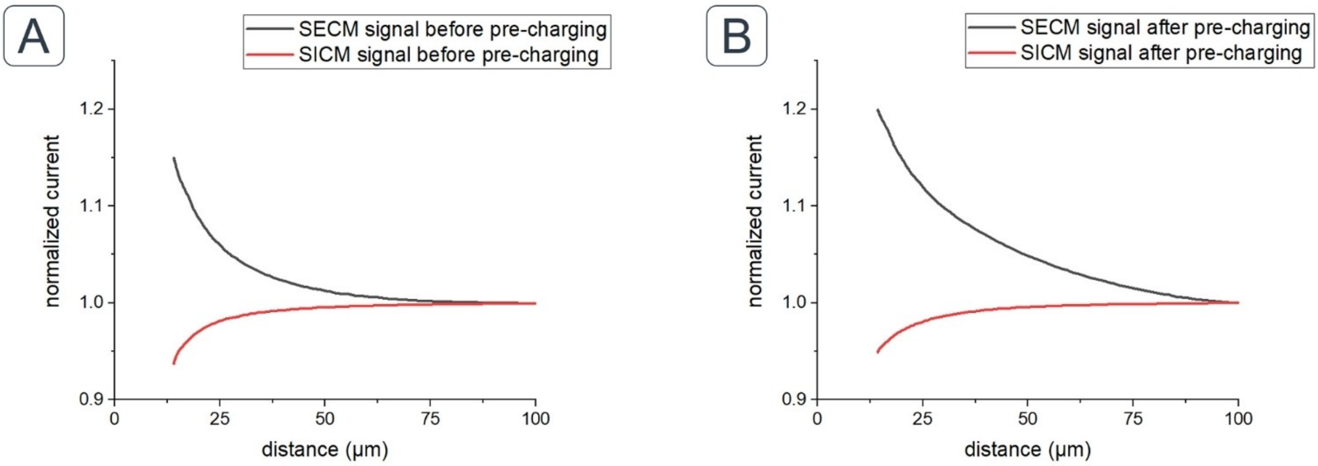

Figure 4. Simultaneous SECM/SICM PACs towards the surface of a Customcells graphite electrode before (A) and after (B) the pre-charging protocol recorded in 1.5 mM Fc in 0.1 M $LiPF_6$ solution (EC:EMC 30/70). SECM probe was a Pt UME ($r = 6.25$ µm, $R_g = 7$), which was polished at a 15 degree angle and mounted in a tilted position at 15°. SICM probe consisted of a Pt wire inserted into a glass capillary (opening diameter 20 µm, total diameter 100 µm) filled with 1.5 mM Fc/Fc^+ solution. Probe potentials were 3.574 V (SECM) or 3.374 V vs $Li/1\ M\ Li^+$ (SICM), quiet time of 15 s, max. approach speed was 10 $\mu m\,s^{-1}$.

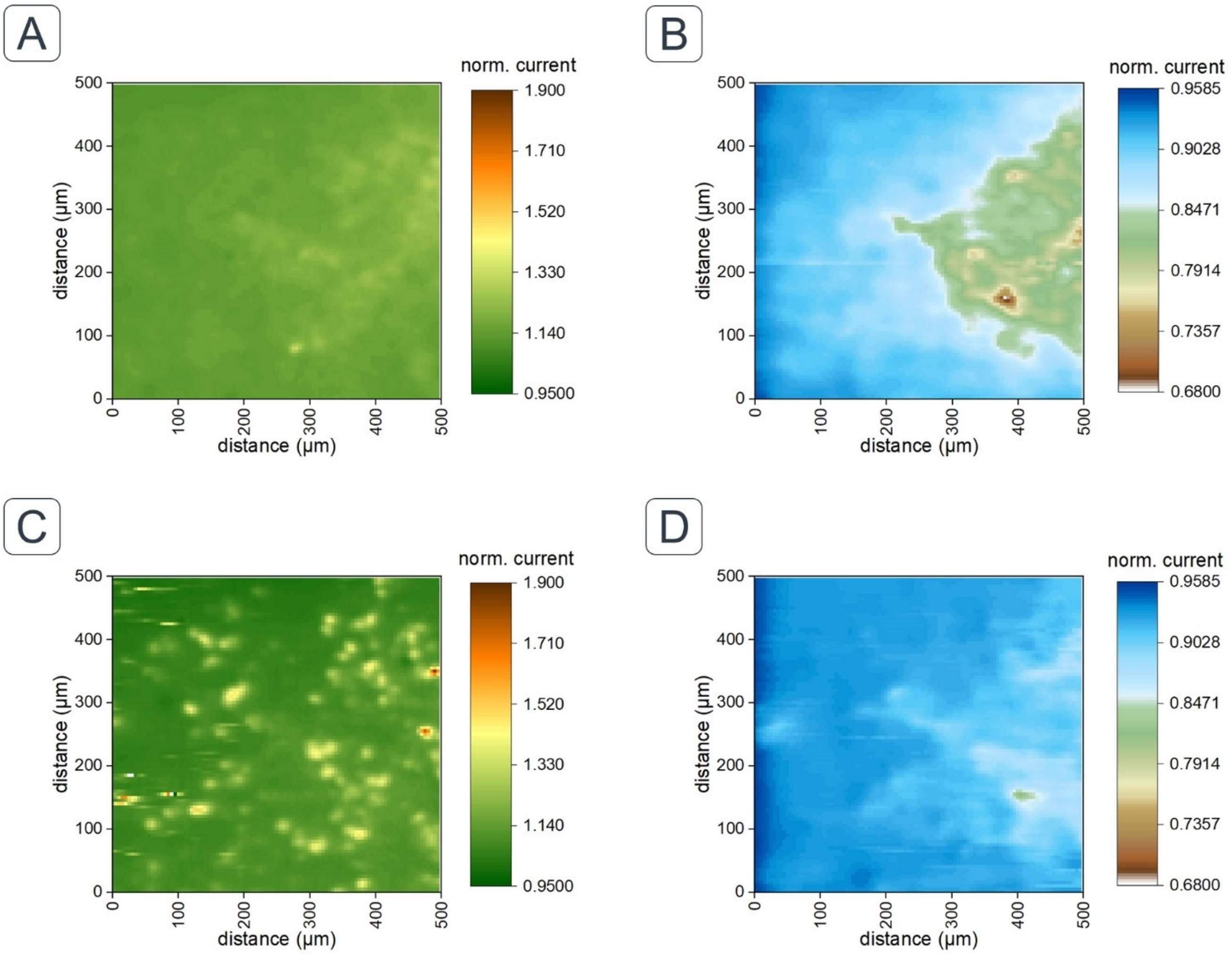

Figure 5. Simultaneous SECM/SICM images from the surface of a Customcells graphite electrode before (A + B) and after (C + D) the pre-charging protocol recorded in 1.5 mM Fc in 0.1 M $LiPF_6$ solution (EC:EMC 30/70). SECM probe was a Pt UME ($r = 6.25$ µm, $R_g = 7$), which was polished at a 15 degree angle and mounted in a tilted position at 15°. SICM probe consisted of a Pt wire inserted into a glass capillary (opening diameter 20 µm, total tip diameter 100 µm) filled with 1.5 mM Fc/Fc^+ solution. Probe potentials were 3.574 V (SECM) or 3.374 V vs. Li/1 M Li^+ (SICM), quiet time of 15 s, movement speed was 50 µm s^{-1}.

electrochemical activity of pristine graphite electrodes is homogeneous.[6,11]

To induce changes in surface characteristics, initial steps towards the formation of a SEI, and repeated Li^+ (de-)intercalation, a pre-charging protocol was applied to the graphite sample after the initial characterisation and mapping of a suitable, representative area by SECM/SICM. During pre-charging, the SECM/SICM probe assembly was retracted from the sample surface to exclude any possible interferences. The protocol consisted of an initial scan from 3.274 to 1.274 V vs. Li/1 M Li^+, followed by cycling between 1.274 to 0.04 V vs. Li/1 M Li^+ for two cycles. Both steps were conducted at a scan rate of 1 mV s^{-1}. Similar conditions had previously been applied in the investigation of graphite electrode samples.[9–11] Passivation of the electrode surface, i.e., reduced electrochemical activity due to the formation of a SEI, is the expected outcome of the pre-charging. The topography, on the other hand, is believed to change minimally, since the SEI thickness is generally accepted to be in the nanometre range.[5,8]

After this pre-charging process, the SECM/SICM probe assembly was moved to the starting position of the PAC before (Figure 4A), and a new approach curve was initiated. The SECM/SICM PACs after pre-charging are shown in Figure 4B. Interestingly, this second PAC terminated at a total travel distance of 9 µm less than the previous one. Most likely, this height difference resulted from solvent uptake. Bülter *et al.*[28] reported swelling of graphite electrodes because of swelling of the binder used in the graphite composite formulation. Another intriguing finding was the fact that the SICM PAC, on the one hand, did not show significant changes, but on the other hand, the course of the SECM curve was altered in a different way than anticipated. A signal decrease resulting from formation of an electronically insulating SEI was expected, but the opposite was measured. In Figure 5C and 5D, SECM and SICM current maps from the same region as in 5A and 5B are shown. The distribution of electrochemical activity (Figure 5C) changed considerably, indicating several local hot spots randomly distributed in the investigated area. Similar results were also observed elsewhere. Bülter *et al.*[6] attributed these local jumps of activity to temporal dissolving of parts of the SEI, terming this phenomenon as short-term events. Zeng *et al.*[11] observed locally high electrochemical activity spots as well in their studies of graphite composite electrodes. They concluded that lithiated graphite was exposed locally as a result of the initially unstable nature of the SEI. Also, other possible explanations are discussed in literature, including speculation on electron tunnelling towards Fc^+ through the SEI, when Fc was present during formation.[29] The majority of the investigated area exhibited typical behaviour correlated with SEI formation, i.e. a decrease in electrochemical activity. Interestingly, the topography of the graphite electrode sample changed between the imaging experiments before and after pre-charging. The elevation on the right side of the imaged area was found to be less pronounced after the SEI formation. In combination with the detected height difference of 9 μm in the PACs before and after pre-charging, it was presumed that these changes in morphology are related to a physical swelling of the surface. Studies by Bülter *et al.*[28] were dedicated to the swelling of pristine graphite composites resulting from solvent uptake. It was found that binder additives in the graphite composite could swell immensely after immersion of the electrode in electrolyte solution, and similar dimensions of sample swelling were observed in their experiments.

Conclusions

Within this contribution we have introduced a simple and straightforward SICM method based on the Fc/Fc^+ redox couple, and a reference electrode for usage in LIB electrolyte. Furthermore, we have designed a probe holding system for working with two scanning probe microscopies at the same time. We have employed the setup in the investigation of a LIB graphite electrode treated with a pre-charging protocol by measuring SECM and SICM simultaneously.

The Fc/Fc^+ SICM probes have been tested regarding their signal stability and reproducibility with a micro milled copper circuit board as model substrate. The signal has been found to be most stable at a potential offset of 0.1 V vs the Fc/Fc^+ reference electrode (corresponding to 3.374 V vs Li/1 M Li^+). PACs have been highly reproducible towards the sample with only minor variations in the total travel distance. Eventually, topographic mapping of the substrate surface has been conducted highlighting the performance of the SICM probes. In further experiments, SICM has been combined with SECM to generate topographical as well as electrochemical activity information of graphite electrodes before and after application of a pre-charging protocol. The findings within these experiments put emphasis on the need of separating the influence of topography and electrochemical activity onto the SECM signal by hyphenation with other scanning probe techniques or other means. This is particularly important in the context of LIB research where typically topography and electrochemical activity of the active electrode material change simultaneously.

The proposed dual-probe approach on SECM/SICM is highly versatile, also enabling hyphenated use of other SPM probes, due to its modular nature. Furthermore, in contrast to a theta-capillary approach, an exchange of defective individual probes is possible. Last, but not least, it is simple to use, with the adjustment of the probe tips being the most complicated step in the setup installation. Then again, the displacement between the active areas of the probe tips limits the application of the dual-probe approach in the achievable resolution. Nanoscale investigations would only be feasible by significant reduction of probe sizes, which in turn would result in highly fragile probes and problems in the tip adjustment. In this regard, an approach with several SPM functions in a single probe would be more straightforward. Nevertheless, the presented SECM/SICM method has the potential to deliver new insights into several LIB related topics. Especially the investigation of industrial type of electrode material with distinct surface topography, as the employed Customcells graphite electrode, is a promising research area. Moreover, studies on novel, promising electrode materials which exhibit significant volume changes during lithium (de-)intercalation, e.g. Si-based electrodes,[30] could benefit from simultaneous SECM/SICM mappings.

Experimental Section

Chemicals and Materials

Dimethyl carbonate (DMC, anhydrous, ≥99%), ethyl methyl carbonate (EMC, 99%), ethylene carbonate (EC, anhydrous, 99%), ferrocene (Fc, 98%), ferrocenium hexafluorophosphate ($FcPF_6$, 97%), and lithium hexafluorophosphate ($LiPF_6$, battery grade, ≥99.99%) were purchased from Sigma–Aldrich (St. Louis, USA). Platinum wire ($r = 6.25$ μm, 99.99%) and platinum wire ($r = 0.25$ mm, 99.99%) were purchased from Advent Research Materials (Oxford, UK) and Goodfellow (Huntingdon, UK), respectively. LIB graphite electrodes (Product ID 11124) were purchased from Customcells (Itzehoe, Germany). Lapping film sheets with particle sizes ranging from 0.1 to 5 μm were purchased from Precision Surfaces International (Houston, USA).

All experiments were conducted in a solution of 1.5 mM Fc dissolved in a mixture of EC:EMC (30:70 by wt.) containing 0.1 M $LiPF_6$. SICM probes and reference electrodes were prepared 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 by wt.). DMC was used to rinse probes and the electrochemical cell between measurement sessions.

SECM and SICM Probe Fabrication

SECM probes were fabricated from soda-lime glass capillaries and platinum wire ($r = 6.25$ μm, 99.99%). The tips of the probes were treated with a custom-made polishing device equipped with lapping film sheets with particle sizes ranging from 0.1 to 5 microns. Regular SECM measurements were performed with a flat probe tip. For SICM-SECM hybrid measurements, the tip of the SECM probe was polished at a 15 degree angle countering the effect of the tilted position in the dual-probe holder. SICM probes were fabricated from soda-lime glass capillaries. Opening diameters of 10 to 30 μm were achieved by defined polishing of the tip. The capillaries were then filled with electrolyte solution (EC:EMC, 30:70 by wt., 0.1 M $LiPF_6$, 1.5 mM Fc, 1.5 mM $FcPF_6$), and a platinum wire

($r = 0.25$ mm, 99.99%) was inserted. A detailed description of the probe fabrication can be found in the supporting information, section SI-1.

Experimental Setup

Experiments and procedures were conducted in an Argon-filled glovebox. Furthermore, the SECM setup was placed on a dampening mat inside a custom-made Faraday cage.

Measurements were conducted with a SECM 920 C system from CH Instruments (Austin, USA) equipped with an electrochemical cell made from polytetrafluoroethylene. Working electrode channel 1 was connected to the SECM probe or to the graphite sample during the pre-charging protocol, respectively. Channel 2 was connected to the SICM probe. As a reference electrode, a platinum wire inserted into a glass tube with a ceramic frit and filled with electrolyte solution (EC:EMC, 30:70 by wt., 0.1 M $LiPF_6$, 1.5 mM Fc, 1.5 mM $FcPF_6$) was used. Auxiliary electrode was a platinum wire. These reference and auxiliary electrodes were utilized in all experimental procedures. Potentials stated within this work were measured with this electrode setup and recalculated to a Li/1 M Li^+ reference system based on the open circuit potential of the Fc/Fc^+ reference of +3.274 V vs. Li/1 M Li^+. A schematic and more instrumental details of the setup are supplied in the supporting information, section SI-2.

Hybrid SECM/SICM measurements were possible due to the use of two probes at once. This was achieved by an in-house built dual-probe holding system shown in Figure 6. The probe holder was made from polyether ether ketone. Two probes could be mounted and installed in the SECM setup at once. In this approach, one probe is installed at a 15 degree angle, which allowed the positioning of both tips in close proximity to each other. The SECM probe was installed in the tilted position and therefore also polished at a 15 degree angle as described before. The distance between the active tip parts (micro disk electrode and capillary orifice) was estimated to be approximately 250 μm by inspection with an optical microscope. The probe holding system is described in more detail in the supporting information, section SI-3.

Two different samples were investigated. As a model substrate in the development of the SICM method, a micro milled copper circuit board was used. Channels with a width of 200 μm were milled into the substrate's surface. Hybrid SECM/SICM measurements were performed with LIB graphite electrodes from Customcells. Samples with a diameter of 4 mm were obtained from a larger foil using a punching iron. For measurements, the small sample was placed on a sample holder made from polyether ether ketone and installed in the electrochemical cell. Microscopic images and surface roughness parameters of the graphite electrode samples were obtained from a VK-X3000 3D laser scanning microscope from Keyence (Neu-Isenburg, Germany).

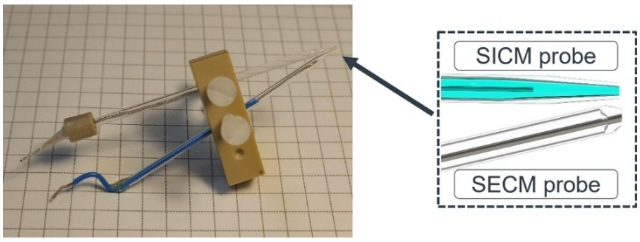

Figure 6. SECM/SICM dual-probe assembly utilized in the experiments. Photograph of the in-house built dual-probe holder with installed SECM and SICM probes and scheme highlighting the probe tip positioning. The distance between the SECM probe micro disk electrode and the opening of the SICM capillary is approximately 250 μm.

Experimental Procedures

For experiments, the samples were installed in the electrochemical cell, which was filled with 5 ml of mediator solution (1.5 mM Fc and 0.1 M $LiPF_6$ in EC:EMC). Within a measurement session, solvent evaporation, essentially the EMC component, takes place. For the typical duration of a session, the changes were in an acceptable range. The slight signal increase of bulk current resulting from the concentration increase of Fc was considered in the results. Levelling was achieved by subsequent probe approach and probe scan curves (PSC) until the substrate tilting was sufficiently corrected for imaging experiments.

Initially, a suitable potential bias of the SICM probe was determined with chronoamperometric measurements. Potential biases of 3.174 V, 3.374 V, and 3.474 V were applied to the SICM electrode, and the current signal was recorded for 15 min. In the proof-of-concept SICM experiments, PACs and images were recorded with a potential of 3.374 V. Quiet time before start of current recording was 15 s. PACs were conducted with a maximum approach speed of 10 $\mu m\,s^{-1}$. Images were recorded with a scan speed of 200 $\mu m\,s^{-1}$, pixel size was 10 μm, and an area of 1000×1500 μm was covered. The SICM probe tip had an opening diameter of 30 μm and a total tip diameter of 150 μm. During imaging, the SICM tip was positioned at a constant height, corresponding to a normalized tip current of 0.7 at the starting point of the measurement.

Prior to the hybrid measurements, the SECM/SICM dual-probe assembly was carefully adjusted under a digital microscope camera. The correct adjustment was verified by PACs towards the sample surface until a satisfactory signal change in both SPM techniques was achieved. In the simultaneous SECM/SICM experiments, PACs and images were recorded with a probe potential of 3.374 V (SICM) or 3.574 V (SECM), respectively. Quiet time before start of current recording was 15 s. PACs were conducted with a maximum approach speed of 10 $\mu m\,s^{-1}$. Images were recorded with a scan speed of 100 $\mu m\,s^{-1}$, pixel size was 5 μm and an area of 500×1000 μm was covered. The SICM probe tip had an opening diameter of 20 μm and a total tip diameter of 100 μm. The SECM tip had a total tip diameter of approximately 90 μm and a micro disk diameter of 12.5 μm. During imaging, the probe tips were positioned at a height of approximately 7 μm above the surface at the imaging starting point.

After the initial morphology and electrochemical activity mapping of the pristine sample, the connection of WE1 was changed from the SECM probe to the graphite electrode and the pre-charging protocol was started. This procedure applied to the graphite electrode samples was adapted and modified from similar experimental conditions reported in literature.[9–11] It consisted of a linear potential sweep from 3.274 to 1.274 V with a scan rate of 1 $mV\,s^{-1}$ followed by cycling in the potential range of 1.274 to 0.040 V with a scan rate of 1 $mV\,s^{-1}$ for two full cycles.

Subsequently, following the completion of the pre-charging protocol, WE1 was connected to the SECM probe again and hybrid SECM/SICM measurements with identical parameters than before pre-charging were conducted.

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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.

Keywords: Electrochemistry · Interfacial Studies · Lithium-Ion Batteries · Scanning Probe Microscopy · Solid Electrolyte Interphase

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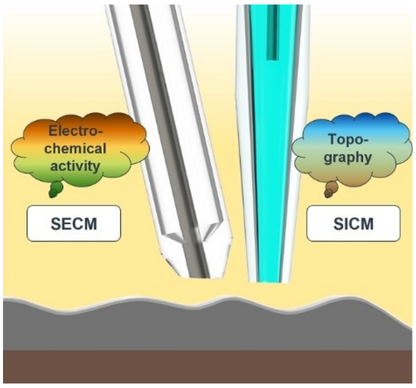
RESEARCH ARTICLE

Hyphenated scanning electrochemical (SECM) and ion conductance microscopy (SICM) in the context of lithium-ion battery (LIB) research is introduced. It represents a powerful approach to generate information about the electrochemical activity and the topography of substrates at the same time. The applicability is showcased with the investigation of a LIB graphite electrode before and after application of a pre-charging protocol.



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Simultaneous Scanning Ion Conductance and Electrochemical Microscopy in Lithium-Ion Battery Research