Supporting Information

Correlative Electrochemical Microscopy for the Elucidation of the Local Ionic and Electronic Properties of the Solid Electrolyte Interphase in Li-Ion Batteries

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S-1. Electrochemical measurements.
All measurements were performed inside an Ar-filled glove box (Jacomex), and the electrochemical measurements were carried out in a three-electrodes coaxial electrochemical cell, in which the working electrode is placed in the centre of the cylindrical counter electrode,[1] and the reference electrode is positioned in the external area of the cylindrical counter electrode.[2] Model anodes (Cu metal) for the SEI formation and a Pt disk microelectrode (platinum wire diameter: 25 µm, Goodfellow) for SECM measurements were used as working electrodes. All potential values are referred to a reference electrode composed of metallic Li (ribbon 99.9%, Sigma Aldrich) inserted in a reservoir separated from the electrochemical cell by a ceramic frit. The reference electrode reservoir was filled with an electrolyte similar to that in the electrochemical cell for the SEI formation procedure and for the FB- and AC-SECM measurements, namely a 1 M LiClO₄ and EC:PC (50/50 wt%) solution. The counter electrode consisted of a cylindrical titanium mesh (Alfa Aesar) coated with carbon nanotubes (CNTs) using polyvinylidene difluoride (PVDF) as binder with a weight ratio of 80/20 (wt). The SECM positioners and the potentiostat (Autolab PGSTAT 302N) were controlled by an in-house programmed software. Electrolytes were prepared using battery-grade chemicals, and all chemicals were stored inside the glove box. For the evaluation of the role of the electrolyte composition of the SEI properties, the SEI was prepared using the salts lithium perchlorate (LiClO₄, 99.99% dry, CAS 7791-03-9, Sigma Aldrich) or lithium hexafluorophosphate (LiPF₆, dry, CAS 21324-40-3, Novolyte) dissolved in the mixture of ethylene carbonate (EC, anhydrous, CAS 57-71-6, Sigma Aldrich) and propylene carbonate (PC, CAS 7664-93-9, Sigma Aldrich) in a ratio of 50/50 wt%. The lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate (1.0 M LiPF₆ in EC:DMC 50/50 (v/v), Sigma Aldrich) was employed in the evaluation of solvent composition. All SECM studies were performed in LiClO₄ in EC:PC electrolyte solution. In feedback-mode SECM ferrocene (Fc, CAS 538-75-0, 98%, Sigma Aldrich) was added as redox mediator with a final concentration of 10 mM in 1 M LiClO₄ and EC:PC (50/50 wt%) electrolyte solution. AC-SECM measurements were performed in 1 mM LiClO₄ and EC:PC (50/50 wt%) electrolyte solution.

S-2. SECM tip characterization.
Disk-shaped microelectrodes are used as SECM tips because of the easier mathematical modelling and available fabrication methods. In conditions where faradaic processes are important, mass transport for microdisk-shaped electrodes occurs mainly by radial diffusion. If the overall electrode process is mass-transport controlled, the current intensity reaches steady-state condition. Literature reports several mathematical expressions for describing the approach curves in the positive and negative feedback modes. Those expressions are employed to describe the tip current as a function of the distance between tip and substrate. The first mathematical description was reported by Kwak and Bard,[3] followed by Amphlett and Denuault,[4] who proposed theoretical approach curves for some determined RG values. Lefrou and Cornut proposed mathematical expressions with the RG as a parameter, and one can obtain theoretical approach curves for positive feedback and hindered diffusion modes.[5] The experimental data can be then fitted by using such equations to determine the geometrical parameters of the tip, such as the electrochemically active area and the radius of the insulating glass wall of the tip. The SECM tip was characterized by performing approach curves in the presence of a redox mediator (10 mM Fc in the electrolyte solution). Approach curves towards a conducting and a flat insulating surface were recorded, and the experimental data were fitted with a theoretical fit (Figure S1). Currents were normalized by the bulk value, whereas the distance (d) in the vertical direction (d) was normalized by the disk-shape radius (r). The microelectrode had a platinum disc radius of 12 µm and a glass wall radius of 70 µm. The deviation from the experimental data to the theoretical fit in the approach curve was used to estimate the minimum vertical distance the tip can be positioned close to the flat surface, and the minimal approach distance value was around 2 µm.

Figure S1. Approach curves for ferrocene oxidation towards a Cu surface (blue dots) and glass slide (black dots). Scatter plot: experimental data. Red straight lines: calculated fit approach curves for a UME with radius = 12.2 µm and RG = 6 for a insulating surface (γ = 0) and conductive surface (γ = ∞).[5-6] Measurement recorded in 10 mM ferrocene (Fc), 1 M LiClO₄ and EC: PC (50/50 wt%). Etip: 3.5 V vs. Li/LiClO₄ frit. Scan increment: 1 µm. Approach curve speed: 10 µm/s.
S-3. Description of the model sample surface and SEI formation procedures.

A model battery electrode sample was selected to reduce the complexity of the evaluation of the electrode surface and to facilitate the development and validation of the technique for investigating SEI defects on battery electrodes. Therefore, flat copper or glassy carbon surfaces were selected as model anode surfaces to form the SEI. In the case of the copper surface, the samples were prepared by exposing the Cu surface of a printed circuit board, PCB, copper thickness 35 µm, Bungard, which was achieved by removing the photoresist polymer layer with acetone. The freshly exposed Cu surfaces were immediately inserted into the glove box to avoid oxidation. Nonetheless, minor partial oxidation cannot be ruled out. The glassy carbon (GC) surface was polished before being assembled in the electrochemical cell. A Cu tape was used as electrical connection with the potentiostat connector. The successful connection between the copper tape and the model sample surface was confirmed using a multimeter, and the resistance was 0 Ω. The sample was used as working electrode in the electrochemical cell, and the compartment was filled with the electrolyte solution. The geometric area of the sample exposed to the solution was around 0.385 cm². The two SEI formation procedures contained three steps of the potential program, schematically shown in Figure S2 (A). First a linear sweep voltammogram was recorded at 1 mV s⁻¹ from the OCP to 0 V vs. RE. In the second step, the potential was held at the cut-off SEI formation potential (e.g. 0 V, or 100 mV, or 200 mV) during i) 12 h (long-term) or ii) 1 h (short-term). As the last step, a linear sweep voltammogram was performed from 0 V to 1.5 V at 1 mV s⁻¹. Note the distinction between the two protocols was just during the second step. The third step was scanning the potential back from the cut-off formation potential to 1.5 V. As control measurement, a last linear sweep voltammetry scan enabled us to detect potential Li deposition by the presence or absence of a cathodic Li stripping peak at 0.1 V.

The evaluation of the two proposed protocols for the formation of the SEI were conducted using the copper surface and 1 M LiClO₄ and EC: PC (50/50 wt%) electrolyte. Furthermore, the short-term protocol (protocol ii) was employed to investigate the role of the electrolyte composition on the properties of the SEI by forming SEIs using different electrolyte composition and current collector material. For these experiments, SEI was formed using 1 M LiClO₄ in EC: PC (50/50 wt%), 1 M LiPF₆ in EC: PC (50/50 wt%) or 1 M LiPF₆ in EC: DMC (50/50 v/v) solution. A summary of parameters applied to the SEI formation in the study is shown in Table S1, and the linear sweep voltammograms were shown in Figure S2 (B)-(I).

Table S1. Summary of data plots and experimental parameters for the SEI formation procedure.

| Data plots in Figures S2 | Data plots in Figures S4 – S8 | Current collector | Electrolyte composition for SEI formation procedure | Potential program for the SEI formation procedure | cut-off potential during SEI formation |
|-------------------------|-----------------------------|------------------|-----------------------------|---------------------------------|-----------------------------|
| (B)                     | (A)                         | Copper           | 1 M LiClO₄ and EC: PC (50/50 wt%) | Long-term, Protocol i           | 0 mV                        |
| (C)                     | (B)                         | Copper           | 1 M LiClO₄ and EC: PC (50/50 wt%) | Short-term, protocol ii         | 0 mV                        |
| (D)                     | (C)                         | Copper           | 1 M LiPF₆ in EC: PC (50/50 wt%) | Short-term, protocol ii         | 0 mV                        |
| (E)                     | (D)                         | Copper           | 1 M LiPF₆ in EC: DMC (50/50 v/v) | Short-term, protocol ii         | 0 mV                        |
| (F)                     | (E)                         | Copper           | 1 M LiPF₆ in EC: DMC (50/50 v/v) | Short-term, protocol ii         | 100 mV                      |
| (G)                     | (F)                         | Copper           | 1 M LiPF₆ in EC: DMC (50/50 v/v) | Short-term, protocol ii         | 200 mV                      |
| (H)                     | (G)                         | Graphite         | 1 M LiPF₆ in EC: DMC (50/50 v/v) | Short-term, protocol ii         | 0 mV                        |
| (I)                     | (H)                         | Glassy Carbon    | 1 M LiPF₆ in EC: DMC (50/50 v/v) | Short-term, protocol ii         | 0 mV                        |
Figure S2. (A) Representative potential profile protocols i) and ii) used to form the SEI. (B)-(F) Linear sweep voltammograms recorded in the first step (black line) and during the third step (red curve) of the SEI formation procedure using (B) protocol i) and (C)-(F) ii). Parameters such as current collector, cutoff potential and electrolyte composition are summarized in Table S1.
S-4. Topographic map of the copper plating surface with SEI.

Figure S3. AFM surface scans of the bare copper surface (A) and the cross-section (B) of the lined indicated in (A). Average roughness: 217.2 nm, RMS roughness Rq: 273.3 nm. Peak-to-valley roughness Rt: 1.380 µm. AFM surface scan (C) and the cross-section (D) of the SEI covered copper surface with a scratch made by a tweezer (PTFE) on the SEI.
S-5. FB-SECM image and sequences of approach curves in one lateral direction (line scan).

All SECM measurements were performed using the fresh formed SEI as sample. After the SEI formation, the coaxial cell was disassembled and reassembled after moving the SEI-modified Cu area in such a way that two distinctly different surface regions are later exposed to the electrolyte, i.e. an area of bare Cu and an adjacent SEI-covered area. FB-SECM images were obtained by the normalization of the steady-state tip current measured at two working distances (perpendicular to the surface or Z-direction) in sequence at each X-, Y-position (pixel) of the rectangular scanning grid. The two working distances were 5 µm, the distance at which the SECM tip response is modulated by the sample, and 200 µm, the distance in the bulk of the solution where no tip-sample interaction is expected. The SECM images present the normalized current $I_{5\mu m}/I_{bulk}$ at each pixel in the Figure 1 in the main manuscript. The lateral increment was 100 µm for mapping a large area in the FB-SECM images. The SECM tip was polarized at 3.5 V vs RE, while the model battery surface was unbiased during the measurements. After acquiring the FB-SECM image, a sequence of FB-mode approach curves was carried out after displacement of the tip position in the X- or Y-direction with a higher lateral resolution than the SECM image. An approach curve is the measurement of the SECM tip current while the tip is moved in vertical direction (d) towards the sample surface. The approach curves were recorded in sequence (tip scanned first in vertical -direction) and then moved to the lateral direction (X- or Y-) for the subsequent approach curves. The line scan crossed the SEI-free surface region to the SEI-covered region known from the FB-SECM image (see schemes in the top in Figure S4). The tip was moved with steps of 1 µm in d-direction during the approach curve and at each 50 µm step size in the line scan in X- or Y-direction (depending on the experiment). The recorded curves are shown in Figure S4; the parameters of the SEI formation are presented in Table S1. The calculated fit approach curves were plotted as straight line and dimensionless kinetics $\kappa$ values for some curves are presented in the caption. The $\kappa$ values are the dimensionless parameter of the first order kinetics constant, $k$ (m s$^{-1}$) and the $\kappa$ is described by the Equation S1.

$$\kappa = \frac{D \cdot k}{a} \quad \text{Equation S1}$$

A plot of the sequences of approach curves as a function of the lateral position, called here a 3-D approach curves plot in the d- and lateral (x- or y-) directions as the $\kappa$ values are plotted in Figure 3 of the main manuscript.
Figure S4. (A)-(H) Schemes (top) indicate the regions where the FB-SECM approach curves were recorded at each FB-SECM image. The sequence of approach curves at each lateral position is shown in the graphics (bottom). Straight line: calculated fit approach curves (UME radius = 12.2 µm and RG = 6) in function of dimensionless $\kappa$ values: line 1 $\kappa = 100$ (conductive sample); line 2 $\kappa = 0.6$; line 3 $\kappa = 0.3$; line 4 $\kappa = 1.5$; line 5 $\kappa = 0.1$; line 6 $\kappa = 0.02$ (inert insulating sample); line 7 $\kappa = 1$. The measurements were recorded from an SEI-free region to an SEI-covered region. Sample parameters are summarized in Table S1. $E_{tip}$: 3.5 V vs RE.
S-6. Global measurements on graphite.

The electrochemical global analysis of a graphite rod surface was performed to confirm the advantages of the local SECM measurements to detect the presence of defects or SEI heterogeneity. The current collector was exchanged to graphite due to the unavoidable Cu oxidation process in the potential range of the Fc oxidation. The graphite rod was polished and placed inside the argon-filled glovebox and assembled as WE in the electrochemical cell as described in the section S-1. An EIS at OCP and a cyclic voltammogram were recorded in 10 mM Fc and 1 M LiClO₄ and EC: PC (50/50 wt%). Afterwards, the cell was filled with 1 M LiPF₆ in EC: DMC (50/50 v/v) solution and the SEI was formed according to the parameters in the Table S1. FB and AC SECM experiments were registered right after the SEI formation and the SECM image is shown in Figure 3 in the main manuscript, while the quantitative FB and AC SECM measurements are shown in Figure S-10. The EIS and cyclic voltammogram (red data in Figure S5) of the SEI-covered surface were carried out after the SECM measurements to avoid polarization of the SEI-covered sample and a concomitant possible modulation of the SEI properties caused by anodic polarization of the samples during global measurements.

Figure S5. Global measurements performed by polarizing the pristine graphite surface (black data) and the covered-SEI graphite (red data). (A) Nyquist plot of the EIS measurement performed at OCP in the frequency range from 100 kHz to 100 mHz, and (B) CVs in the presence of Fc. Both EIS and CV measurements were carried out in 10 mM Fc and 1 M LiClO₄ and EC: PC (50/50 wt%).
S-7. Verification of tip integrity during the FB-SECM measurements.

The integrity of the tip was evaluated by recording cyclic voltammogram in the bulk position before and after each experiment in presence of the redox mediator (Figure S6).

Figure S6. (A)-(H) Cyclic voltammograms were performed in 10 mM Fc and 1 M LiClO₄ and EC: PC (50/50 wt%) before (black curves) and after (red curves) FB-SECM experiments. v: 10 mV/s. Tip was positioned in the bulk of the solution. Table S1 summarizes the parameters of the data set.

S-8. Nyquist plot of the EIS data recorded in the bulk electrolyte and at the working distance of 5 μm.

AC-SECM experiments were recorded in 1 mM LiClO₄ in EC: PC (50/50 wt%). A localized impedance spectrum was recorded at each lateral position (x- or y-) in the same region where the sequence of FB approach curves was previously recorded. The sequence of EIS was recorded at two working distances before moving to the next lateral pixel. At first, the tip was positioned in bulk for recording the bulk EIS spectrum (Figure S7), and then the tip was moved in vertical direction (d) towards the sample surface to record another EIS spectrum at a working distance of 5 μm (Figure S8). Afterwards, the tip was moved laterally (x- or y-) with an increment of 50 μm. The tip was kept at OCP for signal stabilization until the potential drift was below 1 mV s⁻¹, then a sinusoidal potential with an AC amplitude of 10 mV peak-peak was applied at the average OCP potential value. The EIS frequency range was set from 150 kHz to 500 Hz, and 30 frequencies per decade with 100 integration cycles. Lower frequencies were avoiding due to the long time for acquisition considering integrity of the tip.
Figure S7. (A)-(H) A sequence of Nyquist plots while scanning the tip in lateral (x- or y-) direction with a lateral resolution of 50 µm. EIS spectra were recorded using a Pt microelectrode (disk-diameter: 25 µm) positioned in the bulk of the electrolyte. Measurements were carried out in 1 mM LiClO4 EC:PC (50/50 wt%) as electrolyte solution. DC potential: OCP. AC bias: 10 mV (rms). f: 150 kHz to 500 Hz. Sample parameters are summarized in Table S1. Schemes at the top of graphics in Figure S4 indicate the regions where the tip was scanned.
Figure S8. (A)-(H) The sequence of EIS spectra while scanning the tip in lateral (x- or y-) direction with a lateral resolution of 50 µm. EIS spectra were recorded using a Pt microelectrode (disc-diameter: 25 µm) positioned at the working distance of 5 µm over the sample surface. Measurements were carried out in 1 mM LiClO₄ EC: PC (50/50 wt%) as electrolyte solution. DC potential: OCP. AC bias: 10 mV (rms). f: 150 kHz to 500 Hz. Sample parameters are summarized in Table S1. Schemes on the top of graphics in Figure S4 represent the scanned regions.

S-9. Modelling of local EIS response.

All localized EIS data recorded at the tip at different regions of the sample were fitted based on a circuit model described before. Data were processed (Kramers-Kronig test, equivalent electrical circuit fitting and calculation) with a homemade program. For the tip response contribution, a constant phase element (CPEt) was used to represent the double contribution of the Pt microelectrode surface, while a RC element was used to model the possible organic thin layer on the tip surface (RtCt). The tip-sample interaction was represented by an RC element, where Cₕ and Rₕ were, respectively, the double-layer capacitance and the ionic charge transfer resistance of the local sample surface. The EIS spectra obtained in the bulk of the solution were used to deconvolute the tip contribution on the overall response at short working distance.
S-10. Local ionic charge transfer resistance and double layer capacitance over SEI-free and SEI-covered regions.

**Figure S9.** FB-SECM and AC-SECM measurements at the interrogated area covering the SEI formed on graphite (A) and glassy carbon (B). Left Y-axis: calculated $R_s$ values distribution obtained by local EIS measurements at a working distance of 5 µm in the multi-frequency AC-SECM measurements. Right Y-axis: dimensionless parameter of the first order kinetics constant, $k$ (m s$^{-1}$), calculated fit at each approach curve. Right Y-axis: vertical/perpendicular distance of the 3D-plot of the FB approach curves, $d$, in function of lateral distance (x- or y-). Colored background scale: normalized current map in the 3D-plot of the sequence of approach curves as a function of the lateral position, with a perpendicular increment of 1 µm and a lateral increment of 50 µm. $E_{cut-off}$: 3.5 V vs RE.
Figure S10. Plots of the information obtained from FB-SECM and AC-SECM measurements at the interrogated area covering the SEI-free (left) and SEI-covered (right) regions. (A)-(I) Left Y-axis: calculated sample capacitance, $C_s$ values, distribution over the lateral scan obtained by EIS measurement at a working distance of 5 µm in the multi-frequency AC-SECM measurements. (A)-(I) Right y-axis: vertical/perpendicular distance of the 3D-plot of the FB approach curves, $d$, in function of lateral distance (x- or y-). (A)-(I) Colored background scale: normalized current map in the 3D-plot of the sequence of approach curves as a function of the lateral position, with a perpendicular increment of 1 µm and a lateral increment of 50 µm. $E_{\text{tip}}$: 3.5 V vs RE.
S-11. Estimation of local dielectric permittivity ($\varepsilon$) and resistivity ($\rho$).

The dielectric permittivity and resistivity of the SEI were estimated using the mean values of the resistance $R_s$ and the capacitance $C_s$ (Figure 3 in the main manuscript and Figure S8) when the tip was over the SEI. The thickness, $l_{SEI}$, of the SEIs were assumed as 50 nm. The estimated ionic resistivity of the SEI, $\rho$, was determined using Equation S2, where $R_{SEI}$ is the mean value of the ionic charge transfer resistance of the SEI, $A$ is the area, here assumed with the local area of the tip-sample interaction (disc-shape platinum microelectrode radius: 12.5 $\mu$m). While the dielectric permittivity was calculated through the parallel plate capacitor equation, Equation S3, where $C_{SEI}$ is the mean value of the double-layer capacitance of the SEI and the $\varepsilon_0$ is the vacuum permittivity ($8.85 \times 10^{-12}$ F.m$^{-1}$).

Values are shown in Table S2.

\[
\rho = \frac{R_{SEI} \cdot A}{l_{SEI}} \quad \text{Equation S2}
\]

\[
\varepsilon = \frac{l_{SEI} \cdot C_{SEI}}{\varepsilon_0 \cdot A} \quad \text{Equation S3}
\]

Table S2. Estimated permittivity ($\varepsilon$) and ionic resistivity ($\rho$ / mΩ m) for SEIs with thickness $l_{SEI}$ assumed as 50 nm.

| Electrolyte composition for SEI formation/ current collector | Mean $C_{SEI}$ / pF | Estimated $\varepsilon$ | Mean ionic $R_{SEI}$ / Ω cm$^2$ | Estimated ionic $\rho$ / mΩ m |
|------------------------------------------------------------|---------------------|------------------------|-------------------------------|-------------------------------|
| 1 M LiClO$_4$ and EC:PC (50/50 wt%)/ Cu $^i$               | 25.2                | 289.4                  | 2.85                          | 28.0                          |
| 1 M LiClO$_4$ and EC:PC (50/50 wt%)/ Cu $^ii$              | 28.4                | 326.9                  | 0.57                          | 5.6                           |
| 1 M LiPF$_6$ in EC:PC (50/50 wt%)/ Cu $^i$                 | 39.7                | 456.8                  | 2.89                          | 28.4                          |
| 1 M LiPF$_6$ in EC:DMC (50/50 v/v)/ Cu $^i$                | 44.1                | 507.6                  | 0.63                          | 6.1                           |
| 1 M LiPF$_6$ in EC:DMC (50/50 v/v)/ GC $^i$                | 38.7                | 445.4                  | 1.67                          | 18.4                          |

$^i$ SEI formed using the protocol $i$ (long-term procedure)

$^ii$ SEI formed using the protocol $ii$ (short-term procedure)

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Author Contributions.

CSS conceptualization, data curation, formal analysis, investigation, methodology, writing - original draft, editing. AB methodology ASB formal analysis, data curation, investigation, writing – review and editing. EV conceptualization, methodology, writing – review and editing, project administration. WS conceptualization, methodology, writing – review and editing, funding acquisition, project administration.