Supporting Information

Understanding surface reactivity of Si electrodes in Li-ion batteries by *in-operando* scanning electrochemical microscopy

E. Ventosa,[a,]* P. Wilde,[a] A. Zinn,[b] M. Trautmann,[a] A. Ludwig,[b,c] W. Schuhmann[a,c,]*

Experimental Section

Preparation of the Si sample

Si samples were prepared starting from a Si wafer covered with 1.5 μm thermally grown SiO_2 which was coated with a 200 nm Cu film as current collector via magnetron sputtering (DCA) at 200 W DC in an Ar (99.9999 % pure) atmosphere of 0.66 Pa. A thin adhesion layer (Ti, ~ 10 nm) was deposited (100 W DC, 0.66 Ar) between the substrate and the Cu current collector. Prior to deposition of the Si film, an additional Ti/Cu layer was added under the same conditions in order to increase adhesion and conductivity. Finally, a 500 nm Si thin film was deposited at 100 W using a pulsed DC power supply in Ar atmosphere (99.9999 % pure) at 0.66 Pa. The coated wafer was broken into smaller pieces that could be accommodated by the electrochemical cell.

The electrochemical cell

For all experiments a home-made four-electrode open cell, whose main body was made from polyether ether ketone (PEEK), was used. [1-3] The cell contains a four electrode set-up. The Si sample acts as the first working electrode and is located at the bottom of the cell. The area exposed to the electrolyte is 0.125 cm^2. The second working electrode is an ultra-microelectrode that simultaneously acts as the tip of the SECM. A 25 μm Pt tip was used. Prior to any experiment, the UME was polished successively with Al_2O_3 or diamond slurries with particle sizes decreasing from 3 μm to 1 μm to 0.3 μm. A cylindrical stainless steel mesh 316 (*Alfa Aesar*) coated with carbon nanotubes served as a large area counter electrode. As a pseudo reference electrode, a twisted stripe of bare Li (*Sigma Aldrich*) was used.

The electrolyte solution

For the (de-)lithiation processes the electrolyte was a commercially available lithium hexafluorophosphate solution (battery grade, *Sigma Aldrich*). It contained 1 M $LiPF_6$ in ethylene carbonate : dimethyl carbonate (EC:DMC) (1:1 volume ratio) as supporting

electrolyte. The electrolyte employed for all SECM measurements was based on EC:PC (1:1 % wt.) containing 20 mM ferrocene (98% *Sigma Aldrich*) as the redox mediator and 1 M LiClO$_4$ (battery grade, dry, 99.99% *Sigma Aldrich*) as supporting electrolyte.

Optical and atomic force microscopy measurements

An optical microscope (JPK instruments) located inside the Ar-filled glovebox (Jacomex GPT4FF) was employed to record a video during the cycling using an open electrochemical cell.

AFM images of the sample after the first electrochemical cycles were taken *ex-situ* using a Nanowizard II (JPK Instruments) operating in tapping mode.
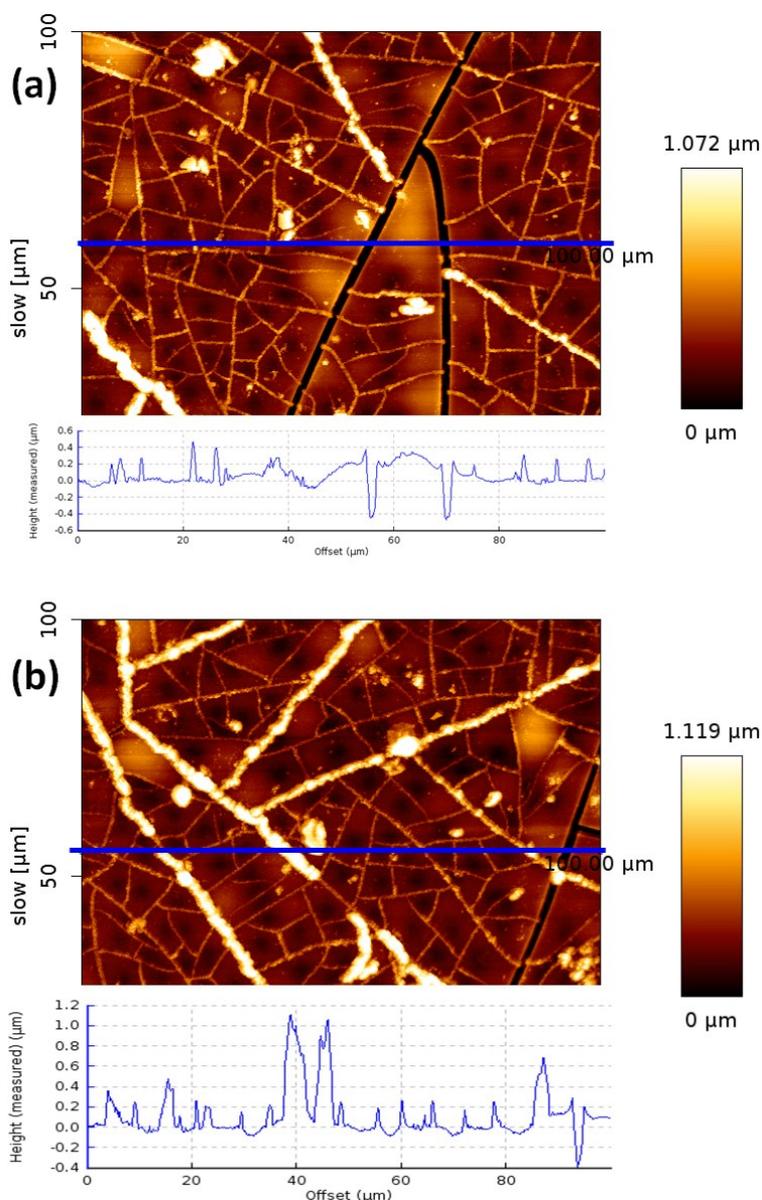
Figure S1. AFM images and their corresponding cross sections.
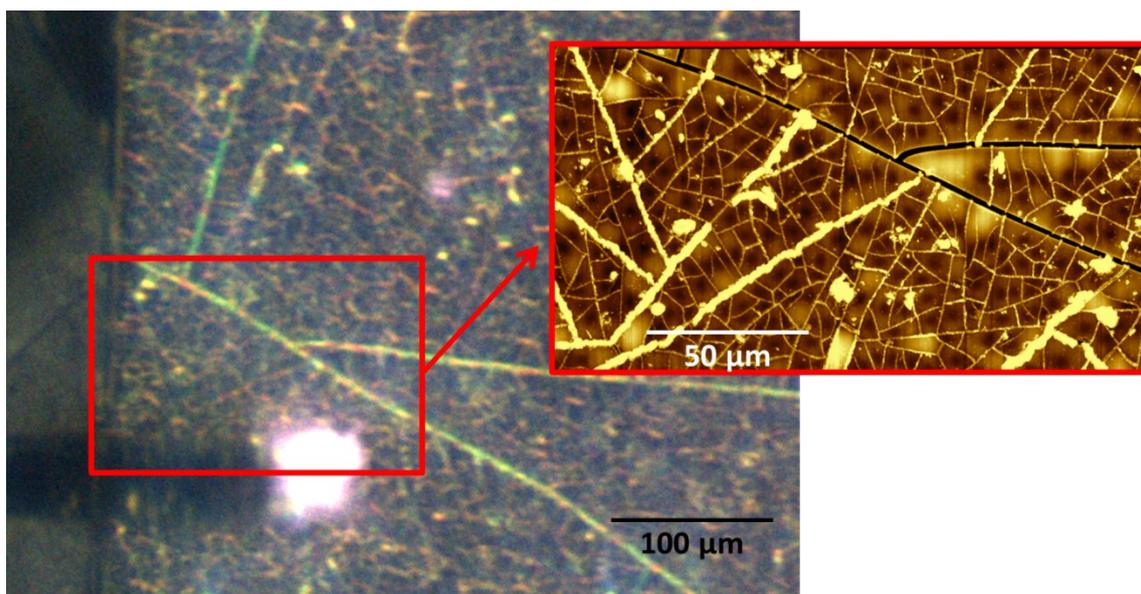
Figure S2. Image taken by optical microscopy together with its corresponding AFM image. The large cracks appearing during the delithiation and observed by optical microscopy correspond to the dark lines in the AFM image (500 nm deep cracks). The bright spot in the optical image is the laser reflecting on the cantilever of the AFM. The bar scale is 50 μm and 100 μm in the optical and AFM image, respectively. The height scale in the AFM image is 1.12 μm.

SECM measurements

Feedback mode SECM provides information about the electrochemical reactivity of a sample surface by probing the reaction rate of a free-diffusing redox mediator present in solution, through the current recorded at the SECM tip.[4] The SECM tip is positioned in close proximity to the sample surface and the measured current is a function of the tip potential and the tip-to-sample distance. In the bulk of the solution the current recorded at the SECM tip is the diffusion limiting one for the oxidation (reduction) of the redox mediator. The normalized feedback current is defined as the ratio of the current recorded at the SECM tip in close proximity of the sample surface (I_T) and the diffusion limiting recorded by the tip far away from the sample (I_{bulk}).

$$\frac{I_T}{I_{bulk}}$$

When approaching the tip to an electrochemically reactive and conductive sample surface, the normalized feedback current is higher than 1 (positive feedback). If an inert or electronically insulating sample surface is approached, the normalized feedback current recorded at the tip is lower than 1 (negative feedback).

SECM measurements were performed inside a glovebox using a custom made *Sensolytics* instrument with special positioner motors (*OWIS*). Prior to any SECM measurement the

potential for the oxidation of the ferrocene used as redox mediator at the UME had to be determined. According to the CV in Figure S3 a potential of 3.6 V vs. Li/Li$^+$ was chosen, a value at which a diffusion limited steady state for the oxidation of ferrocene was reached. In order to determine the tip-to-sample distance for the scans as well as the local SECM measurements. an approach curve was made as can be seen in Figure S4. During the approach negative feedback was observed, which is consistent with the insulating properties of the native surface layer of SiO$_x$.[5] We have prepared a new sample which was transported within an Ar-filled vessel from the sputtering chamber to the SECM glovebox. Therefore, this new sample was never in contact with air and no native SiOx layer was expected. The approach curve to the new sample (figure 2 below) shows a positive feedback, in contrast to the negative feedback observed in the previous samples. This demonstrates that the surface layer of SiOx was not formed during the preparation of the Si films

For the local measurement a distance of 12 µm was chosen and whilst the potential of the tip was held at a constant value of 3.6 V two CV cycles with a scan rate of 0.2 mV s^{-1} were carried out at the sample in the potential range between 3.0 V and 0.005 V. For the SECM images an area of 1500 µm x 500 µm and 1000 µm x 500 µm was chosen. The increment for the measurement was set at 25 µm at a scan rate of 25 µm s^{-1} with a tip to sample distance of 12 µm. The tilt of the sample was calculated using the surface normal calculated with three surface points, which were previously determined by different approach curves of the sample.
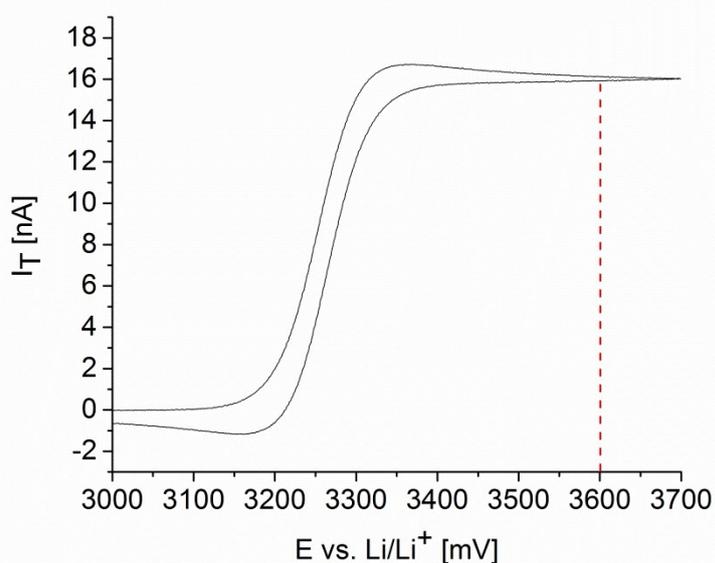
Figure S3. Cyclic voltammogram at the SECM tip immersed in the bulk of the electrolyte. A diffusion limited steady state current was reached at 3.6 V *vs.* Li/Li$^+$.

Origin of the ultrathin SiO$_x$ layer.

After preparation of the Si film, the sample was stored for few days outside the glovebox at room temperature. Si reacts spontaneously with air forming a so-called native thin surface layer of SiO$_x$ leading to the negative feedback observed in the approach curve to this sample (Figure 4).[5] To demonstrate that the SiO$_x$ layer was not formed during preparation of the Si films, one sample was transported within an Ar-filled vessel from the sputtering chamber to the SECM glovebox. Therefore, this new sample was never in contact with air and no native SiO$_x$ layer was expected. The approach curve to the new sample (Figure 4) shows a positive feedback, in contrast to the negative feedback observed in the previous samples. We expect that the thickness of the SiO$_x$ layer in our films is very thin due to two facts: I) it was spontaneously formed at room temperature and II) positive feedback was observed when the Si film was polarized below 2.65 V vs. Li/Li$^+$ (Figure 2a of the main text). The latter shows that the SiO$_x$ layer slows down the electron transfer rate but it does not passivate completely the surface as expected for thicker SiO$_x$ layer.
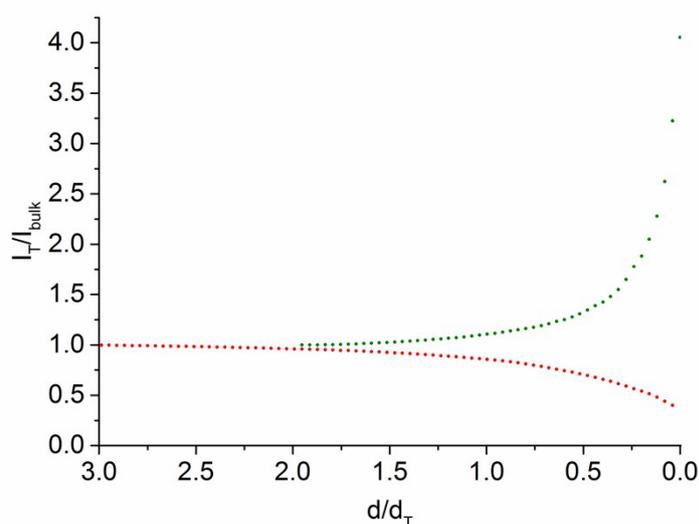
Figure S4. Approach curves to Si electrodes with (red line) and without (green line) SiO$_x$ layer. The potential of the Si electrode and tip were held at 3.0 V and 3.6 V vs Li/Li$^+$, respectively. The normalized current is plotted against the distance of the tip from the sample in μm.

References

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