Supporting information

Impact of the Crystalline $Li_{15}Si_4$ Phase on the Self-Discharge Mechanism of Silicon Negative Electrodes in Organic Electrolytes

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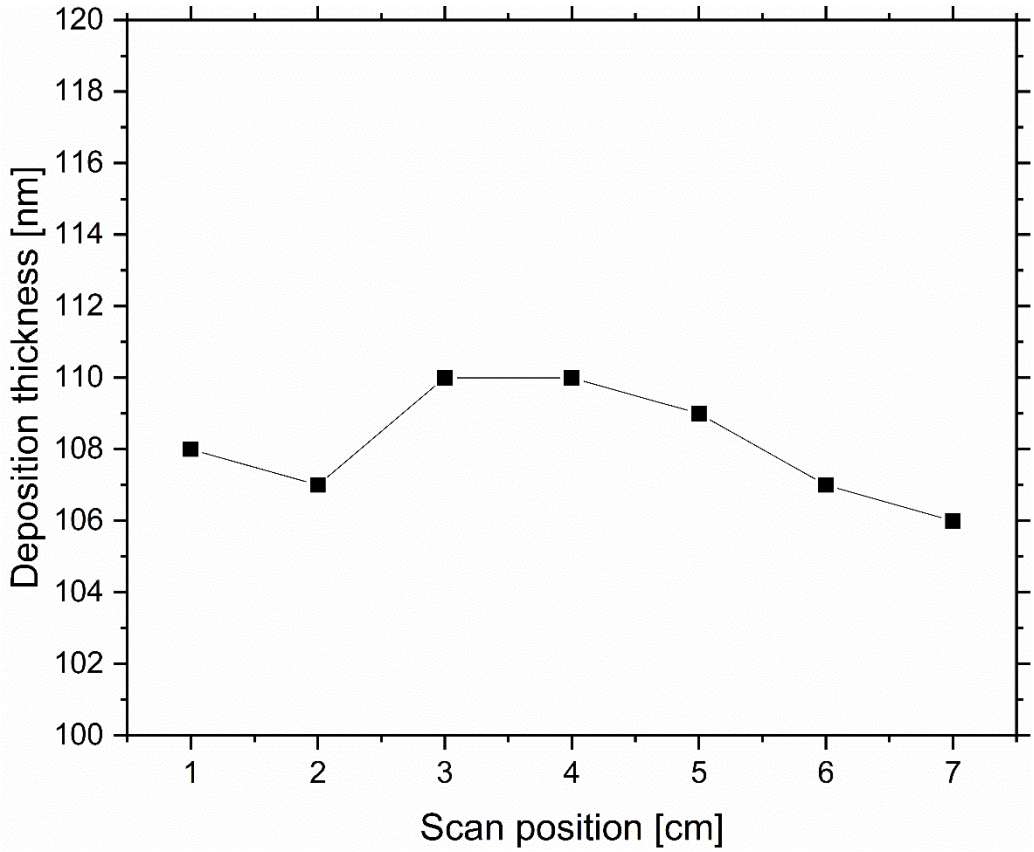

Figure S1. Thickness of the deposited Si thin film along the position of the sample holder. Thickness was calculated from the profilometer scan.

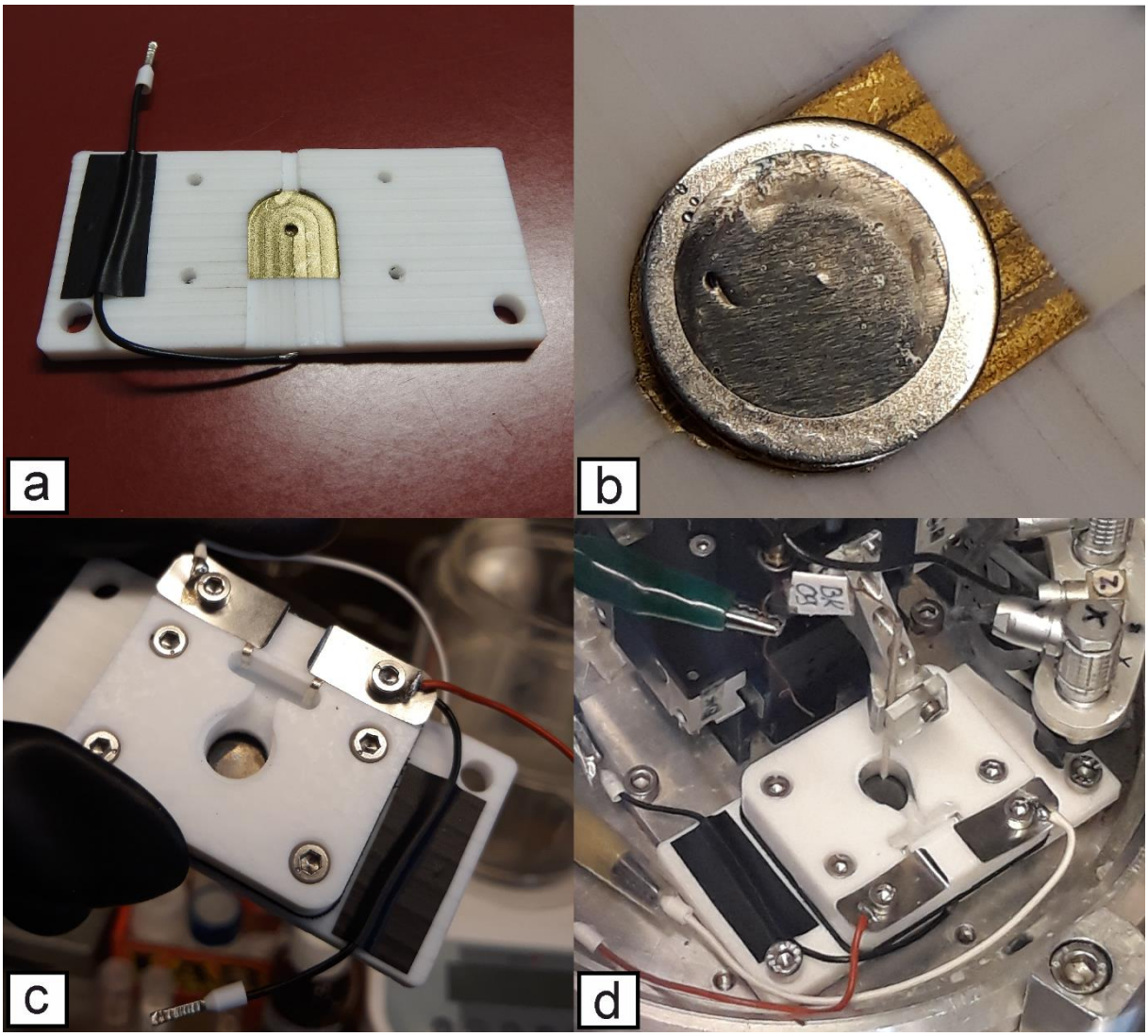

Figure S2. Photographs of the electrochemical cell setup for scanning electrochemical microscopy (SECM). (a) gold-coated lower cell part, (b) Si electrode on stainless steel support, (c) assembled and sealed cell with Li metal counter- and Li metal reference electrodes, (d) cell placed in SECM setup.

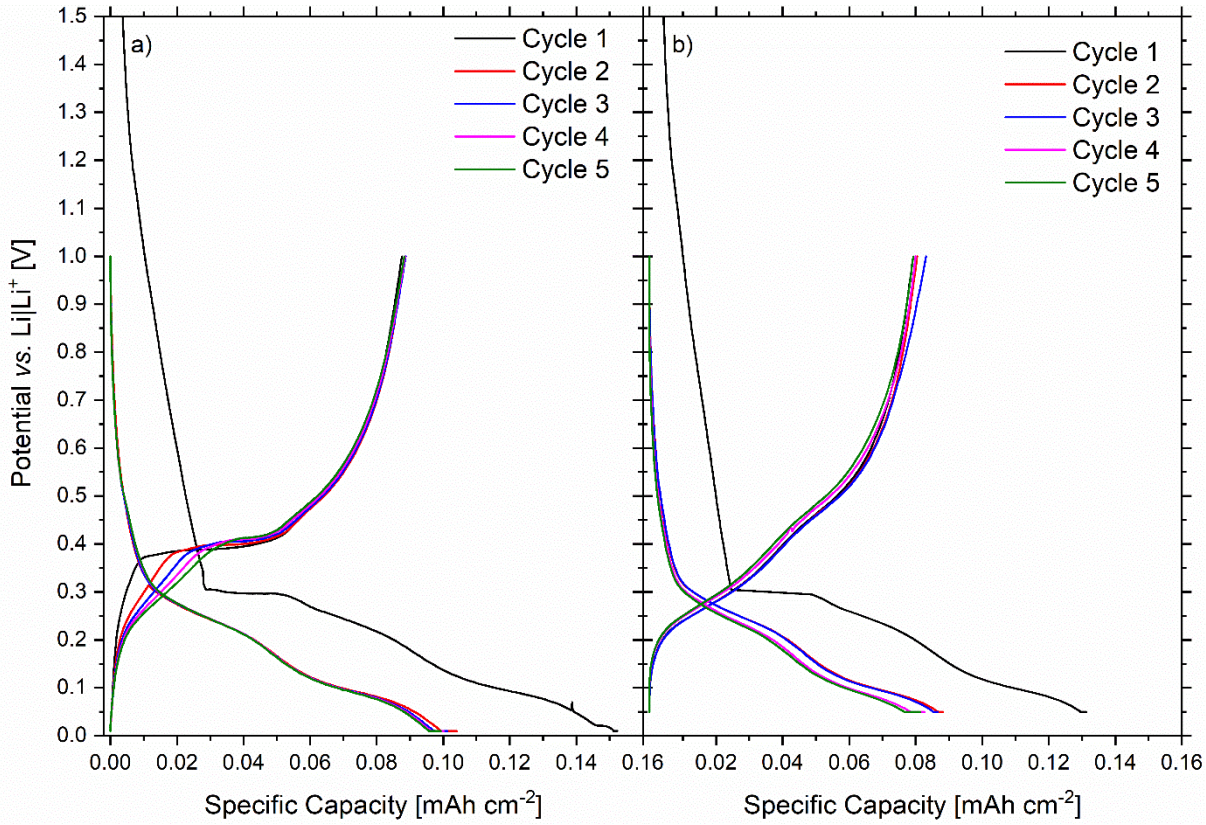

Figure S3. Potential (*vs.* Li|Li$^+$) plotted against the specific charge/discharge capacities for the first 5 cycles of Si thin film negative electrodes at different lower cut-off potentials; (a) U_{Cut} = 10 mV, (b) U_{Cut} = 50 mV *vs.* Li|Li$^+$) in Si || Li metal cells (half-cell setup, three-electrode configuration; WE: 110 nm Si; upper cut-off voltage: 1.0 V *vs.* Li|Li$^+$).

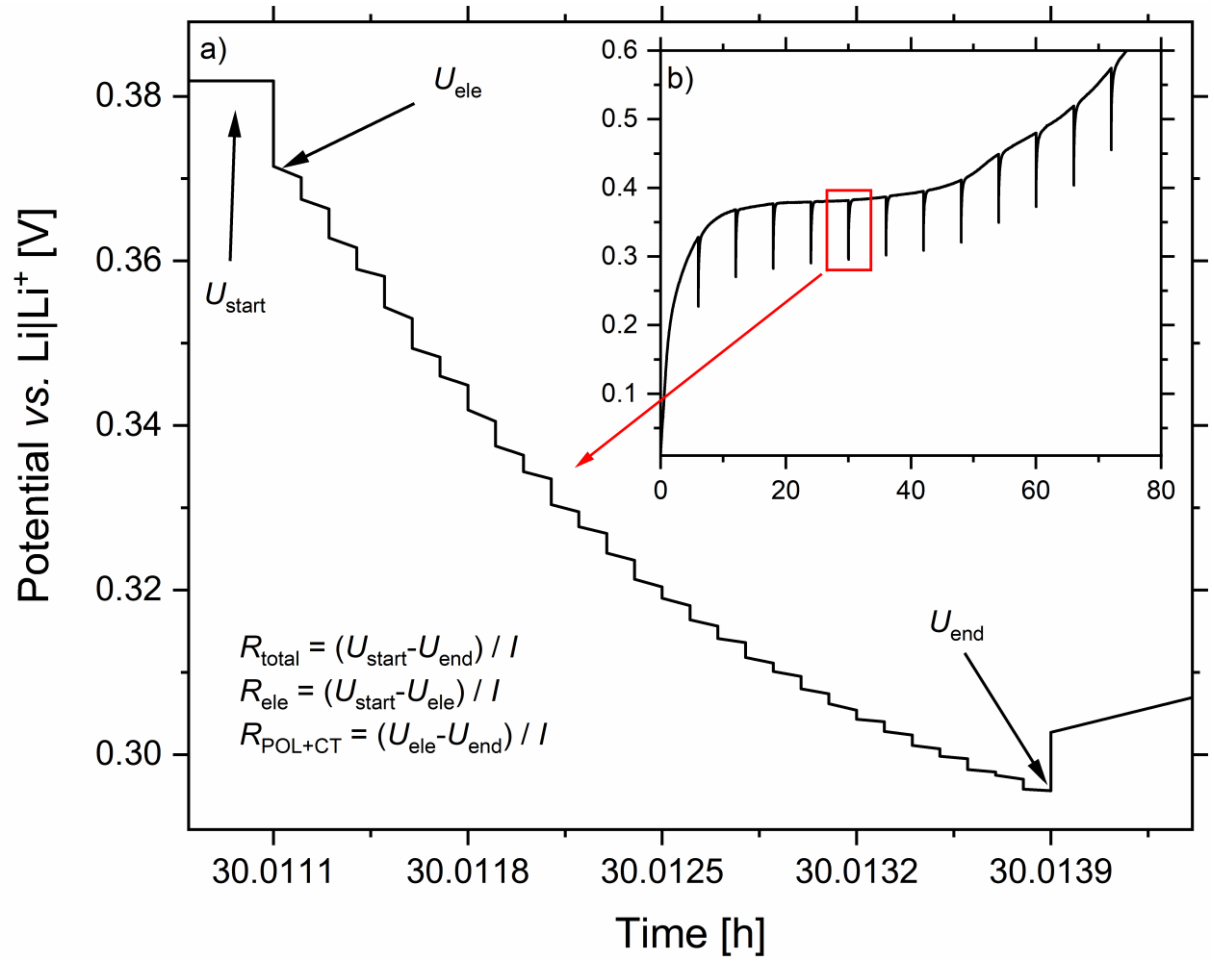

Figure S4. Pulse investigation during self-discharge for U_{10mV}, showing the full potential curve in (b) and the magnification of a single pulse (marked in red) in (a). In (a) all potentials, which are used for calculating the resistances (R_{ele}, R_{POL+CT} and R_{total}) are marked accordingly (U_{start}, U_{ele} and U_{end}). The equations for calculation are also given in the graph, where I is the applied current.

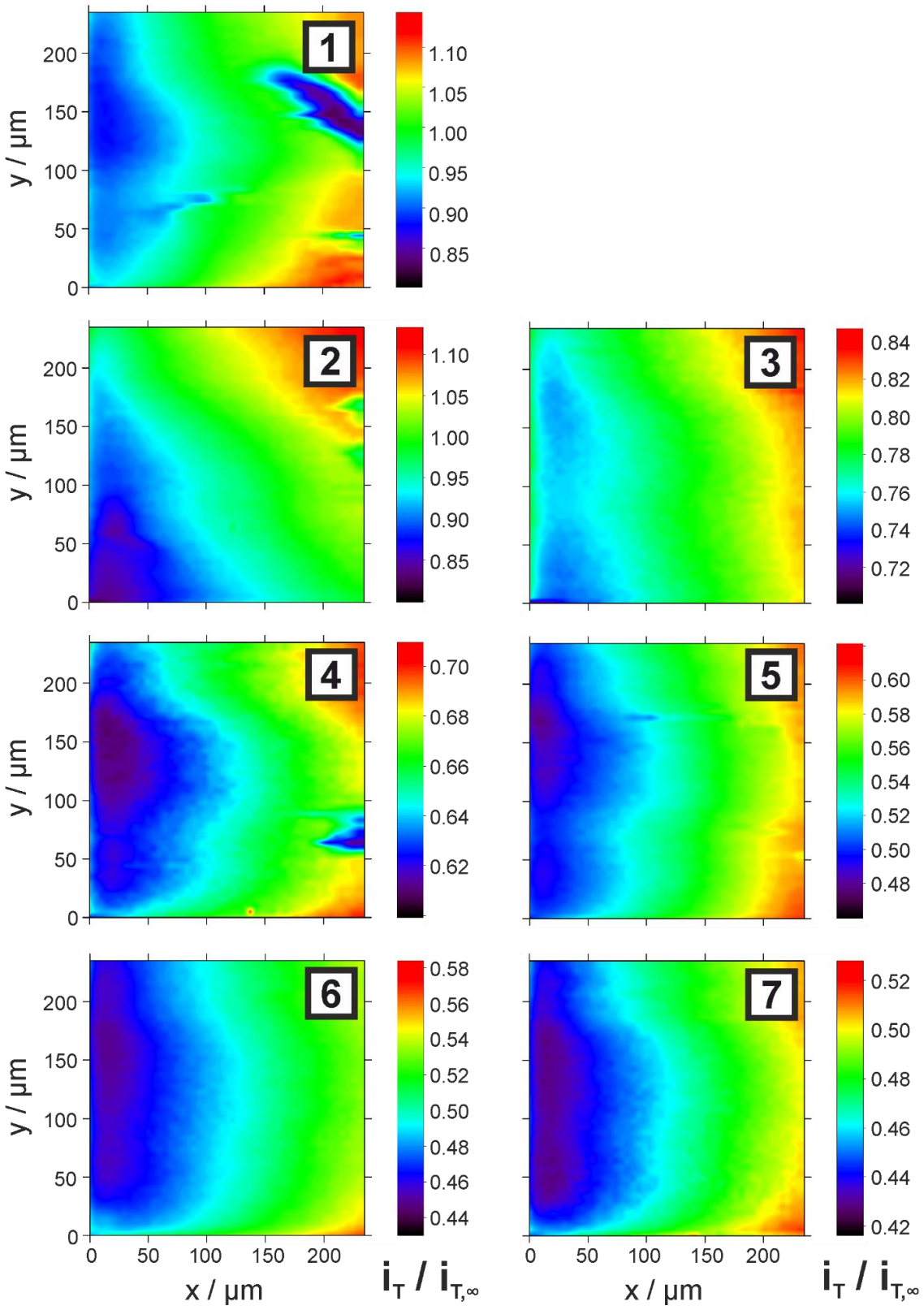

Figure S5. SECM-Image series of a 240 µm × 240 µm area on the Si electrode with U_{Cut} = 10 mV *vs*. Li|Li$^+$. The current is normalized by the microelectrode current $i_{T,\infty}$ in the bulk of the solution before each image. The images in **Figure S5** correspond to **Figures 5a** and **5c**.

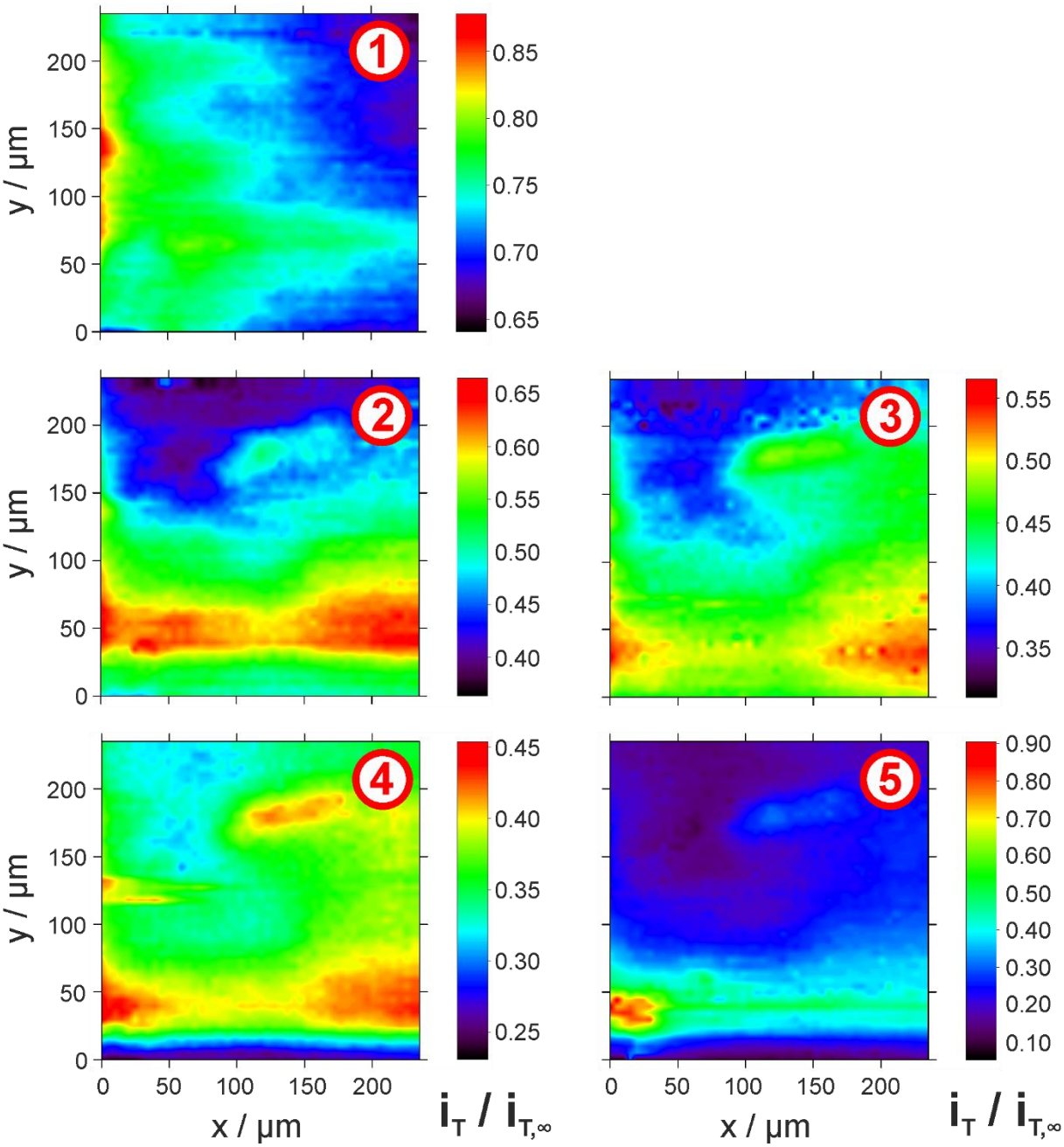

Figure S6. SECM-Image series of a 240 µm × 240 µm area on the Si electrode with U_{Cut} = 50 mV *vs.* Li|Li$^+$. The current is normalized by the microelectrode current in the bulk of the solution before each image. The images in **Figure S6** correspond to **Figures 5a** and **5d**.