

Accelerated Evaluation of the Integrity of the Solid-Electrolyte Interphase on Silicon-Graphite Electrodes during Charge-Discharge Cycles by means of SECM

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Among a variety of emerging anode materials for Li-ion batteries (LIBs), silicon-based electrodes are considered to be among the most outstanding candidates as an alternative to conventional graphite, with a higher gravimetric capacity than graphite, and a lower working voltage.^[1] The stability and integrity of the SEI have been identified as the main limitation of the Si-based battery electrodes. A key challenge of this material is the large volume changes during the lithiation process. Lithiation-induced expansion and shrinking occurring upon (de-)lithiation leads to an unstable solid electrolyte interphase (SEI),^[2] which compromises the protecting character of the SEI and hence limits the long cycle life of corresponding LIBs. We propose scanning electrochemical microscopy (SECM) as a powerful technique to investigate the degradation mechanisms of Si-based electrodes. While the macroscopic evaluation of coulombic efficiency and electrochemical impedance spectroscopy (EIS) measurements only resulted in misleading interpretations of the degradation, SECM results are able to reveal μm -heterogeneities in the surface reactivity in dependence on the number of charge-discharge cycles.

In this work, SEI was systematically prepared on individual Si-carbon anodes by electrochemical aging in a coaxial three-electrode configuration Swagelok cell in 1 M LiPF₆ (EC: DMC) battery grade + 2% w/w vinylene carbonate (VC). Similar conditions were also used for the global impedance analysis before and after SEI formation in the frequency range of 100 kHz to 1mHz. Macroscopic EIS was recorded at the lithiated electrode samples after the aging processes. Afterward, cycled Si-C electrodes were transferred to the SECM cell inside the Ar-filled glovebox. Feedback mode (FB) SECM was used to interrogate the local electronically insulating properties of the SEI following a previously reported protocol.^[3] The local electrochemistry reveals inhomogeneities at an early stage of the cycling process.

The evolution of surface reactivity at the Si-C electrodes during charge-discharge cycling was derived by FB-SECM measurements. Two major processes are superimposed, namely the formation of a protecting SEI, which became more homogeneous during the first cycles, as well as the appearance of an area after prolonged cycling where the increased electron transfer reaction was due to the detachment of active particles.

SECM was demonstrated as a suitable local characterization technique for real-world commercial LIB electrodes with respect to the integrity of the SEI after charge-discharge cycles. This is especially important for next-generation Si-based electrodes due to the volume changes during Li intercalation/deintercalation.

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