

Microelectrochemical in situ observation of battery electrodes

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In our society Li ion batteries are widely used. Intensive research is conducted on next generation batteries such as metal-air batteries. The requirements of high energy density dictate the use of very high (oxidizing) or very low (reducing) potential. These extreme potentials can cause molecular compounds to undergo electron transfer reactions at the interfaces. This is well documented for lithium-ion batteries, where a solid electrolyte interphase (SEI) between the lithiated graphite electrode and the electrolyte is formed by the decomposition of electrolyte components mainly during the first charging process. This layer is critical for the performance and safety of the Li ion batteries [1]. This talk will review a number of approaches to understand charge transport across SEI by using concepts of microelectrochemistry in particular scanning electrochemical microscopy (SECM).

Characterization of the SEI is a challenge, because of the variety of chemically similar components and enclosed electrolyte species. Furthermore, *ex situ* analysis of the SEI requires separation and isolation of the SEI, which may change the content and the structure of the SEI [2]. Recently we used the feedback mode of scanning electrochemical microscopy (SECM) to investigate *in situ* the electron transport at the lithiated graphite (Figure) [3]. 2,5-di-*tert*-butyl-1,4-dimethoxy benzene was identified as a useful SECM mediator providing sufficient stability and sensitivity to study passivation properties of SEI. All measurements were conducted under open circuit conditions of charged negative electrodes. The SECM results show gradual and significant short-term *spatiotemporal* changes of the SEI properties and demonstrate the dynamic and spontaneous behavior of SEI formation, damage and reformation under open circuit conditions above lithiated graphite anodes. The results emphasize that *spatiotemporal* changes of the passivating SEI properties are highly localized and occur preferentially in between the gaps of graphite particles. Significant short-term *spatiotemporal* changes of the SEI properties clarifies that electrolyte reduction still occurs after SEI formation at localized spots. This methodology has also been applied to highly ordered pyrolytic graphite [4], lithiated silicon [5], lithium metal [6].

These examples are examples for intensive attempts to use electrochemical microprobes to assess in situ properties of interfaces in modern batteries [7, 8]. Using a related setup for the investigation of nonaqueous lithium-air batteries, the fate of oxygen reduction products has been investigated. It shows that also during discharge considerable amounts of superoxide diffuse into the organic electrolyte. Soluble intermediates were identified by reaction with selective fluorogenic dyes and quantified by cyclic voltammetry at a microelectrode [9].

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