

Abstract

Electrochemical systems and rechargeable battery systems, in particular, are essential to the transition from fossil fuels to renewable energy sources. The overall performance of a battery system is critically dependent on the processes that occur at the electrolyte interface of the electrode. Still, in-depth understanding of the interfacial processes remains limited due to experimental challenges associated with interface studies and due to the high complexity of battery systems. This work focuses on studies of three distinct electrode/electrolyte interphases which differ in their chemical composition, complexity, and whether a solid phase is present between the electrode and the electrolyte or not. The core findings are obtained using two principal methods, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS).

In the first study, a model system consisting of a thin film gold electrode and a carbonate electrolyte is probed using dip-and-pull ambient pressure XPS (APXPS). By monitoring the drop in electrostatic potential at the electrode|electrolyte interface with operando dip-and-pull APXPS, the meniscus electrochemistry is shown to be significantly affected by a severe iR drop along the meniscus. The meniscus resistance is estimated to be 1000-times higher than the resistance of the bulk electrolyte and is shown to be particularly problematic for conducting *operando* studies of faradaic processes. Strategies to minimize measurement artefacts due to the iR drop are proposed.

The second system of interest is the solid electrolyte interphase (SEI) that forms on composite silicon graphite electrodes (Si/g electrodes) when three distinct combinations of additives are added to the electrolyte. Based on the analysis of XPS spectra collected from composite Si/g electrodes, the structural fragments present in the SEI are proposed. By complementing the information obtained from XPS with EIS measurements, we correlate the SEI chemical composition and thickness to the electrochemical properties of Si/g. Moreover, we demonstrate the importance of performing electrochemical measurements in a way that allows the individual contributions of each electrode to be distinguished.

In the third study, the interphase between Li metal and carbonate electrolyte is modified by applying a coating onto Li metal electrode surface. The applied coating consists of a biopolymer and LiNO_3 and has previously been shown to suppress dendrite growth. A series of EIS measurements are conducted to determine the mechanism of mass transport through the coating. Transmission line model (TLM) of the studied system is constructed and verified by comparing TLM-based simulations with experimentally observed trends. Finally, the usefulness of the constructed TLM is demonstrated by employing the TLM to determine the transport parameters of a new system, namely, a system in which the liquid electrolyte has been replaced by a polymer electrolyte.

Keywords: electrode electrolyte interphase, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, mass transport, electrochemical processes