Revealing Interfacial Reactions in Li-ion Batteries under Working Conditions

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Lithium-ion batteries (LIBs) are a key enabling technology for the transition from fossil fuels towards increased use of renewable energy sources. Although LIBs are already widely used in portable electronics and the rapidly expanding electric vehicle market, more widespread deployment requires improved cycle-lifetimes. These are currently limited by side-reactions that occur primarily at the electrode-electrolyte interfaces, and understanding the nature of these reaction is critical to the design of materials solutions to mitigate LIB degradation. However, obtaining chemical information with nm-scale interface sensitivity is a significant challenge given these interfaces are typically buried between a bulk electrode and dense electrolyte environment. [1,2]

Here we introduce and apply complementary interface-sensitive methods based on X-ray spectroscopies and neutron reflectometry, adapted for observing electrode-electrolyte interfaces in electrochemical environments. This includes *membrane-based* approaches which we have been involved in developing over recent years to perform *operando* x-ray photoelectron and absorption spectroscopy (XPS/XAS).[2-5] These rely on reaction cells sealed with X-ray/electron-transparent membranes such as thin (<100 nm) silicon nitride or graphene membranes that remain impermeable to liquids. We demonstrate how these approaches can monitor the evolution of solid-liquid interfaces under electrochemical control, [5] including solid-electrolyte interphase (SEI) formation on Li-ion battery anodes. This is complemented by neutron reflectometry (NR) which reveals the precise thickness of the layers formed on electrode surfaces with sub-nm depth resolution, even for light elements such as Li, C, O.

We will further discuss our recent progress in probing buried interfaces using Hard X-ray Photoelectron Spectroscopy (HaXPES), including electrode-electrolyte interfaces in solid-state batteries.[6] These are being developed as part of an effort within the UK's Faraday Institution to implement new battery characterization capabilities, and we expect them to be valuable in understanding a wide range of interfacial reactions across the electrochemical sciences.

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