Soft X-ray spectroscopy of electrochemical interfaces

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Lithium-ion batteries (LIBs) are key to the transition from fossil fuels towards increased use of renewable energy sources. However, more widespread deployment requires improvements in energy density, cost and cycle-lifetime. Various cathode and anode materials are under consideration for next-generation LIBs, and the interfacial stability of these materials in contact with the electrolyte is a critical consideration. Interface-sensitive *operando* characterization techniques are urgently needed to reveal the reactions occurring in working batteries.[1,2]

I will present our recent *ex-situ* studies of Ni-rich $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) cycled vs. Graphite in full cells, where electrochemical signatures of cell degradation are linked to surface chemistry changes taking place on the electrodes as revealed with Hard X-ray Photoelectron Spectroscopy (HaXPES). This reveals thickening of electrode-electrolyte interphases with cycling, the growth of a reduced surface layer at the cathode, and incorporation of transition metals at the anode due to cross-over from cathode.

Despite these insights, ex-situ measurements nevertheless can't capture the intermediate species involved in interface degradation. We therefore introduce several *operando* approaches for resolving the structural and chemical evolution of electrochemical interfaces.[3-8] This includes *in situ* deposition of thin lithium layers onto solid electrolytes,[6,7] and enclosed reaction cells sealed with thin (<100 nm) X-ray-transparent silicon nitride membranes that allow studies with liquid electrolytes.[8] We demonstrate how these approaches can monitor reactions at electrode-electrolyte interfaces under electrochemical control, including solid-electrolyte interphase (SEI) formation on Li-ion battery anodes.

References

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