

What Can Soft X-rays Tell Us About Fuel Cells and Batteries?

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In this talk, I will discuss the application of a variety of soft x-ray spectroscopy techniques to study metal oxide cathodes within intermediate temperature ($T \sim 500 - 700 \text{ }^\circ\text{C}$) solid oxide fuel cells (IT-SOFCs) and Li-ion batteries. I will restrict myself to manganese containing oxides and careful *ex-situ* measurements at various stages of fabrication and operation. Despite not being true *in-situ* measurements, one can still obtain technologically relevant information. These studies also highlight the suitability of *in-situ* soft x-ray spectroscopy techniques going forward (i.e. at NSLS-II). I will focus on Mn *L*- and O *K*-edge x-ray absorption spectroscopy (XAS), Mn *L*-edge resonant photoemission spectroscopy (RPES) and O *K*-edge x-ray emission spectroscopy (XES). I will demonstrate how these soft x-ray techniques can be employed to correlate the evolution of Mn charge state (Mn *L*-edge XAS) with the modification of both the topmost occupied (Mn *L*-edge RPES and O *K*-edge XES) and bottommost unoccupied (O *K*-edge XAS) states during electrochemical activity. Moreover, I will also show how these measurements can be directly compared to density functional theory (DFT) calculations.

The first example regards the enhanced oxygen reduction reaction (ORR) catalytic activity observed after many hours of operation (often referred to as the "burn-in" phenomenon) of Sr-doped LaMnO₃ cathodes within IT-SOFCs. After elucidating the electronic structure of pristine samples using Mn *L*-edge RPES and O *K*-edge XAS/XES, the evolution of the Mn charge state and electronic structure of rapidly quenched samples prior to and after the "burn-in" was successfully traced. Severe Sr enrichment at the surface occurs upon exposure to elevated temperatures prior to the bias, which results in insulating character that severely reduces the initial performance of the IT-SOFC. After the burn-in (i.e. 90 hours of 1 V bias), the greatest changes occur in the Mn charge state with only subtle changes in the oxygen environment.[1] The second example refers the nature of (pseudo) Jahn-Teller distortions within electrochemically delithiated Li_xMnPO₄. Upon delithiation the evolution of the Mn charge state from 2+ to 3+ was confirmed by Mn *L*-edge XAS; the corresponding distortion of the MnO₆ environment with the change in charge state was observed using hard x-ray spectroscopy of the Mn *K*-edge. The resultant evolution of the electronic structure associated with the severe local distortion in the Mn³⁺ configuration was examined by O *K*-edge XES/XAS combined with DFT. The excellent agreement between predicted and observed the local distortion and evolution of the electronic structure provides confidence in DFT calculations of the hole and electron polaron formation and migration energies of Li_xMnPO₄. [2] Similar DFT calculations have previously explained the reduced electrochemical performance of LiMnPO₄ compared to LiFePO₄. [3]

References

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- [3] S. P. Ong, V. L. Chevrier and G. Ceder "Comparison of small polaron migration and phase separation in olivine LiMnPO_4 and LiFePO_4 using hybrid density functional theory" **Phys. Rev. B** 83 (2011) 075112