Energy-tuned photoelectron spectroscopy of lithium-ion battery cathodes: revealing oxygen redox activity and investigating new materials

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With the quest to find better performing electrode materials for Li-ion batteries becoming hotter by the day, advanced spectroscopic techniques are being employed to better understand the processes at interfaces of the battery components and deeper in the bulk of the active materials. One of those techniques is energy-tuned photoelectron spectroscopy (XPS), typically performed at synchrotron facilities, which offers the possibility to irradiate a sample with soft or hard X-rays and detect electrons with kinetic energies up to 10,000 eV. This builds up a true surface vs. bulk picture including formation of solid electrolyte interphases on anodes, oxidation products on cathodes and redox activity in the bulk of particles, such as that of transition metals or oxygen.

A class of cathode materials which are of particular interest are those exhibiting oxygen redox activity, providing capacity beyond that of the traditional transition metal redox. We have investigated a number of such lithium-excess Ni, Co, or Mn oxide materials, which are known to exhibit oxygen redox, by energy-tuned XPS. The analysis reveals important details of the differences between surface and bulk, which DFT calculations have helped rationalise.

Lithium-rich oxyfluorides (Li_2MO_2F where M = V, Fe, Mn etc.) are another class of material that have gained increased attention in recent years. These cathode materials have promising potential with high theoretical capacities (420 mA h g^{-1} for Li_2VO_2F) at ~2.5 V with minimal volume expansion, but suffer from local structural instabilities. We are using energy-tuned XPS to study their degradation mechanisms and how they might be mitigated using transition metal doping or coatings.

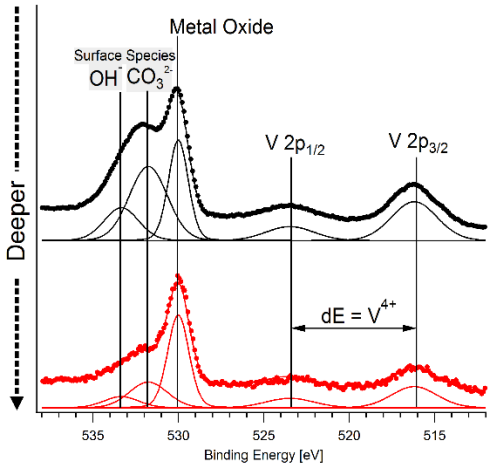

Figure 1. O 1s and V 2p XPS spectra of a Li_2VO_2F electrode for the EU H2020 'LiRichFCC' project, at two photon energies; 2005 eV (black), 6015 eV (red).