ELECTROLYTE ADDITIVES FOR LITHIUM- AND MANGANESE-RICH LAYERED CATHODE MATERIALS: AN XPS STUDY

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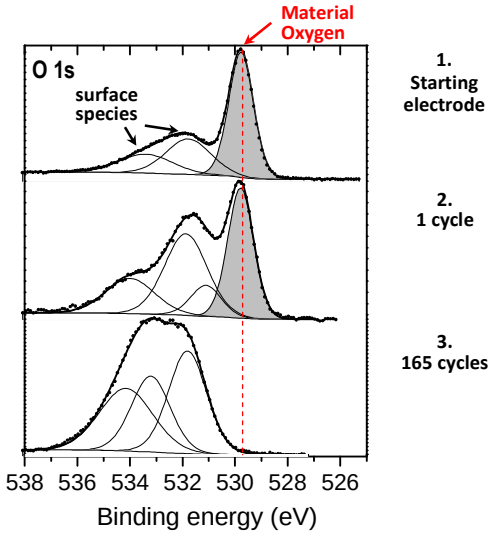
Lithium- and manganese-rich layered oxides $Li_{1+x}(Mn_{1-y-z}Ni_yCo_z)_{1-x}O_2$ (LMR-NMC) are able to reach reversible capacities higher than 250 $mAh.g^{-1}$, much more than conventional positive electrode materials. To achieve such capacities, they need an electrochemical activation by increasing the upper voltage limit of the first cycle (up to 4.8 V vs. Li^+/Li). Further cycling also requires rather high potentials to take full advantage of the great capacities of these materials. However, usual liquid electrolytes (organic carbonate solvents mixtures) undergo oxidative reactions at the electrode surface at high potentials (~ 4.5V vs. Li^+/Li). To prevent such reactions, one solution is to use electrolyte additives that are able to form a passivating film at the positive electrode/electrolyte interface.

In this presentation, I will discuss the effect of three additives. Two organic: Vinylene Carbonate (VC), Succinic Anhydride (SA), and one inorganic: Tris(2,2,2-trifluoroethyl) phosphite (TTFP). Electrochemical characterisation revealed the beneficial effect of such additives. X-ray Photoelectron Spectroscopy (XPS) investigation of surface/interface mechanisms has shown that these additives not only improve the anodic stability of the electrolytes in contact with the positive electrode surface, but also act on the LMR-NMC material itself. Especially, it was shown that the presence of the additive improves the efficiency of the electrochemical activation step on the material.



XPS O 1s spectra of LMR-NMC electrodes before cycling, and after 1 cycle and 165 cycles, in half cells with EC/PC/EMC/DMC + 1M $LiPF_6$ + 5 wt. % TTFP electrolyte