

### Tender XPS studies of the interfacial reactivity between the high-voltage cathode, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ , and the electrolyte

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#### Introduction

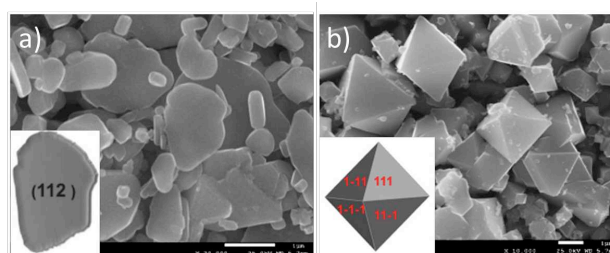
With a 4.7 V voltage vs.  $\text{Li}^+/\text{Li}$  and a capacity of 147 mAh  $\text{g}^{-1}$ ,  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  is an attractive cathode material for high-energy and high power applications such as electric and plug-in hybrid vehicles[1]. However, it operates at voltages above the oxidation limit of conventional electrolytes, which reduces cycle life. Common decomposition products observed after cycling include organic and inorganic species such as  $\text{ROCO}_2\text{M}$ ,  $-(\text{OCH}_2)_n-$ ,  $\text{Li}_x\text{PF}_y$ , and  $\text{Li}_x\text{PF}_y\text{O}_z$ [2]. While most electrode-electrolyte interface work is carried out with large, aggregated particles, it has been shown<sup>2</sup> through the use of single crystal electrodes that the crystallographic orientation can have an effect on the reactivity with the electrolyte.

In this work, we use tender X-ray photoelectron spectroscopy (TXPS), with  $h\nu = 3$  keV and 4 keV, provides photoelectron probing depth of more than 10 nm and 15 nm respectively, as well as surface sensitivity, to compare how well defined  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  crystals with different prominent (111) and (112) surface facets react with conventional carbonate-based electrolyte over electrochemical cycling. This is a powerful technique capable of nondestructively probing atomic and chemical species at the solid/solid interface between the decomposition products and the  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  crystals.

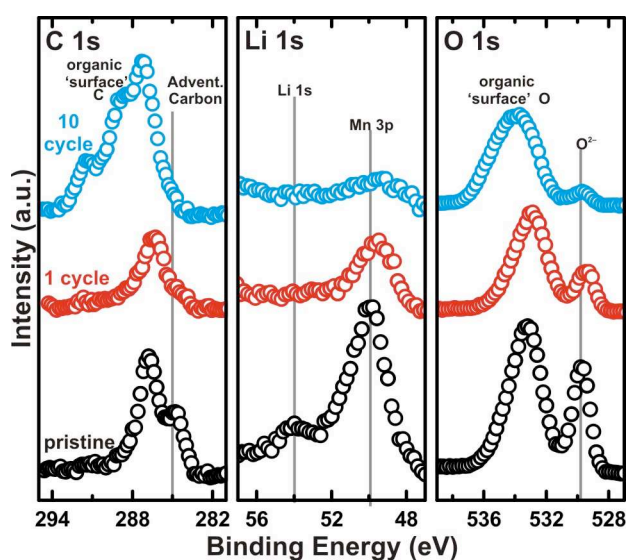
#### Results

Large, well-crystallized micron size  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  crystals with prominent (112) and (111) facets, shown in **Figure 1a and b**, and referred to as plates and octahedrons, respectively, were synthesized by a molten salt technique [4]. Electrochemical testing was done in coin cells; the electrodes were prepared without carbon additive or binder in order to detect the deterioration products on  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  only. The electrolyte consisted of 1.2M  $\text{LiPF}_6$  in EC:DEC 1:1 %v/v, Celgard 2400 was used as separator and a lithium foil as counter electrode. The cells were electrochemically cycled between 3.5 V – 4.9 V, opened in a glove box and transferred in an inert environment into the TXPS endstation on beamline 9.3.1 at the Advanced Light Source where TXPS spectra were acquired at  $h\nu = 3$  keV and 4 keV. **Figure 2** shows the C 1s, Li 1s/Mn 3p, and O 1s spectra for the pristine octahedrons, and after 1 and 10 cycles. As the octahedron samples are electrochemically cycled, a significant amount of new carbon species are formed at higher binding energies. The attenuation to the lithium (Li 1s), manganese (Mn 3p) and oxide ( $\text{O}^{2-}$ ) of the  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  spectra intensity with electrochemical cycling supports the formation of various oxygen containing ‘surface’ (non-oxide) species such as organic compounds, thus suppressing the amount of signal that can be detected from the crystals underneath. The growth of different organic containing ‘surface’ species is also evident in the broadening of the higher binding energy O

1s peak, and new features in the C 1s spectra upon reaching 10-cycles. By comparing the interface species formed at the octahedron/electrolyte interface to that of the plates/electrode interface using TXPS we will be able help identify key factors contributing to the octahedron (111) crystals enhanced cycling capabilities [4] from that of the plate (112) crystals.



**Figure 1.** SEM images of crystalline  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  particles with prominent a) (112), b) (111), plates and octahedrons respectively.



**Figure 2.** C 1s, Li 1s and O 1s TXPS spectra taken at  $h\nu = 4$  keV of pristine, 1 electrochemically cycled and 10 electrochemically cycled binder free electrodes comprised of well defined octahedron  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  crystals.

#### References:

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