

## In Situ Fluorescence Spectroscopy Studies of Interfacial Processes on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ High-Voltage Cathodes

Angelique Jarry\*, Simon F. Lux, Hugues Duncan, Guoying Chen, Robert Kostecki

Environmental Energy Technologies Division  
Lawrence Berkeley National Laboratory  
1 Cyclotron Road, Berkeley, CA 94720, USA  
\*ajjarry@lbl.gov

Significant improvements in energy density, safety, and lifetime of lithium-ion batteries are necessary to allow their rapid adoption for automotive applications. One approach is to find and develop cathode materials with higher operating potentials. Spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode with a redox potential of 4.7 V vs.  $\text{Li}/\text{Li}^+$  and a capacity of 147 mAh/g is an attractive alternative to conventional cathodes, such as  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$ .

The importance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  particle morphology in achieving optimal rate capability and stability has been demonstrated<sup>1</sup>. However, these high operating voltages are at the edge of the thermodynamic stability window for standard carbonate-based electrolytes, and the side reactions between the electrode and electrolyte can have a significant influence on the performance and lifetime of the battery<sup>2</sup>. A fundamental understanding of the physical and chemical processes that govern the complex electrode/electrolyte interactions is essential to the development of new battery materials. In this work, the interfacial reactivity of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  single crystals with specific surface crystal orientation was probed using fluorescence spectroscopy.

The presence of a large fluorescence background is a common phenomenon observed in cycled high-voltage cathodes. In fact, it provides direct evidence for the presence of decomposition products formed on the surface of the electrodes. The strong fluorescence signal can also be used to sense and characterize degradation processes and soluble reaction products that diffuse into the electrolyte. In situ fluorescence measurements were carried out during charge/discharge using a spectro-electrochemical cell. Carbon- and binder-free  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  electrodes with different particle morphology were investigated (Figure 1).

The initial fluorescence response of the model  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  single crystals was similar to the signal observed for a regular polycrystalline material. The fluorescence rises at the beginning of the nickel oxidation and then slowly vanishes upon relithiation. Insoluble products of the electrolyte oxidation tend to accumulate at the surface of the electrode forming a thin layer contributing to a gradual increase of the fluorescence background signal whereas soluble compounds diffuse away into the electrolyte. All electrodes showed a steady increase of the fluorescence background with cycling. However, for the octahedrons the intensity of the fluorescence background remains unchanged after the first cycle whereas fluorescence on the platelets seem to keep growing after every cycle. Electrolyte oxidation products formed on  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  octahedrons tend to passivate the material more effectively during the initial charge/discharge cycles.

Interestingly  $\text{LiMn}_2\text{O}_4$  spinel does not produce any fluorescent signal during charging/discharging processes whereas the beginning of the  $\text{Ni}^{2+}$  oxidation in  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  correlates with the fluorescence signal rise. This suggests that nickel is mainly responsible for the observed oxidation of the electrolyte<sup>3</sup>.

The formation of photoluminescent active species is not only influenced by the electrode material and the electrolyte but also by the crystalline orientation of the particle surface. The mechanism of these side reactions and their impact on the Li-ion system electrochemical performance of Li-ion systems will be discussed.

### References

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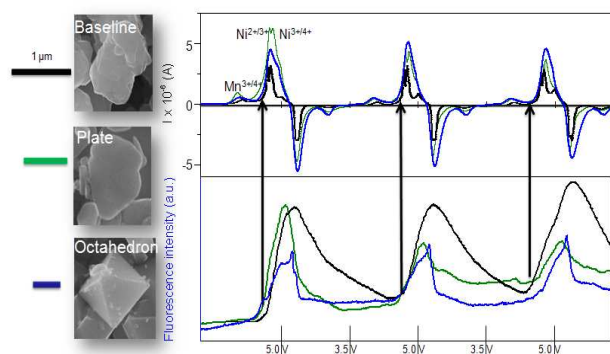


Figure 1. SEM images (left), electrochemical data (right-top), and corresponding integrated fluorescence intensity (right-bottom) of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  baseline (black), plate (green) and octahedron (blue) particles in EC:DEC 1:2 1M  $\text{LiPF}_6$