

EELS and HRTEM Analysis of Surface Phase in Nanostructured $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ Battery Materials

F. Cosandey^{*}, N. Marandian Hagh^{**} and G.G. Amatucci^{**}

^{*} Department of Materials Science and Engineering, Rutgers University, Piscataway NJ 08854

^{**} Energy Storage Research Group (ESRG), Rutgers University, North Brunswick, NJ 08902

The Ni doped $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel (Fd-3m) structure is an excellent candidate as Li-ion cathode material for high voltage battery applications due to its high capacity (> 130 mAh/g) with good room temperature cycling and high rate capabilities.. In order to improve the battery performance at high temperatures (60 °C), we have introduced a surface modification process involving treatments in hydrofluoric (H-treated) or phosphoric (P-treated) acids followed by high temperature annealing. The surface modified $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel show drastically improved impedance and capacity retention with enhanced cycle life and rate capabilities over the untreated spinel. In this paper, we present EELS compositional and Mn valence map results as well as structural phase identification by combined HRTEM and image simulations showing the formation of a new surface phase induced by the surface acidic and annealing treatments.

The detailed description of sample preparation methods with electrochemistry results are presented elsewhere [1]. High resolution images (HRTEM) were obtained using a JEOL JEM 2010F operating at 197 kV. The EELS maps were obtained with a Gatan GIF spectrometer and 0.3 nm probe size. Multislice HRTEM images simulations were performed on spinel as well as various modified ordered phases using JEMS program [2].

A STEM image of a P-treated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ nanoparticle is shown in Figure 1a with the corresponding Mn (Fig.1b), O (Fig.1c) and Ni (Fig.1d) elemental maps. It can be seen that the concentration of Mn is higher at the surface with a corresponding decrease in surface O content. This change in surface composition is accompanied by a change in valence state of Mn from Mn^{4+} in the bulk to Mn^{3+} at the surface. This decrease in valence state was obtained from a quantitative analysis of the increase in Mn L_3/L_2 white line intensity ratio as depicted in Fig.1e.

A HRTEM image of the standard $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ in a [110] ZA orientation with the corresponding FFT pattern are shown in Figure 2a and 2b respectively. The HRTEM image is consistent with the Fd-3m spinel structure. The HRTEM image of the P-modified $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ in a [110] ZA orientation with the corresponding FFT pattern are shown in Figure 2c and 2d respectively. Extra (110), (210), (310) type reflections are observed in this P-treated sample. Similar results are observed for the H-treated sample. These extra reflections can be attributed to the ordered ($\text{P4}_3\text{32}$) spinel [3] phase or to the cubic primitive (Pd-3m) cell. However, image analysis using dynamical HRTEM image simulations seems to indicate that this surface phase corresponds to a modified $\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_{4-\delta}$ ($\text{P4}_3\text{32}$) phase with a fraction of Mn atoms in the Li site.

- 1 N. Marandian Hagh and G.G Amatucci, ECS Transactions, **11**, (2007)
- 2 <http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/jems.html>.
- 3 J.-Kim et al., Chem. Mater. **16**, (2004), p.906.

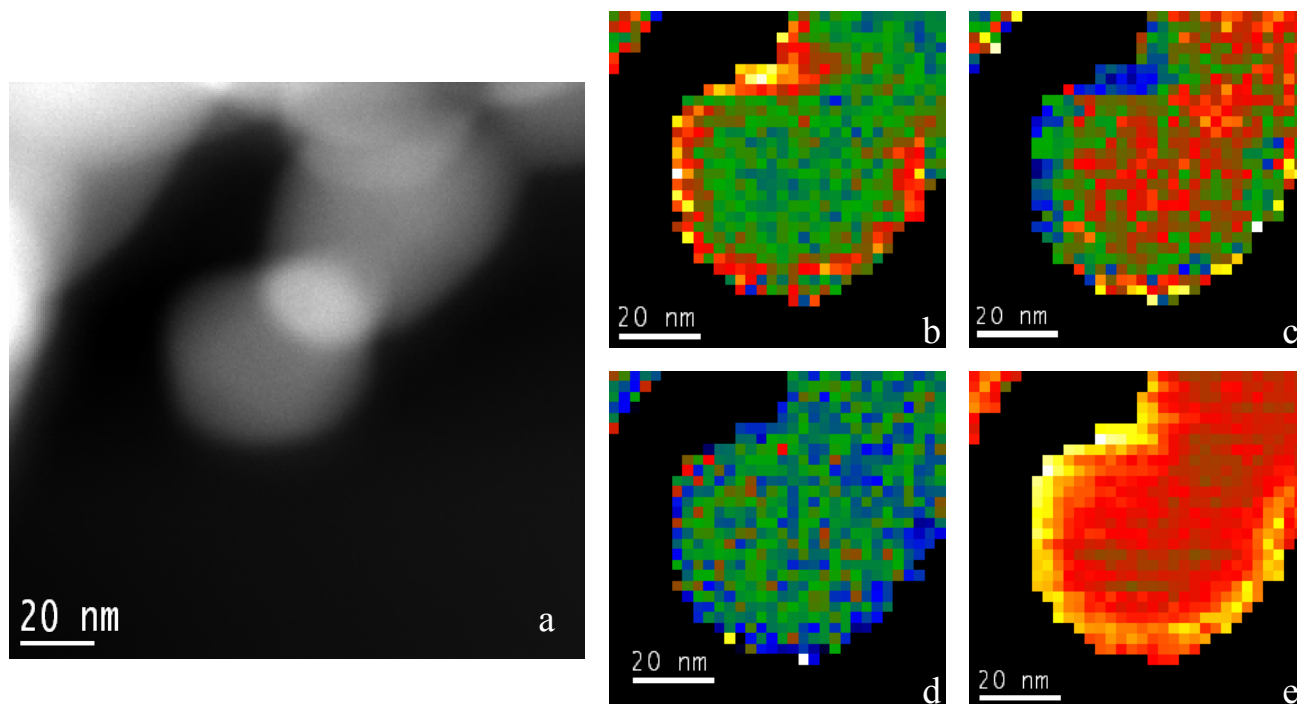


Fig. 1. (a) DF STEM image of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ nanoparticle with corresponding elemental EELS maps showing distribution of (b) Mn, (c) O, (d) Ni and in (e) Mn L_3/L_2 line intensity ratio.

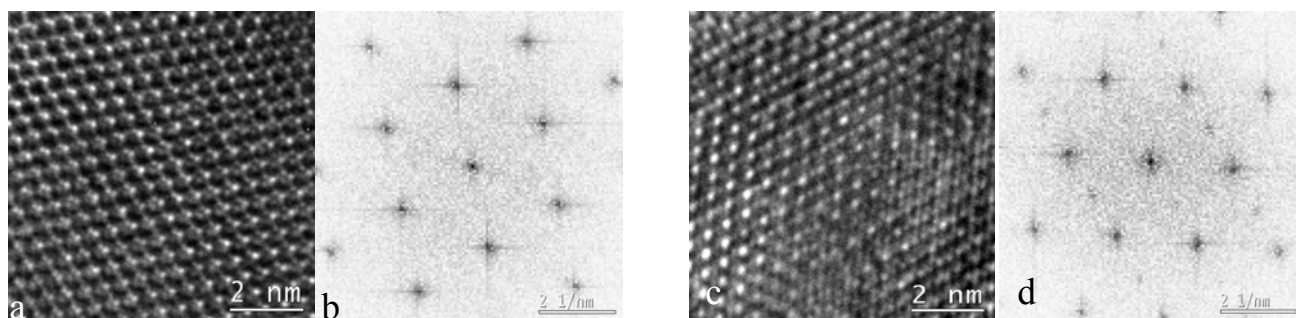


Fig. 2. (a) [110] zone axis HRTEM image of STD $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ with in (b) the corresponding FFT (c) [110] zone axis HRTEM image of P-treated $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ with in (c) the corresponding FFT showing extra superlattice reflections.