

Compositional and Chemical Segregation in $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ Cathode Materials Characterized by Atom Probe Tomography and Scanning Transmission X-ray Microscopy

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Li-ion batteries are one of the most widely used rechargeable energy sources, with a two times higher voltage than aqueous batteries, six times higher gravimetric specific energy compared to the lead acid battery [1], and a high energy density [2]. Layered $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ (LMNO) nanoparticles have shown to be a very promising next generation high capacity cathode material for Li-ion batteries. However, there is still a debate as to the structure, cation ordering and distribution in the cathode, both before and after cycling [3,4]. In addition, the layered cathode has shown a trend to transform to spinel phase after high voltage cycling [5]. This important structural change would result in capacity fading and poor rate performance, limiting its application in heavy-duty electric vehicles. These important structural, compositional and chemical changes can be clarified using a combination of atom probe tomography (APT), scanning transmission x-ray microscopy (SXTM) and transmission electron microscopy (TEM) analysis.

Recent scanning TEM x-ray energy dispersive spectroscopy (STEM-EDS) tomography results have indicated the segregation of Ni at surfaces and grain boundaries. It has been proposed that this clustering acts as a barrier to the Li [6]. Moving forwards, an effective means of detecting Li is needed. Laser-assisted, local electrode atom probe (LEAP) combines a time of flight mass spectrometer with a point projection microscope capable of position sensing to perform atomic scale imaging of materials with sub-nanometer (<0.2 nm) spatial resolution in three dimensions and parts-per-million (ppm) composition sensitivity [10], and is capable of detecting Li. LMNO nanoparticles have been prepared for APT analysis by a focused ion beam liftout and analyzed in a LEAP 4000XHR with a UV laser. In addition to confirming Ni and Mn segregation observed previously by STEM-EDS, the atom probe reconstructions demonstrate that the Li preferentially segregates to Mn-rich regions over the Ni-rich regions (Fig. 1a,b). In addition, LMNO before and after cycling were examined using STXM on Advanced Light Source beamlines 5.3.2.1 and 11.0.2. Examination of the oxygen K-edge evidenced the emergence of a peak at 533.5 eV in samples after cycling, predominantly located at surfaces. This feature is additionally observed in spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ materials only after cycling, and has been previously linked to lithiation, potentially suggesting a surface-rich segregation [7,8].

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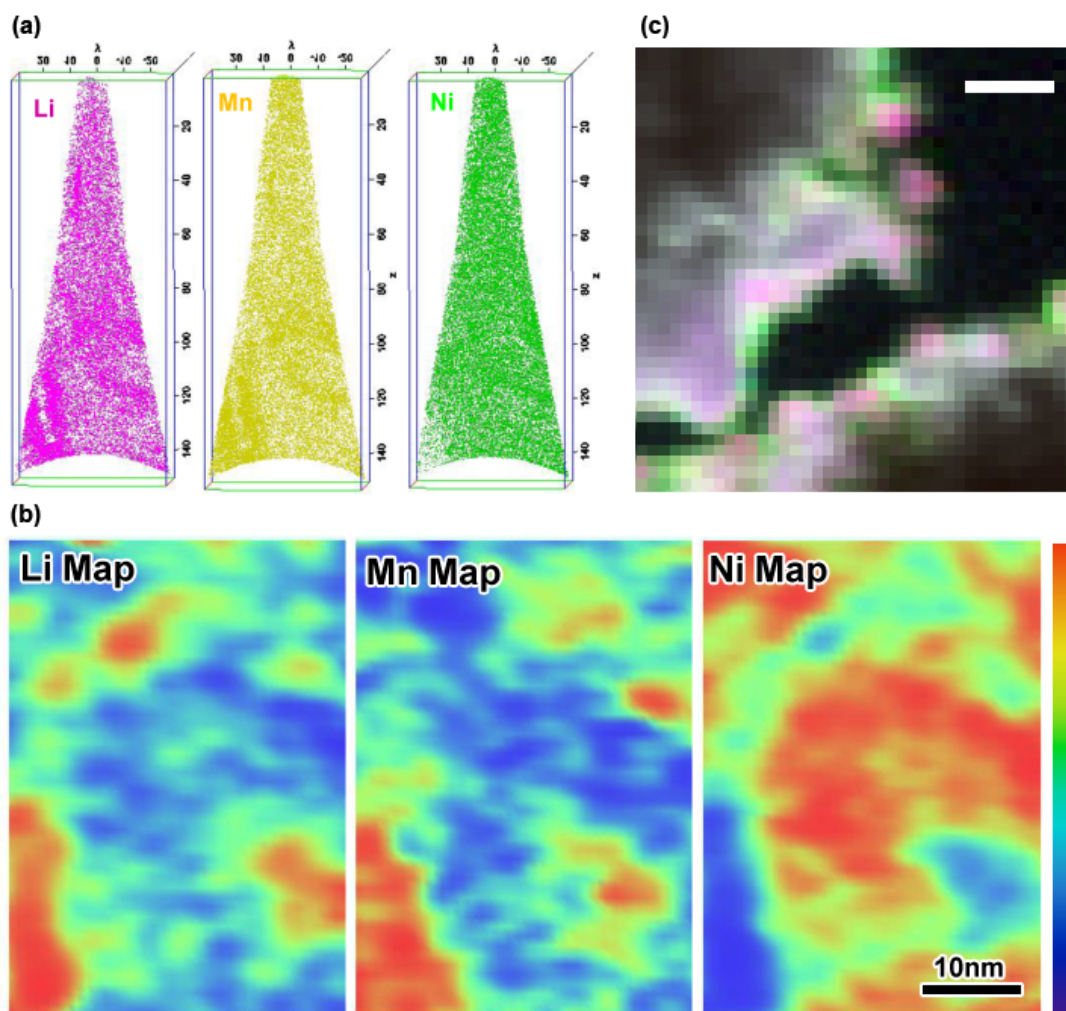


Figure 1: (a) APT reconstructions separately showing the Li, Mn, and Ni ions for a typical uncycled $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ particle and (b) density maps from a sliced subsection of the reconstruction demonstrating the segregation of the Mn and Ni, along with correlation of the relative density of the Li with the Mn. (c) A three-color map extracted from a STXM stack of the oxygen K edge for cycled LMNO, demonstrating the spatial variation of features at ~ 529.2 eV (red), ~ 531.6 eV (blue), and 533.5 eV (green). The scale bar is 600 nm.