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Determination of Mn Valences in $Li_{1-x}Mg_xMn_2O_4$ Using Monochromated EELS in an Aberration-Corrected STEM

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Mixed-valent transition metal oxides have attracted much of attention for the applications as insertion cathode materials. Among various materials, Lithium-manganese-oxides ($Li_yMn_2O_4$) of spinel structure have demonstrated as an effective lithium insertion electrode for rechargeable lithium batteries [1]. The concept of using the Mn_2O_4 framework of a spinel, where Li and Mn occupy the tetrahedral and octahedral sites, respectively, is based on the three-dimensional interstitial space for Li^+ ion transport, and the framework remains intact over a broad range of Li composition ($0 \leq y \leq 2$). Here we explore the same framework flexibility for Mg insertion with help of STEM/EELS.

Compared to the widely used X-ray absorption spectroscopy for the study of insertion cathode materials, STEM/EELS provides a powerful probe for the local electronic structure. Key developments in aberration correction have allowed for better than 1 Å STEM imaging resolution and an increased probe current over previous instruments [2]. The large probe current has led to better signal/noise ratio in EELS and improved sensitivity. However, the range of energy loss that can be studied is limited, in case of AMn_2O_4, the accessible loss edges by EELS are these of Mn L and O K, and the interpretation of L edges present a significant challenge.

Here, we report on the EELS study of $LiMn_2O_4$ and delithiated and Mg inserted $Li_{1-x}Mg_yMn_2O_4$ nanocrystals. The EELS experiments were carried out using a monochromated Themis Z STEM (Thermo Fisher Scientific) operated at 300kV. The microscope is equipped with a DCOR Probe Cs corrector and a post-column Gatan Imaging Filter (GIF) Quantum with dual EELS detectors. A FWHM of 0.15 eV is obtained using monochromated EELS. For STEM imaging, high angle annual dark-field (HAADF) and annual bright-field (ABF) images are acquired. For EELS, dual EELS spectra were acquired simultaneously in STEM mode over an area, the low-loss spectra provide a measurement of the nanocrystal thickness and reference for spectra quantification, while the core loss spectra were recorded for the O-K and Mn-L edges. Figure 1 shows an example of STEM/EELS characterization of $LiMn_2O_4$ and Mg inserted $Li_{1-x}Mg_yMn_2O_4$. The spectra shown were averaged over the observed nanocrystal. Compared the reported Mn L edges for different Mn oxidation states, the Mn L-edge for $Li_{1-x}Mg_yMn_2O_4$ resembles that of nanoparticles of Mn_3O_4 [3].

The above results will be discussed based on the combined EDX and diffraction analysis of $Li_{1-x}Mg_xMn_2O_4$ nanocrystals [4]. Specifically, we will provide direct evidence of Mg insertion and its quantification based on electron diffraction. We will then use these data and modeling to interpret the Mn-L edges observed by STEM/EELS [5].

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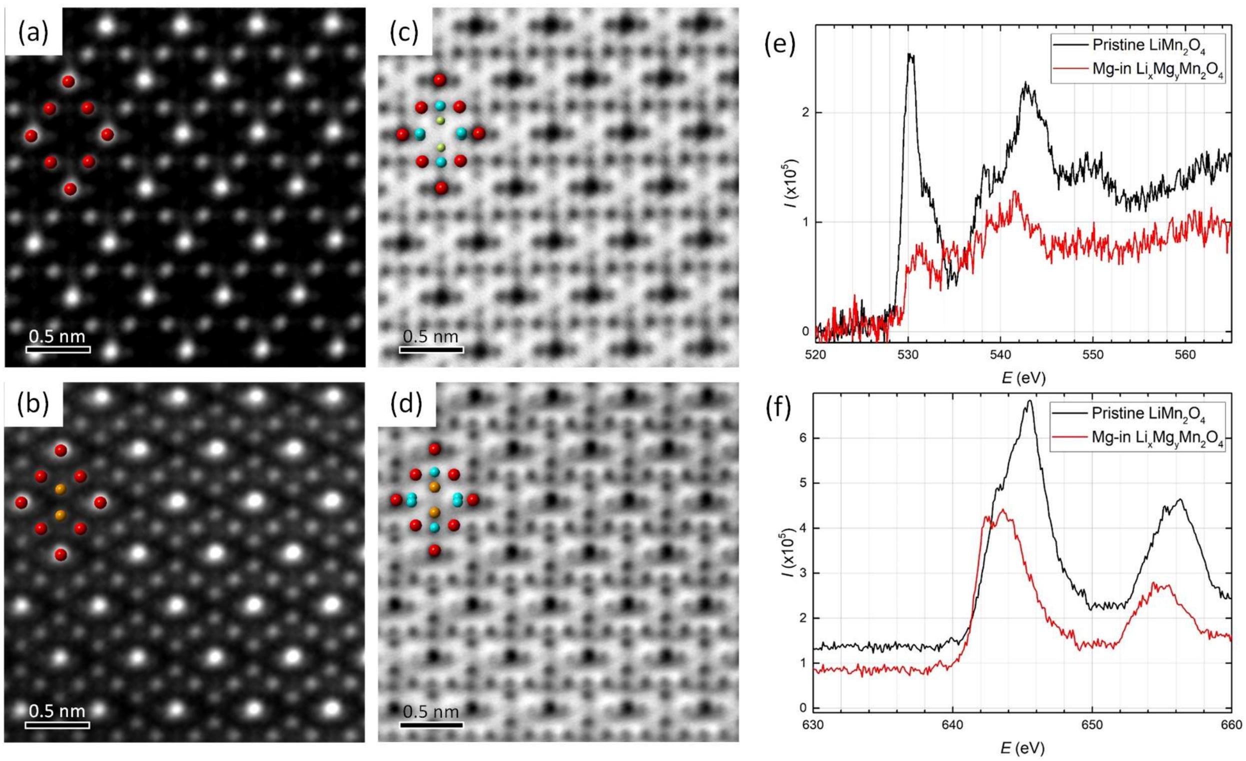

Figure 1. (a) and (b) HAADF-STEM image of $LiMn_2O_4$ and Mg Mn_2O_4 respectively. (c) and (d) ABF-STEM image of $LiMn_2O_4$ and Mg Mn_2O_4 respectively. (e) O-K edges and (f) Mn-L edges.

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