

In Situ TEM Studies of Lithiation/de-lithiation in Chemically-complex Alloys

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Ever growing demand for high capacity, energy density and stable energy storage devices has grabbed intense attention in materials science research area especially emerging field of high entropy materials (HEMs) toward developing novel and advanced electrode materials to boost next-generation Li-ion batteries performance. Chemically-complex alloys and oxides have attracted more interest since 2015 and mostly on five-component equimolar compositions [1-3]. Here we extend this concept to compositionally complex (non-equimolar) oxides and introduced new solid solution transition-metal-based (Fe,Cu,Mg,Mn,Ni)₃O₄ high entropy oxide (HEO) for use in Li-ion batteries.

Structural and chemical characterization of these high entropy materials were carried out using aberration corrected STEM, energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) confirmed single phase spinel crystal structure of high entropy solid solution and homogenous distribution of compositional elements (**Figure 1**). High angle annular dark field imaging (HAADF), which is a Z-contrast imaging technique and can resolve the transition metal atoms, has been utilized in this research (**Figure 2**).

This research focuses on shedding light to the structural chemistry, interactions among multiple metal cations and complex electrochemical reactions of this new materials during lithiation and de-lithiation science obtained via powerful in-situ TEM. We explored the chemical and electrochemical reactions, structural stability, phase transformation of HEO during charging and discharging, to elucidate more in-depth knowledge about underlying mechanisms and accurate model for atomic structure engineering of entropy stabilization to design electrochemistry. In-situ STEM-EELS studies showed that each individual metal cations of HEO has critical role in the subsequent electrochemical properties. we found transition metal HEO undergoes reversible conversion reaction mechanism via reducing active metal ions during lithiation, while Mg provides the structural stabilization role of nanoparticles during redox reactions [4].

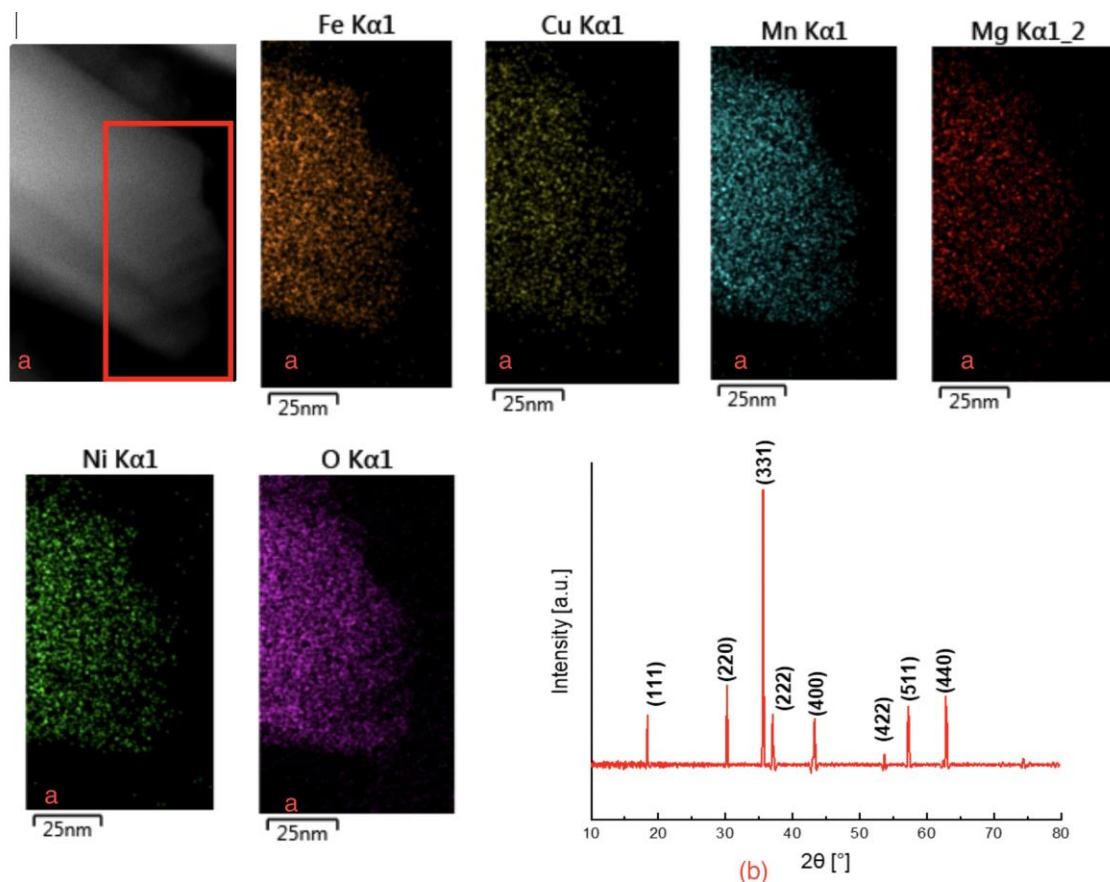


Figure 1. (a) EDS elemental mapping images of Fe, Cu, Mg, Mn, Ni and O in the HEO, (b) XRD diffraction pattern of the HEO shows well indexed planes of the spinel (cubic $Fd\bar{3}m$ space group) structure.

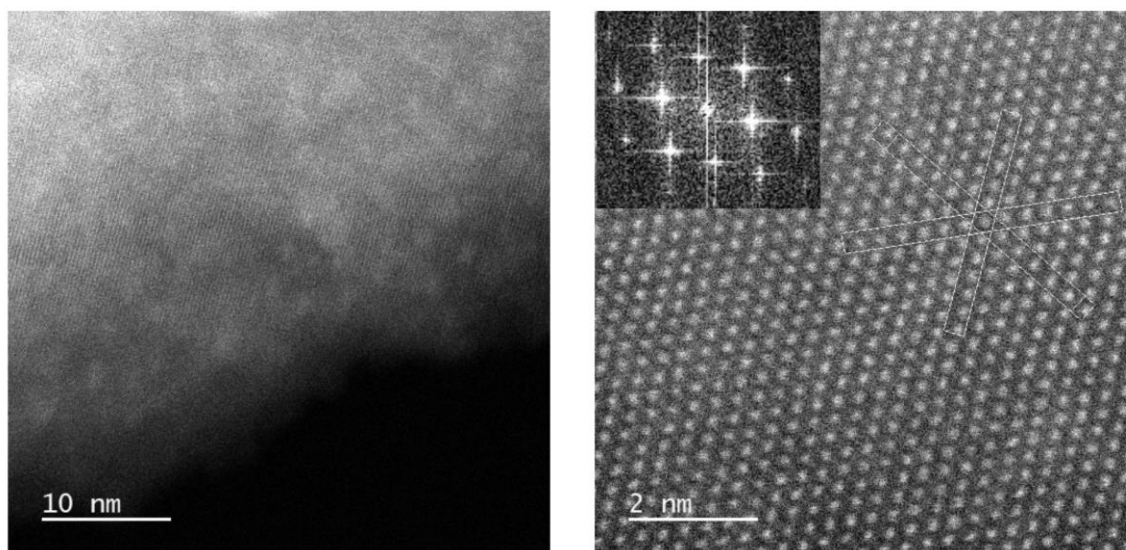


Figure 2. HAADF-STEM images of HEO (Inset is the FFT of the HEO).

References

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