

Spatially Resolved Characterization of Phases in LiFePO₄ Battery Cathodes Using Low Loss Electron Energy-loss Spectroscopy

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Lithium iron phosphate (LiFePO₄) has considerable potential for automotive applications due to its high rate capability, reasonable energy density and environmentally benign nature [1]. However, performance degradation seen after thousands of cycles at high charging-rates (C-rates) has been a point of major concern [2]. Studies of the aging mechanism suggest that phases (LiFePO₄/FePO₄) formed in the cathode during discharge influence the aging profile [3]. These phases have been investigated recently using x-ray and neutron diffraction [4, 5]. While these methods provide insights into crystal structure and unit cell volume changes associated with phase changes between LiFePO₄ and FePO₄, their ability to provide spatially resolved measurements of quantities such as Li and Fe concentration at the nano-scale is severely limited. Such measurements are key to confirming the presence or absence of the phases mentioned above and solid solution phases (Li_xFePO₄). With recent advances in aberration corrected electron microscopy, electron energy-loss spectroscopy (EELS) performed in the scanning transmission electron microscope (STEM) has emerged as a leading technique to obtain spatially resolved measurements of chemistry, structure and bonding. Previously, researchers have used shifts observed in core-loss peaks of iron and oxygen to study the delithiation of FePO₄ host lattice [6-8]. However, these ionization edges have relatively small inelastic scattering cross sections, and consequently, a relatively high electron dose is required to achieve acceptable signal-to-noise ratios in the data resulting in significant electron beam damage to the specimen. The low energy-loss region of the spectrum (0-40 eV) can be very useful since (i) the intensity is much larger compared to the core-loss spectrum and (ii) lesser collection time is required which significantly lowers the risk of beam damage to the material. In this study, we explore the use of low loss EELS to characterize the nominally pure LiFePO₄ powder with trace amounts of FePO₄ which is typical of phase mixtures that is present during phase transformation within the LiFePO₄ battery cathode at the nanoscale during aging.

Fig.1a shows the XRD pattern of the LiFePO₄ standard (Sigma-Aldrich, > 97% purity). The pattern shows the presence of both LiFePO₄ and FePO₄ phases. The relative intensities of the peaks show that FePO₄ was present in small quantities which was consistent with the 97% purity rating of the sample. EELS spectra were collected on the aberration corrected FEI Titan microscope at an accelerating voltage of 300kV. The energy resolution was 0.8eV and data were acquired in an energy window containing the peaks associated with the bulk plasmon, Li-K and Fe-M excitations. Fig. 1b shows three EELS spectra recorded from different regions of a single nanoparticle agglomerate of LiFePO₄. These spectra are compared with EELS database spectra for Fe₂O₃ and LiF. The first interesting observation is that the energy of the bulk plasmon peak (E_p) or valence electron peak appears to vary across regions of the nanoparticle. Similar valence electron peak shifts (> 1eV) have been observed by McComb and Howie [9] in dealuminated zeolite crystal. According to them the peak shifts are due to dealumination in the zeolite unit cell. The process of dealumination was observed more easily by the consequent shift in plasmon/valence energy than by core loss energy shifts. In our study, similar valence electron peaks shifts are observed in the range 22-25 eV between different regions of the LiFePO₄ particle. This is presumably due to a change in valence electron density or the unit cell volume, or both. In this case such

shifts are presumably associated with local variations in lithium concentration. Similarly Li-K and Fe-M_{2,3} edges shifted to lower energy-losses when compared with database spectra. More significantly, some spectra show only one of the ionization edges i.e., Li-K or Fe-M while others contain both excitations. This variation suggests the existence of compositional inhomogeneity across the same particle as we had earlier seen with valence electron peak shifts. The ability to observe such small peak shifts in STEM-EELS provides a platform to characterize phase changes occurring during the delithiation process in the LiFePO₄/FePO₄ microstructure. Analysis performed in this study on the standard LiFePO₄ particle will form the basis for studies on particles of composite cathode material in order to correlate low loss EELS data with the evolution of phases with aging in these materials [9–11].

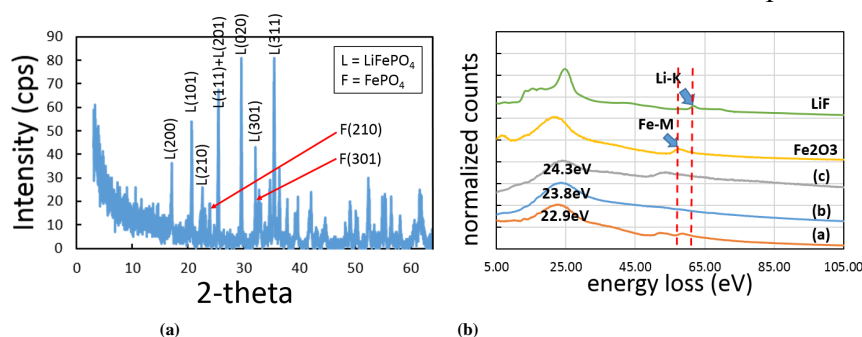


Fig. 1: (a) XRD spectrum of a standard nanoparticle showing LiFePO₄ and FePO₄ peaks; (b) EELS spectra from different regions

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