

Probing the Local Chemical and Structural Ordering of Iron Oxyfluoride

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Scanning transmission electron microscopy (STEM)-electron energy loss spectroscopy (EELS) has been used for studying local structure of the energy related materials. High resolution (Cs-corrected) STEM is regarded as a promising technique to observe morphological evolution and atomic arrangement inside single particles. Combining with EELS technique, one could probe the local chemical structure therefore to give the high spatial resolution information on the chemical evolution, which information could not be obtained by other characterization techniques, such as X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).

In the iron fluorite system used for the cathode for Li-ion battery, conversion reaction behavior of FeF_2 was investigated using STEM-EELS technique.[1-2] The importance of the local morphological evolution on the reversibility was identified by comparing highly reversible FeF_2 and irreversible CuF_2 . FeO nanoparticles (< 5 nm) interconnected each other to form bicontinuous network inside LiF matrix while larger CuO particles (5- 12 nm) were isolated by surrounding LiF after lithiation. In contrast to simple phase behavior of FeF_2 ($\text{FeF}_2 + 2\text{Li}^+ + \text{e}^- = 2\text{LiF} + \text{FeO}$), multiple phase coexist together in $\text{FeO}_{1-\delta}\text{F}_{1+\delta}$ cathode during cycling, implying the complexity in the morphological and chemical evolution during the reaction.[3] The separation of O-based phase (rocksalt Li-Fe-O(-F)) and F-based phase (LiF, amorphous FeF_2) was identified from the literature, but how the O/F-based phases are distributed inside the single particle is not clear yet. In addition, valence state of Fe and its distribution in $\text{FeO}_{1-\delta}\text{F}_{1+\delta}$ during cycling is a critical issue to understand the reaction. Since Fe atom has variety of valence states (e.g., Fe_0 , Li-Fe-O, amorphous FeF_2), the Fe valence distribution could inform the phase distribution inside the single particle as a function of Li content. In this respect, high resolution characterization is expected to be the most suitable analytical tool to study the single particle behavior of $\text{FeO}_{1-\delta}\text{F}_{1+\delta}$ cathode to complement the bulk measurement techniques in the literatures.

Here, we studied morphological and chemical evolution of well-ordered ellipsoidal $\text{FeO}_{0.7}\text{F}_{1.3}$ nanoparticle during cycling to understand the impact of O-substitution to FeF_2 [4]. Morphological evolution depending on Li content during cycling was traced by HAADF imaging. Spatial distribution of constituent elements (i.e., Li, Fe, O, F) and valence state of Fe at pristine, discharged (1.5 V) and recharged (4.5 V) $\text{FeO}_{0.7}\text{F}_{1.3}$ single particle was identified via high resolution EELS (< 1 nm) to track the O/F distribution, redox reaction of Fe, and corresponding atomic rearrangement during the Li storage/release reaction.

References

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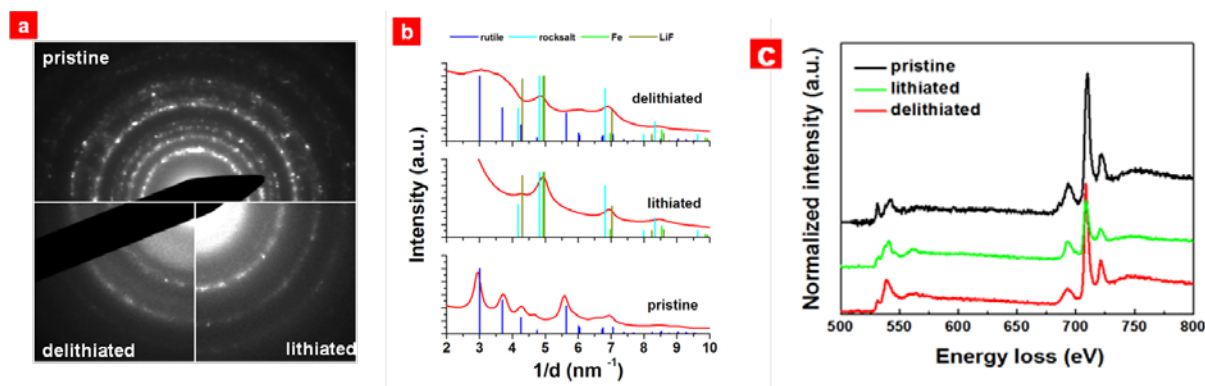


Figure 1 Diffraction pattern (a,b) and EELS spectra(c) of pristine, delithiated and lithiated samples.

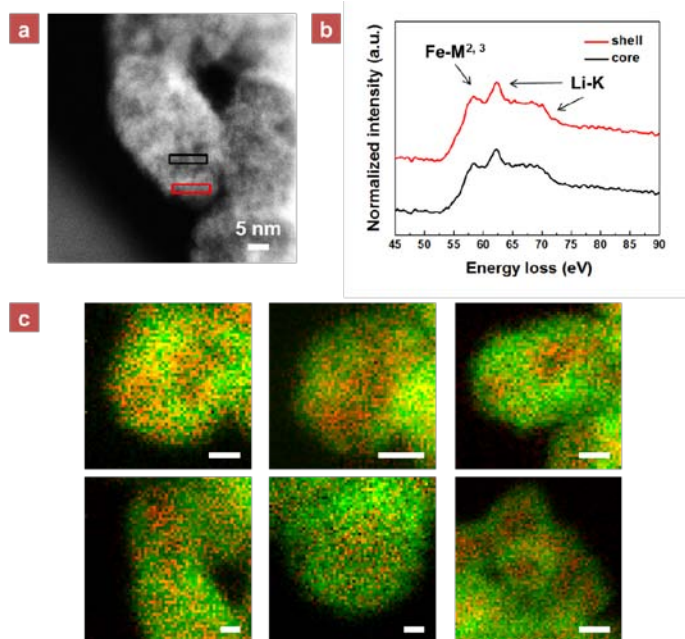


Figure 2 (a)ADF image of a $\text{FeO}_{0.7}\text{F}_{1.3}$ nanoparticle at the lithiated state. (b) Selected area EELS spectra from the core and shell region. (c) Elemental distribution of Fe (green) and Li (red) (scale bar: 5 nm) of $\text{FeO}_{0.7}\text{F}_{1.3}$ at lithiated state.