

STEM/EELS and Diffraction Study of Phase Transformation in $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$ Nanocomposites after Lithiation/Delithiation

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Recently, transition-metal fluorides have received considerable attention as positive electrodes due to their high specific capacities [1]. Iron oxyfluoride is one of the materials in this group, with a theoretical capacity after complete lithiation of 885 mAh/g. In FeOF conversion materials the transition metal reduces to metallic iron (fully reduction) in contrast to intercalation materials with only partially valence changes [2,3]. In study, the combined techniques of selected area electron diffraction (SAED), and electron energy loss spectroscopy (EELS) have been used to study the structural changes and reversibility of $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$ upon lithiation/delithiation. In addition, ADF-STEM and DF-TEM imaging were used to study size, morphology and distribution of the converted phases.

The SEAD intensity profile of the initial $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$ confirms the existence of rutile phase (Figure 1(a)). Upon Li insertion, the rutile reflections shifted slightly toward higher hkl-spacings, suggesting the expansion of the unit cell associated with reduction of Fe^{3+} to Fe^{2+} . Also (101) and (211) reflections grew in intensities up to 0.8 Li, which is attributed to the formation of new distorted rutile-II phase. Further lithiation up to 1.68 Li leads to both the gradual decrease in rutile II reflections intensities and the formation of two new reflections (around 4.7 nm^{-1} and 6.7 nm^{-1}), which are associated with the formation of converted phases (rocksalt-type and Fe). Figure 2(a) shows ADF-STEM image of the lithiated sample with 1.68 Li, consisting of about 2.3 nm metallic iron (bright contrast). The corresponding Li-K/Fe-M intensity ratio map (Fig. 2(b)) shows phase distribution of rich Li phase (rocksalt phase) and low Li phase (metallic iron). The particle size distribution of Fe and rocksalt phase nanoparticles measured from the lithiated sample with 1.68 Li ADF-STEM and DF-TEM images is shown in Figure 2(c), with average particle size of about 3.6 nm. This indicates the significant particle size reduction of the initial electrode particle size with 15 nm to the converted phases (Fe^0 , $\text{Li}_{0.7}\text{Fe}^{2+}_{0.5}\text{O}_{0.7}\text{F}_{0.3}$, and LiF) with 3.6 nm upon lithiation.

Upon delithiation, the I_1 and I_2 reflections corresponding to the cubic phases can be observed up to full recharge as shown in the SAED intensity profiles during delithiation of Figure 1(b). In addition, broad and diffuse reflections are observed above 1.02 Li, which are associated with the formation of an amorphous phase. The delithiated samples with amorphous rutile and rocksalt phases have been found to intermix and recrystallize under low dose electron beam irradiation into a rutile-type phase with long-range order.

The Fe valence state was determined with nanometer spatial resolution by measuring the relative intensity of EELS Fe-L₃ and Fe-L₂ lines during cycling. Figure 3 shows the plot of the experimentally measured Fe valence states as a function of Li content for discharge (lithiated) and recharge samples. High and low Fe valence states has been measured for the lithiated samples above 1 Li and the valence difference is largest for the sample with 1.68 Li, suggesting the formation of converted phases with two different valence states (Fe^0 , $\text{Li}_{0.7}\text{Fe}^{2+}_{0.5}\text{O}_{0.7}\text{F}_{0.3}$ upon lithiation. Upon full recharge (delithiated electrode), the measured average Fe valence state returns back to its initial value of $\text{Fe}^{+2.7}$ (c.f. Figure 3).

References

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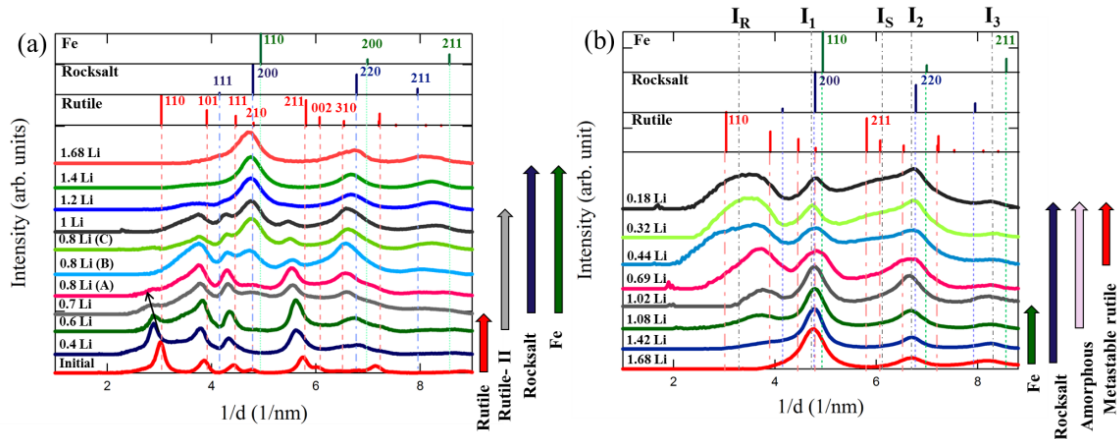


Figure 1. SAED intensity profile of $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$ as a function of Li content for (a) lithiated, and (b) delithiated samples.

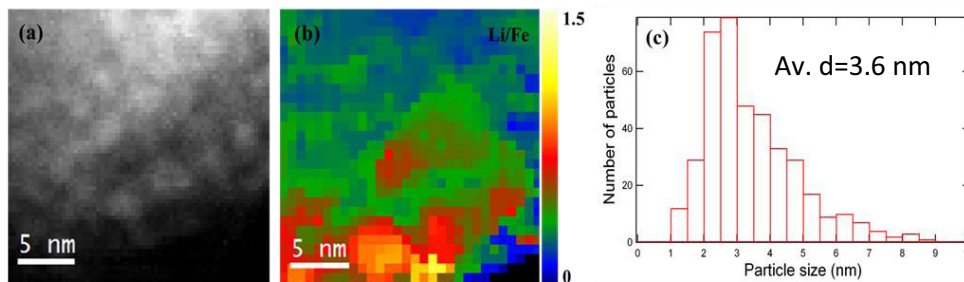


Figure 2. (a) ADF-STEM image of the lithiated $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$ with 1.68 Li, b) corresponding Li-K/Fe-M EELS intensity ratio map, and (c) particle size distribution of Fe and rocksalt phases obtained from DF-TEM for lithiated sample with 1.68 Li.

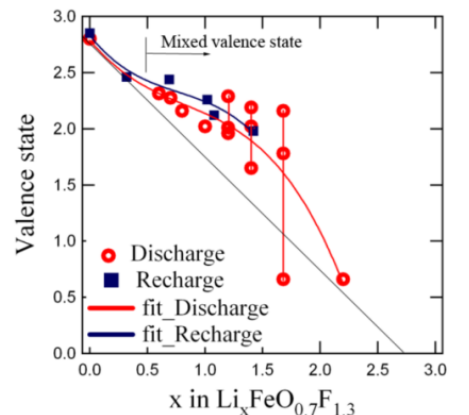


Figure 3. Fe valence state calculated from Fe L_3 over L_2 intensity ratio as a function of Li content x for the lithiated and delithiated $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$ samples.