

Structural transformation of conversion  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  nanocomposite electrode upon lithiation/delithiation  
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Recently, transition-metal oxides and fluorides have received considerable attention as electrodes due to their unique high specific capacities [1,2]. Among this group of materials, iron oxyfluoride has 885 mAh/g theoretical specific capacity upon fully lithiation. However, FeOF has low electronic conductivity and therefore this cathode material is enabled via synthesis of FeOF/C nanocomposite by mechanical milling with carbon. [3,4]. In this study, we have followed structural changes upon lithiation and delithiation by scanning transmission electron microscopy (STEM) combining selected area electron diffraction (SAED) and electron energy loss spectroscopy (EELS) techniques.

Figure 1 shows voltage profile of  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  at 60°C under a constant current of 50mA/g. The filled dots represent the conditions used for the ex-situ TEM experiments.

It was found that the first region (Figure 1) from 0 to 0.6 Li content corresponds to an intercalation reaction. In this region lithium inserted into  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  (rutile structure) accompanied with the unit cell expansion, which is associated with reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . In the second region (Figure 1) from 0.6 to 1.68 Li, a new converted Li-Fe-O-F phase with rocksalt-type structure is forming while the intercalated rutile-type phase is decreasing. Therefore, lithiated  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  with 1.68 Li contains rocksalt type phase (Li-Fe-O-F), LiF and metallic Fe. Upon recharge process, diffraction patterns show reconversion to metastable rocksalt type structure and amorphous rutile type phases.

Energy-loss Spectroscopy (EELS) was used to investigate the distribution of lithium and the valence state of iron via measuring Fe  $L_3/L_2$  line intensity ratio with nanometer spatial resolution [4]. Figure 2 shows the measured Fe valence states from lithiated and delithiated samples as a function of Li content. Figure 2 shows Fe valence state decreased/increased upon lithiation/delithiation and complete reversibility of Fe valence state. Also it can be observed the existence of two phases with different Fe valence states above 0.6 Li during lithiation, which is corresponding to the formation of converted phases, ( $\text{Fe}^0$  and  $\text{Li}_{0.7}\text{Fe}^{2+}_{0.5}\text{O}_{0.7}\text{F}_{0.3}$ ). Figure 3 shows phase separation of  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  with 1.68 Li. Figure 3(a) is the annular dark field STEM image of the lithiated FeOF with 1.68 Li. The corresponding Fe-L and O-K concentration maps (Figure 3b and 3c respectively) show phase distribution of rich Fe phase ( $\text{Fe}^0$ ) and O-K phase ( $\text{Li}_{0.7}\text{Fe}^{2+}_{0.5}\text{O}_{0.7}\text{F}_{0.3}$ ).

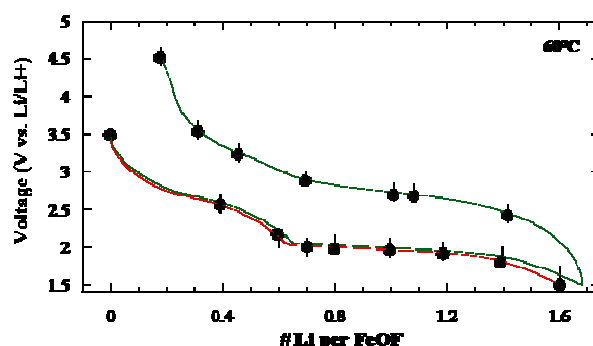


Figure 1. Electrochemical behavior of  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  for the first discharge and recharge.

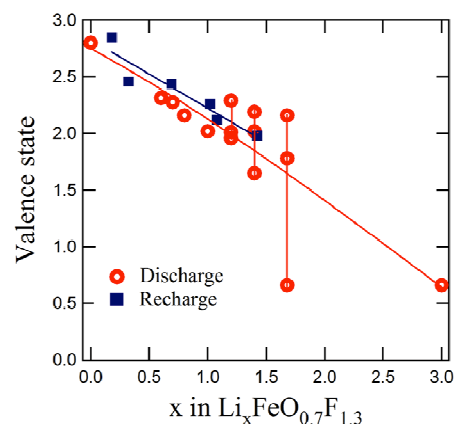


Figure 2. Fe valence states of  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  during lithiation and delithiation as a function of Li content.

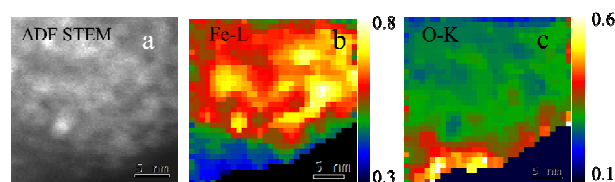


Figure 3 (a) Annular dark field STEM image of the lithiated  $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$  with 1.68 Li with corresponding concentration map of (b) Fe-L and (c) O-K .

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#### References

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