EELS Determination of Li Distribution and Fe Valence Mapping in Lithiated FeOF/C Nanocomposite Battery Materials

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Positive electrodes for Li-ion batteries have been developed recently based on transition metal fluoride (FeF_3, $FeOF$, FeF_2, CuF_2….)/C nanocomposites [1]. The high specific capacity in these materials is obtained by using all the oxidation states of Fe from Fe^{+3} to Fe^0 during discharge and charge cycles. To investigate battery electrode materials, electron energy loss spectroscopy (EELS) is unique as with this technique, the local Li distribution and Fe valence state can both be determined with nanometer scale spatial resolution. In this study, we have used Scanning Transmission Electron Microscope (STEM) combined with EELS spectroscopy to determine the Li spatial distribution and the Fe valence state in FeOF/C nanocomposites positive electrodes.

This STEM-EELS analysis was done using a JEOL 2010F equipped with a Gatan GIF 200 spectrometer and with a Hitachi 2700 STEM equipped with an Enfina spectrometer. In order to minimize electron beam damage and F loss, the samples were cooled to LN_2 temperatures and imaged with a total electron dose not exceeding 10^4 C/cm^2. Both lithiated (discharged) and de-lithiated (re-charged) FeOF/C nanocomposites electrodes were analyzed by EELS. The Fe valence state was obtained by measuring the Fe L_3/L_2 intensity ratio [2]. The L line intensities were obtained using either a 5.1 eV window or by taking the positive component of the EELS spectra second derivative.

The low loss EELS signal for the lithiated sample to 1.5 V is shown in Fig. 1 revealing the superposition of the Li-K edge and Fe-M edge. The Li-K edge has two prominent peaks whose energies are separated by 6.6 eV. In addition to the two prominent Li peaks, there is a third one located at a distance of 4.2 eV from the first peak. The existence of these peaks is indicative of the presence of two Li-base compounds LiF and possibly a new Li-Fe-O phase. The Li-K/Fe-M intensity map is shown in Fig.2b with the corresponding STEM-ADF depicted in Fig.2a. This figure reveals the presence of Li and Fe rich phases with a spatial distribution in the 3-5 nm range. At this voltage the expected phases are $LiF+Fe^0+Li_xFe^{n+}O_y$ [3]. At the surface, a Li rich phase is observed corresponding to mixed $LiF-Li_2CO_3$ solid electrolyte interface (SEI) surface layer.

Upon lithiation, the Fe valence state decreases as represented by the decrease in Fe-L_3/L_2 intensity ratio shown in Fig.3. At the lowest voltage of 0.8V, Fe is in the metallic state. Upon recharge to 4.5 V, the Fe in the electrode returns to its initial Fe^{+3} valence state and the electrode converts back to the initial rutile FeOF structure. At 1.5 V, the valence state is not uniform and the microstructure is composed of a mixture of high and low valence state phases as depicted in Fig. 4b. The O-K concentration map shown in Fig.4a has a similar distribution as the valence map of Fig. 4b which indicates that the oxygen rich phase is also the phase with highest valence state. A quantitative analysis of the Fe L_3/L_2 intensity ratio using standard compounds (Fe^0, $Fe^{2+}F2$ and $Fe^{3+}OF$) indicate a valence state in the 2.2-2.4 range for this $Li_xFe^{n+}O_y$ phase.

References
[1] G.G. Amatucci and N. Pereira, *J. Fluorine Chem*. 128 (2007) 243
[2] F. Cosandey et al. *Microscopy and Microanalysis*, 13 (2007) 1-9
[3] N. Pereira et al, J. *Elechtrochem. Soc*., 156 (2009) A407-A416
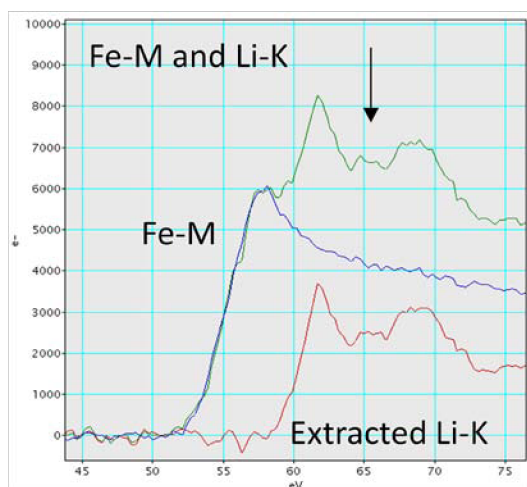[4] This research was supported by NECCES, a DOE-BES-EFRC funded center under Grant Number DE-SC0001294

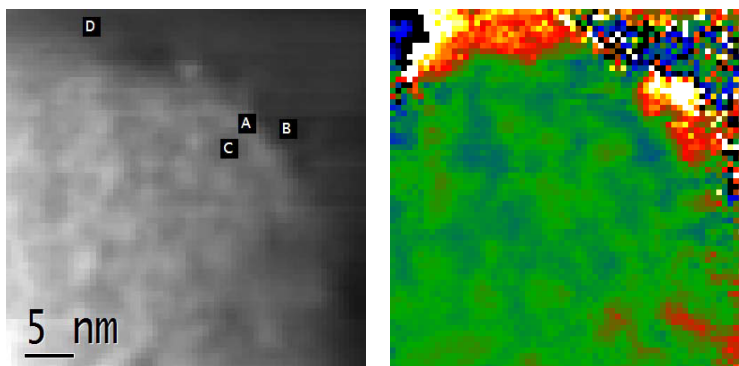Figure 1: Fe-M and Li-K edges from FeOF/C positive electrode discharged to 1.5V

Figure 2. (a) ADF-STEM image and (b) Li-K/Fe-M signal intensity ratio map taken from FeOF/C discharged to 1.5V
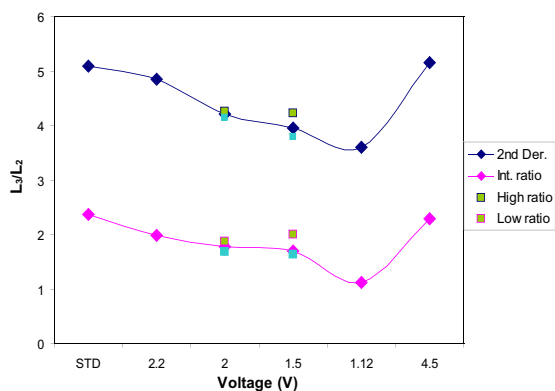

Figure 3: Fe L_3/L_2 intensity ratio as a function of discharge and charge voltages measured using either the second derivative or with a 5.1 eV window method.
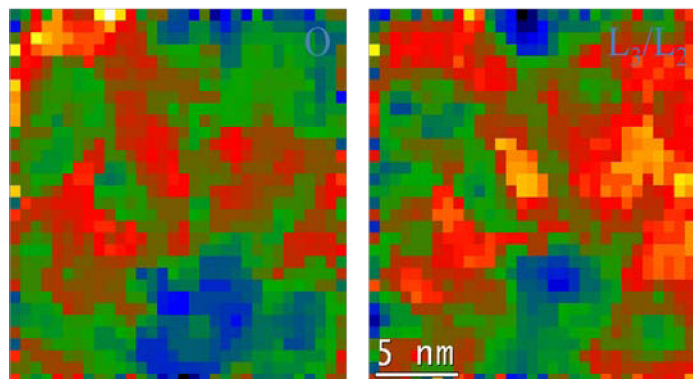

Figure 4: (a) O-K concentration map and (b) Fe L_3/L_2 intensity map taken from FeOF/C discharged to 1.5V