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EELS Compositional Imaging of FeF_2-C Nanocomposite Used as a New Positive Electrode in Li-Ion Batteries

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Carbon ferrous fluoride (FeF_2-C) nanocomposite is a new type of positive electrodes for Li-Ion batteries, which has been introduced recently [1-3]. The electronic and ionic properties of this material have been improved drastically by transforming this insulator material into FeF_2 nano domains with 8-12 nm particle size range embedded in a conductive carbon matrix. The utilization of the full reduction of the Fe^{2+} in FeF_2 to Fe^{o} is the main reasons which led to four times increase in capacity as compared to the conventional $LiCoO_2$ based materials. The exact reaction mechanisms and phase transformation which are accompanying the charging and discharging $FeFe_2$-C material are still not fully understood. Therefore, EELS spectroscopy and spectrum imaging were used to investigate the elemental and valence distribution associated with the lithiation process.
The FeF_2-C cathode materials taken at various lithiation stages (as synthesized, 20 hrs, 42 hrs, and fully discharged) were prepared for TEM analysis. HRTEM images were conducted using TOPCON 002B TEM operated at 200 kV. EELS spectrum imaging was conducted using Philips CM200 FEG TEM equipped with Gatan Imaging Filter (GIF) operating in STEM-mode at 200kV. Because of the high sensitivity of the FeF_2 material to electron beam, an under-focused STEM probe with a diameter of ~ 2nm was used. In addition time series with stationary probe were also conducted. Compositional as well as valence maps in the 2-nanometer scale were collected from all the above samples to investigate the lithiation process (FeF_2 +2Li ↔2LiF+Fe).
Compositional EELS images were collected from the as synthesized sample and at various lithiation stages. Figure 1 shows compositional images of the as synthesized FeF_2 electrode (before lithiation). The elemental maps of this electrodes show almost homogenous distribution of both Fe and F throughout the sample. However, the Fe valence map ratio (Fe-L_3/L_2) showed some regions of Fe^{+3}, because of the presence of the double peaks in the Fe-L_3 from individual spectrum and the higher Fe-L_3/L_2 ratio [4,5]. Elemental maps of electrode which has been discharged for 42 hrs (figure 2) shows fluorine rich and iron rich regions. Investigation of individual EELS spectra from the samples shows that the Fe rich regions consists of metallic Fe while remaining regions show signals from both Fe and F(figure 2). These chemical maps show a consistent transformation of FeF_2 into Fe and LiF nanodomains upon reaction with Li ions. These results are in a complete agreement with the expected lithiation reaction mentioned above. These results are the first steps in the analysis of these highly beam sensitive materials using EELS compositional mapping and additional work is underway to shed some light on the atomistic mechanism of the lithiation process.

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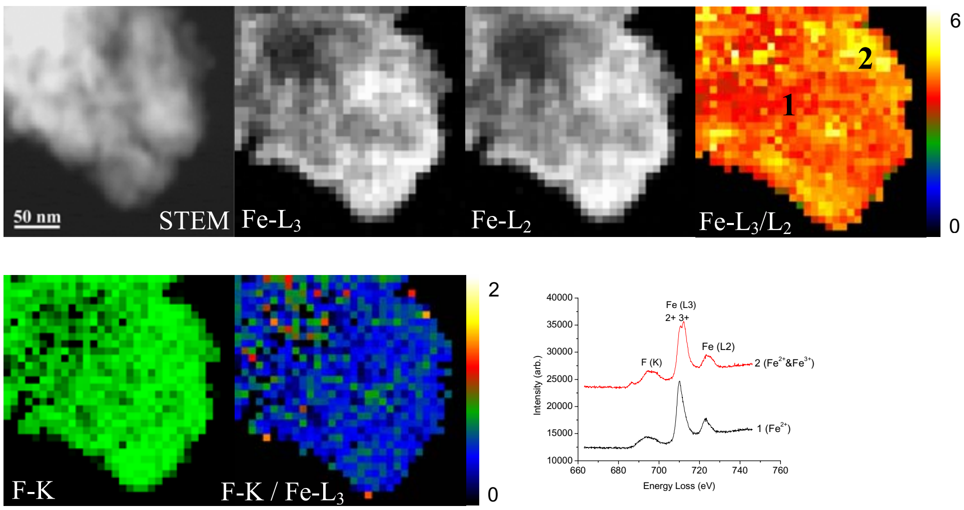

Figure1., EELS maps of the as synthesized electrode, (STEM image, $Fe-L_3$, $Fe-L_2$, $Fe-L_3/L_2$, F-K, $F-K/Fe-L_3$ maps and EELS spectra correspond to spots 1 and 2 shown in $Fe-L_3/L_2$ map). Each image is 256 by 256 nm in size

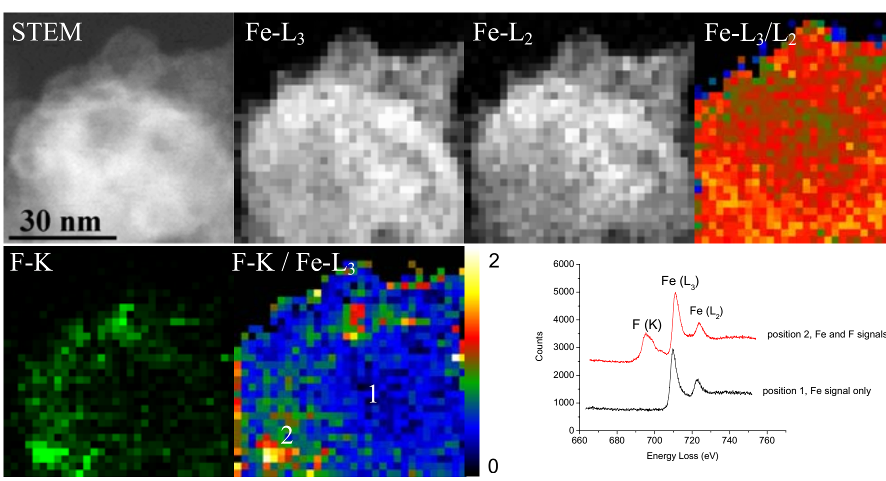

Figure 2., EELS maps of the FeF_2-C electrode discharged for 42 hrs, (STEM image, $Fe-L_3$, $Fe-L_2$, $Fe-L_3/L_2$, F-K, $F-K/Fe-L_3$ maps and EELS spectra correspond to spots 1 and 2 shown in $F-K/Fe-L_3$ map. Each image is 256 by 256 nm in size

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