

## EELS Analysis of Radiation Induced Structural Transformations in Fluoride Compounds

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A new type of positive electrode for Li-ion batteries has been developed recently based on transition metal fluoride compounds ( $\text{FeF}_3$ ,  $\text{FeOF}$ ,  $\text{FeF}_2$ ,  $\text{CuF}_2$ , ...)[1]. In order to understand redox evolution and microstructural changes during discharge and recharge processes we are performing EELS analysis combined with high spatial resolution spectrum imaging. However, in view of the high beam sensitivity of fluoride compounds, it is necessary to understand the effect of radiation induced structural transformations caused by the high intense electron beam. In this study, we performed an EELS analysis of structural changes in fluoride compounds caused by irradiation with an intense nanometer-sized electron probe. One advantage of using EELS is that it can provide information on both the F loss and the associated changes in oxidation state of the transition metal. The results are presented in terms fluorine loss and electronic fine structure changes of the transition metals.

The EELS spectra were obtained with a Gatan GIF-200 spectrometer attached to a JEOL 2010F equipped with thermionic field emission source operated at 197 kV. The EELS energy resolution was 1.2 eV. Metal fluorides are sensitive to radiation damage and all EELS spectra were taken in STEM mode with a 0.3 nm probe size and 0.2 nA probe current. The valence state of the transition metal has been followed from changes in  $L_3$  peak energy and  $L_3/L_2$  intensity ratio. For measuring the EELS peak intensities, we used the positive intensity under the second derivative.

The time evolution of the EELS spectra for the standard  $\text{FeF}_3$  material under beam irradiation is shown in Fig. 1(a). The initial EELS spectrum is represented by the Fe  $L_{23}$  white lines and F  $K$ -edge. In addition, there is a small pre-peak at the F- $K$  edge in  $\text{FeF}_3$  which is due to the mixing of the F- $2p$  with Fe- $3d$  electrons indicative of covalent bonding [2]. This F pre-peak has also been observed in  $\text{FeOF}$  and seems to be associated with  $\text{Fe}^{3+}$  state as it does not appear for  $\text{FeF}_2$ . Upon beam irradiation, this pre-peak decreases quickly after only 5 sec exposure time, indicative of a transformation from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . This rapid change in valence state is also represented by the decrease in Fe-  $L_3$  peak energy as depicted in Fig. 1(b). The Fe  $L_3/L_2$  intensity ratio is dependent on the d band occupancy and hence to the charge state of the transition metal cation. Fig. 1b shows the variation of the ratio between  $L_3$  and  $L_2$  lines versus exposure time. A decrease in Fe  $L_3/L_2$  intensity ratio corresponds to a decrease in the oxidation state of iron ions from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and finally to  $\text{Fe}^0$ . As shown previously [2] the  $L_3/L_2$  intensity ratio continues to decrease with changes in valence state from  $\text{Fe}^{2+}$  to  $\text{Fe}^0$  although the  $L_3$  peak energy remains almost constant.

The time evolution of the EELS spectra for copper fluoride ( $\text{CuF}_2$ ) nano particles is shown in Fig 2(a) and (b). The initial EELS  $\text{CuF}_2$  spectrum is represented by the F- $K$  edge and by the Cu- $L_3$  and Cu- $L_2$  white lines. After beam exposure, we observed a broad but prominent peak about 40 eV above the Cu- $L_3$  ionization threshold in  $\text{CuF}_2$ . This post peak becomes dominant after long exposure (25 sec), indicative of complete conversion to metallic copper. The absence of  $L_{23}$  white lines for metallic copper is due to a filled  $3d$  band. A similar post peak is visible in the spectra of copper

reported by Leapman et al. [3]. During beam exposure, the F-*K* edge decreases in intensity with a sharp decrease in Cu-*L*<sub>3</sub> peak intensity as well as an increase in *L*<sub>3</sub> peak energy associated with the change in oxidation state from Cu<sup>2+</sup> to Cu<sup>0</sup>. The evolution of both of these features for various beam exposure time is shown in Fig 2(b).

## References

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- [2] F. Cosandey et al, *Microsc. Microanal.* 13 (2007) 87.
- [3] R. D. Leapman, L.A. Grunes and P.L. Fejes, *Phys. Rev. B* 26 (1992) 614.

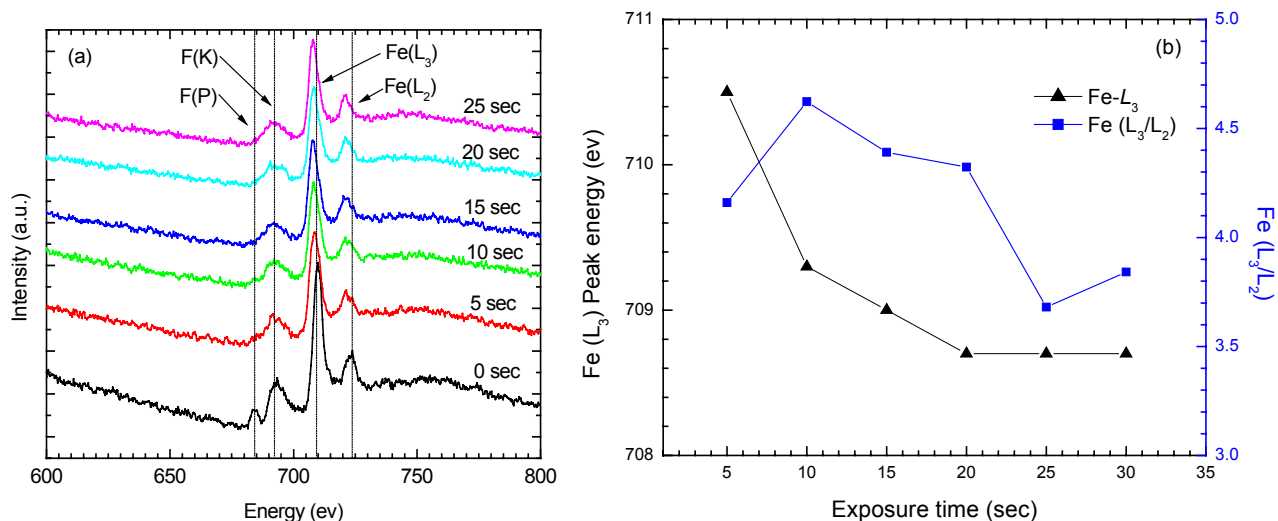


FIG. 1. (a) Time evolution of Fe *L*<sub>23</sub> white lines and F-*K* edge of FeF<sub>3</sub> with in (b) the variation of Fe *L*<sub>3</sub> peak energy and *L*<sub>3</sub>/*L*<sub>2</sub> intensity ratio as a function of beam exposure time.

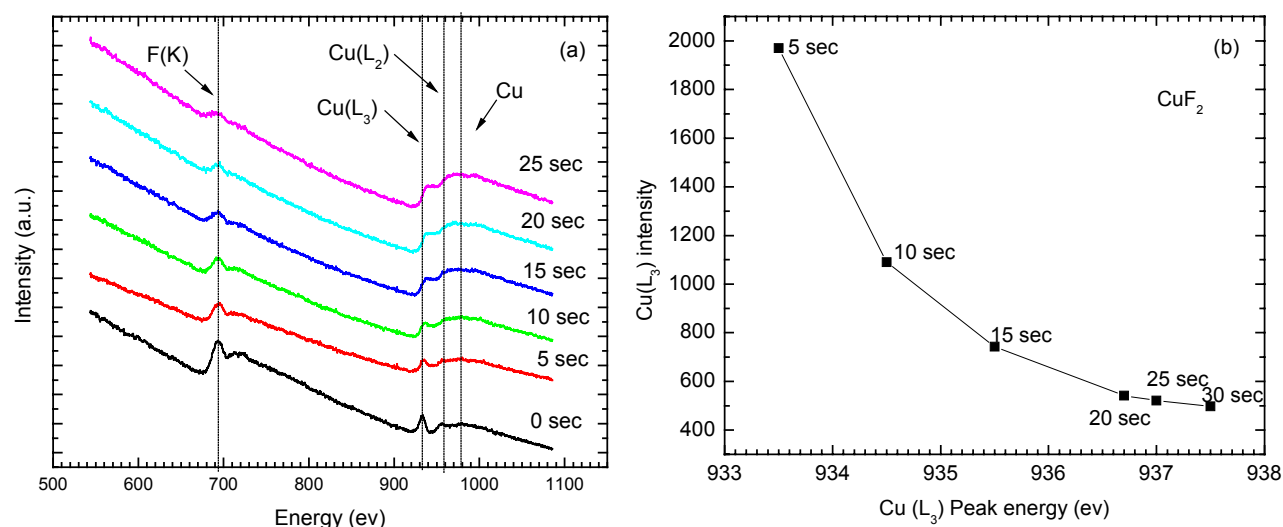


FIG. 2. (a) Time evolution of Cu *L*<sub>23</sub> white lines and F-*K* edge of CuF<sub>2</sub>, with in (b) the variation of Cu *L*<sub>3</sub> peak intensity and peak energy for various beam exposure times.