Recently, we have synthesized a new type of positive electrodes for Li-Ion batteries based on FeF$_2$/C nanocomposites [1-3] with 8-12 nm particle size. In these nanocomposites, we have measured battery capacities that exceed those based on the standard LiCoO$_2$ electrode. The measured high capacity rely on a complete reduction of Fe according to the following reaction:

$$x\text{Li}^+ + xe^- + Fe^{x+}F_x = x\text{LiF} + Fe^{0}$$

Two iron fluorides nanocomposites have been studied namely FeF$_2$/C and FeF$_3$/C with initial x=2 and x=3 valence states respectively. In this paper, we report TEM studies on the electrochemical conversion processes, performed with a Hitachi HF200 and Gatan PEELS. Specifically, we used EELS spectroscopy to follow the valence state of Fe during battery charge and discharge processes.

**EELS spectroscopy of standard compounds:** In order to follow quantitatively the chemical state of Fe during charge and discharge processes, we have examined first the standard LiF, Fe, FeF$_2$, and FeF$_3$ compounds that are expected to occur during the electrochemical reactions. Representative EELS spectra for fluorine K edge and iron L edge from FeF$_2$ and FeF$_3$ are shown in Fig.1a and 1b respectively. The L edge of Fe is characterized by the two L$_3$ and L$_2$ white lines resulting from the transition of electrons from the spin-orbit split levels 2p$^{3/2}$ and 2p$^{1/2}$ to unoccupied 3d states. The other peak observed at 693.4 eV corresponds to the fluorine K edge resulting from a transition of electrons from the 1s level to unoccupied 2p states. For FeF$_3$, there is an additional pre-peak marked P$_1$ located at 684.6 eV. The existence if this pre-peak can been attributed to a forbidden 1s to 3d transition indicating that the unoccupied 2p states hybridized with 3d Fe orbital giving rise to significant covalent effects in FeF$_3$ [4]. For iron compounds, the L$_3$ peak energy as well as the L$_3$/L$_2$ peak intensity ratio increases with increasing valence state of Fe allowing an unambiguous determination of Fe valence state [5].

**Effects of beam exposure on phase stability.** Fluoride compounds are extremely electron-beam sensitive and in this study we have investigated the effects of electron beam exposure on chemical evolution of standard FeF$_2$ and FeF$_3$ compounds by recording the Fe L and F K EELS spectra as a function of time (Dose~1x10$^{-6}$Cm$^{-2}$/s). For FeF$_2$, the electron beam induces a surprising phase transformation as shown in Fig. 2. First, a second L$_3$ peak is observed 1.1 eV higher in energy and second, a prepeak P$_1$ starts to form as marked by an arrow. After about 20 s of beam exposure a spectra similar to the FeF$_3$ (c.f.Fig.1a) is observed. For longer times, not shown here, the EELS spectra reveal the disappearance of the prepeak P$_1$ followed by complete disappearance of the fluorine K peak. Finally, after long exposure, a spectrum typical of metallic Fe is observed. Both the shift in Fe L$_3$ peak energy and the formation of the F pre-peak P$_1$ are indicative of the formation of an intermediate FeF$_3$ structure before complete transformation to metallic Fe. For an initial FeF$_3$ structure, fluoride dissociation and complete transformation to metallic Fe is observed.

**EELS spectroscopy of lithiation process.** In order to follow quantitatively the valence state of iron, after discharge and during re-charge processes, we have examined by EELS spectroscopy the as synthesized FeF$_3$/C and FeF$_2$/C nanocomposites as well as positive electrode material taken at various stages of lithiation process corresponding to discharge voltages of 1.5 V and recharge voltages of 3.4 V and 4.5 V. For TEM observations, samples were obtained by disassembling the electrochemical cells containing positive electrode in powder form [1, 2]. After full discharge of FeF$_2$/C and FeF$_3$/C nanocomposite electrodes, metallic Fe is observed as expected from the electrochemical reaction shown above. Upon recharging to 4.5V, Fe reverts back to a F$^{2-}$ state as shown in Fig.3. This observation holds true regardless of the initial FeF$_2$/C or FeF$_3$/C nanocomposites structure. This result is an indication that the only fully reversible electrochemical reaction occurs for FeF$_3$/C nanocomposites.
References


Fig.1. Characteristic EELS spectra for standard compounds (a) FeF₂ and (b) FeF₃

Fig.2. Effect of electron beam exposure (time) on the evolution of EELS spectra for an initial FeF₂ compound

Fig.3. EELS spectrum of an initial FeF3/C nanocomposite discharged and recharged to 4.5V and comparison with FeF₂ and FeF₃ compounds,