For Li-ion batteries, transition metal fluoride/carbon nanocomposites have been under extensive investigation as cathode materials due to their high theoretical capacity between 500 to 800 mAh/g [1,2]. In this study, the structural changes of FeOF/C positive electrode during lithiation/delithiation have been studied as a function of number of cycles (up to 20) under constant cycling current of 50 mA/g and at 60°C. ADF-STEM imaging technique combined with electron energy loss spectroscopy (EELS) were used to track the chemistry of surface layer (SEI) forming on FeOF/C cathode and to determine the bonding characteristics of phases present after cycling. This analysis was done at 200 kV with the JEOL 2010F equipped with Gatan 200 GIF spectrometer having an energy resolution of 0.9 eV.

Upon lithiation-delithiation cycling, the STEM-EELS analysis revealed the formation of a SEI layer as shown in the ADF-STEM image depicted in Fig. 1a. The thickness of this SEI layer is in the range of 20 to 40 nm. The corresponding O-K, F-K and Li-K EELS spectra for the delithiated sample after 20 cycles taken from regions marked 1 and 2 are shown in Fig.1b and 1c respectively. The F-K, O-K, and Li-K vary considerably between these two different regions (1 and 2) suggesting different chemistry in these two different parts of the sample. The edge of the active electrode (region 1) contains only lithium, carbon, fluorine, and oxygen associated with a solid electrolyte interphase (SEI) layer at the cathode. In addition different chemical state is observed for the O-K edge with a pre-peak present in FeOF/C electrode which is missing in the SEI layer (region 1). Quantitative analysis of SEI layer chemistry gives a composition corresponding to Li$_{0.45}$C$_{0.2}$O$_{0.05}$F$_{0.3}$. Figure 2a and 2b show the Li-K and F-K edge spectra respectively taken from region 1 (edge) and comparison with possible electrolyte decomposition compounds (LiF, Li$_2$CO$_3$) and with polymer binder (PDVF). The Li-K and F-K EELS spectra from region 1 can be identified as characteristic of LiF [3] from the presence of a post peak in the F-K edge and the separation the separation between the F-K and Li-K peaks of 24.6 eV and 7.2 eV respectively. An additional a small peak marked by an arrow in Fig.2b is also observed in the SEI F-K edge spectrum. This peak with energy of 708.3 eV has been attributed to Fe-L$_3$ line. Furthermore, the energy value of this peak is indicative of ionic Fe with Fe$^{+2}$ valence state. We have observed that this SEI layer thickness increases with cycle number.


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Fig. 1: (a) ADF-STEM image of the fully recharged FeOF/C cathode after 20 cycles, with the corresponding EELS spectra from region 1 and 2, (b) O-K, F-K and Fe-L$_{3,2}$ edges, and (c) Fe-M and Li-K edges.

Fig. 2: EELS spectra taken from SEI layer (region 1 from Fig. 2a) with (a) Li-K edge, (b) F-K edge and comparison with possible standard phases (LiF, Li$_2$CO$_3$ and PVDF). There is an extra peak on the SEI F-K edge at 708.3 eV which has been attributed to the presence of Fe-L$_{3}$ peak with Fe$^{2+}$ state.