

STEM/EELS Analysis of Conversion Reactions in Cycled FeOF/C

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Transition metal fluoride/carbon nanocomposites have been under extensive investigation in the past ten years due to their theoretical high capacity in the range of 500 to 800 mAh/g [1]. 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) and selected area electron diffraction (SAED) were used to track the phase evolution of FeOF/C and chemical composition with bonding characteristics of phases present after cycling.

Upon lithiation, the STEM-EELS and diffraction analysis revealed an initial transition from rutile FeOF to rocksalt (Li-Fe-O-F) followed by partial conversion to LiF and Fe at 1.5V [2, 3]. The effect of cycling did not affect significantly the formation of these phases but the amount of crystalline LiF increased with increasing cycle number. The SAED intensity profiles of fully recharged (delithiated) samples after different number of cycles are shown in Fig 1. For the first re-charged cycle, the intensity profile reveals the co-existence of broad amorphous reflections (I_R and I_S reflections) in addition to rocksalt-type (I_1 and I_2 reflections) reflections [3]. As the number of cycles increased, the intensity profiles show that the I_R and I_S reflections (associated with an amorphous rutile-type phase) decreased in intensity. The ADF-STEM image at first recharge does not show any contrast, however the ADF-STEM image after 20 cycles contains bright contrast, which is attributed to the existence of unreacted metallic iron. This presence of Fe nanoparticles indicates that the converted phases (LiF and Fe) did not fully recombine upon delithiation. Fig. 2 shows the ADF-STEM image and the corresponding O-K, F-K and Li-K EELS spectra for the recharged sample after 20 cycles taken from two different regions (marked 1 and 2). The F-K, O-K, and Li-K vary considerably between these two different regions (1 and 2) suggesting different chemistry in two different parts of the sample. The edge of the active electrode (region 1) contains only lithium, carbon, fluorine, and oxygen elements associated with a solid electrolyte interphase (SEI) layer at the cathode. Figure 3a and 3b show the comparison between the Li-K and F-K edge spectra of the region 1 (edge) with possible electrolyte decomposition compounds (LiF, Li_2CO_3) and polymer binder (PDVF). The Li-K and F-K EELS spectra from region 1 can be identified as characteristic of LiF [2]. An additional small peak marked by an arrow in Fig.3b is also observed in the SEI F-K edge spectrum. This peak with energy of 708.3 eV could be attributed to Fe- L_3 line. We have observed that the amount of this SEI layer increased with the number of cycles. This loss of active material (LiF and Fe) and incomplete reconversion of LiF and Fe to the amorphous rutile-type phase may be the cause for the observed capacity loss during cycling.

References

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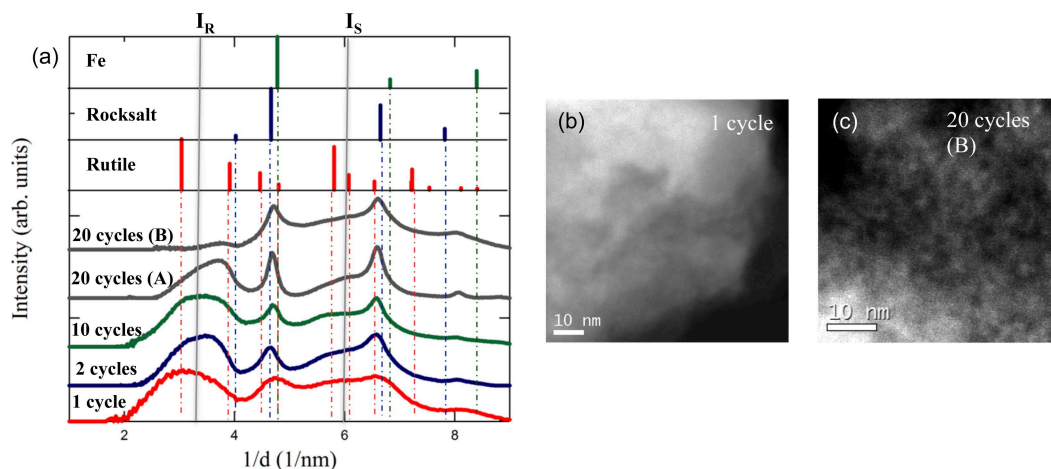


Fig 1. (a) SAED intensity profile of the delithiated FeOF/C as a function of cycle number, and the corresponding ADF-STEM images of the fully recharged electrode after (b) 1 cycle, and (c) 20 cycles take from corresponding SAED profile marked (B).

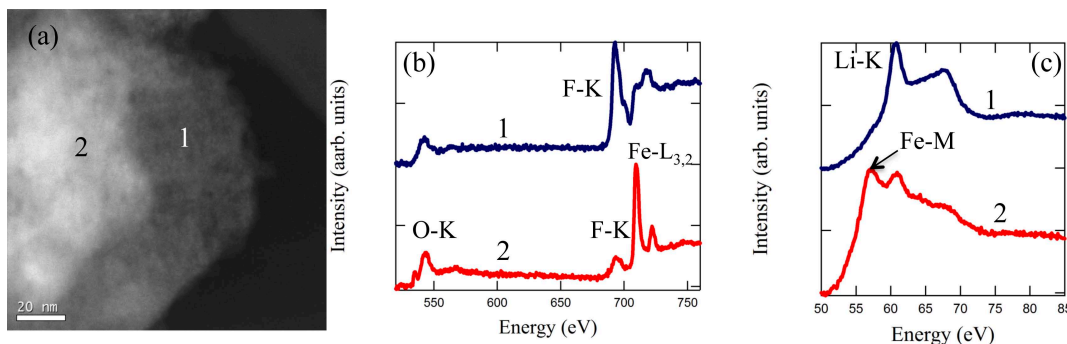


Fig 2. (a) ADF-STEM image of the fully recharged electrode after 20 cycles, and the corresponding EELS spectra from region 1 and 2, (b) O-K, F-K and Fe-L_{3,2} edges, and (c) Fe-M and Li-K edges.

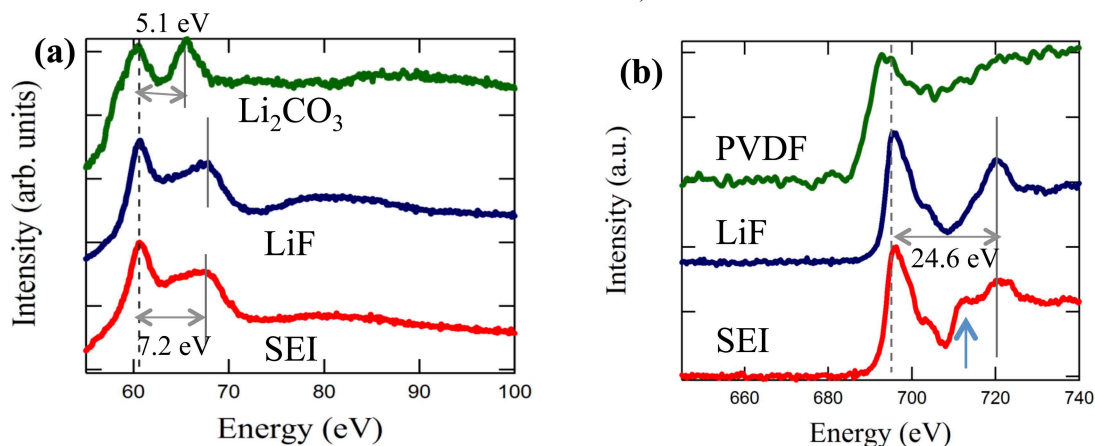


Fig 3. EELS spectra taken from SEI layer (region 1 from Fig. 2a) (a) Li-K edge, (b) F-K edge and comparison with possible standard phases (LiF, Li₂CO₃ and PVDF).