EELS determination of Li distribution and Fe valence mapping in lithiated FeOF/C nanocomposite electrode materials

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Amongst the techniques to investigate Li-ion battery materials, electron energy loss spectroscopy (EELS) play a unique role as Li distribution, chemical state and valence of transition metals (charge transfer) can all be determined with nanometer scale spatial resolution. In this work, we use EELS to investigate new positive electrodes for Li-ion batteries based on transition metal fluoride (FeF₃, FeOF, FeF₂, CuF₂....)/C nanocomposites [1]. The high specific capacity in these new electrodes is obtained by using all the oxidation states of Fe from Fe⁺³ to Fe⁰ during discharge cycles via a complete conversion process. In this study, we used Scanning Transmission Electron Microscopy (STEM) combined with EELS to determine the Li spatial distribution, its chemical state and the Fe valence state in FeOF/C nanocomposite electrodes during charge and discharge processes.

This STEM-EELS analysis was done using a JEOL 2010F equipped with a Gatan GIF 200 spectrometer and with a Hitachi 2700 STEM equipped with an Enfina spectrometer. In order to minimize electron beam damage and F loss, the samples were cooled to LN_2 temperatures and imaged with a total electron dose not exceeding 10^4 C/cm². Both lithiated (discharged) and delithiated (re-charged) FeOF/C nanocomposites electrodes were analyzed by EELS. The Fe valence state was obtained by measuring the Fe L₃/L₂ intensity ratio [2,3]. The L line intensities were obtained using either a 4.5 eV window or by taking the positive component of the EELS spectra second derivative.

An ADF STEM image of a FeOF/C cathode material discharged to 1.5V is shown in Fig.1a with the corresponding low energy EELS signal (c.f. Fig. 1b) taken from area marked A revealing the superposition of the Li-K and Fe-M edges. The extracted Li-K edge has two prominent peaks whose energies are separated by 6.6 eV. In addition to the two prominent Li peaks, there is a third one located at a distance of 4.2 eV from the first peak. The existence of these peaks is indicative of the presence of two Li-base compounds (LiF) and a new Li-Fe-O-F cubic phase. The Li-K/Fe-M intensity map shown in Fig.1c from the area depicted in Fig.1a reveals the presence of Li and Fe rich phases with a spatial distribution in the 3-5 nm range. At this voltage the expected phases are LiF+Fe⁰+Li_xFeⁿ⁺O_yF_z [3]. At the surface, a 10-20 nm thick Li rich phase (c.f. Fig 1d) is observed corresponding to a mixed LiF-Li₂CO₃ solid electrolyte interface (SEI) surface layer.

Upon lithiation, the Fe valence state decreases as represented by a decrease in the Fe-L₃/L₂ intensity ratio. At the lowest voltage of 0.8V, all Fe is in the metallic state. At the intermediate discharge voltage of 1.5 V, the Fe valence state is not uniform and the microstructure is composed of a mixture of high and low valence state phases as depicted in Fig. 2b. The O-K concentration map shown in Fig.2a has a similar distribution as the valence map of Fig. 2b which indicates that the oxygen rich phase is also the phase with highest valence state. A quantitative analysis of the Fe L₃/L₂ intensity ratios using standard model compounds (Fe⁰, Fe²⁺F₂ and Fe³⁺OF) as reference indicate a Fe valence state of 2.3 for this cubic Li_xFeⁿ⁺O_yF_z phase. Upon recharge to 4.5 V, all the Fe in the electrode returns to its initial Fe⁺³ valence state with the electrode material converting back to its initial rutile FeOF phase. [4].

References

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Figure 1. (a) ADF STEM image of FeOF/C discharged to 1.5V and (c) corresponding Li-K over Fe-M intensity ratio map. (b) Li-K and Fe-M edges taken from area marked A in (c) with top curve the superposed Li-K and Fe-M edges, middle curve is the reference metallic Fe edge and lower curve the extracted Li-K edge. (d) Li-K edge taken from area marked B in (c)



Figure 2. (a) O concentration map (at%) of lithiated (discharge) FeOF/C to 1.5V and (b) corresponding Fe L_3/L_2 intensity ratio map. The oxygen rich phase corresponds to the one with the higher Fe valence state