

Electron Diffraction Study of Phase Formations during Lithiation of FeOF/C Nanocomposite Battery Materials

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Iron oxyfluoride nanocomposites (FeOF/C) are newly developed positive electrodes for lithium-ion batteries [1]. In contrast to Li intercalation materials [2] where the intercalation process restricts valence changes of transition metals, these new positive electrode materials convert into new phases where the transition metal is completely reduced to the metallic state (full reduction) [1]. Bulk FeOF has low electronic conductivity and in order to improve the electrochemical performance, FeOF/C nanocomposites with 15 nm initial particle size were synthesized by mechanical mixing [1]. Electrochemical data of voltage versus Li content reveal three sequential structural changes which are at present not fully understood. In this study, we report selected area diffraction (SAED) results on the phase changes that occur during charge and discharge cycles.

In this work, the SAED diffraction analysis was done using a JEOL 2010F. Both lithiated (discharged) and de-lithiated (re-charged) FeOF/C nanocomposites positive electrodes were analyzed by TEM. In addition, SAED intensity profiles were simulated by JEMS to determine the structure and possible existence of various phases formed at different voltages.

After synthesis, the SAED pattern of FeOF/C, reveals a single phase with rutile crystal structure. As mentioned previously, the FeOF/C discharged voltage profile to 0.8 V shows three specific regions. In the first region from 3.5 to 2.2 V, lithium intercalates into FeOF/C and the diffraction pattern still reveals a rutile structure as shown in Fig. 1(a). However, in the second region from 2.2 to 1.5 V, FeOF/C converted into intermediate phases with different structures. Upon discharged to 1.5 V, LiF+Fe+Li-Fe-O phases are formed. The SAED pattern (c.f. Fig. 1(b)) showed the superposition of BCC Fe and a rocksalt structure corresponding to the Li-Fe-O phase. The experimental intensity profile of FeOF/C at 1.5V has a similar intensity profile as the one simulated by JEMS, thus confirming the presence of a rocksalt structure (Fig. 2). Occasionally, reflections associated with LiF are also observed. In the third region corresponding to complete discharged to 0.8 V, Li-Fe-O converts into Fe+Li₂O phases with all the Fe now fully converted to the metallic state. This can be seen in the SAED pattern shown in Fig. 1(c) which reveals the superposition of both Fe and LiF phases. The third Li₂O phase has not been detected because it might be amorphous. Upon complete recharge (lithiation) to 4.5V, it is observed that the electrode transforms back into its crystalline FeOF rutile structure as shown in Fig. 1(d). This is also confirmed by comparison of experimental intensity profile with simulation. Therefore, the FeOF/C experiences a complete reversible reconversion reaction. Further characterizations are in progress to determine the exact intermediate Li-Fe-O phase composition and Fe valence state formed during lithiation and delithiation processes.

References

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- [2] K. Mizushima, et al, *Mater. Res. Bull.* 15, (1980), 783–789.
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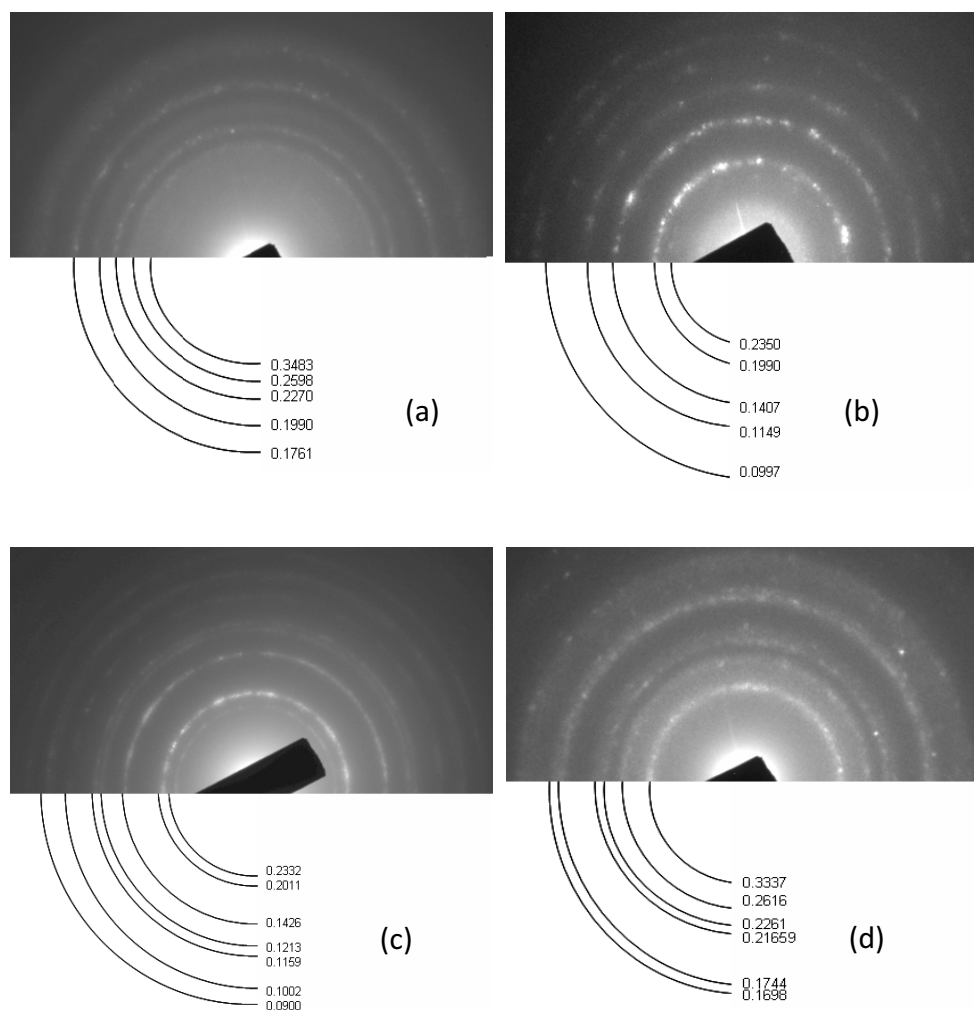


FIG. 1 SAED pattern of FeOF/C as a function of discharge voltages of a) 2.2 V, b) 1.5V, c) 0.8 V and recharge voltage of d) 4.5 V.

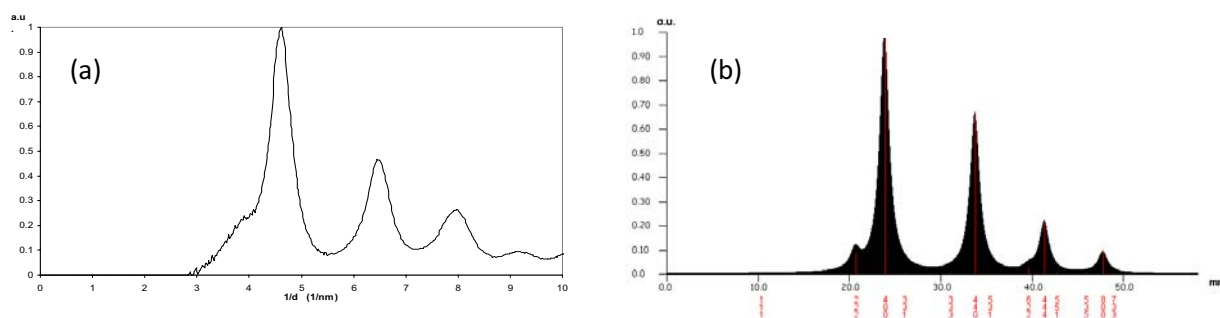


FIG. 2. SAED intensity profile for FeOF/C discharged to 1.5V, a) Experimental SAED pattern, b) Simulated intensity profile with LiFeO₂ rocksalt structure