

Transport and Hysteresis of Iron Fluoride and Oxyfluoride Conversion Electrode Materials

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Iron Metal Fluoride positive electrode materials have become an intriguing material as candidates for next generation lithium batteries (1). As compared to intercalation positive electrodes, conversion batteries can provide up to three times the capacity as the transition is reduced. One characteristic which exists in all conversion electrode materials is the presence of hysteresis. Various views have been proposed on the origin of this phenomena with no conclusive answer. In order to identify the near thermodynamic reaction potential of a number of metal fluoride conversion materials, potentiostatic intermittent titration (PITT) was used to follow the true voltage curve. These experiments proceeded with very small step 10mV and low current cutoffs approaching $C/1000$.

Figure 1 is a PITT voltage profile of rutile FeF_2 nanocomposites that was discharged and charged at 10mV step with a 0.4mA/g cut-off. At 1.77V, FeF_2 is converted into Fe^0 and LiF . The theoretical voltage of this conversion reaction is 2.66V which is $\sim 900\text{mV}$ difference. In reconversion, the delithiation step occurs at 2.71V, resulting in a highly asymmetric hysteresis with a total of 1V. In Figure 2, the voltage profile of FeOF shows that upon lithiation the conversion step takes place at 2.06V. In delithiation, the reconversion of this material occurs at 2.80V which indicates a 800mV difference in hysteresis for FeOF . Despite the low current cutoffs that allowing these materials to move equilibrium, both FeF_2 and FeOF show some presents of a hysteresis. This indicates that there is some limiting factor preventing full lithiation of these materials without a large driving force.

From these experiments, diffusion coefficients were calculated for both the discharge and charge profiles in order to establish the kinetic aspect of the conversion reactions. In the PITT study, at each voltage step there is a current response that decays exponentially. By plotting the natural log vs time response; there will be a linear slope that can be used to determine the diffusion coefficient (2). To contrast these diffusion measurements, electrochemical impedance spectroscopy "EIS" was utilized to extract the impedance using two different methodologies. One is by looking at the nyquist plot; a typical plot will consist of a semi-circle follow by a 45° slope and then move up to infinity which marks the limiting low frequency resistance, R_L . The diffusion coefficient is defined by the initiation of the 45° slope to R_L . The other method of calculating diffusion is by using the Warburg impedance. By taking the slope of $\text{Re}(Z)$ vs $\omega^{-1/2}$, the warburg coefficient can be extracted to calculate the diffusion coefficient (3).

For FeF_2 , the current in the conversion step from $x=0.07$ to $x=1.36$ in Figure 1 displays a non-Cottrellian behavior at that point from $t=7\text{h}$ to $t=88\text{h}$ shown in Figure 3. The diffusion coefficient was found to be $2.07 \times 10^{-12} \text{ cm}^2/\text{s}$. On reconversion, diffusion is $2.01 \times 10^{-11} \text{ cm}^2/\text{s}$. In FeOF , the diffusion coefficient is $4.65 \times 10^{-12} \text{ cm}^2/\text{s}$ upon conversion for discharge at $x=0.76$. On charge, this was $1.53 \times 10^{-11} \text{ cm}^2/\text{s}$ at $x=0.96$. These coefficients show that both FeF_2 and FeOF have distinct asymmetry in their reactions and non obvious pseudointerinsertion behaviour

especially in delithiation.

This paper will expand on these results with inclusion of contrasting systems and how these results relate to the mechanism of hysteresis.

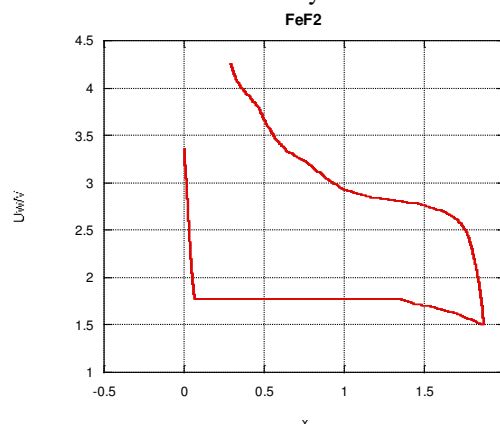


Figure 1. PITT of FeF_2 with 10mV steps and 2mA/g current cut-off.

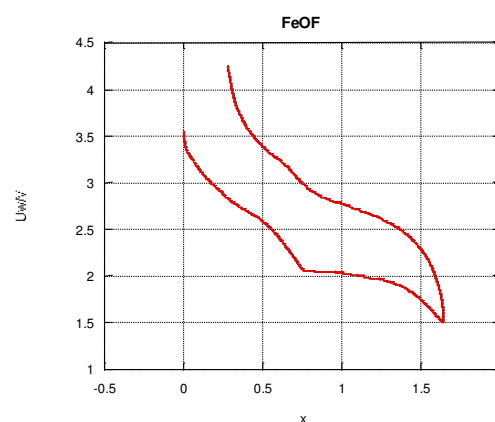


Figure 2 PITT of FeOF with 10mV steps and 2mA/g current cut-off.

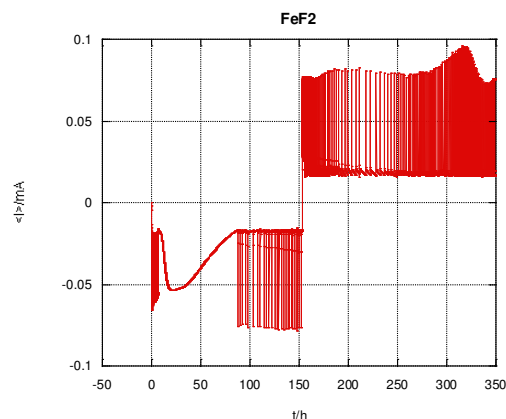


Figure 3. Current vs time of FeF_2 .

Works Cited

1. Badway, F, Cosandey, F, Pereira, N, and Amatucci, G G. Journal of The Electrochemical Society, 150, 10 (2003), A1318-A1327.
2. Ho, C., Raistrick, I. D., & Huggins, R. A. (1980, february). Electrochemical Science and Technology, 127(2), 343-350.
3. Wen, C. J., Boukamp, B. A., Huggins, R. A., & Weppner, W. (1979, December). Journal of the Electrochemical Society, 126(12), 2258-2266.