

## TEM Investigations on FeF<sub>2</sub> based Nanocomposite Battery Materials

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The application of conversion materials in electrochemical storage devices is one of the few options to build batteries with considerably increased energy density, e.g. based on metal fluorides, which react reversibly with lithium. However, as metal fluorides are electrical insulators and show large volume changes during cycling, batteries based on micron-sized particles rapidly lose capacity. In contrast, with nanocrystalline electrode materials high cycling stability and a fast charging and discharging can be achieved. In particular, iron fluorides are an important class due to their low cost and low toxicity. FeF<sub>2</sub> is an interesting cathode material which has a thermodynamic reduction potential of 2.66 V versus lithium and a theoretical specific capacity of 571 mAh g<sup>-1</sup>, which leads to a theoretical gravimetric energy density of 1519 Wh kg<sup>-1</sup> [1]. FeF<sub>2</sub> is an electrical insulator and needs to be in intimate contact with electronic conductors at the nanoscale in order to become electrochemically active. A good choice for this purpose is graphitic carbon. C<sub>F</sub>x has a high thermodynamic reduction potential vs. lithium (4.2 V) so that it can react with iron metal to form FeF<sub>2</sub>, which has a thermodynamic reduction potential of 2.66 V vs. lithium. During the synthesis C<sub>F</sub>x acts both as source of fluoride for the iron and as source of graphitic carbon for the matrix [1].

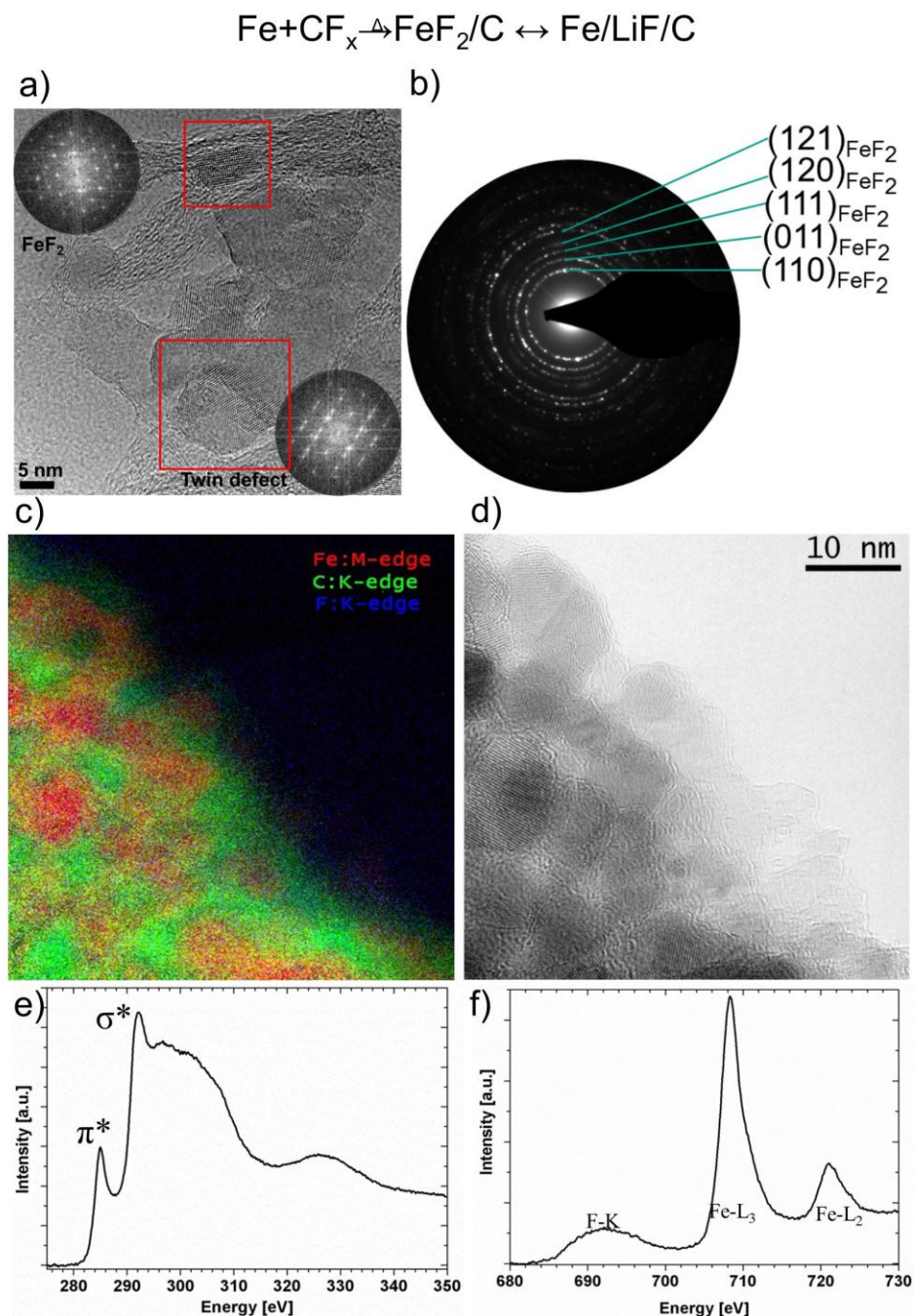
The composite electrode is prepared by reaction of a volatile Fe compound with chemically modified graphite, graphite fluoride (C<sub>F</sub>x) in that case. Iron pentacarbonyl Fe(CO)<sub>5</sub>, a liquid source for iron metal, reacts well inside the C<sub>F</sub>x matrix. HRTEM micrograph and the associated FFT patterns show the FeF<sub>2</sub> nanoparticles in a carbon matrix. The indexed SAED pattern in Fig. 1(b) demonstrates the high crystallinity of the FeF<sub>2</sub> nanoparticles. Fig. 1(c) shows an energy filtered TEM map of the material using the Fe M-edge (red), C K-edge (green) and F K-edge (blue) corresponding to the HRTEM micrograph in Fig. 1(d). Fig. 1 (e) and (f) are the EEL spectra recorded for the area shown in Fig. 1 d). Fig. 1 (f) shows the F K-edge and the Fe L3- and L2-edges. The EELS analysis with the carbon K-edge in Fig. 1 (e) shows well-defined peaks due to transitions of 1s electrons to π\* and σ\* anti-bonding states, which is a clear indication for the graphitic nature of the carbon in the composite (in agreement with the results from Raman studies). The absence of a pre-peak in the F K-edge of Fig. 1(f) together with the position of the Fe L3 edge as well as electron diffraction rules out the presence of FeF<sub>3</sub> [1].

FeF<sub>2</sub> intercalated in different types of carbon have been studied here to understand the structure, morphology and chemical composition of the electrode material. Variation of the size of FeF<sub>2</sub> nanoparticles and their particle size distribution observed from the bright field TEM images corroborates well with results obtained from the X-ray diffraction techniques. Additionally, an effect of variation in the ratio between Carbon to Fluorine have also been studied and will also be presented.

## References:

[1] M A Reddy, B Breitung, V S K Chakravadhanula, C Wall, M Engel, C Kübel, A K Powell, H Hahn, M Fichtner, *Advanced Energy Materials* 5 (2012), p. 1-6. doi:10.1002/aenm.201200788 and references therein.

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**Figure 1.** (a) Bright field TEM image with inset of FFT patterns and (b) SAED pattern depicting the crystallinity of  $\text{FeF}_2$  (c) An energy filtered TEM map using the Fe M-edge (red), C K-edge (green) and F K-edge (blue). (d) Corresponding HRTEM micrograph. e,f) Electron energy loss spectra recorded for the area shown in Figure (a).