

Supporting Information

Microwave-assisted fluorolytic sol-gel route to iron fluoride nanoparticles for Li-Ion batteries

Lidia Di Carlo, Donato E. Conte, Erhard Kemnitz and Nicola Pinna

Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2, 12489
Berlin (Germany)

Experimental procedures.

All products were used as received, except when specified.

Synthesis of graphene oxide and partially reduced graphene oxide.

Graphene oxide (GO) was synthesized following a modified Hummers method¹². 1 g of graphite powder (<20 µm, Aldrich) was suspended in 20 mL of concentrated H₂SO₄ (J. T. Baker, 95-97%) and first pre-oxidized with 2.5 g of K₂S₂O₈ (Sigma Aldrich, ≥99%) and 2.5 g of P₂O₅ (Fluka, >97%) under stirring. The resulting suspension was heated at 80 °C for 5 h, after which the solid was recovered by centrifugation, repeatedly washed with water to neutrality and dried. Oxidation was performed starting from 1 g of pre-oxidized graphite in 46 mL of concentrated H₂SO₄. Addition of 1 g of NaNO₃ (ABCR, 98%) and 6 g of KMnO₄ (ABCR, 98%) was performed under vigorous stirring and in ice bath. After 5 days at room temperature, water was added and the suspension was heated at 98 °C for 1 h prior to addition of 6 mL H₂O₂ (VWR, 30%). The warm suspension was finally filtered, washed with 2 M HCl (Grüssing, 37%) solution, washed with water to neutral pH and dried under reduced pressure at 120 °C for several hours. In order to partially reduce GO, the obtained black powder was then redispersed in benzyl alcohol (BnOH, Sigma

¹ W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339

² N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, A. D. Gorchinskiy, *Chem. Mater.* 1999, **11**, 771 – 778

Aldrich, Reagent Plus) and microwave treated at 190 °C for 20 min. After repeatedly washing with methanol and drying overnight, the partially reduced graphene oxide (RGO) powder was employed for the synthesis of the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ /RGO composite.

Synthesis of $\text{FeF}_3 \cdot 0.33(\text{H}_2\text{O})$.

Iron fluoride sol was synthesized according to the reported fluorolytic sol-gel method³. Briefly, 10 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ABCR, 98%) were firstly dehydrated for 2h at 65 °C under vacuum. The final product was dissolved in 50 mL of BnOH and then 30 mmol of highly concentrated anhydrous HF in methanol were added. The reactants and the system itself were kept under inert Ar atmosphere along all the process. The solution was stirred 1h at room temperature, and then transferred into a 10 mL SiC vessel used in the microwave reactor Anton Paar Monowave 300. The solution was thermally treated at 150 °C for 10 minutes under stirring (600 rpm). The ramping time was set as 20 °C min^{-1} while the power output was automatically controlled by the instrument itself. The relative profiles are reported in Figure S1. The resulting dispersion was centrifuged and repeatedly washed with methanol. The recovered particles $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ were then dried overnight at 65 °C.

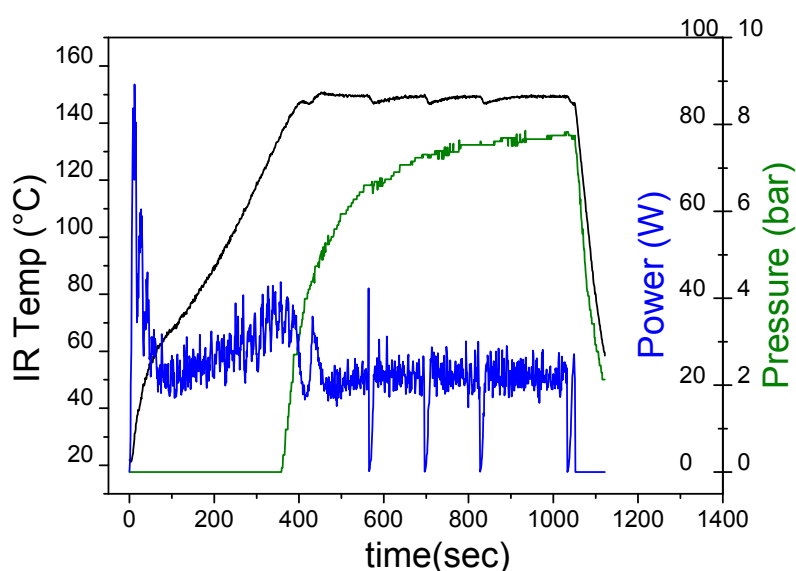


Figure S1: Temperature, Pressure and Power profiles during microwave irradiation of the sol.

³ Y. Guo, P. Gaczyński, K.-D. Becker and E. Kemnitz, *ChemCatChem*, 2013, **5**, 2223-2232

Synthesis of $\text{FeF}_3 \cdot 0.33(\text{H}_2\text{O})/\text{RGO}$ nanocomposite.

120 mg of the as synthesized $\text{FeF}_3 \cdot 0.33(\text{H}_2\text{O})$ along with 44 mg of RGO were dispersed in 7 mL of BnOH and were treated under microwave irradiation for 10 min at 150 °C. The resulting dispersion was centrifuged and repeatedly washed with methanol. The recovered composite powder was then dried overnight at 65 °C.

Characterizations.

X-ray diffractograms were recorded in the Bragg-Brentano geometry using a Siemens D5000 diffractometer equipped with Cu K_α radiation (154.18 pm) in the range $10 < 2\theta < 70^\circ$. The program FullProf was used for lattice parameter and crystallite sizes calculations.

Transmission electron microscopy (TEM) images were recorded on a Philips CM 200 microscope equipped with a LaB_6 cathode and operated at 200 kV.

IR spectra were collected on a Digilab FTIR 3000, Excalibur series in ATR mode configuration in the range $4000\text{--}400\text{ cm}^{-1}$.

Two-electrode cells (EL-Cell GmbH) were assembled in an Ar-filled glove box (MBraun) with the synthesized iron-based fluorides as a working electrodes and lithium foil (Alfa Aesar, 99.9%) as a counter and reference electrode. The working electrodes were prepared by mixing iron-based fluorides powders, carbon black (Timcal, Super C), and poly(vinylidene difluoride) (PVdF, Alfa Aesar) with a weight ratio of 70:10:20 in N-Methylpyrrolidone (NMP, Alfa Aesar, >99%). The resulting slurry was then pasted on commercial aluminum foil, roll pressed (MTI Corp.) and cut into discs. The latter were dried under vacuum at 120 °C overnight (Büchi glass oven) before assembly. Glass fiber from Whatman was employed as the separator. The electrolyte is composed of 1 M LiPF_6 (ABCR, 99.9% battery grade) in a non-aqueous mixture of ethylene carbonate (EC, ABCR, 99%), propylene carbonate (PC, ABCR, 99%) and dimethyl carbonate (DMC, ABCR, 99%) with a volume ratio of 1:1:1. Charge-discharge measurements were performed at room temperature under different rates (0.1 C ~ 1 C) in a voltage range of 1.6–4.4 V vs Li^+/Li^0 on a Bio-Logic VMP3 potentiostat/galvanostat.

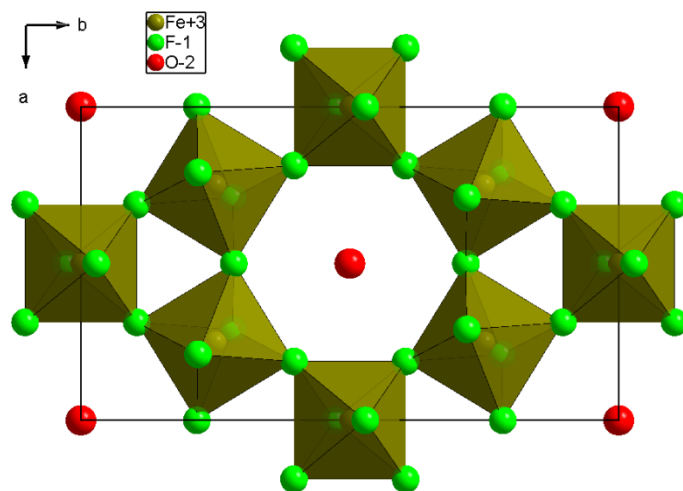


Figure S2: Crystal structure of hexagonal bronze-type $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ viewed along the c axis. The central monodirectional channel is well visible. 1/3 of the channel is occupied by H_2O molecules.

Table S1. Lattice constants and crystallite sizes calculated for the iron fluoride and iron fluoride/carbon composite.

Sample	a (pm)	b (pm)	c (pm)	Cell volume (pm^3)	Crystallite sizes (nm)
JCPDS 76-1216	742.3	1273.0	752.6	$711.17 \cdot 10^6$	/
$\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$	738.7(2)	1277.7(4)	751.2(1)	$709.8(2) \cdot 10^6$	17
$\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{RGO}$	737.1(2)	1281.6(3)	751.4(1)	$709.0(3) \cdot 10^6$	19

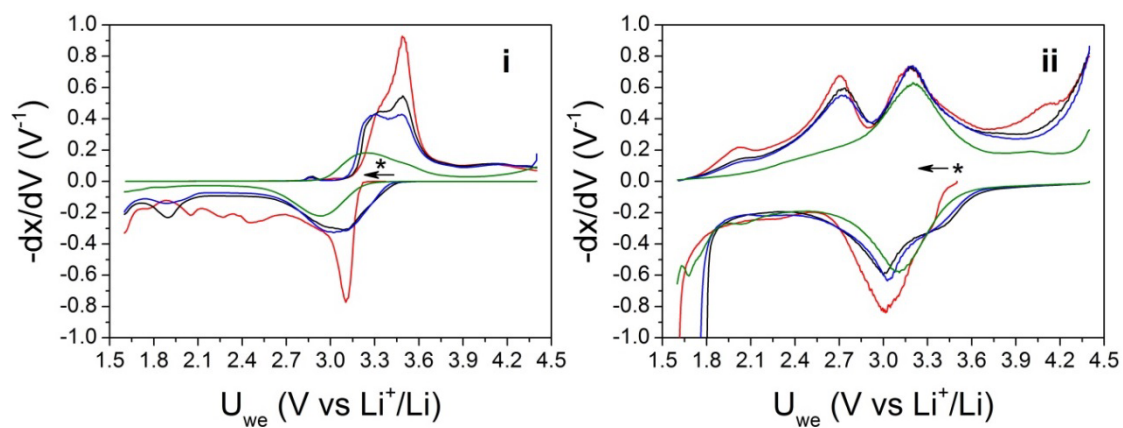


Figure S3: Derivative curve of selected galvanostatic cycles of pure $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ (i) and $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{RGO}$ composite (ii). First cycle (red line), second cycle (black line), third cycle (blue line) and fifty-fifth cycle (green line).

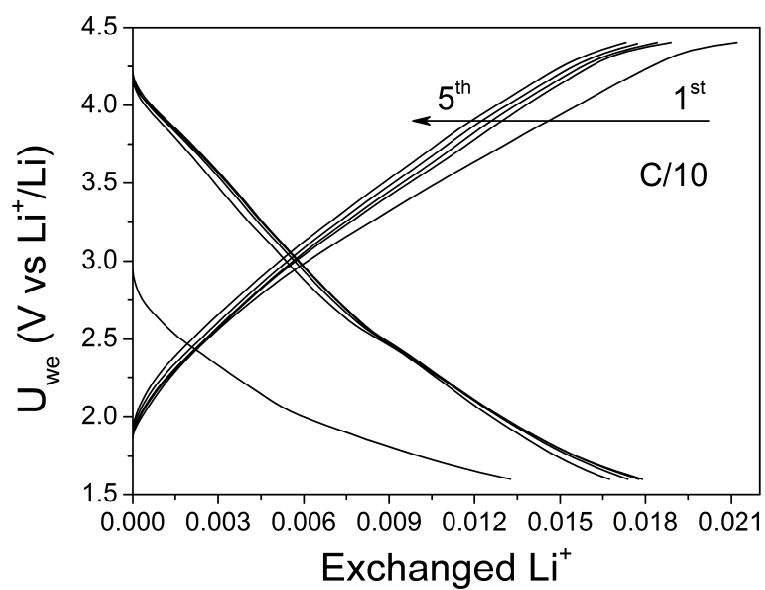


Figure S4: Contribution of the RGO to the galvanostatic profile of the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{RGO}$ composite. Pure RGO was cycled using the same voltage window and electrolyte of the composite material (1.6-4.4 V vs Li^+/Li^0 and 1 M LiPF_6 , EC:PC:DMC).

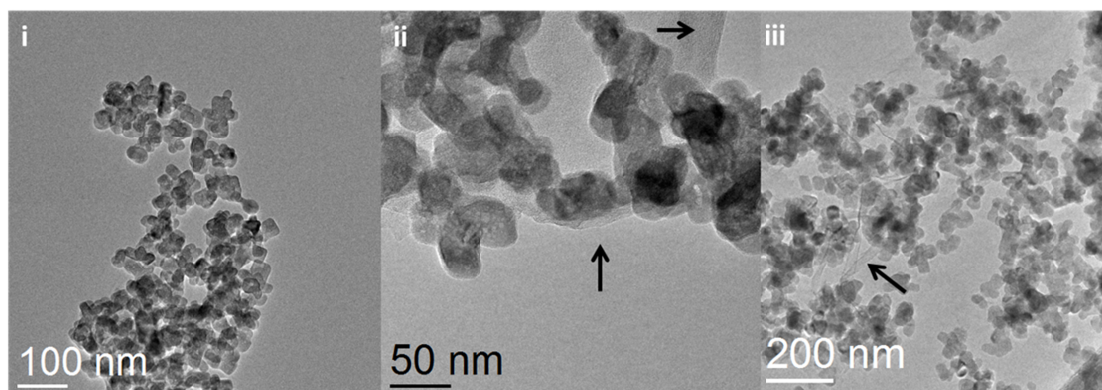


Figure S5: TEM images of (i) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, (ii) a detail of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{RGO}$ along with (iii) an overview image (arrows point the RGO sheets).

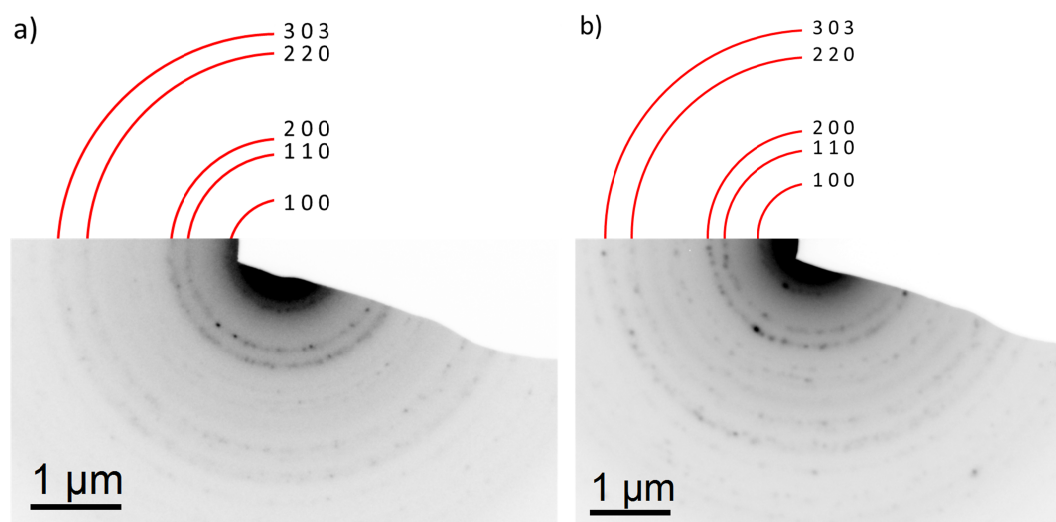


Figure S6: Selected area electron diffraction of (a) $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, (b) and $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{RGO}$. The most intense diffractions are assigned on the figure.