Supporting information

Unravelling lithiation mechanisms of iron trifluoride by operando X-ray Absorption Spectroscopy and MCR-ALS chemometric tools

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Table SI.1

Refined parameters for pyr-FeF_3 sample obtained from the PDF analysis in the 1.5 to 20 Å r-range with Q_{max} = 25 $Å^{-1}$

FeF_3	Pyrochlore (ICSD#202047)	HTB (ICSD#35359)
	F d -3 m	C m c m
a (Å) b (Å) c(Å)	10.3184(9)	7.423 12.73 7.526
Atomic positions	Fe 0 0 0 F 0.3122(4) ¼ ¼	Fe 0 ½ 0 Fe ¼ ¼ 0 F 0 0.2156 0.5511 F 0.1876 0.3962 0.0434 F 0 0.5286 ¼ F 0.2101 0.2176 ¼ O 0 -0.0006 ¼
ADPs ($Å^2$)	Fe 0.005(1) F 0.0154(2)	Fe 0.0072 F 0.164
Relative phase content (wt.%)	0.826 (8)	0.174(8)
Low r sigma ratio R cutoff (Å) Q_{damp} ($Å^{-1}$)	0.57(2) 4.1 0.023(4)	
R_W (%)	16.4	

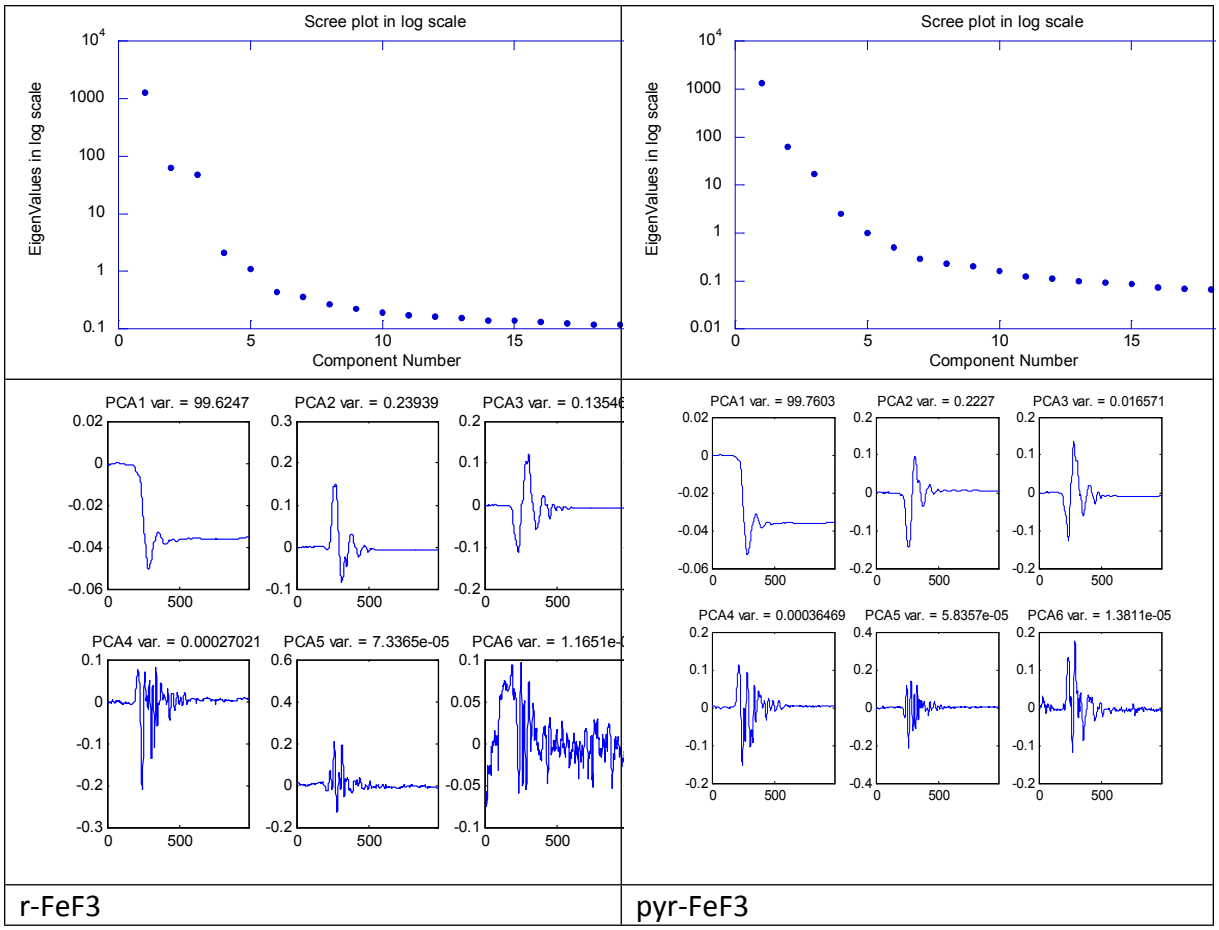

Fig SI 1: a) Scree plot which is the graphical representation of the EigenValue obtained in PCA, b) Plot of the variance versus the energy range in number of points.

We used chemometric tools based on a combination of Principal Component Analysis (PCA) and Multivariate-Curve Resolution Alternating Least Squares (MCR-ALS)[25-28] to analyze the whole XAS dataset measured at Fe K-edge for each FeF3 sample. Thanks to PCA, we can determine the minimum number of independent components required to describe the whole operando dataset obtained during the electrochemical discharge. Then this number of principal components is implemented in the MCR – ALS analysis, which lead up to the reconstruction of the principal orthogonal components required to reproduce the complete dataset. The reconstruction of the spectra was done using the Evolving Factor Analysis (EFA) methods and some constraints were applied especially for the concentration profile of the principal components i) non-negative concentration value, *ii*) unimodality (only one maximum), and *iii*) closure (the sum of the concentration of all components must be equal to one).

The Scree and variance plots obtained from the PCA analysis on the operando XAS spectra indicates that four independent components are required to describe the whole system (fig1 a and b).

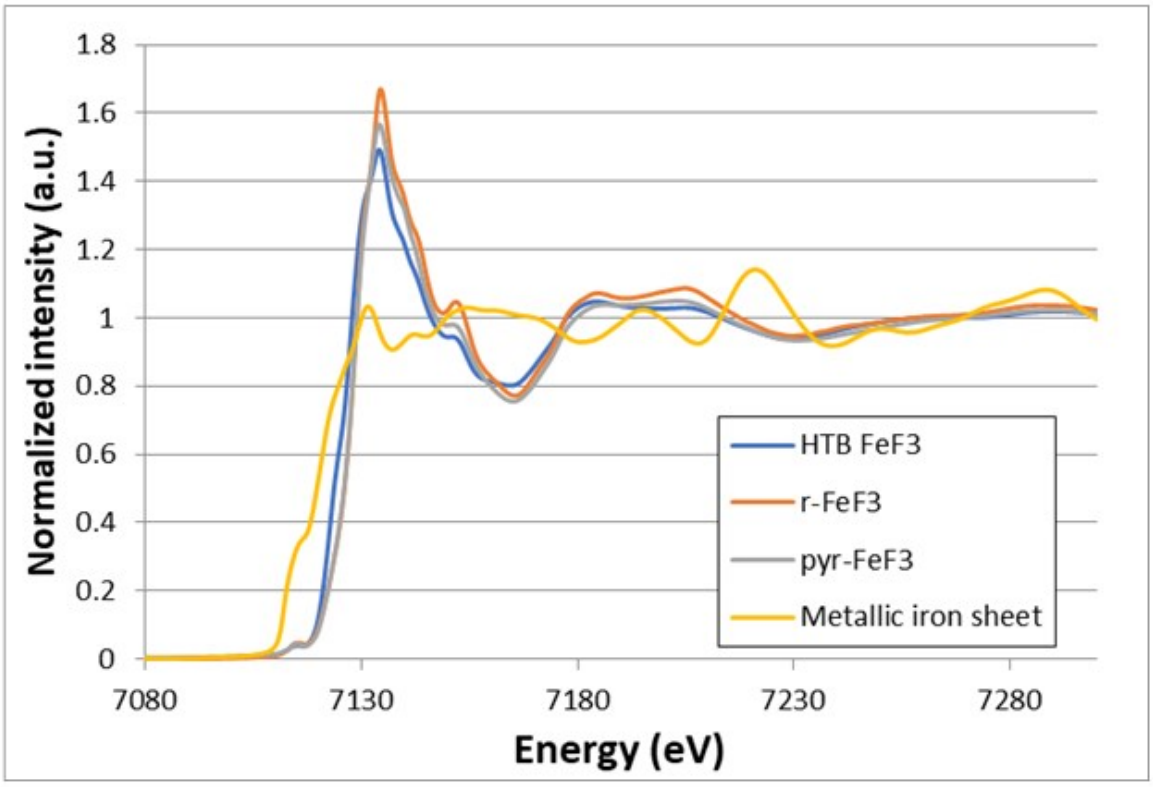

Fig SI 2. XANES of HTB, r-, pyr- FeF_3 compared with metallic iron sheet