Supplementary information

1-XRD Microstructural analysis, data processing:

The microstructural analyses are carried out using a Finger-Cox-Jephcoat pseudo-Voigt profile function without any additional constraints. The full width at half maximum of the Gaussian (H_G) and Lorentzian (H_L) components of the peak profile have an angular dependence given by:

$$H_G^2 = H^2_{ins,G} + U_{d,G} \tan^2\theta + Z_{L,G}/\cos^2\theta$$

$$H_L = H_{ins,L} + X_{d,L} \tan\theta + Y_{L,L}/\cos\theta$$

Where the Gaussian contribution of the crystallite size, $H^2_{L,G} = Z_{L,G}/\cos^2\theta$,
the Lorentzian contribution of the crystallite size, $H_{L,L} = Y_{L,L}/\cos\theta$,
the Gaussian contribution of the microstrains, $H^2_{d,G} = U_{d,G} \tan^2\theta$,
and the Lorentzian contribution of the microstrains, $H_{d,L} = X_{d,L} \tan\theta$.

Both $H^2_{ins,G}$ and $H_{ins,L}$ represent the Gaussian and Lorentzian instrumental contributions to the diffraction peak broadening. $U_{d,G}$, $X_{d,L}$, $Y_{L,L}$, and $Z_{L,G}$ are refinable parameters in the FullProf refinement program. In the case of independent (hkl) broadening (isotropic case), the instrumental and microstrain contributions are essentially Gaussian, and the Lorentzian contribution of the particle size is dominant. From this working hypothesis, the parameters $X_{d,L}$, $Z_{L,G}$ are null, and only $U_{d,G}$ and $Y_{L,L}$ need to be refined.

From $Y_{L,L}$, the average crystallites size is calculated using the following equation:

$$\langle L \rangle = \left(\frac{360}{\pi^2}\right)\left(\frac{\lambda}{Y_{L,L}}\right)$$, and

from $U_{d,G}$, the average maximal microstrain is calculated using the following equation:

$$\langle \varepsilon \rangle = \frac{\pi}{180}\left(\frac{1}{8}\sqrt{\frac{\pi}{ln2}}\right)\sqrt{U\ d,G}$$.

A) x=1

Fe_3S_4, F*d-3m* (n^{o} 227)

a = 9.845(5) Å

microstrain parameters:
$U_{d,G}$ =0.3469 (1), $Y_{L,L}$= 0.6665 (1)

Atom	**Site**	**x,y,z**	**B_{iso}**	**Occupation**
FeIII-A	8b	0.125	0.56 (1)	0.56 (1)
FeII-A	8b	0.125	0.56 (1)	0.44 (1)
FeII-B	16c	0.5	0.86 (1)	0.72 (1)
FeIII-B	16c	0.5	0.86 (1)	0.28 (1)
S	32e	0.2549 (3)	0.65 (5)	1

B) x=0.25

phase 1:$Fe_{2.96}S_4$, F*d-3m* (n^{o} 227)

a = 9.850(5) Å

Atom	**Site**	**x,y,z**	**B_{iso}**	**Occupation**
FeIII-A	8b	0.125	0.83 (1)	1
FeII-B	16c	0.5	0.75 (1)	0.44 (1)
FeIII-B	16c	0.5	0.75 (1)	0.54 (1)
S	32e	0.2549 (3)	1.55 (5)	1

phase 2:Fe_2O_3, F*d-3m* (n^{o} 227)

a = 8.389(1) Å

Atom	**Site**	**x,y,z**	**B_{iso}**	**Occupation**
FeIII-A	8b	0.125	0.74 (1)	1
FeIII-B	16c	0.5	0.57 (1)	0.83 (1)
O	32e	0.2544 (3)	0.92 (5)	1

C) x=0

$Fe_{2.93}O_4$, F*d-3m* (n^{o} 227)

a = 8.381(1) Å

microstrain parameters:
$U_{d,G}$ =1.0769 (1), $Y_{L,L}$= 0.7004 (1)

Atom	**Site**	**x,y,z**	**B_{iso}**	**Occupation**
FeIII-A	8b	0.125	0.42 (1)	1
FeIII-B	16c	0.5	0.72 (1)	0.64 (1)
FeII-B	16c	0.5	0.72 (1)	0.30 (1)
O	32e	0.2544 (3)	0.85 (5)	1

Table 1: Unit cell parameters, atomic positions, isotropic thermal displacements, and occupation rate of each detected phase for the materials synthesized in a) Benzyl-SH (x=1), b) x=0.25, c) Benzyl-OH (x=0) (from the Rietveld analysis). In the case of sample a) and c) microstrains parameters are given (from the whole pattern matching).

2-Morphological characterization

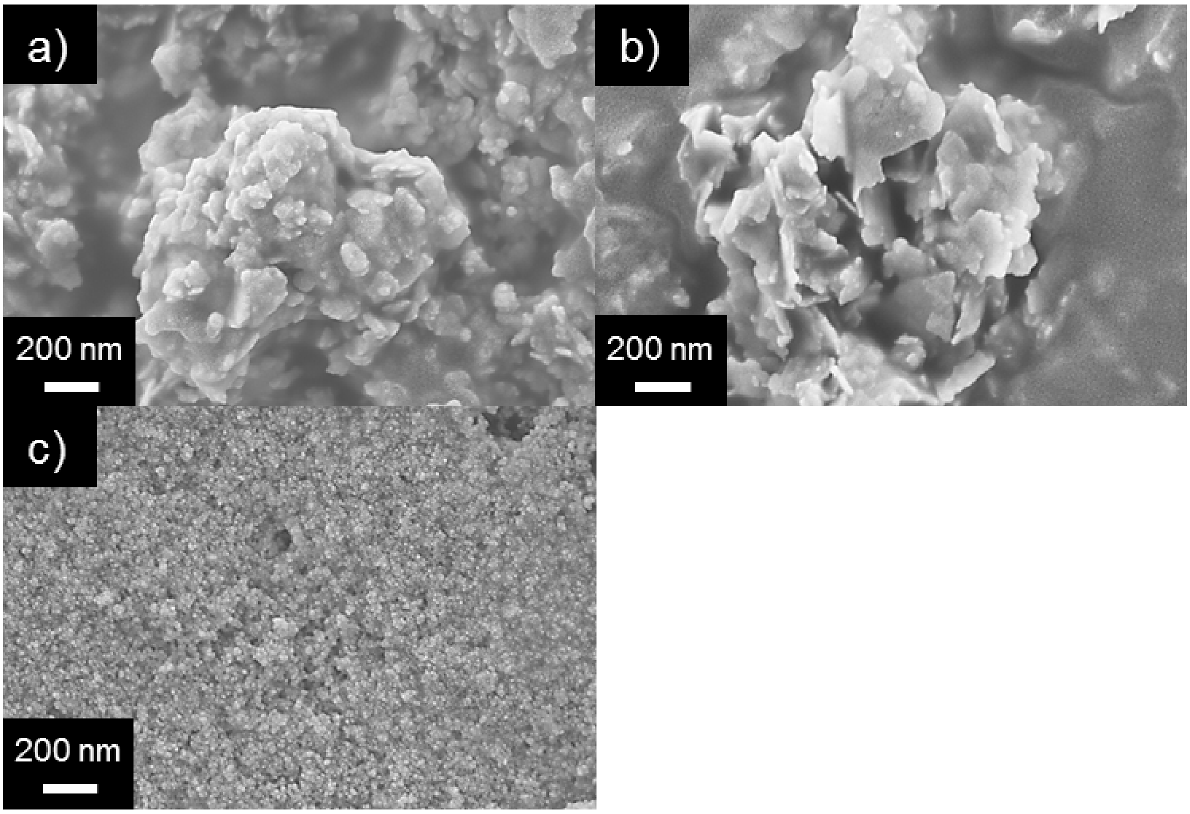

Figure S1: SEM micrograph of a) composite (x = 0.25), b) greigite and c) magnetite powders.

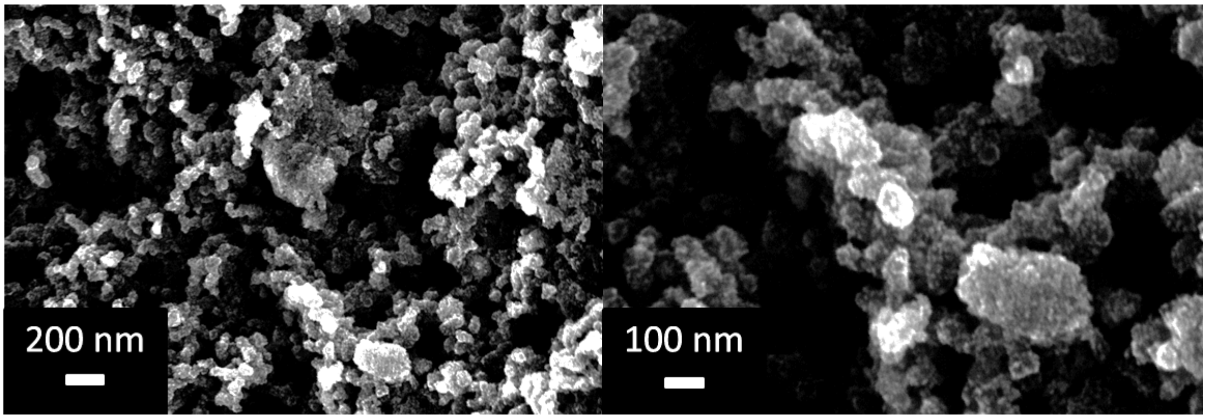

Figure S2: SEM micrographs of electrode prepared with the magnetite (x=0).

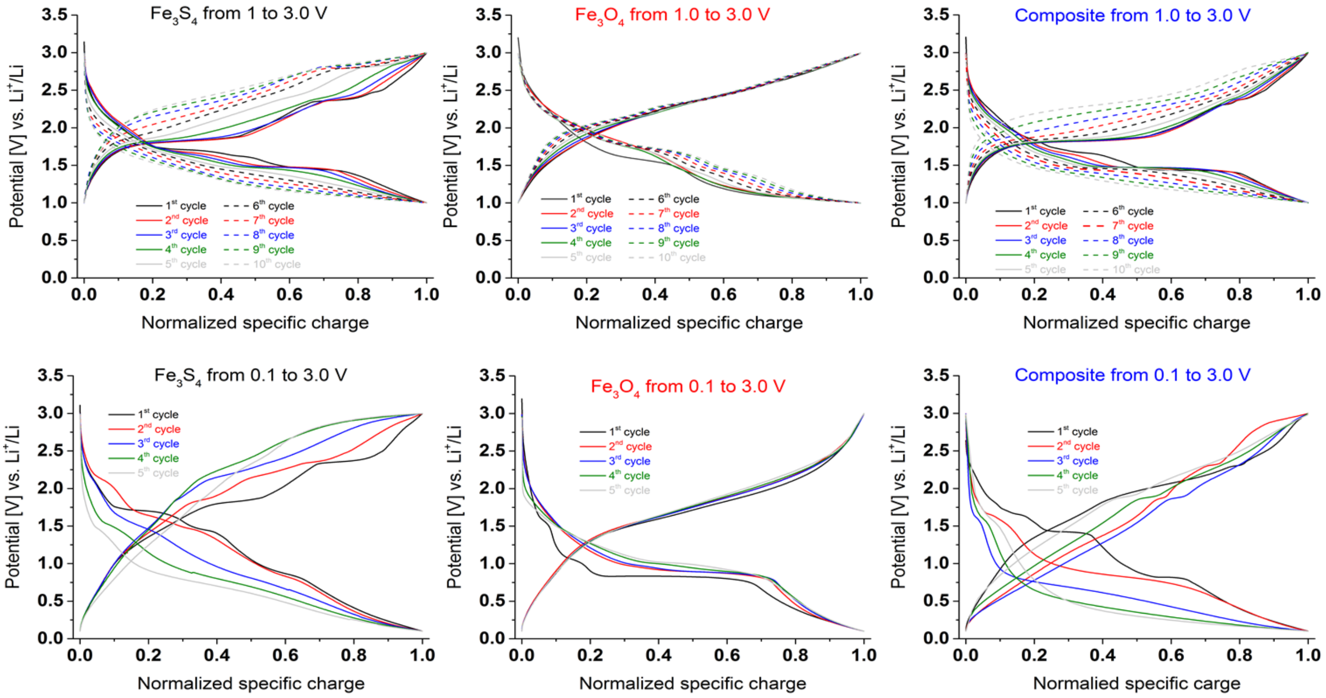

Figure S3: Normalized galvanostatic plot of greigite, magnetite and composite.

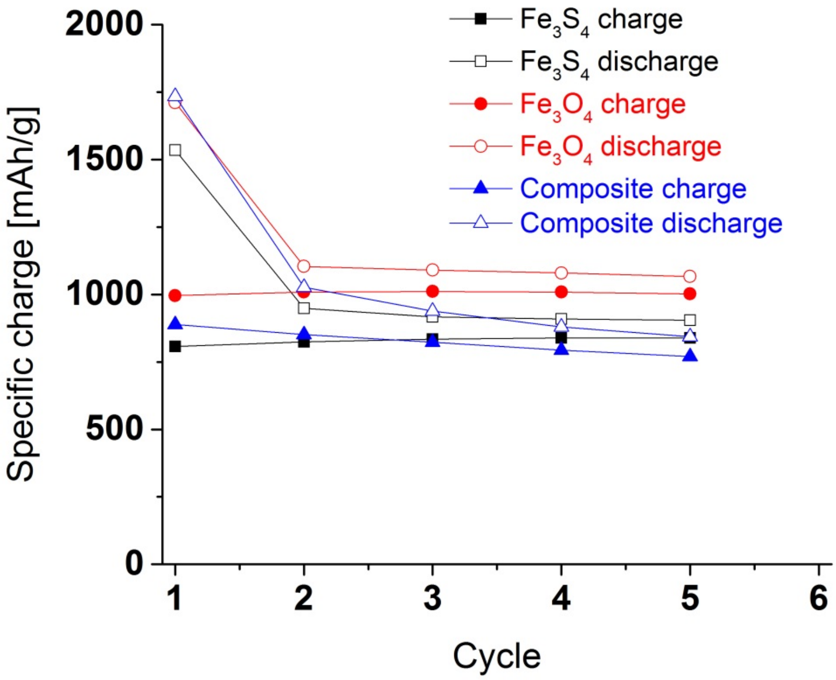

Figure S4: Evolution of the specific charge vs. cycle number of the electrodes composed of active material (greigite, magnetite or composite) and carbon super C65 (1 :1 weight ratio) in 0.1-3.0 V vs. Li^+/Li potential window