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One-pot synthesis by anhydrous sol-gel chemistry and electrochemical study of mixtures of iron sulfide and iron oxide

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Electrochemical reaction

- Expected electrochemical processes with metal oxides/sulfides

  Insertion : $M_yX_z + a\ Li^+ + a\ e^- \rightleftarrows Li_aM_yX_z$

  Conversion: $M_yX_z + 2z\ e^- + 2z\ Li^+ \rightleftarrows z\ Li_2X + y\ M^0$

  M = metal; X = oxygen or sulfur

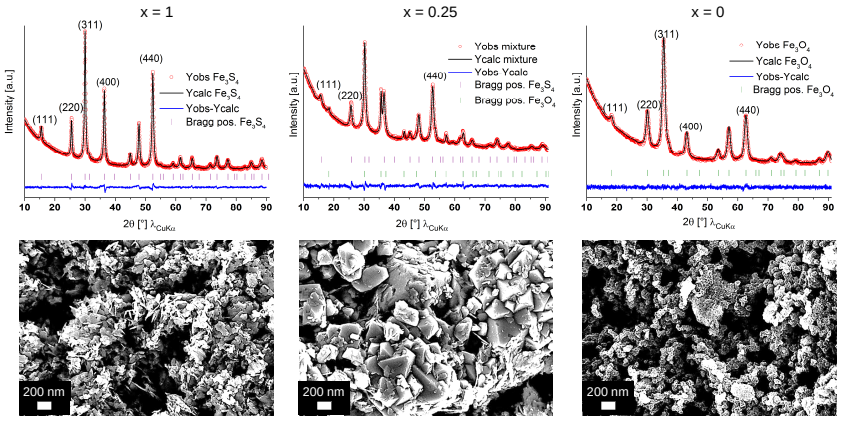
- Magnetite, Fe_3O_4, shows an insertion mechanism for U > 1 V *vs.* Li^+/Li and a conversion mechanism for U < 1 V *vs.* Li^+/Li.
- Gregite, Fe_3S_4, was found to cycle between 0 V and 3 V *vs.* Li^+/Li. [1], but electrochemical processes were not identified.

Synthesis by anhydrous sol-gel route

$Fe(acac)_3$ +  and/or  $\xrightarrow[40h]{175ºC}$ Fe_3O_4 and/or Fe_3S_4

- Benzyl alcohol (b-OH) [2] and benzyl mercaptan (b-SH) [3] are solent and co-reactant simultaneously.
- Formation of nanocrystalline powders at low temperatures.
- Mixtures of b-OH and b-SH: synthesis of one-pot mixtures of iron oxide and iron sulfide or iron oxysulfide ?!?

Analysis (XRD & SEM)



x in x b-SH + (1-x) b-OH [molar ratio]	Detected phases	Crystallinity spinels: $FWHM_{(311)}$
x=1	greigite	0.47 (low, nanopowder)
x=0.25	75% greigite 25% maghemite	0.66 (low) 0.23 (high)
x=0	magnetite	0.98 (low, nanopowder)

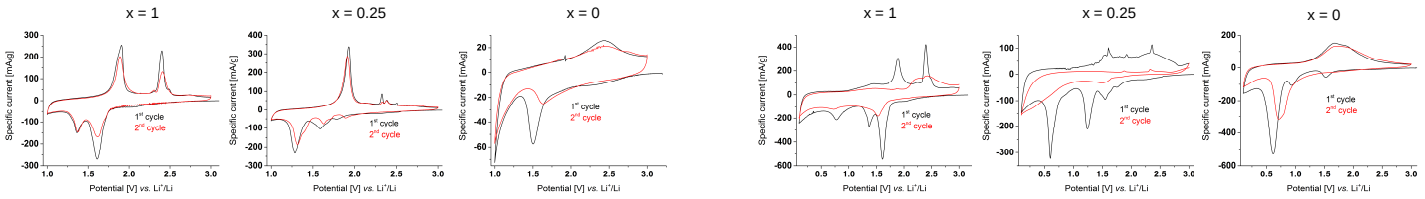
- In mixtures of b-OH and b-SH: formation of greigite and metal oxide(s) (magnetite Fe_3O_4 or maghemite γ-Fe_2O_3).
- The morphology of the particles and the crystallinity of the phases are evolving as a function of x.

Electrochemistry

Cyclic voltammetry in half-cell configuration (50 µV/s, electrolyte $LiPF_6$ 1M in ethylene carbonate/dimethyl carbonate 50/50 by weight)

E = 1.0-3.0 V *vs.* Li^+/Li

E = 0.1-3.0 V *vs.* Li^+/Li



- The greigite shows an insertion mechanism for E >1 V *vs.* Li^+/Li (shape of 1st and 2nd CV cycles are similar) and a conversion mechanism for E < 1 V *vs.* Li^+/Li (shape of 1st and 2nd CV cycles are different).
- The one-pot mixture (x = 0.25), even mostly composed of the greigite, has electrochemical properties close to the maghemite [4].

Conclusions

- The greigite and one-pot iron sulfide-iron oxide crystalline mixtures can be synthesized by anhydrous sol-gel chemistry.
- The reduction mechanisms of the greigite have been determined as an insertion and a conversion mechanism for E > 1 V and E < 1V *vs.* Li^+/Li, respectively.

References and acknowledgement

[1] Paolella et al., Chem. Mater., 2011, 23, 3762.
[2] Pinna et al., Angew. Chem. Inter. Edit., 2008, 47, 5292.
[3] Ludi et al., Chem. Commun., 2011, 47, 5280.
[4] Pernet et al., Solid State Ionics, 1993, 66, 259.

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