Getting more capacity out of Fe-based cathodes for HEV battery applications

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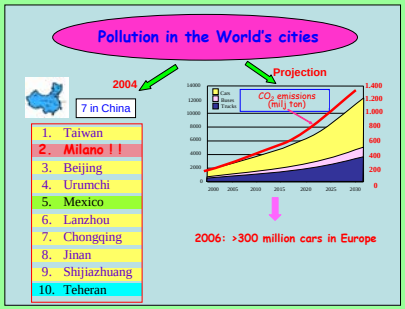
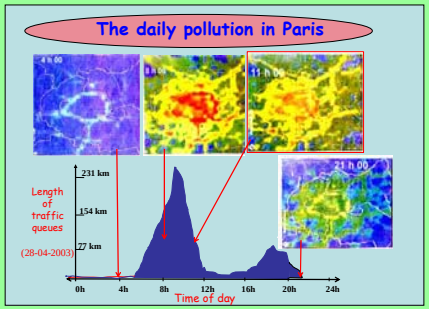
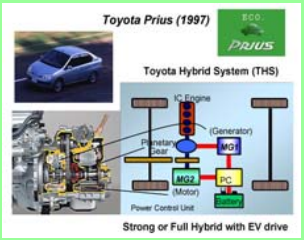
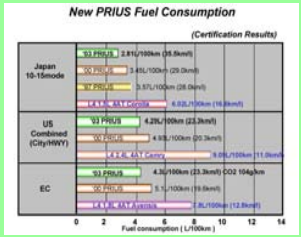
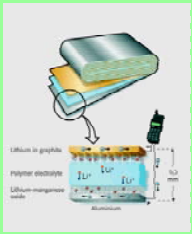




Problem: Urban pollution is fast reaching dangerously high levels . . . and the automobile is a major culprit !



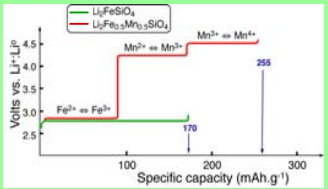




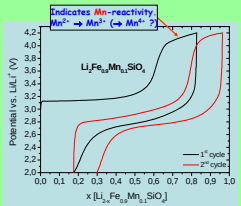
HEVs can improve things → but "Ni-MH" is not enough → we need "Li-ion" !

- $LiFePO_4$ is on its way into HEV batteries – but its capacity is limited: only 170 mAh/g !
- Li_2FeSiO_4 has the same theoretical capacity, since we can only use the Fe^{2+}/Fe^{3+} couple - so Li_2 can only go down to Li_1 ... the capacity would double if we could get down to Li_0 !
- The mixed-ion system $Li_2(Fe_{1-x}Mn_x)SiO_4$ facilitates the possibility of a >1 electron redox reaction" corresponding to:

$$Li^+_2(Fe^{2+}_{1-x}Mn^{2+}_x)SiO_4 \Rightarrow Li^+_{1-y}(Fe^{3+}_{1-x}Mn^{4+}_x)SiO_4 + (1+y)Li^+ + (1+y)e^-$$



e.g., "x=0.5" would give:
- 60% higher V
- 50% higher capacity

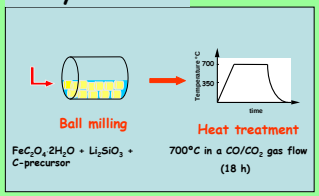


Electrochemical performance of $Li_2Fe_{0.9}Mn_{0.1}SiO_4$. Two redox plateaus ($Mn^{3+}/Mn^{2+}$ at 4.1 V and Fe^{3+}/Fe^{2+} at 3.1V) are distinguishable during the first charge cycle – giving higher voltage and increased capacity !

Our GCEP challenge is to find how to get Mn or some other higher-valent metal-cation to cycle through this redox couple reversibly.

Some techniques to be used . . .

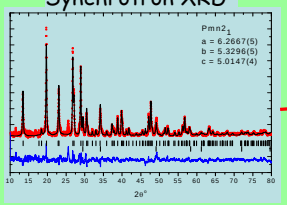
Synthesis

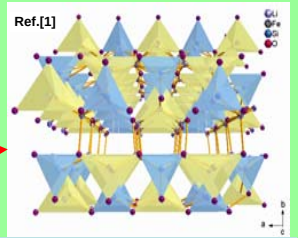


$FeC_2O_4\,2H_2O + Li_2SiO_3 +$ C-precursor

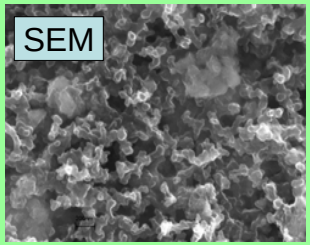
700°C in a CO/CO_2 gas flow (18 h)

Synchrotron XRD



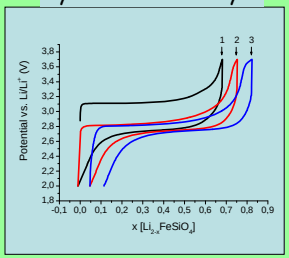


Structure of Li_2FeSiO_4

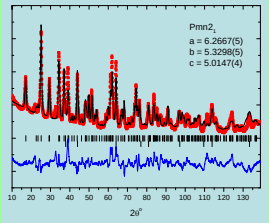


Li_2FeSiO_4 electrode after 25 cycles

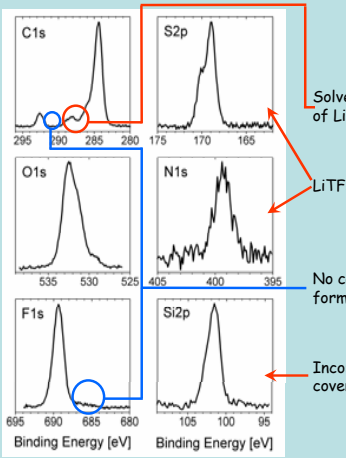
Cyclic voltammetry



Neutron powder diffraction



PES/XPS studies



Solvent reaction products of Li-carboxylate type

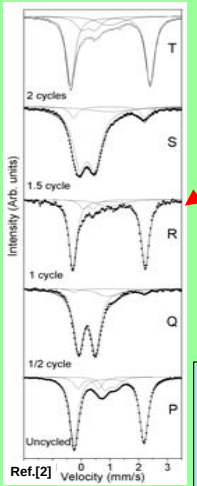
LiTFSI stable on cycling

No carbonates or LiF formed on cycling

Incomplete surface-film coverage

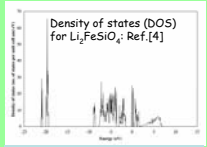
XPS spectra for a cycled Li_2FeSiO_4 electrode

Ref.[3]



Ref.[2]

Mössbauer spectroscopy - tells us the oxidation state of Fe (+2 or +3)



DFT calculations

Some references to this work . . .

[1] A. Nytén, A. Abouimrane, M. Armand, T. Gustafsson & J.O. Thomas, *Electrochem. Comm.*, **7** (2005) 156.

[2] A. Nytén, S. Kamali, L. Häggström, T. Gustafsson & J.O. Thomas *J. Mater. Chem.*, **16** (2006) 2266.

[3] A. Nytén, M. Stjerndahl, H. Rensmo, H. Siegbahn, M. Armand, T. Gustafsson, K. Edström & J.O. Thomas, *J. Mater. Chem.*, **16** (2006) 3483.

[4] P.Larsson, R. Ahuja, A. Nytén & J.O. Thomas, *Electrochem. Comm.*, **8** (2006) 797.