Experimantal details

Lithium iron(II) pyrophosphate ($Li_2FeP_2O_7$) was synthesized by solid state reaction method using lithium carbonate (Li_2CO_3, 99.997%, Aldrich), ammonium dihydrogen phosphate ($NH_4H_2PO_4$, 99.999%, Aldrich) and iron(II) oxalate ($FeC_2O_4.2H_2O$) as the starting materials. $FeC_2O_4.2H_2O$ was prepared by reacting equimolar solutions of Mohr's salt ($(NH_4)_2Fe(SO_4)_2$, ACS reagent, 99%, Sigma-Aldrich) and oxalic acid ($(COOH)_2.2H_2O$, ACS reagent, ≥99% Sigma-Aldrich). The reaction involved is as follows:

$$(NH_4)_2Fe(SO_4)_2.6H_2O+(COOH)_2.2H_2O \rightarrow FeC_2O_4.2H_2O+2H_2SO_4+2NH_3+6H_2O$$

De-ionized (DI) water with resistivity of ~18 $M\Omega cm^{-1}$ obtained using Mill-Q Integral 10 (Millipore) DI water plant was used for preparing the above solutions. Yellow colored precipitate of $FeC_2O_4.2H_2O$ immediately formed as soon as the two solutions were mixed. The precipitate was washed several times and then dried at 343 K overnight before using for the preparation of $Li_2FeP_2O_7$. The starting materials (Li_2CO_3, $NH_4H_2PO_4$ and $FeC_2O_4.2H_2O$) in the ratio of 1:1:1 were mixed thoroughly in an agate pestle-mortar and ground for 2h. The mixture was then transferred to an alumina crucible and heated at 573 K for 5h to ensure the removal of exhaust gases (NH_3, CO_2, CO) and water vapors. This mixture was calcined at 773, 823 and 853 K for 5h, 5h and 10h, respectively with intermittent grinding. All the above calcinations were performed in reductive atmosphere of 85% Ar+15% H_2 to avoid the oxidation of Fe^{2+} ions to Fe^{3+}. X-ray diffraction pattern (XRD) was recorded using PANalytical X'Pert PRO X-ray diffractometer (Cu K_α radiation, λ=1.5418 Å) over a 2θ range of 10 to 90°. The step size was taken as 0.008° and the scan step time was 134 s. SEM images were recorded for the sample sputter coated with gold using Quanta 200 FEG scanning electron microscope. The TGA and DSC data were collected using SDT Q600 (TA instruments) in the temperature range 303 K to 1273 K at a heating rate of 10 $Kmin^{-1}$. Impedance data were collected using the Alpha A impedance analyzer (Novocontrol Technologies) in the frequency range 0.1 Hz to 40 MHz.

Crystallographic data

Fractional atomic coordinates, occupancies and thermal displacement parameter obtained from Rietveld refinement of XRD data for lithium iron(II) pyrophosphate ($Li_2FeP_2O_7$)

Atom	x	y	z	Occupancy	B (Å^2)
Fe1	0.6720(2)	0.5717(2)	0.6971(2)	1.0000	1.93
Fe2	0.8195(2)	0.2828(3)	0.7504(4)	0.6613	1.93
Li5	0.8195(2)	0.2828(3)	0.7504(4)	0.1713	1.93
Fe3	0.0395(5)	0.0784(6)	0.6585(7)	0.3387	1.93
Li4	0.0395(5)	0.0784(6)	0.6585(7)	0.6387	1.93
P1	0.5724(3)	0.6555(3)	0.3736(4)	1.0000	0.92
P2	0.2400(3)	0.5701(4)	0.5645(3)	1.0000	0.92
P3	0.8941(3)	0.7976(3)	0.6168(4)	1.0000	0.92
P4	0.7540(3)	0.0440(4)	0.5222(3)	1.0000	0.92
O1	0.8606(5)	0.1299(7)	0.6164(8)	1.0000	0.62
O2	0.7869(6)	0.0333(7)	0.3851(6)	1.0000	0.62
O3	0.3815(6)	0.5783(7)	0.9747(8)	1.0000	0.62
O4	0.0992(5)	0.5566(7)	0.5649(7)	1.0000	0.62
O5	0.6891(5)	0.3276(7)	0.3332(7)	1.0000	0.62
O6	0.7283(6)	0.4081(7)	0.5673(7)	1.0000	0.62
O7	0.0777(6)	0.2732(6)	0.0271(7)	1.0000	0.62
O8	0.4202(6)	0.2830(7)	0.1941(8)	1.0000	0.62
O9	0.8474(5)	0.6813(7)	0.6820(7)	1.0000	0.62
O10	-0.0102(6)	0.8775(6)	0.7192(6)	1.0000	0.62
O11	0.4911(7)	0.9416(7)	0.7788(6)	1.0000	0.62
O12	0.5552(6)	0.6754(6)	0.5249(8)	1.0000	0.62
O13	0.2949(6)	0.0709(8)	0.1096(7)	1.0000	0.62
O14	0.2302(7)	0.1083(7)	0.4088(7)	1.0000	0.62
Li1	0.443(1)	0.708(2)	0.099(2)	1.0000	0.24
Li2	0.988(1)	0.614(2)	0.418(2)	1.0000	0.24
Li3	0.463(2)	0.568(2)	0.865(4)	1.0000	0.24