### Li(Mn<sub>x</sub>Fe<sub>1-x</sub>)PO<sub>4</sub>/C (x = 0.5, 0.75 and 1) Nanoplates for Lithium Storage Application.

#### **Supporting information**

#### SI-1 Structural and Electrochemical Characterization

Powder X-Ray diffraction (PXRD) patterns were recorded using a D5005 Bruker X-ray diffractometer equipped with Cu Ka radiation. The accelerating voltage and current were 40 kV and 40 mA, respectively. A scan speed of 0.015°/s was used to record the PXRD patterns. The morphology of the product was examined using field emission scanning electron microscope (FESEM) model Jeol JSM-6700F operated at 5 kV and 10 mA and high resolution transmission electron microscope (JEOL JEM-2010). For SEM examination, the sample surface was sputtered with platinum. For TEM studies, the sample was dispersed in ethanol by sonication; a drop was loaded on Cu-grid and dried. For electrochemical studies, composite electrodes were fabricated with the active material, super P carbon black and binder (Kynar 2801) in the weight ratio 70:15:15 using N-methyl pyrrolidone (NMP) as solvent. Super P carbon and active material were mixed through the spex mixer miller for 2 h in an agate 2 mL vial with one ball before making slurry with the Kynar 2801 binder and NMP. Electrodes with a thickness of 10 µm were prepared using an etched aluminium foil (20 µm thick) as current collector using the doctor-blade technique. Lithium metal foil, 1M LiPF6 in ethylene carbonate (EC), diethyl carbonate (DEC) and Dimethyl carbonate (DMC) (1:1:1 v/v) (Merck) and Celgard 2502 membrane were used as counter electrode, electrolyte and separator respectively to assemble cointype cells (size 2016) in an Ar-filled glove box (MBraun, Germany). The geometrical area of the electrode was 2.0 cm<sup>2</sup>. The active material content in the electrode was around  $\sim 1.5$ -2 mg. Further details of cell fabrication have been described previously.<sup>1</sup> The cells were aged for 12 h before measurement. Charge-discharge cycling at a constant current mode was carried out using a computer controlled Arbin battery tester (Model, BT2000, USA) and cyclic voltammetry studies were carried out at room temperature using a computer controlled VMP3 (Bio-logic, France).



**SI-2** PXRD patterns and FESEM images of the LMP synthesized at different  $Mn^{2+}$  moles. (a) LMP- JCPDS standard (Card No 33-0803), (b) 2.2 x  $10^{-3}$  moles, (c) 8.7 x  $10^{-4}$  moles and (d) 2.2 x  $10^{-4}$  moles. \* refers to the impurities. (e) and (f) refer to the SEM images of the product obtained at 8.7 x  $10^{-4}$  moles and 2.2 x  $10^{-4}$  moles respectively.

### **SI-3** Metal Coating

High carbon percentage will significantly decrease the volumetric energy density of LMP rather than the gravimetric energy density. For practical purposes, volumetric/gravimetric energy density and rate capability are the most essential features of electrode materials. Hence, it is essential to reduce the percentage of carbon in LMP/C composites. In case of LFP, earlier reports <sup>2</sup> have confirmed that small amount of 1-5 wt.% silver, gold or copper coating would enhance the LiFePO<sub>4</sub> performance even at high current rates. Furthermore, the density of gold, silver and copper is 19.30 g·cm<sup>-3</sup>, 10.49 g cm<sup>-3</sup> and 8.94 g·cm<sup>-3</sup> respectively. This is much superior to that of carbon.

# Silver coating

Silver nanoparticles coated on the LMP nanoplates were synthesized by the polyol method at 160 °C for 10 min using glycol as the solvent and AgNO<sub>3</sub> as silver source. PXRD pattern of the olivine phase was not found to be altered by the coating of Ag nanoparticles. Due to the low weight percentage used in the synthesis the characteristic peak of silver was not observed in the PXRD pattern. Fig. **SI-3a** presents the TEM and HRTEM images of Ag coated LMP nanoplates. The HRTEM image reveals 5 to 10 nm sized Ag nanoparticles on top of the LMP nanoplates. HRTEM images of the Ag coated LMP shows the lattice spacing for both Ag metal and LMP (**SI-3a**).



Instead of polyol, when a reductant like  $NaBH_4$  was used to coat Ag nanoparticles on LMP nanoplates only a partial coating of the plates was observed. **SI-3b** shows the distribution of silver nanoparticle on the LMP nanoplates using glycol and NaBH<sub>4</sub>.



**SI-3b** Comparison of TEM images of silver coated LMP nanoplates (a, b) Ag coating by glycol (c, d) Ag coating by NaBH<sub>4</sub>

# **Gold coating**

Under similar polyol reduction condition, K[AuCl<sub>4</sub>] was used as gold source and sodium citrate was added to prevent the growth of the gold nanoparticles. However, this procedure was not successful. Gold nano particles were found to be bigger in size around 60-100 nm. In addition, it was found that they were not uniformly distributed around the LMP nanoplates (**SI-3c**).



**SI-3c** TEM images of gold coated LMP nanoplates by polyol reduction at different magnification (a-d).

To surmount this problem, we have used oleic acid and oleyl amine as surfactant and mild reducing agent respectively for the synthesis of small Au nanoparticles on top of the LMP nanoplate. This procedure resulted in a uniform spherical gold nanoparticles with an average size around 10-15 nm covering the surface of LMP nanoplates. TEM images show the (**SI-3d**) distribution of gold nanoparticles around the nanoplates. Fig. **SI-3d** show the HRTEM images of the gold coated LMP plates which depict the clear lattice spacing for gold and LMP plates.



Fig. SI-3d TEM, HRTEM images of gold coated LMP nanoplates by amine reduction.

# **Copper coating**

Cu coating on top of the LMP nanoplates was not successful by any of the method which described previously. In most of the attempts agglomerates of copper nanoparticles were found to be present outside the LMP nanoplates.



**SI-4** PXRD patterns of the LMP synthesized from  $Mn(OAc)_2$  at various temperatures and time (a) 250 °C and (b) 290 °C. The symbol \* refers to impurities.



**SI-5** Galvanostatic charge–discharge cycle curves of LMP nanoplates with various coating: (a) bare, (b) carbon, (c) silver and (d) gold. Current density of 1.71 mA/g (1 C refers to a capacity of 171 mA/g in one h), potential window 2.3–4.5 V, recorded at room temperature.



SI-6 FESEM images of LiMn<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub>/C and LiMn<sub>0.75</sub>Fe<sub>0.25</sub>PO<sub>4</sub>/C.



**SI-7** HRTEM images of (a) LMP, (b)  $LiMn_{0.5}Fe_{0.5}PO_4/C$  and (c)  $LiMn_{0.75}Fe_{0.25}PO_4/C$  nanoplates showing crabon coating at the free surfaces.



**SI-8** Galvanostatic charge–discharge profiles of  $LiMn_{0.75}Fe_{0.25}PO_4/C$  nanoplates at various rates (only selected cycles were given) (a) 5 C (850 mA/g) (b) 7 C (1190 mA/g) (c) 10 C (1700 mA/g) and (d) reversible capacity vs. cycle number plots. Potential window for the cycles was maintained between 2.3–4.5 V and the data were recorded at room temperature

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Electronic Supplementary Material (ESI) for Journal of Materials Chemistry This journal is The Royal Society of Chemistry 2011

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