A Rationally Designed Dual Role Anode Material for Lithium-ion and Sodium-ion Batteries: Case Study of Eco-Friendly Fe_3O_4

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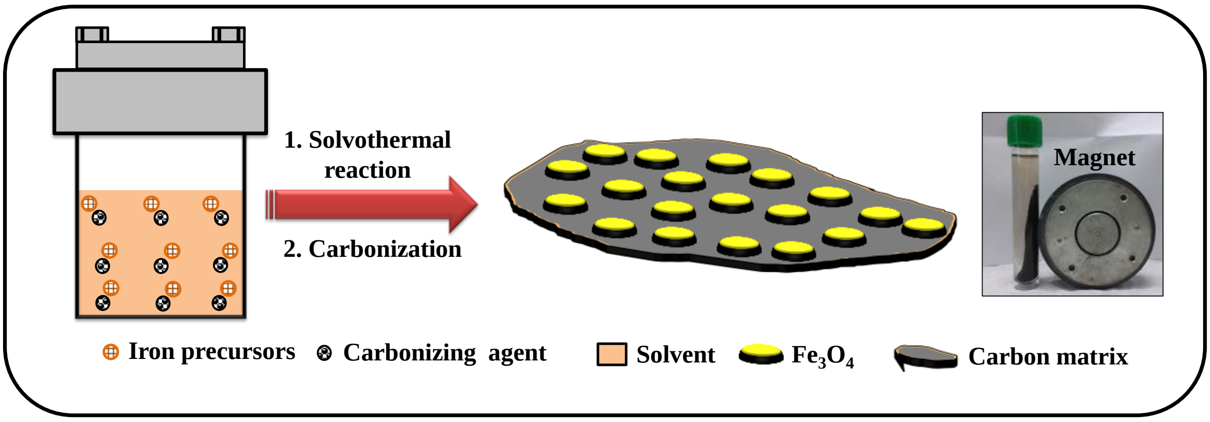

Fig. S1. Schematic depiction of the active material preparation process.

The solvothermal reaction was carried out at 200 ˚C for 16 h. The carbonization was performed at 450 ˚C for 4 h in an inert atmosphere of Argon. The optical photograph shows that the prepared material was magnetic (qualitative test only).

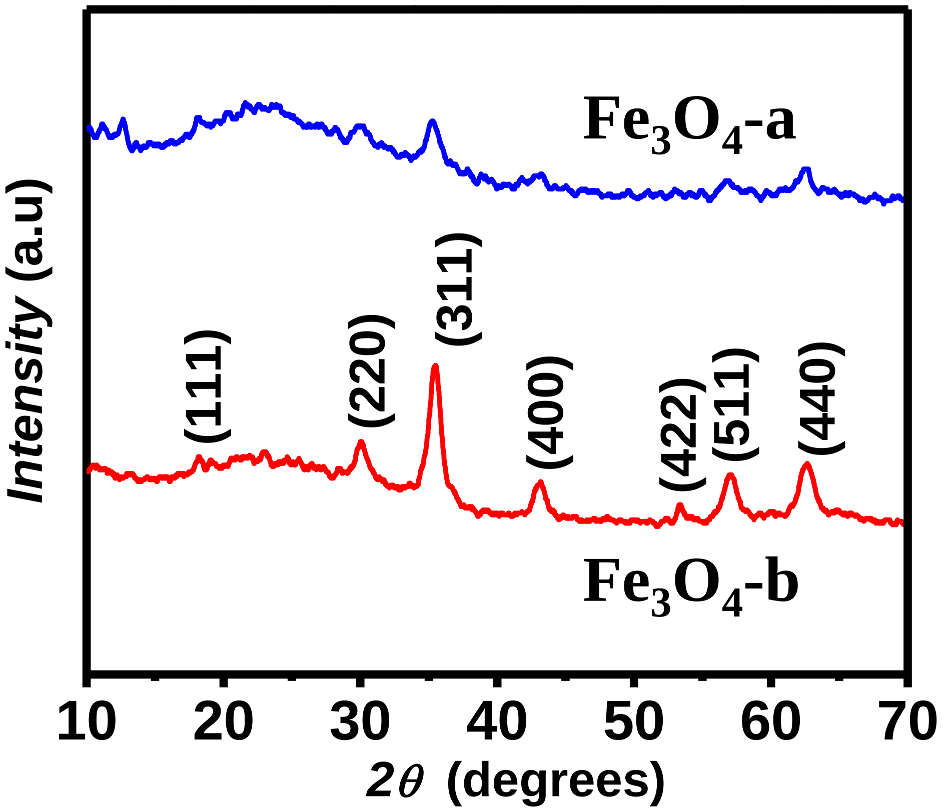

Fig. S2 XRD patterns of the intermediate product obtained after solvothermal reaction at 200 ˚C, before carbonization.

Intermediate product of Fe_3O_4-a appears to be relatively amorphous compared to those of Fe_3O_4-b. The peaks of Fe_3O_4-b indexed here match with the standard pattern of Fe_3O_4 (ICDD card No. 19-0629)

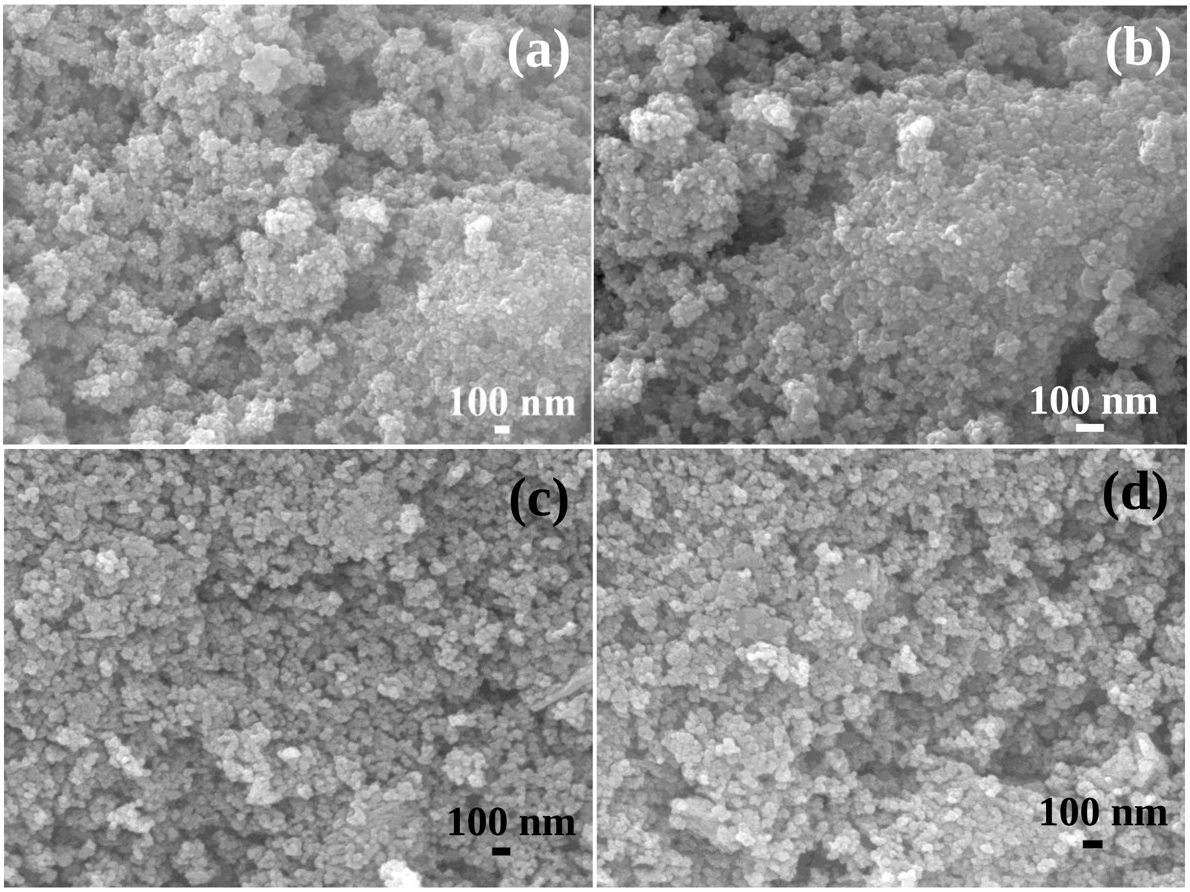

Fig. S3 (a) & (b) FESEM images of the final product of Fe_3O_4-a recorded at different regions. (c) & (d) FESEM images of the final product of Fe_3O_4-b recorded at different regions.

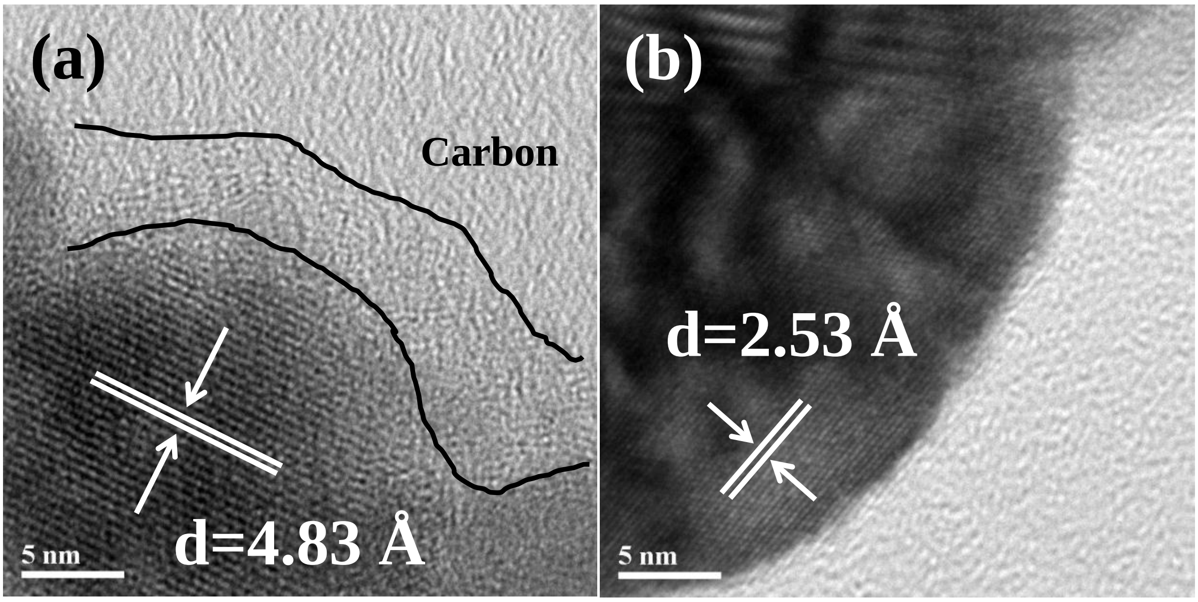

Fig. S4 (a) & (b) HRTEM images of Fe_3O_4-a and Fe_3O_4-b samples.

The HRTEM images clearly reveal the presence of a thin carbon layer surrounding the Fe_3O_4-a particle. However, the same could not be observed in Fe_3O_4-b.

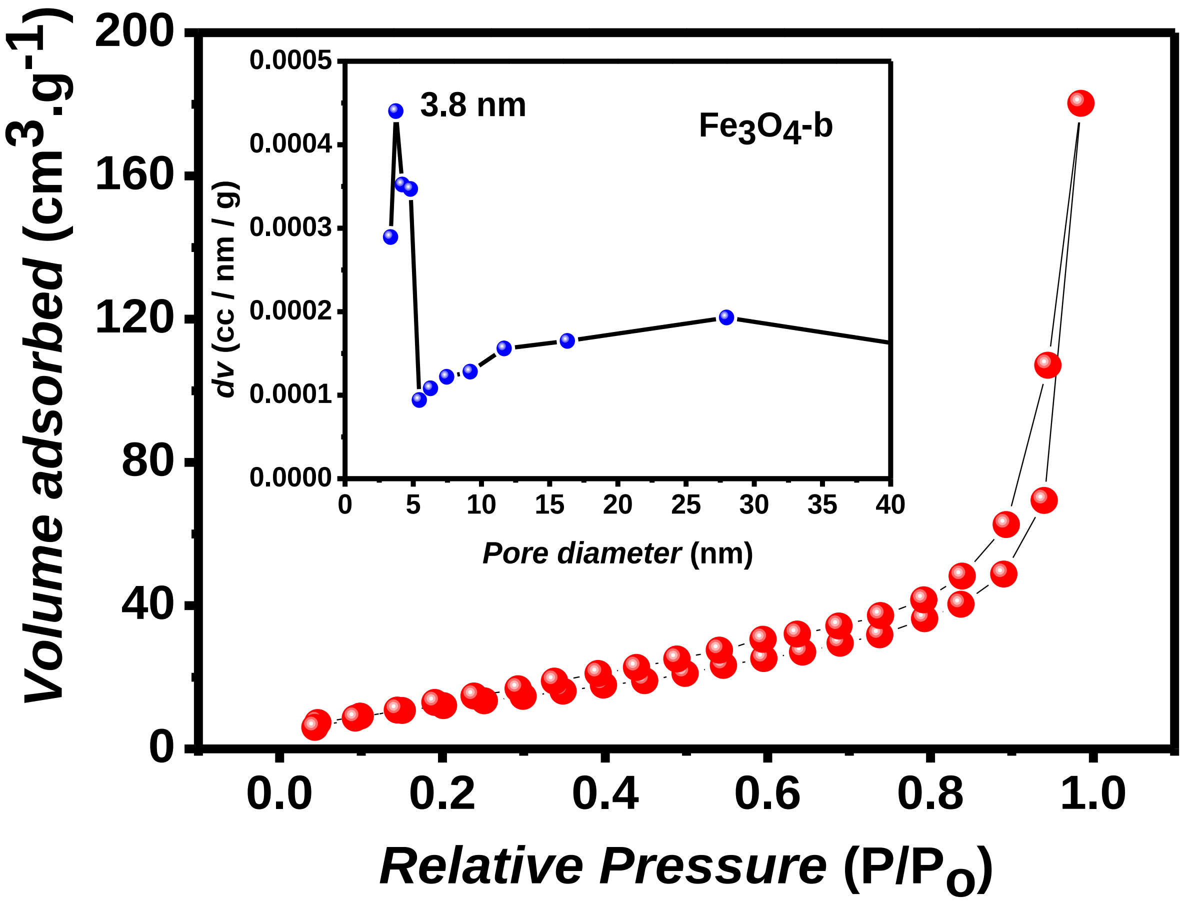

Fig. S5 Nitrogen adsorption and desorption isotherm of Fe_3O_4-b. Inset shows the pore size distribution.

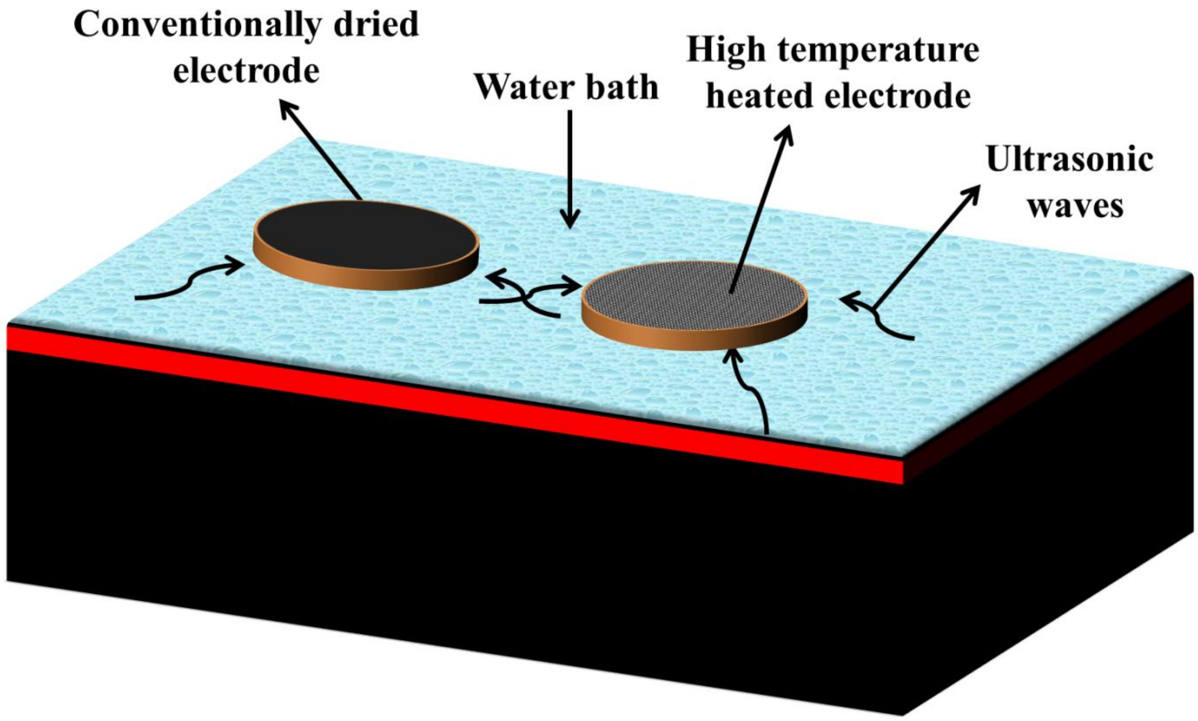

Fig. S6 Schematic of the experimental set-up used for performing qualitative adhesion tests.

For the qualitative adhesion test, the electrodes were first soaked in 40 ml of water. The electrodes were then continuously irradiated with ultrasonic waves over duration of 3 min. The video of this test can be viewed in **http://youtu.be/ZzIpQH-hep0**

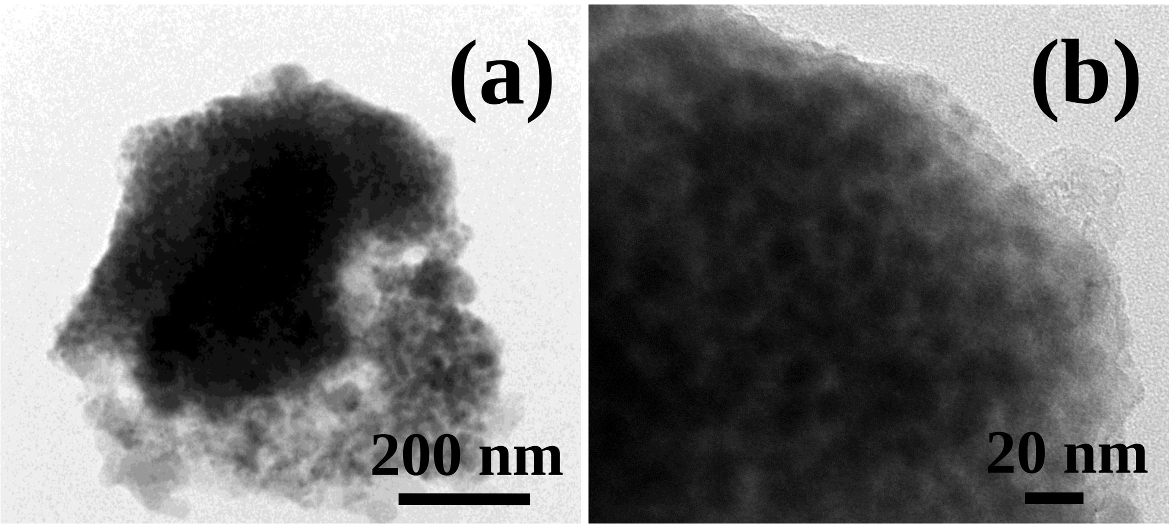

Fig. S7 (a) & (b) TEM images recorded at different magnifications on Fe_3O_4-a after cycling at 12 C.

It could be seen that the carbon matrix firmly holds the active material particles keeping them connected with the main body of the electrode even after cycling at 12 C.

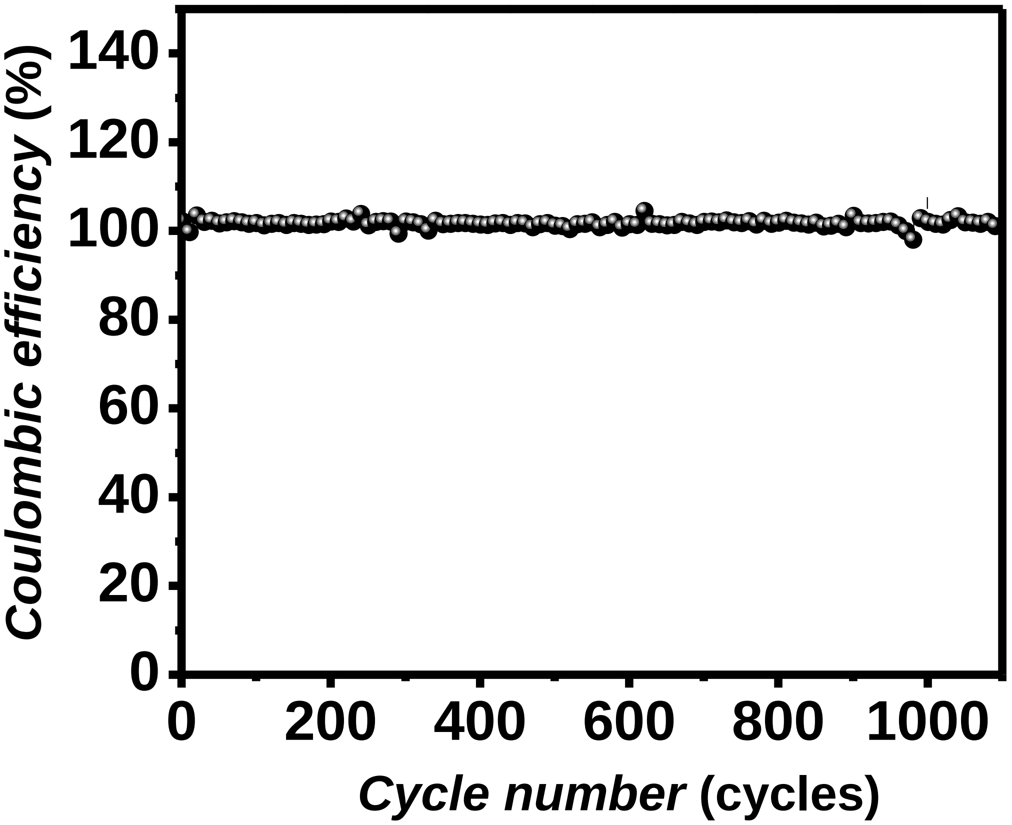

Fig. S8. Variation of coulombic efficiency as a function of cycle number of Fe_3O_4-a *vs.* Li/Li^+ with 13% external carbon additive cycled at 1.2 C rate in the voltage window 0.04-3.0 V.

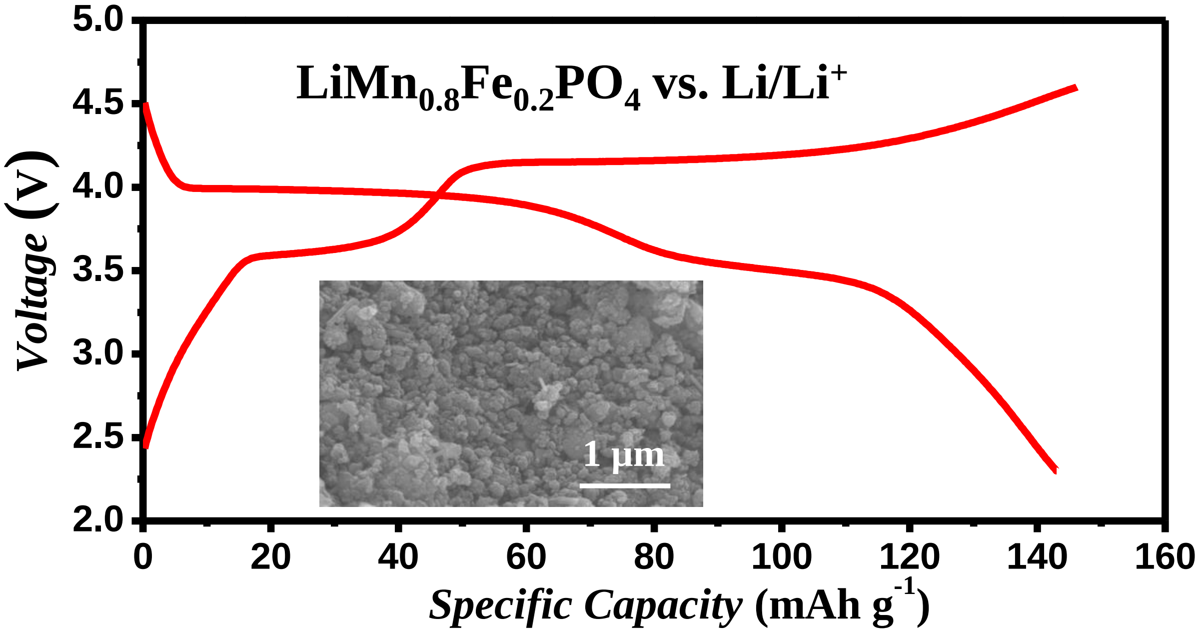

Fig. S9. Voltage profile of $LiMn_{0.8}Fe_{0.2}PO_4$ vs. Li/Li^+ at 0.1 C in the voltage window 2.3 - 4.6 V. More details of the cathode performance will be published elsewhere. [1]

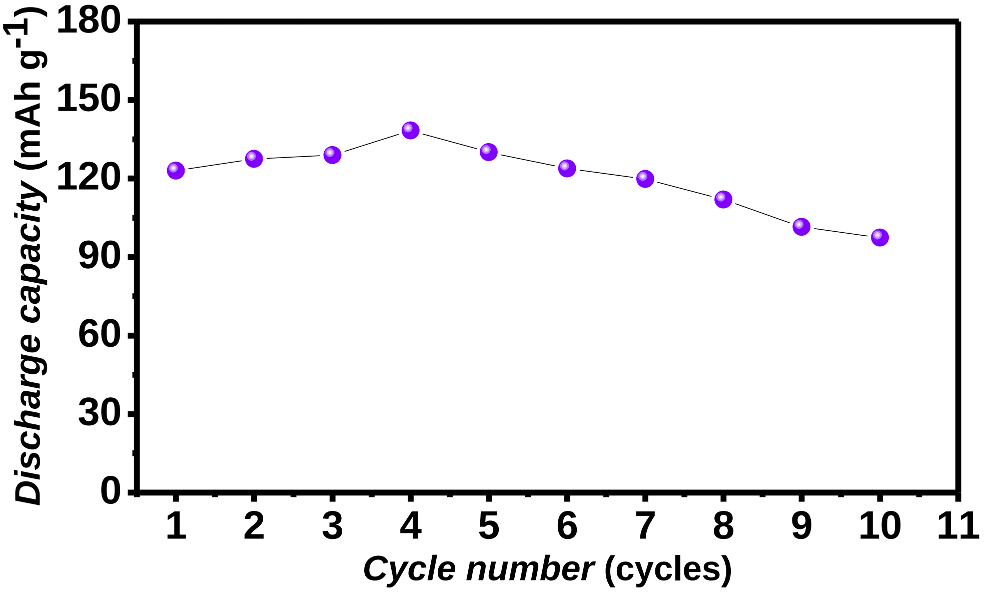

Fig. S10. Discharge capacity *vs.* cycle number of Fe_3O_4-a *vs.* $LiMn_{0.8}Fe_{0.2}PO_4$ at 0.12 C in the voltage window 0.5 - 3.75 V.

The capacity plotted here is shown based on the weight of the cathode. The first formation cycle is not shown here.

Table S1: Comparison of the electrochemical performance of Fe_3O_4 obtained in this work with some of the compelling reports in literature.

Nanocomposite	**Capacity retention after nth cycle with respect to first cycle at a specific current density (%)**	**Carbon content in the test electrodes (%)**	**Rate performance - Capacity delivered at current density ($mAh\ g^{-1}$)**	**Ref**
Fe_3O_4 incorporating rational material and electrode design	No noticeable capacity fade upto 1100 cycles at 1.11 A g^{-1}	28% carbon in the electrode (13% *ex-situ* + 15% *in-situ*)	610 mAh g^{-1} at 11.11 A g^{-1}	This work
Carbon and Fe_3O_4	No noticeable fade upto 100 cycles at 0.39 A g^{-1}	14% CNT	482 mAh g^{-1} at 6.25 A g^{-1}	Ref 2 2012
Carbon coated Fe_3O_4	No noticeable fade upto 100 cycles at 0.1 A g^{-1}	27% 12% *in-situ* + 15% *ex-situ*	418 mAh g^{-1} at 2.5 A g^{-1}	Ref 3 2012
Fe_3O_4 in carbon framework	No noticeable fade upto400 cycles at1.848 A g^{-1} (Total carbon in the electrode 30%)	30% carbon	500 mAh g^{-1} at 2.31 A g^{-1}	Ref 4 2012
Fe-Fe_3O_4 composite	-	10% pitch + 15% acetylene black	711 mAh g^{-1} at 10 A g^{-1}	Ref 5 2012
Nano architectured Fe_3O_4 array electrode	No noticeable fade after 220 cycles at a charge rate of 2.67 A g^{-1}	-	231 mAh g^{-1} at 8 A g^{-1}	Ref 6 2012
Single walled carbon nanotube -Fe_3O_4	92.94% after 60 cycles at 4.36 A g^{-1}	5% SWCNT	550 mAh g^{-1} at 8.72 A g^{-1}	Ref 7 2011
Fe_3O_4 nanoparticle integrated graphene	44% after 80 cycles at 1.85 A g^{-1}	5.5% *in-situ* 10% *ex-situ* 15.5%	192 mAh g^{-1} at 9.26 A g^{-1}	Ref 8 2011
Fe_3O_4-graphene nanocomposite	800 cycles at different current densities.	20% graphene + 10% carbon	180 mAh g^{-1} at 10 A g^{-1}	Ref 9 2011

Graphene wrapped Fe_3O_4	91% after 100 cycles at 0.7 A g^{-1}	13.3% graphene + 10% carbon	520 mAh g^{-1} at 1.75 A g^{-1}	Ref 10 2010
Carbon coated Fe_3O_4 nanowires	No noticeable fade upto 50 cycles at 0.1C rate	25% carbon (10% *in-situ* + 15% *ex-situ*)	600 mAh g^{-1} at 5C	Ref 11 2009
Carbon coated Fe_3O_4 nanospindles	88.3% after 80 cycles at 0.462 A g^{-1}	36.5% carbon (21.5% *in situ*+ 15% *ex-situ*)	190 mAh g^{-1} at 4.62 A g^{-1}	Ref 12 2008

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