Supporting Information

Reducing Li-diffusion Pathways via "Adherence" of Ultra-Small Nanocrystals of LiFePO₄ on Few Layer Nanoporous Holey-Graphene Sheets for Achieving High Rate Capability

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Experimental: Materials and methods:

Phosphoric acid (H₃PO₄), ferric citrate (C₆H₅FeO₇), lithium phosphate (Li₃PO₄), dimethyl formamide (DMF), sulfuric acid (H₂SO₄, 36 N), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂, 30%) and hydrochloric acid (HCl, 12 M) are obtained from SD Fine Chem Ltd (Mumbai). Graphite is obtained from Fluka. Ethylene carbonate (EC), dimethyl carbonate (DMC) and battery grade Lithium hexafluorophosphate (LiPF₆) are obtained from Sigma Aldrich. Milli-Q water (18.2 MΩ·cm at 25 °C) is used all throughout for all the experiments.

Synthesis of graphene oxide (GO) from graphite: Graphitic oxide is prepared by a method similar to that as reported in Ref. [1]. In a 500 ml round bottom flask, 1.5 g of graphite flake (powdered) is mixed by stirring with 0.75 g of sodium nitrate followed by addition of 35.4 ml of concentrated sulfuric acid. The mixture is subsequently cooled to 0 °C in an ice bath. 4.5 g of KMnO₄ is added to the suspension (temperature < 20 °C) under constant agitation. The temperature of the suspension is raised to 35 °C and maintained for 30 min. With the progress of the reaction, effervescence diminishes resulting in thickening of the reaction mixture. At the end of 20 min, the mixture becomes paste-like with a brownish grey color. After 30 min, 69 ml of water is added to the reaction mixture which leads to violent effervescence. The temperature of the reaction mixture is then increased to 98 °C followed by dilution with 210 ml water (after 15 min) and treatment with 1.5 ml of hydrogen peroxide to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. The suspension is filtered while warm to avoid precipitation of slightly soluble salt of mellitic acid formed as a side reaction. After washing the yellowish-brown filter cake three times with water, the graphitic oxide residue is treated with 30% HCl followed by washing with water, ethanol and finally dried at 50-60 °C.

10 mg of this graphitic oxide is dispersed in 100 ml of water and sonicated for 1 h. This leads to the exfoliation of graphitic oxide to graphene oxide (GO).

Preparation of holey-GO (h-GO): Holey-GO is prepared by a method as reported by Zhu *et al.*² Typically, 500 mg of GO is dispersed in 25 ml of water by ultra-sonication for 2 h. This is followed by the addition of 3.5 g of KOH (KOH:GO \approx 7), additional sonication for 20 min and stirring for 6 h (sonicated periodically for 1-2 mins during this 6 h) and finally dried at 120 °C. A paste-like black product is obtained and is first heated to 280 °C for 1 h in air to remove residual water followed by heating at 800 °C under N₂ atmosphere for 1 h in a tubular furnace (quartz tube). A black mass is obtained which is washed several times with water until neutral pH and finally dried at 80 °C. To avoid the corrosion of quartz tube with the KOH in the sample, the inner surface of the tube is wrapped with copper foil.

*Preparation of carbon coated LiFePO*₄ (*LFP-C*) *by sol-gel method*: 30 mmol (183.7 mg) of ferric citrate is dissolved in 25 ml of water at 70 °C for 1 h. Lithium phosphate (0.01 M, 40.5 mg) and ortho-phosphoric acid (0.02 mol, 0.04 ml) are dissolved in 35 ml of water at 70 °C resulting in LiH₂PO₄ (ortho-phosphoric acid is added drop-wise to the solution containing Li₃PO₄ at 70 °C). This reaction mixture is maintained at 70 °C for 1 h followed by drop-wise addition (over a period of 15-20 min) to the ferric citrate solution in hot condition and stirring for additional 1 h. The reaction mixture is then transferred to a crystallization glass dish and allowed to evaporate at 70 °C overnight. The green color gels obtained after complete removal of water is powdered to obtain LiFePO₄ followed by sintering the same at 350 °C for 12 h and carbonization at 700 °C for 7 h in a ceramic boat under continuous flow of 99.999% argon gas to obtain LFP-C.

Synthesis of LFP-h-GO and LFP-1GO composites: 200 mg LFP-C is dispersed in 15 ml of DMF by sonication for 15 min followed by removal of the supernatant. This is repeated for 2-3 times

and the solid mass dried. The sample mass is then mixed with requisite amount of h-GO (according to the weight ratio of h-GO and LFP-C) followed by addition of 5 ml of DMF, sonication for 2 h and finally dried at 180 °C. The LFP-h-GO composite with varying percentage of h-GO is represented as LFP-xh-GO (x = 0.5%, 1%, 2% and 5%). As LFP-1h-GO displays the best half-cell performance, LFP-1%GO (abbreviated as LFP-1GO) is only synthesized for the comparative studies. The synthesis of LFP-1GO is also done using the same method explained above except that 1% of GO is used instead of 1% of h-GO.

Structural and Electrochemical Characterization: The powder X-ray diffraction (PXRD) data are collected on a PANalytical diffractometer using Cu-K α radiation, ($\lambda = 0.1542$ nm). Transmission electron microscopy (TEM) measurements are performed using the Technai F30 transmission electron microscope (300 kV). Fourier transform infrared spectra are recorded on a Perkin Elmer Fourier transform infrared (FTIR) Spectrometer using the Spectrum 2000 software at a spectral resolution of 4 cm⁻¹. The Raman spectra are recorded on a Renishaw Micro-Raman 2000 Spectrometer operated at Nd:YAG laser excitation (wavelength = 532 nm) with a beam spot size of about 2 µm. X-ray photo electron spectroscopy (XPS) data is recorded on an AXIS-Ultra instrument from Kratos using monochromatic Al-K α radiation (225 W, 15 mA and 15 kV). Atomic force microscopy (AFM) images are acquired in the tapping mode using Bruker TESPA AFM probes on a Bruker Dimension Icon[®] instrument. The AFM images are analyzed using NanoScope Analysis v1.40r1 software. The painting of conducting carbon on aluminum foil is done by using the Elcometer Doctor Blade Film Applicator 4340. The cyclic voltammograms are obtained with the CH Instruments (CH608C) in the voltage range of 2-3.8 V at a scan rate of 0.25 mV s⁻¹. The galvanostatic charge/discharge cycling are performed on Arbin Instruments

(Model BT 2000) at different C-rates ($1C = 170 \text{ mA g}^{-1}$) in the voltage range of (2-3.8) V (versus Li⁺/Li).

Electrochemical cell assembly: Electrochemical stability and lithium battery performance studies are tested in SwagelokTM half-cells with lithium foil (Aldrich, thickness = 0.75 mm) as a counter and reference electrode, Whatman glass fiber as separator soaked with 1 M LiPF₆ in EC:DMC (1:1 V/V) as electrolyte. For electrochemical measurements, slurry of active material (LFP-C, LFP-1GO or LFP-xh-GO) is prepared with acetylene carbon black (Alfa Aesar) and polyvinylidene fluoride (PVdF, Kynarflex) in a weight ratio of 80:10:10 in N-Methyl-2pyrrolidone (NMP). This is then cast on a carbon coated aluminum foil and dried at 110 °C under vacuum for 12 h. All cell assembly is done at 25 °C in argon filled glove box (MBraun) (oxygen < 1.0 ppm and H₂O < 1.0 ppm). The galvanostatic intermittent titration technique (GITT) measurements are also carried out using Arbin Instrument (Model BT 2000, Arbin Instruments Corp., USA). GITT measurements consisting of a series of current pulses are applied to the SwagelokTM cells at a current of 0.1 C for 7.5 min each followed by 2 h rest.

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Figure-S1. Thermogravimetric analysis (TGA) profile showing percentage of total carbon (carbon coating on LFP-C + h-GO) in LFP-1h-GO.



Figure-S2. N₂ adsorption-desorption isotherm of h-GO.



Figure-S3. (a) X-ray diffraction patterns of h-GO, GO and graphite and (b) TEM image of graphene oxide (inset: TEM image of GO at scale bar: 50 nm).



Figure-S4. Clear distinction of activated portion (h-GO) and non-activated portion of graphene oxide (GO) in TEM.



Figure-S5. Thermogravimetric analysis (TGA) profiles of h-GO, GO and graphite.



Figure-S6. Powder X-ray diffraction patterns of (a) LFP-1h-GO, (b) LFP-1GO, (c) LFP-bat and (d) reference pattern (JCPDS No. 40-1499).



Figure-S7. Fourier transform infrared (i) and confocal Raman (ii) spectra (excitation wavelength = 532 nm) of (a) GO, (b) h-GO, (c) LFP-1GO, (d) LFP-1h-GO and (e) LFP-C. Inset: plot of ratio of area intensity of D to G bands. The Raman spectra are normalized with reference to the G band.

GO	h-GO	LFP-C	LFP- 1h-GO	Assignments
593				
618	618			
784	730			
832	857			δ (epoxy C-O-C), cyclic edge ether
1057	1010			ν(C-O)
1225				ν(Epoxy C-O)/ ν(C-OH)
1400				O-H bending deformation in carboxylic acids and phenolic groups
1582, 1574	1565	1581 (weak hump)	1580	v(C=C)
1621	1656	1641	1653	ν (C=O) + δ (O-H)
1724				v(C=O)
2855				ν(C-H)
2926				ν(C-H)
2960				ν(C-H)
3194				Phenolic O-H
3391	3362	3334	3422	ν (O-H) of hydroxyl, carboxyl groups and/or H ₂ O

Table-ST1. Important infrared band positions (in cm⁻¹) and assignment for h-GO and LFP-1h-GO (v \rightarrow stretch and $\delta \rightarrow$ bending).

Table-ST2. Important infrared band positions (in cm⁻¹) and assignment for LFP-1h-GO ($\nu \rightarrow$ stretch and $\delta \rightarrow$ bending, Symm \rightarrow symmetric and Asym \rightarrow asymmetric).

LFP-C	LFP-hGO	Assignments
467	468	Li-O oscillations
500	506, 509, 513	
548	549	
576	578	δ _{Asym} (O-P-O)
	597	
636	636	
647	648)	
945, 951,954	946,955, 960	$v_{\text{Symm}}(\text{P-O}) \text{ of } \text{PO}_4^{3-}$
1048	1051, 1055 ∫	
1078	1075	
1095	1083	$v_{Avm}(P-O)$ of PO_4^{3-}
	1095	
1137)	1136	
1581 (very weak hump)	1580 (medium)	v(C=C) from h-GO
1641	1653	$v(C=O) + \delta(O-H)$
3334	3422	ν(O-H)



Figure-S8. (a) Bright field transmission electron microscopy (BF-TEM) and (b) high resolution transmission electron microscopy (HRTEM) images of LFP-bat.



Figure-S9. Energy-dispersive X-ray spectrum (EDS) of LFP-1h-GO.



Figure-S10. Voltage vs. specific capacity plot of LFP-1GO in the initial cycle.

Electrochemical impedance spectra (EIS) of LFP-1h-GO before and after the 1500th galvanostatic cycle

The Nyquist plots of the LFP-1h-GO cathode before cycling (fresh cell) and after 1500th galvanostatic cycles are shown in Figure-S11. The fresh cell impedance spectrum composed of a depressed semicircle (high to medium frequency) and a straight slopping line (low frequency). To get a better understanding of the change of impedance parameters, the Nyquist plots were analyzed by ZViewTM software (Scribner Associates Inc.). Based on the characteristics of Nyquist plot we proposed the simplified equivalent circuit for the observed EIS spectrum as shown as inset of Figure S11. To compensate for the non-ideal behavior of the electrode (e.g. surface roughness and porosity) a constant phase element (CPE) is used to model equivalent circuit instead of a capacitor. Here, R_{el} corresponds to the electrolytic resistance and the contact resistance of the cell components. The semicircle is represented by $R_{CT}//CPE_{DL}$ where R_{CT} is the electrolyte-electrode charge- transfer resistance and CPE_{DL} the related double-layer capacitance. The slope line at low frequency is represented by the bounded Warburg impedance (*Ws*1) of the Li⁺-ions diffusion in the LFP cathode. The assignments of EIS is done according to the persisting assumptions.³⁻⁷

The EIS of LFP-1h-GO at the end of 1500th cycle shows similar behavior as that of the fresh cell with the exception of generation of an additional hump at the high frequency region (1-0.125) MHz. This high frequency semicircle (overlapped with the mid-frequency semicircle) is attributed to the surface film (the solid-electrolyte interface, SEI) and is represented as $R_{\text{SF}}//CPE_{\text{SF}}$, where R_{SF} (= 15.2 Ω) corresponds to resistance and capacitance of the surface film.⁸ However the appearance of very weak hump for the surface film suggest development of too thin layer of the SEI even after 1500th cycle, again indicating superior performance of the electrode.

The increase of charge-transfer resistance to 118 Ω after 1500th cycle from 20.6 Ω of the fresh cell is explained on the basis of change in feasible processes like partial desolvation reaction, adsorption, and surface diffusion of lithium-ions on the electrode surface because of repeated cycling. This increase of R_{CT} along with increase of defects⁹ (eg. antisite defects which blocks channelized 1D movement of Li⁺-ions in LiFePO₄¹⁰) with repeated cycling explains the monotonic decrease of specific capacity of LFP-h-GO cells.

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Figure-S11. Electrochemical impedance spectra of LFP-1h-GO (red) before cycling and (olive) at the end of 1500th cycle. Inset: equivalent circuits used for fitting the impedance data. R_{el} , R_{sf} and R_{CT} stand for electrolytic resistance, resistance of surface film (solid-electrolyte interface) and the charge-transfer resistance respectively. DL stands for double layer and *W*s is Warburg element.



Figure-S12. Galvanostatic cycle performance of LFP-1GO (current rate = 0.1C).



Figure-S13. Coulombic efficiency for LFP-1h-GO (current rate = 0.1C).



Figure S14. Rate capability plot of LFP-1GO.



Figure-S15. Galvanostatic cycle performance of LFP-*x*h-GO: (a) x = 2%, (b) x = 0.5% and (c) x = 5%.

Evaluation of diffusion coefficient of LFP-h-GO and LFP-1GO

The effective Li⁺-ion chemical diffusion coefficients (D_{Li}) for LFP-1h-GO and LFP-1GO are determined from the GITT (c/f Figures 7 and S16) using the Fick's laws and the following equation¹¹

$$D_{Li} = \frac{4}{\pi \tau} \left(\frac{mV}{MS}\right)^2 \left(\frac{\Delta E_S}{\Delta E_{\tau}}\right)^2$$

Here, *m* is the mass of active electrode material and *M* (157.76 g mol⁻¹) and *V* (46 cm³ mol⁻¹) the molar mass and molar volume of LiFePO₄ respectively. τ is the time for which the constant current pulse is applied and ΔE_s and ΔE_t , stands for the change of the steady-state voltage (*E*₀) of the cell for each applied galvanostatic current pulse and the total transient voltage change of the cell during the step, respectively. *S* stands for geometric surface area of the electrode.

For, LFP-1h-GO, M = 157.76 g mol⁻¹, V = 46 cm³ mol⁻¹, S = 0.786 cm², $\tau = 456$ min, $\Delta E_s = 0.001224$ V and $\Delta E_t = 0.015302$ V,

Thus $D_{\text{Li}^+} = 6.3 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$

For LFP-1GO the calculated value (c/f Figure S12b) for $D_{\text{Li}} = 4.7 \times 10^{-13} \text{ cm}^2 \text{ g}^{-1}$

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Figure-S16. Galvanostatic intermittent titration technique (GITT) polarization curve for a single GITT discharge process at plateau potential for (a) LFP-1h-GO and (b) LFP-1GO.