Uncovering Lithium Iron Metaphosphate as a Cathode Material Through Organophosphate Assisted One-Pot Synthesis

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1. Experimental Section

Chemicals: Alpha-iron (III) oxyhydroxide (α-FeOOH, Aldrich Chemica), Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$ Macklin 98 %), Lauric acid ($C_{12}H_{24}O_2$, Macklin, 98 %), n-Hexylphosphonic acid (HPA, Macklin, 98 %), N, N-Dimethylfornanide (DMF, Macklin, 99.5 %), Nafion® perfluorinated resin-aqueous dispersion (Aladdin, 5 wt.% in water), Carbon black (Macklin, xc-72R,10-20 nm), ethanol (CH_3CH_2OH, Macklin, 95 %), Lithium battery electrolyte (KLD-LP07, Canrd, 1.0M LiPF6 in EC:DMC=1:1 vol%) and Separator (Celgard® 2500)

Synthesis of $LiFeO_2$ nanoparticle: $LiFeO_2$ nanoparticle was synthesized following a solid-state method reported by Y.T. Lee et al.[1]

Synthesis of LiFe-HPA: 1 mmol of $LiFeO_2$ nanoparticle was dispersed and ultrasonicated in 6 ml of n-hexane for 30 min. Subsequently, 4 mmol of HPA and 30 g of lauric acid were added. The mixture was heated to 60 ℃ under vigorous stirring, with N_2 gas purged for 1 hour to degas and remove n-hexane and air. Then, the $LiFeO_2$ nanoparticles and HPA in lauric acid solution were heated up to 260 ℃ under N_2 atmosphere and refluxed at this temperature for 6 h. After heating was completed, the mixture was cooled to 60 ℃, followed by the addition of 50 ml DMF and stirring. LiFe-HPA precipitates were then collected by centrifugation. The precipitates were washed three times with DMF and once with ethanol to remove the residues of HPA and lauric acid. After drying in oven at 60 ℃ and grinding treatment, a brown powder was collected.

Synthesis of Lithium iron metaphosphate: The as-synthesized LiFe-HPA powder was placed in an alumina crucible and then placed in a tube furnace for heat treatment under N_2 atmosphere (50 sccm flow rate) until the furnace was cooled down to below 60 ℃.

Material Characterizations: The samples were analyzed using X-ray diffraction (XRD), transmission electron microscopy (TEM), Thermogravimetric analysis (TGA), Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy. XRD patterns were obtained using a SmartLabTM 9 kW X-ray diffractometer (Cu Kα radiation, λ=1.541 Å). TGA was done using SDTQ600 and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Transmission electron microscopy (TEM) measurements were performed on a FEI Talos F200S 200 kV transmission electron microscope, coupled

with a Super-XEDS for dispersive X-ray spectroscopy (EDS) and elemental mapping.

Electrochemical Tests: The electrochemical lithium (de)intercalation performences of $LiFe(PO_3)_3$ were examined with the coin-type (CR2032) half-cell. To make the working electrode (cathode), a uniform slurry of active materials along with acetylene black and poly (vinylidiene fluoride) (PVDF) binder in 80:10:10 (w/w/w) ratio was prepared in minimal amount of N-methyl-pyrrolidone (NMP). The obtained homogeneous slurry was then spread uniformly on a thin aluminum foil and dried at 80 ℃ for 12 h in vacuum before roll pressing. Circular cathodes with a diameter of 10 mm were acquired using a punching machine, and the mass loading of active material was about 1-2 mg cm^{-2}. Lithium metal foil was used as counter electrode, while a Celgard 2500 membrane was used as the separator. For all cells, 60 μL of 1 M $LiPF_6$ in EC/DEC (1:1, v/v) was used as the electrolyte, followed by a 24 h rest at room temperature before testing. Charge/discharge test of the assembled coin cell was carried out with a Neware battery test system under different current densities in the voltage range of 2.0-4.0 V at 25 ℃. Cyclic voltammogram (CV) tests (scan rate of 0.5 mV/s in the voltage range of 2.0-4.0 V) were performed by an Autolab PGSTAT 302 electrochemical workstation. Electrochemical impedance spectroscopy (EIS) measurements were carried out using a three-electrode configuration in 1 M $LiNO_3$ aqueous electrolyte, with a platinum plate and a saturated calomel electrode (SCE) serving as the counter and reference electrodes, respectively. The measurements were performed at 0 V (vs. reversible hydrogen electrode, RHE) over a frequency range from 0.1 to 1.0×10^6 Hz.

The lithium-ion diffusion (D_{Li^+}) coefficients can be obtained from EIS measurements using the following equations[2]:

$$Z_{Re} = R_s + R_{ct} + \sigma\omega^{-1/2} \tag{1}$$

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \tag{2}$$

2. Table

Table S1. Nomenclature and heat-treatment conditions for various samples under N_2 atmospheres.

Sample Name	Temperature (℃)	Holding time (h)
$LiFe(PO_3)_3/C_{1h}$	640	1
$LiFe(PO_3)_3/C_{2h}$	640	2
$LiFe(PO_3)_3/C_{4h}$	640	4
$LiFe(PO_3)_3/C_{6h}$	640	6
LiFe-HPA-N450	450	6
LiFe-HPA-N550	550	6
LiFe-HPA-N600	600	6
LiFe-HPA-N640	640	6
LiFe-HPA-N650	650	6
LiFe-HPA-N700	700	6
LiFe-HPA-N750	750	6
LiFe-HPA-N800	800	6

Table S2. The elemental content of sample LiFe-HPA-N640 and LiFe-HPA-N750 obtained from EDS (the corresponding sampling area are shown in the SEM pictures in Figure S7).

Sample	C (at%)	O (at%)	P (at%)	Fe (at%)	Li (estimated at%)
LiFe-HPA-N640	7.54	47.10	18.16	13.60	13.60
LiFe-HPA-N750	7.99	62.12	15.55	7.18	7.18

Table S3. Mass loss date of LiFe-HPA-N640, LiFe-HPA-N700, LiFe-HPA-N750 and LiFe-HPA-N800.

Sample	Initial Mass(mg)	Final Mass(mg)	Mass Remains
LiFe-HPA-N640	510	202	39.6%
LiFe-HPA-N700	600	246	41%
LiFe-HPA-N750	263	104	39.5%
LiFe-HPA-N800	250	93	37.2%

Table S4. Based on the Warburg coefficient extracted from the low-frequency region, the lithium-ion diffusion (D_{Li^+}) coefficients for samples obtained at different pyrolysis durations were calculated.

Sample Name	Lithium-ion diffusion (D_{Li^+})
$LiFe(PO_3)_3/C_{1h}$	1.64×10^{-15}
$LiFe(PO_3)_3/C_{2h}$	5.81×10^{-15}
$LiFe(PO_3)_3/C_{4h}$	1.9×10^{-14}
$LiFe(PO_3)_3/C_{6h}$	2.01×10^{-14}

3. Figures

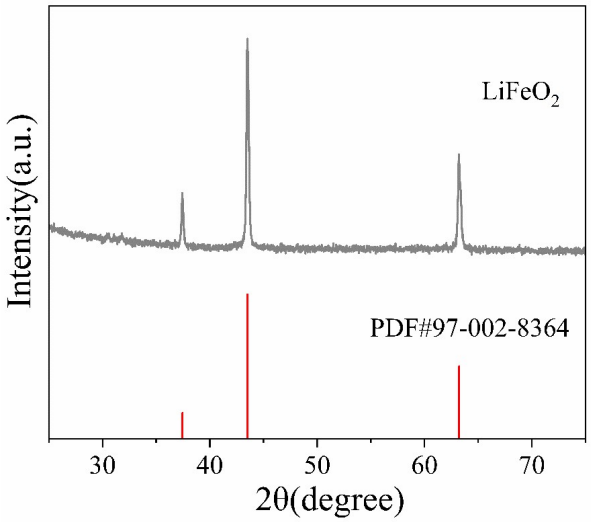

Figure S1. XRD pattern of $LiFeO_2$.

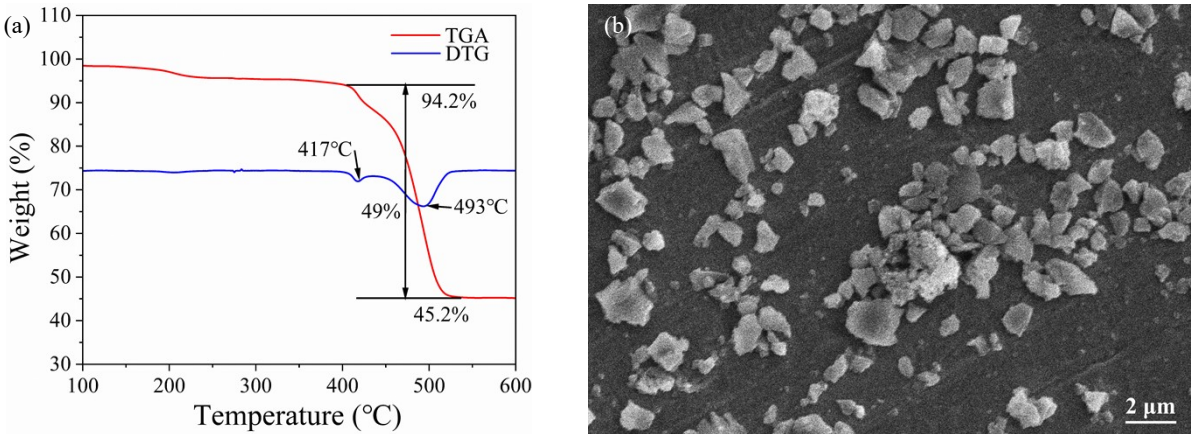

Figure S2. (a) TGA and derivative thermogravimetry (DTG) curves for LiFe-HPA pyrolyzed in N_2 at the rate of 5 °C min^{-1}; (b) SEM image of $LiFe(PO_3)_3/C_{6h.}$

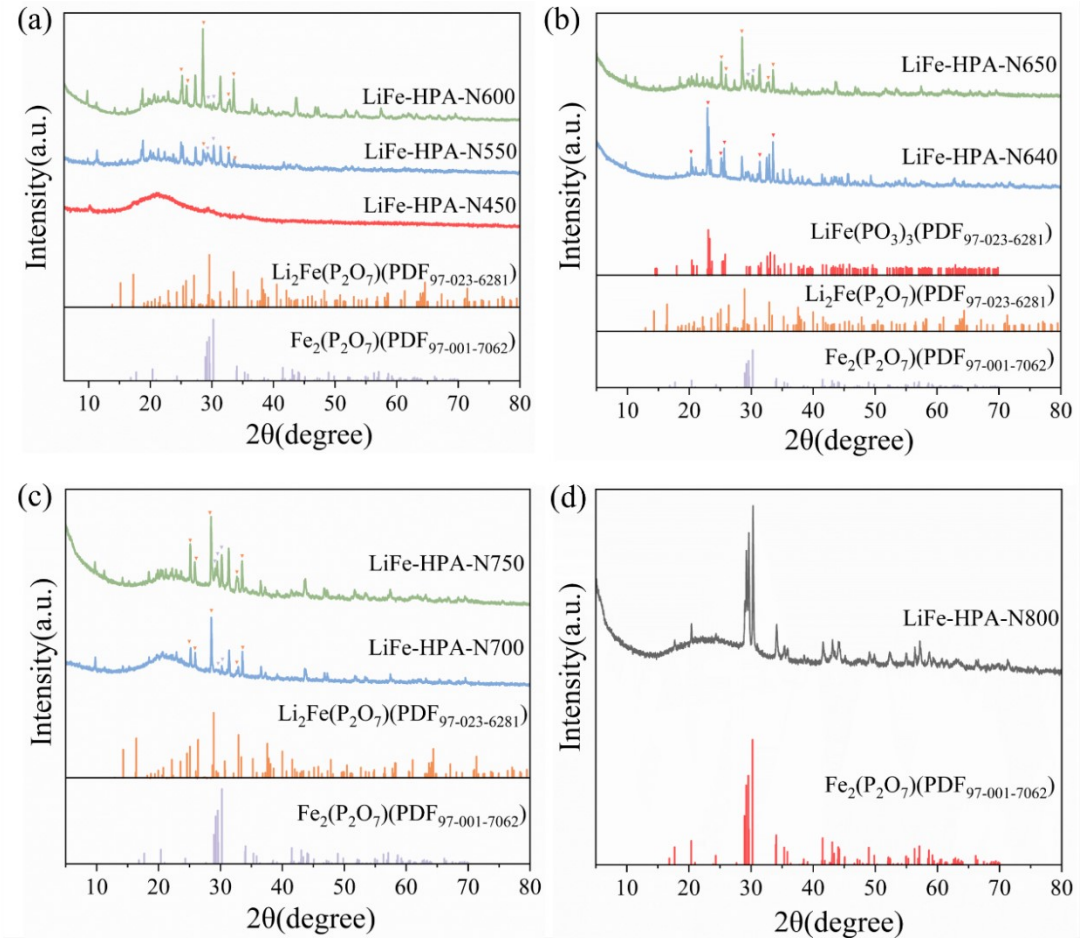

Figure S3. XRD patterns of the products derived from LiFe-HPA at different pyrolysis temperatures.

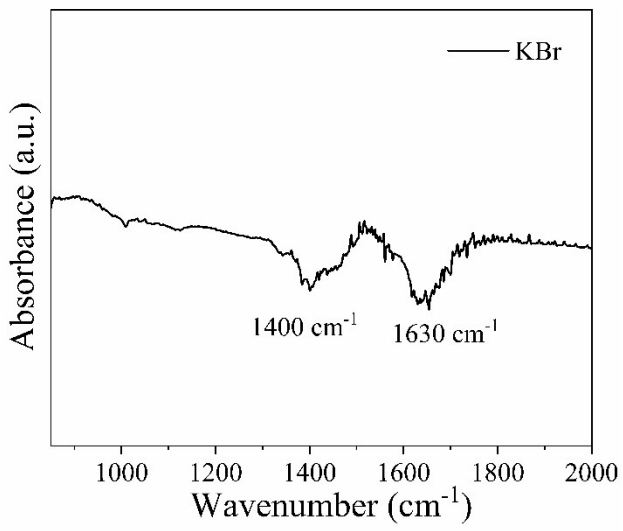

Figure S4. FTIR spectroscopy of KBr.

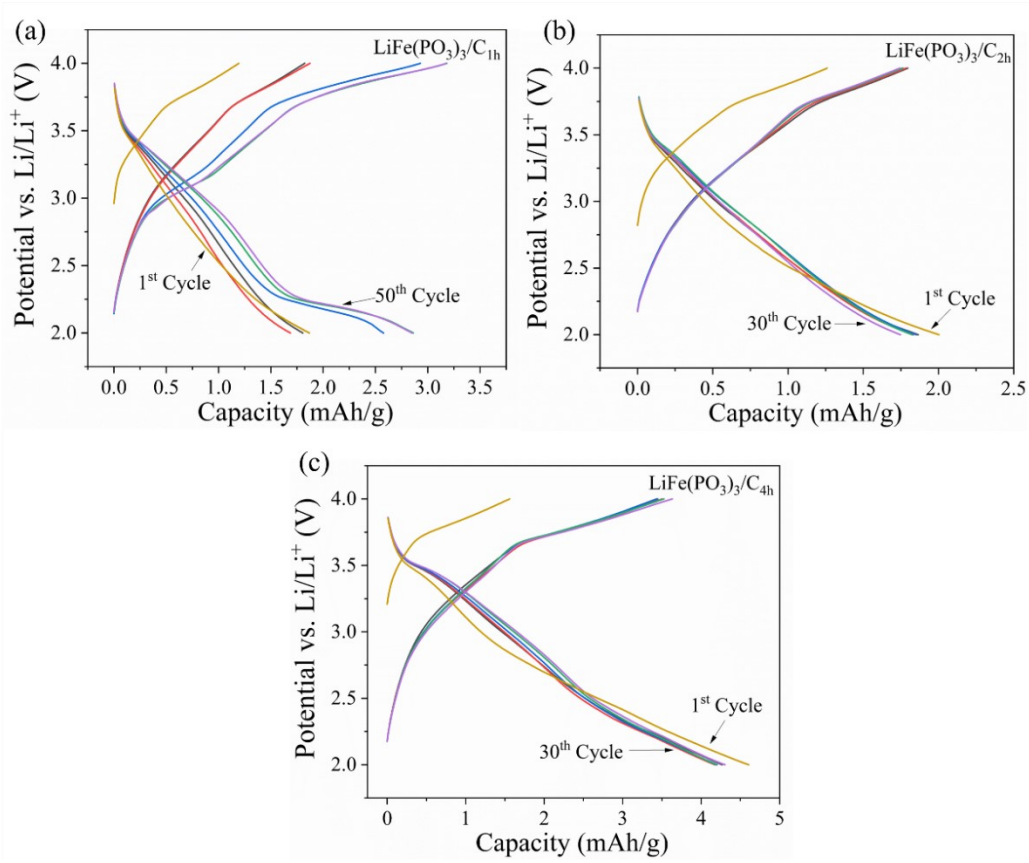

Figure S5. Galvanostatic charge−discharge profiles of (a)$LiFe(PO_3)_3/C_{1h}$, (b)$LiFe(PO_3)_3/C_{2h}$, (c)$LiFe(PO_3)_3/C_{4h}$ cycled between 2.0-4.0 V at a rate of 0.01 C in coin-cell architecture.

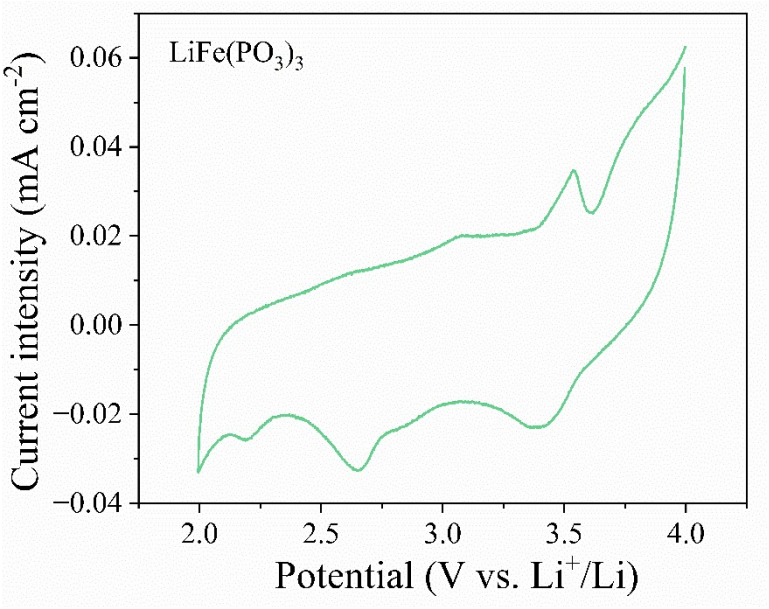

Figure S6. Cyclic voltammetry (CV) of $LiFe(PO_3)_3$ was carried out within 2.0-4.0 V (vs. Li^+/Li) at a scan rate of 0.5 mV s^{-1}.

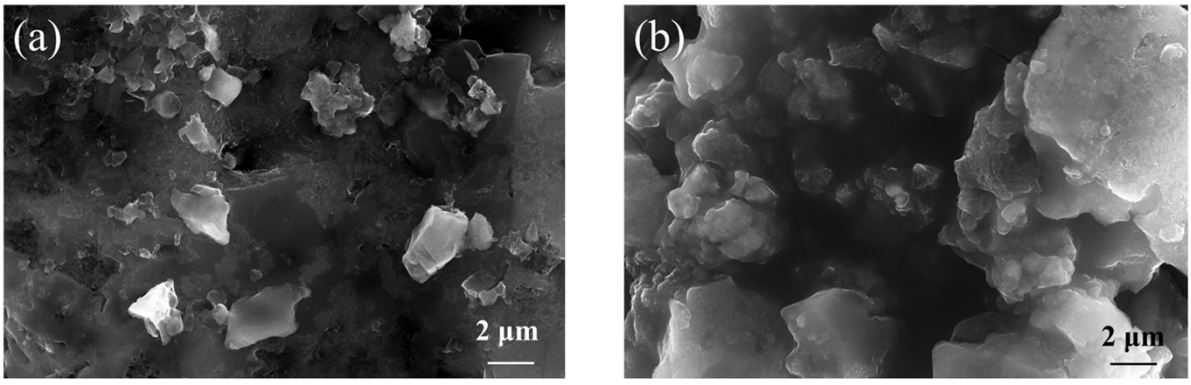

Figure S7. SEM images of (a) LiFe-HPA-N640 and (b) LiFe-HPA-N750 correspond to EDS results in Table S2.

References

1. Y. T. Lee, C. S. Yoon, Y. S. Lee and Y. K. Sun, *Journal of Power Sources*, 2004, **134**, 88-94.

2. F. Meng, Y. Li, S. Wang, D. Luo, X. Zhang, M. Wagner, Z. Tang, Y. Li, D. Kong and L. Zhi, *Energy & Environmental Science*, 2025, **18**, 4775-4786.