

Supporting information

One-pot synthesis of $\text{Li}_2\text{FePO}_4\text{F}$ nanoparticles via supercritical fluid process and characterization for lithium ion battery

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Experimental

$\text{Li}_2\text{FePO}_4\text{F}$ nanoparticles were synthesized from Iron chloride (II) tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Wako, Japan), orthophosphoric acid (H_3PO_4 Wako, Japan) and lithium fluoride (LiF Wako, Japan) in 1:1:4 molar ratios. Ascorbic (Wako, Japan) was used as reducing agent. First, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and H_3PO_4 were dissolved in mixed solvents of water and ethylene glycol (70:30 volume ratio) and LiF was separately dissolved in diluted hydrochloric acid (HCl) with constant stirring at $70\text{ }^\circ\text{C}$ for 1h (LiF is not soluble in water, so HCl was used) the solution was stirred for 30-40 min and then both solution was mixed together, followed by addition of ascorbic acid. Later, the solution mixture (5 ml) was transferred to batch reactors (4 reactors, each 10 ml volume) followed by heating at $400\text{ }^\circ\text{C}$ at high pressure (38 MPa) for about 10-30 min and then reactors were quenched in cold water, the products were recovered through repeated washings using ethanol and water.

Characterization

The powder X-ray diffraction (XRD) analysis was carried out with a Bruker AXS D8 Advance instrument using $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (JEOL

TEM-2100F), Energy dispersive spectroscopy (EDS) was carried out using SU 8000, Hitachi, Japan. TG analysis was performed using TG-DTA 2000S to know the exact carbon content in $\text{Li}_2\text{MnSiO}_4$

Electrochemical measurements

Carbon coating was carried out prior to electrochemical measurements. Active materials was mixed with known amount of carbon materials (acetylene black), the mixture was put into ball milling pot and ball milling process was carried out for above 3h with 240 rpm. After that, the sample was recovered and vacuum dried. Later, the vacuum dried cathode material was ground well with 10 wt% PTFE (poly(tetrafluoroethylene)) binder to make the electrode paste. The weight ratio of active material, acetylene black and PTFE were 80:10:10. The prepared paste was spread uniformly on a 1 cm^2 SUS metal (100 mesh) using the doctor-blade method. The cathode loading was $5\text{--}7\text{ mgcm}^{-2}$. Li metal on a SUS metal mesh was used as a counter and reference electrodes. The electrolyte consist the solution of (18 to 20 ml) 1M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1 by volume). The cell assembly was carried out in a glove box filled with high purity argon gas. The electrochemical performances of the prepared electrode was characterized by galvanostatic charge-discharge (HOKUTO DENKO, Japan) in a potential range between 1.8 V to 4.5 V vs Li/Li^+ .

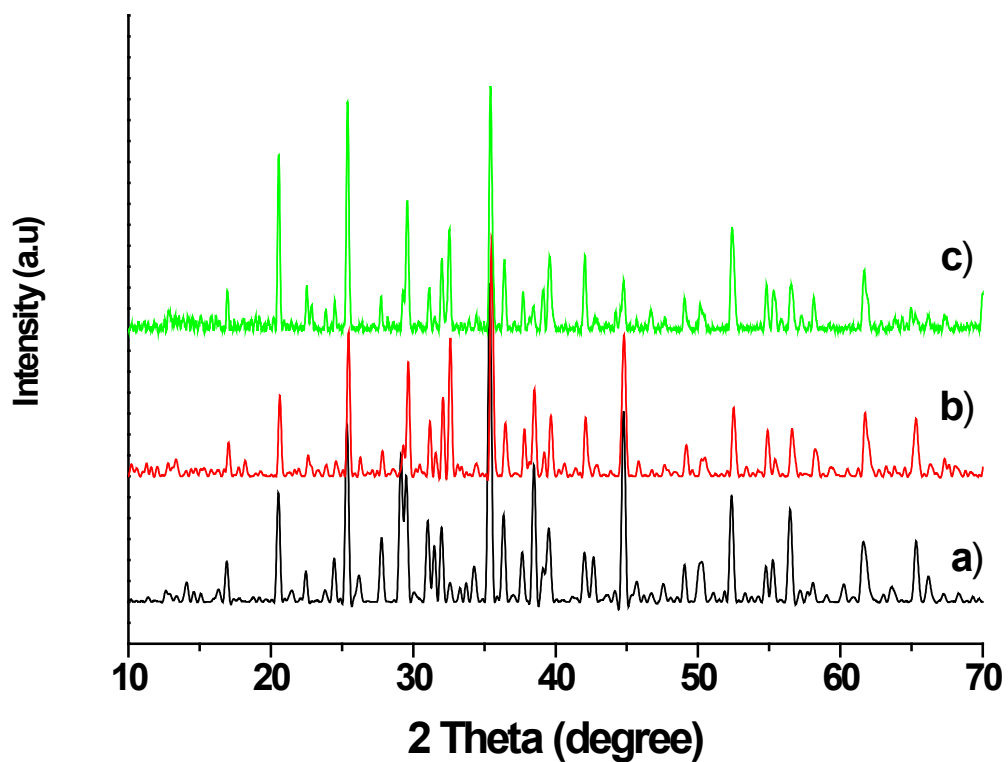


Fig. S1 XRD pattern of as-synthesized particles at 400 °C for 30 min, a) in water, b) ethanol and c) water/ethanol. Majority of the diffraction peaks are matching to LiFePO₄ phase compared with JCPDS#40-11499

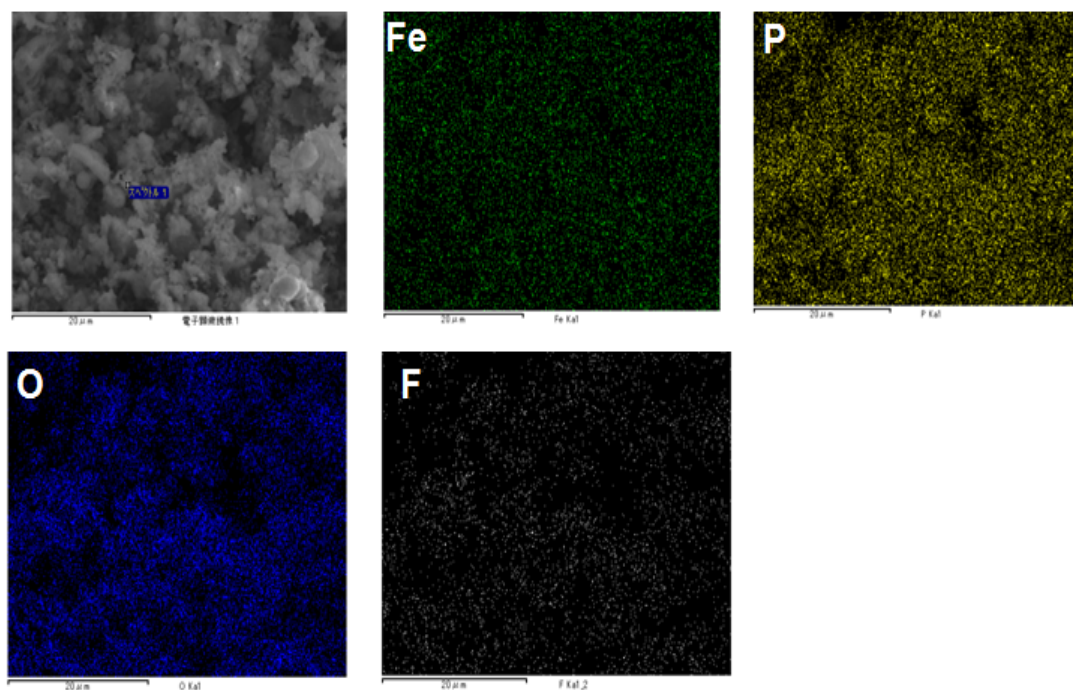


Fig. S2 SEM image and elemental mapping of as-synthesized $\text{Li}_2\text{FePO}_4\text{F}$ nanoparticles at 400 °C for 10 min. Mapping of Fe, P, O and F can be observed.

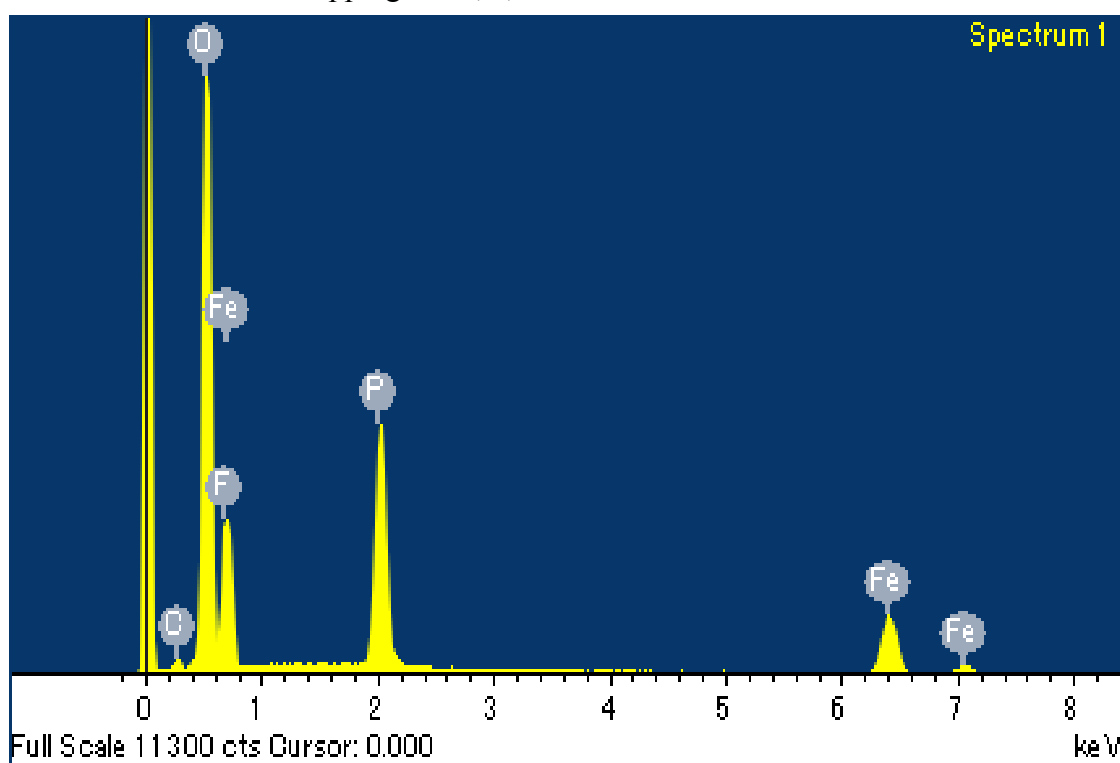


Fig. S3 EDS Spectra of $\text{Li}_2\text{FePO}_4\text{F}$ nanoparticles synthesized at 400 °C for 30 min, showing the presence of Fe, P, O and F and confirming the formation of $\text{Li}_2\text{FePO}_4\text{F}$ phase.

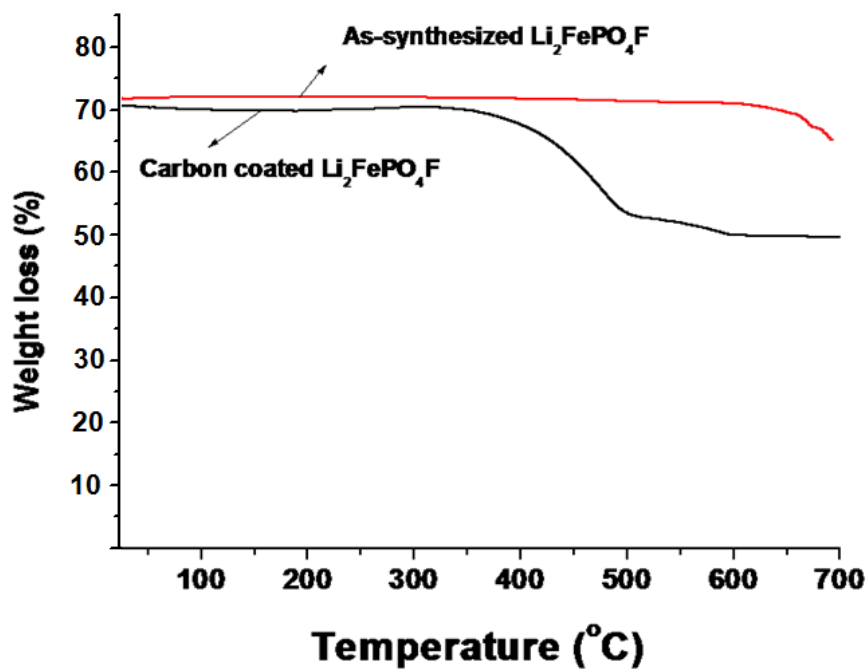


Fig. S4 TG analysis of as-synthesized and carbon coated Li₂FePO₄F nanoparticles at 400 °C for 30 min.

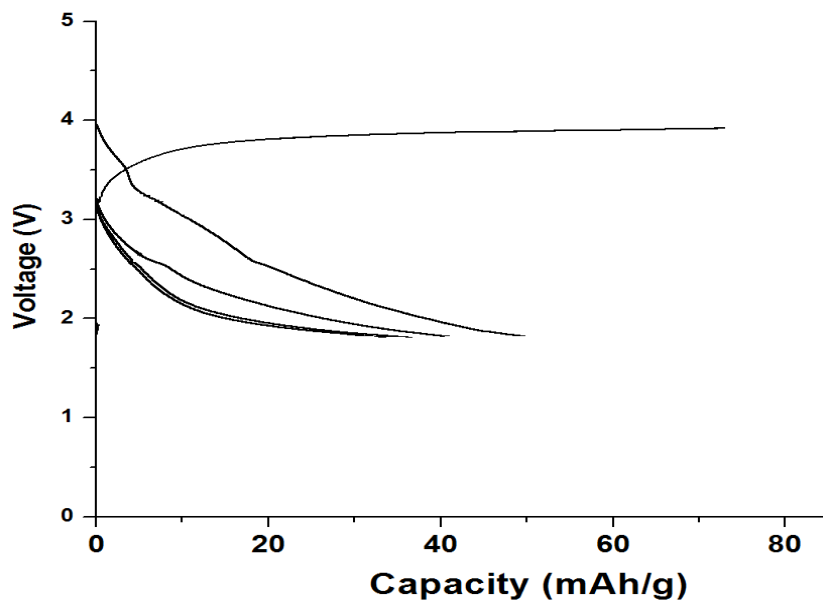


Fig. S5 Charge discharge of as synthesized Li₂FePO₄F at 400 °C for 30 min via supercritical fluid process.