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Supporting Information

Unraveling the dynamic phase transition behavior of $LiMn_{0.7}Fe_{0.3}PO_4$ nanoparticle electrodes for lithium-ion batteries

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Experimental

Morphology and structure characterization: The phase compositions and crystallinity of LMFP were analyzed by X-ray diffraction (XRD, Bruker) with Cu Kα radiation over the 2θ angle range from 10º to 80°. A Zeiss Gemini scanning electron microscope (SEM, Gemini SEM 300) and a transmission electron microscope (TEM, JEOL 2100 Plus) were used to observe the morphologies of samples. The elemental compositions were analyzed with an energy-dispersive X-ray spectrometer (EDS) attached to the SEM instrument. The chemical states (Fe, Mn) of pristine electrode and charged electrodes (4.5 V, *vs.* Li^+/Li) at various C-currents (0.2 C, 2 C and 20 C) were characterized by *ex-situ* X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi).

Electrochemical measurements: The electrochemical performances of LMFP are evaluated using coin-type half-cells (CR2032 size) assembled in an argon-filled glove box (Mikrouna Super 1220). The cathode electrodes were prepared by casting a homogeneous slurry consisting of LMFP (40 wt%), conductive carbon (40 wt%), polyvinylidene fluoride (PVDF, 20 wt%) and N-methyl-2-pyrrolidone (NMP) onto a conventional aluminum foil or a special ultra-thin porous aluminum foil. Then the coated foils were dried in a vacuum oven at 80 °C for 12 h to assure total evaporation of the solvent. These foils were cut into 12 mm diameter discs, each with a controlled active material loading of between 0.35 and 0.45 mg cm^{-2}. The electrolyte is 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1, *v*/*v*/*v*) with 1.0 wt% vinylene carbonate (VC) additive, while Celgard 2400 polypropylene membrane as the separator. The galvanostatic charge-discharge characteristics of the cells are also determined on a Land test system in a voltage range of 2.2-4.5 V at room temperature (25±2 °C), respectively.

To obtain the bulk Li^+ diffusion coefficient (D_{Li+}) of LMFP, we analyze the kinetic investigation of LMFP|Li based on galvanostatic intermittent titration technique (GITT) measurements. The LMFP|Li cell is charged or discharged for 2 min at a pulse current of 0.5

C, followed by a duration of 30 min relaxation to reach thermodynamic steady-state. The diffusion coefficients ($D_{\mathrm{Li+}}$) can be calculated via the following equation:

$$D_{Li^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \quad \left(\tau << L^2/D_{Li^+}\right)$$

where τ is the current pulse time, m_B is the mass of active material, V_M is the molar volume of LMFP, M_B is the molecular mass of LMFP, S is the area of the LMFP electrode, ΔE_s is the variation of steady-state voltage of the cell after a single step; ΔE_t is the total transient voltage change of the cell after employing a galvanostatic current for the time τ; and L is the average thickness of the LMFP sample.

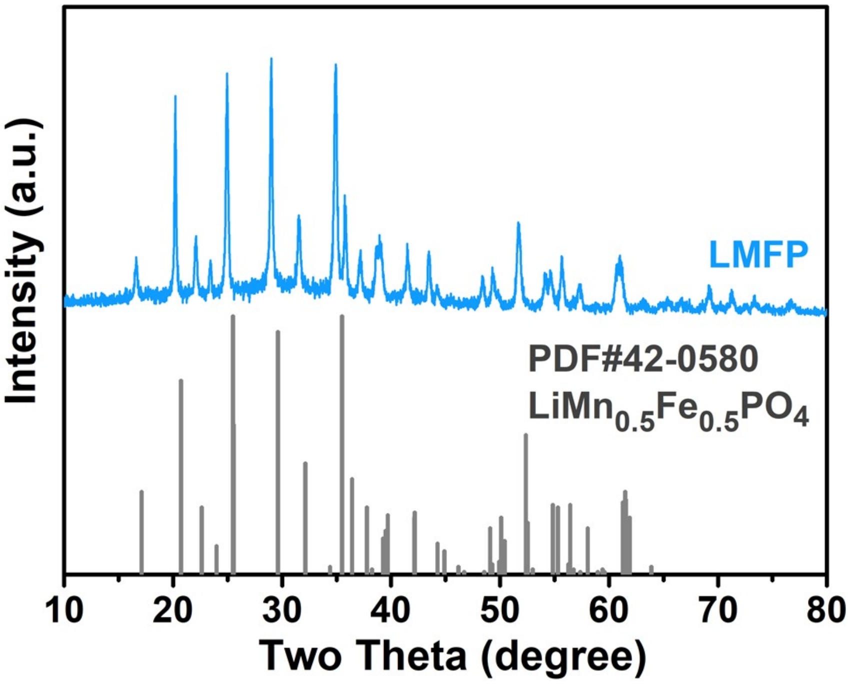

Fig. S1 XRD pattern of LMFP particles.

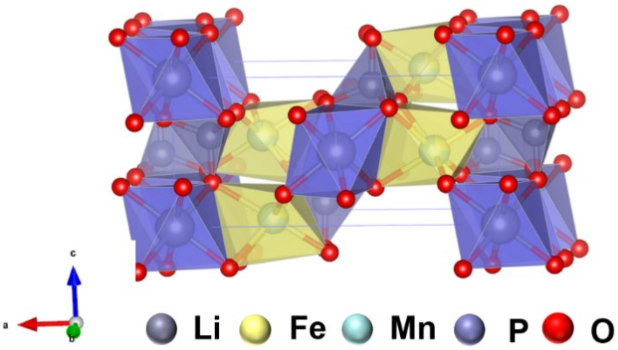

Fig. S2 Schematic crystal structure of LMFP.

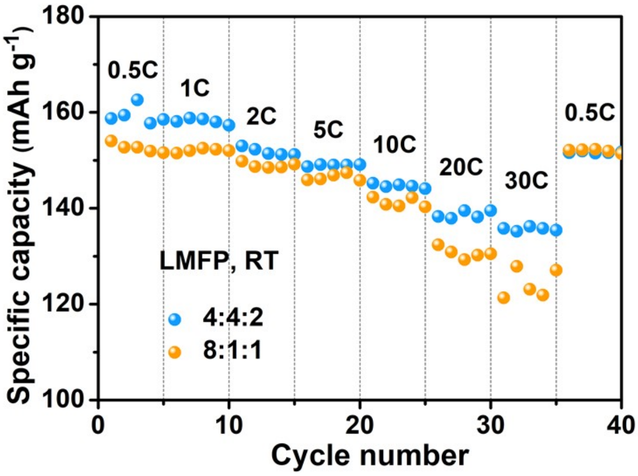

Fig. S3 Rate capability of LMFP electrodes with different compositions (4:4:2 and 8:1:1), while these cells are charged at 0.5 C and discharged at n C.