Supplementary Information

**Nanoparticle shapes of LiMnPO₄, Li⁺ diffusion orientation and diffusion coefficients for high volumetric energy Li⁺ ion cathodes**

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**Electrochemical potential spectroscopy (EPS) Experimental method**

The lithium ion diffusion coefficient was measured in a three-electrode open cell with lithium counter and reference electrodes with 1M LiPF₆ in EC/DMC (Sigma) inside a grounded Faraday cage housed in an argon glovebox. Electrochemical control and measurement were performed using a Bio-Logic SP-300 potentiostat.

Electrochemical Potential Spectroscopy (EPS) is a variant of Potentiostatic Intermittent Titration Technique (PITT) where there is no open-circuit period applied between voltage steps. EPS was performed through chronoamperometric response measurements as 5 mV step voltages are applied. Charging measurements (lithium extraction) start from the initial open-circuit potential, the applied voltage is step-wise increased every 3 minutes until 4.4 V (vs. Li/Li⁺). For the discharge portion (lithium insertion), it is decreased instead, also in 5 mV steps, held for 3 minutes each until 2.5 V (vs. Li/Li⁺).

The current transient response to applied step potential is described by the equation below, where \( l \) as the electrode thickness, \( F \) is Faraday’s constant and \( S \) is the electrode surface area. To avoid the need to calculate the difference between the concentration of the lithium ions at the surface (\( C_s \)) and bulk (\( C_o \)), the EPS-derived lithium ion diffusion coefficient (\( \tilde{D}_{\text{Li,EPS}} \)) was calculated from the slope of the linear portion of the natural log of the current transient \( \ln(i(t)) \) vs. time \( t \). As the slope equates to \( -\frac{\pi^2 \tilde{D}_{\text{Li,EPS}}}{4l^2} \), the \( \tilde{D}_{\text{Li,EPS}} \) can be calculated.

\[
i(t) = \frac{2FS(C_s - C_o)\tilde{D}_{\text{Li,EPS}}}{l} \exp\left(-\frac{\pi^2 \tilde{D}_{\text{Li,EPS}}}{4l^2} t\right)
\]
Fig. S1. TEM image of LiMnPO$_4$ particles synthesized with manganese acetate.

Fig. S2. Rietveld refinement analysis of nano-LiMnPO$_4$. The red is experimental and the blue is calculated. The reliability factors, $R_{wp}$ (weighted profile R-factor) = 1.9663, $R_{exp}$ (expected R-factor) = 0.9665, $R_p$ = 1.4447, GOF (goodness of fit) = 4.1388.
Fig. S3. The pore size distribution of the composites, nano-LiMnPO$_4$ and carbon prepared by hand mixing and ball milling.