Electronic Supplementary Material

**Spinel LiNi_{0.5}Mn_{1.5}O_{4} cathode for rechargeable lithium-ion batteries: Nano vs micro, ordered phase (P4_{3}32) vs disordered phase (Fd\overline{3}m)**

Jingang Yang, Xiaopeng Han, Xiaolong Zhang, Fangyi Cheng\(^\star\), and Jun Chen

*Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China*

Supporting information to DOI 10.1007/s12274-013-0343-5

**Figure S1** (a) XRD patterns and (b) Raman spectra of as-prepared LNMO-MP, LNMO-MF, LNMO-NP, and LNMO-NF. Rietveld refined XRD patterns of the prepared (c) LNMO-MP and (d) LNMO-NF, with experimental data (red dots), calculated profile (cyan line), allowed Bragg reflections (vertical green bars), and difference curve (blue line). Raman mapping of (e) LNMO-MP and (f) LNMO-NF, within a selected area of 10 \( \mu \)m \( \times \) 10 \( \mu \)m. The symbols * and \( \bigstar \) denote P4_{3}32-LNMO and LiNi_{x}O_{1-x}, respectively.

Address correspondence to fycheng@nankai.edu.cn
Figure S2  Cyclic voltammograms (CVs) of the electrodes made with (a) LNMO-MP, (b) LNMO-MF, (c) LNMO-NP, and (d) LNMO-NF. The scan rates are set from 0.1 to 4.0 mV·s$^{-1}$. In the CVs, the redox peaks at 4 V, which are connected with the Mn$^{3+}$/Mn$^{4+}$ couple, are only present in LNMO-MF and LNMO-NF. All electrodes show increased separation potential within the redox couple, decreasing in the order LNMO-MP > LNMO-NF > LNMO-MF ≈ LNMO-NP, as the potential scanning rate ($v$) increases. This result indicates a larger polarization of LNMO-MP and LNMO-NF as compared to LNMO-MF and LNMO-NP, consistent with the analysis in Fig. 4(b). Assuming that the intercalation reaction is controlled by the solid-state diffusion of lithium ions, the dependence of $i_p$ on $v^{1/2}$ can be employed to determine the diffusion coefficient of Li$^+$ ($D_{Li}$) on the basis of the following equation:

$$i_p = 2.69 \times 10^5 n^{3/2}D_{Li}^{1/2}v^{1/2}C_{Li}^0$$

(1)

where $n$ is the number of electrons per reaction species and $C_{Li}^0$ is the bulk concentration of Li$^+$ in the electrode (given as 0.02378 mol·cm$^{-3}$ from the theoretical density of spinel) [S1, S2]. A good linear relationship between $i_p$ and $v^{1/2}$ is observed for the investigated LNMO samples (Fig. S3) and $D_{Li}$ values are calculated to be $8.8 \times 10^{-12}$, $1.1 \times 10^{-10}$, $2.0 \times 10^{-11}$, and $9.1 \times 10^{-11}$ cm$^2$·s$^{-1}$, respectively. The $D_{Li}$ values determined for the four samples are consistent with their rate capabilities.
Figure S3 Plots of the peak (as indicated in Fig. S2) current density versus the square root of the potential scan rate derived from the CVs of (a) LNMO-MP, (b) LNMO-MF, (c) LNMO-NP, and (d) LNMO-NF.

Figure S4 Cycling performance of the prepared LNMO-MP, LNMO-MF, LNMO-NP, and LNMO-NF at discharge rates of (a) 5 C and (b) 20 C. The charge current was kept constant at 1 C rate.

References

[S1] Yang, T. Y.; Zhang, N. Q.; Lang, Y.; Sun, K. N. Enhanced rate performance of carbon-coated LiNi_{0.5}Mn_{1.5}O_{4} cathode material for lithium ion batteries. *Electrochim. Acta* 2011, 56, 4058–4064.