

Liquid-phase Synthesis of Uniformly Nano-sized LiMnPO_4 Particles and Their
Electrochemical Properties for Lithium-ion Batteries

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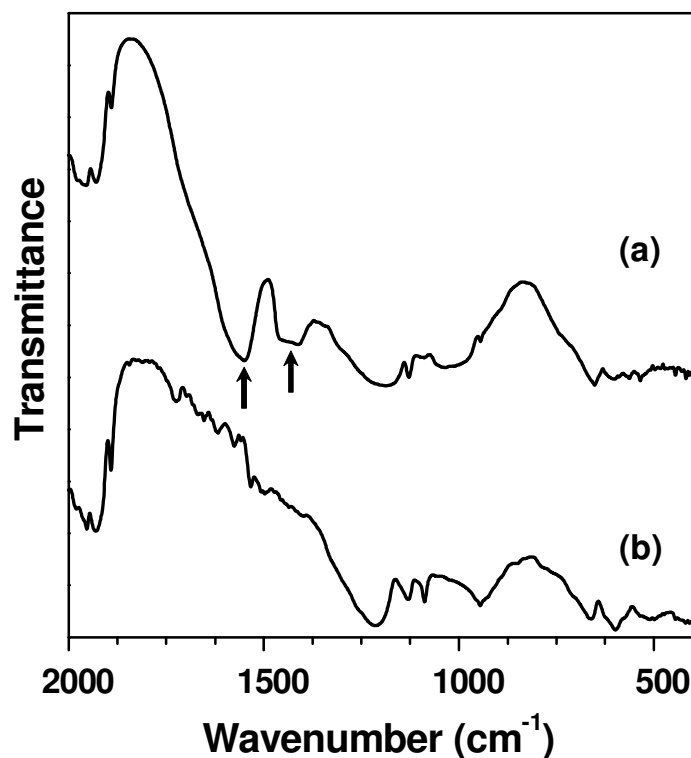


Fig. 1S. FT-IR spectra of (a) LiMnPO₄ particles prepared at 280 °C and (b) LiMnPO₄ powder prepared by a conventional solid-phase synthesis.

The LiMnPO₄ powder was prepared by a conventional solid-phase synthesis as follows: a mixture of lithium carbonate (98 %), dimanganese trioxide (99.9 %) and diphosphorus pentaoxide (98 %) in a Li/Mn/P ratio of 1/1/1 was fired at 500 °C for 15 h in air. The resultant powder was ground and sintered at 800 °C for 36 h in air. The particle size of the LiMnPO₄ powder was ca. 30 μm. FT-IR spectra of the particles were obtained by accumulating 200 iterations with a resolution of 4 cm⁻¹ using a spectrometer (FT-IR, FT/IR-680plus, Jasco). The nano-sized LiMnPO₄ particles gave a spectrum very similar to that of the LiMnPO₄ powder, except for two peaks at around 1450 and 1550 cm⁻¹. Based on the literature, these two bands were identified as symmetric and antisymmetric stretching bands of a carboxyl group, respectively.¹⁷ The gap between these two bands was about 100 cm⁻¹, indicating that oleic acid was attached to the LiMnPO₄ particles.

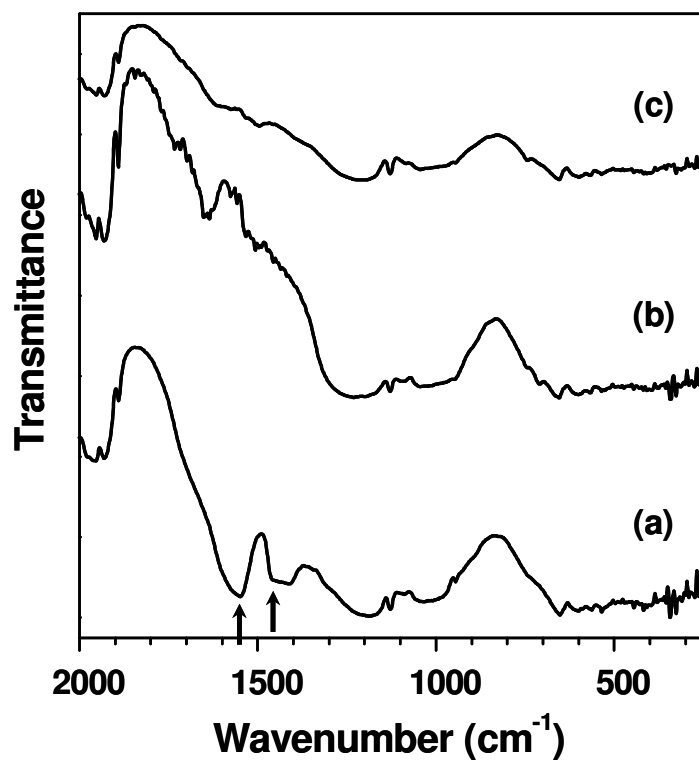


Fig. 2S. FT-IR spectra of LiMnPO_4 particles (a) before and after heat treatment in (b) O_2 or (c) Ar at 500 $^{\circ}\text{C}$ for 1 h.

The peaks at around 1450 and 1550 cm^{-1} , which are assigned to carboxyl groups of oleic acid, disappeared with heat treatment at 500 $^{\circ}\text{C}$ for 1h in Ar and O_2 ; a peak at around 1650 cm^{-1} was observed after heat treatment in O_2 , likely due to Li_3PO_4 . Thus, oleic acid molecules attached to LiMnPO_4 particles could be removed by heat treatment.

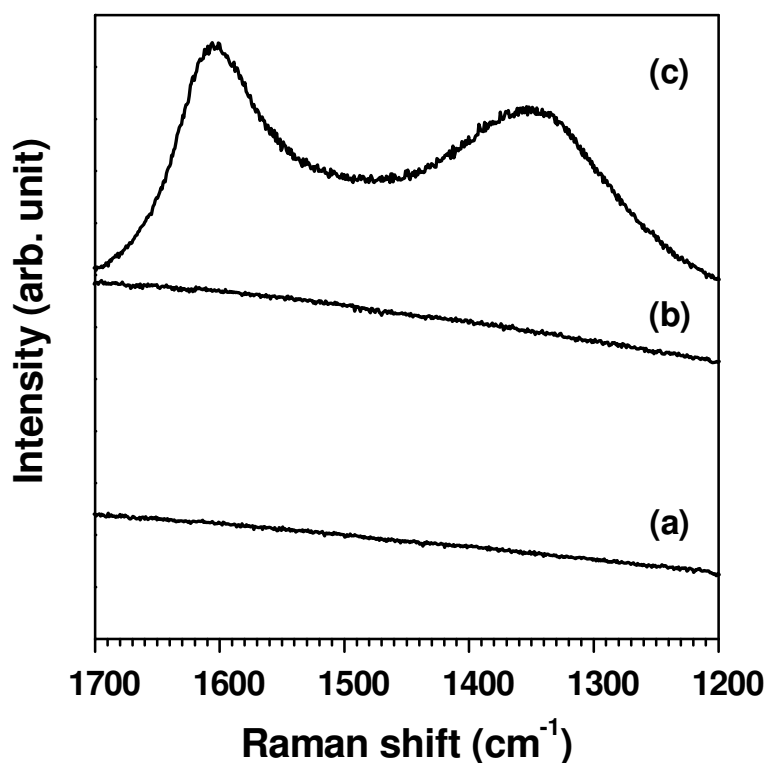


Fig. 3S. Raman spectra of LiMnPO₄ particles (a) before and after heat treatment in (b) O₂ or (c) Ar at 500 °C for 1 h.

Raman spectra were excited using the 514.5 nm line (100mW) of an argon ion laser for 60 s, and the scattered light was collected in a quasi-backscattering geometry (NRS-2100, Jasco). Two broad peaks appeared at around 1360 and 1600 cm⁻¹ after heat treatment in Ar (Fig. S3c), while no peak was observed after heat treatment in O₂ (Fig. S3b). These results indicate that carbonaceous materials with low crystallinity were formed from oleic acid by heat treatment in Ar.