Electronic Supplementary Information for

Bimolecular inducing hierarchical nanoporous LiTi₂(PO₄)₃/C with superior high-rate and cycling performance

Wenwei Sun^a, Jiehua Liu^a*, Xiaoqian Liu^a, Xiaojing Fan^a, Kuan Zhou^a and

Xiangfeng Wei^{a,b}

^a Future Energy Laboratory, School of Materials Science and Engineering, Hefei
^b University of Technology, No.193 Tunxi Road, Hefei, Anhui 230009, China
^b School of Chemistry and Chemical Engineering, Hefei University of Technology, No.193 Tunxi Road, Hefei, Anhui 230009, China
Email: <u>liujh@hfut.edu.cn</u>

Experimental section

Synthesis of LTP based samples

In a typical route, 0.44 g lithium hydroxide monohydrate and 3.51 g phosphoric acid (85 wt%) was added in 5 mL 20 wt% glucose with the aid of ultrasound to obtain a transparent solution. 6.95 g tetrabutyl titanate was first dissolved into 4 ml 2-dimethylaminoethanolamine (DMEA). The above two solutions were fast mixed and transferred into a 20 ml Teflon lining of the autoclave. The autoclave was sealed and then heated at 160 °C for 10 h. After reaction, the obtained power was annealed at 800 °C 10 h with N₂, named LTP/C-1 and LTP-2 was obtained without carbon source added. In order to deeply investigate the effect of the glucose, we anneal the LTP/C-1 at 600 °C 3h to remove the coating carbon of LTP/C-1 named LTP-3. For comparison, LTP/C-4 and LTP/C-5 were obtained as comparative materials when hydrothermal temperature at 180 °C or annealing at 700 °C.

Material Characterization

All X-ray diffraction (XRD) data were examined by the X-ray diffraction (XRD) analysis system (D/MAX 2500V, Rigaku) equipped with a Cu-K α Radiation source(λ =1.54056 Å). The particle size and morphology of the LTP composite was investigated by using scanning electron microscopy(SEM) and the transmission electron microscopy (TEM) were obtained with JEOL JEM-1400 and JEOL 2100F. N₂ adsorption-desorption isotherms were conducted at 77 K on a Micromeritics Tristar 3000 analyzer. The BET surface areas and pore-size distribution curves were concluded using adsorption data. X-ray photoelectron spectroscopic (XPS)

measurements were carried out by using a mono-chromated Al Ka (1486.7 eV) X-ray source at power of 150 W (15 kV×10 mA).

Electrochemical measurements

Electrochemical tests were using coin cells (CR2032) with 1 mol/L LiPF₆ in EC/DMC (1:1 by volume) as electrolyte and lithium foil as counter and reference electrodes. Active material, Super P and PVDF binder in the NMP solution with a weight ratio of 80:10:10. The slurry was painted on aluminum foils fabricating the cathode through dried at 80 °C for 10 h. All cells were assembled in the Ar-filling glove box. Cyclic voltammograms (CV, 2.0–3.5 V) curves were measured at a scanning speed of 0.2 mV s⁻¹ by CHI electrochemical workstation (CHI 760D). For galvanostatic intermittent titration technique (GITT) analysis, the cells were cycled in the potential window of 2.0-3.5 V at a rate of 0.2C. The duration time for LTP/C-1 and LTP-2 was 10 min and 30 min respectively, and the rest time was 5 h. The EIS measurements were performed with a 5 mV voltage amplitude over a frequency range of 0.1 Hz to 100 KHz. Galvanostatic charge/discharge cycling was conducted using a battery tester (NEWAER) at different current rates of 0.2C to 20C, where 1C= 138 mA g⁻¹.



Fig. S1. High-resolution FESEM images of (a) LTP/C-1 and (b) LTP-2.



Fig. S2. (a) XPS full spectrum of the LTP/C-1; (b) $Ti2p_{3/2}$ spectrum of LTP-2.



Fig. S3. The N_2 adsorption-desorption isotherm of LTP-2.



Fig. S4. The GITT curves and Li⁺ diffusion coefficient distribution of (a) LTP/C-1 and (b) LTP-2 at 0.2C.



Fig. S5. XRD patterns of (a) LTP/C-4 and (b) LTP/C-5.



Fig. S6. CV curves of (a) LTP/C-4 and (b) LTP/C-5 at a scan rate of 0.2 mV s⁻¹.



Fig. S7. Cycling performance of (a) LTP/C-4 and (b) LTP/C-5 at a chargedischarge rate of 1C.



Fig. S8. The EIS plots of (a) LTP/C-1 and (b) LTP/C-3.