Electronic Supporting Information

$LiNi_{0.5}Mn_{1.5}O_4$ Microcubes Cathode Materials with Improved Discharge/Charge Performances for Lithium-Ion Batteries

Yanli Fu,[1,2] Liqiong Wu,[1] Shengang Xu,[2] Shaokui Cao,[2] and Xinheng Li[1,]*

[1] The State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Suzhou 215123, China.

[2] College of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

Corresponding Author Email: Xinhengli@licp.cas.cn

Materials and Methods

Synthesis of spinel $LiNi_{0.5}Mn_{1.5}O_4$ mesoporous microcubes

First, MnC_2O_4 precursors were prepared by a micro-emulsion method. Detailed procedures are as follows.1.0 g of cetyltrimethyl ammonium bromide as a surfactant was dissolved in 50 ml of distilled water to form a transparent solution. To the solution, 2.5 mL of 0.2 M $Mn(CH_3COO)_2$ aqueous solution was added. After vigorous stirring for 30 min. at room temperature, 2.5 mL of 0.4 M oxalic acid aqueous solution was added. And the mixed solution was vigorously stirred for 30min. And then, the solution was transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at a temperature of 120℃for 12 hrs and finally cooled to room temperature. The obtained products were centrifuged, washed with ethanol, and dried. Last, the as-obtained products were calcined at 500℃for 10 hrs to turn into Mn_2O_3.To obtain spinel $LiNi_{0.5}Mn_{1.5}O4$, an impregnation method was employed herein. Specifically, Mn_2O_3, $LiCH_3COO•2H_2O$, $Ni(CH_3COO)_2•4H_2O$ with stoichiometric ratio of 1.5:1.0:0.5 were dispersed in 3 mL of ethanol and the mixed solution allowed to evaporate to remove solvent. The remained solid underwent vacuum-drying overnight, and then calcined at 700℃for 6 hrs in air. For comparison, synthesis of spinel $LiNi_{0.5}Mn_{1.5}O_4$ nanowires was conducted following a previous procedure [1].

Structural characterizations

XRD spectra were taken on Bruker D8 ADVANCE powder X-ray diffraction spectrometer with Cu Kα radiation. SEM images were captured by Hitachi S4800 field-emission scanning electron microscopy. Energy dispersive spectra were taken on Quanta FEG 250 environmental scanning electron microscope. TEM images were taken on Tecnai G2 F20 S-TWIN transmission electron microscopy. Surface area analysis was carried out by measuring the N_2 adsorption-desorption isotherms at 77 K on a BELSORP-mini BET measurement instrument. TG/DSC data were recorded on Mettler TGA analyzer. FTIR spectra of the samples were taken on a Nicolet 6700 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Escalab 250 Xi spectrometer.

2.4Electrochemical measurements and mechanical tests

Electrochemical tests were conducted using CR2032 coin-type cell and lithium metal as a counter electrode. The cathodes were fabricated by mixing 80% as-prepared LNMO samples, 10% acetylene black, and 10% polyvinylidene fluoride (PVDF) in N-methy-2-pyrrolidone to form a homogeneous slurry. The obtained slurry was coated onto aluminum foil and dried at 70℃for 8 hrs in an oven and at 120℃for 12hrs in vacuum. The dried electrode were treated with 20 MPa load pressure with a mass loading about 1.7 mg/cm^2. The electrolyte used was 1.0 M LiPF6 dissolved in a mixed solution of ethylene carbonate/dimethyl carbonate (EC/DMC, in 1:1 volume ratio). The separator used was a microporous Celgard 2325 membrane. They were all assembled into coin cells in an argon-filled glove box. The cyclic voltammograms (CVs) were carried out at room temperature on PGSTAT101Autolab workstation. The assembled cells were cycled between 3.5–4.95 V at different rates on LAND-CT2001A battery-testing instrument. Mechanical tests were carried out in Agilent UTM150 Nano-stretching tester.

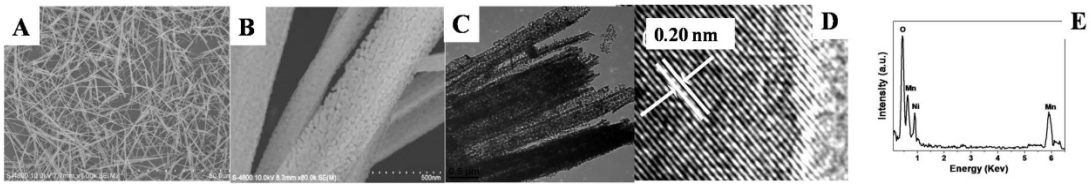

Fig. S1 SEM images (A, B), TEM and HRTEM images (C, D) of the $LiNi_{0.5}Mn_{1.5}O_4$ nanowires. E is EDS spectra of the $LiNi_{0.5}Mn_{1.5}O_4$ nanowires.

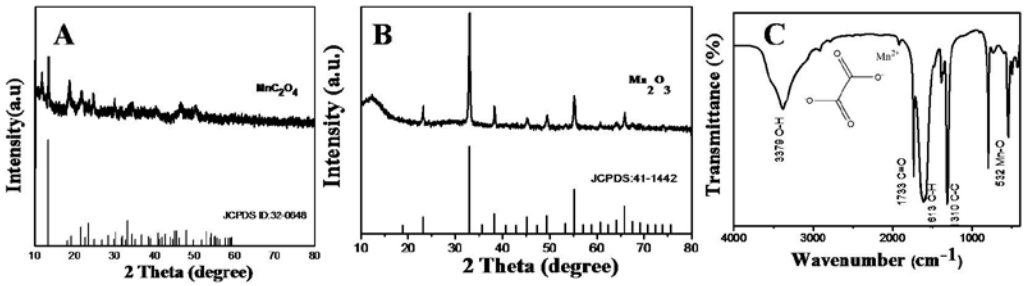

Fig. S2 XRD of MnC_2O_4 (A) and Mn_2O_3 (B), and FTIR spectra of MnC_2O_4.

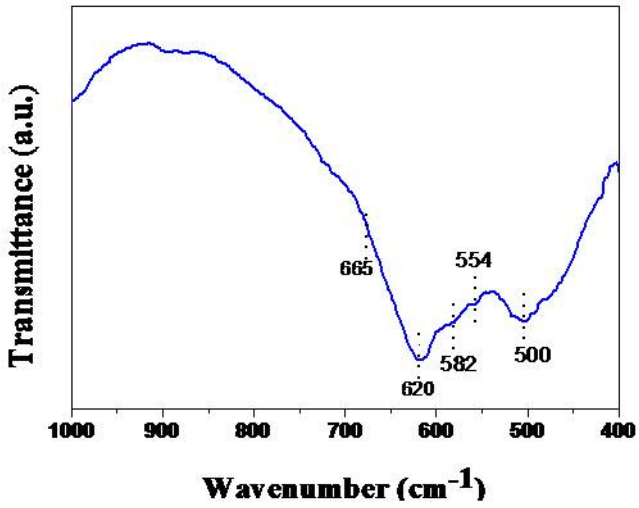

Fig. S3 FTIR spectra of $LiNi_{0.5}Mn_{1.5}O_4$ microcubes, showing a Fd-3m phase.

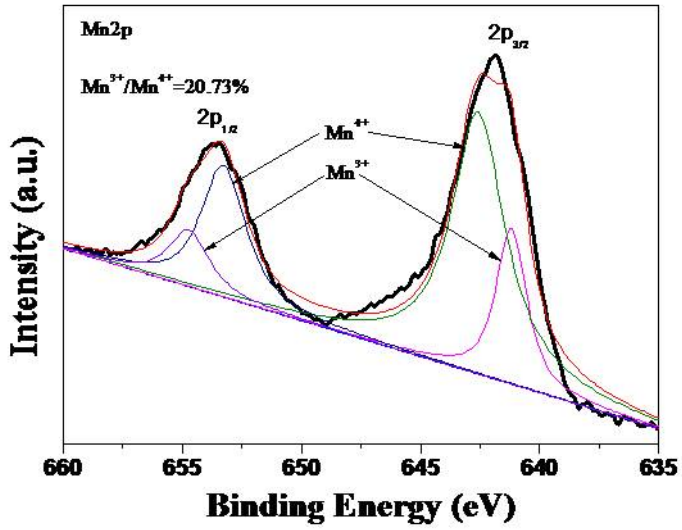

Fig. S4 XPS spectra of $LiNi_{0.5}Mn_{1.5}O_4$microcubes by deconvolution, indicating the existence of Mn^{3+}.

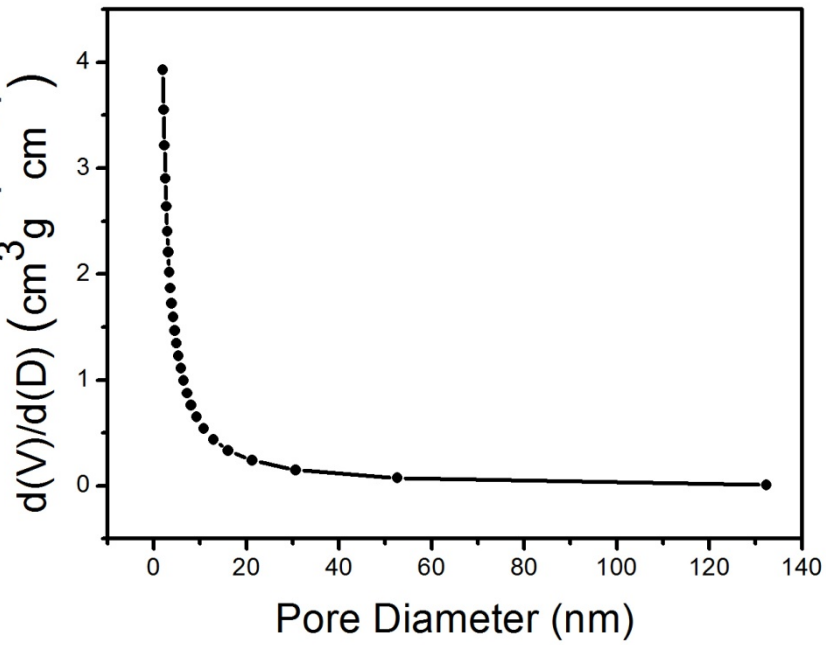

Fig. S5 The pore size distribution of the $LiNi_{0.5}Mn_{1.5}O_4$ microcubes.

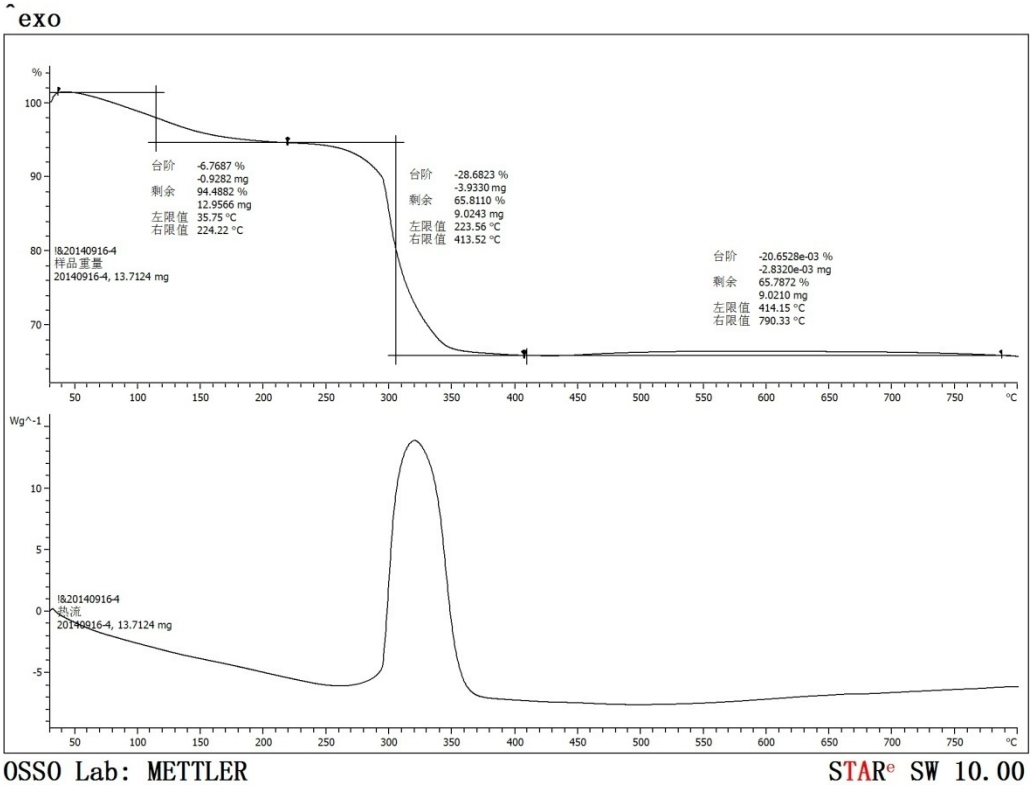

Fig. S6 TG and DSC spectra of the $LiNi_{0.5}Mn_{1.5}O_4$ nanowires, showing decomposition at ca. 305°C.

References

[1] Zhang, X.; Cheng, F.; Yang, J.; Chen, J. $LiNi_{0.5}Mn_{1.5}O_4$ porous nanorods as high rate and long-life cathode for Li-ion batteries. *Nano Lett.* **2013**, *13*, 2822-2825.