Electronic Supporting Information (ESI)

Impact of lithium excess on the structural and electrochemical properties of $LiNi_{0.5}Mn_{1.5}O_4$ high-voltage cathode material

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Experimental Section

The co-precipitation method is widely used to synthesize binary or ternary electrode materials, including $LiNi_{0.5}Mn_{1.5}O_4$. During a typical co-precipitation preparation, Ni and Mn ions are first precipitated by oxalate or carbonate in aqueous solution, the resulting Ni-Mn precursor would be mixed with lithium sources, followed by final calcination. However, ammonia as a complexing agent usually impedes the completely deposition of Ni^{2+} and in turn causes severe Ni-deficit in the final product.[1] In this work, a one-step nonaqueous co-precipitation method was applied to precipitate all the three metal ions (Li^+, Ni^{2+} and Mn^{2+}) at the same time. $LiCH_3COO$, $Mn(CH_3COO)_2$ and $Ni(CH_3COO)_2$ were dissolved in ethanol to prepare a mixed-metal ions solution, then added this solution slowly into an ethanol solution containing required amount of $C_2H_2O_4$. Then the precipitate products were dried overnight at 80 °C. The final spinel materials were obtained by firing the Li-Ni-Mn oxalate precursors at 850 °C for 15h with a heating rate of 3 °C min^{-1} and cooled to 650 °C at a cooling rate of 0.5°C min^{-1}. As shown in Fig. S1, the prepared materials with the designed stoichiometric composition of $Li_{1+x}Ni_{0.5-x}Mn_{1.5}O_4$ (x=0, 0.01, 0.03, 0.05) display high crystallinity and uniform grain size with kinetic preeminent (111) surface facets. The chemical formula ($Li_{1+x}Ni_{0.5-x}Mn_{1.5}O_4$) is nominal. As we know, the amount of lithium is difficult to be measured accurately and lithium could be volatilized at high temperature during solid reaction process. It must be said, though, that what we focus on is the effect of lithium amount on the crystal structure rather than itself.

Characterization and measurements

The crystal structure of the samples was characterised by X-ray diffraction with Cu Kα radiation. The Mn 2p core binding energy of the materials was characterized by X-ray photoelectron spectroscopy (XPS). Raman spectra were recorded with a labRAM HR800. The morphology was observed by a scanning electron microscope (SEM) and transmission electron microscopy (TEM) (Tecnai G2 F30 S-TWIN instrument). The particle size distribution was characterized by a laser particle size analyzer.

Electrochemical tests were performed in CR2032 cells with lithium metal counter electrodes. Cathode slurries were prepared by dispersing the active material, super P conductive carbon, and polyvinylidene difluoride (PVDF) with a w. t. ratio of 85:10:5 in N-methyl pyrrolidone (NMP) solvent. This slurry was then cast onto an aluminum foil and dried overnight under vacuum at 120 °C. The resulting electrode was then punched into disks with an area of 1.13 cm^2. The active material loaded for the individual cell was around 2.7 $mg \cdot cm^{-2}$. Electrolyte solution for high voltage system (~5.0V vs. Li/Li^+) was used, the main composition of the electrolyte is 1.1M $LiPF_6$ in ethylene carbonate (EC)-dimethyl carbonate (DEC) mixture (3:7 ratio by volume) with 1.0 wt. % high voltage additive (Shenzhen CAPCHEM Technology Co. Ltd, China). The coin cells were then assembled under Ar/H_2 (95/5 vol. %) atmosphere in glove box (H_2O, $O_2 \leq 5$ ppm). The galvanostatic charge and discharge cycle tests were carried out at 25±0.5 ºC between 3.5 V and 5.0 V using a battery tester (LAND CT2001A, China). The batteries were charged at 0.1C, and then discharged at various rates. The electrochemical impedance spectroscopy (EIS) was examined by applying an AC voltage of 5 mV.

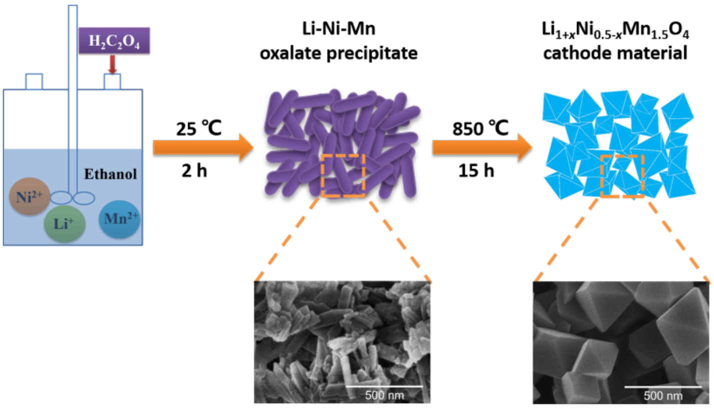

Fig. S1 Schematic drawing of synthesis process by nonaqueous co-precipitation method using oxalate as precipitant.

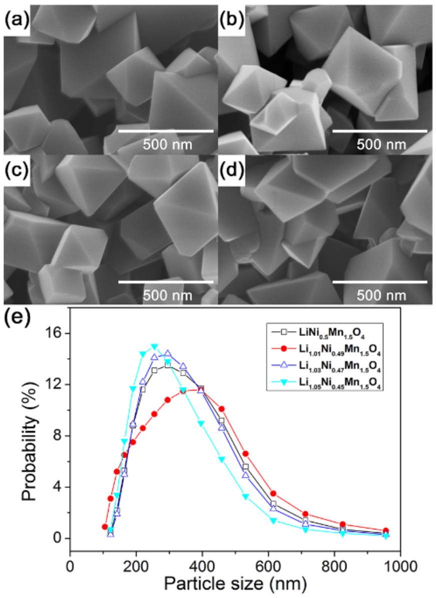

Fig. S2 SEM images of (a) $LiNi_{0.5}Mn_{1.5}O_4$, (b) $Li_{1.01}Ni_{0.49}Mn_{1.5}O_4$, (c) $Li_{1.03}Ni_{0.47}Mn_{1.5}O_4$ and (d) $Li_{1.05}Ni_{0.45}Mn_{1.5}O_4$; (e) distribution of particles size of $Li_{1+x}Ni_{0.5-x}Mn_{1.5}O_4$ samples.

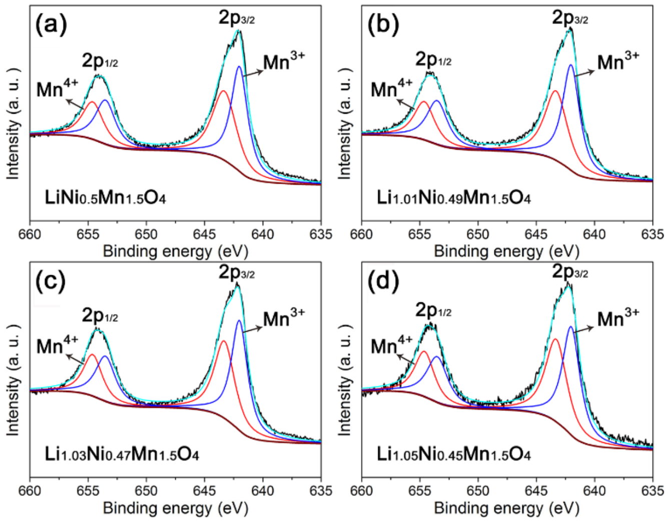

Fig. S3 X-ray photoelectron spectroscopy collected at Mn2p regions of $Li_{1+x}Ni_{0.5-x}Mn_{1.5}O_4$ samples.

Reference

1. Z. Zhu, D. Zhang, H. Yan, W. Li and Qilu, *J Mater Chem A*, 2013, **1**, 5492-5496.