Supporting Information

Synthesis and electrochemical properties of $Li_{1.3}Nb_{0.3}Cr_{0.4}O_2$ as a high-capacity cathode material for rechargeable Lithium batteries

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1 Experimental Section

1.1 Material synthesis

To synthesis $Li_{1,3}Nb_{0,3}Cr_{0,4}O_2$, a mixture of Li_3NbO_4 and $LiCrO_2$ was used as starting materials. A 0.81 g sample of Li_3NbO_4 and 1.19 g of $LiCrO_2$ were first manually mixed inside an argon-filled glove box, using a mortar and pestle. The mixture was then milled under argon atmosphere with a ball-to-powder mass ratio of 15:1 using a SFM-3 high speed vibrating ball mill (1200 r min⁻¹; MTI corp.). The milling time was varied from 2 to 8 h. Li_3NbO_4 was prepared by a conventional solid-state reaction from Li_2CO_3 (99%; Alfa Aesar) and Nb₂O₅ (99.9%; Alfa Aesar) at 950 °C for 24 h in air. $LiCrO_2$ was synthesized from Li_2CO_3 (99%; Alfa Aesar) and Cr_2O_3 (99.9%; Alfa Aesar) at 900 °C for 12 h in argon atmosphere. 10 wt% excess (rather than stoichiometric amount) Li_2CO_3 was used to compensate for possible loss of Li_2O during sintering. The prepared samples were stored in an argon-filled glove box until use.

1.2 Electrochemical measurement

The electrode performance of the samples was examined for as-prepared samples and the samples prepared by ball milling. All the samples (70 wt%) were mixed using a mortar and pestle with 20 wt% carbon black (Alfa Aesar, acetylene black) and 10 wt% polytetrafluoroethylene (PTFE, Sigma-Aldrich) and pasted on aluminum mesh (MTI corp.) as a current collector inside an argon-filled glove box. Li metal foil (China Energy Lithium Co., Ltd) was used as a negative electrode. The electrolyte was 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 vol, battery grade; Shanghai Songjing Amperex Technology Co., Ltd). A polypropylene microporous membrane (Celgard 2400) was used as a separator. CR2032-type coin cells were assembled in an argon-filled glove box with H₂O and O₂ content below 1.0 ppm. Galvanostatic discharge-charge behavior of coin cells was carried out on a Land CT2001 multichannel battery tester between the voltage ranges of 1.0 - 4.8 V at a rate of 10 mA·g⁻¹ in ambient temperature.

1.3 Material characterization

Powder X-ray diffraction (XRD) patterns were collected on an X-ray diffractometer (Bruker D8 Advance, Germany) with Cu-K α radiation ($\lambda = 0.1540$ nm) at 40 kV, 40 mA. Data were obtained over the 2θ range of 10 - 80° for as-prepared materials and electrodes with a scan rate of 1° min⁻¹.

Scanning electron microscope (SEM) images and Energy dispersive X-ray spectroscope (EDX) were captured using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) operated at an acceleration voltage of 10 kV.

Transmission electron microscopy (TEM) images were obtained by using a field emission transmission electron microscope (Tecnai G2 F20 S-Twin) with an acceleration voltage of 300 kV. A bright-field scanning TEM (STEM) image as well as EDX spectra were acquired in STEM mode.

Cr and Nb-K edge X-ray absorption spectra (XAS) of pristine and cycled samples were performed at beamline 8-ID of National Synchrotron Light Sources II (NSLSII-Brookhaven National Laboratory (BNL)). All the XAS spectra were collected in transmission mode at ambient temperature. Analysis of the XAS data was performed by using Athena software package.



Fig. S1. Galvanostatic charge/discharge profiles of $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ in Li batteries at a rate of 10 mA g⁻¹ in the voltage ranges of 1.0 - 4.8 V at room temperature. Data of Li_3NbO_4 and $LiCrO_2$ are also shown for comparison.



Fig. S2. XRD patterns of the binary system of xLi_3NbO_4 - $(1-x)LiMe^{3+}O_2$ (x = 0.43; Me³⁺ = Cr³⁺/Mn³⁺) prepared by the conventional calcination.^{1, 2} Li₂CO₃, Nb₂O₅, Cr₂O₃, and Mn₂O₃ were used as starting materials, and calcined at 950 °C for 24 h in Ar. Based on a binary system for xLi_3NbO_4 - $(1-x)LiMnO_2$ (x = 0.43), a single phase can be obtained as Li_{1.3}Nb_{0.3}Mn_{0.4}O₂. However, if chromium ions (Cr³⁺) are substituted for Li⁺ and Nb⁵⁺ ions in Li₃NbO₄ based on a binary system for xLi_3NbO_4 - $(1-x)LiCrO_2$ (x = 0.43), phase segregation into LiCrO₂ and Li₃NbO₄ is obvious.



Fig. S3. EDX spectra of the as-prapared $Li_{1.3}Nb_{0.3}Cr_{0.4}O_2$ samples.

Element	0	Nb	Cr
Weight percentage (%)	49.19	29.46	21.35
Atomic percentage (%)	80.86	8.34	10.80
Atom ratio		Nb : $Cr = 3 : 3.89$	

Table S1. Chemical analysis of the as-prapared $Li_{1.3}Nb_{0.3}Cr_{0.4}O_2$ samples obtained from EDX spectra of Fig. S3.



Fig. S4. XAS spectra at the Cr K-edges of the $Li_{1.3}Nb_{0.3}Cr_{0.4}O_2$ samples at different charge/discharge states with CrO_x as reference.

References

1. N. Yabuuchi, M. Takeuchi, S. Komaba, S. Ichikawa, T. Ozaki and T. Inamasu, *Chem. Commun.*, 2016, **52**, 2051-2054.

2. N. Yabuuchi, M. Takeuchi, M. Nakayama, H. Shiiba, M. Ogawa, K. Nakayama, T. Ohta, D. Endo,

T. Ozaki, T. Inamasu, K. Sato and S. Komaba, *Proceedings of the National Academy of Sciences*, 2015, **112**, 7650-7655.