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
Weiwen Wang, a Jingke Meng, b Xinyang Yue, b Qinchao Wang, b Xinxin Wang, b Yongning Zhou, b Zhengwen Fu*a and Zulipiya Shadike*c

a Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, 220 Handan Road, Shanghai 200433, P. R. China
b Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, P. R. China.
c Chemistry Division, Brookhaven National Laboratory, Upton, New York, 11973, USA.
* Corresponding author.
E-mail addresses: zwfu@fudan.edu.cn, zshadike@bnl.gov
1 Experimental Section

1.1 Material synthesis

To synthesis Li$_{1.3}$Nb$_{0.3}$Cr$_{0.4}$O$_2$, a mixture of Li$_3$NbO$_4$ and LiCrO$_2$ was used as starting materials. A 0.81 g sample of Li$_3$NbO$_4$ 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$_3$NbO$_4$ was prepared by a conventional solid-state reaction from Li$_2$CO$_3$ (99%; Alfa Aesar) and Nb$_2$O$_5$ (99.9%; Alfa Aesar) at 950 °C for 24 h in air. LiCrO$_2$ was synthesized from Li$_2$CO$_3$ (99%; Alfa Aesar) and Cr$_2$O$_3$ (99.9%; Alfa Aesar) at 900 °C for 12 h in argon atmosphere. 10 wt% excess (rather than stoichiometric amount) Li$_2$CO$_3$ was used to compensate for possible loss of Li$_2$O 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 LiPF$_6$ 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 H$_2$O and O$_2$ 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$\alpha$ radiation ($\lambda = 0.1540$ nm) at 40 kV, 40 mA. Data were obtained over the $2\theta$ 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 spectrocope (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$_3$NbO$_4$ and LiCrO$_2$ are also shown for comparison.
Fig. S2. XRD patterns of the binary system of $x\text{Li}_3\text{NbO}_4-(1-x)\text{LiMe}_3\text{O}_2$ ($x = 0.43$; $\text{Me}^{3+} = \text{Cr}^{3+}/\text{Mn}^{3+}$) prepared by the conventional calcination.\textsuperscript{1,2} $\text{Li}_2\text{CO}_3$, $\text{Nb}_2\text{O}_5$, $\text{Cr}_2\text{O}_3$, and $\text{Mn}_2\text{O}_3$ were used as starting materials, and calcined at 950 °C for 24 h in Ar. Based on a binary system for $x\text{Li}_3\text{NbO}_4-(1-x)\text{LiMnO}_2$ ($x = 0.43$), a single phase can be obtained as $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$. However, if chromium ions ($\text{Cr}^{3+}$) are substituted for $\text{Li}^+$ and $\text{Nb}^{5+}$ ions in $\text{Li}_3\text{NbO}_4$ based on a binary system for $x\text{Li}_3\text{NbO}_4-(1-x)\text{LiCrO}_2$ ($x = 0.43$), phase segregation into $\text{LiCrO}_2$ and $\text{Li}_3\text{NbO}_4$ is obvious.
Fig. S3. EDX spectra of the as-prepared Li$_{1.3}$Nb$_{0.3}$Cr$_{0.4}$O$_2$ samples.
Table S1. Chemical analysis of the as-prepared Li$_{1.3}$Nb$_{0.3}$Cr$_{0.4}$O$_2$ samples obtained from EDX spectra of Fig. S3.

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Nb</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percentage (%)</td>
<td>49.19</td>
<td>29.46</td>
<td>21.35</td>
</tr>
<tr>
<td>Atomic percentage (%)</td>
<td>80.86</td>
<td>8.34</td>
<td>10.80</td>
</tr>
<tr>
<td>Atom ratio</td>
<td>Nb : Cr = 3 : 3.89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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