Supporting Information

A New Layered Sodium Molybdenum Oxide Anode for Full Intercalation-Type Sodium-Ion Batteries

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Experimental

Synthesis

Layered Na$_{0.3}$MoO$_2$ sample was synthesized by a one-step solid-state reaction. A proportionable mixture of reagent grade Na$_2$CO$_3$ (20% excess) and MoO$_2$ was ball-milled under wet condition with alcohol additions for 20 h at 200 rpm. After drying at 80 °C for 12 h, the obtained powder was pressed into pellets. Finally, the pellets were heated at 750 °C for 15 h under an Ar atmosphere. The obtained material was stored in an argon-filled glove box.

Layered Na$_{0.8}$Ni$_{0.4}$Ti$_{0.6}$O$_2$ is prepared as our previous report. The precursors of Na$_2$CO$_3$, NiO and TiO$_2$ were also ball-milled under wet condition with alcohol additions for 20 h at 200 rpm. After drying 80 °C for 12 h, the mixture was pressed into pellets and heated at 900 °C for 20 h under an Ar flow. The as-prepared materials was also stored in an argon-filled glove box.

Characterization

The crystalline structure and ex-situ XRD was characterized by Bruker D8 Advance Diffractometer using Cu Ka radiation. The morphology of as-prepared materials was observed using scanning electron microscopy (SEM, TOPCON DS-720 instrument). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were performed on a FEI Tacnai G2 electron microscope equipped with an X-ray energy dispersive spectroscopy (EDS, BRUKER AXS).

Electrochemical test

The electrochemical experiments were performed using 2032-type coin cells, with sodium metal served as the counter electrode, which were assembled in an argon-filled glove box. The working electrode was prepared by mixing 70 wt% of active material, 20 wt% of carbon black conductive additive and 10 wt% of polyvinylidenefluoride (PVDF) binder onto aluminium foil. Mass loading of the electrode is about 2.5~3 mg/cm$^2$. The working and counter electrodes were separated by glass fiber membrane. The electrolyte was 1 M NaPF$_6$ in ethylene carbonate–diethyl carbonate (EC/DEC, 1 : 1 (v/v)). Galvonostatic charge – discharge was performed on a Hokuto Denko HJ1001SD8 battery tester in the voltage window of 0.05 – 2.0 V. Cyclic voltammetry (CV) was performed on Solartron 1640. For the full cell, the pre-desodiation of Na$_{0.8}$Ni$_{0.4}$Ti$_{0.6}$O$_2$ and pre-sodiation of Na$_{0.8}$MoO$_2$ were performed to carry out the three cycles’ activation. Na$_{0.8}$Ni$_{0.4}$Ti$_{0.6}$O$_2$ /Na half cells were cycled in...
the voltage range of 1.5-4 V at current density of 20 mA/g to get the pre-desodiation of Na$_{0.8}$Ni$_{0.4}$Ti$_{0.6}$O$_2$. And Na$_{0.3}$MoO$_2$/Na half cells were cycled in the voltage range of 0.05-2 V at current density of 20 mA/g to get pre-sodiation of Na$_{0.3}$MoO$_2$. The electrode mass ration of cathode and anode is around 1.2. The full cell is cathode limited and cycled in the voltage of 0.6-3.6 V.

Table S1 The sodium storage properties for reported titanium-based materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Current density</th>
<th>Voltage range</th>
<th>Capacity</th>
<th>Cycle number</th>
<th>Capacity retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$Ti$<em>6$O$</em>{13}$</td>
<td>5 mA/g</td>
<td>0-2.5 V</td>
<td>200 mAh/g</td>
<td>30</td>
<td>40%</td>
</tr>
<tr>
<td>Na$_2$Ti$_3$O$_7$</td>
<td>17.7 mA/g</td>
<td>0.01-2.5 V</td>
<td>135 mAh/g</td>
<td>25</td>
<td>50%</td>
</tr>
<tr>
<td>Na$_2$Ti$<em>3$O$</em>{13}$</td>
<td>12.5 mA/g</td>
<td>0.1-2.5 V</td>
<td>70 mAh/g</td>
<td>50</td>
<td>80%</td>
</tr>
<tr>
<td>Na$<em>{2/3}$Co$</em>{1/3}$Ti$_{2/3}$O$_2$</td>
<td>20 mA/g</td>
<td>0.15-2.5 V</td>
<td>90 mAh/g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$<em>{2/3}$Ni$</em>{1/3}$Ti$_{2/3}$O$_2$</td>
<td>22.5 mA/g</td>
<td>0.2-2 V</td>
<td>75 mAh/g</td>
<td>22</td>
<td>60%</td>
</tr>
<tr>
<td>Na$_{0.3}$MoO$_2$</td>
<td>20 mA/g</td>
<td>0.05-2 V</td>
<td>140 mAh/g</td>
<td>50</td>
<td>85%</td>
</tr>
</tbody>
</table>

Figure S1 The dQ/dV curves of the Na$_{0.3}$MoO$_2$ at current density of 20 mA/g.
Figure S2 Discharge-charge curves of the Na$_{0.3}$MoO$_2$ for the first cycle at current density of 20 mA/g.

Figure S3 Standard XRD pattern of Na$_{0.3}$MoO$_2$ and ex-situ XRD patterns of Na$_{0.3}$MoO$_2$ after first and 1000th cycles.
Na_{0.3}MoO_2 as anode is a typical intercalation-type material based on following reasons:

1. From dQ/dV curves (as shown in Figure S1), it is clear that the position of the peaks do not change between the 1\textsuperscript{st} and 2\textsuperscript{nd} cycles, while for the alloying or conversion reaction, there are obvious change of the peaks position and peak intensity.\textsuperscript{6-9} It would be characterized by the typical intercalation reaction.\textsuperscript{10-12}

2. The reversible capacity is about 146 mAh/g, corresponding to 0.7 reversible sodium ion (de)intercalation in per Na_{0.3}MoO_2. The amount of sodium ions suggests that the sodium ion insertion into the Na_{0.3}MoO_2 to form NaMoO_2 as the following equation:

   \[
   \text{Na}_{0.3}\text{MoO}_2 + 0.7\text{Na}^+ + 0.7\text{e}^- \rightarrow \text{NaMoO}_2
   \]

For the alloying or conversion reaction, more sodium ions will react with the electrode materials.\textsuperscript{9-12}

3. The ex-situ XRD patterns at different charge depths of the first cycle (as shown in the right of Figure S4) display a shift of peak position during the sodium ion insertion into the anode materials. It is a typical phenomenon for the intercalation-type anode.\textsuperscript{13, 14} Due to the low valence state of Mo is sensitive to the O_2, some impurity such as Na_2Mo_2O_7 are formed during the XRD testing in the air environment.
4. From the ex-situ XRD patterns after the 1\textsuperscript{st} discharge as shown in Figure S5, it shows that peaks of Na$_{0.3+x}$MoO$_2$ are obvious and no peaks belonging to Mo metal or NaMo alloys are detected. It suggests that the Na$_{0.3}$MoO$_2$ is a typical intercalation-type anode.\textsuperscript{15, 16}

![Figure S6 Discharge-charge profiles of the sample at different current densities.](image)

![Figure S7 Linear fitting of I$_p$ vs. $\nu^{1/2}$ relationship of the sample.](image)
Figure S8 Charge-discharge profiles of Na$_{0.8}$Ni$_{0.4}$Ti$_{0.6}$O$_2$ for the first three cycles.

The excellent full cell performance should be attributed to the high efficiency of both cathode and anode. For the cathode side, the charge-discharge profiles of Na$_{0.8}$Ni$_{0.4}$Ti$_{0.6}$O$_2$ for the first three cycles displayed a low efficiency (about 80 %), which is caused by the decomposition of electrolyte at high charge cut-off voltage. In the full cell, the cut-off voltage is 3.6 V, which could much reduce the inefficiency of the cathode. Thus, the full cell could present an excellent cycling performance.

Reference:
2. J. Xu, C. Ma, M. Balasubramanian and Y. S. Meng, *Chemical Communications*, 2014, 50, 12564-12567.