Supplementary Material

Correlation of crystal structure and ion storage behavior of MoO$_3$ electrode materials for aluminum-ion energy storage studied with in-situ X-ray spectroscopies

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Figure S1. The XPS spectra of the MoO₃ materials with various crystal phases after insertion of Al³⁺ ion.

Table S1. As-characterized composition of the MoO₃ electrodes with various crystal phases after insertion of Al³⁺ ion deduced by XPS measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al atomic content %</th>
<th>Mo atomic content %</th>
<th>O atomic content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MoO₃</td>
<td>1.33</td>
<td>19.07</td>
<td>79.59</td>
</tr>
<tr>
<td>β-MoO₃</td>
<td>0.14</td>
<td>21.92</td>
<td>77.94</td>
</tr>
<tr>
<td>h-MoO₃</td>
<td>0.98</td>
<td>20.99</td>
<td>78.09</td>
</tr>
</tbody>
</table>
The Electrochemical impedance spectroscopy (EIS) measurements of the various MoO$_3$ electrode materials are shown in Figure S2. The EIS measurements were recorded in a frequency range of $10^5$ to 0.1 Hz at an open circuit potential. In the high-frequency region of Nyquist plots, the intersection with real axis and the diameter of semicircle represent the resistance of electrochemical system ($R_s$) and charge transfer resistance ($R_{ct}$), respectively. There clearly show smaller $R_{ct}$ for the $\alpha$-MoO$_3$ and $h$-MoO$_3$ electrode materials, whereas the $\beta$-MoO$_3$ electrode material has the largest $R_{ct}$. This result indicates that the charge-transfer at the interface for the $\alpha$-MoO$_3$ and $h$-MoO$_3$ electrode materials is relatively easier than that for $\beta$-MoO$_3$. Furthermore, the slope of straight line in the low-frequency region is defined as the diffusion resistance. The slope trend ($\alpha$-MoO$_3$ > $h$-MoO$_3$ and $\beta$-MoO$_3$) indicates that the diffusion resistance of $\alpha$-MoO$_3$ is lower than that of $h$-MoO$_3$ and $\beta$-MoO$_3$, whereas the diffusion resistances of both $h$-MoO$_3$ and $\beta$-MoO$_3$ electrode materials show no significant difference.
The rate performance of the various MoO$_3$ electrode materials is characterized under current density from 1 A g$^{-1}$ to 5 A g$^{-1}$ with potential range from -0.7 V to 0.6 V. It is observed that the charge and discharge gravimetric capacities are decreased with increasing current density, which is attributed to the polarization phenomenon of the MoO$_3$ electrode materials.

Figure S3. Rate performance and variation of charge/discharge capacities of the various MoO$_3$ electrode materials.
Figure S4. (a) The average valence state of Mo in the various MoO$_3$ electrode materials under insertion/extraction of Al$^{3+}$ ion, and (b) the Mo K-edge XANES spectra of the various MoO$_3$ electrode materials together with the reference samples.
Figure S5. The MoO$_6$ octahedral structure in the (a) $\alpha$-MoO$_3$, and (b) $\beta$-MoO$_3$ materials.