Supporting Information

Charge Density of Intercalants inside Layered Birnessite Manganese Oxide Nanosheets Determining Zn-ion Storage Capability towards Rechargeable Zn-ion Batteries

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Computational Methods

All calculations reported in this work were performed by Vienna *ab initio* simulation package (VASP) based on the periodic plane-wave density functional theory (DFT).\(^1\)-\(^3\) The interaction between ion cores and valence electrons was accounted by the projector-augmented wave (PAW) pseudopotentials.\(^4\) The exchange and correlation interactions between electrons were treated within the generalized gradient approximation (GGA) with the Perdev-Burke-Ernzerhof (PBE) parameterization.\(^5\), \(^6\) The additional van der Waals (vdW) contributions were obtained from the semiempirical D2 method of Grimme (DFT-D2).\(^7\) The effect of 3d electron correlation can be improved by considering on-site Coulomb (U) and exchange (J) interactions. On-site Hubbard term U–J values of 3.9 eV were applied for Mn atom.\(^8\), \(^9\) The cut-off energy for the expanded plane-wave basis set was set to 450 eV. The convergence thresholds for full geometry optimizations were set to 10\(^{-5}\) eV and 0.02 eV/Å for each electronic and ionic step. The Brillouin zone integration was sampled *via* the Monkhorst-Pack (MP) with the 2×3×4 \(k\)-points mesh for supercell and 2×3×4 \(k\)-points mesh for bulk.\(^10\) The calculated relative binding \((E_b)\) energy was obtained from the equation as follows:

\[
E_b = E_{\text{Zn}/\text{MnO}_2} - E_{\text{Zn}} - E_{\text{MnO}_2}
\]

where \(E_{\text{Zn}/\text{MnO}_2}\), \(E_{\text{Zn}}\), and \(E_{\text{MnO}_2}\) are the total energies of the adsorbed Zn in the MnO\(_2\) structure, the pristine MMnO\(_2\) structure, and the bulk Zn, respectively.
**Table S1** Elemental analysis, where X=Li, Ca, and Al.

<table>
<thead>
<tr>
<th>Sample</th>
<th>X/Mn Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICP</td>
</tr>
<tr>
<td>Li-MnO₂</td>
<td>0.33</td>
</tr>
<tr>
<td>Ca-MnO₂</td>
<td>0.15</td>
</tr>
<tr>
<td>Al-MnO₂</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* Li detection is not applicable with XRF technique.
**Fig. S1** The TGA curves of the as-prepared MnO$_2$ at a heating rate of 10 °C min$^{-1}$ under air atmosphere.

**Fig. S2** Galvanostatic charge-discharge profiles at different current densities of (a) Li-MnO$_2$ and (b) Ca-MnO$_2$. 

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**Legend**

- Li-MnO$_2$
- Ca-MnO$_2$
- Al-MnO$_2$
Fig. S3 CV profiles as a function of scan rate of (a) Li-MnO$_2$ and (b) Ca-MnO$_2$.

Fig. S4 GITT profiles during discharging process of (a) Li-MnO$_2$ and (b) Ca-MnO$_2$. 
**Fig. S5** XPS profiles after charging/discharging process of (a) Li-MnO$_2$ and (b) Ca-MnO$_2$. 
Table S2 The benchmarking table of capacity and cycling performance for manganese oxide-based cathodes in aqueous Zn-ion batteries.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphology</th>
<th>Electrolyte</th>
<th>Window potential</th>
<th>Capacity</th>
<th>Stability</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MnO₂</td>
<td>nanorod</td>
<td>1 M ZnSO₄</td>
<td>0.7-2.0 V vs. Zn/Zn²⁺</td>
<td>167 mAh g⁻¹ at 42 mA g⁻¹</td>
<td>70% after 30 cycles at 42 mA g⁻¹</td>
<td>[11]</td>
</tr>
<tr>
<td>Bi-α-MnO₂</td>
<td>nanowire</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>0.8-1.9 V vs. Zn/Zn²⁺</td>
<td>325 mAh g⁻¹ at 0.3 A g⁻¹</td>
<td>90.9% after 2000 cycles at 1 A g⁻¹</td>
<td>[12]</td>
</tr>
<tr>
<td>ε-MnO₂</td>
<td>nanosheet</td>
<td>2 M ZnSO₄ + 0.5 M MnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>183.4 mAh g⁻¹ at 0.5 A g⁻¹</td>
<td>83% after 1000 cycles at 5 A g⁻¹</td>
<td>[13]</td>
</tr>
<tr>
<td>β-MnO₂</td>
<td>nanofiber</td>
<td>3 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>288 mAh g⁻¹ at 0.05 C</td>
<td>84.3% after 1000 cycles at 2 C</td>
<td>[14]</td>
</tr>
<tr>
<td>γ-MnO₂</td>
<td>nanowire/fiber</td>
<td>1 M ZnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>219 mAh g⁻¹ at 0.5 mA cm⁻²</td>
<td>37% after 40 cycles at 0.5 mA cm⁻²</td>
<td>[15]</td>
</tr>
<tr>
<td>δ-MnO₂</td>
<td>nanowire</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>&lt;200 mAh g⁻¹ at 0.2 A g⁻¹</td>
<td>40% after 700 cycles at 200 mA g⁻¹</td>
<td>[16]</td>
</tr>
<tr>
<td>δ-MnO₂/C</td>
<td>nanoflower</td>
<td>2.0 M ZnSO₄ + 0.5 M MnSO₄</td>
<td>1.0-1.9 V vs. Zn/Zn²⁺</td>
<td>203 mAh h⁻¹ at 3 A g⁻¹</td>
<td>61.85% after 1500 cycles at 2 A g⁻¹</td>
<td>[17]</td>
</tr>
<tr>
<td>δ-MnO₂</td>
<td>flake</td>
<td>1 M ZnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>233 mAh g⁻¹ at 100 mA g⁻¹</td>
<td>~45% after 50 cycles at 100 mA g⁻¹</td>
<td>[18]</td>
</tr>
<tr>
<td>PANI-intercalated δ-MnO₂</td>
<td>grainy</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>110 mAh h⁻¹ at 3 A g⁻¹</td>
<td>~83% after 5000 cycles at 2 A g⁻¹</td>
<td>[19]</td>
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<tr>
<td>δ-MnO₂</td>
<td>flake</td>
<td>1 M ZnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>252 mAh g⁻¹ at 83 mA g⁻¹</td>
<td>~44.4% after 100 cycles at 83 mA g⁻¹</td>
<td>[20]</td>
</tr>
<tr>
<td>δ-MnO₂/graphite</td>
<td>nanoflower</td>
<td>1 M ZnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>181 mAh g⁻¹ at 200 mA g⁻¹</td>
<td>~90% after 100 cycles at 400 mA g⁻¹</td>
<td>[21]</td>
</tr>
<tr>
<td>Al-intercalated δ-MnO₂</td>
<td>sheet</td>
<td>2 M ZnSO₄</td>
<td>1.0-1.8 V vs. Zn/Zn²⁺</td>
<td>210 mAh g⁻¹ at 100 mA g⁻¹</td>
<td>84% after 2000 cycles at 2 A g⁻¹</td>
<td>This work</td>
</tr>
</tbody>
</table>

References


