Supporting Information

Correlation of intercalation potential with d-electron configurations for cathode compounds of lithium-ion batteries

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\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
 & M-O bond & Li-O bond & \multicolumn{2}{c|}{\(\Delta d\) (Li-O)} \\
 & deli- & Li- & deli- & li- & \\
\hline
LiMn\textsubscript{2}O\textsubscript{4} & 1.93 & 1.95, 2.28 & 2.04 & 2.11, 2.17 & 0.10 \\
LiCoO\textsubscript{2} & 1.96 & 2.03 & 2.01 & 2.12 & 0.11 \\
LiNiO\textsubscript{2} & 1.88 & 1.93 & 2.00 & 2.07 & 0.07 \\
\hline
\end{tabular}
\caption{The M-O and Li-O bond lengths for layered LiMO\textsubscript{2}. The units are \(\text{\AA}\). The “deli” and “li” represent delithiated and lithiated phases, respectively. In the delithiated phase, Li-O bond is measured with Li ions distributed with the fractional coordinates in the lithiated phase. The \(\Delta d\) (Li-O) represents the change of Li-O bond length by the Li\textsuperscript{+} insertion.}
\end{table}

Mn\textsuperscript{3+} cation in LiMn\textsubscript{2}O\textsubscript{4} is so instable within the initial \(R3m\) (without Jahn-Teller distortion) group that the ligand anions are relaxed to form Jahn-Teller distorted octahedron surround the Mn\textsuperscript{3+} cation forming two kinds of Mn-O bonds with different lengths.

Fig S1. The three energy terms involved with intercalation potential. (a) Equations describing the three decomposed intercalation processes, which define the three energy terms. Host *Li and (Li-Host) represent the intercalated state before and after structure relaxation, respectively. (b) Schematic illustration of the relation between the intercalation potential and the three energy terms.

Table S1. The M-O and Li-O bond lengths for layered LiMO\textsubscript{2}. The units are \(\text{\AA}\). The “deli” and “li” represent delithiated and lithiated phases, respectively. In the delithiated phase, Li-O bond is measured with Li ions distributed with the fractional coordinates in the lithiated phase. The \(\Delta d\) (Li-O) represents the change of Li-O bond length by the Li\textsuperscript{+} insertion.
Table S2 The values of energy difference between HS and LS states ($E_{\text{HS}}-E_{\text{LS}}$) obtained with first-principles calculations, the parameterized expressions of the term $E_{\text{HS}}-E_{\text{LS}}$ within CF theory and CF splitting $\Delta$ estimated from the $E_{\text{HS}}-E_{\text{LS}}$ term, in the delithiated phases. The units are eV. The label * means the value is hypothetic, not deduced from $E_{\text{HS}}-E_{\text{LS}}$ term. E.C (HS: LS) represent the d-electron configuration of the cations in HS and LS states.

<table>
<thead>
<tr>
<th>TME</th>
<th>MO$_2$</th>
<th></th>
<th>MPO$_4$</th>
<th></th>
<th>LiMSiO$_4$</th>
</tr>
</thead>
</table>
|     | E.C (HS: LS) | $E_{\text{HS}}-E_{\text{LS}}$ | $\Delta$ | E.C (HS: LS) | $E_{\text{HS}}-E_{\text{LS}}$ | $\Delta$ | E.C (HS: LS) | $E_{\text{HS}}-E_{\text{LS}}$ | $\Delta$
| Mn  | $t^2_g e_g^0$ | 2.50$^*$ | $t^2_g e_g^0 + t^2_g e_g^0$ | -1.17 | $\Delta \alpha -5J_{II}$ | 1.33 | $e^4 e^0 + e^4 e^0$ | -2.97 | $2\Delta \alpha -8J_{II}$ | 0.52
| Fe  | $t^2_g e_g^0 + t^2_g e_g^0$ | -0.76 | $\Delta \alpha -5J_{II}$ | 1.74 | $t^2_g e_g^0 + t^2_g e_g^0$ | -1.53 | $2\Delta \alpha -10J_{II}$ | 1.74 | $e^4 e^0 + e^4 e^0$ | -1.76 | $2\Delta -10J_{II}$ | 1.62
| Co  | $t^2_g e_g^0 + t^2_g e_g^0$ | 0.83 | $2\Delta \alpha -10J_{II}$ | 2.92 | $t^4 e_g^0 + t^4 e_g^0$ | -0.61 | $2\Delta \alpha -8J_{II}$ | 1.70 | $e^4 e^0 + e^4 e^0$ | -0.69 | $\Delta -5J_{II}$ | 1.81
| Ni  | $t^4 e_g^0 + t^4 e_g^0$ | 1.03 | $2\Delta \alpha -8J_{II}$ | 2.52 | $t^5 e_g^0 + t^5 e_g^0$ | 0.24 | $\Delta \alpha -4J_{II}$ | 1.81 | $e^4 e^0$ | 0.80$^*$ |