Supporting information for: Calculated Descriptors of Catalytic Activity for Water Electrolysis Anode: Application to Delafossite Oxides

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Calculation results

Partial density of states (PDOS) of copper delafossite oxides

Figure S1 shows the e_g and t_{2g} components of PDOS of the d states of the B site in CuBO_2 (B = Cr, Mn, Fe, Co, Rh). The PDOS of the 3R-type structure for CuBO_2 (B = Cr, Fe, Co, Rh) closely resembles that of the 2H-type structure. The PDOSs for CuBO_2 (B = Cr, Mn, Fe) are spin-polarized, whereas those for CuBO_2 (B = Co, Rh) are not. These results for CuCoO_2 show that Co-d states are in a low spin state, which is consistent with previous reports.^{12,27} In contrast, the
PDOSs for CuFeO$_2$ do not have a band gap, so they do not reproduce previous experimental results.$^{30-32}$

*The effect of GGA+$U$ on $e_g$ and $t_{2g}$ occupancy of CuFeO$_2$*

We calculated the systems for CuFeO$_2$ with GGA+$U$ $^{33,34}$ to reproduce an experimental band gap. The effect of the choice of effective $U$ value ($U_{\text{eff}}$) was examined. The $U_{\text{eff}}$ values of 0.0 and 7.1 eV$^{30}$ were used for the Cu-d states (hereinafter the $U_{\text{eff}}$ is denoted by Cu-$U_{\text{eff}}$), and values of 0.0, 2.81, $^{31}$ 4.1, $^{32}$ and 7.1 eV$^{30}$ were used for the Fe-d states (hereinafter $U_{\text{eff}}$ is denoted by Fe-$U_{\text{eff}}$).

Figure S2 shows the PDOS of Fe-d states in CuFeO$_2$, calculated using GGA+$U$ with several different $U_{\text{eff}}$ values. The PDOS with Cu-$U_{\text{eff}} = 7.1$ eV are similar to those with Cu-$U_{\text{eff}} = 0.0$ V for each Fe-$U_{\text{eff}}$ value, which suggests that the PDOS of Fe-d states do not interact with the Cu-d states. The PDOS with Fe-$U_{\text{eff}} \geq 2.81$ eV have a band gap. Higher Fe-$U_{\text{eff}}$ values are associated with wider band gaps. Figures S3 show $e_g$ and $t_{2g}$ occupancies as a function of Fe-$U_{\text{eff}}$ for Cu-$U_{\text{eff}} = 0.0$ and 7.1 eV, respectively. Both $e_g$ and $t_{2g}$ occupancies are saturated at Fe-$U_{\text{eff}} \geq 2.81$ eV. We therefore set Cu-$U_{\text{eff}} = 0.0$ and Fe-$U_{\text{eff}} = 2.81$ eV.

*PDOS of delafossite oxides including precious metals*

Table S1 lists structural data for PdBO$_2$ ($B = \text{Cr, Co, Rh}$) and PtCoO$_2$ with a 3R-type delafossite structure.$^{35}$ Figure S4 shows the PDOS of d states of the $B$ site in PdBO$_2$ and PtCoO$_2$. These PDOS of PdBO$_2$ and PtCoO$_2$ are similar to those of CuBO$_2$ for the same $B$ element. Table S1 also shows the calculated $e_g$ and $t_{2g}$ occupancies of PdBO$_2$ and PtCoO$_2$. 

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Electronic states of copper delafossite surfaces

The $t_{2g}$ occupancy of the bulk material has a close to linear relationship with the OER activity of delafossite oxides. This indicates that the $t_{2g}$ occupancy of the bulk is likely to be correlated with that of the surface, although the electronic states of the bulk are different from those of the surface. To grasp the difference between the electronic states of an ideal surface and those of the bulk, we investigated a slab model using DFT calculations. Figure S5 illustrates the slab model of Cu$BO_2$ ($B = \text{Cr, Co}$) used in our calculations. Cr and Co were adopted as the $B$ element, since our bulk calculations showed the $t_{2g}$ occupancy for Cr to be the lowest, whereas that for Co is the highest. The plane direction is (001), and the slab model consists of four Cu-$BO_6$ layers with oxygen-terminated surfaces. The top three layers of the slab were optimized. The surface unit-cell was set at (2 $\times$ 2). Spurious electronic interactions between periodic images in the slab calculations were eliminated using the effective screening medium (ESM) method.\textsuperscript{36,37}

Figures S6 and S7 show the PDOS of the d states of the $B$ site in the top three layers, and the $e_g$ and $t_{2g}$ states of the $B$ site in the bulk. Table S2 lists the calculated $B$-O and Cu-O bond distances in each layer. The PDOS near the Fermi energy ($E_F$) in the second and third layers for both CuCrO$_2$ and CuCoO$_2$ are similar to those in the bulk of each substance. In contrast, the PDOS in the first layer is slightly different from that in the bulk, an effect caused by surface relaxation (Table S2). There are up-spin states just above $E_F$ for CuCrO$_2$, whereas there are both up- and down-spin states just above $E_F$ for CuCoO$_2$. These unoccupied states localized in the top surface are $t_{2g}$ states that slightly reduce the $t_{2g}$ occupancy in the top surface. The ratio of the unoccupied
t$_2$g states just above $E_F$ to total occupied states is $\approx 6\%$ for CuCrO$_2$ (low t$_2$g occupancy), and $\approx 3\%$ for CuCoO$_2$ (high t$_2$g occupancy). The degrees of decrease in the t$_2$g occupancy in the top surface appear to be independent of the $B$ element, and thus linearity is maintained in the relationship between the t$_2$g occupancy of the bulk and OER activity.

The t$_2$g orbital of Co$^{3+}$ in the low spin state (Figs. S1 (f), (g)), where ACoO$_2$ has high OER activity, is fully filled. Oxygen-related intermediate species produced during OER are not likely to adsorb onto the delafossite surface. Our slab calculations suggest that the unoccupied states of the Co site in the surface just above $E_F$ are likely to enhance the binding of Co with intermediates. The fully-filled t$_2$g states of Co$^{3+}$ enhance OER activity, which suggests that the rate-limiting reaction is likely to be the desorption process of the intermediates. It will be necessary to investigate in more detail how the unoccupied states of the $B$ site in the surface affect the binding of intermediates to the $B$ sites and the OER process.

*The relationships between the calculated and experimentally-determined e$_g$ occupancies in perovskite oxides*

Figure S8 shows the e$_g$ and t$_2$g components of PDOS of the d states of the $B$ site in perovskite oxide, LaBO$_3$ ($B = \text{Cr, Co, Ni, Fe}$). Here, the PDOSs were calculated in bulk, and the crystal structures of LaBO$_3$ were based on the literature.$^9$ The PDOSs for LaBO$_3$ ($B = \text{Cr, Co, Fe}$) are spin-polarized, whereas that for LaNiO$_3$ is not. It should be noted that the Co-d states in LaCoO$_3$ are not in a low spin state. This is consistent with the experimental results.$^9$
Figure S9 shows the relationship between the calculated and experimentally-determined e_g occupancies of the B site in LaBO_3. Here, the calculated e_g occupancies were estimated on the basis of the PDOS, and the experimentally e_g occupancies were based on the literature. We found these occupancies to have a linear relationship, which suggests that the catalyst descriptor estimated using bulk DFT calculations can extend to other transition metal oxides. In our present calculations, only perovskite oxides of LaBO_2 were calculated. In the future, the calculated e_g or t_2g occupancy of active sites in more complicated perovskite oxides (ex. A'A'B'B'O_3) should be examined to correlate them with the OER activity.

ADDITIONAL REFERENCES


Figure S1. $e_g$ and $t_{2g}$ components of partial density of states (PDOS) of $d$ states at the $B$-site in CuBO$_2$ ($B =$ Cr, Mn, Fe, Co, Rh) with 3R-type, 2H-type, and crednerite structures. Positive and negative DOS values respectively represent the spin-up and spin-down DOS.
Figure S2. $e_g$ and $t_{2g}$ components of PDOS of Fe-d states in 3R-type CuFeO$_2$ calculated using GGA+$U$ with several different $U_{\text{eff}}$ values. Positive and negative DOS values respectively represent the spin-up and spin-down DOS.
Figure S3. (a) $e_g$ and (b) $t_{2g}$ occupancies of 3R-type CuFeO$_2$ as a function of Fe-$U_{\text{eff}}$ for Cu-$U_{\text{eff}} = 0.0$ and 7.1 eV.
Table S1. Structural data and calculated $e_g$ and $t_{2g}$ occupancies of PdBO$_2$ ($B = \text{Cr, Co, Rh}$) and PtCoO$_2$ with the 3R-type structure.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$u$</th>
<th>$e_g$</th>
<th>$t_{2g}$</th>
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<tr>
<td>PdCrO$_2$</td>
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<td>1.09</td>
<td>0.11</td>
<td>a</td>
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<td>PdCoO$_2$</td>
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<td>a</td>
<td>2.00</td>
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<td>PdRhO$_2$</td>
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<td>18.08</td>
<td>0.11</td>
<td>a</td>
<td>1.81</td>
</tr>
<tr>
<td>PtCoO$_2$</td>
<td>2.83</td>
<td>17.84</td>
<td>0.11</td>
<td>a</td>
<td>1.99</td>
</tr>
</tbody>
</table>

$^a$ Reference 35
Figure S4. \( e_g \) and \( t_{2g} \) components of PDOS of the d states of the \( B \) site in Pd\( B\)O\(_2\) (\( B = \) (a) Cr, (b) Co, (c) Rh) and (d) PtCoO\(_2\). Positive and negative DOS values respectively represent the spin-up and spin-down DOS.
Figure S5. Cross-sectional view of slab model of CuBO$_2$ ($B = $ Cr, Co). This slab model was visualized using VESTA.$^{21}$
Figure S6. PDOS of Cr-d states in the (a) first, (b) second, and (c) third layer, which are denoted as the atoms circled in Fig. S5. (d) $e_g$ and $t_{2g}$ components of PDOS of Co-d states in bulk CuCrO$_2$. Positive and negative DOS values respectively represent the spin-up and spin-down DOS.
Figure S7. PDOS of Co-d states in the (a) first, (b) second, and (c) third layer, which are denoted as the atoms circled in Fig. S5. (d) $e_g$ and $t_{2g}$ components of PDOS of Co-d states in bulk CuCoO$_2$. Positive and negative DOS values respectively represent the spin-up and spin-down DOS.
Table S2. Calculated $B$-O and Cu-O bond distances in each layer of the CuBO$_2$ ($B$ = Cr, Co) surface.

<table>
<thead>
<tr>
<th>Layer</th>
<th>CuCrO$_2$</th>
<th>CuCoO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr-O (Å)</td>
<td>Cu-O (Å)</td>
</tr>
<tr>
<td>1st layer</td>
<td>1.91</td>
<td>1.85</td>
</tr>
<tr>
<td>2nd layer</td>
<td>1.98</td>
<td>1.86</td>
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<tr>
<td>3rd layer</td>
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<td>1.87</td>
</tr>
<tr>
<td>4th layer</td>
<td>1.96</td>
<td>1.90</td>
</tr>
</tbody>
</table>
Figure S8. $e_g$ and $t_{2g}$ components of PDOS of the d states of the $B$ site in LaBO$_3$ ($B = \text{Cr, Fe, Co, Ni}$). Positive and negative DOS values respectively represent the spin-up and spin-down DOS.
Figure S9. The relationship between calculated and experimentally-determined $e_g$ occupancies of the $B$ site in perovskite oxide $\text{LaBO}_3$ ($B = \text{Cr, Co, Fe, Ni}$).