SUPPORTING INFORMATION

Theoretical Inspection of TM-P4C Single-Atom Electrocatalyst: Ultra-High Performance for bifunctional Oxygen Reduction and Evolution Reactions

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Calculation methods

The OER performance on TMP4 in acid condition is investigated via the four-electron pathway. In the first step, TMP4 takes one H2O molecule from the solvent and releases one (H\(^{+}\)+e\(^{-}\)) pair, leading to the formation of *OH. Next, one (H\(^{+}\)+e\(^{-}\)) pair continues to separate from *OH, leaving *O. Then, another H2O molecule joins in and reacts with *O to form *OOH with the release of one (H\(^{+}\)+e\(^{-}\)) pair. At last, *OOH can generate O2 and go back to * with one (H\(^{+}\)+e\(^{-}\)) pair releasing. The four elementary steps of OER can be described as:

\[
\begin{align*}
* + \text{H}_2\text{O} & \rightarrow *\text{OH} + (\text{H}^{+} + \text{e}^{-}) \quad (1) \\
*\text{OH} & \rightarrow *\text{O} + (\text{H}^{+} + \text{e}^{-}) \quad (2) \\
*\text{O} + \text{H}_2\text{O} & \rightarrow *\text{OOH} + (\text{H}^{+} + \text{e}^{-}) \quad (3) \\
*\text{OOH} & \rightarrow * + \text{O}_2 + (\text{H}^{+} + \text{e}^{-}) \quad (4)
\end{align*}
\]

in which * denotes P4C. To avoid the calculation of the free energy of O2 gas, the experiment reaction energy of 2H2O → O2 + 2H2 (4.92 eV) is taken into account. Moreover, the energy of (H\(^{+}\)+e\(^{-}\)) pair can be replaced by half of the H2 molecule at 298 K. Hence, the free energy change of each step can be written as:

\[
\begin{align*}
\Delta G_1 &= \Delta G_{*\text{OH}} \\
\Delta G_2 &= \Delta G_{*\text{O}} - \Delta G_{*\text{OH}} \\
\Delta G_3 &= \Delta G_{*\text{OOH}} - \Delta G_{*\text{O}} \\
\Delta G_4 &= 4.92 - \Delta G_{*\text{OOH}}
\end{align*}
\]

where \(\Delta G_{*\text{OH}}, \Delta G_{*\text{O}},\) and \(\Delta G_{*\text{OOH}}\) are the adsorption free energy of *OH, *O and *OOH, respectively. Assuming that the small obstacles in the (H\(^{+}\)+e\(^{-}\)) pair transfer are negligible, the OER reaction is thus only determined by the free energy change of each elementary step. The step with the greatest increasing change of OER is defined as the potential-determining step. To evaluate the catalytic activity, the OER overpotential (\(\eta_{\text{OER}}\)) is defined as:

\[
\eta_{\text{OER}} = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e - 1.23 \quad (9)
\]

A catalyst with lower \(\eta_{\text{OER}}\) possesses better OER activity. The process of ORR is the reverse reaction of OER. Similarly, the overpotential of ORR (\(\eta_{\text{ORR}}\)) can be written as:

\[
\eta_{\text{ORR}} = \max\{-\Delta G_1, -\Delta G_2, -\Delta G_3, -\Delta G_4\}/e + 1.23 \quad (10)
\]

In addition, for a given electrode process \(\text{O} + ne \rightarrow \text{R}\) at a certain electric potential \(E\), the concentrations of the reactant and product can be linked by the well-known Nernst equation:
\[ E = E^0 + \frac{RT}{nF} \ln \frac{C_0}{C_R} \]  

(11)

Where \( E^0 \) is the equilibrium potential of the reaction in the standard state, \( R \) is the universal gas constant, \( T \) is the temperature, \( n \) is the electron transfer number, \( F \) is the Faraday constant, and \( C_0/C_R \) are the concentrations of the oxidation/reduction states in the reaction. From this, the exchange current density \( j_0 \) is given by

\[ j_0 = nFkC_0 \exp\left[- \frac{aF}{RT}(E_{eq} - E_0)\right] \]  

(12)

Where \( k \) is the electrode reaction rate constant, \( E_{eq} \) is the equilibrium potential, and \( a \) is the transfer coefficient. Thus, the electrochemical polarization equation for the electrode (Butler–Volmer equation) is derived as follows:

\[ j = j_0 \left[ \exp\left(- \frac{aF}{RT}\eta\right) - \exp\left(\frac{(1-a)F}{RT}\eta\right)\right] \]  

(13)

where \( \eta = E - E_{eq} \) is the overpotential for deviation from the equilibrium potential and \( j \) is the overall current density. As one of the most important experimental activity descriptors, the exchange current density \( j_0 \) can be used to explore the catalytic activity of different catalysts. However, because the reaction rate constant \( k \) and transfer coefficient \( a \) in Equation 12 are unknown and variable, it is virtually impossible to compute \( j_0 \) theoretically. The Nørskov electrochemical catalysis model defines the rate constant \( k \) for a reaction as follows:

\[ k = k_0 \exp\left[- \frac{\Delta G_{max}}{k_BT} \right] \]  

(14)

where \( k_b \) is the Boltzmann constant and \( \Delta G_{max} \) is the change in free energy for the rate-determining step. In the electrochemical polarization model, \( k_0 \) can be defined as

\[ k_0 = \frac{k_BT}{h} \]  

(15)

Where \( h \) is Planck’s constant. Here, we combine Equation 13-15 to estimate a solution for the calculation of the specific value of \( j_0 \):

\[ j_0 = nFC_0 \frac{k_BT}{h} \exp\left[- \frac{\Delta G_{max}}{k_BT} \right] \]  

(16)

Therefore, the overall electrode current density \( j \) can be calculated according to the overpotential \( \eta \):

\[ j = nFC_0 \frac{k_BT}{h} \exp\left[- \frac{\Delta G_{max}}{k_BT} \right] \left[ \exp\left(- \frac{aF}{RT}\eta\right) - \exp\left(\frac{(1-a)F}{RT}\eta\right)\right] \]  

\[ \approx nFC_0 \frac{k_BT}{h} \exp\left[- \frac{\Delta G_{max}}{k_BT} \frac{aF}{RT}\eta\right] \]  

(17)
Table S1. The correction of zero-point energy (ZPE) and the entropy of adsorption species. T is the room temperature (298.15 K) and * represents TM-P4-C.

| Systems | TS | ZEP | Systems | TS | ZEP | Systems | TS | ZEP |
|---------|----|-----|---------|----|-----|---------|----|-----|
| Ti-P4-C |    |     | Zr-P4-C |    |     | Hf-P4-C |    |     |
| *OH     | 0.17 | 0.31 | *OH     | 0.15 | 0.32 | *OH     | 0.14 | 0.33 |
| *O      | 0.10 | 0.07 | *O      | 0.10 | 0.06 | *O      | 0.10 | 0.06 |
| *OOH    | 0.20 | 0.45 | *OOH    | 0.15 | 0.44 | *OOH    | 0.21 | 0.44 |
| V-P4-C  |    |     | Nb-P4-C |    |     | Ta-P4-C |    |     |
| *OH     | 0.14 | 0.32 | *OH     | 0.15 | 0.31 | *OH     | 0.15 | 0.32 |
| *O      | 0.08 | 0.07 | *O      | 0.08 | 0.07 | *O      | 0.08 | 0.07 |
| *OOH    | 0.24 | 0.43 | *OOH    | 0.14 | 0.44 | *OOH    | 0.14 | 0.44 |
| Cr-P4-C |    |     | Mo-P4-C |    |     | W-P4-C  |    |     |
| *OH     | 0.10 | 0.34 | *OH     | 0.11 | 0.34 | *OH     | 0.11 | 0.34 |
| *O      | 0.06 | 0.08 | *O      | 0.07 | 0.07 | *O      | 0.07 | 0.08 |
| *OOH    | 0.22 | 0.42 | *OOH    | 0.22 | 0.42 | *OOH    | 0.23 | 0.41 |
| Mn-P4-C |    |     | Ru-P4-C |    |     | Re-P4-C |    |     |
| *OH     | 0.12 | 0.34 | *OH     | 0.13 | 0.13 | *OH     | 0.09 | 0.36 |
| *O      | 0.06 | 0.08 | *O      | 0.07 | 0.07 | *O      | 0.06 | 0.08 |
| *OOH    | 0.23 | 0.42 | *OOH    | 0.23 | 0.42 | *OOH    | 0.21 | 0.41 |
| Fe-P4-C |    |     | Rh-P4-C |    |     | Os-P4-C |    |     |
| *OH     | 0.11 | 0.35 | *OH     | 0.12 | 0.34 | *OH     | 0.13 | 0.34 |
| *O      | 0.08 | 0.06 | *O      | 0.08 | 0.05 | *O      | 0.06 | 0.07 |
| *OOH    | 0.23 | 0.42 | *OOH    | 0.21 | 0.43 | *OOH    | 0.23 | 0.42 |
| Co-P4-C |    |     | Pd-P4-C |    |     | Ir-P4-C |    |     |
| *OH     | 0.11 | 0.34 | *OH     | 0.08 | 0.33 | *OH     | 0.11 | 0.35 |
| *O      | 0.08 | 0.06 | *O      | 0.12 | 0.04 | *O      | 0.08 | 0.06 |
| *OOH    | 0.20 | 0.43 | *OOH    | 0.17 | 0.42 | *OOH    | 0.21 | 0.43 |
| Ni-P4-C |    |     | Ag-P4-C |    |     | Pt-P4-C |    |     |
| *OH     | 0.12 | 0.34 | *OH     | 0.16 | 0.32 | *OH     | 0.13 | 0.34 |
| *O      | 0.11 | 0.04 | *O      | 0.07 | 0.03 | *O      | 0.09 | 0.06 |
| *OOH    | 0.21 | 0.43 | *OOH    | 0.27 | 0.41 | *OOH    | 0.23 | 0.43 |
| Cu-P4-C |    |     | Au-P4-C |    |     |         |    |     |
| *OH     | 0.14 | 0.33 | *OH     | 0.14 | 0.34 |         |    |     |
| *O      | 0.06 | 0.08 | *O      | 0.10 | 0.05 |         |    |     |
| *OOH    | 0.23 | 0.42 | *OOH    | 0.25 | 0.42 |         |    |     |
Table S2. Summary of TM-P average bonds length ($d_{TM-P}$), binding energies ($E_b = E_{TM-P4-C} - E_{P4-C} - E_{TM-atom}$), and bader charge transfers (q, from TM to P4-C) on TM-P4-C. $E_{TM-P4-C}$, $E_{P4-C}$ and $E_{TM-atom}$ are the energies of TM-P4-C, P4-C and TM single atom, respectively.

|     | d/Å  | E/eV | q  |
|-----|------|------|----|
| Ti  | 2.29 | -6.59| 1.20|
| V   | 2.19 | -6.38| 1.18|
| Cr  | 2.14 | -5.57| 1.12|
| Mn  | 2.11 | -5.29| 1.02|
| Fe  | 2.09 | -5.24| 0.95|
| Co  | 2.07 | -5.27| 0.96|
| Ni  | 2.08 | -5.22| 0.95|
| Cu  | 2.17 | -3.90| 0.52|
| Zr  | 2.43 | -7.48| 1.36|
| Nb  | 2.32 | -7.22| 1.27|
| Mo  | 2.26 | -6.91| 1.15|
| Ru  | 2.23 | -6.84| 1.13|
| Rh  | 2.26 | -6.68| 1.05|
| Pd  | 2.82 | -4.17| 0.66|
| Ag  | 3.02 | -2.10| 0.33|
| Hf  | 2.40 | -8.85| 1.66|
| Ta  | 2.31 | -8.58| 1.58|
| W   | 2.25 | -8.17| 1.46|
| Re  | 2.22 | -7.91| 1.41|
| Os  | 2.23 | -8.16| 1.42|
| Ir  | 2.25 | -7.51| 1.31|
| Pt  | 2.77 | -5.22| 0.68|
| Au  | 2.93 | -2.75| 0.46|
Figure S1. The optimized structures of TM atoms embed graphene sheet with the tetra-coordinates P.
Figure S2. The calculated free energy diagrams of TMP4 systems at electrode potential of 0V and 1.23V.
Figure S3 Partial density of states of d orbitals for transition metal embedded P4C systems, dotted and red lines represent the Fermi level and d-band center of TM atoms, respectively.
Figure S4. The density of states and the charge density difference of intermediates adsorption on CoP4.