Rational Design of Bifunctional ORR/OER Catalysts Based on Pt/Pd-Doped Nb$_2$CT$_2$ MXene by First-Principles Calculations

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**Figure S1** The structures of terminated Nb$_2$C, a) Nb$_2$CO$_2$, b) Nb$_2$CF$_2$, and c) Nb$_2$C(OH)$_2$.

**Figure S2** a) The Frequency distribution of geometrically optimized Nb$_2$CF$_2$, b) Temperature equilibrium curve and energy fluctuation curve obtained from molecule dynamic simulation.
Figure S3 The reaction paths and the activation barriers of a) ORR on Nb$_2$C(OH)$_2$ and b) OH groups recovery.
Figure S4 The structures of the recombinant catalysts, with a) Pt/Pd single atoms on O-terminated Nb$_2$C, b) Pt/Pd single atoms on F-terminated Nb$_2$C, and c) Pt/Pd single atoms on OH-terminated Nb$_2$C.
**Figure S5** The electronic locational functions (ELF) of a) Pt/Pd single atoms on Nb$_2$C(OH)$_2$ and b) functional terminated Nb$_2$C and Pt/Pd single atoms on Nb$_2$CO$_2$ and Nb$_2$CF$_2$. 
Figure S6 The adsorption properties of O\textsubscript{2} molecules on a) Nb\textsubscript{2}CF\textsubscript{2}, Nb\textsubscript{2}C(OH)\textsubscript{2} and b)-d) Pt/Pd single atoms modified Nb\textsubscript{2}CF\textsubscript{2}, Nb\textsubscript{2}CO\textsubscript{2} and Nb\textsubscript{2}C(OH)\textsubscript{2}, respectively.
Figure S7 The adsorption properties of H$_2$O$_2$ molecules on a) Pt/Pd single atoms modified Nb$_2$CF$_2$, and b) Pt/Pd single atoms modified Nb$_2$CO$_2$. 
**Figure S8** The reaction competition of O$_2$ hydrogenation (path 2) or dissociation (path1) at the first step of ORR, a)-h) represented Nb$_2$CO$_2$-Pd, Nb$_2$CO$_2$-Pt, Nb$_2$CF$_2$-Pd, Nb$_2$CF$_2$-Pt, Nb$_2$CO$_2$-V$_0$-Pd, Nb$_2$CO$_2$-V$_0$-Pt, Nb$_2$CF$_2$-V$_f$-Pd, Nb$_2$CF$_2$-V$_f$-Pt, respectively.

**Figure S9** Changes in Gibbs free energy differences (ΔG) of elementary reaction steps along the 4-e-pathway toward ORR and OER, with a) ΔG for Nb$_2$CO$_2$, and b) ΔG for Nb$_2$CF$_2$, respectively.
Figure S10  

a) The structure of Nb-deficit vacancies immobilized with single Pt atoms; b) the charge transfer differences (CDD) of the structures of Nb$_2$CO$_2$-V$_\text{Nb}$-Pt, Nb$_2$CF$_2$-V$_\text{Nb}$-Pt, Nb$_2$CO$_2$-V$_\text{Nb,O}$-Pt and Nb$_2$CF$_2$-V$_\text{Nb,F}$-Pt; c) H$_2$O$_2$ molecule adsorbed on the Nb-deficit structures with or without the functional vacancies.
Figure S11  a) The adsorption properties of OOH on the Nb-defected MXenes; b)-c) the reaction paths and barrier of O$_2$ dissociation on Nb$_2$CO$_2$-$V_{Nb}$-Pt and Nb$_2$CF$_2$-$V_{Nb}$-Pt; d)-e) the reaction competition in the first step of ORR on Nb$_2$CO$_2$-$V_{Nb,O}$-Pt and Nb$_2$CF$_2$-$V_{Nb,F}$-Pt, respectively.
Figure S12 The properties a) and structures b) of molecules (O$_2$, CO, H$_2$O and double O$_2$) adsorbed on Nb$_2$CF$_2$-V$_r$-Pt, where $D_{m-s}$ represented the distance between the adsorbents and substrate, $D_{m-m}$ and $DI_{m-m}$ were the bond lengths of molecules in vacuum and increased bond lengths of the activated molecules, respectively.
Figure S13  a) Schematic diagram of possible reaction pathways for ORR.  b) The possible reaction pathways for the ORR on Nb$_2$CF$_2$-V$_{1}$-Pt.
Figure S14 The adsorption structures of O$_2$ on a) Nb$_2$CO$_2$-V$_0$-Pt, Nb$_2$CO$_2$-V$_0$-Pt$_6$Pt$_1$, Nb$_2$CO$_2$-V$_0$-Pt$_6$Pt$_2$ and b) Nb$_2$CF$_2$-V$_f$-Pt Nb$_2$CF$_2$-V$_f$-Pt$_6$Pt$_1$, Nb$_2$CF$_2$-V$_f$-Pt$_6$Pt$_2$. c)-d) the scheme of noble metal utilization on Pt(111) and IrO$_2$(110), respectively.
**Figure S15**  
(a) The charge density differences (CDD) of Nb$_2$CO$_2$-V$_0$-Pt$_0$Pt$_1$, Nb$_2$CO$_2$-V$_0$-Pt$_0$Pt$_2$, Nb$_2$CF$_2$-V$_1$-Pt$_0$Pt$_1$, and Nb$_2$CF$_2$-V$_1$-Pt$_0$Pt$_2$.  
(b) The CDD of a single or a double O$_2$ adsorbed Nb$_2$CF$_2$-V$_1$-Pt$_0$Pt$_1$ and Nb$_2$CF$_2$-V$_1$-Pt$_0$Pt$_2$.

**Figure S16**  
(a) The top view of the solvation system and b) the solvation model with adsorbed intermediates.

**Table S1.** The adsorption properties of the reaction molecule O$_2$ on Nb$_2$CT$_X$, in which $E_{\text{ads}}$-O$_2$ was the adsorption energies and Q was the number of charge transfer from catalysts to O$_2$. And $\eta^{\text{ORR}}$ and $\eta^{\text{OER}}$ were the overpotentials toward ORR and OER.

<table>
<thead>
<tr>
<th>Properties</th>
<th>$E_{\text{ads}}$-O$_2$(eV)</th>
<th>$\eta^{\text{ORR}}$(V)</th>
<th>$\eta^{\text{OER}}$(V)</th>
<th>Q(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$_2$C</td>
<td>-11.47</td>
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<td>---</td>
<td>1.23</td>
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<tr>
<td>Nb$_2$CO$_2$</td>
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<td>1.04</td>
<td>0.94</td>
<td>0.17</td>
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<tr>
<td>Nb$_2$CF$_2$</td>
<td>-0.22</td>
<td>1.04</td>
<td>1.53</td>
<td>0.21</td>
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<td>Nb$_2$C(OH)$_2$</td>
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Table S2. The adsorption energy of an O₂ molecular on different catalysts, where Eₐₐ₅₀ , Eₐₐ₅₁ and Eₐₐ₅₂ represented the adsorption energies of O₂ on noble metals which was labeled as Pt₀, Pt₁ and Pt₂ and Ir₀, Ir₁, Ir₂ respectively.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Eₐₐ₅₀(eV)</th>
<th>Eₐₐ₅₁(eV)</th>
<th>Eₐₐ₅₂(eV)</th>
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</thead>
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<tr>
<td>Nb₂CO₂-VₐO⁻</td>
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<td>0.41</td>
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<tr>
<td>Pt₀Pt₁</td>
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<tr>
<td>Nb₂CO₂-VₐO⁻</td>
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<td>0.65</td>
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<tr>
<td>Pt₀Pt₂</td>
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<td>Nb₂CF₂-V₁-Pt₀Pt₁</td>
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<tr>
<td>Nb₂CF₂-V₁-Pt₀Pt₂</td>
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<td>0.56</td>
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<tr>
<td>Pt(111)-Pt₀Pt₁</td>
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<td>Pt(111)-Pt₀Pt₂</td>
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<tr>
<td>IrO₂(110)-Ir₀Ir₁</td>
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Table S3. Charge transfer during the reactions, Q-0, Q-1, Q-2 were the charge number that noble metals gained from the supports, Q₁-O₂ and Q₂-O₂ were the charge number of the first and second O₂ molecule captured from catalysts.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Q-0(e)</th>
<th>Q-1(e)</th>
<th>Q-2(e)</th>
<th>Q₁-O₂(e)</th>
<th>Q₂-O₂(e)</th>
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<tr>
<td>Nb₂CO₂-V₀-Pt₀Pt₁</td>
<td>0.47</td>
<td>0.42</td>
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<td>0.48</td>
<td>0.45</td>
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<td>Nb₂CO₂-V₀-Pt₀Pt₂</td>
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<td>0.57</td>
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<tr>
<td>Nb₂CF₂-V₁-Pt₀Pt₁</td>
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<td>0.36</td>
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<td>0.42</td>
<td>0.41</td>
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<tr>
<td>Nb₂CF₂-V₁-Pt₀Pt₂</td>
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<td>0.48</td>
<td>0.53</td>
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Table S4 The energy corrections and the adsorption free energies in ORR and OER on all the catalysts.

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<tr>
<th></th>
<th>ΔZPE</th>
<th>TΔS</th>
<th>ΔG</th>
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<th>ΔZPE</th>
<th>TΔS</th>
<th>ΔG</th>
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<td></td>
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<td>Nb₂CF₂</td>
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<tr>
<td>*OOH</td>
<td>0.51</td>
<td>0.26</td>
<td>3.35</td>
<td>0.51</td>
<td>0.27</td>
<td>3.65</td>
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<tr>
<td>*O</td>
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<td>0.19</td>
<td>0.39</td>
<td>0.13</td>
<td>0.22</td>
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<tr>
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<td>Nb₂CO₂-Pd</td>
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<td>Nb₂CF₂-Pd</td>
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<td>*OOH</td>
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<td>*O</td>
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<td></td>
<td>Nb₂CO₂-Pt</td>
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<td>Nb₂CF₂-Pt</td>
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<tr>
<td>*OOH</td>
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<td>0.50</td>
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<td>3.92</td>
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<tr>
<td>*O</td>
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<tr>
<td>*OH</td>
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<td>0.51</td>
<td>0.39</td>
<td>0.13</td>
<td>0.52</td>
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<tr>
<td></td>
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<td>Nb₂CF₂-Vₐ-Pd</td>
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<tr>
<td>*OOH</td>
<td>0.52</td>
<td>0.26</td>
<td>4.20</td>
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<td>0.26</td>
<td>4.16</td>
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<tr>
<td>*O</td>
<td>0.11</td>
<td>0.13</td>
<td>2.51</td>
<td>0.10</td>
<td>0.10</td>
<td>3.04</td>
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<tr>
<td>*OH</td>
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<td>1.14</td>
<td>0.40</td>
<td>0.13</td>
<td>0.93</td>
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<tr>
<td></td>
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<td>Nb₂CF₂-Vₐ-Pt</td>
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<tr>
<td>*OOH</td>
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<td>3.81</td>
<td>0.51</td>
<td>0.28</td>
<td>3.85</td>
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<tr>
<td>*O</td>
<td>0.11</td>
<td>0.10</td>
<td>2.38</td>
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<td>2.25</td>
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<td>*OH</td>
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<td>0.39</td>
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<td>0.83</td>
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Table S5 The solvation energies corrections ($\Delta$Sol) and the free energies after considering the salvation effect ($\Delta G_{Sol}$) on the selected catalysts (Nb$_2$CO$_2$-V$_O$-Pt and Nb$_2$CF$_2$-V$_F$-Pt).

<table>
<thead>
<tr>
<th></th>
<th>$\Delta$Sol</th>
<th>$\Delta G_{Sol}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>*OOH</td>
<td>*O</td>
</tr>
<tr>
<td>Nb$_2$CO$_2$-V$_O$-Pt</td>
<td>-0.57</td>
<td>-0.50</td>
</tr>
<tr>
<td>Nb$_2$CF$_2$-V$_F$-Pt</td>
<td>-0.45</td>
<td>-0.59</td>
</tr>
</tbody>
</table>
The poison resistance of Nb$_2$CF$_2$-V$_f$-Pt

To evaluate the poison resistance of Nb$_2$CF$_2$-V$_f$-Pt, we studied the adsorption properties of CO, H$_2$O and multiple O$_2$ on the selected catalyst. As shown in Figure S12a, the $E_{\text{ads}}$ represented the adsorption energies of several molecules on Nb$_2$CF$_2$-V$_f$-Pt. It revealed that the catalyst had the strongest binding strength to O$_2$ molecules, with the largest $E_{\text{ads}}$ (0.55 eV). Then followed by the H$_2$O molecule (0.49 ev), which indicated that O$_2$ was adsorbed first in the reaction. As to the CO and the second O$_2$, the adsorption energies were only 0.38 and 0.23 eV, respectively, which manifested that Nb$_2$CF$_2$-V$_f$-Pt had the resistance to CO poisoning, moreover multiple O$_2$ wouldn’t prevent the subsequent reactions. Besides, the distance between the adsorbents and substrate ($D_{m-s}$) was shortest and the increased bond length of the activated molecules ($D_{I_{m-m}}$) was the longest on the adsorbed O$_2$ (Figure S12). It indicated that the O$_2$ were activated to the greatest extent among these adsorbates, which further demonstrated that Nb$_2$CF$_2$-V$_f$-Pt will not be poisoned during the catalytic process.

The reaction energies barriers of ORR/OER on Nb$_2$CF$_2$-V$_f$-Pt

Although there were three possible reaction pathways (I-III) in the schematic diagram (Figure S13a), association mechanism of ORR was more feasible on Nb$_2$CF$_2$-V$_f$-Pt (II) (Figure S13b), where the adsorbed O$_2$ molecule went through a sequential coupled proton-electron transfer process to form H$_2$O through the following reactions:

\[
\begin{align*}
* + \text{O}_2 + \text{H}^+ + e^- & \rightarrow \text{*OOH (R1-II)} \\
\text{*OOH} & \rightarrow \text{O}^* + \text{OH}^* \text{ (R2-II)} \\
\text{*OOH} + \text{H}^+ + e^- & \rightarrow \text{*O + H}_2\text{O (R2-IIa)} \\
\text{OOH}^* + \text{H}^+ + e^- & \rightarrow 2\text{*OH (R2-IIb)} \\
\text{*O} + \text{H}^+ + e^- & \rightarrow \text{*OH (R3-IIb)} \\
2\text{*OH} + \text{H}^+ + e^- & \rightarrow \text{*OH} + \text{H}_2\text{O (R3-IIa)} \\
\text{*OH} + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O (R4-II)}
\end{align*}
\]

After the *OOH was formed, it dissociated to *O and *OH with an activation barrier of 0.50 eV. This was followed by two possible reaction paths. One was the OH* hydrogenation to
release a H$_2$O molecule (R4-IIa) firstly and then the remained *O was reduced to *OH and H$_2$O (R5-IIa) with activation barriers of 0.71, 0.62 and 0.73 eV, respectively. The other path was the *O reduced to form *OH and H$_2$O with activation barriers of 0.69 and 0.75 eV. In addition, the OER on Nb$_2$CF$_2$-V$_F$-Pt is followed by a reversed process of ORR, in which the absorbed H$_2$O species directly dissociated to *OH and dissociative H atom in the first step with an energy barrier of 0.67eV. Then the produced *OH met with two reaction bench. In path IIa, the *OH further dissociated to *O and H atom, then the remained *O captured a H$_2$O and dissociated to *O and *OH with an activation barrier of 0.75 and 0.70 eV, respectively. While in path IIb, *OH combined with a H$_2$O molecule to form 2*OH and then dehydrogenated to *O and *OH with an energy barrier of 0.88 and 1.03 eV, respectively. Therewith, the produced *O and *OH synthesized to the *OOH and finally separated out O$_2$ with energy barriers of 0.67 and 53eV, respectively.

**The Solvation effect**

Based on previous studies, a single ice-like bilayer of water is a reasonable model able to provide sufficient water molecules to describe solvation effects.$^1$ To fit the size of water bilayer, the repeating unit of Nb$_2$CO$_2$-V$_O$-Pt and Nb$_2$CF$_2$-V$_F$-Pt was increased from 3×3 to 7×5, and the water layer was constructed in a 2×3 repeating unit including 24 H$_2$O molecules (Figure S16). The energy correction of the solvation energy (ΔSol) was defined by the following equations (equation 1-2):

$$\Delta \text{Sol} = E_{\text{tot}} - E_{(\text{sur} + \text{adsorbate})} - E_{\text{water}} + E_{(\text{sur} + \text{water})} \quad (1)$$

$$\Delta \text{G} = \Delta \text{E} + \Delta \text{ZPE} - T\Delta \text{S} + \Delta \text{Sol} + x \text{eU} - 4\text{eU} \quad (2)$$

where $E_{\text{tot}}$, $E_{(\text{sur} + \text{adsorbate})}$, $E_{\text{water}}$, and $E_{(\text{sur} + \text{water})}$ represent the computed electronic energies of the surface with the adsorbates as well as the single water layer, the surface with the adsorbates only, the single water layer, and the surface with single water layer only, respectively. The number of transferred electrons x was 1-3 for the OOH*, O*, and OH* intermediates, respectively.

Results in Table S5 indicated that the intermediates involved in ORR and OER were stabilized to different extents by interacting with environmental water molecules via hydrogen
bonds. As shown, OH* had larger solvation energy compared to OOH* due to its ability to form a more polarized structure on the Nb₂CO₂-V₀-Pt and Nb₂CF₂-V₁-Pt surface. The adsorption of these intermediates was able to keep the binding network in the water bilayer via formation of hydrogen bonds with the neighboring *H₂O molecules. The hydrogen bonds interaction between water bilayer and the intermediates had a certain influence on the whole ORR process of Nb₂CO₂-V₀-Pt and Nb₂CF₂-V₁-Pt, and the overpotentials were changed (0.49V and 0.43 V). Besides, the rate-limiting steps of OER were turned to *O+H₂O →*OOH + H⁺ + e⁻ both on Nb₂CO₂-V₀-Pt and Nb₂CF₂-V₁-Pt. Accompanying with this, the OER overpotentials shifted from 0.39 to 0.64 V (Nb₂CO₂-V₀-Pt) and from 0.37 to 0.40 V (Nb₂CF₂-V₁-Pt). The above results indicated that, although water indeed influenced the absolute adsorption energy and free energy of the reactions, it didn’t significantly affect the general trend of the inherent catalytic properties.

**More calculation details**

The overall ORR reaction in the acidic environment was written in Eq (3), like that occurs on the cathode of a fuel cell in discharge:

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}
\]  

(3)

According to literatures, this ORR reaction proceeded via the 4-electron transfer pathways as shown in Eq 3a-3d:

\[
*+ \text{O}_2 (g) + \text{e}^- + \text{H}^+ \rightarrow *\text{OOH}
\]  

(3a)

\[
*\text{OOH} + \text{e}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} (l) + *\text{O}
\]  

(3b)

\[
\text{O}^* + \text{e}^- + \text{H}^+ \rightarrow *\text{OH}
\]  

(3c)

\[
*\text{OH} + \text{e}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} (l) + *
\]  

(3d)

In which * denoted an activity site on the catalyst, (l) and (g) represented liquid and gas phases, respectively. The adsorption energies of O-containing intermediates on the catalysts were
calculated by Eq (4)-(7):

\[
\Delta E_{O*} = E_{O*} - E_* - [E_{H_2O} - E_{H_2}]
\]  
\[\text{(4)}\]

\[
\Delta E_{OH*} = E_{OH*} - E_* - [E_{H_2O} - 1/2E_{H_2}]
\]  
\[\text{(5)}\]

\[
\Delta E_{OOH*} = E_{OOH*} - E_* - [2E_{H_2O} - 3/2E_{H_2}]
\]  
\[\text{(6)}\]

Where \(E_*\), \(E_{OOH*}\), \(E_{OH*}\), and \(E_{O*}\) referred to the total energies of the catalyst substrate without and with the adsorption of OOH, OH and O, respectively. And \(E_{H_2O}\) and \(E_{H_2}\) were the total energies of free H\(_2\)O and H\(_2\) molecules in gas phases, respectively. For each step, the reaction Gibbs free energy \(\Delta G\) was defined by the Eq (7)

\[
\Delta G = \Delta E + \Delta \text{ZPE} - T \Delta S + \Delta G_U + \Delta G_{pH}
\]  
\[\text{(7)}\]

Here, \(\Delta \text{ZPE}\) was the zero-point energy which could be obtained from the calculation of vibrational frequencies for the adsorbed species. \(\Delta S\) was the entropy of the reaction. In fact, the \(\Delta \text{ZPE}\) and the entropy of the adsorbed O-containing intermediates on different catalysts were found to have similar values (Table S4).

The OER was the reverse reaction of ORR that described in Eq (8):

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+
\]  
\[\text{(8)}\]

with the 4-electron transfer pathways given in Eq 8a-8d:

\[
\text{H}_2\text{O} (l) + * \rightarrow ^*\text{OH} + e^- + \text{H}^+
\]  
\[\text{(8a)}\]

\[
^*\text{OH} \rightarrow \text{O}^* + e^- + \text{H}^+
\]  
\[\text{(8b)}\]

\[
\text{H}_2\text{O} (l) + ^*\text{O} \rightarrow ^*\text{OOH} + e^- + \text{H}^+
\]  
\[\text{(8c)}\]

\[
^*\text{OOH} \rightarrow ^*+ \text{O}_2 (g) + e^- + \text{H}^+
\]  
\[\text{(8d)}\]
The computational $\Delta G$ for each step was used to determine the rate-determining step during the reactions. The theoretical maximum free energy change for ORR ($\Delta G_{\max}^{123}$) and OER ($\Delta G_{\max}^{123'}$) at equilibrium potential was obtained by

$$\Delta G_{\max}^{123} = \max \{ \Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d \} + 1.23V$$  \hspace{1cm} (9)$$

$$\Delta G_{\max}^{123'} = \max \{ -\Delta G_a', -\Delta G_b', -\Delta G_c', -\Delta G_d' \} + 1.23V$$  \hspace{1cm} (10)$$
References