

Theoretical insights into the hydrogen peroxide oxidation and reduction reactions on low-index Pt surfaces

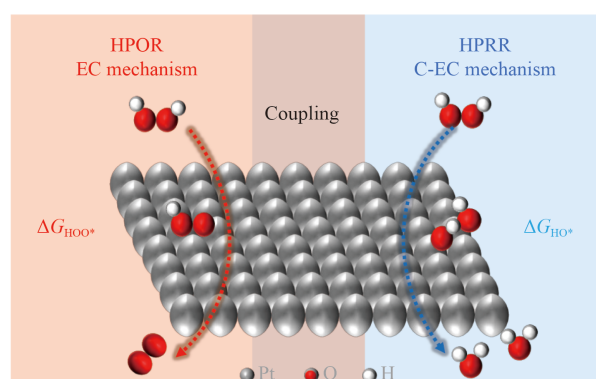
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Abstract: Hydrogen peroxide (H_2O_2) oxidation and reduction reactions (HPOR/HPRR) are pivotal in various innovative electrochemical energy conversion devices. A comprehensive understanding of these mechanisms is critical for catalyst design and performance improvement in these applications. In this work, we systematically investigate the HPOR/HPRR mechanisms on low-index Pt surfaces, specifically Pt(111), Pt(100) and Pt(110), through density functional theory (DFT) calculations combined with the computational hydrogen electrode (CHE) model. For HPOR, all the low-index Pt surfaces exhibit a unified potential-determining step (PDS) involving the electrochemical oxidation of hydroperoxyl intermediates (HOO^*). The binding free energy of HOO^* (ΔG_{HOO^*}) emerges as an activity descriptor, with Pt(110) exhibiting the highest HPOR activity. The HPRR mechanism follows a chem-electrochemical (C-EC) pathway. The rate-determining step (RDS) of HPRR is either the cleavage of the HO–OH bond (chemical) or the reduction of HO (electrochemical), depending on their respective activation energies. These activation energies are functions of the HO^* binding free energy, ΔG_{HO^*} , establishing ΔG_{HO^*} as the descriptor for HPRR activity prediction. Pt(111) and Pt(100) are identified as the most active HPRR catalysts among the studied metal surfaces, although they still experience a significant overpotential. The scaling relationship between ΔG_{HOO^*} and ΔG_{HO^*} reveals a thermodynamic coupling of HPOR and HPRR, explaining their occurrence on Pt surfaces. These findings provide important insights and activity descriptors for both HPOR and HPRR, providing valuable guidance for the design of electrocatalysts in H_2O_2 -related energy applications and fuel cells.

Key words: HPOR; HPRR; Pt low-index surfaces; density functional theory



Hydrogen peroxide (H_2O_2) oxidation reaction (HPOR, $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{e}^- + 2\text{H}^+$; $E = 0.695$ V vs. RHE) and H_2O_2 reduction reaction (HPRR, $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$; $E = 1.78$ V vs. RHE) play key roles in various innovative electrochemical devices, such as H_2O_2 electrolyzer^[1–2], direct- H_2O_2 fuel cell^[3–7], H_2O_2 sensors^[8–11], energy-storage systems with H_2O_2 as an energy carrier^[12], two-electron electrochemical oxygen pump^[13], and two-electron zinc-air batteries^[14]. Additionally, HPRR is also involved in the oxygen reduction reaction, which is the key reaction in the cathode of hydrogen fuel cells^[15]. A comprehensive understanding of the HPOR/HPRR mechanisms can guide

the design of electrocatalysts for these energy applications.

Researchers have made significant progress in understanding the HPOR/HPRR mechanisms through well-designed electrochemical experiments^[16–20]. The HPOR was proposed to occur through two distinct mechanisms. One mechanism proposed for a polycrystalline platinum (Pt) electrode is a non-electrochemical process. In this case, HPOR occurs at potentials where Pt–OH forms, which then drives the HPOR through a chemical step: $2\text{Pt}(\text{OH}) + \text{H}_2\text{O}_2 \rightarrow 2\text{Pt} + \text{O}_2 + 2\text{H}_2\text{O}$ ^[21]. In contrast, an electrochemical (EC) process was identified for a single-crystal Pt(111) electrode. The study investigated the pH-dependent

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catalytic activity of HPOR on Pt(111) and suggested that the mechanism involves two consecutive proton-coupled electron transfer (PCET) steps^[22]. For the HPRR, two mechanisms were proposed^[23–28]. Researchers examined the kinetic parameters of HPRR on metal catalyst, typically associated with Tafel slopes of 120 mV/decade, suggesting that HPRR is controlled by the initial charge transfer process and follows an EC mechanism^[27]. Other studies observed much larger Tafel slopes than 120 mV/decade for HPRR^[28], indicating the presence of a chemical step prior to the electrochemical process, known as the chem-electrochemical (C-EC) mechanism. These findings provide valuable insights into the HPOR/HPRR mechanisms. In summary, the mechanism of HPOR is generally accepted to follow a structure-dependent pathway: the chemical mechanism dominates on polycrystalline Pt, while the electrochemical mechanism is valid for Pt(111), thus presenting no major controversy. In contrast, the mechanism of HPRR is still debated. This is mainly because electrochemical measurements on different catalysts have produced inconsistent kinetic observations. However, the information obtained from electrochemical tests is still insufficient to fully explain the key intermediates, the rate-determining step (RDS), and effective descriptors to reveal the microscopic mechanisms of these reactions.

Theoretical calculations can provide detailed descriptions of reaction barriers and intermediate structures, helping to predict the RDS in the reaction pathways. Our group previously investigated the HPOR on the transition metal and nitrogen co-doped carbon (M-N-C) materials and metal phthalocyanine catalysts through the density functional theory (DFT) calculations^[1–2,29]. We found that the binding free energy of hydroperoxyl intermediates (HOO^*), ΔG_{HOO^*} , is the activity descriptor for HPOR on these types of catalysts, confirming that HPOR follows an EC mechanism. While Pt-based catalysts are recognized as the most active catalysts for HPOR/HPRR, our understanding of the mechanisms involved in these reactions is primarily based on extensive electrochemical experiments, as mentioned above. There are few theoretical calculations related to these mechanisms, with early computational research primarily focused on examining the adsorption behavior of H_2O_2 on low-index Pt crystal surfaces^[30–33]. Therefore, further theoretical investigations on Pt surfaces are essential to gain a comprehensive understanding of HPOR/HPRR mechanisms.

In this study, we systematically investigated the HPOR/HPRR mechanisms on calculations and the computational hydrogen electrode (CHE) model, as illustrated in Figure 1. For HPOR, we identify the electrochemical oxidation of HOO^* as the potential-determining step (PDS) across all Pt surfaces, with ΔG_{HOO^*} determining the thermodynamic limiting potential (U_L) and serving as a descriptor. For HPRR, we reveal a C-EC mechanism, where the overall reaction is controlled by the competitive activation energies (ΔE_a): the chemical cleavage step of the HO–OH bond and an electrochemical reduction of hydroxyl (HO^*).

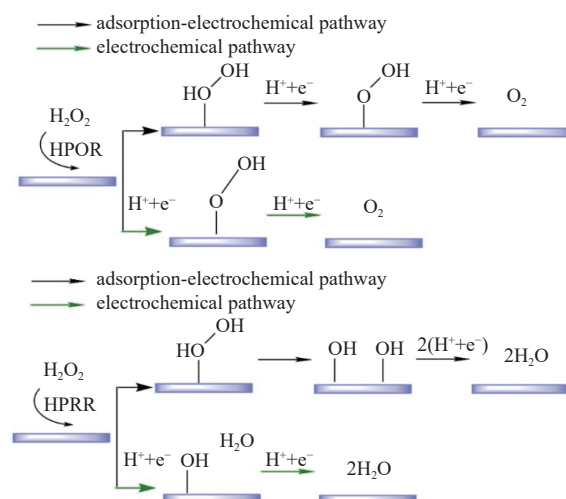


Fig. 1 Schematic illustration of the HPOR/HPRR reaction pathways over the Pt low-index surfaces

Crucially, both ΔE_a values are functions of the HO^* binding free energy (ΔG_{HO^*}), making ΔG_{HO^*} a reliable descriptor for predicting the HPRR activity. Pt(110) exhibits optimal activity for HPOR, while Pt(111) and Pt(100) show superior activity for HPRR. Notably, the intrinsic scaling relationship between ΔG_{HOO^*} and ΔG_{HO^*} enables the construction of a dual-activity volcano plot. The crossover region in this plot first establishes a mechanistic explanation for the experimentally observed reaction coupling phenomena. These mechanistic insights establish fundamental design principles for developing advanced electrocatalysts in H_2O_2 -based energy conversion systems.

1 Computational details

The Periodic density function theory (DFT) calculations were performed using the Vienna Ab-Initio Simulation Package^[34]. The exchange-correlation was described by the Perdew-Burke-Ernzerhof functional within the generalized gradient approximation (GGA)^[35]. The projector-augmented wave (PAW) method was employed to calculate electronic structures^[36]. The cut-off energy for all calculations was set to be 400 eV. Four layers were used to model three low-index Pt planes. A unit cell size of $(2\sqrt{3} \times 2\sqrt{3})$ was used for Pt(111), and a unit cell size of (3×3) was used for both Pt(100) and Pt(110), with sampling by $(4 \times 4 \times 1)$ Monkhorst–Pack k-point grid. The bottom two layers of the slab were fixed, while the top two layers, together with adsorbates and water, were allowed to relax. The conjugate gradient algorithm was employed for structure and transition state optimizations, with the convergence criterion set to a maximum Hellmann–Feynman force below 0.03 eV/Å. To ensure a reliable representation of an isolated system, a vacuum spacing of 15 Å was applied to minimize interactions between periodic images. Vander Waals interactions were incorporated into the calculations using the DFT-D3 dispersion correction method introduced by Grimme^[37]. To validate the feasibility of the EC pathway of

HPRR, a simulation without explicit water molecules was conducted. In this model, an adsorbed water molecule was introduced as the proton donor, aiming to examine whether hydrogen peroxide can be directly hydrogenated *via* an electrochemical step. The location and energy of the transition state were determined using the climbing image nudged elastic band (CI-NEB) method with four images between the initial and final states^[38–39].

The explicit solvent model is a viable approach to incorporate solvent effects^[40]. On the Pt(111) surface with hexagonal symmetry, water molecules tend to form dense, ice-like grids, stabilized significantly by a hexagonal hydrogen bond network. To simulate the explicit solvent model, a $2\sqrt{3}\times 2\sqrt{3}$ -R30° hexagonal water bilayer on Pt(111) was employed^[41–42]. Two stable square-arranged water structures on Pt(100) were obtained at coverages of 4/5 and 2/3 ML, with the 2/3 ML coverage being more thermodynamically stable, as reported previously^[43]. Accordingly, in the present work, the 2/3 ML coverage structure was chosen for the computational calculations.

As for the Pt(110) surface, no stable water structures have been reported. Thus, we evaluated the approximate surface energy of 4/5 and 2/3 ML coverage water structures on Pt(110) using the method proposed by Paul Clabaut et al.^[44] and found that the 2/3 ML coverage remains more thermodynamically stable. The water structures of 4/5 and 2/3 ML on Pt(110) are shown in Figure S1, and the detailed discussion can be found in the supporting information. The optimized water structures on the three Pt surfaces are shown in Figure S2. Ideally, the most thermodynamically stable surface water structure should also correspond to the lowest adsorption free energy of the intermediate. As shown in Figure S3, both configurations enable HO* to form hydrogen bonds with three neighboring water molecules. However, under the thermodynamically more stable 2/3 ML coverage, the adsorption free energy of HO* is unexpectedly higher than that under 4/5 ML. The reason for this discrepancy remains to be further investigated. Nevertheless, we believe that the thermodynamically more favorable water structure better aligns with the general principle for selecting surface water models.

The binding free energy (ΔG) was calculated using the computational hydrogen electrode (CHE) model proposed by Nørskov et al.^[45]. In this model, the electrode potential (U) is defined relative to the reversible hydrogen electrode (RHE), enabling the construction of free energy diagrams of electrochemical reactions. This method computes the binding free energy of each reaction intermediate at a given electrode potential as follows:

$$\Delta E_{\text{DFT}} = E_{\text{total}} - E_{\text{slab}} - E_{\text{ref}} \quad (1)$$

$$\Delta G(U) = \Delta E_{\text{DFT}} + \text{ZPE} - T\Delta S - neU \quad (2)$$

where E_{total} represents the total energy of intermediate and substrate, E_{slab} refers to the energy of the clean surface, and E_{ref} denotes the energy of k water molecules ($k = 0, 1$) and p hydrogen molecules ($p = 0.5, 1, 1.5$) in the gas phase. ΔE_{DFT}

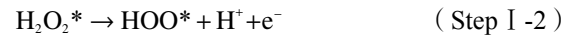
can be corrected to binding free energy, $\Delta G(U)$, by adding zero-point energy (ZPE), entropy, and electron energy as different electrode potential (neU), where T is 298.15 K, n represents the number of electrons transferred, and e is the elementary charge of an electron. In this study, all calculations were carried out at the single-site level, neglecting interactions between adsorbed species. Therefore, the potential influence of H_2O_2 concentration on adsorption energies and reaction kinetics was not considered.

2 Result and discussion

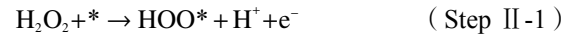
2.1 Adsorption of H_2O_2 and the intermediates involved in HPOR/HPRR

We systematically investigated the HPOR/HPRR mechanisms on three low-index platinum surfaces through comprehensive DFT calculations.

The HPOR pathway proceeds *via* the initial chemisorption of H_2O_2 (Step I -1), followed by two PCET processes leading to the formation of O_2 (Steps I -2 and I -3), detailed as follows:



Alternatively, a parallel pathway bypassing the initial adsorption step may occur:

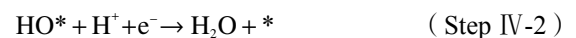
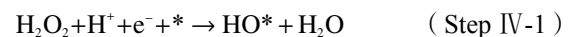


For HPRR, both C-EC and EC pathways were elucidated:

C-EC pathway of HPRR, initiated by the chemisorption of H_2O_2 (Step III-1), followed by a chemical cleavage of the HO–OH bond to form two HO* intermediates (Step III-2, chemical step). Subsequently, the two HO* intermediates undergo two PCET steps to form two H_2O molecules (Steps III-3 and III-4):



EC pathway of HPRR proceeds through sequential PCET steps with a single HO* intermediate:



In the HPOR mechanism, the intermediates H_2O_2^* and HOO^* are involved. For HPRR, the intermediates include

H_2O_2^* , two HO^* species, and a single HO^* species. Through comprehensive DFT simulations, we identified the preferred adsorption configurations of H_2O_2 and intermediates involved in HPOR/HPRR in the presence of a water overlayer on the three low-index Pt surfaces, as shown in Figure 2. In Figure 2(a), it is demonstrated that H_2O_2 prefers to adsorb at the top site on all three surfaces, with one O atom bonded to a Pt atom. Figure 2(b) indicates that HOO^* adsorbs at the top site of a Pt atom *via* monodentate and perpendicular adsorption on the Pt(111) surface and Pt(110). On the Pt(100) surface, HOO^* adsorbs at the bridge site, where the non-hydrogenated O atom forms bonds with two Pt atoms. Figure 2(c) displays the co-adsorption configurations of two HO^* intermediates, with the top site remaining in the favored position across all surfaces. In Figure 2(d), a single HO^* prefers to adsorb at the top site for Pt(111) and Pt(110). In contrast, on the Pt(100) surface, the bridge site is favored for HO^* adsorption. With the above discussion, the following sections will discuss the intrinsic characteristics of the HPOR/HPRR, elucidating effective descriptors. The detailed calculation functions and data are displayed in the supporting information and Table S1. Notably, the adsorption free energy of H_2O_2 exhibits a positive value, which is inconsistent with the expected physical behavior. This apparent overestimation stems from the choice of surface water as the reference state. Since surface water retains only vibrational degrees of freedom compared to gas-phase water, its entropy is lower, leading to an overestimated adsorption free energy^[46]. Moreover, the adsorption behavior of H_2O_2 is notably influenced by surface charge^[22], making the analysis more intricate. In our discussion, we do not identify the adsorption step as the RDS of the overall process.

2.2 HPOR mechanisms on low-index Pt surfaces

Figure 3(a) illustrates the free energy diagrams of the HPOR pathway that involves H_2O_2 adsorption at the equilibrium potential ($U^0 = 0.695 \text{ V}$). Using water as the reference state, H_2O_2 is generated *via* two proton-electron transfers, followed by another two to form O_2 . To reconcile the electrode's electron transfer framework, we explicitly treat H_2O_2 reacting with $2(\text{H}^+ + \text{e}^-)$ in both HPOR and HPRR. Among the three Pt surfaces, H_2O_2 adsorption is relatively more favorable on Pt(111). Similarly, Step I -3 is uphill on all three Pt surfaces and is identified as PDS. The energy barrier of Step I -3 follows the trend: $\text{Pt}(110) < \text{Pt}(111) < \text{Pt}(100)$, with the activity sequence: $\text{Pt}(110) > \text{Pt}(111) > \text{Pt}(100)$. A similar analysis for the pathway (Figure 3(b)), which bypasses surface adsorption, identifies Step II -2 as the PDS, maintaining identical surface activity trends due to the shared ΔG_{HOO^*} .

The U_L represents the minimum electrode potential required to drive an electrochemical reaction, ensuring the overall step is thermodynamically downhill. Figure 3(c) shows the influence of adsorption on U_L . Here, U_L is defined as the maximum of U_{L1} and U_{L2} , both being functions of ΔG_{HOO^*} , expressed as follows:

$$U_{L1} = \Delta G_{\text{HOO}^*} - \Delta G_{\text{H}_2\text{O}_2^*} \quad (3)$$

$$U_{L2} = 4.92 - \Delta G_{\text{HOO}^*} \quad (4)$$

$$U_L = \max(U_{L1}, U_{L2}) \quad (5)$$

The gray-shaded region in the figure indicates that the U_L is lower than U^0 , implying that the reaction is thermodynamically forbidden.

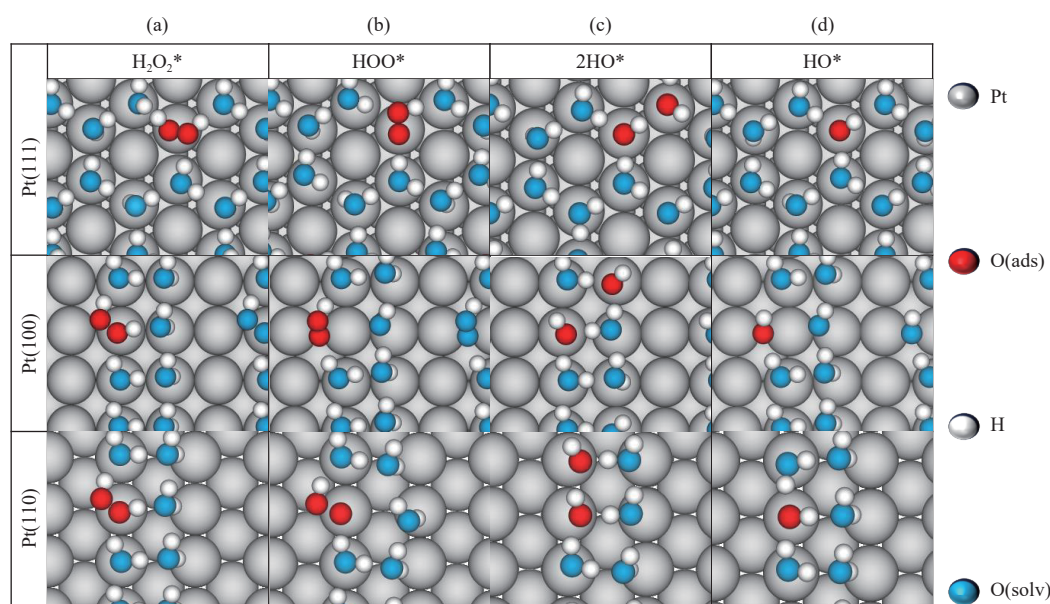


Fig. 2 Top views of the optimized configurations for (a) H_2O_2^* , (b) HOO^* , (c) two HO^* and (d) one HO^* on the three low-index Pt surfaces

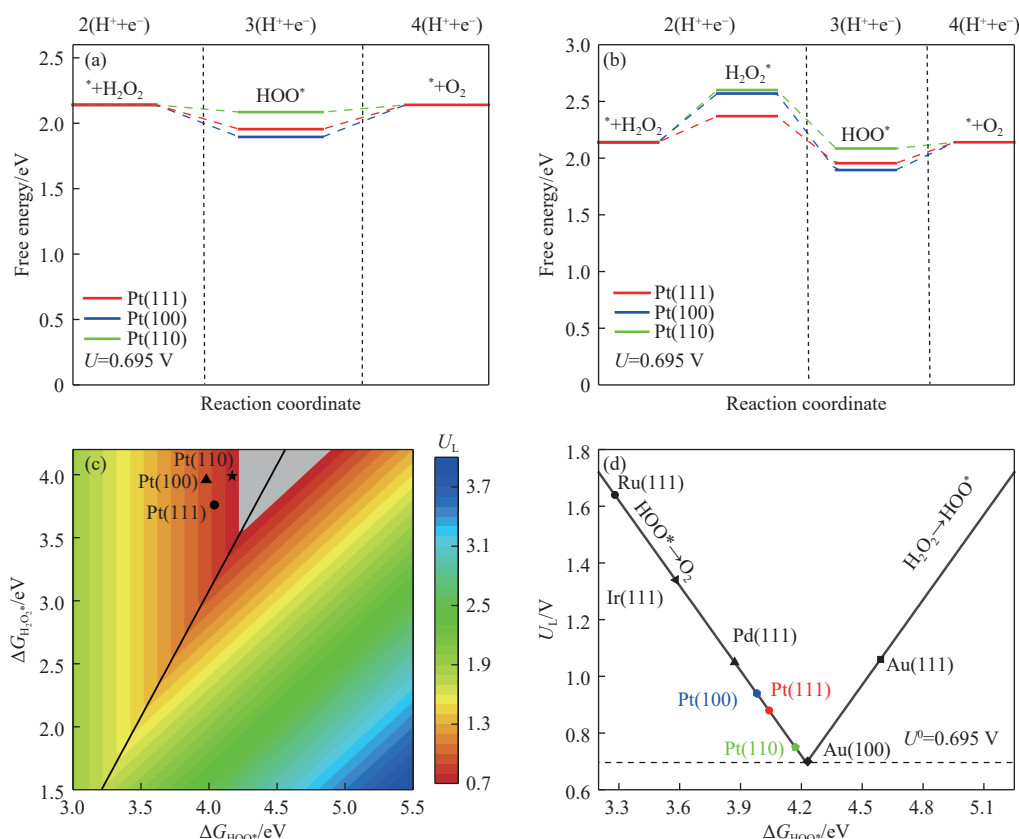


Fig. 3 (a) Free energy diagrams for HPOR with H₂O₂ adsorption at U⁰ = 0.695 V vs. RHE. (b) Free energy diagrams for HPOR without H₂O₂ adsorption at U⁰ = 0.695 V vs. RHE. (c) Contour plot of U_L for HPOR versus ΔG_{H₂O₂*} and ΔG_{HOO*} of HPOR in the C-EC pathway. (d) Volcano plot of U_L for HPOR as a function of ΔG_{HOO*}. The ΔG_{HOO*} values for other metal catalysts are obtained from Kulkarni et al.^[47–48]

The solid line denotes the condition where U_{L1} equals U_{L2}. To the left side of the solid line, Step I -3 is the PDS with U_L = U_{L2}. To the right side, Step I -2 is the PDS with U_L = U_{L1}. When ΔG_{H₂O₂*} approaches 3.53 eV and ΔG_{HOO*} approaches 4.225 eV, U_L is closest to U⁰, indicating the optimal reaction activity. For the three Pt surfaces positioned on the left side, Step I -3 is the PDS, and U_L is determined by Eq. (4).

Figure 3(d) shows the volcano plot of U_L versus ΔG_{HOO*} for the pathway that bypasses H₂O₂ adsorption. The U_L is defined as the maximum of U_{L1} and U_{L2}, which are functions of ΔG_{HOO*}, expressed as follows:

$$U_{L1} = \Delta G_{HOO^*} - 3.53 \quad (6)$$

$$U_{L2} = 4.92 - \Delta G_{HOO^*} \quad (7)$$

$$U_L = \max(U_{L1}, U_{L2}) \quad (8)$$

At the peak of this plot, the HPOR occurs at a thermodynamic overpotential (η) of 0 V, corresponding to an ideal ΔG_{HOO*} value of 4.225 eV. Here, η is defined as the difference between U_L and U⁰. To the left of the peak, strong HOO* binding results in Step II -2 being the PDS of the reaction. Conversely, on the right side of the peak, weak HOO* binding leads to Step II -1 becoming the PDS. Since only one HOO* intermediate is involved, it serves as a

descriptor for predicting HPOR activity. For all low-index Pt surfaces, Step II -2 is identified as the PDS. Among these, Pt(110) has a ΔG_{HOO*} value closest to 4.225 eV, resulting in an η of 0.055 V, lower than the η of 0.185 and 0.245 V predicted for the Pt(111) and Pt(100), respectively. Notably, Pt(110) exhibits the highest HPOR activity among the three low-index surfaces.

To further validate the applicability of the descriptor proposed in this work, we also evaluated the HPOR activity of metal catalysts using ΔG_{HOO*} values obtained from Kulkarni et al.^[47–48]. The ΔG_{HOO*} values for Pd(111) and Au(111) fall on opposite sides of the volcano plot, positioned further from the peak compared to the three Pt surfaces. This positioning indicates relatively lower HPOR activity for Pd and Au relative to Pt, consistent with the experimental results^[49]. Additionally, Ru(111) and Ir(111) exhibit excessively strong adsorption of HOO* intermediates, resulting in weak HPOR activity. In contrast, Au(100), located near the volcano peak, is predicted to show superior HPOR activity.

For all three Pt surfaces, free energy diagrams confirm the strong HOO* binding free energies as a limiting factor for reaction rates. ΔG_{HOO*} can be considered a descriptor to predict the HPOR activity of Pt surfaces. Pt(110) with optimal ΔG_{HOO*} value exhibits the highest HPOR activity.

2.3 HPRR mechanisms on low-index Pt surfaces

Figure 4(a) shows the C-EC pathway free energy diagram for HPRR (solid line) at an electrode potential of 0.9 V. Among all three Pt surfaces, the Pt(111) surface shows relatively easier adsorption of H_2O_2 . In addition, the chemical process (Step III-2) and the PDS (Step III-3 and Step III-4) contribute to the overall reaction. Using U_L as a metric for assessing catalytic activity is not reliable. Instead, we employ activation energy (ΔE_a) as an alternative metric to better reflect catalytic activity.

We define ΔE_{a1} as the activation energy of Step III-2. It is expressed as a function of ΔG_{HO^*} :

$$\Delta E_{a1} = 0.3698\Delta G_{\text{HO}^*} - 0.0621 \quad (9)$$

The coefficients and intercepts were obtained by fitting the data extracted from the literature based on the Brønsted–Evans–Polanyi (BEP) relationship^[50–51], as shown in Figure S4. This approach was chosen to efficiently capture the activity trends of different catalysts^[52]. Notably, instead of explicitly identifying the transition state structures, we adopt a semi-quantitative approach to estimate ΔE_{a1} . However, this approximation introduces deviations due to the absence of explicit transition state

calculations.

We define ΔE_{a2} and ΔE_{a3} as the activation energies of Step III-3 and Step III-4. The constant-charge model in the CHE framework makes it unsuitable for calculating potential-dependent activation barriers. Although grand-canonical density functional theory (GC-DFT) enables the accurate determination of potential-dependent transition states^[53–54], its practical application is limited by the high computational cost associated with large-scale interface models and extensive sampling. Alternatively, estimating activation energies using the BEP relationship is intended to capture general activity trends rather than to precisely locate the transition state. Thus, the ΔE_{a2} and ΔE_{a3} at different electrode potentials are estimated using Eq. (11) and Eq. (12), as proposed by Tripković et al.^[55]:

$$U_0 = \Delta G_i^0 / e \quad (10)$$

$$\Delta E_{a2} = 0.5(\Delta G_{2\text{HO}^*} - \Delta G_{\text{HO}^*} - eU) + E_{a0} \quad (11)$$

$$\Delta E_{a3} = e\beta(U_0 - U) + E_{a0} = \beta(\Delta G_{\text{HO}^*} - eU) + E_{a0} \quad (12)$$

where U_0 is the reversible potential, corresponding to the limiting potential at which this step is thermoneutral. ΔG_i^0 is the reaction free energy at 0 V versus RHE. β is the transfer coefficient with a value of 0.5^[56–57].

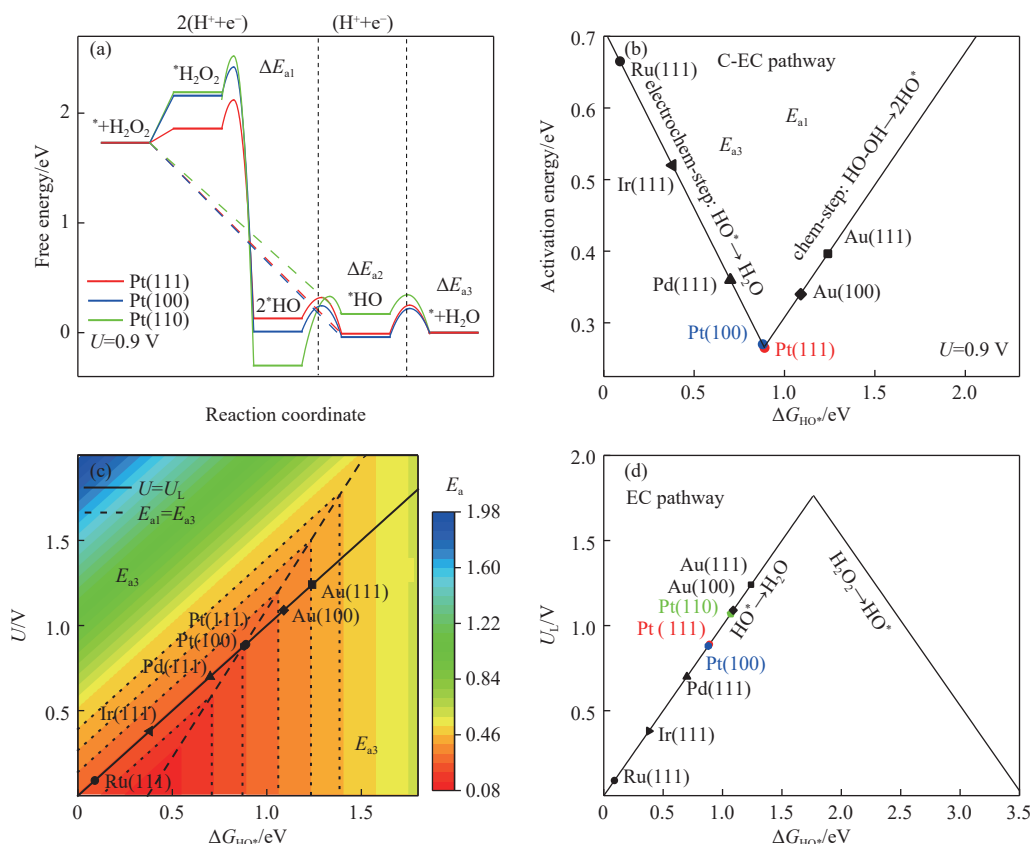


Fig. 4 (a) Free energy diagrams for HPRR at $U = 0.9$ V vs. RHE. The solid line represents the C-EC pathway, while the dashed line represents the EC pathway. (b) A volcano plot of activation energy of HPRR versus ΔG_{HO^*} at $U = 0.9$ V vs. RHE in the pathway with Step III-4 serves as the PDS. (c) Contour plot of activation energy of HPRR as a function of ΔG_{HO^*} at various U in the C-EC pathway, with Step III-4 serving as the PDS. (d) A volcano plot of U_L of HPRR as a function of ΔG_{HO^*} in the EC pathway

The ΔG_{HO^*} values for other metal catalysts were obtained from Nørskov et al.^[47–48]

E_{a0} is the activation energy of 0.26 eV when the electrode potential reaches the U_0 , representing the intrinsic barrier for proton transport from the bulk water to the specific site. eU is the potential-related term in the electrochemical step. The ΔE_a is the maximum of ΔE_{a1} , ΔE_{a2} and ΔE_{a3} , and a smaller ΔE_a indicates higher activity, expressed as:

$$\Delta E_a = \max(\Delta E_{a1}, \Delta E_{a2}, \Delta E_{a3}) \quad (13)$$

As shown in Figure 4(a), on the Pt(111) surface, the adsorbed H_2O_2 dissociates into the two HO^* species, with a ΔE_{a1} of 0.260 eV. The subsequent electrochemical step, Step III-4, involving an uphill process with a ΔE_{a3} of 0.265 eV, emerges as the PDS of HPRR. The PDS on Pt(100) surface is the same as that on Pt (111), with a slightly higher ΔE_{a3} of 0.270 eV. On the Pt(110) surface, the adsorption of a single HO^* species is weak, while the co-adsorption of HO^* is relatively stronger, making Step III-3 the PDS with a greater ΔE_{a2} of 0.36 eV. The low free energy of the co-adsorption of HO^* suggests poisoning or site blocking, thereby limiting the overall HPRR activity on Pt(110). In conclusion, the observed activation energy establishes the activity sequence as Pt(111) > Pt(100) > Pt(110).

When considering Step III-4 as the PDS ($\Delta E_a = \max(\Delta E_{a1}, \Delta E_{a3})$) under an electrode potential of $U = 0.9$ V, we construct a volcano plot illustrating the ΔE_a versus ΔG_{HO^*} using Eq. (9) and Eq. (12), as shown in Figure 4(b). The volcano apex at $\Delta G_{HO^*} = 0.888$ eV according to the optimal Sabatier condition, where ΔE_a reaches its minimum. Pt(111) and Pt(110) are very close to this peak, resulting in a high HPRR activity. Since Step III-3 is the PDS for Pt(110), this surface is not shown in Figure 4(b). Furthermore, we applied this model to other metal catalysts, with ΔG_{HO^*} values obtained from Kulkarni et al.^[47–48]. Pd(111) and Au(111) are located on the left and right sides of the volcano plot, respectively, with Pd being closer to the peak. Accordingly, Pd exhibits higher activity toward HPRR than Au, though slightly inferior to that of Pt, which is consistent with experimental observations^[49]. Based on the volcano plot, Au(100) is anticipated to possess favorable HPRR activity. In contrast, Ru and Ir are predicted to exhibit low activity due to their overly strong adsorption of HO^* intermediates. These results suggest that ΔG_{HO^*} can serve as a descriptor for HPRR activity.

Figure 4(c) shows the $\Delta E_a = \max(\Delta E_{a1}, \Delta E_{a3})$ as a function of ΔG_{HO^*} at different U , where Step III-4 serves as the PDS. The U_L determines the onset potential and is solely related to the removal of HO^* , which is expressed as:

$$U_L = \Delta G_{HO^*} \quad (14)$$

The solid line represents the U_L for Step III-4. The inclined dotted lines represent the contours of ΔE_{a3} , while the vertical dotted lines represent the ΔE_{a1} . The dashed line represents the condition where ΔE_{a1} equals ΔE_{a3} . On the left side of the dashed line, ΔE_{a3} is higher than ΔE_{a1} , while on the right side, ΔE_{a1} surpasses ΔE_{a3} . The intersection of the solid and dashed line represents that at the onset of HPRR,

ΔE_{a1} and ΔE_{a3} are identical with the ΔG_{HO^*} value of 0.871 eV, corresponding to the optimal catalytic activity. Pt(111) and Pt(100) near this intersection point are ideal HPRR catalysts. When $U = U_L$, where ΔG_{HO^*} is lower than 0.871 eV (as observed in Pd), the activation energy of the electrochemical step, Step III-4, is higher and becomes the RDS, and the activity increases with the overpotential. As ΔG_{HO^*} weakens more than 0.871 eV (as seen with Au), Step III-2 becomes the RDS, and the activity is independent of the overpotential.

Figure 4(a) also illustrates the free energy diagram of HPRR through the EC pathway (dashed lines) at 0.9 V vs. RHE. Analysis of the three low-index Pt surfaces reveals that the PDS corresponds to the conversion of HO^* to H_2O (Step IV-2). Figure 4(d) shows a volcano-type relationship between U_L and ΔG_{HO^*} . For the two reaction steps of HPRR, U_L is defined as the lower value between U_{L1} and U_{L2} , expressed as:

$$U_{L1} = 3.53 - \Delta G_{HO^*} \quad (15)$$

$$U_{L2} = \Delta G_{HO^*} \quad (16)$$

$$U_L = \min(U_{L1}, U_{L2}) \quad (17)$$

According to the volcano plot, the HPRR activity of Au(111) is predicted to be higher than that of Pt(111). However, experimental observations contradict this prediction, with Pt(111) demonstrating significantly better HPRR activity^[49]. This discrepancy challenges the validity of the EC pathway for describing HPRR on these metallic surfaces. It is worth noting that Au(111) already represents one of the weakest HO^* binding surfaces among known metal catalysts. Therefore, no data points appear on the weak-binding side of the volcano plot.

Comparative analysis of the C-EC and EC pathways (Figure 4(a)) suggests Step IV-2 in the EC pathway is thermodynamically favored due to its highly exothermic nature. However, our calculations using the climbing image nudged elastic band (CI-NEB) method for the ΔE_a of this step failed to converge, indicating unexpected kinetic limitations. This issue may arise from the limited proton-accepting capability of H_2O_2 as a Brønsted acid during the reaction process. Instead, the activity sequence predicted by the C-EC pathway shows better alignment with experimental observations across Pt, Pd and Au catalysts. Therefore, we propose that the HPRR follows the C-EC pathway. The C-EC pathway successfully explains the purely electrochemical control for HPRR on strongly adsorbing catalysts and the chemical-electrochemical mixed control on weakly adsorbing catalysts. Furthermore, it clarifies the HPRR failing to reach the theoretical onset potential of 1.76 V, as weak HO^* adsorption not only elevates the onset potential but also impedes critical $HO-OH$ bond cleavage.

2.4 The coupling of HPOR and HPRR

Experimental studies have revealed significant coupling

between HPOR and HPRR on the Pt surfaces^[58–60]. The associated potential loss consequently reduces the efficiency of hydrogen peroxide-based energy conversion devices^[59]. To elucidate this phenomenon, we analyze the U_L derived from the HPOR and the C-EC pathway for HPRR with Step III-4 as the PDS. As described above, the ΔG_{HOO^*} and ΔG_{HO^*} serve as activity descriptors for HPOR and HPRR, respectively. Utilizing the established linear scaling relationship between ΔG_{HOO^*} and ΔG_{HO^*} ($\Delta G_{\text{HOO}^*} = \Delta G_{\text{HO}^*} + 3.2$)^[47], we plotted the U_L of HPOR and HPRR as functions of ΔG_{HO^*} in Figure 5. Notably, our calculated results also follow this linear trend. As shown in Figure S5, both OH^* and OOH^* exhibit hybridization between the O $2p$ orbitals and the metal d -band. When the d -band center of the metal shifts, the adsorption strengths of both intermediates change concurrently, giving rise to the observed scaling relationship. Compared to HO^* , HOO^* exhibits a broader hybridization range and significant hybridization above the Fermi level. As a result, HOO^* has weaker adsorption than OH , leading to an energy difference of approximately 3.2 eV. The electronic structure of different metal surfaces simultaneously affects the adsorption strength of both HO^* and HOO^* , which leads to the intrinsic coupling between HPOR and HPRR.

As shown in Figure 5, the red-shaded region indicates where HPOR tends to occur. The blue-shaded region is split into two parts: when ΔG_{HO^*} is less than 0.871 eV, the HPRR is governed by electrochemical steps; when ΔG_{HO^*} is greater than 0.871 eV, the HPRR is controlled by chemical steps.

Notably, an overlapping area is observed where $\Delta G_{\text{HO}^*} > 0.86$ eV. In this overlapping region, the U_L for HPRR is higher than that for HPOR, indicating the co-occurrence of HPOR and HPRR, known as the coupling of HPOR and HPRR. This coupling is especially favorable when ΔG_{HO^*} lies between 0.871 and 1.025 eV. Pt(111) and Pt(100), positioned within the overlapping region, are significantly conducive to the coupling of HPOR and HPRR.

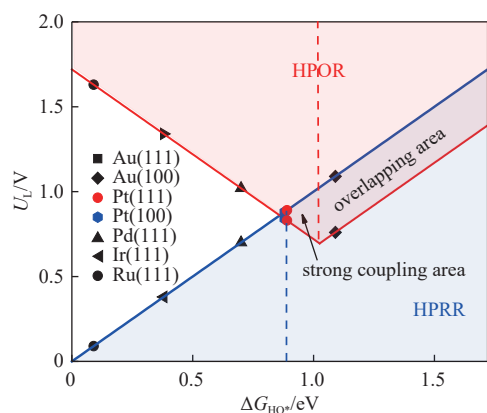


Fig. 5 U_L of HPOR and HPRR as a function of ΔG_{HO^*} . U_L obtained from the EC mechanism for HPOR and C-EC mechanism for HPRR with Step III-4 as the PDS. The red line represents the U_L of HPOR, while the blue line represents the U_L of HPRR. The ΔG_{HO^*} values for other metal catalysts are obtained from Nørskov et al^[47–48].

Au also falls within the overlapping range, but the coupling between HPOR and HPRR is limited due to the relatively weak adsorption of HO^* , which hinders the chemical step and is not reflected in the analysis of U_L . For Pd, Ru and Ir, which are situated outside of the overlapping region, the coupling of HPOR and HPRR is theoretically unlikely to occur. Ultimately, the coupling of HPOR and HPRR arises from the linear scaling relationship between HOO^* and HO^* . The optimal ΔG_{HO^*} is 1.025 eV for HPOR and 0.871 eV for HPRR. On Pt surfaces, where ΔG_{HO^*} is close to these optimal values, exhibit high HPOR/HPRR activities, leading to a strong coupling between HPOR and HPRR.

To mitigate the efficiency losses of H_2O_2 -related energy transfer applications caused by the coupling of HPOR and HPRR, we propose two strategies to decouple these reactions. One strategy involves disrupting the scaling relationship between ΔG_{HOO^*} and ΔG_{HO^*} by manipulating adsorption properties, such as altering the configuration of intermediates or inducing a second adsorption site^[61–62]. Another strategy is to alter the adsorption site of intermediates, leveraging the ensemble effect to control the reaction pathway. For instance, using single-atom hot-spots alloys increases the binding energy of HO^* co-adsorption, $\Delta G_{(\text{HO-Pt} + \text{HO-M})}$, which raises the activation energy of the cleavage of the HO-OH bond. Consequently, this approach possibly suppresses HPRR activity and improves HPOR selectivity. These strategies may provide valuable insights into the design of effective catalysts.

3 Conclusion

We conducted a comprehensive investigation into the HPOR/HPRR mechanisms on three low-index Pt surfaces using DFT calculations and the CHE model. For HPOR, the predicted activity follows $\text{Pt}(110) > \text{Pt}(111) > \text{Pt}(100)$, where the electrochemical oxidation of HOO^* is the PDS. The ΔG_{HOO^*} is identified as the activity descriptor with an optimal value of 4.225 eV. For HPRR, comparative analysis of C-EC and EC pathways confirms the dominance of the C-EC mechanism, aligning with experimental observations. The ΔE_a for both the chemical and electrochemical steps is a function of ΔG_{HO^*} . ΔG_{HO^*} can act as a descriptor for HPRR activity, with the predicted activity order being $\text{Pt}(111) > \text{Pt}(100) > \text{Pt}(110)$. Furthermore, our investigation revealed that the scaling relationship between ΔG_{HO^*} and ΔG_{HOO^*} leads to a strong coupling of HPOR and HPRR on Pt surfaces. Overall, this study enhances our understanding of HPOR and HPRR on Pt surfaces and provides valuable guidance for developing more efficient electrocatalysts, advancing H_2O_2 -related energy applications.

Declaration of Competing Interest

The authors declare no conflict of interest.

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基于理论计算的低指数 Pt 表面过氧化氢氧化还原反应机理研究

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摘 要: 过氧化氢 (H_2O_2) 的氧化还原反应 (HPOR/HPRR) 在多种新型电化学能量转换装置中具有重要作用。深入理解其反应机理对于催化剂的设计与性能优化具有关键意义。本工作基于密度泛函理论 (DFT) 计算, 并结合计算氢电极 (CHE) 模型, 系统研究了低指数铂表面 (Pt(111)、Pt(100) 和 Pt(110)) 上 HPOR/HPRR 的反应路径。对于 HPOR, 所有低指数 Pt 表面均呈现出统一的电位决定步骤, 即 HOO^* 中间体的电化学氧化。 HOO^* 的结合自由能 (ΔG_{HOO^*}) 可作为 HPOR 活性描述符, 其中, Pt(110) 晶面活性最佳, 其 HOO^* 吸附自由能 (ΔG_{HOO^*}) 为 4.17 eV, 最接近理想值 4.225 eV。HPRR 则遵循化学-电化学 (C-EC) 路径, 其速率决定步骤可能为 $\text{HO}-\text{OH}$ 键的化学解离或 HO^* 的电化学还原, 具体取决于两者的活化能高低。这些活化能与 HO^* 的结合自由能 (ΔG_{HO^*}) 相关, 从而确立 ΔG_{HO^*} 为预测 HPRR 活性的关键描述符。在活化能相关的火山图中, 最优材料的 ΔG_{HO^*} 为 0.888 eV, Pt(111) 与 Pt(100) 面接近这一值, 因而表现出很高的 HPRR 活性, 尽管仍存在较大的过电位。此外, ΔG_{HOO^*} 与 ΔG_{HO^*} 之间的线性关系揭示了 HPOR 与 HPRR 之间的热力学耦合, 为其在 Pt 表面上的耦合提供了解释。本研究结果不仅加深了对 HPOR 和 HPRR 反应机制的理解, 也为过氧化氢相关能量装置与燃料电池中电催化剂的设计提供了重要的理论指导。

关键词: 过氧化氢氧化反应; 过氧化氢还原反应; 低指数铂表面; 密度泛函理论

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