Circumventing the Sabatier Principle in Electrocatalysis:
the Case of Oxygen Reduction Reaction on Au(100) in Alkaline Medium

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Abstract: The barriers for elementary steps in the oxygen reduction reaction (ORR) catalyzed on Au(100) in alkaline solution are mapped out by ab initio molecular dynamics simulations. Due to the relatively weak binding energy of O2 and oxygenated species, the calculated O–O dissociation barrier at ~0.5 eV is indeed considerably higher than the association barrier (< 0.1 eV) to form adsorbed HOO*, pushing ORR towards the thermodynamically less favorable 2e− pathway. However, the kinetics is changed above the equilibrium potential for the association channel ~0.7 V (RHE) where the 2e− pathway is switched off. Thereafter, the 4e− pathway becomes active as the O–O dissociation barrier at ~0.5 eV is not prohibitive. For the subsequent reduction steps, the weak binding energies of oxygenated species on Au(100) are actually an advantage, making Au(100) as good an ORR catalyst as Pt. It also makes the outer sphere electron transfer to O2 as the eventual rate determining step, as supported by the j-E polarization curve, showing a small ORR current extending close to the overall 4e− ORR equilibrium potential of 1.23 V. It provides an example on how the ORR activity volcano curve based on the Sabatier Principle can be circumvented in electrocatalysis.

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Introduction

Pt is the best catalyst for oxygen reduction reaction (ORR).\textsuperscript{1,3} It can be explained by the well-known Sabatier Principle for catalysis: the binding energy between the reactant and the catalyst should be neither too strong nor too weak. It should be strong enough so that the bonds in the reactant are activated, but not too strong to block the subsequent desorption of products.\textsuperscript{4,5} For ORR, this principle can be expressed as a volcano curve, obtained by plotting the ORR catalytic activity against the adsorption energy of oxygenated species calculated by density functional theory (DFT).\textsuperscript{6} Among metal catalysts, Pt indeed occupies the central position, with moderate adsorption energy for oxygenated species and the highest catalytic activity, which is consistent with the Sabatier Principle. Much of the current search for a better catalyst for ORR, which is one of the key challenges in fuel cell technology, relies on this principle, with efforts directed at either lowering the content of the expensive Pt or finding materials with binding energy of oxygenated species close to the center of the ORR volcano curve.\textsuperscript{2,5,7}

In contrast, Au has been cited as an example of unfavorable catalytic activity for ORR, as the adsorption energies of oxygenated species are weak, putting Au near the volcano’s foothill.\textsuperscript{6} It explains the experimental observations that ORR on Au electrodes generally goes through the 2e\textsuperscript{−} pathway, leading to the formation of H\textsubscript{2}O\textsubscript{2} or OOH\textsuperscript{−} depending on the pH, which is less efficient for producing current than the 4e\textsuperscript{−} pathway on Pt catalysts.\textsuperscript{8-15} However, when the electrode potential is above 0.7 V (RHE) in alkaline solution, the ORR on Au(100) becomes a 4e\textsuperscript{−} process, and in fact the current is slightly better than that on Pt(111).\textsuperscript{8-9,16} While this has been observed only on Au(100) within a narrow potential window (0.7~1.0 V RHE), it does fall into an important range for the optimal performance of fuel cells and pose a challenge to the Sabatier Principle and the ORR volcano plot.\textsuperscript{17}

A number of factors have been suggested, such as the presence of either OH* or OOH*,\textsuperscript{12-13} the promotion effects of H\textsubscript{2}O solvent,\textsuperscript{17-18} or the disproportionation of HOO\textsuperscript{−}.\textsuperscript{19} The formation of OOH* in the presence of H\textsubscript{2}O\textsuperscript{18} and the stability of OOH* in the presence of OH*\textsuperscript{20} have been examined by DFT calculations. For ORR in alkaline solution, it has been suggested that the initial and the rate determining step (RDS) is an outer sphere reaction, with O\textsubscript{2} capturing an electron from the electrode.\textsuperscript{21-22} For ORR on Au(100), such an outer sphere process has been examined systematically.\textsuperscript{23-26} Nonetheless, the overall mechanism remains unclear and disputed.\textsuperscript{27-28}
It’s well known that mapping out the reaction path for an electrochemical reaction is challenging, due to the complexity in the interfacial region, the dynamic nature of electrode processes in the presence of a solution layer, and the difficulties to deal with the effects of electrode potential. In recent years, it has become possible to simulate such reactions with more realistic models, including explicit solvent water molecules and DFT based AIMD (ab initio Molecular Dynamics) simulations for the solvation and entropic effects. Relevant to our current study are recent AIMD simulations of ORR reaction steps on Pt(111) in both acid and alkaline solutions. Based on the changes in the kinetics of the hydrogenation of OH* and the two competing hydrogenation channels of O* with varying electrode potential, a consistent account can be worked out for the main electrochemical observations, including the irreversible feature in the oxide region of the cyclic voltammogram, the starting potential for the decrease of ORR current, the high onset overpotential, and the shape of the polarization curve.

In this paper, we report the results of AIMD simulations on the ORR mechanism on Au(100) in alkaline solution. The kinetic factors underlying the excellent performance in the 4e\textsuperscript{−} ORR region are identified. The mechanism is analyzed in comparison to the ORR mechanism on Pt(111), and the \( j-E \) polarization curve is re-examined in light of these new mechanistic understandings, demonstrating how the Sabatier Principle and the ORR volcano curve are circumvented.

Results and Discussions

**Spin state and \( O_2 \) adsorption on Au(100)**

\( O_2 \) molecule is a diradical with its ground state being a triplet. When an \( O_2 \) is put close to Au(100), DFT calculations could lead to artificial change in the spin and the triplet state of \( O_2 \) could not be conserved. Geometric optimization would produce the structure shown in Figure 1a, with \( O_2 \) in the singlet state. Such an \( O_2^* \) is only 0.16 eV lower in energy than a triplet \( O_2 \) far away from Au(100), in agreement with previous reports. However, it would be incorrect to attribute this structure to physisorption, just based on its low adsorption energy. The Au–O distance is around 2.2 Å, comparable to the Au–O distance of 2.01–2.07 Å in \( \text{Au}_2\text{O}_3 \) crystal. The Bader charge on \( O_2^* \) is at \(-0.5\text{e}\), while the O–O distance upon adsorption is elongated to 1.33 Å, a significant increase from the O–O distance of either triplet \( O_2 \) (1.21 Å) or singlet \( O_2 \) 1.23 Å. In
other words, it’s actually a chemisorbed structure, with Au–O bonding interactions, superoxide O–O bond and significant negative charge on \( \text{O}_2^* \).

![Figure 1: Optimized adsorption structure for \( \text{O}_2^* \) on Au(100) by spin polarized DFT calculations with the spin state forced to stay as either singlet or triplet. (a) singlet adsorbed structure (chemisorption); (b) triplet adsorbed structure (physisorption); (c) the minimum potential energy paths for the singlet and triplet state, respectively, obtained from elastic band calculations with Configuration 0 being an \( \text{O}_2 \) at 6 Å above the surface and Configuration 9 being adsorbed \( \text{O}_2^* \).](image)

A more realistic evaluation of the interaction between \( \text{O}_2 \) and Au(100) is obtained by spin-polarized calculations with spin restriction to force the system to stay either as a triplet or a singlet. In the triplet state, a physisorbed \( \text{O}_2 \) is indeed optimized, as shown in Figure 1b. Furthermore, without spin transformation, a triplet \( \text{O}_2 \) approaching Au(100) passes through a flat energy surface into a shallow physisorption well, as shown in Figure 1c. Here, it is instructive to compare the cases of Si(100) and Au(100). On Si(100), a triplet \( \text{O}_2 \) can have significant bonding interaction with Si, which traps \( \text{O}_2 \) on the surface and guarantees its eventual spin transformation to the energetically much more favorable singlet state.\(^{42}\) On Au(100), an adsorbed triplet \( \text{O}_2 \) is actually
slightly more stable than an adsorbed singlet O\(_2\) (although only by about 0.007 eV), and without bonding interaction between triplet O\(_2\) and Au atoms the probability for spin transformation is low. An incoming O\(_2\) would be easily bounced back by Au(100), in agreement with the well documented observations that Au surfaces are inert to O\(_2\).\(^{43-44}\)

On the other hand, a singlet O\(_2\) is more reactive, as expected. On Au(100), the potential energy drops over 1 eV as O\(_2\) approaches the surface (Figure 1c), leading to the chemisorbed singlet O\(_2\) (Figure 1a). With the energy gap between singlet and triplet O\(_2\) being also around 1 eV, it indicates that the Au–O bonding energy is just about enough to compensate for the spin transformation from triplet to singlet O\(_2\). However, it does not mean that a chemisorbed singlet O\(_2\) could easily desorb, which has to proceed along the singlet potential energy surface with a barrier of 1 eV.

In an electrochemical environment, an O\(_2\) in its triplet ground state could capture an electron from the electrode by an outer sphere charge transfer, producing an O\(_2^-\) which is stabilized by polar solvents and brought to the electrode surface as a chemisorbed O\(_2^*\).\(^{21-22}\) On Au(100), such a reaction step has been analyzed theoretically by Schmickler and coworkers and identified as the RDS for ORR in alkaline solution.\(^{23-27}\) Experimentally, there are now convincing evidences for chemisorbed O\(_2^*\), usually as superoxide, and also for HOO* and H\(_2\)O\(_2^*\) on gold electrode surfaces, based on in situ vibrational spectroscopic studies, either by Surface Enhanced Raman Scattering\(^{19, 45-47}\) or Surface Enhanced Infrared Reflection/Absorption.\(^{48-49}\) In alkaline aqueous solution, the O–O stretching feature for adsorbed superoxide was observed at 1130 or 1150 cm\(^{-1}\).\(^{19, 47}\) A similar feature was also observed in O\(_2\) saturated DMSO solution, which was definitely due to O\(_2^*\), rather than HOO* or H\(_2\)O\(_2^*\), since the highly polar DMSO solvent was aprotic.\(^{46}\) We shall later discuss the kinetic implication of such an outer sphere step, after mapping out the barriers for the elementary reactions following O\(_2\) chemisorption on Au(100) in alkaline solution and in an electrochemical environment.

**Associative vs dissociative pathway**

There are two pathways for ORR on an electrode surface. The dissociation pathway is initiated by the stretching of O–O* bond, while the association pathway is initiated by the attack of H on an adsorbed O\(_2^*\), with the H provided either via a solvated proton or via a H\(_2\)O molecule. For ORR on Pt(111), these two steps are not really independent of each other, as demonstrated by AIMD based thermodynamic integration and metadynamics (MTD) simulations.\(^{34, 37}\) The barrier
for breaking the O–O* bond on Pt(111) is low (0.1–0.2 eV), while the reaction energy for the formation O* or OH* is significantly more exergonic than that for the formation of HOO*. When HOH…O–O* distance is shortened to simulate the H attack on O₂*, the O–O* bond is often perturbed and broken, leading to OH*/O*, instead of HOO*. When O–O* bond distance is stretched to simulate its breaking, the O* atom would often pick up a H from the solution layer, producing again OH*/O* rather than HOO*. With both the H attack on O₂* and the stretching of O–O* leading to O–O* dissociation, ORR on Pt(111) is dominated by the 4e⁻ pathway.³⁷

Figure 2: Results of a metadynamics simulation with \(d_{\text{OH}}\) (HOH…O–O* distance) as the collective variable (CV). (a) the time evolution of \(d_{\text{OH}}\). The designated H atom would no longer approach the O₂* after the 123rd Gaussian hill (3.7 ps). (b) free energy surface obtained by collecting Gaussian hills up to 123rd Gaussian hill; (c) a snapshot structure of OOH* during the metadynamics simulation.

On Au(100), the H attack on O₂* does lead to HOO*, again as observed in MTD simulations with HOH…O–O* distance as the collective variable (CV),

\[
O_2 + H_2O \rightleftharpoons HOO^* + OH^*. \tag{R1}
\]
But the O–O* bond is maintained during the reaction. The calculated free energy barrier of 0.03 eV, shown in Figure 2, is very low, in agreement with the previous observation of spontaneous HOO* formation on Au(100) in acid solution during AIMD simulations.\textsuperscript{28} On the other hand, with O–O* distance as the CV, the MTD simulation results on Au(100) are similar to those on Pt(111), leading to O–O* dissociation, with a H often picked up along the way,

\[
O_2^* + H_2O \rightleftharpoons 2OH^* + O^*.
\]  
(R2)

The calculated free energy barrier is averaged to about 0.48 eV (Table 1), in line with recently estimated value of 0.68 eV,\textsuperscript{26} but significantly lower than the earlier estimate of 2.06 eV without considering the solvation effects of H\textsubscript{2}O.\textsuperscript{6} At the potential of zero charge, the associative channel is clearly favored on Au(100), due to its lower activation barrier, and the 2e\textsuperscript{−} ORR should be the dominant pathway as observed in experiments.

<table>
<thead>
<tr>
<th>Charge [e]</th>
<th>O\textsubscript{2} dissociation barrier (eV)</th>
<th>HO\textsubscript{2}O dissociation barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q=-0.5)</td>
<td>0.50±0.09</td>
<td>—</td>
</tr>
<tr>
<td>(q=0.0)</td>
<td>0.48±0.09</td>
<td>0.47±0.15</td>
</tr>
<tr>
<td>(q=1.0)</td>
<td>0.56±0.12</td>
<td>—</td>
</tr>
<tr>
<td>(q=2.0)</td>
<td>0.41±0.04</td>
<td>—</td>
</tr>
<tr>
<td>(q=2.5)</td>
<td>0.45±0.11</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 1: Average O–O dissociation barrier obtained by MTD simulations with O–O distance as the CV, and \(q\) being the extra charged added to the slab. More details are provided in the Supporting Information (Figure S1 and S2; Table S1 and S2).

A further reaction step between HOO* and H\textsubscript{2}O is also facile,

\[
\text{HOO}^* + H_2O \rightleftharpoons \text{HOOH} + \text{OH}^*.
\]  
(R3)

with a small barrier again around 0.03 eV, leading to the formation and desorption of H\textsubscript{2}O\textsubscript{2} and the completion of 2e\textsuperscript{−} ORR. We also examined the dissociation of O–O bond in HOO* and found an average barrier around 0.47 eV, again being kinetically unfavorable compared to H\textsubscript{2}O\textsubscript{2} formation. It indicates similar O–O bond strength in O\textsubscript{2}\textsuperscript{*} and HOO*.

\textit{4e\textsuperscript{−} ORR at high potential}
However, the kinetics favoring HOO* formation (R1) and 2e\textsuperscript{−} ORR can be changed by raising the electrode potential. In alkaline solution, the standard reduction potential for the 4e\textsuperscript{−} pathway
\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^-, \]  
(R4) is 0.401 V (SHE), while for the 2e\textsuperscript{−} pathway,
\[ \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{HO}_2^- + \text{OH}^-, \]  
(R5) it’s only −0.076 V (SHE).\textsuperscript{50-51} At pH=13, the equilibrium potential for R5 in RHE is 0.69 V, while the transition from 2e\textsuperscript{−} to 4e\textsuperscript{−} also occurs around 0.7 V (RHE).\textsuperscript{15} This is not a coincidence. The free energy surface for reaction for HOO* formation (R1) is quite flat, with both the barrier and the free energy change for R1 being small (Fig. 2b). As the electrode potential is raised, R1 would soon become energetically unfavorable. The turning point should be none other than the equilibrium potential for R5, above which R5 is reversed, and so are the related elementary steps, R1 and R3. Yet, while the 2e\textsuperscript{−} pathway is henceforth closed due to thermodynamics, the dissociation channel (R2) is now opened up, since its barrier of 0.48 eV is accessible at room temperature. ORR on Au(100) now becomes a 4e\textsuperscript{−} process, and the calculated barrier for O–O* cleavage is in reasonable agreement with the experimentally measured value of 0.6 eV for ORR.\textsuperscript{15}

The dissociation of O–O* bond is followed by the formation of O* and OH*, and eventually by the desorption of OH*. While the production of OH* is known to be promoted by the presence of water,\textsuperscript{17-18} OH* desorption could be a key factor in determining the ORR current.\textsuperscript{52} Again, it’s instructive to compare the relevant steps on Pt(111) and Au(100). Hydrogenation of O* could go through two possible channels, either
\[ \text{O}^* + \text{H}_2\text{O} \rightarrow 2\text{OH}^*, \]  
(R6) or
\[ \text{O}^* + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^* + \text{OH}^- \]  
(R7)
While R7 involves charge transfer from the electrode to the solution, R6 does not, and therefore R6 does not generate reduction current. As discussed earlier, both could sometimes take place during the dissociation step when a nascent O* reacts with a nearby H\textsubscript{2}O.

The crucial link between R6 and R7 is the equilibrium,\textsuperscript{38}
\[ \text{OH}^* + \text{e}^- \rightleftharpoons \text{OH}^- \]  
(R8) which is the final reduction step and always generates current. Below the equilibrium potential of R8, R6 would be followed by OH* desorption. Above this potential, OH* desorption is stopped as OH* becomes more stable than OH\textsuperscript{−}. It also affects O* reduction even when it goes through R7,
as the product OH− near the electrode surface should be followed by OH− adsorption. The sum of R7 and the reverse R8 is equivalent to R6, and no net reduction current would be produced. In other words, above the equilibrium potential of R8, the ORR current shall be stopped.

The value of this equilibrium potential varies with the metal. On Pt(111), the value is 1.03 V (RHE),53 which is responsible for the large onset overpotential for ORR current.3,37-38 On Au(100), the cathode scan peak for OH* desorption is at 1.1 V (RHE) and the equilibrium potential should be close to 1.2 V (RHE).15 The higher value on Au(100) is partly due to the smaller OH* adsorption energy. Furthermore, as recently demonstrated in our AIMD simulations,52 hydrated OH− can be stabilized by the unusual type of hydrogen bond interaction OH−…Au, which also favors OH* desorption. The puzzle of the excellent ORR performance on Au(100) in the high potential 4e− ORR region is explained by the fact that OH* desorption is quite facile on Au(100), while the barrier for O–O* cleavage (R2) is just around 0.5 eV.

Rate determining step

In light of the important role of R8 as the RDS for ORR on Pt(111) and the significant higher equilibrium potential of R8 on Au(100) (~1.2 V RHE) than that on Pt(111) (~1.0 V RHE), it is worthwhile to re-examine their respective current (j) – electrode potential (E) curves, as shown in Figure 3. In the 0.9 < E < 1.0 V (RHE) region, the ORR currents on Pt(111) and on Au(100) are nearly the same (Figure 3a). However, in 1.0 < E < 1.18 V, there is still a small cathodic current on Au(100) (Figure 3b).
Figure. 3 The polarization curves for ORR (positive scan) on different electrodes: (a) before and (b) after deducting the background current for double layer charging as well as for pseudo-capacitive charge for H$_2$O|OH* redox. Insert shows the magnified $j$-$E$ in the 0.7 to 1.3 V region.

There are two complicating factors in this region: a significant double layer charging current and a significant pseudo-capacitive current due to the formation/reduction of Au oxide. The latter current, due to the presence of Au oxide during previous positive scans, produced a small cathodic peak ca 1.05 V, superimposed on the $j$-$E$ curve for the alkaline ORR on Au(100), as reported in two independent studies.\textsuperscript{14-15} The presence of small ORR current in $1.0 < E < 1.18$ V region has therefore not been carefully examined before. To eliminate the double layer charging current, we have subtracted the $j$-$E$ curve measured in Ar saturated solution from the ORR (O$_2$ saturated) $j$-$E$ curve. To eliminate the Au oxide reduction current, we use the data obtained only from positive scans. The corrected $j$-$E$ shows a small cathodic current in $1.0 < E < 1.18$ V on Au(100), very close to the overall ORR equilibrium potential at 1.23 V (see the blow up in Figure 3b).

Such an observation is related to the RDS for ORR on Au(100) in this potential region. In alkaline solution, the 4e$^-$ ORR process involves four essential steps: O$_2$ adsorption, O–O* bond
dissociation, O* hydrogenation to OH*, and OH* desorption. For the ORR on Au(100), OH* desorption is active up to 1.2 V RHE. O* hydrogenation should also be active, since R6 and R7 are energetically more favorable than R8. Both O* hydrogenation and OH* desorption can be ruled out as the RDS.

The barrier for O–O* bond dissociation does not change significantly at elevated electrode potential according to our MTD simulations with positive charges added to the slab. The calculated barrier remains around 0.5 eV, as listed in Table 1, although more structural distortions are observed for the surface Au atoms, in line with previous experimental studies. These results indicate that the 4e− ORR on Au(100) is unlikely to be blocked by the suspension of O–O* bond cleavage. Furthermore, if it was the RDS, there would be an accumulation of O2* on Au(100) above 0.9 V (RHE). But in a recent surface enhanced Raman study, the signal for O–O* actually disappears in that potential region.

By exclusion, it leaves the first step, O2 adsorption, as the RDS, which has been suggested before, based on the well-known low adsorption probability of O2 on Au surfaces, and studied in details by Schmickler and co-workers using a combination of theoretical modelling, DFT and classical MD calculations. Our calculation results lend further supports to this suggestion. As discussed earlier, an O2 molecule in its triplet ground state could hardly adsorb on Au surfaces at room temperature. The presence of water molecules in the electrode interfacial region does not facilitate the transformation of triplet O2 into the more reactive singlet state. The more likely adsorption route is for an electron to be transferred to the outer sphere,

\[ \text{O}_2 + e^- \rightleftharpoons \text{O}_2^-, \quad (R9) \]

which does become energetically more favorable in the presence of water by the solvation of O2−. It is also more favorable in alkaline solution since the metal surface is less positively charged in the ORR potential range, as compared to that in acid solution.

While O2− is formed in the outer sphere, it is close to the electrode and could readily adsorb on a positively charged Au(100),

\[ \text{O}_2^- \rightarrow \text{O}_2^* + e^- . \quad (R10) \]

Overall, R9 followed by R10 would not produce current. However, our calculations show that in the presence of water, O2* is even more negatively charged with a population of −1.1e and forms strong hydrogen bonds. With the singlet desorption path as prohibitive as shown in Figure 1c and the association channel blocked at high electrode potential, O2* could only follow the 4e− ORR
pathway, through $O_2^*$ dissociation, OH* formation and OH* desorption, all of which are quite facile, even up to 1.2 V RHE.

In other words, once $O_2^-$ is adsorbed on Au(100), it would be consumed by ORR. The standard potential for R9 is around $-0.28 \text{ V}$, and at $pH=13$ it would be 0.5 V (RHE). When the electrode potential is raised above 0.5 V, the ORR current does not drop to zero due to the irreversible nature of R10, although the amount of $O_2^-$ in the outer sphere should decay exponentially with the increasing overpotential and so should the ORR current. By +0.9 V (RHE), there is only a small amount of $O_2^-$ produced, and R9 should indeed be the RDS. Such an exponential decay implies a linear Tafel plot with a slope around 120 mV/decade for the one electron transfer reaction R9, in agreement with recently reported experimental value.\textsuperscript{15}

This decay could further extend to $E > 1.0 \text{ V}$ (RHE), although in this region there are other complicating factors. The adsorption sites on Au(100) would be partially blocked due to the enhanced presence of OH* and O* at high potential, which would hinder R10. When $E$ is close to 1.2 V, OH* desorption would also slow down. Such factors could have impacts on the rather low $O_2^-$ concentration in this potential region and cause significant shifts in the equilibrium R9. The decay in ORR current would be faster than that expected from an exponential function. But, as long as OH* desorption remains active, which is the case up to 1.2 V (RHE),\textsuperscript{15} there would still be ORR current. It explains the small ORR current in the corrected $j$-$E$ curve for $E > 1.0 \text{ V}$ (RHE), up to 1.18 V (RHE), which is close to the equilibrium potential for the overall ORR at 1.23 V.

The difference between the ORR activity on Au(100) and that on Au(111) would be another interesting problem for further study. Previously it has been attributed to difference in the OH* adsorption energy,\textsuperscript{26} while the relevant reaction barriers are still unknown. There is also the possibility that the barrier for the outer sphere electron transfer is larger on Au(111) since the potential of zero charge is larger on Au(111) ($\approx-0.5 \text{ eV}$) than that on Au(100) ($\approx-0.3 \text{ eV}$).\textsuperscript{57}

Conclusions

When the Sabatier Principle and the ORR activity volcano curve are applied to ORR on Au(100), it is reasoned that the weak interactions between oxygenated species and Au surface make the O–O* dissociation difficult, which leads to the formation of HOO*/H$_2$O$_2$ through the 2e$^-$ pathway, rather than the formation of O*/OH*/H$_2$O through the 4e$^-$ pathway. However, such an analysis, based on the shallow adsorption well observed in vacuum studies, is inadequate in an
electrochemical environment. With significant charge transfer to O$_2^*$ stabilized by water molecules in the interfacial region, the O–O$^*$ dissociation barrier ~0.5 eV on Au(100) is hardly prohibitive. O–O$^*$ dissociation is inaccessible only because the association barrier to form HOO$^*$ at less than 0.1 eV is considerably lower.

More importantly, reaction mechanisms and the corresponding kinetics can be changed. In the case of alkaline ORR on Au(100), it can be changed by electrode potential. The associative 2e$^-$ pathway is switched off around 0.7 V (RHE), which leaves the dissociative 4e$^-$ pathway as the only accessible process. The weak adsorption energy of oxygenated is now turned into an advantage: the OH$^*$ desorption is facile on Au(100), with an equilibrium potential close to 1.2 V (RHE), which makes Au(100) a better ORR catalyst than Pt(111), in the high potential region.

Our calculations further show that O–O$^*$ dissociation, OH$^*$ desorption and O$^*$ hydrogenation remain accessible at elevated electrode potential up to 1.2 V (RHE), close to the theoretical ORR limit of 1.23 V. It supports the suggestion that the outer sphere electron transfer to O$_2$ is the RDS, and makes it possible to observe a flat ORR $j$-$E$ curve extending into 1.0 < $E$ < 1.2 V.

The current endeavor for better ORR catalysts is largely based on the imitation of Pt, focusing on finding materials with the adsorption energies of oxygenated species comparable to those on Pt. But the 2e$^-$ to 4e$^-$ ORR transition on Au(100) demonstrates that the Sabatier Principle, as represented by various volcano plots based solely on the consideration of adsorption energies, can be circumvented. These results also point to a new strategy based on the imitation of Au(100), embodying an ORR mechanism distinct from that on Pt. Lower adsorption energies, away from the narrow center of the ORR volcano curve, could actually be an advantage, if the challenge to facilitate O$_2$ adsorption onto the electrode surface could be met.

**Supporting Information**
Computational Details; Experimental Methods; Additional Metadynamics Results.

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