Metal-Free Electrocatalysts for Oxygen Reduction to Hydrogen Peroxide

Zhe Wang, Dustin K. James, and James M. Tour*

Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), as an environmentally friendly and highly efficient oxidation reagent, is now widely and increasingly used in many areas. The traditional anthraquinone synthesis process, however, is energy and capital intensive with low efficiency. Electrochemically reducing oxygen (O\textsubscript{2}) to H\textsubscript{2}O\textsubscript{2} with metal-free catalysts is considered a promising alternative. This work describes the two-electron oxygen reduction process from both thermodynamic and kinetic aspects and summarizes the designing rules for effective H\textsubscript{2}O\textsubscript{2} formation catalysts. This includes tuning the binding energy of the intermediate species, the concentration of dissociation active sites, and adjusting the dielectric constant of solvents. These principles are successfully applied to the design of various metal-free catalysts by proper structure engineering and heteroatom doping, which shows both high activity and efficiency. Furthermore, pH and temperature effects are presented with a view toward reaction optimization. An outlook of future challenges is also discussed.

1. Introduction

Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), as a green and highly efficient oxidant, is now playing an essential role in modern society with various applications ranging from disinfectants to water treatment, from paper and pulp bleaching to propylene oxide generation, and as a result, the market is now over $5 billion and is expanding rapidly.\[1,2\] Recent needs for widespread disinfectants during the COVID-19 pandemic are highlighting the special role of this environmentally friendly chemical oxidant.\[3\] Nevertheless, most H\textsubscript{2}O\textsubscript{2} is produced through the traditional capital, energy, and waste intensive 70-year-old anthraquinone process.\[1\] Expensive catalysts and complicated processes including extraction, distillation, and purification as well as transportation and storage fees impede further reduction of the cost.\[1,4,5\] Direct electrochemical synthesis of H\textsubscript{2}O\textsubscript{2} from air and water with renewable energy under mild conditions is considered a promising alternative, which could permit local generation to minimize transportation and storage costs.\[4\] Various catalyst candidates include metal,\[6\] metal alloys,\[7,8\] and single-atom catalysts.\[9,10\] However, metal dissolution remains a problem for the catalysts.\[11,12\] Thus, metal-free catalysts could be an alternative.\[13–15\]

As an intermediate of the traditional four-electron oxygen reduction reaction (ORR), H\textsubscript{2}O\textsubscript{2} is more active than water and is a kinetic product rather than the most stable thermodynamic product water (Figure 1a). Understanding the kinetics of two-electron and four-electron ORR processes could help in the rational designing of catalysts with high selectivity and efficiency for H\textsubscript{2}O\textsubscript{2} generation. Although several review articles regarding two-electron ORR catalysts have been published, few of them considered the kinetic process.\[16–18\] In this perspective, we will highlight the thermodynamic and kinetic mechanisms in the ORR processes and describe possible tuning factors. Recent processes on metal-free catalysts for reducing O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2} are summarized and analyzed. pH and temperature, as part of the reactor design, are discussed.

2. Theoretical Guidance for Tuning the Selectivity of ORR Catalysts

Electrochemical ORRs, including both two-electron and four-electron pathways, could be described with the following equations.

\[
\begin{align*}
\text{O}_2 + 2e^- + 2H^+ & \rightarrow \text{H}_2\text{O}_2 \quad E^0 = 0.70 \text{ V} \\
\text{O}_2 + 4e^- + 4H^+ & \rightarrow 2\text{H}_2\text{O} \quad E^0 = 1.23 \text{ V}
\end{align*}
\]

According to the standard potentials, the four-electron pathway oxygen reduction is thermodynamically preferred. Also,
Figure 1. Theoretical calculations of the electrochemical oxygen reduction to H₂O₂. a) Free energy diagrams of both two-electron and four-electron pathways on PtHg(110), together with theoretically calculated volcano plots for the two-electron pathway (blue) and four-electron pathway (red) of oxygen reduction with the formation free energy of *OH or *OOH as a descriptor. U represents the theoretical equilibrium potentials for the ORR process on different catalysts. Reproduced with permission.[21] Copyright 2013, Springer Nature. b) Free energy diagrams for bifurcating two-electron pathways and four-electron pathways of the ORRs at different dielectric constants (ε). Blue lines show the activation of O₂ molecules. Red and green lines represent two-electron pathways and four-electron pathways, respectively. Structure 1 represents the model molecule, N-doped colloidal graphene, and structure 2 was reduced from structure 1 through a one-proton, two-electron pathway. Structure 3, the peroxygraphic enion, was generated when structure 2 reacts with an oxygen molecule. Structure 4 shows the transition state of O–O bond cleavage in structure 3, and structure 5 is the final product of the O–O bond cleavage process. Reproduced with permission.[21] Copyright 2016, American Chemical Society. c) Free energy diagrams for the ORR process on Pt(111) at 0.9 V versus reversible hydrogen electrode (RHE). *A and *B both represent active sites. Reproduced with permission.[21] Copyright 2014, American Chemical Society.

under certain circumstances, H₂O₂ generated from the two-electron pathway could be reduced to H₂O in the following equation

\[ \text{H}_2\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad E^0 = 1.76 \text{V} \] (3)

or disproportionated in the following equation.

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad E^0 = 1.06 \text{V} \] (4)

Thus, it is critical to design suitable catalysts and systems so as to produce H₂O₂ with high efficiency and to avoid further reduction. A suitable descriptor of the kinetic process could help to understand the mechanism and to better engineer catalyst structures.

Considering that both two-electron and four-electron ORR processes share the same step in the following equation

\[ \text{O}_2 + * + e^- + \text{H}^+ \rightarrow *\text{OOH} \] (5)

where * denotes an active site, and that according to experiments, the formation free energy of *OH (ΔG^f_{*OH}) is linear to the formation free energy of *OOH (ΔG^f_{*OOH}), which is normally used as a descriptor of the four-electron ORR process, and ΔG^f_{*OOH} had a volcano relationship with both two-electron and four-electron ORR theoretical potential and could be a suitable candidate to demonstrate how ORR branches.[19] A smaller ΔG^f_{*OOH} indicates a strong interaction between catalysts and *OOH, dissociating the O–O bond and promoting the four-electron ORR process, whereas an increased ΔG^f_{*OOH} preserves the O–O bond. However, it is worth noting that if ΔG^f_{*OOH} is too large, it results in low activity. Thus, catalysts located near the top of the volcano plot could be ideal for a highly efficient two-electron ORR process with zero theoretical overpotential (Figure 1a).

Local hydrophilicity of catalysts on the catalytic active sites is also critical for the kinetic process (Figure 1b).[20] A hydrophobic surface limits the accessibility of electrolytes at the interface, causing a much lower local dielectric constant (ε) comparing with that in the electrolyte. Density functional theory (DFT) calculations have shown that the dielectric constant influences the energy barriers of *OOH dissociation and H₂O₂ formation and the stability of the corresponding product. Smaller dielectric constants raise both the energy barrier and the energy of H₂O₂, inhibiting the two-electron process.

In addition, a direct kinetic analysis by calculating the energy of transition states could be applied to provide detailed mechanisms and insights regarding the ORR process.[21] Figure 1c shows the various pathways for the ORR. Noting that O–O scission could happen during the following steps

\[ \text{O}_2*_{A} + *_{B} \rightarrow \text{O}^*_{A} + \text{O}^*_{B} \] (6)

\[ \text{OOH}^*_{A} + *_{B} \rightarrow \text{OH}^*_{A} + \text{O}^*_{B} \] (7)

\[ \text{H}_2\text{O}_2^*_{A} + *_{B} \rightarrow \text{OH}^*_{A} + \text{OH}^*_{B} \] (8)

where *_{A} and *_{B} both represent active sites, and all these steps are irreversible. Controlling the concentration of *_{B} by isolating active sites is more suitable for H₂O₂ generation and could be an efficient strategy for H₂O₂ catalyst design.[16,22] The calculated kinetic volcano plot matched the potential limiting volcano as well as experimental data, illustrating a similar active trend, whereas, additionally, it shows why the two-electron ORR process could happen with high selectivity.[22,23]
3. Synthetic Approaches of Metal-Free Two-Electron ORR Electro catalysts

3.1. Development of Pure Carbon Catalysts

As is described in the abovementioned section, catalysts with isolated active sites for the ORR with a moderate \( \Delta G_{\text{SOOH}} \) could be ideal for \( \text{H}_2\text{O}_2 \) generation. Although well-defined graphene or graphite was considered inert in electrocatalysis, defect engineering of carbon materials could active these inexpensive and abundant materials.\(^{[24,25]} \) Since 1939, carbon materials have been used in electrochemical \( \text{H}_2\text{O}_2 \) generation.\(^{[26]} \) Bao and co-workers studied the ORR performance in 0.1 m potassium hydroxide (KOH) of microporous carbon and mesoporous carbon, both of which exhibited >70% selectivity for \( \text{H}_2\text{O}_2 \) with an early onset potential (Figure 2a).\(^{[13]} \) However, as the mesoporous structure improved the electrochemical accessibility and local hydrophilicity, it showed better activity, selectivity, and stability compared with those showing a microporous structure. DFT calculations together with spectroscopic characterizations illustrated that sp\(^2\) carbon defects, especially double vacancies with pentagon and heptagon rings, are the most active sites for the two-electron ORR process. Tao et al. have found that graphene prepared by thermally expanding graphite oxide showed high selectivity to \( \text{H}_2\text{O}_2 \) with the electron transfer number ranging from 2.31 to 2.65 in 0.2-0.4 V versus RHE in 0.1 KOH.\(^{[27]} \) Chorkendorff and co-workers tested the ORR performance of various commercial carbon black materials, and the Faradaic efficiency (FE) of \( \text{H}_2\text{O}_2 \) reached over 80%.\(^{[28]} \) With the aid of X-ray photoelectron spectroscopy (XPS) and prompt gamma-ray activation analysis/neutron activation analysis (PGAA/NAAN) analysis, it is suggested that the FE is not related to the trace amount of metal in carbon black, or the oxygen concentration or nitrogen content (Figure 2b). Hydrogen concentrations, however, were correlated to FE changes, suggesting that aliphatic-like carbon sites could play a role in the \( \text{H}_2\text{O}_2 \) generation. Nevertheless, this is harder to mechanistically envision. In addition, graphite (81% current efficiency at 6.4 A m\(^{-2}\) when \( \text{pH} = 2 \))\(^{[11]} \) 33% current efficiency at 10 A m\(^{-2}\) in \( \text{Na}_2\text{SO}_4 \) with a pH of 3\(^{[29]} \) 91.3% current efficiency in 1 m NaOH\(^{[30]} \), carbon nanotubes (CNTs; 40–61% current efficiency in 0.05 m \( \text{Na}_2\text{SO}_4 \) with a pH of 3.6\(^{[31]} \), carbon sponge\(^{[32]} \) and ordered mesoporous carbon (40.0% current efficiency in 0.1 m \( \text{Na}_2\text{SO}_4 \)\(^{[33]} \) >90% in 0.1 m KOH\(^{[34]} \) were found to be potential catalysts for the two-electron ORR as well.

3.2. Heteroatom-Doped Carbon Materials

Apart from adjusting the structure of pure carbon materials, heteroatom doping provides another control element to modify the electronic structure, active sites types, the hydrophilicity of carbon materials, and concentrations of \( \delta_{\text{A}} \) and \( \delta_{\text{B}} \)\(^{[24,35]} \) We will summarize, here, recent progress on nonmetal doping for \( \text{H}_2\text{O}_2 \) electrocatalysts.

3.2.1. O-Doped Carbon Materials

It was first found in 1987 that the ORR activity of carbon materials could be enhanced through oxidizing treatment.\(^{[36]} \) Since then, carbon materials with different oxygen-containing functional groups have been successfully synthesized by various methods, resulting in enhanced performance. For example, modifying electrode surface with quinone molecules could afford 100% \( \text{H}_2\text{O}_2 \) generation in 0.1 m KOH.\(^{[14]} \) Santos and co-workers enhanced the \( \text{H}_2\text{O}_2 \) selectivity of Vulcan XC 72R and Printex L6 materials by increasing their hydrophilicity with nitric acid treatment.\(^{[39]} \) Cui and co-workers extended this concept and achieved 90% \( \text{H}_2\text{O}_2 \) selectivity in both alkaline and neutral solutions by oxidizing various carbon materials such as CNTs, super P (SP), and acetylene black (AB) with different oxidizing methods.\(^{[14]} \) The selectivity and current density are both related to oxygen concentrations in the catalysts (Figure 3). The removal of the oxygen functional groups resulted in a larger overpotential and lower performance, indicating that these groups were potential active sites. DFT calculations illustrated theoretical overpotentials as well as the rate-limiting steps on typical oxygen functional groups, of which C–O–C groups on the basal plane showed the highest activity. A similar correlation between oxygen concentration and \( \text{H}_2\text{O}_2 \) selectivity was also confirmed by Lu et al.\(^{[39]} \) and Xia et al.\(^{[40]} \) Aside from oxidizing methods, reducing methods could be another choice to introduce certain types of oxygen-containing groups. Kim et al. found that both few-layered mild reduced graphene oxide (F-mrGO) and annealed F-mrGO showed high selectivity to \( \text{H}_2\text{O}_2 \), the active sites of which were assigned to basal planes and ring ether groups at the edges, respectively, with the aid of in situ Raman, near-edge X-ray absorption fine structure (NEXAFS), and other spectroscopic methods (Figure 4).\(^{[41]} \) By controlling the annealing temperature, specific types of functional groups could be generated, changing the onset potential as well as the ORR selectivity. As a result, the activity trend here is not linear with absolute oxygen concentration. F-mrGO(600), which was annealed at 600 °C, exhibited the best ORR performance (overpotential <10 mV, \( \approx 100\% \) \( \text{H}_2\text{O}_2 \) selectivity in 0.1 m KOH), whereas F-mrGO(300), annealed at 300 °C, showed worse ORR activity compared with F-mrGO. Changing reaction conditions and adding additives such as KOH and KBH\(_4\) helps produced similar functional groups.\(^{[40,41]} \) Han et al. prepared a set of oxidized graphene nanoplatelets (GNPs) containing different functional groups using ball milling methods.\(^{[42]} \) It was illustrated that quinone-enriched structures could enhance \( \text{H}_2\text{O}_2 \) production effectively (98% \( \text{H}_2\text{O}_2 \) yield at 0.75 V vs RHE in 0.1 m KOH) as determined by X-ray absorption near-edge structure (XANES), XPS, Fourier transform IR (FTIR) spectra, and electrochemical tests. High ORR activity of quinone structures was also confirmed by testing standalone molecules with different oxygen-containing groups, such as phenanthrenequinone, anthraquinone, naphthenetetracarboxylic dianhydride, perylenetetracarboxylic dianhydride, dibenzoxodiazin, and dibenzofuran.

Catalyst structures are critical to the kinetic electron transfer process and local hydrophilicity as well. As shown in Figure 5a, graphitic-ordered mesoporous carbon (GOMC) catalyst exhibited a vertically stacked graphitic nanosheets array structure with abundant edge sites.\(^{[42]} \) At 0.75 V (vs RHE), GOMC-catalyzed \( \text{H}_2\text{O}_2 \) production was 28 times faster than that provided by a basal-plane-rich CNT. The production rate and electron transfer kinetic could be further enhanced by adjusting oxygen
concentration. Similarly, the two-electron ORR activity of edge-enriched nanowire-templated 3D fuzzy graphene (NT-3DFG) is directly related to the electrochemical surface area and exposed edge density (Figure 5b).

3.2.2. N-Doped Materials

Similar to oxygen, nitrogen has a larger electronegativity than carbon, enabling N-doping to be a method to redistribute...
In addition, moderated surface N functionality was found to be a selectivity (75% in 0.1 M KOH compared with N-doped selectivity). Bao and co-workers found that F doping was recently found to be a selectivity of F-doping and showed selectivity in N-doped catalysts. The interface between KOH and N-doped was found to be good precursors for N-doped carbon catalysts for H$_2$O$_2$ generation. Park et al. synthesized a set of MNC with different nitrogen contents along with microporous activated nitrogen-doped carbon (ANC) (Figure 6a). It was found that the two-electron ORR process is not only related to N content but also to pore sizes. The mesoporous structure had a special local environment, promoting mass transport and preventing H$_2$O$_2$ from a further reduction on the catalyst surface, which was also found in other catalysts.

Zhang et al. changed the nitrogen functionality ratios while keeping the porous structure the same in the graphene-covalent organic frameworks (G-COF) catalysts by annealing the G-COF precursor at different temperatures. Although the nitrogen content in G-COF-950 is lower than those in G-COF-750 and G-COF-550, it showed the best H$_2$O$_2$ selectivity (75% in 0.1 M KOH), indicating that it is graphitic N, not the total N content, that was critical for the highly selective two-electron ORR process on N-doped carbons (Figure 7a). Li et al. synthesized N-rich few-layered graphene (N-FLG) from melamine and glyicine and successfully adjusted the pyrrolic N concentration by varying the mass ratio of precursors. Electrochemical tests and XANES results indicated the correlation between the two-electron ORR process and pyrrolic N concentration. N-FLG-8 could achieve over 95% H$_2$O$_2$ selectivity with long stability in 0.1 M KOH solution. Strasser and co-workers used N-doped CMK-3 as an example and illustrated that pyridinic N could be active sites in acidic solution. In addition, moderated surface N functionality density isolated active sites and prevented O–O bond dissociation of H$_2$O$_2$. Eigler and co-workers demonstrated that in-plane carbon lattice-defect concentrations can also affect ORR selectivity in N-doped graphene (Figure 7b). N-doped graphene from o xo-functionalized graphene (oxo-G) with lower in-plane carbon lattice-defect concentrations exhibited better H$_2$O$_2$ selectivity (over 82% in 0.1 M KOH).

### 3.2.3. Other Heteroatom-Doped Materials

DFT calculations illustrated that other heteroatom doping, e.g., B, P, S, Si, and halogens, could also adjust the electronic structure and Δ$G_{\text{OOH}}$ of catalysts. Coding strategies show synergistic effects in some systems. Bao and co-workers found that B, N codoped carbon (BN-C) exhibited a larger H$_2$O$_2$ current and smaller overpotential in 0.1 M KOH compared with N-doped carbon (N-C), which was directly correlated with both B and N concentrations. The interface between h-BN domains and graphene was identified as the active site for H$_2$O$_2$ generation with the help of X-ray spectroscopies and DFT calculations. Similarly, O and N codoping showed a synergistic effect, and 100% H$_2$O$_2$ selectivity was achieved in a COOH-terminated nitrogen-doped carbon aerogel. In N, S codoped carbon materials, N was found in a direct relationship with catalytic performance, whereas S caused the opposite effect. This phenomenon was in accord with the results in S-doped carbon, which showed only 20% H$_2$O$_2$ selectivity. F doping was recently found to be a successful strategy to enhance the H$_2$O$_2$ activity and selectivity of carbon materials (97.5% H$_2$O$_2$ selectivity in 0.05 M H$_2$SO$_4$, 89.5% current efficiency when at pH 7)$.^1$ Furthermore, N, F codoping could combine the early onset and large current of N-doping with the high H$_2$O$_2$ selectivity of F-doping and show 89.6% FE when at pH 13.$^2$

### 4. System Parameters

In addition to catalyst designs, parameters of the reaction system are also of great importance to maintain high efficiency in the industrialization of H$_2$O$_2$ generation, many of which have been summarized in the literature.$^{12,17,63}$ We will focus, here, mainly on two critical points that are not often discussed: pH and temperature.

#### 4.1. pH

The influence of pH exists in at least three aspects. First, when pH is higher than 11.6, H$_2$O$_2$ molecules deprotonate and exist in...
high concentration as HO$_2^-$, and as a result, the two-electron pathway of the ORR process changes, as in the following:

$$O_2 + 2e^- + H_2O \rightarrow HO_2^- + OH^-$$  \hspace{1cm} (9)

Theoretical potential increases by 60 mV compared with that in acidic solution.

Second, the mechanism of two-electron oxygen reduction on the catalyst could be different, as shown in the following:

$$O_2 + e^- + H_2O \rightarrow \bullet OOH + OH^-$$  \hspace{1cm} (10)

$$\bullet OOH + e^- \rightarrow \bullet + HO_2^-$$  \hspace{1cm} (11)

It was also suggested that in some cases, the coherently coupled proton-electron transfers may not happen directly on the surface of the catalyst. Thus, the ORR performance would change accordingly. As shown in Figure 8a–c, N-doped single-wall carbon nanohorns (CNHs) exhibited very high FE (nearly 98% at 0.30 V vs RHE) in acidic solution, which decreased with increased pH. A similar trend was observed in hierarchically porous carbon (HPC) (Figure 8d). However, mesoporous carbon hollow spheres (MCHS) reached their highest FE in neutral electrolytes (0.1 M phosphate-buffered saline (PBS)) and smallest Tafel slope in the alkaline electrolyte (0.1 M KOH) (Figure 8e,f).

Third, pH could influence the stability of the reactor, especially the ion exchange membrane. Although H$_2$O$_2$ with electrolytes could be used on certain occasions, in most cases, pure H$_2$O$_2$ aqueous solution is more desirable. Considering energy efficiency and environmental requirement, ion exchange membranes are the most promising separation methods. However, the stability of the anion exchange membrane remained a bottleneck due to structure properties, limiting the design of the reactor.

### 4.2. Temperature

The temperature has contradictory effects on H$_2$O$_2$ generation. On the one hand, the diffusion coefficient of O$_2$ molecules increases as the temperature rises, which helps increase the H$_2$O$_2$ current density. Conversely, higher temperature means a lower dissolved O$_2$ concentration and a faster decomposition rate of H$_2$O$_2$. Experiments showed that the decomposition of H$_2$O$_2$ did not show an obvious difference at 20 and 30 °C, but it was enhanced dramatically at 50 °C. However, it was also observed that the catalysts favored the four-electron ORR process at a low temperature (≤50 °C) while switched to the two-electron process at a higher temperature (25 °C). The overall effect of temperature depends on the various conditions and catalyst composition.

### 5. Outlook

Electrochemical oxygen reduction to H$_2$O$_2$ with metal-free catalysts is now rising as a promising path with the rapid growth of...
Figure 5. Representative oxidized carbon catalysts with different structures for selectively reducing \( \text{O}_2 \) to \( \text{H}_2\text{O}_2 \). a) Transmission electron microscopy (TEM) images of GOMC, heterogeneous electron transfer rate constant, and mass activity at 0.75 V (vs RHE) as a function of O contents. Reproduced with permission.[42] Copyright 2018, Wiley. b) Scanning electron microscopy (SEM) images, linear sweep voltammetry (LSV) polarization curves of NT-3DFG with different edge densities, and proposed active sites for the ORR process. Reproduced with permission.[43] Copyright 2020, American Chemical Society.

Figure 6. Representative N-doped carbon catalysts with different microstructures for selectively reducing \( \text{O}_2 \) to \( \text{H}_2\text{O}_2 \). Schematic of reducing \( \text{O}_2 \) to \( \text{H}_2\text{O}_2 \) on MNC and ANC, polarization curves on RRDE along with corresponding \( \text{H}_2\text{O}_2 \) selectivity of MNC and ANC in 0.5 M \( \text{H}_2\text{SO}_4 \). Reproduced with permission.[47] Copyright 2014, American Chemical Society.
renewable energy. Both thermodynamic and kinetic analyses have been applied to better understand the mechanism, which demonstrated the principles for the catalyst design: adjusting active site structure to achieve moderate OOH binding energy, increasing hydrophilicity to reduce local dielectric constant, and isolating active sites to avoid catalyzing O–O bond dissociation. These principles have been successfully applied in the practice of various strategies such as carbon defect engineering and heteroatom doping. Despite all this, as a rapidly developing area, some fundamental questions remained to be explored. For example, what are the real active sites for the two-electron ORR process? It was found that the catalytic performance of oxidized carbon materials is related to oxygen functional groups. However, recent work indicated that the carbon defects generated during the oxidation process also play an important role. Effects may be more complicated in N-doped and other heteroatom-doped materials. Further exploration can help understand the catalytic process and design better catalysts. Also, the stability of catalysts must be considered during material design, as they are in contact with highly active oxygen species. One example is, although N-doped catalysts showed good activity in acidic electrolytes, N concentrations decreased significantly after electrolysis, indicating possible performance decay.

Besides catalyst designs, integrated design of reactors was also developed, key parameters of which like pH and temperature are even more important for industrialization. The efficiency and long-term stability of the whole system should be evaluated properly.

Finally, as a representative practice of combined theory and experiments, electrochemical two-electron oxygen reduction may shed light on even more complicated systems such as nitrogen reduction to ammonia and CO₂ fixation.
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Conflict of Interest

The authors declare no conflict of interest.

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