Catalyst Design for Electrochemical Oxygen Reduction toward Hydrogen Peroxide

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Precise electrochemical synthesis under ambient conditions has provided emerging opportunities for renewable energy utilization. Among many promising systems, the production of hydrogen peroxide (H₂O₂) from the cathodic oxygen reduction reaction (ORR) has attracted considerable interest in past decades due to the increasing market demands and the vital role of ORR in the electrocatalysis field. This work describes recent advances in cathodic materials for H₂O₂ synthesis from 2e⁻ ORR. By using Pt as a stereotype, the tuning knobs are overviewed, including the intrinsic binding strength of oxygenated species, the intermediate diffusion path and the isolation of Pt–Pt ensembles that enable 2e⁻ ORR pathway from 4e⁻ total reduction. This knowledge is successfully applied to other transition metal systems and leads to the discovery of more efficient alloy catalysts with balanced improvement on both activity and selectivity. In addition, mesostructure engineering and heteroatoms doping strategies on carbon-based materials, which significantly boost the H₂O₂ production efficiency as compared to intact carbon sites, are also reviewed. Finally, future directions and challenges of transferring developed catalysts from lab scale tests to pilot plant operations are briefly outlooked.

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1. Introduction

Hydrogen peroxide (H₂O₂) as a versatile and environmentally benign oxidant is an essential component in modern industries with numerous applications ranging from chemical synthesis to water treatment, from textile bleaching to aerocraft propelling etc.¹² The annual production of H₂O₂ commodity in 2015 has exceeded 5 million tons,¹³ mostly by the energy and waste intensive anthraquinone process within capital plants, for which downstream vacuum distillation and purification steps are needed before its transportation to end users. As an alternative, electrochemical synthesis is driving a global trend for decentralized H₂O₂ generation and onsite application in considering its mild reaction conditions as well as its green inputs starting from air, water and renewable energy without fossil fuel consumptions.⁴⁻⁶

Partial electrochemical O₂ reduction to H₂O₂ (O₂ + 2H⁺ + 2e⁻ → H₂O₂) is emerging as a promising route for distributed hydrogen peroxide synthesis,⁷⁻⁹ in addition to the other 4e⁻ reduction pathway (O₂ + 4H⁺ + 4e⁻ → 2H₂O) intensively studied in fuel cells and metal-air batteries.¹⁰⁻¹² For an associative O₂ reduction, both 2e⁻ and 4e⁻ pathways share the same reactive intermediate of *OOH:

\[
\begin{align*}
O₂ + \cdot + (H^+ + e^-) & \rightarrow *\text{OOH} \\
*\text{OOH} + (H^+ + e^-) & \rightarrow H₂O₂ + * \\
\text{or} \quad *\text{OOH} + 3(H^+ + e^-) & \rightarrow 2H₂O + *
\end{align*}
\]

The critical knob branching ORR pathway locates at the binding strength of *OOH species. As shown in Figure 1a, Siahrostami et al. predicted an oxygen reduction volcano plot using the adsorption energy of oxygenated species, ΔG_{HOOH} or ΔG_{HOH}, as the descriptor.¹³ They disclosed that on the left side of the volcano peak (strong *OOH binding with small ΔG_{HOOH} value), it is more downhill in free energy to form H₂O₂; this means the selectivity towards the 4e⁻ pathway will dominate over the 2e⁻ pathway, as is the case for Pt and Pd. On the right side (weak *OOH binding with large ΔG_{HOOH} value) of the volcano peak, there is a high activity for both H₂O₂ and H₂O formation as the 2e⁻ and 4e⁻ leg overlap with each other. From the theoretical view, moving rightwards from the peak of the two-electron volcano weakens the interaction with *O and *OOH, increasing the selectivity but lowering the activity. In this context, proper structural engineering of catalytic materials is needed for a balanced improvement on H₂O₂ selectivity and activity.
Here in this progress report, we will pinpoint fundamental understanding and recent tuning strategies on Pt for 2e\(^{-}\) ORR from the well-known 4e\(^{-}\) pathway, these knowledges could be further applied to develop other transition metal catalysts toward efficient \(\text{H}_2\text{O}_2\) production. Other key advances like metalloid-doped carbon materials and transition metal single atom coordinated motifs are overviewed. At last, challenges and perspectives for scaling up promising catalysts from lab tests to pilot plants operation are forecasted.

2. Tuning Knobs for ORR Selectivity on Pt

Pt electrode is most well known for its capability of reducing \(\text{O}_2\) into \(\text{H}_2\text{O}\) toward a fully release of chemical energy into electricity. On the other hand, 2e\(^{-}\) ORR for onsite hydrogen peroxide generation as noted above is of increasing interest recently. Therefore, the ORR reaction pathway tuning on these intensively investigated Pt-based model systems is an important step from the fundamental understanding of reaction mechanism to the development of more efficient \(\text{H}_2\text{O}_2\) production catalysts.

2.1. Development of Monometallic Pt Catalysts

Earlier electrochemical studies suggest that ORR occurs through a serial pathway of “two step” two-electron process with \(\text{H}_2\text{O}_2\) as intermediate, and if the catalyst nanoparticles are sparsely distributed, there will be room for \(\text{H}_2\text{O}_2\) escaping before its fully reduction to \(\text{H}_2\text{O}\).[14] Following this line, Pt loading and interparticle spacing should be straightforward parameters to fine tune the \(\text{H}_2\text{O}_2\) selectivity. Inaba et al. observed a \(\approx 67\%\) \(\text{H}_2\text{O}_2\) selectivity at 0.05 V versus RHE on 5.7 \(\mu\text{g}_{\text{carbon}}\text{-cm}^2\) Pt/C-cast glassy carbon electrode within 1 m \(\text{HClO}_4\), which decreases with an increase in agglomeration of Pt/C catalyst loading up to 56.7 \(\mu\text{g}_{\text{carbon}}\text{-cm}^2\).[15] This phenomena have also been verified by different research groups.[16–19] Compton and co-workers investigated a series of Pt nanoparticles modifies glassy carbon electrode with Pt surface coverages from 0.46% to 1.96% and nanoparticle size distribution from 29 to 136 nm.[20] They found that the nature of oxygen reduction depends on the delicate interaction between diffusion and chemical kinetics. Under the condition of small particle size, the intermediate is easier to diffuse, and oxygen reduction on platinum approximates to a 2e\(^{-}\) reduction producing \(\text{H}_2\text{O}_2\) rather than a 4e\(^{-}\) reduction producing \(\text{H}_2\text{O}\). Besides, the intrinsic electron transfer coefficient is also suggested to be affected by the size of the Pt nanoparticles. Figure 1b shows uniform arrays of Pt nanoparticle reported by Zou and co-workers with more controlled size and interparticle distance.[21] \(\text{H}_2\text{O}_2\) selectivity is revealed to increase with the decrease of Pt nanoparticles size and the increase of particles spacing.[21,22] From a theoretical view, smaller-sized Pt nanoparticles exhibit lower binding energy for oxygenated species, which is favorable for retaining *OOH toward the 2e\(^{-}\) ORR pathway.[23]

Isolating large Pt ensembles is demonstrated to be another effective way to improve \(\text{H}_2\text{O}_2\) selectivity. Markovic et al. reported that chemically modified platinum with a self-assembled monolayer of calix[4]arene molecules could positively shift the onset potential for \(\text{H}_2\text{O}_2\) generation by \(\approx 300\text{mV}\) as compared to a clean Pt(111) surface, together with a predominant 2e\(^{-}\) ORR below 0.6 V versus RHE in 0.1 m \(\text{HClO}_4\) (Figure 1c).[24] Similar effects of halogen anions adsorption,[25–28] cyanide ion modification,[29] ammonia adsorption,[30,31] and Se-/S-modification[32] to tune up \(\text{H}_2\text{O}_2\) selectivity at 0.05 V versus RHE on 5.7 \(\mu\text{g}_{\text{carbon}}\text{-cm}^2\) Pt/C catalyst, which proceeds via an end-on adsorption configuration of \(\text{O}_2\) followed by a nondissociative desorption of \(\text{H}_2\text{O}_2\) as suggested by the authors. As an extreme case of Pt dispersion, Choi et al. deposited an amorphous carbon layer to isolate the Pt sites (Figure 1d).[33] Up to \(\approx 48\%\) \(\text{H}_2\text{O}_2\) selectivity is observed in 1 m \(\text{HClO}_4\) on this Pt@C catalyst, which proceeds via an end-on adsorption configuration of \(\text{O}_2\) followed by a nondissociative desorption of \(\text{H}_2\text{O}_2\) as suggested by the authors. As an extreme case of Pt dispersion, Choi et al. further extend this isolation concept into atomically dispersed Pt catalyst over high sulfur-doped zeolite-templated carbon substrate with a relatively high Pt loadings of 5 wt% as shown in Figure 1e.[34]
An early onset potential of $\text{H}_2\text{O}_2$ production at 0.71 V versus RHE is demonstrated together with a high $\text{H}_2\text{O}_2$ selectivity up to 96% in 0.1 m $\text{HClO}_4$. Due to the fast development of nanotechnology and methodology, catalytic motifs can be precisely designed and engineered at atomic level. Sub-nanometric Pt clusters or even atomically
dispersed Pt sites are more often adapted for 2e\textsuperscript{-} ORR. Bian and co-workers comparatively investigate H\textsubscript{2}O\textsubscript{2} selectivity over a series of graphene supported Pt, for which isolated Pt atom catalyst exhibits a H\textsubscript{2}O\textsubscript{2} selectivity up to 95% in 0.1 m KOH while larger crystalline Pt nanoparticles show preference of 4e\textsuperscript{-} ORR with increasing particle size.\[36\] Figure 1f shows the dispersion of 0.35 wt% Pt/TiN catalyst with a H\textsubscript{2}O\textsubscript{2} selectivity up to 65% in 0.1 m HClO\textsubscript{4} and a mass activity of 78 A per gram Pt at an overpotential of 0.05 V.\[37\] The same group further investigated the effect of support on monoatomic platinum catalysts.\[38,39\] Atomically dispersed Pt over TiC is found to show a higher H\textsubscript{2}O\textsubscript{2} selectivity than Pt/TiN, which is associated with a less exothermic process of O\textsubscript{2} adsorption and a weaker interaction with the former Pt-TiC surface as suggested by DFT calculations.\[38\] Lin and co-workers prepared a series of Pt adatom modified AuCu nanoaerogels (Figure 1g),\[40\] with a H\textsubscript{2}O\textsubscript{2} selectivity up to 91.8% after composition optimization. The synergistic effect of AuCu alloys and the favorable mass and electron transfer by employing robust 3D hybrid porous architecture are counted for this observed H\textsubscript{2}O\textsubscript{2} selectivity. More recently, Li et al. developed a hollow nanosphere catalyst constructed by dispersing Pt atoms over amorphous CuS\textsubscript{x} support with a high concentration of single atomic Pt sites (≈24.8 at\%).\[41\] The strong Pt–S interaction ensures that the Pt atom would preferentially coordinate with sulfur without the formation of Pt clusters. This catalyst can consistently reduce O\textsubscript{2} into H\textsubscript{2}O\textsubscript{2} with selectivity of 92%–96% over a wide potential range of 0.05–0.7 V versus RHE in acidic HClO\textsubscript{4} electrolyte (Figure 1h).

2.2. Development of Pt-Based Alloy Catalysts

Alloying Pt with another host metal is also an effective strategy to isolate platinum sites for 2e\textsuperscript{-} ORR. Siahrostami et al. have initially screened over 30 alloy catalysts using DFT calculations for potential cathodic H\textsubscript{2}O\textsubscript{2} generation catalyst,\[13\] and pinpointed PtHg\textsubscript{4} as a promising candidate with a suitable HOO\textsuperscript{*} binding energy close to the summit of 2e\textsuperscript{-} ORR volcano plot (Figure 1a). Experimentally, they synthesized a stable Pt@Hg/C alloy catalyst comprising a Pt core and a Pt–Hg shell as shown in Figure 2a. This alloy catalyst exhibits a high H\textsubscript{2}O\textsubscript{2} selectivity of above 90% between 0.3 and 0.5 V and a mass activity of 26 ± 4 A g\textsuperscript{-1} at an overpotential of 50 mV. Similar concept on Pt–Pd\[42\] and Pt–Au\[43,44\] alloys have also been demonstrated. By employing a well-defined Pt(111) single crystalline surface, Behm et al. prepared Au\textsubscript{4}Pt\textsubscript{1} /Pt (111) surface alloy electrodes with varied Au surface contents and explored their ORR performance (Figure 2b).\[43\] For Au-rich surfaces (>50%), the catalytic...
properties of the surface alloys shift towards that of polycrystalline Au, with an increasing tendency for H$_2$O$_2$ formation. A rational design of alloying components and composition is expected to further improve H$_2$O$_2$ production performance. Theoretically, cuboctahedral nanoclusters of Pt$_{79}$Au$_{19}$@Pt$_{60}$, Co$_{29}$@Pt$_{60}$ and Au$_{10}$Co$_{9}$@Pt$_{60}$ enclosed by well-defined (111) facet have been screened for 2e$^-$ versus 4e$^-$ ORR, in which ternary Au$_{10}$Co$_{9}$@Pt$_{60}$ is identified as most efficient and selective for H$_2$O$_2$ formation based on reaction free energies and activation barriers analysis. Experimentally, Ni-coated Au–Pt (Au–Pt–Ni) nanorods are found to be selective for H$_2$O$_2$ generation. The epitaxial growth of Ni over Au–Pt core with continuous lattice fringes is suggested to fine tune the electronic property of surface sites, leading to a H$_2$O$_2$ selectivity up to 95% and a current density of 1.01 mA cm$^{-2}$ (=192.9 A g$^{-1}$(noble metal)) at an overpotential of 150 mV (Figure 2c).

3. Non-Pt Based Catalysts

3.1. Nanostructure Design of Transition Metal Catalysts

As noted above, the selectivity of ORR toward H$_2$O$_2$ is determined by the competitive pathways of *OOH direct protonation versus that of O–O bond dissociation into *O, which are intrinsically varied on different metal surfaces. Figure 3a shows the ORR activity trend for a range of bulk metals as derived from either a limiting potential volcano of thermodynamic analysis (solid line) or a kinetic volcano from microkinetic modeling (dotted line). Similar to bulk Pt, the model surfaces like Pd(111) and Ag(100) locating at the left leg of the volcano show a strong affinity for oxygenated species, thus proceeding mainly the 4e$^-$ pathway to H$_2$O. In contrast, a weak interaction on Au(111) and Ag(111) surfaces would result in a lower overall ORR activity but a higher H$_2$O$_2$ kinetic current density as shown in Figure 3b, which is in good harmony with earlier experimental results on single crystalline electrodes.

On the basis of high H$_2$O$_2$ selectivity over Au model surfaces among various transition metal candidates, Jirkovsky et al. have employed Au(111) as the substrate and computationally screened several electroactive surface containing discrete guest transition metal atoms as Au-M reactive centers. As illustrated in Figure 3c, three alloying elements of dispersed Pd, Pt, or Rh are least favored for *O–O and *OH dissociation reactions, which should display higher H$_2$O$_2$ production selectivity than pure gold. Experimentally, they carried out a colloidal synthesis to prepare carbon-supported cube-octahedral Au nanoparticles (Figure 3d) and an impregnation-reduction method to prepare a series of Au$_{x}$Pd$_{y}$/C catalysts with different Pd contents (Figure 3e). A maximum $\approx$90% H$_2$O$_2$ selectivity can be achieved on Au/C at the potential window from 0.4 to 0.5 V versus RHE in 0.1 M HClO$_4$ and decreases with increasing overpotential. An optimum Pd doping of 8% improves the H$_2$O$_2$ selectivity to $\approx$95% and suppresses its further reduction H$_2$O$_2$ at negative potential regions to sustain a higher H$_2$O$_2$ production performance. Thereafter, Pizzutillo et al. carried out a more detailed components screening of Au$_{x}$Pd$_{y}$/C and a stability test on the bimetallic system by accelerated degradation protocol, revealing that incorporating trace amount of Pd could enhance the onset potential (and activity) for H$_2$O$_2$ generation while at the sacrifice of selectivity.

Sanchez-Sanchez and Bard employed scanning electrochemical microscopy method to screen H$_2$O$_2$ selectivity in acidic ORR over different metal electrodes. For Cu and Ag, a noticeable change from 2e$^-$ toward 4e$^-$ path is observed as the potential becomes more negative, while Hg proceeds an exclusive 2e$^-$ pathway for entire ORR potential window studied. This unique selectivity makes Hg an ideal host to isolate other catalytic metals like Ag(-Hg), Pt(-Hg), and Pd(-Hg) shown in Figure 3b. Taken Pd metal for example, bulk Pd is known to be selective for the complete reduction of oxygen to water because it can efficiently catalyze both O–O bond scission and O–H bond formation. Shown in Figure 3f are the representative STEM-EDX images of core–shell structured Pd–Hg nanoparticles with an anisotropic thickness of Hg-enriched shell. This delicate arrangement of isolated Pd sites surrounding by Hg matrix leads to a H$_2$O$_2$ selectivity of $\approx$95% within a potential window between 0.35 to 0.55 V versus RHE in 0.1 M HClO$_4$. In addition to the alloying strategy to isolate active sites, Figure 3g demonstrates another approach of fabricating amorphous Pd nanocatalyst at a size distribution below 5 nm by in situ electrochemical deposition. Both the STEM image and the EXAFS pattern suggest the lack of long-range structural Pd–Pd or Pd–O arrangements for the deposited amorphous Pd. In sharp contrast to the crystalline Pd and PdO counterparts, this amorphous Pd catalyst delivers a potential-averaged H$_2$O$_2$ selectivity of 95.1%.

There are some reports on alternative transition metal-based catalysts like CoS$_2$, MnO$_2$, octahedra shaped Mn$_{1.5}$Co$_{0.5}$O$_4$, nanoporous Mn–Ru oxide for cathodic H$_2$O$_2$ generation. However, major challenges remain as narrow applicable potential range for 2e$^-$ pathway, metal oxide catalyzed H$_2$O$_2$ decomposition etc., which should be carefully addressed before their practical operations.

3.2. Defects and Heteroatoms Engineering on Carbon-Based Catalysts

Carbon-based materials like carbon particle pack, polytectic graphite, glassy carbon etc. have been employed in electrocatalytic H$_2$O$_2$ production system for a long time, mainly due to their inexpensive and earth abundant nature as well as widely tunable surface and structural properties to boost electrocatalytic performance. Herein, we will summarize some recent progress on the carbon structural engineering by defective sites and mesostructured design, as well as by both metal- and metal-heteroatoms doping.

Bao and co-workers comparatively investigated the ORR performance on microporous and mesoporous carbon materials in 0.1 M KOH. The mesoporous structure provides greater electrochemical accessibility and an overall improved activity, selectivity and stability as compared to the microcarbon. Through synergistic spectroscopic characterizations and DFT calculations, the sp$^3$-type defects, especially these double-vacancy defective types with nonhexagonal ring members, are identified as the active sites for 2e$^-$ ORR. Graphitic carbon edges have been reported to exhibit superior electrocatalytic properties than those...
of basal carbons owing to the modified local electronic structure.[71,72] Joo et al. have extended this concept into cathodic \( \mathrm{H}_2\mathrm{O}_2 \) production. As shown in Figure 4a, they prepared a graphitic ordered mesoporous carbon (GOMC) catalyst with periodic hexagonal array mesostructures. This edge-enriched nanocarbon catalyst exhibits about 28 times higher activity for \( \mathrm{H}_2\mathrm{O}_2 \) production than a basal plane-rich carbon nanotube (CNT) with a \( \mathrm{H}_2\mathrm{O}_2 \) selectivity over 90%.[73] With the aid of Tafel slope and electrochemical impedance spectroscopic analysis, the authors pointed out that the first electron transfer ability from carbon to \( \mathrm{O}_2 \) molecule (known as \( \mathrm{O}_2 \) activation) is a prime determinant of the ORR activity. Chorkendorff et al. screened seven commercially available carbon (GOMC) catalyst with periodic hexagonal array mesostructures. This edge-enriched nanocarbon catalyst exhibits about 28 times higher activity for \( \mathrm{H}_2\mathrm{O}_2 \) production than a basal plane-rich carbon nanotube (CNT) with a \( \mathrm{H}_2\mathrm{O}_2 \) selectivity over 90%.[73] With the aid of Tafel slope and electrochemical impedance spectroscopic analysis, the authors pointed out that the first electron transfer ability from carbon to \( \mathrm{O}_2 \) molecule (known as \( \mathrm{O}_2 \) activation) is a prime determinant of the ORR activity. Chorkendorff et al. screened seven commercially available carbon materials for \( 2e^- \) ORR and revealed that \( \mathrm{H}_2\mathrm{O}_2 \) selective materials have higher contribution from the C1s peak component correlated with aliphatic-type defects and edge carbon atoms, as opposed to intact graphitic carbon motifs.[74] To determine the carbon defects content, Raman spectroscopy has also been reported in literature for which the intensity ratio of D band to G band serves as a descriptor correlating \( \mathrm{H}_2\mathrm{O}_2 \) selectivity with intrinsic \( \mathrm{sp}^3-C \) bond and defects distribution.[75] Metalloid doping is another widely deployed strategy to create defective carbon motifs. Though N-doped carbon has been reported to be active for \( 4e^- \) ORR,[76,77] there are actually a variety of C–N coordination structures such as pyridinic, pyrrolic or quaternary, which in turn give rise to the possibility of searching more selective \( 2e^- \) ORR catalysts. By using N-butyl-3-methylpyridinium dicyanamide as precursor and commercial silica nanoparticles as hard templating, Fellinger et al.[78] reported a mesoporous N-doped carbon material that delivers \( 2e^- \) transfer at the potential window of 0.1 to 0.3 V versus RHE in 0.1 M \( \mathrm{HClO}_4 \). Figure 4b shows a representative image of N-doped carbon with 3.4–4.0 nm well-ordered mesopores. The good mass transport boosts acidic \( \mathrm{H}_2\mathrm{O}_2 \) selectivity over 90% in a wide potential window from 0.0 to 0.5 V.[79] More recently,
Sun et al. explored the N-doping effect on commercial CMK-3 carbon (Figure 4c) and correlate the H₂O₂ product yield with other physicochemical properties including surface area and interfacial zeta potential. It is suggested that N-functionalities play a beneficial role at low active surface site density; however, they appear to be detrimental for the H₂O₂ selectivity at high contents. Fornasiero and co-workers developed a class of single-wall carbon nanohorns catalysts with N-doping as shown in Figure 4d. This carbon nanohorn catalyst exhibits a H₂O₂ Faradaic efficiency up to 98% in acidic media, which is ascribed to the optimized N-doping content and the suitable porosity.

Besides the above studies on N-doped carbons, different dopants like B, F, and S have been explored to tune the activity of carbon catalyzed H₂O₂ generation. Notably, oxidized carbon material like activated carbon is an emerging class of efficient catalysts for 2e⁻ ORR. Figure 4e plots the limiting potential volcano of H₂O₂ pathway as a function of ΔG_{OOH}. Over different types of oxygen functional groups screened, the C=O=C groups located either on the basal plane or at the edge of the graphene, and the −COOM at the armchair edge are most active for H₂O₂ production. Experimentally, a facile surface oxidation approach of carbon nanotubes could enhance H₂O₂ selectivity up to 90% in both basic and neutral media, verifying the theoretical description. Following this line, other catalysts like air-annealed carbon black, mildly reduced graphene oxide, etc. have been disclosed for selective O₂ reduction to H₂O₂. On the basis of beneficial effects from oxygen functional group and N-dopants, Han et al. investigated the N-doping effect onto oxo-functionalized graphene and clarified the role of in-plane carbon lattice defects on H₂O₂ selectivity (Figure 4f).

Earlier studies on molecular complexes suggested M−N₇ coordination structure could be active for H₂O₂ production. Transition-metal single atom motifs coordinated in carbon matrix are emerging as highly selective H₂O₂ production catalysts bridging earlier homogeneous research fundamentals with more-efficient heterogeneous electrocatalysts design. As compared to their bulk metal counterparts, single atom catalysts with strong ensemble
and ligand effects hold the potential to break scaling relations for the adsorption of reaction intermediates, i.e., \(^*\)O, \(^*\)OOH and \(^*\)OH, making room for \(\Delta G_{HOO^*}\) and \(\Delta G_{O^*}\) tuning toward a balanced improvement on \(H_2O_2\) production activity and selectivity.[95] Shown in Figure 5a,b are representatives of Co–N–C sites anchored on carbon substrates. Zhang et al. synthesized a Co–N\(_x\)–C site and oxygen functional group comodified carbon catalyst, exhibiting a \(H_2O_2\) selectivity over 80% in 0.1 m KOH and an early onset potential at 0.79 V versus RHE.[96] Co–N\(_x\)–C moiety is suggested to contribute to the reactivity and oxygen functional groups are suggested to contributed to the 2e\(^-\) ORR selectivity. Figure 5b shows a Co–N\(_4\)/graphene catalyst with the similar designing strategy that Co–N\(_4\) moieties are surrounded by the desired configuration of electron-rich oxygen atoms from graphene oxide substrates.[97] As a result, this synergy effect delivers a kinetic current density of 2.8 mA cm\(^{-2}\) at 0.65 V in 0.1 m KOH with \(\approx 82\%\) \(H_2O_2\) selectivity and maintains 98.7% activity after 110 h operation. More recently, Liu and co-workers carried out a detailed kinetic analysis on Co–NC single-atom catalyst for 2e\(^-\) ORR in acidic media.[98] By tuning electrolyte pH and \(O_2\) partial pressure, they observed a \(H^+\) reaction order of \(-0.05\) to \(-0.07\) and a \(O_2\) reaction order of 0.53–0.9 within an overpotential of 0 to 250 mV, suggesting the first electron transfer step (\(O_2 + * + e^- \rightarrow *O_2^-\)) to be the rate-limiting step for \(H_2O_2\) synthesis at this onset region (Figure 5c).

It is noted that these isolated M–X–C motifs have strong capabilities in tuning intrinsic binding strength with reaction intermediates, i.e., \(^*\)O, \(^*\)OOH and \(^*\)OH, making room for \(\Delta G_{HOO^*}\) and \(\Delta G_{O^*}\) tuning toward a balanced improvement on \(H_2O_2\) production activity and selectivity.[95] Shown in Figure 5a,b are representatives of Co–N–C sites anchored on carbon substrates. Zhang et al. synthesized a Co–N\(_x\)–C site and oxygen functional group comodified carbon catalyst, exhibiting a \(H_2O_2\) selectivity over 80% in 0.1 m KOH and an early onset potential at 0.79 V versus RHE.[96] Co–N\(_x\)–C moiety is suggested to contribute to the reactivity and oxygen functional groups are suggested to contributed to the 2e\(^-\) ORR selectivity. Figure 5b shows a Co–N\(_4\)/graphene catalyst with the similar designing strategy that Co–N\(_4\) moieties are surrounded by the desired configuration of electron-rich oxygen atoms from graphene oxide substrates.[97] As a result, this synergy effect delivers a kinetic current density of 2.8 mA cm\(^{-2}\) at 0.65 V in 0.1 m KOH with \(\approx 82\%\) \(H_2O_2\) selectivity and maintains 98.7% activity after 110 h operation. More recently, Liu and co-workers carried out a detailed kinetic analysis on Co–NC single-atom catalyst for 2e\(^-\) ORR in acidic media.[98] By tuning electrolyte pH and \(O_2\) partial pressure, they observed a \(H^+\) reaction order of \(-0.05\) to \(-0.07\) and a \(O_2\) reaction order of 0.53–0.9 within an overpotential of 0 to 250 mV, suggesting the first electron transfer step (\(O_2 + * + e^- \rightarrow *O_2^-\)) to be the rate-limiting step for \(H_2O_2\) synthesis at this onset region (Figure 5c).

It is noted that these isolated M–X–C motifs have strong capabilities in tuning intrinsic binding strength with reaction intermediates for boosting desired catalytic pathways, i.e., by varying different metal atom centers and/or by varying different adjacent coordinative dopants. In fact, modulating the local coordination environment of transition-metal single atoms has been demonstrated as an effective way in tuning their catalytic activity, selectivity and stability.[99–102] In a latest work, our group pinpointed Fe–C–O as an efficient \(H_2O_2\)
catalyst, with an unprecedented onset of 0.822 V versus RHE in 0.1 m KOH to deliver 0.1 mA cm\(^{-2}\) \(\text{H}_2\text{O}_2\) current, and a high \(\text{H}_2\text{O}_2\) selectivity of above 95% in both alkaline and neutral pH.\(^{[103]}\) To better investigate the structure–activity relationship, state-of-the-art atomic structure characterizations have been carried out including scanning TEM, synchrotron radiated X-ray absorption spectroscopy as well as statistic atom probe tomography analysis derived from a \(\approx 9\) million ions (atoms) dataset (Figure 5d). Fe–C–O motifs are identified as the active center for 2e\(^{-}\) ORR by the synergistic experimental approaches and DFT calculations, in sharp to the well-known 4e\(^{-}\) ORR pathway on Fe–C–N. Qiao and co-workers came up with a multicomponential catalyst design by anchoring high-loading Mo single atoms (\(\approx 13.47\) wt% Mo content) onto porous oxygen, sulfur-doped graphene frameworks,\(^{[104]}\) for which Mo–O/S–C motifs are assigned as the active center contributing to \(\approx 95\%\) \(\text{H}_2\text{O}_2\) selectivity in 0.1 m KOH. As another representative of metal atom centers tuning, Kim et al. prepared a series of noble metal single atom catalysts supported on CNTs via a “trapping-and-immobilizing” method consisting of SiO\(_2\)/carbonaceous layer/CNT composite structures and screened their 2e\(^{-}\) ORR performance in 0.1 m HClO\(_4\) as shown in Figure 5e.\(^{[105]}\) Atomically dispersed Pt/CNT is identified as the most selective catalyst toward \(\text{H}_2\text{O}_2\) and the selectivity trend could be correlated to the binding energy difference between *OOH and *O species on the M–N\(_4\) moieties investigated.

4. Summary and Outlook

The electrocatalytic reduction of \(\text{O}_2\) into \(\text{H}_2\text{O}_2\) driven by renewable energy is emerging as a green and cost-effective route in precise electrochemical synthesis. In the past years, great efforts have been devoted for this 2e\(^{-}\) ORR field with a synergistic approach from both theoretical modeling on the reaction mechanism and novel catalysts design by specific structure tailoring. As illustrated in Figure 6, we summarize some general principles for efficient \(\text{H}_2\text{O}_2\) production catalyst design in this progress report by using Pt as the model, i.e., a lower binding strength of oxygenated species, a facile intermediate diffusion path and a frustrated Pt–Pt pair or even an atomically isolated Pt site would improve the \(\text{H}_2\text{O}_2\) selectivity. Moreover, these knowledges have been successfully applied to other transition metal systems and lead to the discovery of more efficient alloy catalysts with balanced improvement on both activity and selectivity of 2e\(^{-}\) ORR. For carbon-based materials, proper mesostructure engineering and heteroatoms doping could create more active motifs for \(\text{H}_2\text{O}_2\) production than the intact carbon sites. Following this line, future catalysts development would focus on improving kinetic current densities for a more energy-efficient perspective as well as extending applicable \(\text{H}_2\text{O}_2\) potential window toward a flexible control on products output demand.

Besides these materials’ innovation, researches on reactor architecture optimization have also been explored at pilot scale. For example, using a gas diffusion electrode setup within a channel flow cell\(^{[106]}\) or a solid-state electrolyte configured reactor,\(^{[8]}\) tunable output \(\text{H}_2\text{O}_2\) concentrations at industrial current densities have been demonstrated. To merit requirements in these scaled-up reactors, long-term stability of cathodic catalysts regarding both material structure and product selectivity should be properly addressed, especially given the longtime exposure to superhydroxyl radicals.

At last but not least, the electrochemical reduction of \(\text{O}_2\) to \(\text{H}_2\text{O}_2\) could serve as a representative of precise electrochemical synthesis for a broader trend. The physical and electronic structure engineering for certain active moieties toward 2e\(^{-}\) ORR pathway tuning could provide vital hints for more complex electrochemical synthesis like artificial photosynthesis from \(\text{CO}_2\) fixation and ammonia synthesis from \(\text{N}_2\) reduction.

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Conflict of Interest

The authors declare no conflict of interest.

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electrocatalysis, hydrogen peroxide, oxygen reduction reaction, platinum, single atom catalysts

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