A fundamental comprehension and recent progress in advanced Pt-based ORR nanocatalysts

Yao Wang | Dingsheng Wang | Yadong Li

Department of Chemistry, Tsinghua University, Beijing, China

Abstract
Today, Pt/C catalysts are widely used in proton exchange membrane fuel cells (PEMFCs). The practical applications of PEMFCs still face many limitations in the preparation of advanced Pt-based catalysts, including high cost, limited life-time, and insufficient power density. A kinetically sluggish oxygen reduction reaction (ORR) is primarily responsible for these issues. The development of advanced Pt-based catalysts is crucial for solving these problems when the large-scale application of PEMFCs is to be realized. Herein, we demonstrate the design principle of advanced Pt-based catalysts with an emphasis on theoretical understandings to practical applications. Generally, three main strategies (including strain effect, electronic effect, and ensemble effect) that governing the initial activity of Pt-based electrocatalysts are elaborated in detail in this review. Recent advanced Pt-based ORR catalysts are summarized and we present representative achievements to further reveal the relationship of excellent ORR performance based on theoretical mechanisms. Then we focus on the preparation standards of membrane electrode assembles and testing protocols in practice. Finally, we predict the remaining challenges and present our perspectives with regards to design strategies for improving ORR performance of Pt-based catalysts in the future.

KEYWORDS
catalytic performance, membrane electrode assembles, oxygen reduction reaction, proton exchange membrane fuel cells, Pt-based catalysts

1 | INTRODUCTION
Currently, because of high-efficiency, stable, and environment-friendly advantages, proton exchange membrane fuel cells (PEMFCs) are regarded as a promising energy transformation to solve the energy issues around power sources of automobiles.¹⁻³ Pt-based catalysts as the most promising cathode electrode materials are always used to catalyze the oxygen reduction reaction (ORR) in PEMFCs.⁴ However, the sluggish kinetics of ORR restricts the whole reaction process of PEMFCs.⁵,⁶ Thus, rational design and preparation of advanced Pt-based ORR catalysts widely attract researcher’s attention. To solve these issues, a fundamental understanding of the limiting factors of ORR is the basis to guide correctly the fabrication of ORR catalysts from the insight of nanoscience and nanocatalysis at the atom level. Intrinsic advantages of Pt make it the competent object to catalyze the ORR
process. In 2007, the per-KW cost of 80 kW\textsubscript{net} PEMFCs systems with high-volume manufacturing of 500,000 units had reached about $45/kW\textsubscript{net}, with a $15/kW\textsubscript{net} gap between the long-term cost targets of $30/kW\textsubscript{net}.\textsuperscript{7} However, the high-cost price and scarcity of Pt on the earth are the main bottleneck limitations to their wide commercial applications for industrialization process.\textsuperscript{8–10}

Recently, enormous achievements of advanced Pt-based catalysts have been achieved on theoretical understandings of ORR kinetics, which mainly focus on the following aspects: (i) Understanding the intrinsic mechanisms of ORR kinetics. Due to the complicated the ORR reaction pathway, the reaction kinetics of ORR is limited by adsorption energy and active energy of O\textsubscript{2} molecules on catalyst surface atoms.\textsuperscript{11–15} (ii) Demonstrating the effect factors of ligand effect, strain effect, and ensemble effect of Pt-based catalysts toward ORR. Constructing the corresponding relationships between the design principle of catalysts and the reaction mechanism of ORR is beneficial for preparing advanced Pt-based catalysts.\textsuperscript{16–23} According to the Sabatier principle,\textsuperscript{24} the interactions between catalyst surface/interface atoms and the reactant should be neither too strong nor too weak. Thus, surface engineering strategies based on ligand effect, strain effect, and ensemble effect are widely explored to elaborate the impact of every factor on ORR performance. Usually, implanting a foreign secondary metal into the surface lattice of Pt will induce all the above effects, which is an efficient and facile method for improving the ORR performance. Besides, other synthesis strategies, modification methods, and engineering tactics are also performed to further clarify the relationships between theoretical mechanisms and practical ORR performance, such as, forming Pt skin or skeleton,\textsuperscript{25,26} shaping Pt alloy,\textsuperscript{27} exposing high-index facets,\textsuperscript{28,29} creating multidimensional nanostructure,\textsuperscript{25,30} phase hybrid,\textsuperscript{31} ordered intermetallic Pt-based alloy,\textsuperscript{26} and single atom site catalysts.\textsuperscript{32} (iii) Presenting several advanced Pt-based ORR catalysts. Under these theoretical design principles, extensive works have been developed to accommodate the PEMFC targets. The design of these catalysts fully follows the above design principles of advanced Pt-based electrocatalysts mentioned above. (iv) Elaborating the relationships between laboratory ORR performance and practical applications of the single fuel cell. The relationship between electrochemical performance and advanced materials and morphology in ex situ setups is extremely challenging in terms of reproducibility and reliability; thus further efforts are needed to study catalysts under technically relevant conditions. Figure 1 shows the overview of the topics covered in this review. Finally, we present a

Figure 1: Overview of the topics covered in this review.
perspective of further research directions to point out
the challenges and strategies for next-generation Pt-
based catalysts.

2 | FUNDAMENTAL UNDERSTANDING OF ORR MECHANISM

Due to the complex kinetics of ORR and complicated in-
termediates during the whole ORR process, it is a great
challenge for us to understand the intrinsic ORR mecha-
nism from the atomic or molecular level to design Pt-based
electrocatalysts. It is generally accepted that the com-
plete electron transfer (4e⁻) is in favor of ORR; on the
contrary, the two-electron pathway is undesirable because
its final product is H₂O₂, which will destroy the Nafion
membrane and cause damage to fuel cells. Theoretical
studies reveal that four-electron pathway is preferred to
occur on the Pt crystal facet with (111) under the condition
of oxygen enrichment. Thus, the elemental steps of ORR
are usually presented in the following (*denotes an active
site of catalyst):

Four-electron pathway

\[
\begin{align*}
\text{O}_2 + 4(\text{H}^+ + e^-) & \rightarrow 2\text{H}_2\text{O} \quad E = 1.23\text{V vs. RHE,} \\
1/2\text{O}_2 + 2(\text{H}^+ + e^-) & \rightarrow *\text{O} + 2(\text{H}^+ + e^-) \rightarrow *\text{OH} \quad + (\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O,} \\
\text{O}_2 + 4(\text{H}^+ + e^-) & \rightarrow *\text{OOH} + 3(\text{H}^+ + e^-) \rightarrow *\text{OH} \quad + (\text{H}^+ + e^-) \rightarrow 2\text{H}_2\text{O.}
\end{align*}
\]

Two-electron pathway

\[
\begin{align*}
\text{O}_2 + 2(\text{H}^+ + e^-) & \rightarrow \text{H}_2\text{O}_2 \quad E = 0.70\text{V,} \\
\text{O}_2 + 2(\text{H}^+ + e^-) & \rightarrow *\text{OOH} + (\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O}_2.
\end{align*}
\]

The electroreduction of O₂ will go through two dif-
ferent pathways based on whether the bond-breaking of
*OOH or not. The optimized catalyst possesses strong
binding energy, which is beneficial for splitting of O–O
bond. This review is based on the Pt-based catalysts, so
the strong oxygen-binding energies on Pt sites facil-
itate the form of *O to some extent, namely the four-
electron pathway. Furthermore, the binding free energies
of intermediate, such as *OOH, *OH, *OH, derived from
complete reduction is shown in Figure 2A. It was re-
ported that the binding free energy of intermediates is
linearly related to each other. The *OH-binding free energy
\[\Delta G_{\text{OH}} = 1/2\Delta G_{\text{O}}\] and \[\Delta G_{\text{OH}} = \Delta G_{\text{OOH}}-3.2\] so the \(\Delta G_{\text{OH}}\)
could be used as a descriptor to evaluate the ORR
performance. According to the Sabatier principle, the
interactions between the catalyst surface atoms and the
reactants/intermediates should be neither too strong nor
too weak, revealing the presence of maximum catalytic
activity to some extent. Figure 2B shows the ORR ac-
tivity plot for different metals as a function of *OH binding
free energy. We can clearly see that, in this volcano plot, an
ideal ORR catalyst should locate on the peak, whose
overpotential is minimum. In other words, for metals that
bind oxygen-containing species too strongly, the generation
of H₂O₂ rooting from the further reduction of *OH will
control the pace of the reaction, while for metals that bind
oxygen-containing species too weakly, the ORR perfor-
mance will be determined by activity/dissociation of O₂ and
deep reduction of *OOH. Among these metals, Pt is the best
candidate for ORR, while there is still higher binding energy
of about 0.2 eV in comparison with the plot peak. Thus,
decreasing the d-band center of Pt-based catalyst is
crucial for improving ORR performance.

Under the above discussions, many researchers made
everous efforts to further explore the specific activities of
different Pt-based alloy catalysts from the theoretical and
experimental aspects. In theory, Figure 2C shows that Ni and
Co are the best two promising elements for optimizing the
binding free energy of adsorbed oxygen-containing species
on Pt. Similarly, enormous literatures relating to Pt-based
catalysts (alloying with Ni, Co, Fe, V, Ti etc.) were reported
and established an obvious linear relationship between the
ORR catalytic activity and metal d-band center under the
experimental conditions. The Stamenkovic et al. reported
that the transition metals (Ni, Co, Fe, Ti, V) from the
fourth-period alloy with Pt would form a “volcano-shaped”
relation, focusing on the ORR activity and d-band center
for Pt-rich surfaces and Pt-skeleton surfaces. It can be obtained
from Figure 2D that the Pt₃Co alloy catalyst is the best al-
ternative for replacing conventional Pt/C catalyst. In addi-
tion, from the positions of Pt₃Ti and Pt₃V in the polt, it can
be obtained that the d-band center is too far from the Fermi
level, the surface possesses lower coverage of OH⁻ and an-
ions, while the binding energy of O₂ and the intermediates
are too weak to ensure a turnover rate of ORR. Thus, the
rational design of Pt-based catalysts from the viewpoint of
optimizing binding free energy of oxygen-containing species
on surface-active sites is of great importance and efficiency
for enhancing ORR performance.

3 | DESIGNING PRINCIPLE OF HIGH-PERFORMANCE PT-BASED ORR ELECTROCATALYSTS

Considering the sluggish kinetics of ORR, rational de-
signing novel-structured Pt-based electrocatalysts with
excellent performance is of great importance and
significance for fuel cells. Usually, as shown in Figure 3, improving the activity and durability of Pt-based catalysts mainly follows three aspects: (i) increasing the number of Pt active sites; (ii) improving the intrinsic activity of every exposing Pt active sites; (iii) and enhancing the intoxicating behavior of Pt active sites. The previous discussions demonstrate that modulating the electronic structure and coordination environment of surface Pt active sites are beneficial for downshifting the d-band center of Pt, optimizing the interactions between the oxygen-containing species and surface Pt atoms. So far, enormous works have been made to tune/modify the exposing Pt active sites. From theoretical insight, this review will elaborate the relationships between the ORR performance and Pt-based catalysts from strain effect, ligand effect, and ensemble effect.

### 3.1 Strain effect

The surface strain engineering of Pt-based catalysts has obtained researcher’s attention due to its immense potential in modulating the electrocatalytic performance. Strain effect can tune the lattice fringe of surface Pt atoms to improve the electrocatalytic activity while the foreign metals are introduced into the depths of nanocatalysts greater than 1 nm. Strain effect usually appears combining with ligand effect and synergistic effect through tuning the d-band center of Pt-based catalysts and modulating the binding energies of reactants, intermediates, and products. The nature of strain effect formation is lattice
mismatch, which tunes the adsorption or desorption energies via changing the d-band center position. It has been confirmed\textsuperscript{16,58} that the strain effect is based on the long-distance modulation, within six monolayers of catalyst near-surface, while the ligand effect is limited in the two-surface atomic layer. Usually, the calculations of strain effect are based on the distorted percentage of the Pt lattice between the conventional and advanced Pt-based catalysts. It can be defined as follows:

$$S_{\text{Pt}} = \frac{\alpha_{\text{advanced}} - \alpha_{\text{conventional}}}{\alpha_{\text{conventional}}} \times 100\%.$$ \textsuperscript{56}

Where the $\alpha_{\text{advanced}}$ is the lattice value of advanced Pt-based catalyst, the $\alpha_{\text{conventional}}$ is the lattice value of pure conventional Pt particle.

The change of d-band center in the compressive strain case is illustrated in Figure 4A,B, where Ni atom (stands for small metal atoms) is inserted into the lattice or deposited on a Pt bulk with larger lattice spacing. The d-bandwidth will decrease due to the d states overlap of different interfacial metal atoms. On the contrary, if Pt atoms are deposited onto the Ni surface or inserted into Ni surface lattice, the contracted Pt d-bandwidth increases and the xd-band center also downshifts (Figure 4C,D). The recent reports\textsuperscript{65} demonstrate that compressive strain will downshift the d-band center of Pt, triggering a strong interaction. Please note that this rule is only suitable for the late transition metals with a half-filled d-band.

It is accepted that, for ORR, the compressive strain behavior is beneficial for improving the Pt-based catalytic performance. For example, Du et al.\textsuperscript{66} revealed that 52% enhancement and 35% reduction of ORR performance were obtained through depositing 5 nm Pt layers onto the nanofilm under the compressive and tensile conditions, respectively, in comparison with pure nanofilm. On the contrary, Bu et al.\textsuperscript{67} documented that suitable tensile strain can also enhance the ORR performance in the calculations of theoretical exploration. Thus, the cross-light about tensile strain effect will limit the ORR performance should be further study.

Tuning the surface strain behavior is an efficient method for improving the ORR activity of Pt-based nanocrystals. Thus, as mentioned above, to understand the intrinsic behavior of long-distance effect as well the exact number of atomic layers, excluding the influence of interfacial reconstructions and nanocatalyst geometries, is fundamental to understand the strain effect in designing the electrocatalysts with some specific functions. As shown in Figure 5, Wang et al.\textsuperscript{68} documented a strategy

\textbf{FIGURE 3}  Schematic illustration of general designing principle for advanced Pt-based electrocatalysts toward ORR. ORR, oxygen reduction reaction
FIGURE 4  (A) Schematic illustration of the tensile lattice strain behavior. (B) The changes in the Ni d-band structure upon the tensile strain. (C) Schematic illustration of the tensile lattice strain behavior. (D) The changes in Pt d-band structure upon the compressive strain. Reproduced with permission, copyright 2013, Nature Publishing Group

FIGURE 5  (A) Mechanism of the generation of intrinsic strain in 2D transition metal nanosheets. $h$ is the height of an atomic layer. (B) Surface stress of fcc(111) and hcp(111) surfaces compared to the bulk modulus. (C) Ratio of the pressure ($p$) of close-packed surfaces, induced by surface stress, and the bulk modulus for 11 transition metals. (D) Potential energy profile of strained versus unstrained Pd(111) slabs with thicknesses of 8 ML, 4 ML, and 2 ML. (E–G) Intrinsic in-plane strain of fcc(111), fcc(100), and the [110] direction of unreconstructed fcc(110) slabs, with thicknesses from 1 ML to 12 ML. See the supplementary materials for results for the reconstructed fcc (110) surface. Reproduced with permission, copyright 2019, AAAS. ML, monolayer
to demonstrate the intrinsic surface strain in the two-dimensional nanosheets. They found that the attractive interactions of surface atoms would cause a tensile strain, which was equivalent to lead a force of 100 MPa onto the catalyst’s surface and resulting in about 10% contraction stress. In addition, the exact stress value is inversely proportional to the thickness of the nanosheets.

3.2 | Ligand effect

Ligand effect usually occurs on the interfaces of different atoms with dissimilar electronegativity (possessing different d-band center) that makes for the electronic charge transfer between them.\textsuperscript{68,69} The ligand effect can weaken the difference of electronegativity and make the whole catalyst in the lowest energy state. For Pt-based catalysts, alloying Pt with transition metals (such as Ni, Fe, Co)\textsuperscript{2,70–72} is in favor of weakening the d-band center via electron donation (Figure 6A). In the year 2007, Stamenkovic et al.\textsuperscript{73} (Figure 6B) revealed that the Pt\textsubscript{3}Ni (111) surface is ten times more active toward ORR than Pt(111) surface and ninety times more active than commercial Pt/C catalysts. This is because the Pt\textsubscript{3}Ni(111) surface possesses an unusual electronic structure (d-band center position) and arrangement of surface atoms in the near-surface region. Herein, it is noted that the facet effect is another non-negligible factor for influencing the ORR catalytic performance. As is also shown in Figure 6B, exposed (111)-facets Pt\textsubscript{3}Ni shows an enhanced ORR activity than (110) and (100) facets.

However, for Pt-based catalysts, the transition metals will easily be oxidized under an oxygen environment.\textsuperscript{74,75} Additionally, the rigorous electrolytes and high potential also accelerate the dissolution of the catalyst surface.\textsuperscript{8,71,76,77} Thus introducing another element with low electronegativity than O onto catalyst surface to tune the electronic effect of Pt atoms is a promising effective in keeping the initial activity. Sung Jong Yoo’s group\textsuperscript{74} used N-containing polymers to modify the PtCo nanoparticles, to modulate the electronic structure of surface Co, and finally resulting in a highly active and durable Pt-based ORR electrocatalyst (Figure 6C–E). The introduction of N-containing polymers could conduce to the electron donation from Co to Pt, avoiding the further oxidation of surface Co atoms. In addition, this strategy can also improve the stability of PtCo catalysts. It was reported that alloyed Mo-Pd (or Pt) possessed an unrivaled catalytic ORR performance than other alloys, while excessive passivation of surface Mo hindered the exposure of surface-active sites. Thus, Wang et al.\textsuperscript{52} introduced S as “active auxiliary” to modulate the surface Mo atoms of ultralong jagged Pt\textsubscript{85}Mo\textsubscript{15}. On the one hand, they found that S modified Pt\textsubscript{85}Mo\textsubscript{15} catalyst possessed an excellent electrocatalytic performance than bare Pt\textsubscript{85}Mo\textsubscript{15} nanowires. On the other hand, the implantation of S element also changed the surface structure of ultralong Pt\textsubscript{85}Mo\textsubscript{15} nanowires, exposing more active sites than initial intact, as shown in Figure 6F–H. Further evidence demonstrated that S element could prevent the further oxidation of Mo and then lead to enough electron transfer from Mo to Pt (Figure 6J–I).

3.3 | Ensemble effect

Ensemble effect also called “dual active sites effect” is based on the Langmuir–Hinshelwood (L–H) principle\textsuperscript{51,78,79} which is different from the electronic transfer behavior existing on the two neighboring active sites of catalyst (inter-)surface. Nanomaterials, including Pt-metal, Pt-oxide, Pt-hydroxide, Pt-sulfide, Pt-Ionic liquids, and so on, possessing rich interfaces usually induce the ensemble effect. Alloying Pt with transition metals not only changes the electronic effect of Pt but also generate an additional impact on adsorbing the interactants.\textsuperscript{80–83} In the practical application of PEMFCs, cathodic electrocatalysts often suffered from the poison phenomenon, which will decrease the performance of fuel cells.\textsuperscript{84,85} Considering the preparation technology and toxicity resistance, oxophilic elements (such as Ru, Mo, Sn) are preferred to alloy with Pt. Figure 7A shows the schematic illustration of poison resistance of typical Pt-Ru alloy based on the L–H pathway.\textsuperscript{51,88–90} It can be clearly seen that the implantation of Ru into the catalyst surface can easily adsorb the OH\textsuperscript{−}, which is in favor of the oxidation/removal of poisonous CO intermediate. Apart from the oxophilic metals, the oxophilic hydroxide can also be applied to modify the Pt-based catalysts to increase their toxicity resistance. Huang et al.\textsuperscript{56} reported platinum–nickel hydroxide–graphene (Pt/Ni(OH)\textsubscript{2}/rGO) ternary hybrids with long-standing life by enhancing the CO oxidation ability (Figure 7B). In a basic solution, abundant free OH\textsuperscript{−} is suggested to be adsorbed on the defective Ni(OH)\textsubscript{2} and is beneficial for CO oxidation via Langmuir–Hinshelwood (L–H) pathway. The CO stripping experiment (Figure 7C) of Pt/Ni(OH)\textsubscript{2}/rGO revealed that the introduction of Ni(OH)\textsubscript{2} is in favor of decreasing the oxidation potential of CO. In addition, it is seen from the CV curve of CO oxidation that a new peak emerges for Pt/Ni(OH)\textsubscript{2}/rGO in comparison with bare Pt/rGO catalyst. The first peak can be ascribed to CO oxidation at Pt sites near Ni(OH)\textsubscript{2}, and the second peak can be ascribed to the CO oxidation at Pt sites far from Ni(OH)\textsubscript{2}. This result further demonstrates that the addition of Ni(OH)\textsubscript{2} is beneficial for CO oxidation and removal.
In addition, the introduction of oxyphilic species not only enhances the poison resistance but also changes the reaction pathway during the ORR process. Shen et al.\textsuperscript{87} report a new concept of utilizing dual active sites for the ORR via engineering Pt–oxide interfaces. Figure 7D shows the TEM image of a typical Pt–Cu–Ni nanoparticle combined with the SnO\textsubscript{x}, and this catalyst shows a 40% enhancement of specific activity toward ORR, which is ten times higher than pure Pt-Ni-Cu catalyst. Further evidence and density functional theory (DFT) calculations demonstrate that an altered dual-site cascade mechanism wherein the first two steps occur on SnO\textsubscript{x} sites and the remaining steps occur on adjacent Pt sites, allowing a significant decrease in the energy barrier, as shown in Figure 7E,F.

4 | RECENT REPRESENTATIVE ADVANCED PT-BASED ELECTROCATALYSTS WITH HIGH ORR PERFORMANCE

Under the guidance of theoretical understandings mentioned above, enormous research breakthroughs were obtained and mainly focused on the surface structure and
composition regulation, as well as morphology control at the micro-nano scale. However, these achievements are usually based on the cumulations of strain effect, ligand effect, and ensemble effect. One efficient strategy for increasing the ORR performance is alloying Pt with desired secondary metals, which triggers the strain effect, ligand effect, or both. Figure 8 shows the recent advanced Pt-based ORR catalysts with high activity and stability. It can be seen that Mo-Pt3Ni/C, J-Pt NWs/C, PtPb@Pt, PtNi BNSs/C, and PtNi@Pd/C, as well as other Pt-based catalysts with nanoframe structures, all show the high mass activities, specific activities, and electrochemical active surface area (ECSA) values. In general, the specific activity stands for

![Figure 7](image1.png)

**Figure 7** (A) Schematic illustration of poison resistance of Pt-Ru alloy based on Langmuir–Hinshelwood (L–H) pathway. Reproduced with permission, copyright 2019, Elsevier B.V. (B) Schematic illustration showing the bifunctional interaction between Ni(OH)2 and adjacent Pt sites for the dissociate adsorption of water molecules and subsequently the oxidative removal of CO on Pt sites via the L–H pathway. (C) CO stripping experiments of Pt(Ni(OH)2)/rGO-4 in 1 M KOH. Reproduced with permission, copyright 2019, Nature Publishing Group. (D) HRTEM image of SnOx/Pt–Cu–Ni(60) nanoparticles. (E) DFT models of O, OH, and OOH adsorption on SnOx/Pt–Cu–Ni. (F) Scheme of the dual-site cascade mechanism on SnOx/Pt–Cu–Ni. Reproduced with permission, copyright 2016, American Chemical Society. DFT, density functional theory.

![Figure 8](image2.png)

**Figure 8** Summary of specific activity, mass activity, and ECSA reported in recent efforts for ORR.

![Graph](image3.png)

**Graph** Mass Activity (A/mg_n) and Specific Activity (mA/cm^2_n)
the intrinsic activity of catalysts, which can be used to evaluate the catalytic performance of a single Pt active site. The mass activity can be used to predict the real usage of Pt, which is significant for their practical applications. Thus, the high mass activities, specific activities, and ECSA values are the most conventional and the most intuitive standards for evaluating the ORR performance of catalysts. Next, we will further reveal the essential reasons why these Pt-based catalysts possess such high ORR performance based on several typical catalysts from the insight of atomic-level engineering.

In the early age of designing Pt-based electrocatalysts, alloying Pt with other transition metals is a facile and efficient strategy for improving ORR performance. As we know, the oxygen-binding energy is often related to the coupling of adsorbate (O_{ad}) and d-band position of Pt-based alloys, which are tuned easily by the doped transition metals. Figure 9A–C shows the Mo-PtNi/C nanocrystals reported by Huang et al.91 via surface modification, which possesses enhanced ORR performance after Mo addition. The mass activity is 6.98 A/mg_{Pt}, which is about 70 times higher than commercial Pt/C. The DFT calculations reveal that Mo prefers to deposit on the superficial vertex and edge of particles. Furthermore, Cao116 documented that Mo could balance the concentration of surface element and increase the vacancy formation energy of transition metals on the catalyst surface, which was beneficial for preventing the dissociation of transition metals. The enhanced ORR performance is attributed to the ligand effect and strain effect. In terms of Pt-M catalysts, Pt-M intermetallic particles also show an enhanced ORR performance. In comparison to Pt-based alloy with atoms being randomly distributed in the Pt fcc lattice, which is usually etched from the alloy due to corrosive environment and high potentials, the ordered intermetallic compounds combine metallic and ionic bonding, which forms an ordered atomic lattice with specific stochiometry and crystal structure. Several Pt-M intermetallic catalysts, such as PtCo,118 PtFe,111 PtCu,119, and PtNi,117 are also reported.

Core-shell structure plays an important role in ORR catalysts, which are composed of catalytically active Pt shells and cheap cores to utilization. The core not only supports the Pt shell but also tune the electronic structure of Pt shell. Huang et al.67 presented highly uniform PtPb@Pt (core@shell) nanoplates with dramatically ORR performance, as shown in Figure 9D–J. These nanoplates show a 55 m^2/gPt of ECSA values, 7.8 mA/cm^2 of specific activity and 4.3 A/mg_{Pt} of mass activity, of which are attributed to large biaxial tensile strain effect for ORR. In addition, introducing the lanthanide (lanthanum, cerium, samarium, gadolinium, terbium, dysprosium, thulium, or calcium) into the Pt bulk also enhance the ORR performance by tuning the bulk lattice parameters and follows a high peaked “volcano” relation curve (Figure 9K,L).120 The Pt-based nanoframe catalyst also shows an excellent ORR activity. As shown in Figure 9M, Yang group reported a 3D Pt_{3}Ni nanoframe25 with a two atomic layer of Pt via PtNi_{3} transformation, which exhibits an extraordinary performance toward ORR. This nanoframe structure can expose more surface Pt active sites and mass transfer, as well as stable structure for long-term tests.

Constructing the 1D structure with surface modification strategy, including composition and structure engineering, is beneficial for boosting ORR performance. Huang et al.92 presented an ultralong jagged Pt nanowires (donates J-Pt NWs) with a diameter of 2–3 nm, which exhibited an outstanding ECSA value (118 m^2/g_{Pt}) and mass activity (13.6 A/mg_{Pt}) for ORR (Figure 10A–C). This exceptional performance is dominated by ultralong structure and high Pt exposure degree, as well as ligand effect of Pt and Ni. This structure is fabricated by the electrochemical dealloying method, which can induce a Pt-richment on the surface, resulting in a high ORR performance. A stable high-index faceted Pt skin on zigzag-like PtFe nanowires was reported by Guo’s group,96 which selectively exposed active surfaces and judiciously tuning the near-surface composition of electrode materials and showed an enhanced electrocatalytic performance. Further exploration reveals that the combination of 1D structure and exposed high-index facets, as well as Pt-skin surface, is the promoter for optimizing the adsorption energy under the impact of ligand and strain effect. Furthermore, solid nanowires structure is disadvantageous for high utilization of the internal atoms, thus excavating the internal unreacted atoms to fabricate a hollow nanotube is efficient for reducing the usage of Pt. Xia et al.57 (Figure 10D–F) fabricated a branched PtNi alloy nanocages with a Pt-skin structure, as well as high-index facets exposed on nanocages. And this catalyst shows high specific activity (5.16 mA/cm^2_{Pt}) and mass activity (3.52 A/mg_{Pt}). The experiments and DFT calculations demonstrate that stain and ligand effect are the principal factors for excellent ORR performance. Generally, a hollow structure can usually be presented via nanospheres, nanocages polyhedrons, and nanotubes. The synthesis strategies of hollow structure include galvanic replacement, de-alloy method, and other template sacrifice methods.25,121–123

Apart from the above-discussed strategies, another method for minimizing the Pt element without compromising the catalytic ORR performance is to reduce the dimension down to clusters and even separately distributed metal atoms, which can greatly increase the atom utilization efficiency, potentially to
FIGURE 9  (A) The average site occupancies of the second layer of the PtNi nanoparticle and the Mo-PtNi nanoparticle at 170°C as determined by means of a Monte Carlo simulation. Representative HAADF-STEM images of the (B) Pt3Ni/C and (C) Mo-Pt3Ni/C catalysts. Reproduced with permission,91 copyright 2019, AAAS. (D) TEM image of PtPb@Pt hexagonal nanoplates. (E) A model of one single hexagonal nanoplate, (F) HAADF-STEM image from in-plane view, (G) HAADF-STEM image from out-of-plane view. (H) and (I) are high-resolution HAADF images from the selected areas in (E). (J) The schematic atom models of the nanoplate showing the top interface [(110) Pt//(100)PtPb] and the side interface [(110)Pt//(001)PtPb]. Reproduced with permission,67 copyright 2016, AAAS. (K) Schematic view of the bulk structure of a Pt5M (illustrated for Pt5Tb), showing Pt5Tb. (L) Relation between the lattice parameter of Pt5M and the covalent radius of the lanthanide atoms. The dotted line shows the linear fit. Reproduced with permission,120 copyright 2016, AAAS. (M) Schematic illustrations and corresponding TEM images of the samples obtained at four representative stages during the evolution process from polyhedral to nanoframes. Reproduced with permission,25 copyright 2018, AAAS
100 percentage.\textsuperscript{124–126} Atomic site catalysts, including single-atomic site catalysts and diatomic site catalysis, are being pursued as economical alternatives to boosting their commercial applications in PEMFCs due to lower Pt usage and high performance triggered by nearby highly stable coordination atoms. Liu’s group documented a strategy of fabricating highly active and stable ORR electrocatalyst with ultralow-loading Pt usage by carbonization of Co-containing Zn-based zeolitic imidazolate frameworks (Figure 10G,\textsuperscript{126} This catalyst shows an exceptional mass activity of 8.64 A/mg\textsubscript{Pt} performed by rotating disk electrode (RDE), which attributes to highly dispersed Pt atoms and ligand effect of Co-N-C active node. On the other hand, using carbon materials as the support of ORR catalyst possesses the superiorities of high conductivity and high surface area and enhancing anticorrosion ability.

5 | PRACTICAL APPLICATIONS OF SINGLE FUEL CELL

Furthermore, to investigate the practical applications of well-defined catalysts in fuel cell fields, constructing a custom membrane electrode assembly (MEA) and single MEA fuel cell are necessary for evaluating the
performance of advanced electrocatalysts, as shown in Figure 11. The relationship between electrochemical performance and advanced materials (e.g., electrocatalyst kinetics, conductivity, surface functionality) and morphology (e.g., pore structure, interfaces) in ex situ setups is extremely challenging in terms of reproducibility and reliability.\textsuperscript{127-129} Thus, further efforts are needed to study catalysts under technically relevant conditions. Obtaining reliable data via ex situ electrochemical evaluation of advanced ORR electrocatalysts by RDE voltammetry was highly dependent on the electrode morphology. Once protocols were established to reliably produce uniform electrodes, the expected catalyst activity was reproducibly observed. Thus, the practical performance of ORR catalysts in the fuel cells is different greatly from RDE because of rigorous conditions and difficult preparation technology in MEA. Simultaneously, in the process of automated MEA preparation, gas diffusion media, ionomers, polymer electrolyte membranes (PEMs), and electrode structures are also mainly considered and designed for use in next-generation fuel cells. Noting that in the MEA process, the dissolution of the exchange membrane under the high work potential will cause a decrease in the catalytic performance of the catalyst to the same extent. Thus, the mature preparation technology and rational design principle of MEA are recommended in fuel cells.

The US DOE has documented a series of operating protocols and targeted ORR electrocatalysts for transportation applications in 2020, as shown in Tables 1 and 2. Under the guidance of this protocol, enormous advanced Pt-based catalysts were designed precisely, as mentioned above. Apart from the design of advanced catalysts, the loading usage of Pt, pore structure of carbon, and preparation of catalyst-coated layer are also the key factors for high-performance of MEA. Gasteiger and coworkers reported a benchmark to test the MA of Pt cathode electrocatalysts in MEA by contrasting corresponding activity and stability under the conditions (0.9 V vs. RHE).\textsuperscript{128} To make clear the intrinsic mechanism, the Kongkanand group developed a high-power density development of the cathode electrocatalysts as a supplement to verify the Gasteiger’s conclusion.\textsuperscript{129} They found that the O\textsubscript{2} transport resistance seriously affected the availability of Pt active sites. In addition, the carbon support also limits the performance of MEA by constructing the pore distribution.\textsuperscript{128} Today, the highest performance of commercialized cathode electrocatalyst for PEMFCs was reported by Yang group\textsuperscript{129} was porous carbon-supported Pt\textsubscript{x}Ni\textsubscript{1−x} nanoparticles, of which initial mass activity is 0.64 A/mgPGM at 0.9 V without IR.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig11.png}
\caption{(A) Preparation of catalysts and performance tests of ORR. (B) Illustration of single fuel cells and practical tests. Reproduced with permission,\textsuperscript{129} copyright 2013, American Chemical Society. ORR, oxygen reduction reaction.}
\end{figure}
compensation. The test condition is 150 kPa abs back pressure H2/O2 at 80°C. In addition, this catalyst still exhibits a 0.513 A/mgPGM mass activity after 30,000 CV cycles between 0.6 and 1.0 V. In the future, how to transfer the laboratory scale catalyst to large-scale commercial industry successfully is the challenge for applications of PEMFCs.

**TABLE 1** Technical targets: MEA for transportation applications

| Characteristic                  | Units | 2020 Targets |
|--------------------------------|-------|--------------|
| Cost                           | $/kWnet | 14           |
| Durability with cycling        | Hours | 5000         |
| Start-up/shutdown durability    | Cycles | 5000         |
| Performance @0.8 V             | mA/cm² | 300          |
| Performance @ rated power (150 kPabs) | mW/cm² | 1000        |

*Need to meet or exceed at temperatures of 80°C up to peak temperature, with < 10% drop in rated power after the test.

*With less than 5% decrease in voltage at 1.2 A/cm².

*With maximum inlet RH of 40%. Rated power operating point depends on MEA temperature and is defined as the voltage at which \( V = 77.6/(22.1 + T [°C]) \), based on \( Q/ΔT = 1.45 \text{ kW/°C} \), with an approximation of MEA temperature as equal to stack coolant outlet temperature.

PEMFCs as a next-generation energy conversion mode attracted people’s attention in 1840. However, high production costs, immature production process, and rare reserves of Pt resource make it impossible for commercialized production. Thus, from the viewpoint of electrocatalysts, an in-depth understanding of the ORR mechanisms on Pt surface is necessary to better design the advanced Pt-based catalysts with high ORR performance. In addition, we have described the influence factors (strain effect, ligand effect, and ensemble effect) from the theoretical understandings to practical applications (reported advanced Pt-based ORR catalysts). Especially, the highest mass activity has enhanced to 13.6 A/mgPGM for PtNi catalysts, which reveals that there is a large room to improve for Pt-based ORR catalysts. However, for MEA applications, there are still big gaps to skip.

In the future, the design of advanced Pt-based ORR electrocatalysts should follow these principles to obtain excellent performance. (i) Narrowing the structure to one dimension of Pt-based electrocatalyst, the 1D nanostructure can reduce the embedded points at the interface between the electrode and catalyst to take full advantage

**TABLE 2** Technical targets: Electrocatalysts for transportation applications

| Characteristic                         | Units          | 2020 targets |
|----------------------------------------|----------------|--------------|
| Pt group metal total content (both electrode) | g/kW (rated, gross) @ 150 kPabs | 0.125         |
| Pt group metal (pgm) total loading (both electrode) | mg PGM/cm² electrode area | 0.125        |
| Mass activity                          | A/mg PGM @ 900 mVir-free | 0.44         |
| Rated power density                    | mW/cm²geo²    | 1000         |
| Loss in initial catalytic activity     | % mass activity loss | <40          |
| Loss in performance @ 0.8 A/cm²        | mV             | <30          |
| Electrocatalyst support stability      | % mass activity loss | <40          |
| Loss in performance @1.5 A/cm²         | mV             | <30          |

*Rated power operating point depends on MEA temperature and is defined as the voltage at which \( V = 77.6/(22.1 + T [°C]) \), based on the target of \( Q/ΔT = 1.45 \text{ kW/°C} \), with an approximation of MEA temperature as equal to stack coolant outlet temperature.

*Based on MEA gross power at 150 kPa abs. Measured at 0.692 V and 90°C, satisfying \( Q/ΔT < 1.45 \text{ kW/°C} \). At 250 kPa abs status is 0.12 g/kW.

*Mass activity in A·mg⁻¹ @ 150 kPa absolute (abs) back pressure at 900 mV IR-corrected on H2/O2, 100% humidity, 80°C, anode stoichiometry 2; cathode stoichiometry 9.5.

*Rated power density in mW/cm²geo² @ 150 kPa abs pressure at \( V = (77.6/(22.1 + T [°C])) V \) based on target of \( Q/ΔT = 1.45 \text{ kW·°C}^{-1} \), on H2/air, humidified to 59°C dew point, anode stoichiometry 1.5; cathode stoichiometry 1.8.

*Durability test performed 30,000 square wave cycles between 0.6 V (3 s) and 0.95 V (3 s) on H2/N2, 100% humidity, 80°C.
of the catalyst. At the same time, the 1D shape possesses excellent electronic transmission, high utilization of Pt, and stable structure. While the 1D nanostructure still faces the same difficulties in dispersing, length increasing, and MEA tests. (i) Engineering high-indexed facets, nanocrystals with high-indexed facets will possesses abundant active sites compared with low indexed facets due to amounts of stepped atoms on the surface. The undercoordinated surface Pt atoms make it possible to optimize the adsorption/desorption energy of intermediates, which will accelerate the reaction kinetics. However, the unstable structure of Pt-based high-indexed facets facile reconstructed is a key obstacle for further practical applications because of its high surface energy and amounts of unstable structure of Pt. Therefore, the hollow nanostructure, the subnanometer-thick walls of hollow nanostructured Pt-based catalysts not only reduces the usage of Pt weigh but also increase the utilization of Pt. In addition, the high mass transport and electronic excursio and atomic contraction effect rooting from the fold surface are all beneficial for enhanced ORR performance. Furthermore, collaborative adoptions of these abovementioned will lead to exponential growth toward ORR performance. For example, Xia and coworkers reported hollow PtNi nanobranched nanostructure showed a 3.52 A/mgPt of mass activity, which is 14 times higher as compared with a commercial platinum on carbon (Pt/C) catalyst. Thus, rational design and engineering of the structure of Pt-based catalysts at the atomic level based on the theoretical principle is promising for generating next-generation ORR catalysts toward PEMFCs.

ACKNOWLEDGMENTS

This study was supported by the National Key R&D Program of China (2018YFA0702003, 2016YFA0202801), National Natural Science Foundation of China (21890383, 21671117, 21871159), Science and Technology Key Project of Guangdong Province of China (2020B010188002), and Beijing Municipal Science & Technology Commission (No. Z191100007219003).

ORCID
Yao Wang https://orcid.org/0000-0001-9578-9128
Dingsheng Wang https://orcid.org/0000-0003-0074-7633

REFERENCES
1. Debe MK. Electrocatalyst approaches and challenges for automotive fuel cells. Nature. 2012;486:43-51.
2. Wang W, Lei B, Guo S. Engineering multimetallic nanocrystals for highly efficient oxygen reduction catalysts. Adv Energy Mater. 2016;6:1600236.
3. Centi G. Smart catalytic materials for energy transition. SmartMat. 2020;1:1005.
4. Tauster SJ, Fung SC, Baker RT, Horsley JA. Strong interactions in supported-metal catalysts. Science. 1981;211:1121-1125.
5. Wan S, Wu JD, Wang DP, et al. Co/N-doped carbon nanotube arrays grown on 2D MOFs-derived matrix for boosting the oxygen reduction reaction in alkaline and acidic media. Chinese Chem Lett. 2020. https://doi.org/10.1016/j.cclet.2020.04.040
6. Wang N, Miao RK, Lee G, et al. Suppressing the liquid product crossover in electrochemical CO2 reduction. SmartMat. 2021;1:1-5.
7. James BD, Huya-Koudajo M, Houchins C. 2017. Updated. https://www.hydrogen.energy.gov/pdfs/progress17/v_e_5_james_2017.pdf
8. Gasteiger HA, Markovic NM. Just a dream—or future reality? Science. 2009;324:48-49.
9. Wei Z, Zhu Y, Liu J, et al. Recent advance in single-atom catalyst. Rare Met. 2021. https://doi.org/10.1007/s12598-2020-01592-1
10. Stephens IEL, Rossmeisl J, Chorkendorff I. Toward sustainable fuel cells. Science. 2016;354:1378-1379.
11. Zhang T, Anderson AB. Oxygen reduction on platinum electrodes in base: theoretical study. Electrochim Acta. 2007;53:982-989.
12. Anderson AB, Roques J, Mukerjee S, Murthi VS, Markovic NM, Stamenkovic V. Activation energies for oxygen reduction on platinum alloys: theory and experiment. J Phys Chem B. 2005;109:1198-1203.
13. Albu TV, Anderson AB. Studies of model dependence in an ab initio approach to uncatalyzed oxygen reduction and the calculation of transfer coefficients. Electrochim Acta. 2001;46:3001-3013.
14. Fu X, Wan C, Zhang A, et al. Pt3Ag alloy wavy nanowires as highly effective electrocatalysts for ethanol oxidation reaction. Nano Res. 2020;13:1472-1478.
15. Zhong L, Li S. Unconventional oxygen reduction reaction mechanism and scaling relation on single-atom catalysts. ACS Catal. 2020;10:4343-4318.
16. Strasser P, Koh S, Anniyev T, et al. Lattice-strain control of the activity in dealloyed core-shell fuel cell catalysts. Nat Chem. 2010;2:454-460.
17. Kitchin JR, Norskov JK, Barteau MA, Chen JG. Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals. J Am Chem. 2004;120:10240-10246.
18. Wu J, Bai X, Ren Z, et al. Multivalent Sn species synergistically favours the CO2 into-HCOOH conversion. Nano Res. 2021;14:1053-1060.
19. Liu J, Wang P, Fan J, Yu H, Yu J. Hetero-phase MoC2-Mo2C nanoparticles for enhanced photocatalytic H2-production activity of TiO2. Nano Res. 2021;14:1095-1102.
20. Wang Y, Zhou H, Sun H, et al. Implanting Mo atoms into surface lattice of Pt3Mn alloys enclosed by high-indexed facets: promoting highly active sites for ethylene glycol oxidation. ACS Catal. 2019;9:442-455.
21. Schalow T, Brandt B, Starr DE, et al. Size-dependent oxidation mechanism of supported Pd nanoparticles. Angew Chem Int Edit. 2006;45:3693-3697.
22. Wieckowski A, Savinova ER, Vayenas C. Catalysis and electrocatalysis at nanoparticle surface. New York: Marcel Dekker; 2003.
23. Lv H, Wang Y, Xu D, Liu B. Engineering porous architectures in multicomponent PdCuBP mesoporous nanospheres for electrocatalytic ethanol oxidation. Nano Res. 2021. https://doi.org/10.1007/s12274-021-3301-7
24. Cheng J, Hu P. Utilization of the three-dimensional volcano surface to understand the chemistry of multiphase systems in heterogeneous catalysis. J Am Chem Soc. 2008;130:10868-10869.
25. Chen C, Kang Y, Huo Z, et al. Highly crystalline multi-metallic nanostructures with three-dimensional electrocatalytic surfaces. Science. 2014;343:1339-1343.
26. Wang D, Xin HL, Hovden R, et al. Structurally ordered intermetallic platinum-cobalt core-shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts. Nat Mater. 2013;12:81-87.
27. Lim B, Jiang M, Camargo PHC, et al. Pd-Pt bimetallic nanodendrites with high activity for oxygen reduction. Science. 2009;324:1302-1305.
28. Yu T, Kim DY, Zhang H, Xia Y. Platinum concave nanocubes with high-index facets and their enhanced activity for oxygen reduction reaction. Angew Chem Int Edit. 2011;50(12):2773-2777.
29. Xia BY, Wu HB, Wang X, Lou XW. Highly concave platinum nanostructures with high-index facets and enhanced electrocatalytic properties. Angew Chem Int Edit. 2013;52:12337-12340.
30. Yang CH, Nosheen F, Zhang ZC. Recent progress in structural modulation of metal nanomaterials for electrocatalytic CO₂ reduction. Rare Met. 2020. https://doi.org/10.1007/s12598-020-01600-4
31. Zhang Z, Liu G, Cui X, et al. Crystal phase and architecture engineering of lotus-thalamus-shaped Pt-Ni anisotropic superstructures for highly efficient electrochemical hydrogen evolution. Adv Mater. 2018;30:1801741.
32. Liu J, Jiao M, Lu L, et al. High performance platinum single atom electrocatalyst for oxygen reduction reaction. Nat Commun. 2017;8:15938.
33. Keith JA, Jerkiewicz G, Jacob T. Theoretical investigations of the oxygen reduction reaction on Pt(111). ChemPhysChem. 2010;11:2779-2794.
34. Markiewicz M, Zalitís C, Kucernak A. Performance measurements and modelling of the ORR on fuel cell electrocatalysts - the modified double trap model. Electrochim Acta. 2015;179:126-136.
35. O’Hayre RP, Cha SW, Colella WG, Prinz FB. Fuel cell fundamentals. 3rd ed. Hoboken, NJ: John Wiley & Sons Inc; 2016.
36. Jung E, Shin H, Antink WH, Sung YE, Hyeon T. Recent advances in electrochemical oxygen reduction to H₂O₂: catalyst and cell design. ACS Energy Lett. 2020;5:1881-1892.
37. Su C, Lía Y, Cao H, et al. Novel PTFE hollow fiber membrane fabricated by emulsion electrospinning and sintering for membrane distillation. J Membrane Sci. 2019;583:200-208.
38. Holewinski A, Linic S. Elementary mechanisms in electrocatalysis: revisiting the ORR Tafel slope. J Electrochem Soc. 2012;159:H864-H870.
39. Keith JA, Jacob T. Theoretical studies of potential-dependent and competing mechanisms of the electrocatalytic oxygen reduction reaction on Pt(111). Angew Chem Int Edit. 2010;49:9521-9525.
40. Hansen HA, Rossmeisl J, Norskov JK. Surface Pourbaix diagrams and oxygen reduction activity of Pt, Ag and Ni(111) surfaces studied by DFT. Phys Chem Chem Phys. 2008;10:3722-3730.
41. Siáhrostami S, Verdaguer-Casadevall A, Karamad M, et al. Enabling direct H₂O₂ production through rational electrocatalyst design. Nat Mater. 2013;12:1137-1143.
42. Stamenkovic V, Mun BS, Mayrhofer KJJ, et al. Changing the activity of electrocatalysts for oxygen reduction by tuning the surface electronic structure. Angew Chem Int Edit. 2006;45:2897-2901.
43. Stamenkovic VR, Mun BS, Aenz M, et al. Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces. Nat Mater. 2007;6:241-247.
44. Viswanathan V, Hansen HA, Rossmeisl J, Norskov JK. Universality in oxygen reduction electrocatalysis on metal surfaces. ACS Catal. 2012;2:1654-1660.
45. Cheng J, Hu P. Utilization of the three-dimensional volcano surface to understand the chemistry of multiphase systems in heterogeneous catalysis. J Am Chem Soc. 2008;130:10868-10869.
46. Kulkarni A, Siáhrostami S, Patel A, Norskov JK. Understanding catalytic activity trends in the oxygen reduction reaction. Chem Rev. 2018;118:2302-2312.
47. Benck JD, Hellstern TR, Kibsgaard J, Chakrhanont P, Jaramillo TF. Catalyzing the hydrogen evolution reaction (HER) with molybdenum sulfide nanomaterials. ACS Catal. 2014;4:3957-3971.
48. Xue S, Deng W, Yang F, et al. Hexapod PtRuCu nanocrystalline alloy for highly efficient and stable methanol oxidation. ACS Catal. 2018;8:7578-7584.
49. Zhang C, Sha J, Fei H, et al. Single-atomic ruthenium catalytic sites on nitrogen-doped graphene for oxygen reduction reaction in acidic medium. ACS Nano. 2017;11:6930-6941.
50. Choi CH, Kim M, Kwon HC, et al. Tuning selectivity of electrochemical reactions by atomically dispersed platinum catalyst. Nat Commun. 2016;7:10922.
51. George M, Zhang GR, Schmitt N, et al. Effect of ionic liquid modification on the ORR performance and degradation mechanism of trimetallic PdNiMo/C catalysts. ACS Catal. 2019;9:8682-8692.
52. Wang Y, Zheng M, Sun H, et al. Catalytic Ru containing Pt₃Mn nanocrystals enclosed with high-indexed facets: surface alloyed Ru makes Pt more active than Ru particles for ethylene glycol oxidation. Appl Catal B-Environ. 2019;253:11-20.
53. Wang Y, Zhuo H, Zhang X, et al. Interfacial synergy of ultralong jagged Pt₉Mo₁₅-S nanowires with abundant active sites on enhanced hydrogen evolution in an alkaline solution. J Mater Chem A. 2019;7:24328-24336.
54. Kwon T, Jun M, Kim HY, et al. Vertex-reinforced PdCuCo ternary nanoframes as efficient and stable electrocatalysts for the oxygen reduction reaction and the methanol oxidation reaction. Adv Funct Mater. 2018;28:1706440.
55. Maark TA, Peterson AA. Understanding strain and ligand effects in hydrogen evolution over Pd(111) surfaces. J Phys Chem C. 2014;118:4275-4281.
56. Mavrikakis M, Hammer B, Norskov JK. Effect of strain on the reactivity of metal surfaces. Phys Rev Lett. 1998;81: 2819-2822.
57. Slanac DA, Hardin WG, Johnston KP, Stevenson KJ. Atomic ensemble and electronic effects in Ag-Rich AgPd nanoalloy catalysts for oxygen reduction in alkaline media. J Am Chem Soc. 2012;134:9812-9819.
58. Jiao W, Chen C, You W, et al. Tuning strain effect and surface composition in PdAu hollow nanospheres as highly efficient ORR electrocatalysts and SERS substrates. Appl Catal B: Environ. 2020;312:119299.
59. Qin Y, Zhang W, Guo K, et al. Fine-tuning intrinsic strain in penta-twinned Pt-Cu-Mn nanoframes boosts oxygen reduction catalysis. Adv Funct Mater. 2020;30:1910107.
60. Luo M, Guo S. Strain-controlled electrocatalysis on multi-metallic nanomaterials. Nat Rev Mater. 2017;2:17059-17072.
61. Alayoglu S, Nilekar AU, Mavrikakis M, Eichhorn B. Ru–Pt core–shell nanoparticles for preferential oxidation of carbon monoxide in hydrogen. Nat Mater. 2008;7:333-338.
62. Tedsree K, Li T, Jones S, et al. Hydrogen production from formic acid decomposition at room temperature using a Ag-Pd core-shell nanocatalyst. Nat Nanotechnol. 2011;6:302-307.
63. Escudero-Escribano M, Verdaguer-Casadavall A, Malacrriba P, et al. Pt,Gd as a highly active and stable catalyst for oxygen electroreduction. J Am Chem Soc. 2012;134: 16476-16479.
64. Brimaud S, Engstfeld AK, Alves OB, Hoster HE, Behm RJ. Oxygen reduction on structurally well defined, bimetallic PtRu surfaces: monolayer PtRu1−x/Ru(0001) surface alloys versus Pt Film Covered Ru(0001). Top Catal. 2014;57: 222-235.
65. Schnur S, Groß A. Strain and coordination effects in the adsorption properties of early transition metals: a density-functional theory study. Phys. Rev. B. 2010;81:33402.
66. Du M, Cui L, Cao Y, Bard AJ. Mechanoelectrochemical catalysis of the effect of elastic strain on a platinum nanofilm for the ORR exerted by a shape memory alloy substrate. J Am Chem Soc. 2015;137:7397-7403.
67. Bu L, Zhang N, Guo S, et al. Biaxially strained PtPb/Pt core/shell nanoplate boosts oxygen reduction catalysis. Science. 2016;354:1410-1414.
68. Wang L, Zeng Z, Gao W, et al. Tunable intrinsic strain in two-dimensional transition metal electrocatalysts. Science. 2019;363:870-874.
69. Imran K, Ramya K, Chandra Ghosh P, Sarkar A, Rajalakshmi N. Ion immobilized bifunctional electrocatalyst for oxygen reduction and evolution reaction. ACS Appl Energy Mater. 2019;11:7811-7822.
70. Jia Y, Jiang Y, Zhang J, et al. Unique excavated rhombic dodecahedral PtCu3 alloy nanocrystals constructed with ultrathin nanosheets of high-energy [110] facets. J Am Chem Soc. 2014;136:3748-3751.
71. Cui C, Gan L, Heggem M, Rudi S, Strasser P. Compositional segregation in shaped Pt alloy nanoparticles and their structural behaviour during electrocatalysis. Nat Mater. 2013; 12:765-771.
72. Yang S, Liu F, Wu C, Yang S. Tuning surface properties of low dimensional materials via strain engineering. Small. 2016;12:4028-4047.
73. Stamenkovic VR, Fowler B, Mun BS, et al. Improved oxygen reduction activity on Pt3Ni(111) via increased surface site availability. Science. 2007;315:493-497.
74. Jung N, Bhattacharjee S, Gautam S, et al. Discovery of superionic conductors by ensemble-scope descriptor. NPG Asia Mater. 2016;8:237-e237.
75. Ferrando R, Jellinek J, Johnston RL. Nanoalloys: from theory to applications of alloy clusters and nanoparticles. Chem Rev. 2008;108:845-910.
76. Yu L, Zhou TT, Cao S, Tai X, Liu L, Wang Y. Suppressing the surface passivation of Pt-Mo nanowires via constructing Mo-Se coordination for boosting HER performance. Nano Res. 2020. https://doi.org/10.1007/s12274-020-3269-8
77. Greeley J, Stephens IEL, Bondarenko AS, et al. Alloys of platinum and early transition metals as oxygen reduction electrocatalysts. Nat Chem. 2009;1:552-556.
78. Zhao X, Yin M, Ma L, et al. Recent advances in catalysts for direct methanol fuel cells. Energ Environ Sci. 2011;4: 2736-2753.
79. Strmcnik D, Lopes PP, Genorio B, Stamenkovic VR, Markovic NM. Design principles for hydrogen evolution reaction catalyst materials. Nano Energy. 2016;29: 29-36.
80. Antolini E, Salgado JRC, Gonzalez ER. The stability of Pt-M (M = first row transition metal) alloy catalysts and its effect on the activity in low temperature fuel cells—a literature review and tests on a pt-co catalyst. J Power Sources. 2006; 160:957-968.
81. Zhang G-R, Woellner S. Hollowed structured PtNi bifunctional electrocatalyst with record low total overpotential for oxygen reduction and oxygen evolution reactions. Appl Catal B-Environ. 2018;222:26-34.
82. Choi DS, Robertson AW, Warner JH, Kim SO, Kim H. Low-temperature chemical vapor deposition synthesis of pt-co alloyed nanoparticles with enhanced oxygen reduction reaction catalysis. Adv Mater. 2016;28:7115-7122.
83. Chung DY, Jun SW, Yoon G, et al. Highly durable and active PtFe nanocatalyst for electrochemical oxygen reduction reaction. J Am Chem Soc. 2015;137:15478-15485.
84. García-Rodríguez S, Somodi F, Borbáth I, et al. Controlled synthesis of PtSn/C fuel cell catalysts with exclusive Sn-Pt interaction application in CO and ethanol electrooxidation reactions. Appl Catal B-Environ. 2009;91:83-91.
85. Gómez de la Fuente JL, Martínez-Huerta MV, Rojas S, et al. Tailoring and structure of PtRu nanoparticles supported on functionalized carbon for DMFC applications: new evidence of the hydroxyl ruthenium oxide phase. Appl Catal B-Environ. 2009;88:505-514.
86. Huang W, Wang H, Zhou J, et al. Highly active and durable methanol oxidation electrocatalyst based on the synergy of platinum-nickel hydroxide-graphene. Nat Commun. 2015;6: 10035.
87. Shen X, Nagai T, Yang F, et al. Dual-site cascade oxygen reduction mechanism on sino/pt-cu-ni for promoting reaction kinetics. J Am Chem Soc. 2019;141:9463-9467.
88. Lee MJ, Kang JS, Kang YS, et al. Understanding the bifunctional effect for removal of Co poisoning: blend of a platinum nanocatalyst and hydroxyl ruthenium oxide as a model system. ACS Catal. 2016;6:2398-2407.
89. Strmcnik D, Uchimura M, Wang C, et al. Improving the hydrogen oxidation reaction rate by promotion of hydroxyl adsorption. Nat Chem. 2013;5:300-306.

90. Huang L, Zhang X, Wang Q, Han Y, Fang Y, Dong S. Shape-control of Pt-Ru nanocrystals: tuning surface structure for enhanced electrocatalytic methanol oxidation. J Am Chem Soc. 2018;140:1142-1147.

91. Huang X, Zhao Z, Cao L, et al. High-performance transition metal-doped Pt3Ni octahedra for oxygen reduction reaction. Science. 2015;348:1230-1234.

92. Li M, Zhao Z, Cheng T, et al. Ultrafine jagged platinum nanowires enable ultrahigh mass activity for the oxygen reduction reaction. Science. 2016;354:1414-1419.

93. Tu W, Chen K, Zhu L, et al. Tungsten-doping-induced surface reconstruction of porous ternary Pt-based alloy electrocatalyst for oxygen reduction. Adv Funct Mater. 2019;29:1807070.

94. Tian X, Zhao X, Su Y-Q, et al. Engineering bunched Pt-Ni alloy nanocages for efficient oxygen reduction in practical fuel cells. Science. 2019;366:850-856.

95. Huang H, Li K, Chen Z, et al. Achieving remarkable activity and durability toward oxygen reduction reaction based on ultrathin Rh-doped Pt nanowires. J Am Chem Soc. 2017;139:8152-8159.

96. Luo M, Sun Y, Zhang X, et al. Stable high-index faceted Pt skin on zigzag-like PtFe nanowires enhances oxygen reduction catalysis. Adv Mater. 2018;30:1705505.

97. Ao X, Zhang W, Zhao B, et al. Atomically dispersed Fe–N–C decorated with Pt-alloy core–shell nanoparticles for improved activity and durability towards oxygen reduction. Energy Environ Sci. 2020;13:3032-3040.

98. Li K, Li X, Huang H, et al. One-nanometer-thick PtNiRh trimetallic nanowires with enhanced oxygen reduction electrocatalysis in acid media: integrating multiple advantages into one catalyst. J Am Chem Soc. 2018;140:16159-16167.

99. Deng K, Xu Y, Dai Z, et al. Enhanced oxygen reduction and methanol oxidation electrocatalysis over bifunctional PtPdIr mesoporous hollow nanospheres. Chem Asian J. 2019;14:3868-3874.

100. Huang J-F, Tseng P-K. High performance layer-by-layer Pt3Ni(Pt-skin)-modified pd/c for the oxygen reduction reaction. Chem Sci. 2018;9:6134-6142.

101. Wang L, Gao W, Liu Z, et al. Core-shell nanostructured cobalt-platinum electrocatalysts with enhanced durability. ACS Catal. 2018;8:35-42.

102. Choi S-I, Shao M, Lu N, et al. Synthesis and characterization of Pd@Pt-Ni core-shell octahedra with high activity toward oxygen reduction. ACS Nano. 2014;8:10363-10371.

103. Bu L, Shao Q, E B, Guo J, Yao J, Huang X. PtPb/PtNi intermetallic core/atomic layer shell octahedra for efficient oxygen reduction electrocatalysis. J Am Chem Soc. 2017;139:9576-9582.

104. Choi S-I, Xie S, Shao M, et al. Synthesis and characterization of 9 nm Pt-Ni octahedra with a record high activity of 3.3 a/mg(Pt) for the oxygen reduction reaction. Nano Lett. 2013;13:3420-3425.

105. Zhang C, Sandorf W, Peng Z. Octahedral Pt3CuNi uniform alloy nanoparticle catalyst with high activity and promising stability for oxygen reduction reaction. ACS Catal. 2015;5:2296-2300.

106. Park J, Zhang L, Choi S-I, et al. Atomic layer-by-layer deposition of platinum on palladium octahedra for enhanced catalysts toward the oxygen reduction reaction. ACS Nano. 2015;9:2635-2647.

107. Wang X, Vara M, Luo M, et al. Pd@Pt core–shell concave decahedra: a class of catalysts for the oxygen reduction reaction with enhanced activity and durability. J Am Chem Soc. 2015;137:15036-15042.

108. Liu H, Zhong P, Liu K, et al. Synthesis of ultrathin platinum nanoplates for enhanced oxygen reduction activity. Chem Sci. 2018;9:398-404.

109. Kwon H, Kabiraz MK, Park J, et al. Dendrite-embedded platinum-nickel multiframe as highly active and durable electrocatalyst toward the oxygen reduction reaction. Nano Lett. 2018;18:2930-2936.

110. Liu Q, Du L, Fu G, et al. Structurally ordered Fe3Pt nanoparticles on robust nitride support as a high performance catalyst for the oxygen reduction reaction. Adv Energy Mater. 2018;9:1803040.

111. Du XX, Ye Y, Wang XX, Wang JN. Fine-grained and fully ordered intermetallic PtFe catalysts with largely enhanced catalytic activity and durability. Energy Environ Sci. 2016;9:2623-2632.

112. Zhu H, Cai Y, Wang F, Gao P, Cao J. Scalable preparation of the chemically ordered Pt-Fe-Au nanocatalysts with high catalytic reactivity and stability for oxygen reduction reactions. ACS Appl Mater Interfaces. 2018;10:22156-22166.

113. Kim HY, Kim JM, Ha Y, et al. Activity origin and multifunctionality of Pt-based intermetallic nanostructures for efficient electrocatalysis. ACS Catal. 2019;9:11242-11254.

114. Zhang L, Roling LT, Wang X, et al. Platinum-based nanocages with subnanometer-thick walls and well-defined, controllable facets. Science. 2015;349:412-416.

115. He DS, He D, Wang J, et al. Ultrathin icosahedral Pt-enriched nanocage with excellent oxygen reduction reaction activity. J Am Chem Soc. 2016;138:1494-1497.

116. Cao L, Mueller T. Theoretical insights into the effects of oxidation and Mo-doping on the structure and stability of Pt-Ni nanoparticles. Nano Lett. 2016;16:7748-7754.

117. Dubau L, Asset T, Chattot R, et al. Tuning the performance and the stability of porous hollow PtNi/C nanocatalysts for the oxygen reduction reaction. ACS Catal. 2015;5:5333-5341.

118. Wang D, Xin HL, Hovden R, et al. Structurally ordered intermetallic platinum-cobalt core-shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts. Nat Mater. 2013;12:81-87.

119. Kim H, Kwon T, Ha Y, et al. Intermetallic PtCu Nanoframes as Efficient Oxygen Reduction Electrocatalysts. Nano Lett. 2020;20:7413-7421.

120. Escudero-Escribano M, Malacrida P, Hansen MH, et al. Tuning the activity of Pt alloy electrocatalysts by means of the lanthanide contraction. Science. 2016;352:73-76.

121. Chen HM, Liu R-S, Lo M-Y, et al. Hollow platinum spheres with nano-channels: synthesis and enhanced catalysis for oxygen reduction. J Phys Chem C. 2008;112:7522-7526.

122. Gasteiger HA, Kocha SS, Sompalli B, Wagner FT. Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt
123. Zhao D, Zhuang Z, Cao X, et al. Atomic site electrocatalysts for oxygen reduction catalysts for PEMFCs. *Appl Catal B.* 2005; 56:9-35.

124. Wang Q, Chen F, Tang Q, et al. AgPdCo hollow nanospheres electrocatalyst with high activity and stability toward the formate electrooxidation. *Nano Res.* 2020. https://doi.org/10.1007/s12274-020-3220-z

125. Chong L, Wen J, Kubal J, Sen FG, Zou J. Ultralow index facets and enhanced electrocatalytic activity. *Science* 2018;362:1276-1291.

126. Chong L, Wen J, Kubal J, Sen FG, Zou J. Ultralow-loading platinum-cobalt fuel cell catalysts derived from imidazole frameworks. *Science.* 2018;362:1276-1291.

127. Lai J, Niu W, Qi W, et al. A platinum highly concave cube with one leg on each vertex as an advanced nanocatalyst for electrocatalytic applications. *ChemCatChem.* 2015;7:1064-1069.

128. Yarlagadda V, Carpenter MK, Moylan TE, et al. Boosting fuel cell performance with accessible carbon mesopores. *ACS Energy Lett.* 2018;3:618-621.

129. Sasslin MB, Garsany Y, Gould BD, Swider-Lyons KE. Fabrication method for laboratory-scale high-performance membrane electrode assemblies for fuel cells. *Anal Chem.* 2017;89: 511-518.

130. Wu J, Li P, Pan Y-T, Warren S, Yin X, Yang H. Surface lattice-engineered bimetallic nanoparticles and their catalytic properties. *Chem Soc Rev.* 2012;41:8066-8074.

131. Li M, Wang Y, Cai J, et al. Surface sites assembled-strategy on Pt-Ru nanowires for accelerated methanol oxidation. *Dalton T.* 2020;49:13999-14008.

132. Chen Z, Waje M, Li W, Yan Y. Supportless Pt and PtPd nanotubes as electrocatalysts for oxygen-reduction reactions. *Angew Chem-Int Edit.* 2007;46:4060-4063.

133. Kansara S, Gupta S, Sonvane Y, Gajjar PN. Ultrathin Pd and Pt nanowires for potential applications as hydrogen economy. *Mater Today.* 2020. https://doi.org/10.1016/j.mtcomm.2020.101761

134. Xu X, Zhang X, Sun H, et al. Synthesis of Pt-Ni alloy nanocrystals with high-index facets and enhanced electrocatalytic properties. *Angew Chem-Int Edit.* 2014;53:12522-12527.

135. Tian N, Zhou Z-Y, Sun S-G, Ding Y, Wang ZL. Synthesis of tetrahexahedral platinum nanocrystals with high-index facets and high electro-oxidation activity. *Science.* 2007;316: 732-735.

136. Han A, Zhang Z, Li X, Wang D, Li Y. Atomic thickness catalysts: synthesis and applications. *Small Methods.* 2020;4: 2000248.

137. Yang T, Cui C, Rong H, Zhang J, Wang D. Recent advances in platinum-based intermetallic nanocrystals: controlled synthesis and electrocatalytic applications. *Acta Physica-Chimica Sinica.* 2020;9:200347.

138. Schuppert AK, Savan A, Ludwig A, Mayrhofer KJJ. Potential-resolved dissolution of Pt-Cu: A thin-film material library study. *Electrochim Acta.* 2014;144:332-340.
Yadong Li received his B.S. degree from the Department of Chemistry at Anhui Normal University in 1986 and his Ph.D. from the Department of Chemistry at the University of Science and Technology of China in 1998. He joined the faculty of the Department of Chemistry at Tsinghua University in 1999. He was elected as a member of the Chinese Academy of Sciences in 2011. His research interests focus on the synthesis, assembly, and catalytic applications of nanomaterials, clusters, and isolated single-atom sites.

How to cite this article: Wang Y, Wang D, Li Y. A fundamental comprehension and recent progress in advanced Pt-based ORR nanocatalysts. SmartMat. 2021;2:56-75. https://doi.org/10.1002/smm2.1023