Electrochemical Catalysts for Green Hydrogen Energy

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Developing clean and renewable energy resources has become one of the world’s most important challenges, given the double burden of energy scarcity and environmental pollution. For sustainable energy conversion and storage, efficient electrocatalysts play a pivotal role in important energy-related reactions, including oxygen reduction, oxygen evolution, and hydrogen evolution. To satisfy practical requirements, the catalysts need to demonstrate high performance, durability, and acceptable cost. These are primary considerations when designing and preparing various new electrocatalysts. Among the research programs being actively conducted around the world, some promising recent results suggest strong potential alternatives to current expensive noble metal-based catalysts. This review summarizes recent technical advances in the preparation of efficient electrocatalysts.

1. Introduction

The twin trends of increasing global energy demands and environmental pollution have created important challenges and problems. In response, considerable research and development efforts have been focused on innovative alternative energy sources and more efficient energy storage systems.[1–5] Sustainable–renewable energy resources (e.g., hydrogen energy, solar energy, wind energy, wave power, and so on) are particularly attractive approaches for addressing growing energy demand and environmental issues.[6,7] Among them, energy conversion and storage systems, such as fuel cells (FCs),[8–10] metal–air batteries,[11–13] and water electrolysis,[14–17] have received increasing attention.

The heart of these energy conversion and storage technologies is electrochemical reactions, including the oxygen reduction reaction (ORR),[18] oxygen evolution reaction (OER),[19–21] and hydrogen evolution reaction (HER).[22–25] As shown in Figure 1, a water electrolyzer that produces green hydrogen using sustainable energy and a FC generates electric power using hydrogen as fuel via these reactions. However, because the reactions are inherently sluggish, catalysts are required to maximize conversion efficiency. As a result, catalysts are often the key factors determining the efficiency, stability, and cost of energy conversion and storage systems.

The primary catalysts for such reactions are currently Pt-based materials and/or their alloys, but the very limited supply and high cost of Pt are barriers to the widespread commercialization of these systems in various fields.[26] This has driven efforts to discover new alternative catalysts that can deliver a superior combination of high efficiency, durability, and low cost. Generally, two important factors need to be considered in the design of catalysts with enhanced activity. First, the number of active sites will directly influence catalytic activity during the reaction. This feature is related to the specific surface area and the homogeneous dispersion of catalysts on the catalytic supporting materials. Second, the stability of catalyst is associated with the nature of interface between catalyst and support material. This feature is related to the structure of catalysts.

This review provides a critical overview of important developments in new and efficient catalysts (i.e., for ORR, OER, HER, and chemical catalysts). This review is also intended to provide a better understanding of catalysts and the systematic approaches to their development which may lead to new economical catalysts with exceptional performance and stability. This is of particular interest because the catalysts ultimately influence the practical adoption of FCs, water electrolysis, metal–air batteries, and so on.

2. Oxygen Reduction Reaction

FCs, which convert chemical energy into electric energy, are highly efficient, eco-friendly systems running on essentially limitless fuels (e.g., hydrogen and oxygen). Because of their high energy conversion efficiency, FCs are expected to be universally adopted for power generation in various fields, and offer one of the potential solutions to global energy and environmental issues.[27,28]

The anode and cathode materials used in FCs typically consist of Pt nanoparticles (NPs) on activated carbon black (CB). The combination of electrode materials (metals and supports) boosts both the hydrogen oxidation reaction (HOR) and ORR. Because
As a catalyst, in shell structures, among the carbon nanotube (CNT), a variety of high-indexed planes have proven alloy catalysts, to avoid these problems, the carbon supports need to be modified. These factors contribute to the improvement of catalytic activity. Therefore, a controlling size shape of metal NPs is one of the important strategies for highly active catalysts. In the past few years, the relation between the size of Pt NPs and ORR catalytic activities has been very actively studied. Many studies report that the mass activity of ORR catalysts can be maximized Pt NP sizes in the range of 2–5 nm. When Pt NP size is smaller than 2 nm, its mass activity rather decreases. However, the origin of this phenomenon is still controversial, and many studies are currently under investigation to answer why.

### 2.1. Platinum-Based Catalysts

In general, precious metal catalysts, especially platinum (Pt)-based catalysts, have been intensively studied for many years due to their excellent catalytic activity and stability as ORR catalysts. In many studies, Pt has been widely used as a reference catalyst when searching for new catalysts. The catalyst, in which Pt NPs are supported on porous carbon material such as Pt/C, is the most successful commercial ORR catalyst. However, it has a serious problem in the commercialization stage due to its scarcity and cost competitiveness. The research goals of ORR catalyst were summarized by Wei et al. Important research foci are to increase active sites and enhance intrinsic catalytic activity (Figure 2a). Based on this research direction, many studies have developed a number of Pt-based catalysts, including core–shell structures, alloy catalysts, and catalysts with tunable size and shape. Among the precious metals, Pt-based catalysts have been the most amply studied ORR catalysts. Therefore, we will focus on various strategies for Pt-based catalysts in this section.

#### 2.1.1. Size Effect of Pt NPs for ORR Activity

The size of metal NPs is a factor that has a great influence on catalytic activity, and thus studies on controlling NP dimension have also been intensively investigated. Reducing their size can improve catalytic performance due to the following factors: 1) the smaller particles can provide the higher catalytic surface area at given metal loading; 2) the smaller particles have the higher surface energy; and 3) the smaller particles form the larger interface with support. Controlling the shape and size of metal NPs has been studied in various electrocatalyst systems. It is an important factor that has a great influence on the performance of catalysts. An ORR performance according to the plane of Pt NPs, especially the low-index plane, has been extensively studied. Where anions are strongly adsorbed in electrolyte such as \( \text{H}_2\text{SO}_4 \), the ORR activity of Pt(111) surface is dramatically deactivated to be inferior to Pt(100). On the contrary, the ORR activity follows the order of Pt (100) < Pt (110) = Pt (111) in a weakly adsorbed electrolyte such as \( \text{HClO}_4 \). A variety of high-indexed planes have proven to be catalytically more active for ORR. Xia and co-workers successfully synthesized Pt concave nanocubes (NCs) using bromine (Br) as a capping agent to impede the growth of Pt(100). High-resolution transmission electron microscopy (HR-TEM) confirms that Pt concave NCs are mainly composed of (510), (720), and (830) facets. The specific activity of Pt concave NCs at 0.9 V showed three and two times better than Pt cube and cuboctahedra structure, respectively. Although the catalyst showed an excellent specific activity, the efficiency of Pt was not satisfactory due to its relatively large particle size (>15 nm). Furthermore, their ORR activities are improved when one or more facets of Pt NPs are exposed to high-index facets with a Miller index greater than 1. These cases are not limited to the trisoctahedron (hhk), tetrahexahedron (hk0), and trapexezohedron (hhk). In general, the ORR activity is influenced by the factors such as the edges, dense surface phase, and kinks of the high-index planes. However, there is an issue on scalability of catalysts due to the difficulty in stabilization of thermodynamically unstable structure during long-term operation.

#### 2.1.2. Facet Dependence of Pt Nanostructure for ORR Catalytic Activity

Controlling the shape and size of metal NPs has been studied in various electrocatalyst systems. It is an important factor that has a great influence on the performance of catalysts. An ORR performance according to the plane of Pt NPs, especially the low-index plane, has been extensively studied. Where anions are strongly adsorbed in electrolyte such as \( \text{H}_2\text{SO}_4 \), the ORR activity of Pt(111) surface is dramatically deactivated to be inferior to Pt(100). On the contrary, the ORR activity follows the order of Pt (100) < Pt (110) = Pt (111) in a weakly adsorbed electrolyte such as \( \text{HClO}_4 \). A variety of high-indexed planes have proven to be catalytically more active for ORR. Xia and co-workers successfully synthesized Pt concave nanocubes (NCs) using bromine (Br) as a capping agent to impede the growth of Pt(100). High-resolution transmission electron microscopy (HR-TEM) confirms that Pt concave NCs are mainly composed of (510), (720), and (830) facets. The specific activity of Pt concave NCs at 0.9 V showed three and two times better than Pt cube and cuboctahedra structure, respectively. Although the catalyst showed an excellent specific activity, the efficiency of Pt was not satisfactory due to its relatively large particle size (>15 nm). Furthermore, their ORR activities are improved when one or more facets of Pt NPs are exposed to high-index facets with a Miller index greater than 1. These cases are not limited to the trisoctahedron (hhk), tetrahexahedron (hk0), and trapexezohedron (hhk). In general, the ORR activity is influenced by the factors such as the edges, dense surface phase, and kinks of the high-index planes. However, there is an issue on scalability of catalysts due to the difficulty in stabilization of thermodynamically unstable structure during long-term operation.

#### 2.1.3. Synergetic Effect of Pt NPs and Supporting Materials for ORR Activity

For ORR, the most important challenge is increasing both catalytic activity and durability. Typically, Pt NPs are loaded on carbon supports such as CB, carbon nanotube (CNT), graphene, and carbon nanofiber (CNF). The form of catalyst is Pt NPs physically deposited on carbon supports, and thus they prone to be leached and aggregated during operation in corrosive acidic and alkaline electrolytes. To avoid these problems, the carbon supports need to be modified to interact better with the Pt NPs and to improve the structural and/or electronic configuration of the catalysts. Park et al. introduced a new
The Pt NPs were supported on a metal–nitrogen (M–N)x-doped ordered mesoporous porphyrinic carbon (FeCo-OMPC(L)). The Pt content was ultralow, while the catalytic activity of the Pt (5 wt%)/FeCo-OMPC(L) was two times higher than a reference high Pt-loaded catalyst. The improved electrocatalytic activity of the Pt/FeCo-OMPC(L) was correlated with the electronic and geometric effects of the active sites. The results suggest that Pt/FeCo-OMPC catalysts are promising candidates for commercial FCs. Another catalyst, formed of uniform and mesoporous Pt thin films on ionic polymer-doped graphene, showed considerably improved electrocatalytic activity and stability compared with a Pt/C catalyst. Under acidic conditions, Pt/TfGnPs showed onset and half-wave potentials that were positively shifted to 0.58 and 0.53 V (vs Ag/AgCl), respectively, compared with Pt/C catalyst (0.57 and 0.52 V vs Ag/AgCl). More importantly, their electrochemical durability was tremendously improved compared with the Pt/C catalyst.

Figure 2. a) Volcano-like relationships between the catalytic properties and electronic structure of Pt3M alloys. Reproduced with permission.[38] Copyright 2007, Springer Nature. b) Atomic structures of i) icosahedral Pt cluster with 309 atoms and ii) octahedral Pt cluster with 146 atoms. A different color means a different coordination number. Surface strain fields of Pt iii) icosahedral and iv) octahedral nanocrystals with a diameter of 10 nm. Color indicates strain labeled in the color map. Reproduced with permission.[77] Copyright 2012, American Chemical Society. c) The average site occupancies of the second layer of i) the Ni173Pt138 nanocrystal and ii) the Mo23Ni143Pt313 nanocrystal, indicated by iii) colormap. iv) Binding energies for an oxygen atom on the Mo9Ni13Pt78(111) surface, relative to the lowest binding energy. Gray spheres represent Pt atoms, and colored ones represent oxygen sites. Binding energy on the fcc site of Pt(111) surface and Pt8Ni111(111) surface and the peak of Sabatier volcano is labeled for comparison. v) The change in binding energies when a Ni6Pt178 nanocrystal is transformed into a Mo9Ni143Pt78 nanocrystal. Reproduced with permission.[78] Copyright 2015, American Association for the Advancement of Science (AAAS). d) HR-TEM image of Pd–Pt nanodendrite. Reproduced with permission.[44] Copyright 2009, AAAS. e) Kinetic current densities, before and after CV cycling test, recorded at 0.9 V on a variety of polycrystalline Pt3M catalysts versus lattice parameter. f) Relation between the potential necessary to adsorb 1/8, 1/6, 1/4, and 1/3 monolayers (ML) of H (UH) from the cyclic voltammograms (CV) in the H adsorption region in N2-saturated 0.1 M HClO4 on Pt3M and dPt–Pt. Reproduced with permission.[81] Copyright 2016, AAAS. g) Schematic synthesis diagram of carbon-supported and N-doped carbon-coated ordered fct-PtFe NPs. h) Mass and specific activities of the catalysts measured at 0.9 V. Reproduced with permission.[84] Copyright 2015, American Chemical Society.

concept on ORR catalysts to reduce mass transport and overpotential.[59] The Pt NPs were supported on a metal–nitrogen (M–N)x-doped ordered mesoporous porphyrinic carbon (FeCo-OMPC(L)). The Pt content was ultralow, while the catalytic activity of the Pt (5 wt%)/FeCo-OMPC(L) was two times higher than a reference high Pt-loaded catalyst. The improved electrocatalytic activity of the Pt/FeCo-OMPC(L) was correlated with the electronic and geometric effects of the active sites. The results suggest that Pt/FeCo-OMPC catalysts are promising candidates for commercial FCs. Another catalyst, formed of uniform and mesoporous Pt thin films on ionic polymer-doped graphene, showed considerably improved electrocatalytic activity and stability compared with a Pt/C catalyst.[60] More importantly, it exhibited notable stability, with over 95% activity retention after 30 000 cycles of accelerated degradation test (ADT) tests. This stability was attributed to the interconnected mesoporous structure of the Pt thin film and theionic polymer-doped graphene. The concept suggested in this work could be a crucial solution for improving durability. A new graphene support, triazine-functionalized graphene nanonodelets (TfGnPs), was utilized to stably anchor Pt NPs.[61] Pt NPs on TfGnPs (Pt/TfGnPs) demonstrated higher electrocatalytic activity and stability than conventional Pt/C catalyst. This enhancement was associated with the large surface area and nitrogen-doped triazine units in the TfGnPs, which sustained active sites and stabilized the Pt NPs, respectively. Under acidic conditions, Pt/TfGnPs showed onset and half-wave potentials that were positively shifted to 0.58 and 0.53 V (vs Ag/AgCl), respectively, compared with Pt/C catalyst (0.57 and 0.52 V vs Ag/AgCl). More importantly, their electrochemical durability was tremendously improved compared with the Pt/C catalyst.
2.1.4. Hollow Structured Catalysts

The efficiency of metal utilization can be enhanced by increasing available specific surface area with respect to the amount of metal loading. A similar approach to this strategy has been actively studied on the hollow structured NPs. The basic principle of this strategy is to take advantage of surface atoms and nearby atoms that only provide catalytic activity, while the internal atoms do not directly have catalytic activity. Therefore, forming hollow Pt NP structures by leaching core template atoms can be an effective strategy to reduce Pt loading while maintaining catalytic activity. Adzic et al. was successfully synthesized hollow Pt NPs from the removal of template Ni NPs.[62] The hollow Pt NPs show higher ORR activity than a similar size of typical Pt NPs. A compressed deformation approach has also been reported to improve ORR activity by shifting the $\delta$-band center of Pt downward and weakening the adsorption of oxygenated intermediates.[63,64] The Xia’s group reported the structure of Pt nanocages by depositing several layers of conformal Pt shell on the surface of well-aligned Pd nanocrystals and then etching Pd cores.[65] Density functional theory (DFT) calculations prove the principle formation mechanism of Pt nanocage, in which the outermost Pd is integrated during the Pt deposition process and etching starts from the integrated Pd layer. Pt cube and octahedral nanocages composed of {100} and {111} sides were, respectively, formed by the nanoscale Pd cube and octahedral template. The catalyst showed an ORR mass activity of 0.75 A mgPt$^{-1}$ at 0.9 V versus reversible hydrogen electrode ($V_{RHE}$), which is five times higher than commercial Pt/C (0.14 A mgPt$^{-1}$).

2.1.5. Alloy and Doping Effect of Pt Nanostructures for ORR Activity

The ORR activity of Pt is significantly improved by forming Pt alloys with transition metals such as nickel (Ni), cobalt (Co), and manganese (Mn). This strategy has been highlighted to impart unique properties in Pt catalysts in 1993.[66] The enhanced ORR activity of Pt alloys is very closely related to the deformation of electronic structure that affects the adsorption energy between Pt active sites and oxygen-containing species.[67–71] Nørskov et al. proved the volcanic relationship, claiming that the adsorption energy of metal active sites must be in the optimum range to efficiently facilitate the adsorption/desorption of reactants.[72] Markovic’s group also used DFT calculations to establish a similar relationship for the alloy ratios of Pt to other metals.[38] The specific activities of the PtM (M = other metal) alloys show the relationship between volatile position and $\delta$-band center. Their catalytic activities are determined by the reaction between the adsorption energy of the reaction intermediates and the surface coverage by the spectator species (Figure 2a). Interestingly, the Pt$_3$M (M = Fe, Co, or Ni) alloys are located apex of the volcano plot, exhibiting higher ORR activity than other Pt-based catalysts. Based on these results, many groups have experimentally elaborated to improve the ORR activity by controlling the size, shape, and composition of the PtM nanostructures.[73–75] The Pt$_3$Ni(111) truncated-octahedral nanostructure was reported by Wu et al.[76] This structure exhibited 4 and 1.8 times higher ORR mass activity than commercial Pt/C and conventional octahedral Pt$_3$Ni catalysts, respectively. Furthermore, the authors reported a homogeneous icosahedral nanocrystal Pt$_3$Ni catalyst with improved ORR activity.[77] Both studies speculated that the Pt$_3$Ni nanocrystals were bounded to the (111) plane and the ORR performance could be improved by elastic deformation. Molecular dynamic simulations revealed that tensile and compressive surface strains are, respectively, attributed to icosahedral and octahedral particles (Figure 2b). The difference in surface deformation is closely related to the change in electronic structure, which is attributable to improved ORR performance. In addition, a study on the enhanced ORR activity of Pt$_3$Ni(111) via a surface doping strategy was reported by Huang et al.[78] They doped various transition metals. Among them, Mo improved the most enhanced catalytic performance. DFT calculations revealed that the ORR activity was improved by increasing the oxygen binding energy in the central region of the Pt$_3$Ni(111) plane by Mo doping (Figure 2c). A similar study on molybdenum-doped PtNiMo(110) nanocrystals showed exceptionally high catalytic activities for ORR in single FC tests. Its catalytic activity was 3.43 ± 0.35 A mgPt$^{-1}$ at 0.9 $V_{RHE}$ on a rotating disk electrode (RDE) and Pt mass activities of 0.45 A mgPt$^{-1}$ at 0.9 $V_{coul}$ in a membrane electrode assembly (MEA).[79] Compared with undoped PtNi/C octahedral NPs, the higher mass activity and the slightly better durability of the Mo-doped PtNiMo/C octahedral NPs were associated with Ni inclusion in the PtNi alloy. This was because Mo atoms were positioned at the Pt-rich edges and vertices. And also, gallium (Ga)-doped PtNi octahedral NPs supported on carbon (Ga-PtNi/C) displayed much higher ORR activities, which were 11.7 times better mass activity (1.24 A mgPt$^{-1}$) and 17.3 times better specific activity (2.53 mA cm$^{-2}$) than Pt/C catalyst (0.106 A mgPt$^{-1}$ and 0.146 mA cm$^{-2}$).[80] DFT calculations indicated the enhancements were due to the addition of Ga to the PtNi octahedral structure, which increased binding energy with the oxygen intermediate, and thus increased catalytic activity. In addition, compared with PtNi/C and Pt/C catalysts, the Ga-PtNi/C exhibited outstanding durability, and the initial Ni content and octahedral structure of the Ga-PtNi/C were preserved. Furthermore, even after 30,000 cycles of a single-cell stability test, most of the Ga-PtNi octahedral NPs retained their original shape without agglomeration.

In addition to the Pt-Ni system, other PtM systems have also been studied. Xia and co-workers prepared a Pd–Pt alloy catalyst, in which branch-shaped Pt was grown on Pd particles by reducing the Pt salt with Pd nanoseeds. The catalyst showed an excellent ORR activity at room temperature and 60 °C.[44] The ORR activity of Pt–Pd dendrites was due to the exposure of the large surface area and high-index side of the Pt branches (Figure 2d). A Pt/C catalyst stabilized by gold (Au) nanoclusters through the under-potential deposition (UPD) method was reported by Zhang et al.[77] The catalyst displayed an excellent ORR activity. It was because Au clusters increased the oxidation potential of Pt. It was proven by in situ X-ray absorption near-edge spectroscopy (XANES) and voltammetry experiments. Chorkendorff’s group reported eight catalysts of Pt-lanthanide, Pt-alkaline earth catalysts, Pt$_3$M (M = La, Ce, Sm, Gd, Tb, Dy, Tm, and Ca),[81] The volcanic relationship between ORR activities and bulk lattice parameters was plotted (Figure 2e,f). The use of lanthanide shrinkage could control the effect of deformation and was a way
to adjust the activity, stability, and reactivity of these materials. Despite these efforts, a remaining issue on Pt alloys with transition metals is ORR stability due to leaching or melting.\[28,37\]

2.1.6 Core–Shell Structured Catalysts

Core–shell structured Pt bimetallic catalyst is a special type of Pt alloy catalyst, in which the active Pt shell protects supporting transition metal core (e.g., Pd,\[82\] Ni,\[83\] and Cu\[33\]). This strategy mitigates the dissolution of the transition metal core, and can enhance ORR activity through the interaction between Pt and core metal.\[28,36,34\] In addition, as Pt is only used in a small amount on the surface of particles, the use efficiency of Pt increases.\[85,86\] Pt@Ni core–shell octahedron catalysts were prepared via a facet-control synthesis method.\[83\] A Ni octahedron was pierced by Pt atoms along the three orthogonal Cartesian axes, and then Pt atoms were coated along the edges. This peculiar anisotropic diffusion of Pt core atoms, along the (100) vertex and then toward the (110) edges, provided the minimum strain energy for the interaction of Ni–Ni pair. The mass and specific activities of the octahedral skeletal Pt-based nanostructured (OSN)/C catalysts were 0.94 A mg\textsubscript{Pt}\textsuperscript{-1} and 2.8 mA cm\textsuperscript{2}, respectively. The hierarchical skeletal Pt-based nanostructured (HSN)/C catalysts were 1.57 A mg\textsubscript{Pt}\textsuperscript{-1} and 2.7 mA cm\textsuperscript{2}, respectively. The values were much higher than the Pt/C catalyst (0.27 A mg\textsubscript{Pt}\textsuperscript{-1} and 0.36 mA cm\textsuperscript{2}). Molybdenum (Mo)-doped PdPt@Pt core–shell octahedra and ionic block copolymer-functionalized reduced graphene oxide (Mo-PdPt@Pt/IG) were combined to increase interfacial cohesion.\[87\] As a result, the Mo-PdPt@Pt showed distinct configuration benefits, including isolation of the Mo atoms on the vertices and edges of the octahedron, and two to three shell layers of Pt atoms on a PdPt alloy core. Due to the advantages of this configuration, Mo-PdPt@Pt/IG showed considerably improved electrocatalytic activity and durability for ORR in comparison to Pt/C catalyst. Specifically, the mass activity of Mo-PdPt@Pt/IG was 31 times higher than the Pt/C catalyst, while its excellent activities were retained even after 10,000 cycles. To optimize the physicochemical and electrochemical characteristics of Pt@Pd core–shell catalysts, the Pt contents were varied using different amounts of Pt precursors.\[82\] Pd@Pt core–shell NPs were formed by reducing a Pt precursor and growing Pt layers on the surfaces of Pd NPs. The mass activities of the Pt(10%)Pd/C core–shell NPs, produced by Pt(NH\textsubscript{4})\textsubscript{2}Cl\textsubscript{6}·xH\textsubscript{2}O, were 221 mA m\textsubscript{Pt}g\textsubscript{PdCM}\textsuperscript{-1} at 0.85 V\textsubscript{RHE} and 53 mA m\textsubscript{Pt}g\textsubscript{PdCM}\textsuperscript{-1} at 0.9 V\textsubscript{RHE}, which was a significant improvement over the Pt/C catalyst (219 mA mg\textsubscript{Pt}\textsuperscript{-1} at 0.85 V\textsubscript{RHE} and 59 mA mg\textsubscript{Pt}\textsuperscript{-1} at 0.9 V\textsubscript{RHE}). The improved performance of bimetallic Pt–Pd/C catalysts is mostly ascribed to the active Pt surface on a Pd core. A PtCu\textsubscript{x}@Pt/C core–shell structure, formed by the galvanic replacement reaction, exhibited nanoporous Pt surfaces.\[31\] The nanoporous PtCu\textsubscript{x}@Pt structure was produced, when the ratio of Cu to Pt was more than 5. The catalyst also possessed diverse electronic structures, based on the surface configuration in bulk. Among various samples, the PtCu\textsubscript{2}@Pt/C catalyst displayed the best activity and stability for ORR. It is because the d-band downshifts after forming extremely porous Pt layers on the Cu-enriched subsurface layer. A N-doped carbon shell can effectively protect NPs from desorption, aggregation, and dissolution under operating conditions. Ordered face-centered tetragonal (fct) PtFe NPs (fct-PtFe/C) catalysts with a few nanometer sizes were prepared via heat treatment of polydopamine-coated PtFe NPs (Figure 2g).\[88\] When the carbon shell was very thin (below 1 nm), the conservation of NPs was outstanding, and the catalyst showed high electrocatalytic activity. It was because the reactant molecules can penetrate to very thin carbon layer. The mass and specific activities of the resultant fct-PtFe/C catalysts for ORR were, respectively, 11.4 and 10.5 times higher than a Pt/C catalyst (Figure 2h).

2.1.7. Platinum-Based SACs

Currently, Pt single atom catalysts (SACs) have attracted a great attention as promising ORR catalysts. Pt single atoms (SAs) loaded on a carbon-based materials showed an excellent ORR performance with four-electron pathway. The Sun’s group reported a cost-effective catalyst with Pt SAs dispersed on a CB support.\[89\] The catalyst had a low Pt loading (0.09 m\textsubscript{Pt} g\textsubscript{C}\textsuperscript{-1}), and the half-wave potentials were 0.76 and 0.87 V (vs RHE) in acidic and alkaline conditions, respectively. In addition, the catalyst was applied as a cathode for proton-exchange membrane fuel cells (PEMFC), showing a power density as high as 680 mW cm\textsuperscript{2}. Theoretical calculations indicated that Pt SAs are well immobilized by pyridinic nitrogen atoms to be stable against impurities. A catalyst, in which Pt SAs anchored on a carbon support with defects (Pt\textsubscript{1}/BP\textsubscript{defect}), was reported by Liu et al.\[89\] Pt\textsubscript{1}/BP\textsubscript{defect} displayed an enhanced ORR activity, excellent methanol tolerance and stability, as well as an improved Pt utilization. The catalyst was applied as a cathode for PEMFCs, resulting in a maximum power density of 520 mW cm\textsuperscript{2}. Based on the DFT calculations and structure analysis, the Pt SAs stabilized on four carbon atoms in the carbon divacancy (Pt-C\textsubscript{2} site) was identified as active sites for high ORR performance.\[90\]

2.2. Palladium-Based Catalysts

Palladium (Pd) has electronic properties similar to Pt because it is one of the platinum group metals (PGMs). In fact, Pd has shown good activity for ORR, and its cost is only half to one-quarter that of Pt. Therefore, Pd-based catalysts are considered highly attractive alternatives to Pt.\[91\] As a non-Pt catalyst for ORR, Pd–Fe–Mo catalysts, prepared at an optimized atomic ratio (7.5:1.5:1.0) and heat-treated at 500 °C, showed catalytic performance similar to a Pt/C catalyst.\[92\] Their kinetic current density was 32.18 mA m\textsubscript{Pd}g\textsubscript{PdCM}\textsuperscript{-1} at 0.9 V\textsubscript{RHE}. After 3000 cycles, the current density decreased to 6.20 mA m\textsubscript{Pd}g\textsubscript{PdCM}\textsuperscript{-1}, which is significantly better than other non-Pt catalysts. In addition, in practical operating conditions on carbon, the Pd–Fe–Mo catalysts (20 wt%) showed the outstanding performance of 506 mA cm\textsuperscript{2} at 0.6 V\textsubscript{RHE}, qualifying this non-Pt catalyst for ORR. Monodispersed PdFe NPs were prepared by a novel method using a combination of polyl and hydride reductions.\[93\] The resulting PdFe NPs were heat-treated under a reductive atmosphere to induce structural modifications. In this way, the d-band center of the Pd was downshifted, and then the affinity between the Pd and oxygen species was tuned to induce more favorable ORR kinetics. As a result, the mass and area activities
Due to S doping and the formation of edge N¼1.0 V¼0.848 V at a 0.6 V bonds, indicating that the decreased work function of the Fe–N–graphene improved the ORR kinetics. A new approach for the synthesis of Fe–N/C catalysts, the so-called silica-protective-layer assist, was used to generate Fe–N active sites and to control the growth-in-size of Fe-based particles. CNT/PC catalysts with silica coating demonstrated higher activity than the pristine CNT/PC without silica coating. The silica-coated CNT/PC catalysts displayed an excellent electrocatalytic activity and durability in alkaline conditions. Specifically, in an alkaline FC, their cathodes showed the highest current and power densities among nonprecious metal-based catalysts. Their performance in an acidic FC also showed an excellent volumetric current density of 320 A cm⁻².

2.3.2. Preventing Metal Corrosion with Carbon Shell

Fe and Co catalysts confined in several layers of carbon–nitrogen (C–N) shells by applying polyaniline (PANI) as a C–N precursor have been reported by Wu et al.[104] This catalyst showed ORR activity close to the commercial Pt/C, four-electron selectivity (hydrogen peroxide yield < 1.0%) and excellent stability (700 h at Vcell). This result indirectly proved that the corrosion of Fe and Co was protected by the C–N shells. Fe NPs were encapsulated in nitrogenated holey 2D network (C₃N₄) catalysts. The Fe NP cores were encapsulated in electrochemically transparent shells (Fe@C₃N₄) by the in situ sandwiching of a Fe²⁺ precursor in C₃N framework (Figure 3c). The Fe@C₃N₄ catalyst showed better ORR activities than the reference Pt/C in both acidic and alkaline conditions. Moreover, the Fe@C₃N₄ catalysts were corrosion-free after electrochemical testing, even after 650 h, indicating that its abnormal stability stems from indirect-contact electrocatalysis. Defect-free encapsulated Fe NPs in a phena-zine-based fused aromatic porous organic network (Aza-PON) have also been reported.[105] The Fe@Aza-PON catalysts displayed higher performance, with a half-wave potential of 0.839 V½RHE and a Tafel slope of 60 mV dec⁻¹, than Pt/C catalyst (0.826 V and 90 mV dec⁻¹). The resultant Fe@Aza-PON showed excellent durability (zero current loss even after 100 000 cycles) and tolerance against methanol crossover and CO poisoning.

2.3.3. Forming Porous Structure with High Specific Surface Material

Given that the catalytic supports with large specific surface area are generally better to interact with the reactants, the porous activity, Fe@NGnP on CNF was activated by carbon dioxide (CO₂) to produce the Act-CNF-N₃ catalyst, which showed an improved onset potential, similar to a Pt/C catalyst. Its limiting current (−6.3 mA cm⁻²) was even higher than a Pt/C catalyst (−6.0 mA cm⁻²). Using a ball-milling and pyrolysis approach, edge-activated sulfur (S)-doped Fe–N–graphene (EA-SFeNG) was synthesized.[102] Due to S doping and the formation of edge Fe–N sites on the graphene (FeNG), the ORR activity of EA-SFeNG was significantly improved. Its onset potential (Vonset = 1.0 V½RHE) and half-wave potential (V½ = 0.848 V½RHE) were similar to Pt/C catalyst (Vonset = 1.05 V½RHE, V½ = 0.865 V½RHE). The stability of the EA-SFeNG was superior to Pt/C catalyst in alkaline conditions. The improved activity of the EA-SFeNG was attributed to an increase in defect sites and SO₂ bonds, indicating that the decreased work function of the Fe–N–graphene improved the ORR kinetics. A new approach for the synthesis of Fe–N/C catalysts, the so-called silica-protective-layer assist, was used to generate Fe–N active sites and to control the growth-in-size of Fe-based particles. CNT/PC catalysts with silica coating demonstrated higher activity than the pristine CNT/PC without silica coating. The silica-coated CNT/PC catalysts displayed an excellent electrocatalytic activity and durability in alkaline conditions. Specifically, in an alkaline FC, their cathodes showed the highest current and power densities among nonprecious metal-based catalysts. Their performance in an acidic FC also showed an excellent volumetric current density of 320 A cm⁻².

2.3. Non-Noble Metal-Based Catalysts

Noble metal-based catalysts, especially Pt-based catalysts, are a big obstacle for the commercialization stage due to their high cost and durability.[27–93] Currently, ORR researches are focused on the development of cost-effective and reliable catalysts.[96] During the past decades, various non-noble metal-based catalysts have been studied to replace Pt-based ORR catalysts used in FCs. Many studies have been conducted to improve their stability issue. Among them, non-noble metal–nitrogen–carbon complexes (M–N–C) and non-noble metal oxides have demonstrated to be potential alternatives to Pt catalysts.[28,97]

In 1964, Jasinski et al. proved that there was an ORR activity of Co phthalocyanine, and a study on the M–N–C composite as an ORR catalyst began.[98] Since then, many groups have elaborated to improve the ORR performance of M–N–C catalysts. In this section, three major strategies for the development of M–N–C catalysts: 1) improving intrinsic activity by adjusting the composition of M–N–C structure; 2) preventing metal corrosion with carbon shell; and 3) forming porous structure with high specific surface area material.

2.3.1. Improving Intrinsic Activity by Adjusting the Composition of M–N–C Structure

A catalyst, in which iron cations were coordinated to the sites of pyridinic nitrogen atoms in in the micropores of graphitic sheet, was reported by Dodelet’s group.[99] The catalyst was synthesized by ball-milling a carbon support, ferrous acetate, and phenanthroline, followed by successive pyrolysis in an argon and ammonia environment. Interestingly, the continuous pyrolysis process increased the density of active sites. The current density of catalyst electrode in PEMFC was competitive to the Pt-based electrode, while it showed unsatisfactory stability. Later, another Fe-based catalyst was reported using zeolitic imidazolate framework (ZIF-8) with phenanthroline and ferrous acetate.[100] Compared with the previous catalyst, it showed a power density of 0.75 W cm⁻² at a 0.6 Vcell, which clearly demonstrated an improved ORR activity (Figure 3a). It also showed the catalytic performance close to the Department of Energy (DOE) proposed target (300 A cm⁻³ based on non-PGM catalysts; Figure 3b). Although it showed an enhanced ORR activity, an apparent stability reduction of 15% showed unsatisfactory long-term durability. Fe and N codoped graphene nanoplatelets (Fe@NGnP) were developed using a simple method.[101] A small amount of Fe@NGnP coated on CNFs showed an improved catalytic activity and stability for ORR. To further enhance catalytic
structure is an alternative approach to improve the intrinsic activity of nonprecious metal-based catalysts. Müllen’s group developed a non-noble metal catalyst from vitamin B12 (VB12) and the polyaniline-Fe (PANI-Fe) complex. Silica NPs, well-ordered mesoporous silica (SBA-15), and montmorillonite were selected as templates for the formation of porous catalysts (Figure 3d-f). The catalysts from VB12 and silica NPs showed an excellent ORR activity, high four-electron selectivity (electron transfer number >3.95), and enhanced stability (9 mV negative shift of half wave potential after 10 000 CV cycles). Its high catalytic performance should be originated from high Brunauer–Emmett–Teller (BET) surface area (568 m$^2$g$^{-1}$), narrow mesopore size distribution, and uniform distribution of abundant M–N$_x$ active sites. Liang et al. reported a CNT catalyst with Fe–N decoration using hierarchical porous carbon. The catalyst demonstrated high activity, which was associated with efficient transport, and increased active sites and large specific surface area. Based on these advantages, the Fe–N-decorated hybrid catalysts provided an ORR performance similar to commercial Pt/C.

Figure 3. a) Power density curves of as-prepared catalyst (blue stars), a catalyst reported previously (red circles), and Pt/C reference (green squares). b) Volumetric activity (hollow stars or circles) and extrapolated Tafel plots (dash line) of as-prepared catalyst (blue) and a catalyst reported previously (red). The solid gray circle and star represent US DOE volumetric activity targets for the years 2010 and 2015, respectively. Reproduced with permission. Copyright 2011, Springer Nature. c) Schematic representation of the structural evolution of the Fe@C$_x$N catalyst, showing the in situ sandwiching of Fe$^{3+}$ in C$_x$N layers (Fe$^{3+}$@C$_x$N) in NMP, the reduction of Fe$^{3+}$@C$_x$N into Fe$_3$O$_4$@C$_x$N by sodium borohydride, and the subsequent annealing of Fe$_3$O$_4$@C$_x$N into the Fe@C$_x$N catalyst. The structure of the Fe@C$_x$N catalyst consists of Fe NP cores encased in well-ordered nitrogenated graphitic shells (Fe@C$_x$N NPs), which are uniformly distributed on the C$_x$N matrix. Reproduced with permission. Copyright 2018, Elsevier. d-f) TEM and scanning electron microscope (SEM) images of as-prepared C–N–Co catalysts: d) VB12/Silica colloid, e) VB12/SBA-15, and f) VB12/MMT. Insets in (d–f) are the model illustration of the catalysts with various mesoporous structures. Reproduced with permission. Copyright 2013, American Chemical Society.
3. Oxygen Evolution Reaction

In water splitting, the HER and OER, respectively, occur at the cathode and anode. In FCs, the ORR and HOR are generated on the cathode and anode, respectively. HER is a two-electron transfer pathway, while OER is a four-electron transfer pathway. Therefore, OER requires higher energy (i.e., higher overpotential) to overcome the inherent energy barrier. Water is an efficient energy carrier, and studies on electrocatalytic activity for OER have been actively conducted. As a result, diverse catalysts have been reported which exhibit enhanced reaction kinetics and durability in different electrolyte conditions.

3.1. Ruthenium-Based Catalysts

Partially hydrous RuO$_2$ NPs fixed on carbon (x-RuO$_2$@C, $x =$ degree of hydration) was prepared as a catalyst, and the catalyst showed bifunctional properties for OER and HER. Both electrodes with 0.27-RuO$_2$@C displayed smaller potential gaps between HER and OER at different pH values of 0, 7, and 14 than traditional electrodes with different catalysts (e.g., Pt/C for HER and Ir/C for OER). In addition, in FCs, the catalyst also showed bifunctional electrocatalytic activities for HOR and ORR, which are the reverse reactions of HER and OER, respectively.

A lanthanum manganite (LaMnO$_3$) nanofibers (NFs) (LaMnO$_3$ NFs) catalyst was functionalized with RuO$_2$ NPs and nonoxidized graphene nanoflakes (GNFs). The LaMnO$_3$ NFs demonstrated outstanding electrochemical performance in a lithium (Li)–air cell, showing considerably decreased discharge/charge voltage gaps (1.0 V at 400 mA g$^{-1}$) and excellent stability during more than 320 cycles.

3.2. Iridium-Based Catalysts

An iridium (Ir)-decorated carbon electrode with a layered hollow sphere (LHS) was constructed by coating with a catalyst solution containing GO, IrCl$_3$, and polystyrene and subsequent pyrolysis. The electrochemical surface areas of the electrodes were increased approximately six times with respect to GO content. An Ir-decorated carbon electrode with the LHS structure displayed excellent OER activity (current density: 89.99 mA cm$^{-2}$ at 1.6 V_RHE$^{-1}$).

Ir and transition metal alloys with a double-layered nanoframe (DNF) shape were synthesized using different ratios of Ir and transition metals (Ni and Cu). After selective etching, the IrNiCu DNF catalysts possessed a structurally robust rhombic dodecahedral morphology. The IrNiCu DNF displayed superior electrocatalytic activity for OER in acid conditions, compared with an Ir/C catalyst. Moreover, the IrNiCu DN showed excellent durability. This was due to its unique constitution, which impeded the aggregation of NPs and induced a strong rutile IrO$_2$ structure during operation.

Hollow multimetallic nanostructures with well-defined facets can help reduce the loading amount of precious metal while boosting catalytic performance. Hollow octahedral nanocages...
of cobalt (Co)-doped IrCu catalysts were synthesized with controllable morphology and size distribution. The co-doped IrCu octahedral nanocages displayed outstanding electrocatalytic activity and stability for OER in acidic conditions. Their catalytic activity made them one of the most distinctive Ir-based catalysts.

3.3. Iron-Based Catalysts

Developing efficient catalysts that can recycle rusted stainless steel and accelerate the OER is important for ecofriendly society. Zhang’s group reported a strategy for utilizing corroded stainless steel plates as OER electrodes by a hydrothermally combined in situ electrochemical oxidation–reduction cycle (EORC) method. An electrode showed an overpotential of 290 mV (vs RHE at 10 mA cm⁻²) and a Tafel slope of 32 mV dec⁻¹. Its lowered catalytic activity after long-term operation could be regenerated by EORC. An OER catalyst, in which Ni(Fe)OₓHᵧ nanosheet layers were interconnected to stainless steel mesh (SSNNi), was reported by Wei and co-workers. The excellent electron and mass transfer ability of the catalyst was attributed to the very large surface area of 3D structure and the proper contact between the conductive substrate and the active sites. SSNNi electrodes exhibited the Tafel slope and overpotential of 36 mV dec⁻¹ and 230 mV (vs RHE at 20 mA cm⁻²), respectively. FeM/NPC, which combined FeM (M = Ni, Co) particles with nitrogen-doped porous carbon (NPC) as an easy and scalable strategy, was reported by Zhong et al. NPC promoted electron transfer by the efficient dispersion of metal species, and also provided complementary active sites to enhance catalytic activity. The produced catalysts FeNi/NPC and FeCo/NPC showed overpotentials of 310 and 360 mV, respectively, showing similar or better OER activity to RuO₂ (360 mV). This was due to the synergistic effect between FeM and NPC with the enhanced conductivity and high porosity of NPC. In addition, the catalysts were applied for water electrolysis and Zn–air batteries, demonstrating excellent performance and stability. Furthermore, they were also useful for energy storage applications such as Li-ion batteries and supercapacitors.

A fundamental study on the OER activity of FeOₓHᵧ was conducted by the Boettcher’s group. The dependence of FeOₓHᵧ species on several electrode substrates, such as Pt, Pd, Au, Cu, and C, was investigated using chronopotentiometry (CP) and cyclic voltammetry (CV) methods. In Figure 5a, the activity of FeOₓHᵧ follows the order of Au > Pd ≈ Pt ≈ Cu > C. This tendency is due to the adsorption strength of Fe–oxo ion and the substrate. As the adsorption strength is stronger, the more Fe is adsorbed, resulting in a reduction of charge transfer resistance at the interface of FeOₓHᵧ and substrate. As a result, the local atomic and electronic structure of the FeOₓ unit plays an important role in OER catalytic activity.

3.4. Cobalt-Based Catalysts

Sodium cobalt metaphosphate (NaCo(PO₄)ₓ) with a CoO octahedral (CoO₆) structure was synthesized by solid-state heat treatment. The catalyst showed superior activity in alkaline media.
conditions to a RuO₂ catalyst. Specifically, argon-annealed NaCo(PO₄)₃ (NCoM-Cb-Ar) showed remarkably enhanced electrocatalytic activity with a small overpotential (340 mV) and high mass activity (532 A g⁻¹). Efficient charge transfer and chemical interaction between the NaCo(PO₄)₃ and amorphous carbon led to the improved catalytic activity of the NCoM-Cb-Br for OER.

Co-P/Co-N-C/NPC catalysts, prepared from Co-P/Co-N-C and N/P codoped porous carbon (NPC), exhibited an amorphous structure and a high specific surface area (1462.9 m² g⁻¹), and had a number of different active sites, including Co-P, Co-N, and NPC. The Co-P/Co-N-C/NPC catalysts displayed remarkable catalytic activity (η = 374 mV at 10 mA cm⁻²) for OER. In addition, Co-P/Co-N-C/NPC achieved a current density of 10 mA cm⁻² for overall water electrolysis at a cell voltage of 1.59 V, which is similar to that of IrO₂-Pt/C electrodes.

Heterogeneous Co NPs, decorated on a Y₂Ru₂₇Co₂O₇ pyrochlore oxide support, were prepared by an in situ exsolution approach. Efficient electron transfer emerged due to the synergistic effect between the Y₂Ru₂₇Co₂O₇ pyrochlore oxide support and the metallic Co NPs, reducing the energy barrier for COOOH intermediates. As a result, the OER kinetics was effectively expedited in alkaline conditions, resulting in superior OER electrocatalytic activities. The idealized YRCO-560 (Y, Ru, Co, and O elements on YRCO-X, X refers to thermal reduction temperature) catalysts displayed much better OER performance, with the lowest onset potential at a current density of 10 mA cm⁻² and ten times higher mass activity at a potential of 1.48 V RHE, extraordinary Faradaic efficiency (0.958), and excellent durability compared with an IrO₂ catalyst (Figure 5b–d). This concept of heterogeneous catalysts, based on a 3D transition metal anchored on a pyrochlore oxide support, provides effective utilization of nonoxide transition metal-based catalysts for OER by decreasing the energy barrier needed to generate the oxyhydroxide (MOOH) intermediates.

3.5. Copper-Based Catalysts

An electrode consisting of self-assembled copper oxide (CuO) on a stainless steel substrate was prepared by chemical deposition from a CuSO₄ and NH₄OH solution and heat treatment in air. The resultant copper oxide (CuO) catalysts showed a bundle-type morphology of 2D nanosheets. OER for the CuO catalysts occurred at about 1.48 V RHE (η = 250 mV) with a Tafel slope of 59 mV dec⁻¹. Its overpotential of 350 mV at 10 mA cm⁻² was the lowest among Cu-based materials for OER, and it also showed a durability of over 10 h at a current density above 10 mA cm⁻². This result was associated with the properly exposed 2D morphology, which provided an OER-favorable structure and optimum electronic properties.

CuCoOₓ catalysts were prepared with diverse morphologies, including mesoporous nanosheets, cubic, compact-granular, and agglomerated embossed shapes, by hydrothermal reaction in various solvents. They showed outstanding properties for OER in strong alkaline conditions. Specifically, the CuCoOₓ nanosheet displayed exceptional OER activity with a lowest overpotential of ≈290 mV at 20 mA cm⁻² and a Tafel slope of 117 mV dec⁻¹. The outstanding electrochemical activity of the mesoporous CuCoOₓ nanosheet originated from the beneficial electrochemical features of the 2D morphology, with increased electrochemically active areas.

3.6. Metal-Nitride/Metal-Carbide/Metal-Phosphide

3D mesoporous Co₃N₄@amorphous N-doped carbon (AN-C) NCs catalysts, with a well-defined open-framework shape, were synthesized by the nitridation and carbonization of monodisperse Co₃(NC)₄ Prussian blue analogue NC precursors (Figure 5e). The Co₃(N@AN-C NCs catalysts showed excellent activity for OER with a notably low Tafel slope (69.6 mV dec⁻¹), and low overpotential (280 mV at 10 mA cm⁻²). Furthermore, they displayed outstanding stability in alkaline conditions, without showing any notable morphology change or voltage increase. Catalysts composed of metal carbide layers (CuCₓ or NiCₓ) deposited on dendritic Cu (CuCₓ/Cu) and Ni (NiCₓ/Ni) were prepared by an easy electrodeposition approach. They possessed effective catalytic active sites, which had the proper binding energy for favorable electron transfer in OER. The metal carbide decorated on the dendritic metal support offered the proper O binding energy and durability, and consequently the CuCₓ/Cu and NiCₓ/Ni catalysts showed well-defined limiting current densities of −5.19 and −5.11 mA cm⁻², respectively, for OER. According to DFT calculations, the overpotential of the NiCₓ/Ni catalysts was 0.74 eV lower than that of Ni without the NiCₓ layer (Figure 5f,g).

Porous Co-P catalysts were prepared using a simple one-step electrodeposition at a high current density. This technique involved the rapid generation of hydrogen bubbles while Co-P was being deposited, forming a porous Co-P shape. The catalyst showed outstanding electrocatalytic activity and durability for OER, displaying higher electrocatalytic activities (η = 10 mA cm⁻²; 300 mV) comparable with Ir/C (η = 10 mA cm⁻²; 345 mV) and RuO₂ (η = 10 mA cm⁻²; 359 mV) in 1 M aq. KOH solution. The performance was attributed to the efficient charge separation between Co and P in the porous Co-P. Its porosity also provided a high electrochemical active surface area (ECSA). The calculated ECSA of the porous Co-P (118 cm²) was 2.4 times higher than a nonporous Co-P film (49 cm²).

3.7. Nonmetallic Compounds

1D graphitic carbon nitride (g-C₃N₄) nanorods were synthesized by a hydrothermal reaction. Altering the bulk g-C₃N₄ (g-B-CN) to 1D g-C₃N₄ (g-CN) nanorods produced a material with a lot of active sites, increased active surface area, and improved charge transfer. The optimized 1D g-CN exhibited an overpotential of 316 mV RHE at 10 mA cm⁻² in 1 M aq. KOH solution, with a Tafel slope of 125 mV dec⁻¹. The outstanding electrocatalytic properties of 1D g-C₃N₄ were mainly ascribed to the plentiful exposed active sites, due to the 1D structure and oxidized pyridinic N, confirming the importance of detailed morphology tailoring and heteroatom doping.

Phosphorous (P) and sulfur (S) codoped CₓNₓ showed outstanding electrocatalytic OER activity due to synergistic geometric and electronic effects, which increased coordinatively unsaturated sp³-C via structural deformation and increased electrical conductivity by controlling the electronic arrangement with
extra electrons from dopants, respectively. As a result, PCSC-C$_3$N$_4$ (P/S codoped C$_3$N$_4$) showed higher OER/ORR characteristics, with comparable overpotentials, of 0.42 and 0.27 V (theoretical value), respectively, than commercial Pt and RuO$_2$ catalysts.

4. Hydrogen Evolution Reaction

Hydrogen (H$_2$) has received considerable attention to realize hydrogen economy because H$_2$ is one of efficient green energy carriers together with sustainable energy resources. To produce H$_2$ from water splitting, there are two electrochemical reactions—HER and OER. Electrochemical hydrogen production, however, is not efficient enough to meet commercial requirements because water is stable molecule and requires a high overpotential to split into hydrogen and oxygen, resulting in a poor power to gas conversion efficiency.

Many catalysts have been reported to boost HER. Among them, Pt-based catalysts have demonstrated superior performance to others. They have both the lowest overpotential and the highest current density during operation. Nonetheless, their application has been largely limited by high cost and relative scarcity. Developing viable alternatives with high activity and stability at low cost remains an important challenge.

4.1. Platinum-Based Catalysts

The volcano plot in Figure 6a is an indicator that PGMs are located near the apex of the volcanic curve, showing superior HER performance. Among PGMs, Pt, located at the peak of the volcano curve, is the most efficient HER electrocatalyst with a near zero starting overpotential and a small Tafel slope. Based on the Sabatier principle, an optimum M–H bond strength indicates suitable adsorption and desorption of hydrogen on the surface of Pt, leading to high HER activity.
The shape, size, and aspect of Pt NPs are key factors to determine their HER electrocatalytic activity. Generally, the size of NPs is a factor greatly related to catalytic activity. The smaller NP size can provide the more catalytic active sites at the same catalyst loading. However, below critical size dimension, Pt NPs show the opposite trend. For example, the size in the range of 1–3 nm, the specific mass activity decreases as the particle decreases. Theoretical calculations provided a convincing explanation for this phenomenon. The plane surface area of Pt single crystals is more likely involved in catalytic activity because of its lower activation energy than the edge area. Therefore, the smaller sized Pt NPs have the higher edge-to-face ratio, leading to the lower catalytic activity.\(^{[132]}\)

Although many earth-abundant elements, such as transition metal nitrides, sulfides, and phosphides,\(^{[6]}\) have proven their potential for HER catalysts, Pt-based materials are still the best HER catalysts. Unfortunately, however, their high cost and limited availability hinder a wide range of applications. Various efforts have been elaborated to mitigate these shortcomings by improving its utilization efficiency.

The first approach is the size and shape control. As the HER process occurs on the surface of several atomic layers or on the atoms below the surface, increasing the plane surface area of catalysts improves HER performance. Exposing the more Pt(110) surface is proven to be the better HER catalyst.\(^{[132–135]}\) As a result, various researches are focused on the surface engineering of Pt\(^{[136]}\) and controlling edge-to-face ratio.\(^{[65]}\) Therefore, clusters and SACs have recently attracted widespread interest for a new research direction while maintaining high activity and stability with a maximum utilization of Pt active sites.\(^{[132,137–139]}\) However, Pt nanocrystals (Pt NC) tend to sinter and/or agglomerate during catalytic reactions, and their shape control is very limited due to their susceptibility to oxidative etching and high internal strain energy.\(^{[136,140]}\)

The second approach to enhance HER activity is related to catalytic supports. Forming small metal particles on support may sustain catalytic active sites with minimum Pt loading, leading to extreme Pt utilization efficiency. Laasonen and colleagues have developed Pt SAs and subnanometer clusters on single-walled CNTs (Pt@SWCNTs) via an electroplating deposition method.\(^{[137]}\) The Pt@SWCNT with a small Pt loading demonstrated comparable performance with the commercial Pt/C in acidic conditions (Figure 6b). Chen’s group synthesized Pt super-structures functionalized with polyethyleneimine (PEI) (Pt-SSs@PEI).\(^{[141]}\) The molecular structure of PEI induced highly branched Pt NC to improve HER performance. Wang et al. synthesized N-doped CNFs using bacterial cellulose (HN-BC and LN-BC, respectively) doped with low and high proportions of polyaniline.\(^{[142]}\) They fabricated catalysts by immobilizing Pt NCs (\(d = 3–5\) nm) on LN-BC and HN-BC using electrochemical deposition. They claimed that N-doping level was closely related to the HER activity.

The third approach is forming Pt alloy with other transition metals to improve HER performance with minimum Pt loading. Based on the \(d\)-band centroid theory, the \(d\)-band centroid close to the Fermi level indicates relatively strong adsorption, while the far away to that indicates weak adsorption. Therefore, the alloy with \(3d\) transition metals can improve the Pt utilization efficiency by modifying its electron arrangements and coordination environments.\(^{[73,143]}\)

### 4.2. Palladium-Based Catalysts

Pd attracts attention as an alternative HER catalyst to Pt because it is cheaper and its atomic size is similar to Pt with a lattice mismatch of only 0.77%.\(^{[65,144]}\) In addition, Pd has a good hydrogen adsorption capacity in both gas and liquid phases. Bulk Pd undergoes hydrogen adsorption separately on \(\alpha\) and \(\beta\)-phases. The \(\alpha\)-phase arises from low concentrations of hydrogen (H/Pd ratio of 0.03–0.05), while the \(\beta\)-phase is formed from high concentrations of hydride (H/Pd ratio above 0.6).\(^{[145]}\)

Its catalytic performance is sensitive to the size and shape of Pd NPs. Various types of Pd crystals can be formed by thermal dynamic or kinematic control. Various Pd nanostructures were produced by different methods. Pd seed is an important step to determine the shape of Pd nanostructure. Therefore, the catalytic performance of Pd NPs can be improved by seeding to control crystal morphology.\(^{[146]}\)

Pd NPs with different planes showed obvious changes in electronic and geometric structures, which are attributed to improving HER performance at low Pd loading. Jerkiewicz synthesized an octahedral Pd NP with an average tip–tip size of 7.8 nm. These octahedral Pd NPs showed very high H adsorption when compared with bulk Pd or large Pd NPs.\(^{[147]}\) Hydrogen production associated with H adsorption was measured using temperature-controlled CV and thermodynamic analysis, revealing that octahedral Pd NPs adsorbed more H than other Pd nanostructures.

3D NPs have been intensively studied as electrochemical catalysts because of their high specific surface area to provide more active sites. Various porous 3D NP or nanonetwork structures have been produced by chemical etching, Kirkendall effect, Ostwald ripening, and so on. Liu’s group developed Pd NP assemblies (NPAs) with a porous structure with high specific surface area. The catalyst showed a low overpotential of 80 mV at a current density of 100 mA cm\(^{-2}\) and the Tafel slope similar to the commercial Pt/C.\(^{[148]}\) A tunable Pd nanonetwork (PdNN) for HER in alkaline electrolyte was prepared using an easy chemical process with the assistance of a Zn precursor and a surfactant (i.e., cetyltrimethylammonium bromide [CTAB]).\(^{[149]}\) A 3D PdNN exhibited a 2.2 times greater electrocatalytic active surface area compared with a Pt/C catalyst. Other minimally Pd loaded catalysts exhibited high active density and facilitated efficient electron transport. The 3D PdNN showed an overpotential (110 mV@10 mA cm\(^{-2}\)) similar to the Pt/C catalyst. Due to its high crystallinity, monodispersity, and support-free porous nanonetwork, PdNN was proven to be an efficient electrocatalyst for HER with high electrocatalytic activity and durability.

Various support materials have also been actively investigated to improve HER performance. Support materials with high surface area, electrical conductivity, and porosity can boost the activity of Pd-based catalysts. Kelly and co-workers have developed a Pd catalyst supported on tungsten carbide and molybdenum substrates by a physical vapor deposition (PVD) method. The current density of a single-layered Pd on the substrates was doubled. Compared with unmodified carbides, single- and multilayered
Pd catalysts showed superior HER performance. Barman et al. synthesized a porous Pd NPs-carbon nitride composite catalyst (Pd-CN₄) using an ultrasonic mediated method. Porous Pd-CN₄ catalyst showed better HER activity than commercial Pt/Ct in acidic condition. The Pd-CN₄ network structure could be simply formed by the reduction of PdCl₂ in the presence of CN₄ nanosheets during sonication. The excellent HER activity was attributed to the porous nature of catalyst and strong bonding between Pd NPs and CN₄, allowing an efficient charge transfer.[153] Recently, Yang’s group developed Pd(0) NPs@alkyne-poly(vinyl alcohol) (PVA) using a Glaser coupling reaction as a convenient method for the separation and capture of Pd metal. The Pd NPs on carbon networks (PdNPs@CNWs) formed by carbonization showed an excellent HER activity and stability. CNWs allowed an efficient electron transfer and stabilized Pd NPs.[152] Pd and nonprecious metal (i.e., Mn, Co, and Cu) NPs were anchored by four-nitrogen units on CNTs (PdM-N₄/CNTs). On CNTs, the N₄ system led to better dispersion and electrical conductivity.[153] Among samples, PdMn-N₄/CNTs showed the best HER performance (onset potential: 35 mV and overpotential: 71 mV at 10 mA cm⁻²), similar to Pt/C catalyst (35 and 65 mV). Other PdMn/CNTs and Pd/CNTs samples without N₄ units exhibited relatively low HER activity (onset potentials: 45 and 80 mV and overpotentials: 90 and 137 mV, respectively).

4.3. Ruthenium-Based Catalysts

As a cheap alternative to Pt catalysts, ruthenium (Ru) exhibits a similar binding energy with hydrogen (∼65 kcal mol⁻¹).[154] However, Ru has a much stronger cohesive force, which causes it to aggregate into bigger particles, diminishing its catalytic activity and durability. To resolve this problem, Ru@C₄N catalysts, Ru NPs stabilized and uniformly distributed in a nitrogenated holey 2D network structure (C₄N), were prepared. The Ru@C₄N catalysts were formed by the polycondensation reaction of hexaketocyclohexane (HKH) and hexaaminobenzene (HAB) trihydrochloride in the presence of RuCl₃ as a Ru precursor (Figure 6c). The C₄N structure, of uniformly distributed holes (diameter = 0.83 nm) with six nitrogen atoms in each hole, provided a large surface area, with anchoring sites and a conductive platform.[156] The Ru@C₄N catalysts showed high turnover frequencies (TOFs) at 25 mV (0.67 H₂ s⁻¹ in 0.5 Maq. H₂SO₄ solution, 0.75 H₂ s⁻¹ in 1.0 Maq. KOH solution) and small overpotentials at 10 mA cm⁻² (13.5 mV in 0.5 M H₂SO₄ solution, 17.0 mV in 1.0 M KOH solution). The performances of the Ru@C₄N catalysts for HER were similar to, or much better than, Pt/C catalyst.

The mass production of an Ru catalyst, Ru@GnP, for HER was realized using a two-step process.[157] The first step was a mechanochemical reaction between graphite and CO₂ to prepare edge-carboxylated graphitic nanoplatelets (CGnP). The second was the formation of Ru carboxylate complexes between a Ru precursor (RuCl₃) and the CGnP in an aqueous dispersion. After chemical and thermal reduction, Ru NPs (∼2 nm) were evenly formed on the GnP (Ru@GnP). The resultant Ru@GnP showed HER performance superior to a Pt/C catalyst in both acidic and alkaline conditions. The Ru@GnP and Pt/C catalyst showed similar onset potentials in acidic conditions. However, in 1.0 Maq. KOH condition, Ru@GnP had a Tafel slope of 28 mV dec⁻¹, while the Pt/C catalyst was 46 mV dec⁻¹. The result indicated that Ru@GnP had a faster reaction process in alkaline conditions. Therefore, Ru@GnP required only 22 mV to reach a current density of 10 mA cm⁻², which was 11 mV lower than the Pt/C catalyst. In acidic conditions, the overpotential of the Ru@GnP was positively shifted by 2 mV at 10 mA cm⁻² after 10 000 cycles. In alkaline conditions, the polarization curve of the Ru@GnP was negatively shifted insignificantly. The results confirmed the durability of Ru@GnP.

Recently, Ru@MWCNT, Ru on multilayered CNT (MWCNT), was synthesized as a cheap and scalable catalyst. In this study, a method for the formation of evenly distributed and stabilized Ru NPs was developed. The structure of Ru@MWCNT was revealed by the extended X-ray absorption fine structure (EXAFS) study. The result indicated that a strong interaction between the Ru⁴⁺ precursor and carboxylic acid (−COOH) on the partially oxidized surface of MWCNT was associated with particle distribution and stabilization. Ru@MWCNT showed an excellent HER performance in both acid and alkaline media. In addition, the authors reported GC-detected Faradaic efficiency as high as 92.28% at 1.8 V and hydrogen production of 247.65 ± 1.16 L kWh⁻¹ (at 10 mA cm⁻²) using actual water splitting system (Figure 6d-f).[131]

4.4. Iridium-Based Catalysts

Iridium (Ir) has low hydrogen binding energy and is the first element applied for chemical adsorption of hydrogen.[158] Ir(111) has been reported to have a relatively balanced hydrogen adsorption/desorption ability, which has an energy comparable to Pt(100).[159] It is also located at the apex of HER volcano plot (Figure 6a), attracting attention as an alternative to Pt-based catalysts. However, its high cost limits practical uses.

Ir@CON catalysts, in which Ir NPs were embedded and uniformly dispersed in a 3D cage-like organic network (CON), were prepared via a unique and efficient synthesis approach.[159] Ir@CON catalysts showed high TOFs of 0.66 and 0.20 H₂ s⁻¹ at 25 mV and much smaller overpotentials of 13.6 and 13.5 mV at 10 mA cm⁻² in 0.5 Maq. H₂SO₄ and 1.0 Maq. KOH solutions, respectively, than the reference Pt/C catalyst (18 and 23 mV) and Ir/C catalyst (20.7 and 28.3 mV). More importantly, the Ir@CON catalysts exhibited excellent durability for HER. The polarization curve of Ir@CON was negatively shifted by 5.5 mV at 10 mA cm⁻², while the Pt/C catalyst was shifted by 11.24 mV in acidic conditions. However, in alkaline conditions, the Ir@CON and Pt/C catalyst showed increases in overpotential of 11 and 89.8 mV at 10 mA cm⁻², respectively.

Many experiment results and theoretical calculations have proven that an optimal hydrogen adsorption energy is the key for the HER.[160] As a result, studying hydrogen adsorption/desorption energy is very important for the development of catalysts.[155,161] Li et al. studied hydrogen chemisorption by selecting Ir(111) as a theoretical model.[162] Ir NPs were tuned to expose Ir(111) crystal planes using an electronegative carbon/nitrogen matrix. The DOS distributions of hydrogen adsorbates, Ir and IrNC, showed that the surface Ir sites of...
IrNC had stronger hydrogen bonds. The HER performance of IrNC was verified by calculating the free energy.

Heteroatoms on carbon supports are important components for the performance of noble metal-based electrocatalysts because their electronegativity alters electron arrangement of metals. Ir NPs anchored on nitrogen-doped graphene sheets (Ir@NG-750) have been reported. The formation of strong Ir–N bonds inhibits Ir agglomeration, fixes Ir clusters, and acts as an ideal matrix to adjust the electronic structure of the Ir@NG-750 catalyst. DFT calculations indicated that the Ir-pyridinic N site (−0.46 eV) showed adequate hydrogen adsorption energy compared to the Ir-graphene site (−2.72 eV) and Ir-pyrrole N site (−0.77 eV), suggesting that the formation of Ir-pyridinic N enhanced HER catalytic activity.

To date, PGM elements are still the most effective HER electrocatalysts because of their low overpotentials and fast kinetics. However, their high cost and limited supply hinder widespread commercial applications. The electrocatalysts based on the earth-abundant elements would be promising alternatives. However, it is well known that the nonprecious metal catalysts are susceptible to corrosion under strong acid and alkaline conditions and tend to aggregate into larger particles during catalytic cycling. To circumvent this problem, numerous studies have focused on noble metal-free N-doped carbon nanostructures by calcining a mixture of nonprecious metal-based salts and N-rich organic compounds and forming heterogeneous HER electrocatalysts.

4.5. Ni- or Co-Based Catalysts

Ni is widely used as a catalyst for HER in alkaline solutions, and Ni-based electrodes are widely used in practice for a century. Numerous theoretical calculations and experiments have demonstrated that Ni has the minimum free energy for hydrogen adsorption and the maximum HER exchange current density. Many studies have reported that the performance of nonprecious metal HER catalysts is in the order of Ni > Mo > Co > W > Fe > Cu determined by electrochemical techniques. Ni-based catalysts have various Ni forms, whose HER performance is in the order of dendrites > particles > film > commercial foil (Figure 7a,b).

Various methods have been proposed to compensate the disadvantages of Ni metal. A Ni/NiO/CoSe2 hybrid catalyst was prepared using a simple solvothermal reaction and postannealing process. The Markovic’s group prepared nanometer-sized Ni(OH)2 clusters on the surface of Pt electrodes. The edges of the Ni(OH)2 clusters efficiently promote water dissociation (Figure 7c). Unfortunately, the catalyst displayed a poor stability due to the irreversible reaction of Ni in acidic conditions. Qiu et al. reported a catalyst doped with Ni SA on nanoporous graphene. Its catalytic performance was improved by changing the electron arrangement in the sp-d orbital between Ni SA and surrounding carbon atoms in graphene (Figure 7d,e). The empty C–Ni orbital enhanced catalytic activity and stability.

To maximize the HER performance of Ni, various methods were proposed. A 1D NiCoS4 nanowire (NW) catalyst was prepared on 3D Ni foam (NF) by directional growth. The NiCoS4 NW/NF showed distinctive catalytic activity and stability by exposing more active sites at the interface of the electrode and electrolyte. The NiCoS4 NW/NF displayed an overpotential of 210 mV at 10 mA cm−2 and 58.9 mV dec−1 of Tafel slope in 1.0 m aq. KOH solution (Figure 7f,g). This exceptional bifunctional activity and stability allowed alkaline water electrolysis to achieve 10 mA cm−2 at 1.6 V. Based on this result, water electrolysis apparatus for largescale solar-to-hydrogen production was fabricated to induce continuous H2 and O2 evolution. It was possible that the NiCoS4 NW/NF catalyst provided sufficient catalytic activity at 1.68 V. Using atomic layer deposition (ALD), a thin layer of MoN2, which was grown on NF by the sequential exposure of Mo(CO)6 and NH3 at 225 °C, was coated on a 3D nickel foam (NF) substrate with a large surface area (Figure 7h–m). To maximize HER efficiency, the thickness of the MoN2 layer was controlled by the number of ALD cycles. After 700 ALD cycles, MoN2/NF displayed low overpotentials (148 and 125 mV) at 10 mA cm−2 in acidic and alkaline conditions, respectively. In both electrolytes, the increased electrocatalytic activity and durability for HER was related to the uniform and conformal coating. The research demonstrated that forming large-area 3D freestanding catalysts could be used for scalable hydrogen production based on efficient water electrolysis.

The core–shell structured catalysts have demonstrated a good stability against corrosion and agglomeration. Bao et al. reported Co NPs encapsulated in nitrogen-doped carbon (Co@N-C) (Figure 7n,o). Because the unique core–shell structure of Co@N-C could prevent corrosion and aggregation of Co NPs, it showed high stability and catalytic HER activity in a wide range of pH. A similar study, Co NPs on nitrogen-doped graphene film (NGF) (Co@NGF) and Co NPs on B- and N-doped carbon cage (Co@BCN), was also reported as catalysts with high HER stability.

CoSe2-CNT catalysts were synthesized using spray pyrolysis and selenization. Compared with pristine CoSe2 powders (an overpotential of 226 mV at 10 mA cm−2), the CoSe2-CNT catalysts exhibited outstanding HER electrocatalytic activity in acidic conditions with an overpotential of 174 mV at 10 mA cm−2. Furthermore, although the Tafel slope was a little larger than that of a Pt/C catalyst (30.2 mV dec−1), CoSe2-CNT also showed a lower slope (37.8 mV dec−1) than pristine CoSe2 powders (58.9 mV dec−1). The macroporous CNT improved the electrocatalytic activity of CoSe2-CNT by increasing the rate of H2 extraction and minimizing the polarization of the electrode.

Many other nonprecious metal-based electrocatalysts based on molybdenum (Mo), tungsten (W), iron (Fe), and copper (Cu) have also been reported. However, apart from the HER performance, their stability is a critical issue.

4.6. MoS2-Based Catalysts

Nickel phosphide (Ni2P) NPs were grown on MoS2 basal plane (Ni2P/MoS2) by in situ phosphidation of NiMoS4 salt. The conductivity and stability of the Ni2P/MoS2 was improved via hybridization with conductive N-doped reduced graphene oxide (N:RGO) or CNT (N:CNT), to respectively produce...
Ni$_2$P/MoS$_2$/N-RGO or Ni$_2$P/MoS$_2$/N-CNT catalyst. Both catalysts showed HER performance comparable with Pt in acidic media. More meaningfully, they worked well in the high current density region ($>$200 mA cm$^{-2}$), showing them to be a promising candidate for practical HER catalysts.

Using ALD, titanium dioxide (TiO$_2$) was coated on a MoS$_2$ surface (ALD(TiO$_2$)-MoS$_2$) and via in situ electrochemical activation of the MoS$_2$. TiO$_2$ islands were formed on the MoS$_2$ basal plane. The resulting ALD(TiO$_2$)-MoS$_2$ showed extremely localized surface distortions of the MoS$_2$ basal plane, displayed significantly enhanced HER kinetics as a consequence of more favorable hydrogen-binding. 50ALD(Act.)-MoS$_2$ showed an HER current of 28.4 mA cm$^{-2}$ at a potential of $-0.3$ V$_{SHE}$. 50ALD(Act.)-MoS$_2$ also showed excellent durability for the...
HER in acidic conditions without changing the current value at a continuous potential of $-310 \text{ mV}_{\text{SHE}}$ for 16 h. Nickel (Ni)- and cobalt (Co)-incorporated MoS$_2$ nanoboxes were prepared using Ni–Co Prussian blue and (NH$_4$)$_2$MoS$_4$.[185] During the reaction, Ni–Co Prussian blue with a NC-like structure experienced different etching stability between the edge and the plane surface. As a result, Ni–Co-incorporated MoS$_2$ nanosheets were simultaneously formed on these NCs. Because of their structural and compositional advantages, the well-defined Ni- and Co-incorporated MoS$_2$ nanoboxes displayed improved electrocatalytic activity with an onset potential of $125 \text{ mV}$ and a small Tafel slope of $51 \text{ mV dec}^{-1}$ for HER.

MoS$_2$ derivatives were prepared from a distinct melamine-phosphomolybdate (MA-PMo$_{12}$) supermolecular precursor that possessed diverse active sites such as 1T-phase, defects, S vacancies, and exposed Mo edges.[186] Reduced MoS$_2$ (R-MoS$_2$) showed superior performance to most MoS$_2$-based catalysts. Especially, the hybrid R-MoS$_2$/Ni catalysts surpassed the Pt/C catalyst in the particularly significant high-current range (>25 mA cm$^{-2}$), indicating that R-MoS$_2$ catalysts are potential Pt/C alternatives in alkaline conditions.

4.7. Metal-Phosphides

Carbon-shell-coated iron phosphide (FeP) catalysts were synthesized by single-step annealing of iron oxide NPs coated with polydopamine.[187] The FeP NPs exhibited a low overpotential of 71 mV at 10 mA cm$^{-2}$, which was similar to the Pt/C catalyst. It displayed extraordinary stability with an insignificant loss of activity in acidic medium after 10000 cycles.

For HER catalysis, a porous Cu–Co–P structure was formed using a H$_2$ bubble-templated one-step electrodeposition process.[188] Cu played a key role in forming the 3D porous structure and Cu–Co bonding, which were active sites for HER. In addition, P contributed to the enhancement of the electrocatalytic activities of Cu and Co via a chemical shift of the metal–P bonds. The electronegativity had a decisive effect on the electrocatalytic properties of the porous Cu–Co–P. Among the samples, Cu–Co–P$_{20}$ showed the best electrocatalytic activity for HER with an overpotential of 138 mV at 10 mA cm$^{-2}$ with a Tafel slope of 48 mV dec$^{-1}$. After durability tests, its overpotential had increased to 144 from 138 mV, which was only 4.3%. Cu–Co–P$_{20}$ exhibited the largest ECSA (85 cm$^2$) and pore volume. This research proposed a new method of producing Cu–Co–P catalysts using electrodeposition approaches, and showed promise as a practical highly efficient water splitting catalyst.

5. Other Electrochemical Reaction Catalysts

To realize green hydrogen society, technologies for hydrogen storage are equally important to hydrogen production and utilization. In addition to ORR, HER, and OER, many electrochemical catalysts for nitrogen reduction reaction (NRR) and carbon dioxide reduction reaction (CO$_2$RR) have also been studied. While all electrochemical reactions are not covered in this review, NRR and CO$_2$RR are to be briefly discussed in this section.

5.1. Nitrogen Reduction Reaction

The N fixation is essential for fertilizers in agriculture and modern industries. Although air consists of 78% N$_2$, the reduction of N$_2$ into ammonia (NH$_3$) is very difficult because of its inertness. The Haber–Bosch process has been the most efficient method for N$_2$ fixation to date. This process converts N$_2$ and H$_2$ gases into NH$_3$ on the surface of iron-based heterogeneous catalysts under harsh reaction conditions of 400–500 °C and 15–25 MPa.[189] The Haber–Bosch process annually produces 2.45 billion tons of nitrogen-based fertilizers, which consumes 1–2% of the world’s energy supply.[191] However, because of the high energy consumption of the Haber–Bosch process, methods for more efficient nitrogen fixation are being actively searched. Recently, electrochemical NRR into ammonia at ambient condition attracts a lot of attention.[192–195]

DFT calculations suggested the NRR catalytic activity of various transition metal surfaces with respect to applied potentials at ambient condition (Figure 8a).[196,197] Most of the NRR active metals occur in the range of $-0.5$ to $-1.0$ V and show very slow kinetics for NRR. In addition, the NRR active metals have relatively high potentials for HER, which means that HER and NRR are competing each other. While the development of electrochemical NRR is sluggish, many studies suggest very promising and encouraging findings. For example, some Au- and Pd-based electrocatalysts show relatively good yields with high Faraday efficiencies ($>8%$).[198,199] Bao et al. demonstrated that tetrahedral (THH) Au NPs showed efficient reduction of N$_2$ into NH$_3$.[198] The catalyst showed high catalytic activities of 1.648 and 0.102 μg h$^{-1}$ cm$^{-2}$, respectively, for NH$_3$ and N$_2$H$_4$H$_2$O production. Wang et al. reported a defect-rich bismuth (Bi) catalyst, in which defects played a key role for NRR.[200] Defect-rich Bi (110) nanoplates demonstrated an NH$_3$ production rate of 5.453 μg mg$^{-1}$ h$^{-1}$ and a Faradic efficiency of 11.68%, suggesting defect engineering is a good strategy for efficient NRR catalysts.

5.2. Carbon Dioxide Reduction Reaction

Excessive release of CO$_2$ into the atmosphere poses an urgent threat to human society.[200,201] Atmospheric CO$_2$ concentration has sharply risen from 270 to 401 ppm from 1800 to 2015, reaching a global consensus on reduction of CO$_2$ emission.[202,203] To tackle this problem, the energy dependence on fossil fuels is replaced by renewable resources such as solar and wind power.[204–207] However, if the current technology does not generate enough power, the proportion of this renewable energy is limited to only 30% due to its intermittent nature.[208] Therefore, many researches have recently been conducted to capture CO$_2$ and convert into chemical feedstocks and fuels.[208–211] Among them, electrochemical CO$_2$ reduction reaction (CO$_2$RR) using renewable electricity has been a high value-added research field. However, CO$_2$, a very stable linear molecule with strong C=O bonds, requires a high activation barrier for electrochemical conversion. As a result, a high overvoltage is required.[212] In addition, the CO$_2$RR has a complex process involving multiple electron/proton transfer reactions, forming several possible intermediates and products.[213–215]
As shown in Figure 8b,c, the various production rates and Faradaic efficiencies for the reported CO₂RR catalysts are summarized. The state-of-the-art electrocatalyst converts CO₂ into C₁ products (carbon monoxide, formate) by CO₂RR with Faradaic efficiency of over 95% with high production rates (>20 mA cm⁻² in H-type cell, >100 mA cm⁻² in flow cell). On the contrary, because of the reaction mechanism, in which several CO₂ molecules reach the surface of catalyst and must be adsorbed, stepwise transformed, and spatially positioned, an efficient production of more desired multicarbon chemicals (C₂+) has not yet been realized with high selectivity. Therefore, a design of highly selective electrocatalyst is an important prerequisite for the production of C₂+ products.

Recently reported catalysts can produce C₂+ products with Faradaic efficiency of 60%. However, the Faradaic efficiency of C₃+ production is less than 10%. Therefore, developing heterogeneous catalysts for the reductive coupling of CO₂ and C₂+ products is an important challenge.

To develop highly efficient electrocatalysts for specific C₂+ products, several strategies, such as adjusting oxidation state, controlling crystal facet, changing surface ligand, doping hetero atom, and alloying/deallloying, have been suggested. The design of efficient catalysts must consider the specific catalytic action for C–C coupling.

6. Conclusions and Outlooks

In conclusion, this review provides an overview summary of some important new and efficient catalysts for ORR, OER, and HER. These advances contribute to the targeted development of energy and environmental electrocatalysis, for applications including FCs, metal–air batteries, water electrolysis, and chemical reactions.

The importance of energy and environmental electrocatalysis, including for the ORR, OER, HER, and chemical reactions, is increasing all over the world because of growing energy consumption, environmental problems, and so on. This review introduces state-of-the-art catalysts which have strong commercial potential. A variety of electrocatalysts, including noble metals, transition metals, metal alloys, metal-free carbon materials, metal–carbon materials, and so on, have been reported.

To meet commercial demands, the catalysts must provide high efficiency, stability, and low-cost production. To be efficient electrocatalysts, they should have good electrical conductivity and the proper adsorption energy between intermediates and the surface of the electrocatalysts (i.e., not too strong or too weak binding energy to intermediates). In addition, having a good number of redox (lose or gain electrons) centers (active sites) is key to effective electrocatalysis. The durability of the catalysts in electrolytes is also an important factor, especially under high potential: it should not alter their structure, or transform their phase or...
solubility. Size, constitution, morphology, porosity, surface shape, synthesis process, and posttreatment all play pivotal roles in determining catalytic activity and durability.

The approaches to manufacturing these electrocatalysts can be divided into three categories. In the first, heteroatom doping into structures changes the electronic constitution of the materials and enhances their electrical conductivity. In addition to increased electrical conductivity, incorporating other elements in the structure has a significant effect on binding strength with intermediates, boosting electrocatalytic activity. Second, mixing catalysts with other conductive materials (e.g., graphene, CNTs, CNFs, and so on) has been shown to be an effective method of enhancing charge transfer in the electrocatalysts. Finally, tuning the morphology of the catalysts enhances the inherent electrical conductivity, the surface area, and the number of active sites exposed to the electrolyte, leading to improved overall electrocatalytic activity.

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Conflict of Interest

The authors declare no conflict of interest.

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