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Recent advances in the rational design of electrocatalysts towards the oxygen reduction reaction

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ABSTRACT

The quest for low-cost yet efficient non-Pt electrocatalysts for the oxygen reduction reaction (ORR) has become one of the main focuses of research in the field of catalysis, which has implications for the development of the next generation of greener fuel cells. Here, we comprehensively describe the 'big picture' of recent advances made in the rational design of ORR electrocatalysts, including molecule-based, metal-oxide-based, metal-nanomaterial-based and two-dimensional electrocatalysts. Transition metals can fabricate molecular electrocatalysts with N_4 -macrocycles such as porphyrin-class compounds and the so-formed M–N–C active centre plays a crucial role in determining the catalytic performances towards the ORR. Group-IV and -V Transition metal oxides represent another class of promising alternative of Pt-based catalysts for the ORR which catalytic activity largely depends on the surface structure and the introduction of surface defects. Recent advances in synthesis of metallic nanoparticles (NPs) allow for precise control over particle sizes and shapes and the crystalline facets exposed to enhance the ORR performance of electrocatalysts. Two-dimensional materials such as functionalized graphene or MoS_2 are emerging as novel electrocatalysts for the ORR. This review covers various aspects towards the design of future ORR electrocatalysts, including the catalytic performance, stability, durability and cost. Some novel electrocatalysts even surpass commercial Pt/C systems, demonstrating their potential to be alternatives in industrial applications. Despite the encouraging progress, challenges, which are also described, remain to be overcome before the real-world application of novel ORR electrocatalysts.

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1. Introduction

As an ideal primary-energy device that can directly convert chemical fuels into electricity through electrochemical processes, fuel cells use hydrogen or hydrocarbon fuels in which the chemical energy stored is greater than that in common bat-

tery materials and they can be operated at close to room temperature [1]. Fuel cells are thus considered a promising replacement of traditional energy solutions in terms of providing clean, steady and sustainable power to meet the rising global energy demand [2]. It is expected that highly efficient fuel cells will come into widespread commercial use in the areas of

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Fig. 1. Representation of a fuel cell showing the continuous supply of reactants (hydrogen at the anode and oxygen at the cathode) and redox reactions in the cell.

transportation and stationary and portable power generation [3]. When hydrogen fuel is used, water is the only by-product and there is no carbon footprint on the environment. A typical $\text{H}_2\text{-O}_2$ fuel cell follows the reaction

As shown in Fig. 1, H_2 is oxidized at the anode while O_2 is reduced at the cathode, and current thus flows through the circuit [4]. A hydrogen fuel cell can work under alkaline or acidic conditions. In comparison with the hydrogen oxidation reaction, the oxygen reduction reaction (ORR) has much slower kinetics for either alkaline or acidic media [1]. As summarized in Table 1, in acid media, the ORR can proceed by a direct four-electron and four-proton reaction with O_2 to yield H_2O , or can proceed by consecutive two-electron and two-proton steps to yield H_2O_2 followed by H_2O . In basic media, the four-electron direct reduction produces four equivalents of hydroxide, while the two-electron reduced product is one equivalent of hydroxide and one hydroperoxyl anion. The hydroperoxyl anion can then be further reduced by two electrons to three hydroxide ions. The performances and costs of fuel cells therefore largely depend on the ORR electrocatalysts used [5].

Besides slow kinetics, a substantial overpotential arises from the high bond strength of the dioxygen double bond (498 kJ), which prevents the full delivery of the predicted 1.229 V for a hydrogen fuel cell [6]. Platinum (Pt) has an overpotential of ~300 mV for the ORR, and has been regarded as the most promising and practical ORR catalyst for hydrogen fuel cells [7]. However, the scarcity and high cost of Pt are primary barriers in the commercial world [8–10]. In addition, the Pt-based elec-

trode suffers from other issues, including poor long-term stability and the tendency to be deactivated by a catalyst poisoner (e.g., CO) [1,2,11,12].

Attempts to reduce/replace Pt for the electrochemical reduction of oxygen in fuel cells began in the 1960s [13] and have been increasing intensively in recent decades. Even though the amount of Pt needed to achieve the desired catalytic effect can now be reduced by using Pt alloys [14,15] or making core-shell structures with supporting materials [16], the commercial scale-up of production at low cost remains challenging. In this context, much recent effort has been devoted to developing alternative ORR electrocatalysts, including molecular electrocatalysts [5,17–19], metal-nanomaterial-based electrocatalysts [20–25], metal-oxide-based electrocatalysts [2,26] and newly emerging two-dimensional electrocatalysts [27–30]. Although a few outstanding review papers have been published in the field of ORR electrocatalysts recently [2,3,6,12,21–23], a comprehensive coverage of various facets, particularly those investigated in the past 10 years, is still lacking.

The purpose of this review is to give a comprehensive picture of state-of-the-art non-Pt ORR electrocatalysts. The review covers recent developments of various materials used, compares the pros and cons of each material selection, and projects future directions of the development of ORR electrocatalysts.

2. Molecule-based electrocatalysts for the ORR

There have been numerous studies on transition-metal organic complexes as ORR catalyst alternatives since the investigation of transition-metal macrocyclic complexes in the 1960s [13]. Subsequently, the drive to replace expensive noble Pt catalysts for the ORR has led to a large number of molecular electrocatalysts comprising transition metal ions combining with nitrogen functional groups on carbonaceous supports [31]. The performance of these catalysts is directly related to the preparation conditions, such as the synthesis method, metal precursor, ligand structure and carbon support, because nitrogen-containing precursors as well as the metal centre play important roles in forming an active catalyst [32,33]. Later studies have indicated that the pyrolysis of these transition-metal macrocycles can generally improve both the activity and stability of the electrocatalysts [34,35].

2.1. Molecule-based electrocatalysts with N_4 -macrocycles

Research on metal complexes as oxygen reduction catalysts has produced metal macrocycle compounds with many different structures that can promote catalysis for the ORR in acidic, alkaline and neutral conditions [34,36]. The higher ORR cata-

Table 1
Electrochemical reactions for the ORR under different conditions.

Media	Acidic				Alkaline			
	anode	$\text{H}_2 - 2\text{e}^- = 2\text{H}^+$	(2)		$\text{H}_2 - 2\text{e}^- = 2\text{H}^+$	(6)		
Electrochemical reactions	cathode	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$	(3)		$\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- = \text{HO}_2^- + \text{OH}^-$	(7)		
		$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O}$	(4)		$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- = 3\text{OH}^-$	(8)		
	overall	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	(5)		$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$	(9)		

lytic activity has been found to be apt to the transition-metal centre (especially Co or Fe) in N_4 -macrocycles, such as porphyrin-class compounds; e.g., tetramethoxyphenyl-porphyrin, tetraphenylporphyrin, phthalocyanine (Pc) and tetraazaannulene (TCPP) [37–41]. The typical schematic diagram of metal porphyrin structures in Fig. 2 has a central metal M that is bonded with four nitrogen atoms. In principle, M (e.g., Fe, Co, Ni or Cu), N (porphyrin derivatives or other nitrogen-containing macrocycles) and C (carbon support) are necessary for there to be an active site of a molecular ORR electrocatalyst.

The activity of the central transition metal ion in macrocycles largely depends on the electronic structure and interactions between the metal and ligands. The metal redox potential is also an important parameter determining the catalytic activity towards the ORR. Early investigations reported the order of catalytic activities for the ORR as $\text{Fe} > \text{Co} > \text{Ni} > \text{Cu} \approx \text{Mn}$ [42]. Consequently, the transition-metal macrocycles have been extensively studied from the synthetic route to the electrocatalytic mechanism, especially for porphyrin-based compounds where $M = \text{Fe}$ or Co . These metal-porphyrin-type complexes, whether mono- or dinuclear, have been found to enhance the ORR efficiently but via a different mechanism. For instance, reactivity studies for the disproportionation of hydrogen peroxide revealed that O–O bond activation can be enhanced by introducing a proton-transfer component. Dicobalt(II) cofacial bisporphyrins can catalyse such proton-coupled ORR reduces O_2 with a four-electron pathway direct produce water at 80% selectivity [43]. While in the presence of another cobalt porphyrin complex, it has been found that O_2 is reduced via a two-electron scheme in which H_2O_2 is a product [44].

A real alternative to Pt must have at least 1/10 of the volumetric activity of Pt/C because even this activity barely meets the requirement for automotive applications [45]. Only since 2005 have several breakthroughs led to advances in reaching

satisfactory activity of metal-containing molecular catalysts [46,47]. Recently, combining ready-made metal macrocycles with a carbon support seems to be a typical procedure in the preparation of catalysts for an ORR catalytic of this kind [48]. Normally used carbon supports include carbon blacks [49], mesoporous carbons [50] and carbon nanotubes (CNTs) [51]. In 2012, a metalloporphyrin metal-organic framework (MOF) with enhanced catalytic activity for the ORR was synthesized from iron porphyrin and the electrochemical property was investigated as a function of the weight percentage of the functionalized carbon support added to the iron-porphyrin framework [41]. Results showed that the addition of carbon support affected the crystallization process of iron porphyrin in the MOF, increased the porosity and improves the electrochemical charge transfer ability. The carbon-metalloporphyrin hybrid has a facile four-electron pathway for the ORR with catalytic activity comparable to that of Pt/C and is thus a promising Pt-free cathode in an alkaline direct methanol fuel cell. In 2014, a covalent network of porphyrins around multi-walled carbon nanotube (MWNT) surfaces was reported. Cobalt(II) meso-tetraethynylporphyrins are arranged on the nanotube sidewalls through adsorption followed by the dimerization of the triple bonds via Hay coupling [52]. The network is stabilized by multiple π -stacking interactions between the porphyrins and nanotube and by the covalent links between the porphyrins. The nanotube hybrids have been fully characterized and tested as the supported catalyst for the ORR under acidic conditions. Interestingly, compared with similar systems in which monomeric porphyrins are simply physisorbed, MWNT-CoP hybrids have a higher ORR activity associated with a four-electron process, corresponding to the complete reduction of oxygen into water. This is confirmed by the number of electrons (n) involved in the ORR being estimated as 3.82 from rotating ring-disk electrode (RRDE) measurements at -0.05 V

Fig. 2. Left: Schematic diagram of the selected molecular structure of metal porphyrins. Right: (a) Cyclic voltammograms of oxygen reduction on the $(\text{Fe-TPCP})_n$ MOF with different weight percentage (wt%) of graphene; (b) Cyclic voltammograms of oxygen reduction on different modified electrodes in 0.1 mol/L KOH O_2 -saturated at a scan rate of 50 mV/s. The right is reprinted with permission from Ref. [41], © 2012, American Chemical Society.

vs Ag/AgCl. In 2015, Mao and coworkers [53] reported the novel efficient electrocatalyst Co-COF-900, synthesized by pyrolysis in the cobalt covalent organic framework. Results show that O₂ is reduced at –0.50 V to produce HO₂[–] and O₂[–] as the intermediate and both the potential and current responses for the ORR are close to those of commercially available 20% Pt/C. Moreover, from RRDE voltammograms, *n* is calculated to be 3.86 at –0.15 V, suggesting that an almost-four-electron reduction process essentially occurs in the ORR with Co-COF-900 as the catalyst in alkaline media.

In addition, there are alternative approaches for the preparation of the macrocyclic ORR catalyst; e.g., a conjugated Co(II)porphyrinylene-ethynylene-based MOF has been reported and interestingly shows good activity in both alkaline and acidic media [54]. A heterogeneous electrocatalyst containing both FeS and Fe₃C phases for which *o,m,p*-phenylenediamine is used as a nitrogen precursor has been reported [55]. Only a small shift (39 mV) in the half-wave potential is observed after the electrocatalysts have been operated for 5000 cycles. The electrocatalytically active site is identified to be Fe–N₆ complexes ([Fe^{III}(porphyrin)(pyridine)₂]), and the two pyridines are believed to play an important role in the catalytic mechanism.

2.2. Molecule-based electrocatalysts with non-macrocyclic chelating ligands

Since some non-macrocycles, chelating ligands have a coordination chemistry similar to that of N₄-macrocyclic members and it stands to reason that they have reasonable ORR activity. Recently, a series of Cu complexes, including 1,10-phenanthrolines, tris(2-pyridyl)amine triazoles and porphyrins and amino-alkyl ligands, were surveyed [6]. It was found that catalysts with alkyl ligands usually perform poorly owing to their poor electronic conductivity. The forced square planar geometry of the Cu centre and porphyrins also hinders the reactivity performance because open coordination sites are only available above and below the Cu–N₄ plane. Even though Cu complexes with pyridine, imidazole, pyrrole and triazole ligands appear to have much better activity, they face the same obstacle as transition metals other than Co and Fe in that they have much worse overall activity than Pt/C.

In 2013, a series of Fe–N–C catalysts was developed by preparing iron-2,6-bis(2-pyridyl)-pyridine (Fe-TPY) complexes and then treating at 600–900 °C [56]. The optimal Fe loading with the highest potential at 0.5 mA/cm² is 5 wt% while the optimal Fe-to-TPY ratio was determined as 1:5. Electrochemical experiments were carried in an O₂-saturated 0.5 mol/L H₂SO₄ solution and the overall electron transfer number for the catalysed ORR was calculated from the results to be 3.7. In testing on a fuel-cell test station, the open-circuit voltage was recorded as 0.75 V at a cell voltage of 0.21 V, while the current density was 0.38 A/cm² with a maximum power density of 0.08 W/cm². A series of ORR catalysts was fabricated in 2016 by loading 1,10-phenanthroline-cobalt(II) metal complex onto reduced graphene oxide (rGO) surfaces via π – π interaction [57]. The introduction of the N-substituent of

1,10-phenanthroline highly boosted the catalytic activity of the metal complex in terms of the half-wave potential (*E*_{1/2}) and kinetic current density (*J*_k), owing to the downshift of the orbital energy level for the central Co(II) arising from the electron-withdrawing effect of N on 1,10-phenanthroline. The average *n* values for Co complexes reached 3.4–4.0, suggesting that the Co(II)–N₄ structure acts as the active centre of electrocatalysts and is responsible for the highly efficient four-electron pathway, corresponding to the complete reduction of molecular oxygen to OH[–] in alkaline solution. The mechanism for the ORR was found to proceed through a single-cobalt-centre-mediated reduction process.

2.3. Pyrolysis for molecule-based electrocatalysts

Instability in an acidic environment has been problematic for molecule-based electrocatalysts used in ORR since their discovery in the 1960s [13]. Although the stability of these catalysts has greatly improved in recent years, a ~20% loss in performance is still common within the first several hours of operation [58]. This loss in performance is somehow attributed to the oxidative cross-linking of macrocycles, which slowly leach out for some metal centres because of the acidic electrolyte and the oxidative degradation of the macrocycle by H₂O₂ generated during the ORR [59]. In the 1990s, several groups found that both the activities and stabilities of catalysts improved after heat treating Co- and Fe-based tetraphenylporphyrins at 100–1100 °C under Ar [60]. Since then, a broad range of methodologies and materials have been employed to produce active ORR catalysts via heat treatment, and pyrolysis has been considered until now to be a general procedure for preparing metal-based electrocatalysts for the ORR. Despite the remaining difficulties in discerning the controlling parameters when preparing active catalysts, there is good agreement in the literature that the original metal–ligand structure can be replaced by a class of promising metal containing catalysts (M–N_x–C) through pyrolysis. With a typical M–N_x–C active site, where M is a 3d transition metal (e.g., Fe or Co) and *x* = 1–4, both the activity and stability can benefit from these electrocatalysts [61–64]. Besides the pyrolysis of premade carbon-supported nitrogen-containing metal complexes, M–N_x–C catalysts can also be prepared by the pyrolysis of a mixture of small molecular precursors [65]. In recent years, there have been an increasing number of studies on using small molecular precursors instead of ready-made transition-metal complexes as the starting material with which to prepare an M–N–C catalyst.

Although the pyrolyzed process generally has advantages including superior catalyst activity and stability, it is difficult to understand the chemical nature of the active ORR catalytic sites in this case owing to the less-controllable synthetic route. Therefore, the ORR performance of these M–N–C catalysts can only be empirically determined by the type of N-containing molecules and transition metals used, and the catalysts are thus difficult to tune [21]. It is therefore worth mentioning recent works on Co/Fe-based N₄-macrocyclic catalysts exhibiting high catalytic activity and stability in which the active structure is

clearer owing to the avoidance of the pyrolysis step in preparation [52,66,67].

3. Metal-oxide-based electrocatalysts for the ORR

Many transition metal oxides, particularly group-IV and -V metal oxides, are another important category of promising non-precious-metal catalysts for the ORR in both acidic [2] and alkaline [68] solutions; e.g., MnO_x , CoO_x , TiO_x , ZrO_x and IrO_x . Applications of transition-metal oxides to the ORR have been pioneered in the last decade mainly owing to (1) the abundant hydroxyl groups on the surfaces of transition-metal oxides convenient for further functionalization [69], (2) the strong interactions between crystalline constructions of transition-metal oxides helping prevent the aggregation of small metal particles [70] and (3) the obviously higher alkaline corrosion resistance compared with the resistances of noble metals and carbon-based materials [71].

A large family of transition-metal oxides is used as ORR electrocatalysts and has been intensively studied in various fields. For instance, manganese oxides (MnO_x), including MnO , MnO_2 , Mn_3O_4 , MnOOH , Mn_2O_3 and Mn_5O_8 , have been identified as highly active ORR catalysts [72,73]. Although their catalytic activity for the ORR can benefit from oxygen defects in crystalline MnO_x , their practical application to fuel cells is limited by their poor electrical conductivity (10^{-6} – 10^{-5} S/cm) [74]. This problem can be partly solved by coating MnO_x onto functional materials with high conductivity, such as carbon. Ketjenblack-carbon-supported MnO_x nanowires have been shown to be highly active electrocatalysts for the ORR in alkaline solution owing to the abundant active sites for oxygen adsorption and other microscopic features [75]. Recently, it was also found that the covalent hybridization of cobalt oxides, such as Co_3O_4

and CoO , with graphene oxide or CNTs greatly enhanced ORR activity [76,77]. The high catalytic activity of carbon-supported oxide nanoparticles (NPs) may be facilitated by the strong coupling between oxide NPs and the carbon support.

The introduction of surface defects due to metal oxides is believed to be a main reason for the enhanced ORR catalytic activity [2], and the ORR activity on metal oxides therefore largely depends on the surface structure. In recent years, great attention has been paid to the perovskite family of oxides with the general formula ABO_3 [78]. For instance, the ORR activity of pure TiO_x was found to be enhanced by adding certain amounts of Zr and Ta to TiO_x to form binary oxides, such as $\text{Ti}_{0.7}\text{Zr}_{0.3}\text{O}_x$ and $\text{Ti}_{0.5}\text{Ta}_{0.5}\text{O}_x$, and an improvement in ORR activity was also observed for Ru– LaO_x and Ir– VO_x binary oxides relative to the corresponding original metal oxide films [79]. This is probably due to the obviously higher surface area of binary oxides while the specific mechanisms underlying this activity enhancement are still not clear. The $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_x$ -based perovskite oxide was highlighted in 2011 as a competitive candidate of the bifunctional catalyst in ORR catalysis [80]. As a mixed electronic and ionic conductor serving as an intermediate-temperature solid-oxide-fuel-cell cathode material, it facilitates the movement of oxygen anions with fast oxygen exchange kinetics and ionic conductivity. Because MnO_x effectively catalyses the disproportionation reaction of HO_2^- to H_2O , it is possible to catalyse the four-electron reduction of oxygen upon the combination of MnO_x with another material active for the two-electron reduction of oxygen to peroxide. As shown in Fig. 3, an urchin-like $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) perovskite oxide was synthesized in 2013 with urea as a precipitator via the coprecipitation method [81]. Its electrochemical measurements were recorded in a N_2 -saturated 0.1 mol/L KOH solution. When compared with pure carbon, the high activity of the urchin-like LSM/C for the

Fig. 3. (a) SEM image of urchin-like LSM powders; (b) Schematic diagram of the growth of the urchin-like nanostructure; (c) Disk current density (i_d) on the urchin-like LSM/C electrode during the ORR in O_2 -saturated 0.1 mol/L KOH solution; (d) ORR at 2500 r/min in the same solution catalysed by the urchin-like LSM, regular LSM and Pt/C electrocatalysts. Reproduced with permission from Ref. [81], © 2013, Elsevier B.V.

ORR is clearly seen in Fig. 3(c), suggesting that the O_2 reduction reaction proceeds predominantly by four-electron reduction directly to OH^- , which is further supported by Koutecky-Levich (K-L) plots. The experimental results in Fig. 3(d) show that the diffusion-limiting current density of the LSM is about twice that of the regular LSM electrocatalyst. Moreover, this LSM perovskite oxide can be used as a bifunctional catalyst for the ORR and oxygen evolution reaction (OER).

Tuning the crystalline shape, size or components has been demonstrated to be a useful way of improving the catalytic activities of metal oxides [82]. In 2012, strong covalent coupling between oxide NPs and graphene oxide sheets was verified in the $MnCo_2O_4$ -N-doped graphene hybrid developed as a highly efficient ORR electrocatalyst in alkaline conditions [83]. Mn substitution was found to increase the activity of catalytic sites of the hybrid material, further improving the ORR activity relative to that for the pure Co_3O_4 -N species. At the same mass loading, the $MnCo_2O_4$ -N-doped graphene hybrid exhibits both better catalytic activity and better stability than Pt/C in terms of ORR current density at a potential less than 0.75 V vs. the reversible hydrogen electrode (RHE). It is highly desirable but challenging to develop a highly active and durable bifunctional electrocatalyst for the reversible ORR. Novel tube-in-tube nanostructures were successfully synthesized in 2013 for many binary and ternary metal oxides with the carbon nanofiber template; e.g., MCo_2O_4 , where $M = Zn, Co, Mn$ and Ni , and Mn_2O_3 , Co_3O_4 , NiO and Fe_2O_3 [84]. The $MnCo_2O_4$ tube-in-tube structure has an ORR onset potential of about -0.23 V (vs. Ag/AgCl) with the peak current appearing at about -0.43 V. The electron transfer number (n) is derived from the slopes of K-L plots and calculated to be 3.8 throughout the investigated potential range, which suggests that a four-electron reduction mechanism is involved. It is worth mentioning that for these interesting tubular structures of mixed metal oxides without any carbon additive as electrocatalysts for the ORR, the experimental results show remarkable limiting current density that is comparable to that of the same metal oxide with graphene hybrid materials in KOH solution. In 2014, monodispersed metal oxide NPs, including NbO_x , ZrO_x and TaO_x , deposited on carbon black were prepared [85]. The particle sizes of the metal oxides could be well controlled from 1 to 14 nm by adjusting the deposition conditions. Electrochemical measurements suggest that smaller particles have much higher ORR activities than their bulky particles/films, mainly owing to increased surface areas and densities of surface defects and better electrical conductivities.

Besides directly serving as ORR catalysts, many metal oxides, particularly group-IV and -V metal oxides, are chemically stable in acidic electrolytes and have been proposed as catalyst supports to replace carbon. Their associated problems are low electrical conductivity and a lack of adsorption sites for oxygen species on metal oxide surfaces, resulting in extremely low ORR activity in their bulk form. Extensive efforts have been made to solve these issues by surface modification, doping, alloying and forming highly dispersed nanoparticles [86].

4. Metal-nanomaterial-based electrocatalysts for the ORR

Along with tremendous progress made in rational wet chemical synthesis, numerous monodisperse metallic NPs have been obtained with controlled sizes and shapes. Masses of high-quality NPs have high electrocatalytic ORR activity and a structure that is tuneable employing various synthetic methodologies and methods [23,87]. To integrate these metal-containing NPs into an electrocatalytic system, a prerequisite step in which the NPs are immobilized onto a bulk conductive electrode surface is usually performed via drop-casting, chemical self-assembly or other method [88,89]. A successful modification might allow researchers not only to enhance the performance of the resulting devices but also to accurately characterize the electrochemical properties of NPs [23].

4.1. Shape and size control of metal-based NPs

Shape-controlled synthesis offers the advantage of tailoring the active facets of electrocatalysts and maximizing the catalytic active areas, and thus minimizing costs especially for the precious metals used. The successful synthesis of monodisperse NPs allows further study of the size, shape and composition effects on catalysis for the ORR [21]. For instance, studies on single-component Pt NPs have shown that their ORR catalysis is NP-size dependent; among Pt NPs of different size, the smallest (ca. 3 nm) has the best activity [90]. In 2011, monodisperse 5-nm $FePt_3$, $CoPt_3$ and $NiPt_3$ NPs were synthesized and found to have much higher activity for the ORR than Pt [91]. Moreover, the catalytic performance of MPt_3 NPs has a volcano-type dependence on the type of M employed, and $CoPt_3$ NPs have the highest specific and mass activity among the three alloy NP catalysts. In 2012, to test the shape effect on the NP catalysis for the ORR, 13-nm icosahedral $NiPt_3$ NPs were synthesized by the coreduction of $[Pt(acac)_2]$ and $[Ni(acac)_2]$ [92]. Their ORR specific activity is about 50% higher than that of octahedral $NiPt_3$ NPs, revealing that surface strain plays an essential role in their ORR enhancement.

As the only practical electrocatalysts for cathode materials in fuel cells, Pt-based catalysts are expensive and scarce owing to the low abundance of Pt in the Earth's crust. Furthermore, Pt NPs are subject to dissolution, coalescence and poisoning under fuel-cell reaction conditions, which reduces both the active catalyst surface area and the catalytic efficiency for the ORR [21]. In recent decades, many efforts and achievements have been made in dealing with these challenges [20,68] employing different approaches. (1) Nanostructures have been constructed and the exposed facet of Pt NPs has been controlled to increase the catalytic efficiency [93]. It has been reported that 7-nm Pt nanocubes have much higher activities than Pt NPs of other shape in catalysing the ORR in H_2SO_4 [94], suggesting that the shape-dependent ORR activity of Pt NPs depends on the adsorption of sulphate ions on Pt(111) and (100) facets. Moreover, the onset potential gain for 7-nm Pt nanocubes is nearly 50 mV relative to other Pt NPs, while the current density is about four times that of Pt nanocubes of other size at the half-wave potential. It has also been found that Pt nanocubes with exposed high-index planes ($\{730\}$, $\{210\}$ and $\{520\}$ facets) have efficiency per unit surface area 2–4 times that for

low-index planes, such as {111} and {100} [95]. However, the surface structures of such NPs are unstable during the catalysis of ORR reactions, especially in the case of structures with high-index planes [96]. (2) Pt has been alloyed with another metal to generate multimetallic nanocrystals and thus reduce the amount of Pt used. Moreover, the activity and stability of alloyed NPs catalysts has often been found to be better than those of pure Pt NPs owing to the construction of different structures, such as core-shells, branches and anisotropic structures [97]. A Pt-skeleton nanostructure can be obtained by pretreating the mother Pt alloy in an acidified solution or by dealloying via cyclic voltammetry to dissolve the non-noble three-dimensional transition metal and obtain an atomically rough surface composed of Pt atoms, which maintains favourable ORR catalytic properties [98]. In 2014, a versatile route for depositing ultrathin Pt nanocrystal shells demonstrated that the introduction of the Pt precursor at a relatively slow rate and high temperature allowed the deposition of Pt atoms to spread across the entire surface of a Pd nanocube, which generates a uniform shell. The number of Pt atomic layers on each Pd cubic seed could be precisely controlled by simply adjusting the amount of Pt precursor introduced into the reaction solution [99]. (3) Modifying Pt NP surfaces may further improve their operation in the ORR system. The improvement is determined by different functional modification species, such as metal clusters, molecules, ions and organic and inorganic compounds [68]. For instance, the ORR activity on cyanide-functionalized Pt{111} facets in $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ electrolytes is 10–25 times that of the naked Pt{111} facets, where cyanide adsorbed on the Pt surface acts as a third body and consequently selectively blocks the adsorption of sulfuric and phosphoric acid anions [100]. In 2013, a hydrophobic, protic-ionic-liquid-encapsulated Ni–Pt porous NP catalyst supported on carbon was synthesized [101]. With the unique structure, the high O_2 solubility of the ionic liquid is in conjunction with the confined environment of the pores, which is consistent with an increased residence time. The half-cell specific activity of this catalyst is found to be an order of magnitude higher than that of commercial Pt/C under the same test conditions.

4.2. Use of non-Pt noble-metal NPs in advanced electrocatalysts

As mentioned above, great progress has been made toward reducing or replacing the scarce Pt used in electrocatalysts, with non-Pt noble metals considered promising high-performance catalysts for the ORR. Herein we use Au NPs as an example catalyst. In the last several years, Au NPs have been used in advanced electrocatalysts for the ORR with both flexibility and stability [24,25]. In general, shape-controlled monodisperse Au NPs can be generated employing a seed-mediated approach or one-pot synthesis [102–105].

For nanosized Au NPs, the most attractive and investigated electrochemical property is the size-/shape-dependent response towards the ORR [23]. In 2013, Cheng and coworkers reported on a general method of fabricating lightweight and mechanically flexible electrodes from either free-standing

monolayered Au nanorod (NR) superlattices [89] or Au NRs three-dimensionally distributed throughout a paper matrix [24]. Flexible NR electrodes were fabricated via the dexterous self-assembly of Au NRs on sheets of tissue paper that have highly electroactive areas. The three-dimensional close-packed assembly is made uniform across the entire paper sheet to provide high conductivity, which leads to greatly enhanced electrocatalysis towards the ORR and methanol oxidation reaction (MOR) when compared with conventional Au disk electrodes. Remarkably, their conductivity is almost unaffected by repeated bending from -180° to 180° , which suggests that repeated bending does not break the NR electrodes. The electrocatalytic current density for ORR reactions on the NR electrodes is about 30 times that for Au disk electrodes under identical conditions. Around the same time, a robust chemical-tethering approach of immobilizing Au NPs onto indium tin oxide (ITO) glass electrode surfaces was reported by the same group [25]. As shown in Fig. 4, monodisperse 20-nm nanospheres (NS20s), 45-nm nanospheres (NS45s) and 20-nm $\times$ 63-nm NRs have been chemically attached to an ITO surface to form submonolayers without any aggregation, and their size- and shape-dependent electrocatalysis toward the MOR and ORR have been systematically investigated. Results indicate strong electrocatalytic activities toward both the MOR and ORR for all three types of NP-modified ITO electrodes, while the mass current densities highly depend on the particle size and shape; i.e., smaller particles lead to higher catalytic current densities per unit mass because of the greater surface-to-volume ratio. All three types of NP-modified electrodes are virtually indefinitely stable during ORR reactions without observable aggregation. More interestingly, such a chemical modification strategy (e.g., immobilizing NPs onto a bulk conductive electrode surface [106,107]) may serve as a general route to fabricating highly stable, customizable electrocatalytic electrodes for a wide spectrum of applications in the fields of sensors and fuel cells. In 2014, Guo and coworkers [108] made calculations based on density functional theory to predict that core/shell Au/CuPd NPs with a 0.8- or 1.2-nm CuPd_2 shell have similar surface strains and compositions and may surpass Pt in catalysing the ORR. Monodisperse M/CuPd NPs have been synthesized by the coreduction of palladium acetylacetonate and copper acetylacetonate in the presence of Ag (or Au) NPs with controlled shell thicknesses. The catalysis for the ORR has been evaluated in 0.1 mol/L KOH solution. $\text{Ag/Cu}_{37}\text{Pd}_{63}$ and $\text{Au/Cu}_{40}\text{Pd}_{60}$ catalysts with 0.75- and 1.1-nm shells are predicted to be more efficient than commercial Pt catalyst. Results shows their mass activity reaching 0.20 A/mg of noble metal at -0.1 V vs Ag/AgCl in 4 mol/L KCl, which is more than 3 times the activity for commercial Pt (0.06 A/mg Pt). Fig. 5 summarizes the performance of the catalysts.

4.3. Other transition-metal-based nanostructural catalysts

Morphology catalyst layers have mass transport limitations. Specifically, it has been demonstrated that optimizing the thickness and porosity of the catalyst using metal-containing NPs at the cathode can affect the performance of ORR catalysts

Fig. 4. TEM and SEM images of Au NP and Au-NP-modified electrodes; Modification procedures and current-voltage curves of ITO/APTMS/PSS/Au NP electrodes (APTMS = (3-aminopropyl)trimethoxysilane, PSS = poly(sodium 4-styrenesulfonate)). Reproduced with permission from Ref. [25], © 2013, American Chemical Society.

Fig. 5. (a) ORR catalytic mechanism on metal NPs; (b) TEM image of Au/Cu₄₀Pd₆₀; ORR polarization curves (c) and summary of ORR mass activity (d) for Ag/Cu₃₇Pd₆₃ and Au/Cu₄₀Pd₆₀ in O₂-saturated 0.1 mol/L KOH solution at -0.1 V and 20 °C. Scan rate: 10 mV/s. Rotation rate: 1600 r/min. (e) ORR polarization curves of Au/Cu₄₀Pd₆₀ NPs at different rotation rates. (f) K-L plots of the ORR from Au/Cu₄₀Pd₆₀ NPs. Reproduced with permission from Ref. [108], © 2014, American Chemical Society.

[89,109]. Transition-metal–nitrogen–carbon (M–N–C)-containing nanomaterials have thus been recognized as another promising alternative class of Pt catalysts for the ORR owing to their high activity in both alkaline and acidic electrolytes. Although the nature of the active sites in M–N–C catalysts is still not fully understood, in general both the M–N moieties and the nitrogen dopants within the carbon matrix are of great importance for the enhanced ORR [110]. For instance, the specific surface area and the structure of the catalysts largely determine the accessibility of the active sites and thus the eventual electrocatalytic performance.

Silica NPs are often used as rigid templates with which to fabricate porous M–N–C catalysts during carbonization with

appropriate metal and nitrogen precursors, before the template is removed to give different types of porous nanoscale features. In 2013, different nanostructures were prepared from similar silica NP templates, including interconnected vesicle-like frameworks, a linear array of mesoporous structures and nanosheet-like structures [111]. A high N/Co content and abundant active sites with a homogeneous distribution were revealed for these samples. One of the samples has obviously higher activity for the ORR in an acidic medium, indicating a larger Brunauer–Emmett–Teller (BET) surface area and well-defined porous structure, and the mesopore size thus plays an important role in improving the ORR performance. In 2014, a series of novel micro-mesoporous Fe–N–C catalysts

were directly synthesized by the simple pyrolysis of different nitrogen heterocyclic compounds and iron chlorides using the same hard template [112]. It was revealed that the sample synthesized by annealing 2,2-bipyridine and Fe chelates at 900 °C had the most positive ORR onset and half-wave potential in both acid and alkaline media. The best ORR performance probably arises from the optimized balance between the active site density and capability of mass and charge transport.

Carbon nanomaterials, such as nitrogen-doped CNTs, carbon nanocapsules and graphene, have been found to be highly active for the ORR [113,114]. It is thus believed that the activities of transition-metal NPs can be further improved by combining the NPs with nanocarbon structures, thereby forming enhanced ORR catalysts. In 2010, Chen et al. [115] reported the direct synthesis of TiN NPs on carbon black using a mesoporous graphite-like composite as a template. The BET surface area and pore volume of the sample were 194 m²/g and 0.64 cm³/g, respectively. The so-prepared catalyst for the ORR was examined in 0.1 mol/L H₂SO₄. An onset potential of 0.84 V vs. RHE was observed with a high cathodic current associated with the ORR. The carbon-black-supported electrocatalyst had constant ORR performance during 1000 cycles of charging–discharging treatment at 0.6–1.0 V vs. RHE under a N₂ atmosphere, which indicates high durability of the materials as cathode catalysts. In 2014, a Co-containing MOF with polyhedral cages was used as a template during the preparation of porous Fe–N–C catalysts in which Fe–N active sites were accurately fabricated with nitrogen-doped graphene (NG) nanocomposites [116]. Although the original MOF structure could not be obtained after pyrolysis, it is important to generate graphitic carbon materials with a large surface area and porous feature, accommodating a high density of catalytic sites. The resultant N–Fe catalysts with an abundant graphene structure from the MOF has superior ORR activity in both aqueous and nonaqueous solutions. In 2014, NGA-supported Fe_xN NPs were prepared via the hydrothermal assembly of GO and FePc and used as efficient ORR catalysts [117]. FeN is rich in nitrogen and therefore generates Fe–N–C structures more efficiently for maximizing the density of M–N–C active sites on a graphene

surface. In addition to having small size, FeN NPs facilitate the evolution of Fe–N–C sites owing to the effective interface effect, and thus provide excellent catalytic activity for the ORR that surpasses that of commercial Pt/C.

In 2016, Guo and coworkers [118] developed a facile controllable synthesis of complex-metal-oxide multilevel nanotubes with tuneable interior structures. As shown in Fig. 6, this interface-modulated approach can be effectively applied to fabricate wire-in-tube and tube-in-tube nanotubes of various metal oxides through electrospinning followed by controlled heat treatment. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images indicate that the multilevel nanotubes consist of outer shrinkable tubes having a diameter of ~200 nm with inner thin wires (~40 nm in diameter) or inner tubes (~110 nm in diameter, ~10 nm in wall thickness) for wire-in-tube or tube-in-tube nanotubes, respectively. All the multilevel nanotubes have ORR activity probably owing to their large specific surface area and mass transport, which are suitable for the ORR. Moreover, shrinkable CoMn₂O₄ tube-in-tube nanotubes have both excellent electrochemical activity and stability. When acting as an ORR catalyst, CoMn₂O₄ tube-in-tube nanotubes have excellent stability with about 92% current retention after 30,000 s, which is higher than that of commercial Pt/C (81%).

5. Two-dimensional electrocatalysts for the ORR

Graphene is structured as single-layer graphite of two-dimensional *sp*² carbon atoms with close-packed conjugated hexagonal lattices, and has attracted much attention from researchers since its rediscovery in 2004 [119]. There is no doubt that the rediscovery of graphene opens a new period in the development of many scientific fields including catalysis [69]. Electrocatalysts for the ORR also greatly benefit from its unique structure and properties, such as huge surface area, ultrahigh electrical conductivity and excellent chemical stability. Moreover, transition-metal-containing cocatalysts can be immobilized on graphene by intermolecular interactions of the defects and functional groups present on graphene's surface,

Fig. 6. Left: Schematics of the formation of shrinkable metal-oxide wire-in-tube (I) and tube-in-tube nanotubes (II); Right: SEM images of shrinkable CoMn₂O₄ wire-in-tube (a) and tube-in-tube (b) nanotubes; Schematic illustration of shrinkable tube-in-tube nanotubes with efficient O₂ diffusion and fast mass transport in the ORR (c); LSV (linear sweep voltammetry) curves of different nanotubes in O₂-saturated 0.1 mol/L KOH at 5 mV/s (d). Reproduced with permission from Ref. [112], © 2016, Tsinghua University Press and Springer-Verlag Berlin Heidelberg.

contributing to improved stability and catalytic activity. Although different kinds of catalyst supports have been explored in the last several years, to the best of our knowledge, the most popular and practical electrocatalysts for the ORR are still graphene-based-material-supported catalysts, despite graphene-based material not having all the properties of an ideal supporting material for fuel-cell ORR electrocatalysts.

In 2012, a graphene-metalloporphyrin MOF with enhanced catalytic activity for the ORR was synthesized by reacting pyridine-functionalized graphene with iron porphyrin [41]. The cited work points to the use of bifunctionalized rGO as building blocks in MOF synthesis and as a structural reinforcement filler that can extend and enhance the functionalities of the MOF by affecting the crystallization process of the MOF and enhancing the electrocatalytic properties of the composite. The rGO and pyridinium linker act synergistically with the iron-porphyrin catalysts to provide a facile four-electron ORR pathway with a much higher selectivity for the ORR and weaker methanol crossover effects compared with Pt catalyst. In 2015, via direct reaction between iron group metals (i.e., Fe, Co and Ni) and a carbon source, a series of transition-metal carbide nanocrystalline M_3C (M : Fe, Co, Ni) encapsulated in graphitic shells supported with vertically aligned graphene nanoribbons (GNRs)

was synthesized [120]. Hot-filament chemical vapor deposition and a direct reaction are advantageous in obtaining high-purity carbide nanocrystals at relatively low temperature. The M_3C GNRs have superior electrocatalytic activity for the ORR, including a low Tafel slope (39, 41 and 45 mV/dec for Fe_3C GNRs, Co_3C GNRs and Ni_3C GNRs, respectively), positive onset potential (~ 0.8 V), high electron transfer number (~ 4) and long-term stability (no obvious drop after testing for 20,000 s). In 2016, Jiang and coworkers [121] developed a new class of bifunctional oxygen electrocatalysts based on ultrafine transition-metal-oxide NPs, such as NiO, FeO and NiFeO, embedded in an amorphous MnO_x shell, where the embedded NP core contributes to the high OER activity and the porous amorphous MnO_x shell functions as an effective ORR catalyst and provides effective structural confinement of the metal-oxide NP core. The synthetic route of the core-shell structure was shown in Fig. 7, the best performance was obtained for $NiFeO@MnO_x$, which had a potential gap, ΔE , of 0.798 V that provided a current of 3 mA/cm² for the ORR and 5 mA/cm² for the OER in 0.1 mol/L KOH solution, better than gaps for Ir/C (0.924 V) and Pt/C (1.031 V). Most importantly, $NiFeO@MnO_x$ has superior stability owing to the outstanding structural confinement effect of the amorphous MnO_x , achieving ΔE of 0.881 V after 300 cy-

Fig. 7. General synthetic procedure of a metal-oxide@ MnO_x core-shell and the confinement of ultrafine NiO within amorphous MnO_x . The insert shows LSV curves for the ORR and OER on metal-oxide@ MnO_x structures at a scan rate of 10 mV/s and rotation rate of 1600 r/min. Reproduced with permission from Ref. [121], © 2016, The Royal Society of Chemistry.

cles, better than the 1.093 V obtained for state-of-the-art Ir–Pt/C oxygen electrocatalysts.

Templates play an important role in determining the performance of electrocatalysts for the ORR in many cases, but not always. In 2013, a facile template-free coprecipitation route was designed for the fabrication of well-ordered NiCo_2O_4 spinel nanowire arrays [122]. The as-prepared NiCo_2O_4 spinel nanowire arrays have been characterized by X-ray diffraction (XRD), SEM, TEM, BET, and X-ray photoelectron spectroscopy (XPS) analyses. BET results show that NiCo_2O_4 spinel nanowire arrays have a mesoporous (ca. 8 nm) structure and a high specific surface area of $124 \text{ m}^2/\text{g}$. The catalytic activity of NiCo_2O_4 spinel nanowire arrays for the ORR in 0.1 mol/L KOH solution has been studied using an RRDE. RRDE results show that the NiCo_2O_4 spinel nanowire array catalyst has excellent catalytic activity for the ORR. The ORR mainly favours a direct four-electron pathway, which is close to the behaviour of the Pt/C (20 wt% Pt on carbon) electrocatalyst under the same test conditions. Chronoamperometric and cyclic voltammogram tests show that the NiCo_2O_4 spinel nanowire array catalyst has excellent stability and reversibility for the ORR.

Recent experimental and theoretical studies on graphene doping revealed the possibility of making p- and n-type semiconductors by substituting C atoms with heteroatoms (e.g., B, N, F, P and S) [123–127]. As shown in Fig. 8, the doped heteroatoms can modify the electronic band structure of graphene and consequently tune the mechanical properties and electrocatalytic activity. In 2011, Liang and coworkers [76] reported a hybrid material consisting of Co_3O_4 nanocrystals grown on rGO as a high-performance bifunctional catalyst for the ORR. As suggested in Fig. 9, although Co_3O_4 or graphene oxide alone has little catalytic activity, their hybrid has surprisingly high ORR activity that is further enhanced by the nitrogen doping of graphene. A more-positive ORR peak potential and a higher peak current are observed for the Co_3O_4 =N-doped graphene hybrid, which has catalytic activity similar to that of freshly loaded Pt/C catalyst in terms of current density in KOH (1–6 mol/L) electrolyte solutions. The observations are in good agreement with calculation results indicating that the ORR catalysed by NG– Co_3O_4 is a four-electron process. The hybrid also has superior durability relative to Pt/C catalyst in 0.1–6-mol/L KOH, with little decay in ORR activity over 25,000 s of continuous

operation while the Pt/C catalyst exhibited a 20%–48% decrease in activity. Moreover, the same hybrid is highly active for the OER, meaning it is a high-performance non-precious-metal-based bicatalyst for the ORR and OER. The unusual catalytic activity arises from synergetic chemical coupling effects between Co_3O_4 and graphene. In 2012, a cost-effective synthesis of NG was developed using cyanamide as a nitrogen source and graphene oxide as a precursor, which led to high and controllable nitrogen contents (4.0% to 12.0%) after pyrolysis [128]. NG thermally treated at 900 °C has a stable methanol crossover effect, high current density ($6.67 \text{ mA}/\text{cm}^2$) and high durability ($\sim 87\%$ after 10,000 cycles) when catalysing the ORR in alkaline solution. Furthermore, Fe NPs can be incorporated into NG with the aid of Fe(III) chloride in the synthetic process. This allows one to examine the effect of non-noble metals on the electrocatalytic performance. Remarkably, NG supported with 5 wt% Fe NPs has an excellent methanol crossover effect and high current density ($8.20 \text{ mA}/\text{cm}^2$) in an alkaline solution. Moreover, Fe-incorporated NG has an almost-four-electron transfer process and superior stability in both alkaline ($\sim 94\%$) and acidic ($\sim 85\%$) solutions, thus outperforming Pt- and NG-based catalysts.

Although electrocatalysts supported by graphene have been shown to work in fuel cells with reasonable performance, they unfortunately also have intrinsic drawbacks; e.g., carbon supports are not stable enough for these practical catalysts in a fuel cell, which hinders commercialization [68,129]. Carbon corrosion at high electrode potentials or high temperature in the presence of oxygen has been identified to be the major contributor to catalyst failure. In fact, as shown by Eq. (10), carbon corrosion is thermodynamically possible above 0.207 V versus the standard hydrogen electrode [130], which results in the separation of the metal-containing active site from the carbon support and consequent performance loss and thus the low durability of fuel cells. There is thus great interest in exploring stable alternatives as a replacement of carbon materials for the catalyst support.

Besides graphene, an increasing number of two-dimensional nanomaterials have attracted tremendous attention in recent years. Among these two-dimensional materials, transition-metal dichalcogenides (TMDs) with a layered

Fig. 8. Doping of a graphitic carbon structure with heteroatoms to develop different constructions.

Fig. 9. (a) Low-magnification TEM images of the $\text{Co}_3\text{O}_4/\text{N-rmGO}$ hybrid (reduced mildly oxidized graphene oxide (rmGO)); (b) Chronoamperometric responses (percentage of current retained versus operation time) of the $\text{Co}_3\text{O}_4/\text{N-rmGO}$ hybrid and Pt/C on carbon-fibre-paper electrodes kept at 0.70 V versus RHE in O_2 -saturated KOH electrolytes (1 mol/L); Rotating-disk voltammograms of the $\text{Co}_3\text{O}_4/\text{rmGO}$ hybrid (c) and $\text{Co}_3\text{O}_4/\text{N-rmGO}$ hybrid (d) in O_2 -saturated 0.1 mol/L KOH with a sweep rate of 5 mV/s at the different rotation rates indicated. Insets in (c) and (d) show corresponding K-L plots at different potentials. Reproduced with permission from Ref. [76], © 2011, Macmillan Publishers Limited.

structure similar to that of graphite are a focus of research [131]. Most layered TMDs have the composition MX_2 (M = transition metal; X = chalcogen, S, Se, Te). Because of the low electrical conductivity and low surface-to-volume ratio of the bulk form, extensive efforts have been made to enhance the ORR performance by surface modification, doping and forming highly dispersed NPs [86]. Additionally, recent interest has been directed towards two-dimensional MoS_2 in which highly defected sheets afford great catalytic activity owing to the larger number of exposed edges [132].

In 2016, Chua et al. [131] investigated the effect of doping with p-dopants Nb and Ta on bulk TMDs (MoS_2 and WS_2) and its effect on the ORR. All the materials were found to be more catalytic with a more positive onset potential in comparison with bare GC (glassy carbon). The WS_2 group of materials appears to underperform in comparison with the MoS_2 group of materials in terms of catalytic efficiencies for the ORR, with the undoped MoS_2 having the most positive onset potential for the ORR (0.78 V versus RHE). Unfortunately, doping with Ta or Nb does not obviously enhance the catalysis of the TMD for the ORR [131]. However, other works obtained positive results; a series of sandwich-like conjugated nanosheets was successfully developed using 4-iodophenyl-functionalized MoS_2 as a template [133]. Following direct pyrolysis, two-dimensional MoS_2 /nitrogen-doped porous carbon (M-CMP-T) hybrids were obtained with large specific surface areas and hierarchical po-

rous structures. In these hybrids, both sides of the single-layer MoS_2 nanosheets are uniformly decorated with nitrogen-doped porous carbon layers for good interfacial contact. M-CMP-T hybrids have been used for the electrochemical catalysed ORR with high activity and selectivity and for the construction of excellently performing supercapacitors. As shown in Fig. 10, the electron transfer number per oxygen molecule (n) for the ORR was calculated from the LSV curves at different rotation rates (400–1600 r/min) and potentials (−0.4 to −0.9 V) using the K-L equation. The K-L plots show a good linearity for all potentials. These results indicate a lower energy consumption and operation voltage for M-CMP-T hybrids in comparison with corresponding MoS_2 -free counterparts.

6. ORR electrocatalysts based on other porous carbon structures

Porous materials can provide large catalytic surface areas and facilitate electron transfer near the electrode surface. While two-dimensional electrocatalysts are a hot spot of research in the field of ORR electrocatalysis as mentioned in the last section, the two-dimensional materials tend to agglomeration on the electrode surface owing to strong π – π stacking and van der Waals interactions, thus reducing the surface area of the electrode, hindering electrolyte diffusion, slowing the electrochemical reaction rate and consequently limiting practical

Fig. 10. (a) ORR process taking place at the surface of the M-CMP-T hybrids under an alkaline condition; (b) Current-voltage curves for N_2 - and O_2 -saturated 0.1 mol/L KOH; (c) LSV curves at different rotation rates in O_2 -saturated 0.1 mol/L KOH at 5 mV/s (inset: K-L plots); (d) RRDE curve for a rotation speed of 1600 r/min (inset: calculated electron transfer number (n) against the potential); (e) LSV curves at 1600 r/min and a scan rate of 5 mV/s; (f) Galvanostatic charge/discharge curves at a current density of 0.2 A/g. Reprinted with permission from Ref. [133], © 2016, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

application in energy devices [134]. Porous materials have the potential to circumvent this limitation [135]. The three-dimensional porous morphology of carbon-based materials is promising in terms of raising the ORR performance via enhanced mass transfer and electron transfer reactions. Three-dimensional nanoarchitectures provide a high BET surface area and abundant active sites that are vital for good electrocatalytic performance, further accelerating ORR reaction kinetics [136].

Similar to the case of doping graphene, the combination of the three-dimensional porous carbon nanostructures with different active components provides opportunities to enhance ORR activity and durability. In 2014, Ye et al. [137] reported a novel vein-leaf-type three-dimensional structure CNF@NG composed of carbon nanofibers and NG linked by carbon-carbon bonds as shown in Fig. 11. CNF@NG has current density of 5.0 mA/cm² at 0.4 V vs. RHE, which is much higher than values for NG (2.5 mA/cm²), CNF + NG (1.4 mA/cm²) and

Fig. 11. (a) Polarization curves of various electrocatalysts on glassy carbon electrodes and the chronoamperometric response ($i-t$) at 0.4 V vs. RHE in different electrolytes corresponding to electrochemical activity and stability of the catalysts, respectively; (b) Compositional line profile across the CNF@NG; (c) Scheme of the CNF@NG vein-leaf complex structure for enhancing electron transfer; (d) EIS spectra of CNF@NG, NG and CNF in O_2 -saturated 0.1 mol/L KOH solution; (e) Scheme of the complex interpenetrated three-dimensional network structure of CNF@NG, which facilitates the mass transfer. Reproduced with permission from Ref. [137], © 2014, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

CNF (1.2 mA/cm^2). The onset potential on CNF@NG is 0.93 V vs. RHE, which is only ca. 0.1 V more negative than that on the commercial Pt/C catalyst, demonstrating the excellent electrocatalytic activity of CNF@NG. Moreover, CNF@NG has $E_{1/2}$ of 0.80 V vs. RHE, making it one of the most active metal-free ORR catalysts. The electron transfer numbers (n) are calculated based on Koutecky-Levich (K-L) plots as being between 3.6 and 4.0 over the potential range of 0.2 to 0.7 V vs RHE, indicating a more efficient $4e^-$ -dominated ORR process, with a performance approaching that of Pt/C catalysts. As shown in Fig. 11, such an interconnected three-dimensional network facilitates both the electron transfer and mass diffusion for electrochemical reactions.

Besides this, transition-metal (especially Fe or Co)-nitrogen-carbon containing materials have been recognized as another promising class of porous carbon-based electrocatalysts for the ORR because of their high ORR activity in both alkaline and acidic electrolytes. In 2015, Lin and coworkers [138] reported the design and synthesis of a new family of non-precious metal catalysts termed heterometalporphyrins. Two types of porphyrinic monomers are first made via porphyrin synthesis, which is followed by metallization with Fe or Co. Subsequent carbonization is performed to convert the porous and robust polymers into heterometalporphyrinic carbons. During cyclic voltammetry measurements in 0.1 mol/L KOH solution, the Co-incorporated and Fe-incorporated samples have highly positive ORR potentials of 0.83 and 0.86 V versus RHE, respectively.

Porous carbon-based materials can be derived from biomass that is readily available to provide inexpensive and renewable carbon precursors. Several successful demonstrations have shown how to synthesize unique porous carbon nanomaterials from natural biomass [110,127,139,140]. With high

specific surface area, large pore volume and good conductivity, these biomass-derived functional nanomaterials have great potential for electrochemical applications. In 2014, Chen et al. [141] reported novel nitrogen-doped nanoporous carbon nanosheets derived from a conveniently available plant, *Typha orientalis*. As shown in Fig. 12, the preparation of the sample involves a facile hydrothermal process at low temperature followed by annealing in a NH_3 atmosphere. Among all products, N-doped nanoporous carbon nanosheets NCS-850 has the highest surface area of $898 \text{ m}^2/\text{g}$ and the largest total pore volume of $0.52 \text{ cm}^3/\text{g}$ according to XPS characterization. The XRD patterns indicate the amorphous nature of carbon in the products. Rotating-disk-electrode and RRDE measurements were made to investigate the ORR activities. The NCS electrode reveals a four-electron pathway for the ORR with high current, with NCS-800 having the highest onset potential and reduction current. The durability of the catalysts was examined as shown Fig. 12 according to the current-time ($i-t$) chronoamperometric response of the NCS-800 and Pt/C electrodes at 0.10 V (vs. RHE) in O_2 -saturated 0.1 mol/L KOH at a rotation rate of 800 r/min . After $10,000 \text{ s}$, the commercial Pt/C suffered a 23.3% decrease in current density, while NCS-800 had a 16.0% loss in current density. In 2014, Pan et al. [142] demonstrated another successful example of metal-free nitrogen-doped porous carbon nanosheets derived from biomass. Dead ginkgo leaves were used as precursors and annealed in a tube furnace at 1100°C for 5 h under Ar flow to produce a carbonized sample with a high surface area of $1436.02 \text{ m}^2/\text{g}$. The net peak current density reached about 3.26 mA/cm^2 , which is higher than that without NH_3 post-treatment. Furthermore, the value of $E_{1/2}$ is close to that at the Pt/C electrode (-0.154 V vs. -0.135 V , $\Delta E_{1/2} = 19 \text{ mV}$).

Fig. 12. (a) Preparation of the nitrogen-doped nanoporous carbon nanosheet NCS-800 from the plant *Typha orientalis*; (b) SEM images of NCS-800; (c) rotating-disk-electrode voltammograms in O_2 -saturated 0.1 mol/L KOH solution at room temperature for NCS-800 and Pt/C. Reproduced with permission from Ref. [143], © 2014, The Royal Society of Chemistry.

7. Conclusions and future perspectives

This review recounted recent advances in the development of non-Pt electrocatalysts covering a broad spectrum of material selections ranging from molecular materials to metal oxides to metallic nanomaterials to novel two-dimensional materials. For molecular electrocatalysts, the M–N–C active centre plays a crucial role in governing the catalytic performances towards the ORR, which has been shown to be affected by the synthesis method and choices of metal precursors, ligand structure and carbon support. Studies also indicate that pyrolysis improves both the activity and stability of transition-metal macrocycle-based electrocatalysts. However, this technique is disruptive and has poor repeatability towards controlling active sites, while the underlying mechanisms are also poorly understood. Transition metal oxides, particularly group-IV and -V metal oxides, represent another class of promising alternative of Pt-based catalysts for the ORR. Their catalytic activity largely depends on the surface structure and the introduction of surface defects constitutes a dominant strategy for the enhanced ORR catalytic activities in both acidic and alkaline solutions. However, there are issues of low electrical conductivity and a lack of adsorption sites for oxygen species on the metal oxide surfaces, which results in extremely low ORR activity for the bulk form. Recent advances have demonstrated solutions involving surface modification, doping, alloying and forming highly dispersed NPs. Important advances in the wet-chemistry synthesis of metallic NPs allow for precise control over particle sizes and shapes and the crystalline facets exposed. This has led to better understanding of designer metallic nanocatalysts. Some optimized systems outperform commercial Pt/C catalysts albeit the long-term stability in a real-world environment has yet to be validated. It is noted that two-dimensional materials are emerging as novel electrocatalysts for the ORR. In particular, functionalized transition-metal dichalcogenides (e.g., MoS₂) have outstanding catalytic performances. Another aspect for a practical ORR catalyst is the supporting material, which affects the electrocatalysis performance. Until now, the most commonly used supporting substrates for the ORR have been carbon-based materials that suffer from corrosion.

Proton exchange membrane fuel cells (PEMFCs) are electrochemical devices that can efficiently convert chemical energy directly into electrical energy. In a typical practical PEMFC, the membrane electrode assembly contains the anode and cathode, both of which conduct electrons, and reactants; e.g., protons in acidic conditions and hydroxide ions in alkaline conditions. At the anode, the fuel (typically H₂) is oxidized to form protons and electrons. At the cathode, oxygen is reduced to form H₂O. Because the ORR is ~5 times slower than the hydrogen evolution reaction (HER), the ORR electrocatalysts inside the cathode catalyst layers are considered to be the most critical components for fuel cell performance [59]. Currently, the state-of-the-art and most practical electrocatalysts for PEMFCs are still carbon-supported Pt catalysts [27]. Although most examples reviewed here concern results obtained without realistic devices, several demonstrations in recent decades have shown volumetric activity and stability comparable to

that of the commercial Pt/C [76,81,118,121,143].

Although the novel catalysts discussed here have still not reached the commercialization stage, recent rapid progress suggests their potential use in the near future. In particular, improvement in the rational design and synthesis of various nanostructured ORR catalysts with controllable size, shape, composition, and surface morphology has provided important insights into the nature of the catalytic activity and stability. Scalable synthesis and real-world evaluation may be the focus in the next stage of development.

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Graphical Abstract

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Recent advances in the rational design of electrocatalysts towards the oxygen reduction reaction

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This review gives a comprehensive overview of recent progress in the search of non-Pt electrocatalysts towards the oxygen reduction reaction, including molecules, metal oxides, metal nanomaterials and two-dimensional materials.

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氧还原电化学催化剂研究的最新进展

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摘要: 燃料电池可以在接近室温条件下将氢或烃类中蕴含的巨大化学能通过电化学途径直接转化为清洁、稳定、可持续的电, 因而被视为极有前景的、能够满足日益增长的世界能源需求的终极解决方案之一。在一个典型的氢燃料电池中, 氢在正极氧化而氧在负极还原, 从动力学角度说, 氧还原反应(ORR)比氢氧化反应进行的慢得多。无论是在酸性还是碱性条件下, 氧的还原都可以一个四电子过程或是两个双电子过程进行, 当然在酸性和碱性环境中反应的机理不同。铂一直是最有效的ORR催化剂, 但受到价格昂贵、稳定性差和易中毒等因素的制约, 目前非铂催化剂成为越来越引人瞩目的发展方向。本综述试图从分子催化剂、金属纳米材料催化剂、金属氧化物催化剂和新兴的二维材料催化剂等方面, 选取近十年来最能代表ORR电化学催化剂方面成就的例子分析其优缺点, 并为今后该领域的研究提供一些有益的思路。

典型的分子催化剂是卟啉类化合物, 当这种四齿的N₄配体与过渡金属特别是铁、钴络合时, 往往显示出良好的ORR催化性能, 多数情况下其中的过渡金属中心、配体和碳支撑体系共同组成催化剂的活性中心。在另一些报道中, 邻菲罗啉或是连吡啶型N₂化合物也可以作为配体使用。第四和第五副族的很多金属形成的不同价态的氧化物都具有氧还原活性, 比如MnO_x, CoO_x, TiO_x, ZrO_x, IrO_x等。金属氧化物表现出易于修饰, 不容易团聚和抗腐蚀等诸多优点, 而其良好的ORR性能与

表面的缺陷密切相关, 因此钙钛矿型氧化物 ABO_x 也引起人们的广泛关注, 人们可以通过调节氧化物的晶型、尺寸和组成来获得更好的催化性能. 近年来随着液相合成技术的发展, 人们可以制备出理想形状和尺寸的单分散纳米粒子, 然后通过旋涂、自组装等手段将其修饰到合适的电极上以获得增强性能的ORR催化剂. 通过形状与尺寸调控, 或组合成其它复杂的纳米结构, 都有可能提高催化活性或是稳定性, 因此有关纳米催化剂的研究日趋增多. 在此基础上, 考虑到石墨烯的可修饰性和良好的电化学性能, 纳米材料复合石墨烯所形成的二维或三维结构也可提供很好的氧还原催化性能, 而 MoS_2 代替石墨烯作为支撑物所构成的二维催化剂也是值得注意的研究方向.

综上所述, 尽管现有的非铂催化剂仍难以完全满足商业化的要求, 设计理念和合成方法的快速发展有望在不远的将来解决这一难题. 而设计合成可控尺寸、形状、组成和表面形貌的纳米催化剂在很大程度上将加速这一进程.

关键词: 氧还原反应; 电催化剂; 纳米材料; 分子电催化剂; 二维材料

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