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## Review

# Progress in non-platinum catalysts with applications in low temperature fuel cells

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## ABSTRACT

Non-platinum catalysts have recently attracted significant attention with regard to their potential applications in low temperature fuel cells. This review summarizes the progresses in the development of these catalysts to date, including anode and cathode catalysts. Anode catalysts based on metal carbides, Pd alloys, and perovskite oxides are described, focusing on their catalytic activity. The non-platinum cathode catalysts include transition metal macrocyclic compounds, metal nitrides, and metal oxides. Particularly, various aspects are discussed in detail, including active sites, metal-support interactions, and the preparation parameters for transition metal macrocyclic compounds. All the compounds reviewed are considered promising candidates that may find commercial applications as non-platinum anode and cathode catalysts for fuel cells.

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## 1. Introduction

Low temperature fuel cells operating below 100 °C, such as hydrogen/oxygen fuel cells (also known as proton exchange membrane fuel cells, or PEMFCs) and direct methanol fuel cells (DMFCs), show potential as alternative power sources for vehicles. This is because of the advantages that they offer, including high energy conversion efficiency, high power density, low or zero pollution, quick start-up, no loss of electrolyte, and long lifetime [1]. DMFCs are considered especially promising alternative power supplies for mobile and other portable devices because the fuel is readily obtainable, they possess high specific energy densities and are capable of functioning at low temperatures [2,3]. Many research works have been carried out to improve catalyst activities, develop methanol-resistant membranes, synthesize methanol-tolerant cathode catalysts, and

optimize the electrode structures [4]. Pt and its alloys are catalysts for the most commonly used DMFCs because Pt exhibits remarkable activity for both oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR). Pt catalysts do, however, have the disadvantage of inactivation induced by intermediates formed during the MOR. In addition, the strong O=O bond (498 kJ/mol) slows the reaction rate at the cathode and necessitates the use of significant quantities of Pt. From the point of view of economics, therefore, there is a requirement to develop fuel cells that operate either with low Pt loadings or non-Pt electrocatalysts. This paper presents several different non-platinum anode and cathode catalysts with applications in low temperature fuel cells and discusses their prospects for future development.

## 2. Non-platinum anode catalysts

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This section reviews progress in non-platinum anode catalysts, including those with applications in hydrogen/oxygen fuel cells, direct ethanol fuel cells (DEFCs) and DMFCs. In a DMFC, the MOR mechanism involves a six electron process ( $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ ) that occurs spontaneously as long as the anodic potential is equal to or slightly greater than 0.046 V. Unfortunately, this process produces intermediates such as HCHO, CO-like compounds, which are adsorbed on the electrode surface and result in poisoning of Pt-based catalysts [5]. In addition to this drawback, fuel cells employing Pt-based catalysts will also be difficult to commercialize because of the high cost of the material. As a result of continued research into the commercialization of fuel cells, several candidates that may function as non-Pt catalysts have been identified, including metal carbides, Pd alloys, and perovskite oxides.

### 2.1. Metal carbides

Metal carbides, including tungsten carbide (WC) and molybdenum carbide ( $\text{Mo}_2\text{C}$ ), possess a similar electronic structure to that of Pt and thus exhibit Pt-like catalytic activity for a wide range of reactions. Since the use of these compounds was first proposed by Levy et al. [6] in the 1960s, their catalytic performances have been studied through a series of experiments [7]. Metal carbides have subsequently shown remarkable performance when employed as anode catalysts of fuel cells, although WC still exhibits unstable catalytic behavior. The stabilization of the metal carbides has been attempted through the synthesis of bimetallic or multiple W-containing metal carbides [8]. A tungsten-molybdenum carbide prepared via the introduction of molybdenum into WC exhibited enhanced catalytic activity and higher stability during methanol oxidization. This tungsten-molybdenum carbide demonstrated best performance with the ratio  $\text{Mo}/(\text{W}+\text{Mo})$  of 0.2. This improved activity results from the modified catalyst introducing a new reaction path that does not generate intermediates that may poison the catalyst.

Recently, WC films have shown potential for use as anode electrocatalysts in DMFCs owing to their stability at anode potentials below 0.6 V [9].  $\text{W}_2\text{C}$  films, however, do not exhibit a stable voltage region. They are, for example, easily and immediately oxidized to  $\text{W}_x\text{O}_y$  species during cyclic voltammetry (CV) in a  $\text{H}_2\text{SO}_4$  solution (0.5 mol/L) saturated by  $\text{N}_2$ . Methanol adsorption on a WC film results in cleavage of the O–H bond with the formation of an intermediate methoxy species ( $\text{CH}_3\text{O}$ ). Additional results based on testing of WC films have suggested a synergistic effect based on adding small amounts of Pt to the film, which may accelerate the subsequent dissociation of the methoxy intermediate.

The catalytic properties of nanocomposite metal carbides are dramatically influenced by both morphology and structure. Variations in the catalytic performances of these materials typically are caused by differences in their adsorption properties, which in turn are derived from their surface characteristics, such that exceptional catalytic activity is exhibited by nanostructured catalysts with unique surface crystal structures and large specific surface areas [10]. Several  $\text{Co}_6\text{Mo}_6\text{C}_2/\text{graph}$

ite carbon ( $\text{gC}$ ) nanocomposites, which may be prepared using much less energy than traditional high temperature synthetic processes, have been used to prepare  $\text{Pt-Co}_6\text{Mo}_6\text{C}_2/\text{gC}$  catalysts that require less Pt in comparison with commercial Pt/C catalysts [11]. These  $\text{Pt-Co}_6\text{Mo}_6\text{C}_2/\text{gC}$  catalysts have demonstrated superior activity and stability in acidic solution due to a synergistic effect between the  $\text{Co}_6\text{Mo}_6\text{C}_2$  support and the active Pt metal. A similar synergistic effect between WC and Pt has also been identified in previous work [12].  $\text{Pt-Co}_6\text{Mo}_6\text{C}_2/\text{gC}$  shows promise as a stable material because its half-wave potential decreases only 6 mV after 1000 cycles, compared with a decrease of 27 mV for Pt/C. In addition, the  $\text{Pt-Co}_6\text{Mo}_6\text{C}_2/\text{gC}$  catalyst shows no obvious loss of active surface area, whereas a loss of approximately 20% is observed for Pt/C. These results indicate that  $\text{Co}_6\text{Mo}_6\text{C}_2/\text{gC}$  is much more stable than carbon supported under the same testing conditions.

Modified WC is another potential anode material for DMFC applications, and Rh/WC, Ni/WC, and Au/WC were all prepared by Kelly et al. [13] using a physical vapor deposition method. These materials exhibited high catalytic activity for C–H bond scission and for the formation of CO and  $\text{H}_2$ . Temperature-programmed desorption tests showed that the overall catalytic activity of these materials during methanol decomposition was in the order  $\text{WC} > \text{Rh/WC} > \text{Ni/WC} > \text{Pt/WC} \gg \text{Au/WC}$ . These data suggest that Rh/WC and Ni/WC could potentially be used as alternatives to Pt/WC and Au/WC for the purpose of accelerating methanol decomposition.

As can be seen from the above discussion, metal carbides have been investigated not only as non-platinum catalysts but also as potential support on which to load Pt. Owing to their significant catalytic activity for methanol oxidation and high CO tolerance, these catalysts show promise but require further research so as to allow their eventual commercialization as high surface area/high dispersion catalysts. The following aspects would be beneficial: exploring new methods of preparing the catalysts with low cost, low energy consumption, and environment-friendly; applying novel preparation technologies to optimize the catalytic structure, increasing the specific surface area and active center amounts of metal carbides by means of nanotechnology, doping and surface modification; taking advantage of the synergistic effect between metal carbides and doping materials to develop methods of preparing metal carbides with dramatically improved catalytic activity; improving our understanding of the chemical state of the surface and interface of these materials, and employing structural modifications on the nanoscale to enhance their catalytic activity.

### 2.2. Pd alloys

Palladium and Pd-based catalysts have shown great potential as anode catalysts because Pd is similar to Pt in terms of catalytic properties and CO tolerance, but is lower cost and has higher raw material reserves [14–16]. The electrocatalytic activity of Pd-metal (Pd-M) during the MOR originates from bifunctional mechanisms and the ligand effect (electronic effect) [17]. The bifunctional mechanism in the MOR requires the presence of two types of active sites: one for methanol adsorp-

tion and dissociation, another for water adsorption and activation. The ligand effect on the metal alters the electronic properties of the Pd, lowering its CO adsorption energy, and facilitating the oxidation of adsorbed CO ( $\text{CO}_{\text{ads}}$ ) at low potentials.

In early work, binary and ternary Pd-based alloys were widely used as anode catalysts for low temperature fuel cells [18,19]. In these studies, the improved catalytic activity and durability of Pd alloys were achieved by the addition of non-platinum metals such as Fe, Mo, Co, or Ni [20]. CV measurements of PdMo alloy revealed that both the catalytic activity and the stability of the electrocatalyst are enhanced when PdMo/C nanoparticles was prepared via a simultaneous thermal decomposition method [21]. The catalytic activity of Pd<sub>90</sub>Mo<sub>10</sub> in a DMFC at 80 °C was close to that of as-synthesized Pt, and the former also exhibited a high tolerance for methanol poisoning. Research concerning the direct formic acid fuel cell (DFAFC) also showed that the modification of Pd with Sb, Sn, Pb, and other metals increased the rate of the oxidation reaction and eliminated CO poisoning, such that the rate of the oxidation reaction using a PdPb catalyst was 4 times that obtained when using a Pd catalyst after 3 h [22–25]. Furthermore, the rate of the oxidation reaction was increased by approximately 2.5 and 1.25 times when using PdSb and PdSn, respectively. Unfortunately, the problem of CO poisoning of the catalyst during formic acid oxidation has not yet been completely solved and thus it remains necessary to improve the stability and CO tolerance of catalysts to prevent significant performance loss.

Different catalyst morphologies can result in changes in catalytic activity by modification of Pd content. As an example, PdNi films with different Pd contents showed different MOR activities in CH<sub>3</sub>OH (1 mol/L) with H<sub>2</sub>SO<sub>4</sub> (0.5 mol/L) [26]. Polarization curves revealed that the Pd-Ni alloy with the highest Pd concentration possessed the highest activity, which can be explained by the decreasing crystallites sizes with increasing Pd loads. The application of Pd-based electrocatalysts to the hydrogen oxidation reaction (HOR) in H<sub>2</sub>/O<sub>2</sub> PEMFCs has also been studied. Pd-Ni alloys supported on tungsten carbide (referred to as PdNi/WC) were used as anode catalysts and exhibited power density of 230 mW/cm<sup>2</sup> owing to the strong interaction between the alloys and the WC [27]. The long-term stability of these materials, demonstrated by the lack of any obvious performance degradation after 100 h of continuous operation, means that they are attractive as anode catalysts.

The type of electrolyte medium (acidic or alkaline) has been found to have a significant impact on the performance of the catalyst. A series of Pd-Sn binary alloys were synthesized as anode electrocatalysts with different Pd/Sn ratios using SnCl<sub>2</sub> and K<sub>2</sub>PdCl<sub>4</sub> as precursors, for use in DMFCs [28]. The order of peak current density during the EOR in a mixture of 0.5 mol/L KOH and 0.5 mol/L ethanol was Pd<sub>86</sub>Sn<sub>14</sub> > Pd<sub>75</sub>Sn<sub>25</sub> > Pd<sub>47</sub>Sn<sub>53</sub> > Pd (JM), and so the Pd<sub>86</sub>Sn<sub>14</sub>/C catalysts showed the best catalytic activity. Although Pd<sub>47</sub>Sn<sub>53</sub>/C had the lowest current density among the Pd-Sn/C catalysts, it exhibited a peak potential approximately 60 mV more negative than that of Pd/C (JM), attributed to the high degree of alloying in Pd-Sn, which results in the observed increase in catalytic activity based on variation

in the electronic structure of Pd. A prior study has proposed that the optimum Sn content for the EOR in an acidic medium is in the range of 25% to 38% [29], while the optimum Sn content in Pd-Sn catalysts in alkaline media has been shown to be 14%. This difference can be explained by the fact that Pd interacts with adsorbed OH more readily in alkaline media than in acidic solutions.

Future work regarding these new catalytic systems will be required to increase the Pd current density and improve electrochemical stability, owing to the requirement for reactions in direct alcohol fuel cells (DAFCs) to break strong C–C bonds in highly alkaline medium. However, Pd nanoparticles supported on non-noble metal oxides or tungsten carbides represent promising catalysts that have the advantages of low metal content and improved activity and stability. Another desirable future improvement would be the development of easier synthetic means of reducing the particle size of the Pd-M alloy.

### 2.3. Perovskite oxides

Perovskite oxides are widely used as catalysts and electrode materials because of their unique structural characteristics and excellent conductivity. These materials are divided into two types, ABO<sub>3</sub> and A<sub>2</sub>BO<sub>4</sub>, where A is a rare earth metal (such as Sr, Ba, La, or Ce) or alkaline earth metal ion, and B is a transition-metal ion (such as Co, Fe, Ni, Cu, or Ru) [30]. The performance of A<sub>2</sub>BO<sub>4</sub> materials as catalysts can be altered significantly by replacing either A or B with other metals either partially or completely. For example, the MOR activity of La<sub>2-x</sub>Sr<sub>x</sub>NiO<sub>4</sub> (0 < x < 1) is enhanced by increasing the value of x, and LaSrNiO<sub>4</sub> (in which x = 1) exhibits a maximum oxidation current density 50.9 mA/cm<sup>2</sup> without CO poisoning [31].

Partial or complete replacement of A and B induces various valence electron transfers in the perovskite crystal and leads to increased conductivity and improved performance, thus making these compounds potential candidates for anode materials. In particular, perovskite oxides have extensive applications in alkaline solution for the MOR because of their superior corrosion resistance compared with precious metals in acidic media. The alkaline surface of perovskite oxides also contributes to the adsorption of methanol and desorption of H<sup>+</sup>. Recent research on the MOR in alkaline solution revealed that perovskite oxides with high conductivity and which allow the effective diffusion of oxygen ions exhibit significant catalytic activity at a high polarization potential at room temperature [32]. During the MOR, methanol is adsorbed on transition metal ions, followed by O–H and C–H bond scission, which generates electrons and H<sup>+</sup> required for the complete oxidation of methanol assisted by OH<sup>-</sup>. Because of the high oxygen content of perovskite oxides, active oxygen species readily react with C to form CO<sub>2</sub>, thus avoiding the CO poisoning, which occurs with Pt/C.

In order to realize future commercialization of perovskite oxides in fuel cells, various combinations of perovskites loaded with different amounts of Pt have been investigated and have demonstrated excellent efficiency, improved catalytic activity and stability. A variety of ABO<sub>3</sub>/Pt materials (La and Sr at the A site, and Ru at the B site), offering decreased cost as a result of

lower Pt loadings (1%, 5%, 10%, and 15% Pt), exhibited electrocatalytic activity comparable to that of Pt-Ru alloy for methanol and ethanol oxidation [33]. The polarization curves for methanol electrooxidation by various catalysts showed that the onset potential for ARuO<sub>3</sub>/Pt was very close to that of the Pt-Ru alloys (~0.25 V), especially in the case of LaRuO<sub>3</sub> with 15 wt% Pt, which offers several advantages owing to its onset potential negative shift compared with SrRuO<sub>3</sub> with 15 wt% Pt. Similar behaviour of these catalysts was also observed during ethanol oxidation. It was additionally found that ABO<sub>3</sub>/Pt catalysts with 3 to 5 times lower Pt loadings produced current densities comparable to those of standard Pt-based catalysts in methanol and ethanol. The results may be explained by the formation of hydroxide on the catalyst surface, which in turn promotes the oxidation process [34].

Based on our knowledge of the effects of the specific surface area of catalysts, it would be beneficial to develop methods for the preparation of nanoscale perovskite oxides to further improve their catalytic activity and thus obtain enhanced electrochemical oxidation rates.

### 3. Non-platinum cathode catalysts

The development of non-platinum cathode catalysts is required to address the issue of cost associated with Pt catalysts. Debe [35], with the 3M Fuel Cell Components Program, has expounded the goals of the U.S. Department of Energy (DOE) with regard to automotive fuel cells. Currently, the automobile industry employs cathodes containing 0.4 mg Pt/cm<sup>2</sup> or more, and future work is focused on reducing cathode loadings without performance loss or durability degradation. Several different materials have been studied as non-platinum cathode catalysts, including transition metal macrocyclic compounds, metal nitrides, and metal oxides. In order to prepare active non-Pt catalysts, many synthetic methods have also been developed, such as heat treating carbon-supported organometallic complexes [36,37], pyrolyzing metal and carbon precursors in an ammonia or acetonitrile atmosphere [38–40], heat treating carbon and transition metal salts in a nitrogen environment [41] and mixing N-containing ligands with a cobalt oxide sol, followed by entrapment in a carbon-supported polypyrrole matrix [42]. One goal is to achieve a current density in the ORR of 300 A/cm<sup>2</sup> using non-noble metal catalyst by 2015, but many difficulties remain in reaching this target, owing to the complexity of the ORR process, which involves both adsorption and charge transfer. During the design and preparation of these catalysts, the processes by which O<sub>2</sub> is adsorbed on the catalyst surface should be taken into account so as to allow oxygen molecules to efficiently adsorb during the four-electron process [43]. The following is a summary concentrating on progress in the field of non-platinum cathode catalysts in recent years, along with a discussion of potential future work.

#### 3.1. Transition metal macrocyclic compounds

Transition metal macrocyclic compounds contain phthalocyanine (Pc), triallylamine (TAA), tetramethoxyphenylporphy-

rin (TMPP), tetraphenylporphyrin (TPP) or other macrocyclic structures with multidentate ligands that are chelated with a transition metal ion M (such as Fe, Co, Mn, or Ni). They can be widely used as cathode catalysts for the ORR in neutral, acidic or alkaline media. Significant efforts have been made to explore transition metal macrocyclic compounds because it has been demonstrated that CoPc shows catalytic activity for the ORR, although its poor stability makes it difficult to employ in low temperature fuel cells because of the decomposition of macrocyclic compounds in acidic environments [44]. Subsequently, researchers have found that transition metal macrocyclic compounds such as Co-porphyrin and CoTAA also have catalytic activity for the ORR, and that their catalytic activity and chemical stability can be enhanced by heat treating transition-metal N<sub>4</sub>-macrocycles at 600 to 1000 °C under an inert gas [45,46]. Some aspects of transition metal macrocyclic compounds have dramatic impacts on their performance during the ORR. These factors include active sites, metal-support interactions and treatment conditions and are discussed in detail in the following sections.

##### 3.1.1. Active sites

In 1989, Wiesener et al. [47] reported a series of metal phthalocyanine macrocycles that showed decreasing catalytic activities towards the ORR in the order Fe > Co > Ni > Cu ≈ Mn. Further research work subsequently proved that metal macrocyclic compounds using Fe or Co as the center atom showed the highest catalytic activity for the ORR compared to other non-precious metals. Their catalytic activity mainly depends on the interaction between metal and ligands, especially with regard to variations in electron density caused by the electronic effect resulting from macrocyclic ligands [48]. Transition metal (M)-N macrocyclic structures such as MN<sub>4</sub> and MN<sub>2</sub> are presently considered to be the active sites in these materials, but there is still intense debate concerning the nature of the active sites in non-platinum cathode catalysts.

Some researchers believe that metal center ions promote the formation of catalytic active sites although it is unclear whether the metal itself acts as the active site. The link between metal ions and catalysis is explained by the linear relationship between catalytic activity and redox properties noted by Randin [49] and developed based on investigations of FePc and CoTAA by Beck [50]. The metal center is oxidized when O<sub>2</sub> adsorbs on the metal ion in the phthalocyanine, following which O<sub>2</sub> is partially reduced to the superoxide. The metal redox potential is also an important parameter in the ORR, and more highly positive M<sup>III</sup>/M<sup>II</sup> potentials are associated with higher metallophthalocyanine activity. Based on the above theory, research concerning active compounds containing metals and different ligands can be used to explore the catalytic mechanism. FeTMPP supported on carbon black contains two types of active sites [51]: the FeTMPP molecules adsorbed on O-containing functional groups of the carbon support and the “free” FeTMPP molecules. The former accelerates the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>, while the latter promotes the subsequent four-electron reduction of O<sub>2</sub> to H<sub>2</sub>O with the formation of H<sub>2</sub>O<sub>2</sub> following the redox conversion of the central Fe<sup>III</sup> to Fe<sup>II</sup>.

The quantity of transition metal atoms also has an effect on the active sites. A series of Co-ED/PPy-CNF catalysts were synthesized in order to explore their ORR activity [52]. The results showed that catalytic activity could be improved by increasing the amount of Co in the catalyst. In H<sub>2</sub>SO<sub>4</sub> solution (0.5 mol/L), at a scan rate of 5 mV/s, the ORR current measured with Co-ED/PPy-CNF-0 (without Co) was 0.004 mA (0.6 V vs NHE) but increased significantly to a value of 0.43 mA when the Co-ED/PPy-CNF-10 (10% Co) catalyst was tested under the same conditions. A Fe-ED/PPy-CNF catalyst displayed the same trend as Co-ED/PPy-CNF, but its catalytic activity was slightly lower than that of the Co catalysts. In a H<sub>2</sub>/O<sub>2</sub> fuel cell, the current density using Co-ED/PPy-CNF-10 was as much as 0.7 A/cm<sup>2</sup> at 0.4 V, compared with only 0.53 A/cm<sup>2</sup> for the Fe-ED/PPy-CNF-10 at the same potential. This obvious contrast can be ascribed to the difference in the active nitrogen content resulting from the different transition metals.

Both N content and the type of N-containing active functional groups (such as pyridine-N or graphite-N) have an effect on the formation of ORR active sites. The amount of N in the Fe-pyridinic catalyst synthesized by Kothandaraman et al. [53] varied from 0.12% to 0.24% and was correlated to catalytic activity (current density), which varied from 0.07 to 1.9 mA/cm<sup>2</sup> at a catalyst loading of 0.5 mg/cm<sup>2</sup>. These results show that iron associated with pyridinic N forms an active site that exhibits catalytic activity in the ORR. Similarly, Wei et al. [54] reported a significant increase in catalytic activity of Co-N/C with increasing surface N content. Lefevre et al. [55,56] considered FeN<sub>4</sub>/C or CoN<sub>4</sub>/C as the catalytic active sites, at which pyridinic N was associated with a metal center, while Ruggeri et al. [57] proposed that surface pyridinic N connected with iron to form the catalytically active site. Recently, Wood et al. [58] prepared highly active catalysts that showed a current density of 19 A/cm<sup>2</sup>. This work was performed using a metal-doped nitrogen source with an Fe content of 6 μg/cm<sup>2</sup> (the same amount of iron as was used in Ruggeri's work), although the surface nitrogen concentration was twice that of the catalyst used by the Ruggeri group.

The combination of metal and macrocycles has been shown to induce increased activity at the active sites. Cobalt-polypyrrole-carbon (Co-PPy-C) synthesized by the Los Alamos National Laboratory (LANL) [59] showed remarkable stability (no obvious degradation after 100 h continuous operation) in both H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air FCs. Cobalt was entrapped in the polypyrrole matrix, generating a cobalt porphyrin configuration in which Co atoms are linked to the pyrrole unit with the formation of Co-N sites without destruction of the polymeric structure. In the potential range between 0.50 and 0.20 V, the current density generated by the Co-PPy-C cell was more than one order of magnitude greater than that delivered by Co/C, while the maximum power density was 16 times higher. This increased activity can be explained by charge transfer processes and the formation of macrocycle-metal bonding between Co and polypyrrole.

### 3.1.2. Metal-support interactions

Supports play an important role in catalytic activity, stabil-

ity, and utilization. The applications of new carbon supports in DAFs have been investigated to enhance the performance of the active components, focusing on accelerating the removal of water produced by the ORR from the active sites and generating vacancies to allow reaction with O<sub>2</sub> [60]. Extensive research has shown that modifying the electron transfer between the support and the active metal component can change the reaction rate and activation energy. Two effects have been proposed [61,62]: structural promotion, which stabilizes the active metal component via the support material, and synergetic promotion, which generates a new catalytic entity based on the energetic interaction between support and active metal.

Carbon materials exert an influence on catalytic activity and stability, which will vary with the type of carbon and its surface properties. CNTs (carbon nanotubes) modified with phthalocyanines (Pc) were reported to improve the electrocatalytic properties of transition metal macrocyclic compounds owing to the adsorption of Pc on the CNTs and the subsequent formation of "molecular phthalocyanine electrodes" [63]. It also has been reported that FePc and CoPc have the ability to promote the four-electron oxygen reduction to H<sub>2</sub>O without the formation of H<sub>2</sub>O<sub>2</sub> [64,65]. With the addition of MWNT, the performance of CoPc/MWCNT at 45 °C exhibited a maximum power density of 100 mW/cm<sup>2</sup>, which is close to the 120 mW/cm<sup>2</sup> delivered by a commercial Pt/C catalyst (Tanaka Co.), although FePc/MWCNT exhibited only 60 mW/cm<sup>2</sup> under the same condition [66].

Owing to its unique properties, carbon can be used not only as a modified support but also to increase the quantity of active sites. A non-platinum N-doped carbon catalyst, prepared by pyrolyzing a mixture of phenolic resin, a Ketjen black carbon support (KB), and a cobalt phenanthroline complex, showed varying catalytic activity for the ORR when prepared with different KB contents [67]. When the ratio of KB:phenol resin = 1.0:1.0 (noted as KB1.0), the ORR current density at 0.7 V was increased 30-fold compared with the current density seen with catalysts without KB and was 2.5 times greater than the density resulting from catalysts noted as NC (N-doped carbon catalyst) + KB0.2. A cell containing a NC + KB1.0 showed a voltage of 0.41 V, which was approximately twice that of a cell incorporating NC + KB0.4. These results imply that carbon materials are effective at increasing the catalytic activity. Based on similar conclusions reached by Ikeda et al. [68], jagged carbon edges at which carbon atoms bond to graphite-like nitrogen are considered to act as active sites, producing higher ORR activity than carbon bonded to pyridine-like nitrogen. The improved catalytic activity also depends on the quantity of surface carbon atoms, especially the number of active catalytic sites exposed at the surface.

The introduction of other materials to supports has been researched as a means of further improving performance. Carbon-supported TiO<sub>2</sub>-transition metal macrocycle catalysts, which exhibit the high ORR activity of transition metal macrocyclic compounds as well as their semiconductor properties and which promote the decomposition of H<sub>2</sub>O<sub>2</sub> resulting from TiO<sub>2</sub>, showed improved stability and methanol tolerance compared with the corresponding metal macrocycles [69].

### 3.1.3. Treatment conditions

The treatments applied to catalysts can be divided into thermal and chemical methods. It has been demonstrated that both catalytic activity and stability can be improved via heat treatment and that differences of heat treatment temperatures lead to the formation of a variety of active sites. The main species generated at the surface of CoPcTc on carbon black followed by treatment at 600–700 °C included Co-N and Co-C, accompanied by the formation of a CoN<sub>4</sub>/C structure. These modifications improved the catalysis of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> because of the CoN<sub>4</sub> incorporated into the carbon [70]. Similarly, the MN<sub>2</sub>/C structure generated on heat treatment temperatures above 700 °C showed high catalytic activity and selectivity during the direct reduction of O<sub>2</sub> to H<sub>2</sub>O. Heat treatment is often employed in the case of Fe- and Co-based macrocycles, and PANI-C, PANI-Co-C, PANI-FeCo-C, and PANI-Fe-C were synthesized as cathode catalysts for H<sub>2</sub>-O<sub>2</sub> fuel cells at elevated temperatures in the range of 400 to 1000 °C in a N<sub>2</sub> atmosphere (Pt/C was used as the anode catalyst) [71]. Single cell tests showed that PANI-Fe-C exhibited higher activity for oxygen reduction compared with that of PANI-Co-C, although PANI-FeCo-C showed the most promising ORR activity, stability, and durability (remaining stable after 700 h discharging at a constant potential of 0.4 V) among the catalysts. Its declination in average current density was 18 mA/h for PANI-FeCo-C after the second 24 h test, while the losses of PANI-Fe-C and PANI-Co-C were as high as 90 and 130 mA/h, respectively.

Efforts have also been made to explore the selectivity of catalysts through chemical treatment. In an investigation of Co-based macrocyclic compounds, CoTMPP exhibited different selectivity for methanol and formic acid following by different chemical treatments [72]. The rotating disk electrode (RDE) results obtained in that study are provided in Table 1 based on quantitative analysis of the catalytic selectivity for oxygen reduction in oxygen-saturated electrolytes. The values of  $\Delta E_{\text{methanol}}$  in this table represent the difference of  $E_{1/2}$  and  $E_{1/2\text{methanol}}$ , and it was found that those materials with small value of  $\Delta E_{\text{methanol}}$  were more selective for the ORR in the presence of methanol. The results indicated that a CoTMPP electrode pretreated with KOH can act as an alternative catalyst material in a direct formic methanol fuel cell.

In addition to the common pretreatments for catalysts, the ORR activity of metal macrocyclic compounds is also greatly improved by chemical pretreatment on supports. With the development of surface analysis techniques, the mechanism by which catalytic activity is improved by interactions between support and metal should be elucidated and further improved.

**Table 1**

Electrochemical performance of a non-Pt catalyst prepared using various chemical treatments [72].

Catalyst	$E_{1/2}$	$E_{1/2\text{methanol}}$	$\Delta E_{\text{methanol}}$	$E_{1/2\text{formic}}$	$\Delta E_{\text{formic}}$
CoTMPP (none)	0.44	0.36	0.08	0.26	0.18
CoTMPP (KOH)	0.42	0.39	0.03	0.34	0.08
CoTMPP (HCl)	0.41	0.36	0.05	0.39	0.02
CoTMPP (H <sub>2</sub> SO <sub>4</sub> )	0.42	0.34	0.08	0.39	0.03
CoH <sub>2</sub> TMP (none)	0.45	0.41	0.04	0.40	0.05

It is known that surface oxygen-containing functional groups are increased by chemical pretreatment of supports, which in turn ensures strong bonding of the support to the metal macrocyclic compounds. In addition, the N and C contents of the active surface also increase significantly during chemical pretreatment, accompanying by the formation of M-N<sub>4</sub>-C catalytic active sites.

In general, transition metal macrocyclic compounds exhibit promising ORR activity, but their use is still restricted owing to the cost of macrocyclic materials and the requirements of complicated preparation processes, such as high temperature thermotreatment. It will therefore be especially important to develop desirable synthetic methods in order to reduce the cost and facilitate the preparation processes of these catalysts. For example, a series of Co-porphyrin ORR catalysts [73] synthesized via microwave radiation heating technology, has demonstrated better catalytic performances than materials made using traditional reflux heating. Based on our present knowledge of these catalysts, the following are some desirable future goals: (1) exploring new synthetic methods (such as microwave, ultrasonic, plasma or infrared radiation) in order to achieve nanocatalysts with high specific electrochemical surface areas and high dispersions; (2) modifying the surface properties of catalysts (for example, increasing the quantity of surface active sites by sulfidizing), and (3) selecting new reaction media, such as ionic fluids, which allow preparation of these compounds under mild conditions.

### 3.2. Metal nitrides

Transition metal nitrides, which exhibit hydrogen and oxygen chemisorption similar to that of Pt, can be described as a kind of metal compounds with the incorporated nitrogen atoms. The incorporation of either graphite N or pyridine N plays an important role in the improvement of the ORR activity of these compounds, owing to coordination between the nitrogen and carbon atoms and the encapsulated metal ions in the carbon matrix [74–78]. Two kinds of active centers have been proposed by Koslowski et al. [79]: a CFeN<sub>2</sub> center and a Fe<sub>3</sub>C (Fe<sup>0</sup>) center. The formation of the FeN<sub>4</sub> macrocyclic structure was found to be accelerated by heat treatment at 900 °C in a nitrogen source in combination with a Fe loading as high as 0.1%, which is beneficial to the four-electron reaction pathways in the ORR. The Co-N- and Fe-N-based precursors are thought to be superior to the separated N-containing precursors and metal salts [80]. CoFeN/C treated by a series of pyrolysis, leaching, and re-pyrolysis exhibited very similar activity to that of Pt/C because of the efficiently catalytic active sites induced by the heat treatment. Unit cell tests demonstrated a maximum power density of 177 mW/cm<sup>2</sup> and an open circuit potential (OCP) of 0.97 V for CoFeN/C, whereas the maximum power density and OCP obtained using the Pt/C catalyst were 196 mW/cm<sup>2</sup> and 1.04 V, respectively.

Modification of catalysts on carbon materials has also been applied to enhance the stability of the catalyst, with the exception of doping N. In Bryon's work [81], the stability of Fe-N-C was improved by increasing the degree of graphitization, re-

sulting in increases in the specific surface area and quantity of functional groups. A mixture of g-C<sub>3</sub>N<sub>4</sub> (based on a precursor thermally polymerized from dicyandiamide and employed as the N source), FeCl<sub>3</sub>, and graphite oxide (GO) was heated in an NH<sub>3</sub>/N<sub>2</sub>H<sub>4</sub> atmosphere at 80–100 °C, producing a powdery mixture of FeCl<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>/rGO, then carbonized, acid-treated, and pyrolyzed to give a material referred to as Fe-N-rGO. The ORR activity of Fe-N-rGO was substantially lower than that of Fe-N-C<sub>60</sub>, but it exhibited greatly more improved stability during H<sub>2</sub>/O<sub>2</sub> cell tests.

In other work, graphene has been combined with transition metal nitrides because of its high specific surface area and high conductivity. Fe-N-G employed as a cathode catalyst for a microbial fuel cell (MFC) was produced by heat treatment of a mixture of Fe salt, g-C<sub>3</sub>N<sub>4</sub>, and chemically reduced graphene [82]. Linear sweep voltammetry (LSV) tests showed that the Fe-N-G catalyst had a more positive onset potential and increased reduction current densities as compared to the pristine graphene (P-G) catalyst. The Fe-N-G-MFC achieved a maximum power density of 1149.8 mW/m<sup>2</sup>, which is 2.1 times the power density obtained using a Pt/C-MFC cell (561.1 mW/m<sup>2</sup>) and much higher than that of the P-G-MFC (109 mW/m<sup>2</sup>). These results demonstrated that the Fe-N-G materials can be an excellent alternative to expensive Pt catalysts in MFC applications.

Although the stability of catalysts is improved by transition metal nitrides, the resulting catalytic activity is still far lower than that of Pt. It is expected that the catalytic activity of these compounds may be greatly improved by better understanding their surface structures and states and by optimizing their compositions (for example, incorporating new carbon materials such as graphene) and structure (for example, increasing the number of active functional groups via N-doping).

### 3.3. Metal oxides

Metal oxides are typically used in alkaline electrolytes for the ORR because they tend to be unstable and decompose in acidic media. The catalysts that exhibit excellent ORR catalytic activity include ZrO<sub>2</sub>, TiO<sub>2</sub>, SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Co<sub>3</sub>O<sub>4</sub>, and other transition metal oxides prepared via a sputtering method. These materials have been found to be stable in the potential range associated with the ORR and exhibit no activity for methanol oxidation [83,84]. Their catalytic activity decreases in the order of ZrO<sub>2-x</sub> > Co<sub>3</sub>O<sub>4-x</sub> > TiO<sub>2-x</sub> > SnO<sub>2-x</sub> > Nb<sub>2</sub>O<sub>5-x</sub>. ZrO<sub>2-x</sub> exhibits the most promising catalytic activity due to the ORR selectivity of zirconium oxides.

Perovskite oxides such as ABO<sub>3</sub>, where A is a rare earth metal and B is a transition metal, are widely used as cathode catalysts in fuel cell mainly because of their electronic and ionic conductivity as well as the oxygen-vacancy that they contain and which allows lattice ion transfer. The ORR activity of perovskite oxides is associated with the e<sub>g</sub> (δ\*-orbital occupation) and the B-site in the A-B-O structure. For LaCu<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>, the onset potential for the ORR is 0.8 V (vs NHE) in KOH electrolyte (0.1 mol/L) saturated with O<sub>2</sub>, which indicates a four-electron reduction of O<sub>2</sub> to H<sub>2</sub>O [85]. For LaCu<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>, LaMnO<sub>3</sub>, La-

CoO<sub>3</sub>, and LaNiO<sub>3</sub>, the specific activity current can be reached at potentials of 781(±5), 834(±24), 847(±3), and 908(±8) mV (vs RHE), respectively. The perovskite oxides above have exhibited promising potential and enhanced electrocatalytic activity, especially LaMnO<sub>3</sub> and LaNiO<sub>3</sub>, which have shown intrinsic ORR activity comparable to that of Pt/C in alkaline media.

Metal oxides exhibit high catalytic activity for oxygen reduction in alkaline environments, but their stability in acidic media is low. Although these compounds have the advantages of low cost and high methanol tolerance, the application of metal oxides has not been widely realized yet because of low conductivity and poor stability in electrolytes.

## 4. Conclusions and outlook

Over the past decade, great progress has been made in the field of non-Pt catalysts; however, compared with traditional Pt-based catalysts, these materials still require complicated preparation processes and exhibit relatively low catalytic activity and stability. In order to enhance the catalytic activity of these compounds, it will be necessary to develop novel methods and associated technologies to improve the process by which they are prepared as well as the dispersion of active components. In summary, we propose the following future research goals concerning non-Pt catalysts for low temperature fuel cell applications.

(1) Achieving nanometer scale distribution and nanostructured catalytic materials using advanced technologies and methods that are low in cost and energy consumption. These advances will be associated with rapid future developments in materials science, which will allow a better understanding of the catalytic mechanism based on novel preparation techniques and characterization methods, and will allow the synthesis of new non-platinum catalysts offering high activity, excellent chemical and electrochemical stability and long lifetimes.

(2) Designing non-Pt catalysts supported by new carbon materials that make use of the unique properties of these materials to induce dramatic changes in particle shape, size and spatial distribution as well as charge transfer between the support and the metal. As an example, multi-dimensional carbon nanomaterials should be developed as support in mixed catalysts, so as to create channels for mass transportation and electron and proton transfer that enhance the utilization of catalytic particles. The decreasing active areas and increasing resistance of catalyst layers can be reduced by generating unique three dimensional catalyst structures that allow efficient access of reactants to the catalyst.

(3) Optimizing synthetic conditions. The properties of catalytic materials typically depend on particle size, dispersion, morphology and surface characteristics, all of which are influenced by synthetic parameters such as reagents, temperature and pretreatment, et al. Future intensive study of nanotechnology should allow low temperature, adjustable synthetic procedures, thus providing a basis for preparing catalysts with small particle sizes, high dispersion, and large quantities of active sites.

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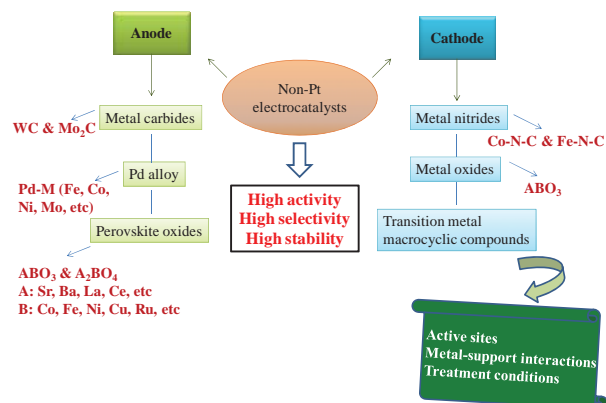
## Graphical Abstract

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## Progress in non-platinum catalysts with applications in low temperature fuel cells

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This review presents a summary of research to date concerning non-platinum anode and cathode catalysts. The review of anode catalysts focuses primarily on metal carbides, Pd alloys, and perovskite oxides, while transition metal macrocyclic compounds, metal nitrides, and metal oxides are considered cathode catalysts.



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## 低温燃料电池非铂催化剂研究进展

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**摘要:** 简要综述了近年来低温燃料电池阳极和阴极催化剂的研究进展. 阳极催化剂主要介绍了金属碳化物、Pd合金以及钙钛矿型氧化物三种, 讨论了阳极催化剂对燃料氧化过程的催化活性和抗CO中毒能力; 阴极催化剂则重点介绍了过渡金属大环化合物、氮化物以及氧化物, 并较详细地阐述了过渡金属大环化合物的反应活性中心、金属-载体相互作用以及化合物制备条件. 由于阴极非铂催化剂存在制备过程较复杂、中间产物过氧化物易破坏催化剂结构等问题, 仍需探索新型的非铂催化剂.

**关键词:** 燃料电池; 非铂催化剂; 甲醇氧化; 氧还原反应

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## 1. 前言

低温燃料电池工作温度一般低于100 °C, 包括氢氧燃料电池(也被称作质子交换膜燃料电池或PEMFC)和

直接甲醇燃料电池(DMFC). PEMFC具有能量转换效率高、零污染、可在室温快速启动、无电解液流失、寿命长、比功率与比能量高等优点, 主要用作汽车动力电源, 是城市清洁能源的不二选择<sup>[1]</sup>. 而DMFC具有燃料来源

丰富、结构简单、能量密度高、储存携带方便、工作温度低、安全性高及绿色环保等特点,因而更加适用于便携式移动装置和电动车等的新型电源<sup>[2,3]</sup>,成为低温燃料电池的主要研究方向.目前DMFC的研发工作大都集中在寻找新型的质子交换膜、合成高活性和高选择性的电催化剂以及电极结构的优化等方面<sup>[4]</sup>.DMFC的催化剂主要包括Pt及Pt合金,分别对氧还原反应(ORR)和甲醇氧化反应(MOR)具有活性,但是甲醇在阳极氧化产生的中间产物CO能使Pt催化剂中毒,使其活性降低.此外,阴极反应中O=O键能(498 kJ/mol)较高,阴极反应速率较低,需较大的Pt用量.同时Pt基催化剂价格昂贵使电池成本居高不下,亟需研发高性能、低成本的低铂或非铂催化剂.

本文较系统地介绍了多种低温燃料电池阳极和阴极非铂催化剂的国内外研究现状,并探讨了非铂催化剂的发展趋势.

## 2. 阳极非铂催化剂

阳极非铂催化剂在氢氧燃料电池、直接乙醇燃料电池(DEFc)以及DMFC的应用已取得一定进展.直接甲醇燃料电池中甲醇氧化反应是一个6电子过程( $\text{CH}_3\text{OH} + \text{H}_2\text{O} = \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ ),理论上阳极电位只要等于或稍大于0.046 V,该反应就能自发进行;但实际上甲醇氧化过程中通常伴随有中间产物,如HCHO及类CO化合物的生成,这些物质吸附在电极表面导致催化剂中毒<sup>[5]</sup>,同时Pt基催化剂的成本居高不下阻碍了燃料电池催化剂商品化进程.为解决这些问题,研究人员在开发非Pt催化剂方面做了大量工作.本文从金属碳化物、Pd合金和钙钛矿型氧化物三个方面阐述阳极非铂催化剂的研究进展.

### 2.1. 金属碳化物

金属碳化物中最常见的具有催化作用的是WC和Mo<sub>2</sub>C,它们具有与Pt相似的结构,其催化活性与Pt相似,在甲醇氧化反应中甚至更高,被誉为“准铂催化剂”.

自Levy等<sup>[6]</sup>发现WC具有与Pt相似的催化性质以来,人们相继做了一系列验证WC催化性质的实验<sup>[7]</sup>.他们发现,WC的催化行为很大程度上受到制备方法的影响,但是对于那些Pt催化的反应而言,WC仍具有较高的催化性能.其后较多工作开始围绕W以及含W的二元或多元金属碳化物展开. Kawamura等<sup>[8]</sup>认为,在含W的二元金属碳化物中添加Mo对甲醇的催化活性最大,且当Mo/(W+Mo)比为0.2时最高.这是由于Mo移走了甲醇氧化过程中某些有毒中间产物,或者使甲醇氧化按另外一个没有毒性中间产物生成的反应路径进行.由于WC膜

在低于0.6 V的阳极电势下能稳定存在,近年来也开始成为DMFC中一种极具潜力的甲醇氧化阳极催化剂.2005年Zellner等<sup>[9]</sup>发现在N<sub>2</sub>饱和的H<sub>2</sub>SO<sub>4</sub>溶液(0.5 mol/L)中进行循环伏安测试(CV),W<sub>2</sub>C膜不稳定易被氧化成W<sub>x</sub>O<sub>y</sub>物种.而WC膜上甲醇的分解导致O-H键断裂;同时生成CH<sub>3</sub>O物种.此时少量Pt修饰的WC膜产生协同效应可加快甲氧基的分解.

催化剂的形貌和结构对阳极催化性能的影响也很大.罗远来等<sup>[10]</sup>认为这是由于电化学反应过程中所涉物种在各晶面上完全不同的吸附行为造成的.一些纳米结构的催化剂具有独特的晶面和较高的比表面积,因而对甲醇氧化具有特殊的催化活性.近期Ma等<sup>[11]</sup>制备出一种纳米结构的Co<sub>6</sub>Mo<sub>6</sub>C<sub>2</sub>/C,其化学稳定性和电化学稳定性均良好,当它负载较低量的Pt时,其在酸性介质中的催化活性和稳定性可达到商品Pt/C的水平.且较低温度下制备,能耗远低于传统的高温方法.循环伏安测试结果表明,Pt-Co<sub>6</sub>Mo<sub>6</sub>C<sub>2</sub>/C的催化活性比Pt/C更高,可能原因是Co<sub>6</sub>Mo<sub>6</sub>C<sub>2</sub>/C载体与高活性的Pt之间产生协同效应,其机理与WC与Pt产生的协同效应相同<sup>[12]</sup>.Pt-Co<sub>6</sub>Mo<sub>6</sub>C<sub>2</sub>/C催化剂经1000次循环后半波电位降低6 mV,而Pt/C催化剂降低27 mV,可见其稳定性更高.Pt/C活性面积的损失高达20%,而Pt-Co<sub>6</sub>Mo<sub>6</sub>C<sub>2</sub>/C几乎没有明显损失,表明相同条件下Co<sub>6</sub>Mo<sub>6</sub>C<sub>2</sub>/C载体比碳载体更稳定,使催化剂也趋于稳定.

另外,向二元金属碳化物中掺入其他元素也是一种改善催化性能的普遍方法.2011年,Kelly等<sup>[13]</sup>采用物理气相沉积法制备的Rh/WC,Ni/WC和Au/WC都对C-H键断裂形成CO和H<sub>2</sub>的过程产生催化活性,其中Rh/WC和Ni/WC对甲醇分解活性稍高.程序升温脱附结果显示,各催化剂在甲醇分解过程中活性大小依次为:WC > Rh/WC > Ni/WC > Pt/WC >> Au/WC.由此可见,在促进甲醇分解方面Rh/WC和Ni/WC更具优势.

总的来说,金属碳化物对甲醇阳极氧化具有一定的催化活性以及较好的抗CO性能,使其不仅能被直接用作非铂催化剂,同时可作为一种有效的载体来负载Pt.相关研究将向着高比表面、高分散性、实用性等方向发展:(1)探索实现低成本、低耗能的绿色制备方法;(2)采用纳米技术和原理,探索优化碳化物颗粒纳米结构、提高比表面积、增加活性中心的制备工艺;(3)对碳化物进行掺杂及表面改性,利用碳化物和掺杂材料的协同效应,探索制备高催化活性的金属碳化物材料;(4)提高对碳化物表界面化学状态的理论认识,采用表界面微观修饰,

改变其本征原子结构, 进一步提高催化活性.

## 2.2. Pd合金

Pd基催化剂的催化性能与Pt极为相似, 但Pd储量远高于Pt<sup>[14]</sup>, 因而其成本低得多, 同时具有很好的抗CO毒化能力<sup>[15,16]</sup>, 因此Pd催化剂具有巨大的潜力. 二元Pd-M催化剂在甲醇氧化过程中的双功能机理和配体效应, 使其成为一种很好的甲醇阳极催化剂<sup>[17]</sup>. 甲醇氧化反应过程需两种活性位: 一种用于甲醇分子的吸附和分离, 另一种用于吸附和活化水分子. 而配体效应则是金属M改变Pd的电子特性, 降低CO的吸附能, 促进吸附CO在较低电位下发生氧化.

早期研究<sup>[18,19]</sup>采取添加Fe, Co, Mo和Ni等非贵金属的方法来改善催化活性和持久性, 其中Pd-Co-Mo三元合金被广泛应用于低温燃料电池的阳极<sup>[20]</sup>. 2008年Sarkar等<sup>[21]</sup>采用热分解法制备了一系列纳米级PdMo/C催化剂, Pd-Mo合金的循环伏安曲线和旋转圆盘电极测试表明, 该催化剂活性和稳定性明显高于Pd催化剂, 其中Pd<sub>90</sub>Mo<sub>10</sub>在工作温度为80°C的DMFC中的催化活性与Pt相似, 且可有效抵抗甲醇中毒. 对于甲酸燃料电池, 自1970年代就有人发现, 向Pd中添加Sb, Sn和Pb等金属元素可增加甲酸氧化速率, 并抑制CO中毒<sup>[22-25]</sup>. 研究表明, PdPb催化剂对甲酸的氧化速率是Pd的4倍, 是PdSb的2.5倍, 相比PdSn增加了25%, 但没有彻底解决甲酸氧化过程中CO中毒问题, 使用3 h后电池性能大幅衰减, 需要进一步提高催化剂稳定性和抗CO中毒能力.

通过调节电流密度、溶液的pH值及温度等条件可以改变催化剂的形貌, 从而使催化剂获得不同活性. 一系列具有不同Pd含量的PdNi膜在CH<sub>3</sub>OH(1 mol/L)+H<sub>2</sub>SO<sub>4</sub>(0.5 mol/L)的电解液中表现出不同的MOR活性<sup>[26]</sup>. 极化曲线显示, Pd含量最高的Pd-Ni合金具有最高的活性, 原因可能是随着Pd浓度的增加晶体尺寸反而减小. 除了DMFC, Pd基电催化剂同样可用于H<sub>2</sub>/O<sub>2</sub>燃料电池氢燃料的氧化反应(HOR). 负载在WC上的Pd-Ni合金(标记为PdNi/WC)用作H<sub>2</sub>/O<sub>2</sub>燃料电池阳极催化剂时最大功率密度可达到230 mW/cm<sup>2</sup>, 其原因是PdNi合金与WC之间形成一种强有力的结合<sup>[27]</sup>. 稳定性测试表明100 h连续运行后电池性能没有发生明显衰减, 这使得PdNi/WC成为一种具有前景的阳极催化剂.

电解液的类型(酸性或碱性)对催化剂性能产生显著影响. 以Du等<sup>[28]</sup>的研究为例, 在0.5 mol/L KOH + 0.5 mol/L乙醇溶液中, 以SnCl<sub>2</sub>和K<sub>2</sub>PdCl<sub>4</sub>为前体制备的一系列不同Pd/Sn比的纳米催化剂的乙醇氧化峰值电流密度

大小依次为Pd<sub>86</sub>Sn<sub>14</sub> > Pd<sub>75</sub>Sn<sub>25</sub> > Pd<sub>47</sub>Sn<sub>53</sub> > Pd (JM). 尽管该系列中Pd<sub>47</sub>Sn<sub>53</sub>/C的氧化峰电流很小, 但是它的峰电位相比商用Pd/C负移了60 mV, 原因是Pd-Sn较高的合金度极大地改变了Pd的电子结构, 更利于催化活性的提高. Antolini等<sup>[29]</sup>曾预测Pt-Sn合金中Sn的理论最优含量为25%~38%, 然而Du等<sup>[28]</sup>将碱性介质中Pd-Sn催化剂Sn的最优含量精确到14%, 体现了Pd在碱性介质中更易与OH<sub>ads</sub>相结合.

对于直接醇类燃料电池, Pd类催化剂最主要的缺点是在活性较高的强碱性介质中C-C键不易断裂, 因此需要设计新的Pd催化体系来增大电流密度, 以维持较好的电学稳定性; 同时, Pd的纳米颗粒与非贵金属氧化物或碳化钨相结合, 也可形成金属载量低且活性和稳定性均较好的催化剂. 所以, 应探索更容易的合成方法, 以减小Pd-M纳米颗粒的尺寸.

## 2.3. 钙钛矿型氧化物

钙钛矿类复合氧化物具有独特的结构特征和优异的导电性, 被广泛用作催化剂材料和电极材料. 它可分为ABO<sub>3</sub>和A<sub>2</sub>BO<sub>4</sub>两种类型, 前者属于六方晶系, 后者属于八面体结构. 其中A通常为稀土或碱土金属元素, 如Sr, Ba, La和Ce等; B是第三周期过渡金属元素, 如Co, Fe, Ni, Cu和Ru等<sup>[30]</sup>. 在A<sub>2</sub>BO<sub>4</sub>型氧化物中, A或B位被其它元素部分或全部取代使催化剂的性能发生明显变化. Singha等<sup>[31]</sup>采用溶胶凝胶法制备了A<sub>2</sub>BO<sub>4</sub>结构的La<sub>2-x</sub>Sr<sub>x</sub>NiO<sub>4</sub> (0.0 < x < 1.0)钙钛矿氧化物催化剂, 常温下在1 mol/L KOH + 1 mol/L CH<sub>3</sub>OH溶液中的电化学测试结果表明, La<sub>2-x</sub>Sr<sub>x</sub>NiO<sub>4</sub>催化剂对CH<sub>3</sub>OH氧化的电催化活性随x数值的增加而增加; 至x = 1时, CH<sub>3</sub>OH氧化电流密度达到最大值50.9 mA/cm<sup>2</sup>, 并且催化剂没有发生CO中毒现象.

将A位和B位元素部分或全部取代后, 因化合价变化而导致晶体内部产生可移动的电子, 可增加催化剂的导电性, 改善其催化性能, 因而钙钛矿类复合氧化物被较多地用作DMFC阳极电催化剂. 需要特别指出的是钙钛矿型氧化物在碱性甲醇燃料氧化过程中的应用更为广泛, 这是由于酸性介质将催化剂限制在耐腐蚀的贵金属, 而采用碱性电解质可使催化剂的活性得到大幅度提升, 不再受贵金属的限制. Hu等<sup>[32]</sup>综述了近年来碱性溶液中各种甲醇氧化催化剂的研究进展, 认为钙钛矿型氧化物室温下具有高电导率和有效的氧离子扩散能力, 在高的极化电位下对甲醇显示高的催化活性, 过渡金属离子吸附甲醇, 然后OH<sup>-</sup>作用下, O-H和C-H断裂给出电子

和 $H^+$ ,使甲醇完全氧化.正是由于钙钛矿型稀土氧化物含氧丰富,“活性氧”易与C反应生成 $CO_2$ ,从而避免类似Pt/C中毒现象发生.

同时为满足DMFC商业化的要求,在钙钛矿型氧化物中加入Pt以提高阳极催化剂活性和稳定性成为该研究领域的另一热点. Lan等<sup>[33]</sup>制备了一系列 $ABO_3/Pt$ 型催化剂(A位为La或Sr, B位为Ru),这类催化剂对甲醇和乙醇的电催化活性与PtRu合金的非常接近,降低了Pt的载量(Pt的载量分别为1%, 5%, 10%和15%),使得成本降低. 通过比较上述一系列催化剂上甲醇氧化的极化曲线可以看出,  $ARuO_3/Pt$ 型催化剂的起始电位接近PtRu催化剂( $\sim 0.25$  V), 其中  $LaRuO_3 + 15\%$  Pt的起始电位相比  $SrRuO_3 + 15\%$  Pt的更负,因而更具有优势,同时对乙醇的氧化过程也具有相似的特性. 所制备的 $ABO_3/Pt$ 型催化剂的Pt载量低于Pt基催化剂的3~5倍,但在甲醇和乙醇的氧化电流密度与Pt基催化剂相当,其可能机理<sup>[34]</sup>是钙钛矿型氧化物表面[OH]形成促进了氧化过程的进行.

从提高催化剂的比表面积考虑,采用不同方法制备纳米级钙钛矿类氧化物也能对甲醇的电化学氧化反应表现出较高的催化活性.

### 3. 阴极非铂催化剂

为解决Pt基催化剂的高成本问题,亟待开发阴极非铂催化剂. 2012年,美国3M燃料电池专家Debe<sup>[35]</sup>在对汽车工业燃料电池电催化剂面临的挑战与展望中总结了美国能源部提出的目标. 目前汽车工业燃料电池阴极Pt用量为 $0.4$  mg Pt/ $cm^2$ 甚至更高,未来的工作应集中在不降低电池性能和持久性的前提下减少阴极贵金属用量. 阴极非铂催化剂包括过渡金属大环化合物、过渡金属氮化物和过渡金属氧化物等,这类催化剂常见的制备途径有:对碳载有机金属复合物进行热处理<sup>[36,37]</sup>,在氨水或丙酮中高温分解碳前体和金属前体<sup>[38-40]</sup>,在含氮环境中对碳和过渡金属盐进行热处理<sup>[41]</sup>,或者将含氮配体与Co的氧化物形成溶胶加入到碳载吡咯基体中<sup>[42]</sup>形成大环类化合物等. 针对非贵金属催化过程中氧还原电流密度值提出的明确目标是2015年达到 $300$  A/ $cm^2$ ,然而低温燃料电池阴极ORR反应是一个复杂的过程,仍然面临较多困难. 设计和制备这类催化剂时应充分考虑到 $O_2$ 在催化剂表面的吸附方式,使氧分子朝着有利于4电子反应发生的方向进行吸附<sup>[43]</sup>.

#### 3.1. 过渡金属大环类化合物

过渡金属大环化合物一般由酞菁(Pc)、三烯丙基胺

(TAA)、四甲氧基苯基卟啉(TMPP)、四苯基卟啉(TPP)等具有多齿配位作用的大环结构与过渡金属离子M(如Fe, Co, Mn和Ni等)螯合形成,可作为ORR催化剂用于中性、酸性以及碱性各种介质,并已广泛应用于燃料电池中. 人们在过渡金属大环化合物方面进行了大量的研究,发现该类化合物对ORR反应均有一定的催化活性. 早在1965年, Jasinski<sup>[44]</sup>就发现Co酞菁对ORR反应有催化活性,但水解作用和过氧化物造成的大环分解使其在酸性环境中稳定性很差,难以用于低温燃料电池. 后来研究人员相继发现,卟啉和CoTAA等过渡金属的大环化合物对ORR反应也具有一定的催化活性,并且通过惰性气体保护下 $600\sim 1000$  °C高温热处理 $N_4$ -金属大环化合物的方式可提高催化活性和化学稳定性<sup>[45,46]</sup>.

研究发现,影响过渡金属大环化合物氧还原性能的主要因素包括:活性中心、金属-载体的相互作用及处理条件等,如下所述.

##### 3.1.1. 活性中心

1989年Wiesener等<sup>[47]</sup>报道了一系列金属-酞菁大环化合物氧还原活性大小依次为 $Fe > Co > Ni > Cu \approx Mn$ . 后来也证实了非贵金属中以Fe和Co为中心的过渡金属大环化合物具有最高的氧还原催化活性. 但是有关阴极非铂催化剂活性中心的讨论依然激烈. 过渡金属大环化合物的活性取决于金属与配体之间的相互作用,对于一个给定的中心离子而言,催化活性取决于大环配体对中心离子的电子效应所引起的电子密度的变化<sup>[48]</sup>. 也有人认为,金属只是促使催化活性位形成,而仍无法完全解释清楚金属本身是否是活性位,目前大部分研究者认同的活性位有 $MN_4$ 和 $MN_2$ .

Randin<sup>[49]</sup>首先提出氧还原特征与催化活性之间存在线性关系. 后来Beck<sup>[50]</sup>在对FePc和CoTAA研究的基础上提出了新的观点: $O_2$ 首先吸附在Pc分子中的金属离子上,进而金属被氧化,分子态的氧部分被还原成过氧化物;并且,金属的还原电位也是重要因素, $M^{III}/M^{II}$ 电位比越正,金属-Pc的活性就越高. 基于上文,可以对金属与不同配体组成的化合物进行活性优劣的筛选,以便进一步探讨活性机理. Radyushkina等<sup>[51]</sup>认为,炭载FeTMPP存在两种活性中心:一种是吸附于碳载体表面含氧官能团上的FeTMPP分子,另一种是FeTMPP自由分子. 前者对 $O_2$ 转化为 $H_2O_2$ 的过程有加速作用,后者促进 $O_2$ 向 $H_2O$ 转化的4电子过程,但在中心离子 $Fe^{III}/Fe^{II}$ 被还原后伴随着中间产物 $H_2O_2$ 的产生.

Oh等<sup>[52]</sup>为探究Co和Fe含量对氧还原反应活性的影

响,制备了一系列Co-ED/PPy-CNF催化剂,实验证明,随着Co含量增加,催化活性明显改善.在 $\text{H}_2\text{SO}_4$ 电解质溶液(0.5 mol/L)中以5 mV/s的速度扫描,Co-ED/PPy-CNF-0(不含Co时)氧还原电流仅为0.004 mA(0.6 V vs NHE),而相同条件下Co-ED/PPy-CNF-10(Co含量为10%)的氧还原电流可达0.43 mA,但是Co本身并不是氧还原反应的直接活性中心. Fe-ED/PPy-CNF催化剂中Fe含量对其活性的影响也有着与Co-ED/PPy-CNF相似的趋势,催化活性略次于Co基催化剂.在 $\text{H}_2/\text{O}_2$ 燃料电池中,Co-ED/PPy-CNF-10在0.4 V时电流密度为0.7 A/cm<sup>2</sup>,Fe-ED/PPy-CNF-10相同电位下电流密度仅为0.53 A/cm<sup>2</sup>,原因是使用不同种类金属造成了催化剂中活性氮含量的差异.

催化剂中N含量和含N活性官能团(如吡啶-N,石墨-N等)的类型均与氧还原反应活性位的形成相关.Kothandaraman等<sup>[53]</sup>制备的Fe-吡啶催化剂阴极载量为0.5 mg/cm<sup>2</sup>,当掺入0.12%~0.24% N时,催化活性(即电流密度)从0.07升至1.9 mg/cm<sup>2</sup>,表明Fe与含N的吡啶之间构成了氧还原反应的催化活性位.同时,Wei等<sup>[54]</sup>发现,随着表面氮含量的增加,Co-N/C催化活性也大幅度提高.Lefevre等<sup>[55,56]</sup>曾指出,吡啶-N与金属中心相连的 $\text{FeN}_4/\text{C}$ 或 $\text{CoN}_4/\text{C}$ 可能是催化活性位;Ruggeri等<sup>[57]</sup>也提出吡啶-N可连接铁原子形成催化活性位.随后Wood等<sup>[58]</sup>直接将金属掺入到氮源中制备了一系列Fe含量为6  $\mu\text{g}/\text{cm}^2$ 的高效催化剂(与Ruggeri等<sup>[57]</sup>所制备的催化剂Fe含量相同),前者氧化电流密度达到19 A/cm<sup>2</sup>,但表面氮元素的含量是后者的2倍,这也有力证明了Fe原子并不是活性中心.

金属与大环化合物之间的结合情况也会影响过渡金属大环化合物的活性位.美国洛斯阿拉莫斯实验室<sup>[59]</sup>采用无需高温热解的常规化学方法合成了Co-PPy-C,该催化剂在 $\text{H}_2/\text{O}_2$ 和 $\text{H}_2$ /空气燃料电池中连续运行100 h电池性能无明显衰减现象.聚吡咯将Co原子包裹在基体中形成的结构类似于Co-卟啉的原子结构,Co原子与PPy单体上的N原子相连形成Co-N活性位,因此该项工作在不破坏聚合物结构的前提下构建了Co-N活性中心.在0.50~0.20 V电位范围内,Co-PPy-C的电流密度值相比Co/C高出一个数量级,最大功率密度更是高达后者的16倍.可见,吡咯与Co原子之间的交互作用致使电荷转移到金属中心,进一步促使金属-大环化合物之间强力结合.

### 3.1.2. 金属-载体的相互作用

载体对提高催化剂活性、稳定性和利用率等同样起到重要作用.Tang等<sup>[60]</sup>针对近年来新型碳载体在直接醇燃料电池中的应用进行了总结,认为应加速ORR的产物( $\text{H}_2\text{O}$ )从活性位上移除以便腾出“空位”为反应物( $\text{O}_2$ )达到活性位参加反应提供场所,以最大限度利用活性组分.同时,载体与活性金属之间的电荷转移影响活化能,进一步影响催化反应的速率.Schwab<sup>[61,62]</sup>曾提出载体对金属的影响有两种类型:结构效应,载体稳定活性组分;协同效应,载体和金属间强相互作用促使在界面形成新的活性位.碳材料在提高催化剂活性和稳定性方面起重要作用,其种类及表面性质对催化剂活性影响很大.近年来研究发现,经酞菁(Pc)修饰的碳纳米管可有效改善复合物的电催化性能,Pc分子强吸附在碳纳米管上形成“Pc分子电极”<sup>[63]</sup>.研究表明<sup>[64,65]</sup>,FePc和CoPc均可促进 $\text{O}_2$ 还原成 $\text{H}_2\text{O}$ 的4电子过程,避免中间产物 $\text{H}_2\text{O}_2$ 的形成.Kruusenberg等<sup>[66]</sup>分别合成了FePc/MWCNT和CoPc/MWCNT阴极催化剂,组成膜电极在45 °C工作温度下对单电池的性能进行测试,CoPc/MWCNT的最大功率密度达到100 mV/cm<sup>2</sup>,非常接近Pt/C(Tanaka公司提供)的(120 mV/cm<sup>2</sup>),而相同条件下FePc/MWCNTs的仅为60 mW/cm<sup>2</sup>.

碳材料除了用作载体和修饰载体,也因其独特的性能而被用于增加催化剂的活性位.Onodera等<sup>[67]</sup>通过高温分解酚醛树脂、Ketjen炭黑和钴的邻二氮杂菲复合物获得氮掺杂的非贵金属催化剂,进一步改变Ketjen炭黑(KB)的含量来考察该类非贵金属催化剂在氧还原反应中的催化活性.当KB与酚醛树脂含量比为1:1(标记为KB1.0)时,0.7 V的电位下对应的氧还原电流密度是不添加KB时的30倍,同时是KB0.2时的2.5倍.将不同含量KB的氮掺杂非贵金属阴极催化剂组装成PEFCs,在80 °C工作温度和0.8 V的电位下测试开路电位,NC + KB1.0的开路电位为0.41 V,约为NC + KB0.4的2倍,说明碳材料的添加可有效增加活性位.这与Ikeda等<sup>[68]</sup>的结论相似,即催化剂的活性中心位于碳的齿状边缘,边缘那些与石墨状掺杂氮相连的碳原子具有比吡啶-N相连的C原子更高的氧还原活性.此外,该类催化剂活性的改善不仅取决于其比表面积以及Co和其它表面原子的含量,更取决于暴露在表面的催化活性位数量.

向载体中引入其它物质来改善催化性能也成为目前一个研究方向.邢巍课题组<sup>[69]</sup>利用过渡金属大环化合物对氧还原的较高催化活性以及 $\text{TiO}_2$ 的半导体性质和催化 $\text{H}_2\text{O}_2$ 分解的性质,制备了炭载 $\text{TiO}_2$ -过渡金属大

环化合物复合催化剂, 因 $\text{H}_2\text{O}_2$ 能被 $\text{TiO}_2$ 及时分解掉, 因此与相应的金属大环化合物相比, 其稳定性有所提高; 与Pt/C催化剂相比, 其耐甲醇性能好, 同时极大地降低了成本。

### 3.1.3. 处理条件

研究充分表明热处理有利于提高氧还原催化活性和稳定性, 目前普遍认为, 不同的热处理温度产生不同的活性位。Lalande等<sup>[70]</sup>先将CoPcTc吸附到炭黑上, 发现在600~700 °C时表面主要产物是Co-N和Co-C, 并存在部分 $\text{CoN}_4$ ,  $\text{CoN}_4$ 与碳结合形成 $\text{CoN}_4/\text{C}$ 结构, 有利于 $\text{O}_2$ 转换为 $\text{H}_2\text{O}_2$ 。一旦热处理温度超过700 °C, 形成的 $\text{MN}_2/\text{C}$ 结构对 $\text{O}_2$ 直接还原成 $\text{H}_2\text{O}$ 的过程具有较高的催化活性和选择性。Wu等<sup>[71]</sup>在 $\text{N}_2$ 气氛中于400~1000 °C合成了PANI-C, PANI-Co-C, PANI-FeCo-C, PANI-Fe-C, 并作为 $\text{H}_2/\text{O}_2$ 燃料电池的阴极(阳极均采用Pt/C)。单电池测试显示, PANI-Fe-C比PANI-Co-C表现出较高的氧还原活性, 其中PANI-FeCo-C的氧还原活性、稳定性和寿命最高(最大功率密度可达到0.55 W/cm<sup>2</sup>)。在0.4 V恒电位下进行700 h的性能测试后, PANI-FeCo-C的稳定性仍保持较好, 前24 h电流密度仅衰减3%, 接下来的24 h平均电流密度损失为18 mA/h, 而PANI-Fe-C和PANI-Co-C损失分别高达~90和130 mA/h。

不同化学处理方法对催化剂的选择性同样有着显著影响。Olson等<sup>[72]</sup>的研究表明, 经不同化学处理的Co基大环化合物对甲醇和甲酸催化存在不同的选择性。用旋转圆盘电极进行循环伏安扫描, 电解液为0.5 mol/L的 $\text{H}_2\text{SO}_4$ ,  $\text{O}_2$ 饱和, 经不同化学处理得到的CoTMPP在电解液中 $E_{1/2}$ ,  $E_{1/2 \text{ methanol}}$ ,  $\Delta E_{\text{methanol}}$ ,  $E_{1/2 \text{ formic}}$ ,  $\Delta E_{\text{formic}}$ 数据如表1所示, 其中 $\Delta E_{\text{methanol}}$ 由公式 $\Delta E_{\text{methanol}} = E_{1/2} - E_{1/2 \text{ methanol}}$ 算得。表1中数据可用于定量分析该类催化剂在混合反应试剂中对氧还原的选择性。 $\Delta E_{\text{methanol}}$ 值较低时甲醇存在下氧还原反应选择性更高, 而较高则有利于甲醇的氧化反应。相比于甲醇燃料, 甲酸在CoTMPP电极上更易被吸附和发生氧化, 因此CoTMPP可以作为甲酸燃料电池的催化材料。

除了对催化剂的处理, 对载体进行化学预处理也能极大地提高金属大环化合物的氧还原活性。随着表面分析技术的发展, 载体与金属之间相互作用对催化活性影响的机理也得到完善。经化学预处理后, 载体表面含氧官能团增多, 可将金属-大环复合物牢固地“粘结”在载体上; 另一方面, 碳载体化学预处理后, 催化剂表面活性的N和C原子含量会显著增加, 有利于形成M-N<sub>4</sub>-C催化

活性中心。

总的来说, 过渡金属大环化合物对氧还原反应具有较高的催化活性, 但原料价格昂贵, 制备过程也比较复杂(需要高温热处理等), 为获得高活性需经过一系列复杂的处理过程, 其催化性能与Pt催化剂相比也存在差距。因此, 选择更加先进的合成技术尤为重要。马紫峰课题组<sup>[73]</sup>采用微波辐射加热技术制备了一系列的Co-卟啉氧还原催化剂, 其催化性能比传统的有机加热回流反应制得同类催化剂的更高。因此, ORR电催化剂的未来研究重点将是: (1)探索新的合成方法(如微波法、超声法、等离子技术以及红外辐射等), 合成出具有高比表面积且高度分散的纳米尺寸催化剂; (2)对催化剂的表面进行修饰(如通过硫化处理增加表面活性位的数目); (3)选取新型的反应介质, 如离子流体, 在更为温和的条件下完成制备过程。

### 3.2. 过渡金属氮化物

过渡金属氮化物是一种新型非Pt催化剂, 具有与Pt相似的氢和氧化学吸附行为, 其结构主要是氮原子插入到过渡金属晶格中所生成的一类金属填充型化合物。

最新的研究表明, 掺入碳材料的石墨-N和吡啶-N对改善氧还原反应有重要作用, 同时过渡金属促进氮原子与碳原子之间的结合, 使金属离子被包裹在碳基体中<sup>[74-78]</sup>。Kosłowski等<sup>[79]</sup>发现,  $\text{FeN}_4$ 大环化合物中存在 $\text{CFeN}_2$  ( $\text{Fe}^{2+}$ )和 $\text{Fe}_3\text{C}$  ( $\text{Fe}^0$ )两种活性中心。 $\text{Fe}^{2+}\text{N}_4$ 结构有利于氧还原反应中的4电子反应途径, 在氮源中以900 °C热处理且催化剂中Fe含量大于0.1%时更有利于形成 $\text{Fe}^{2+}\text{N}_4$ 。Li等<sup>[80]</sup>发现, 含氮的Co-N-和Fe-N-前体明显优于分离的氮前体和金属盐, 由于热处理对形成高效活性位起重要作用, 经高温分解、过滤、再次高温分解制得CoFeN/C催化剂其开路电位为0.97 V, 最大功率密度为177 mW/cm<sup>2</sup>, 而商品Pt/C催化剂的分别为1.04 V和196 mW/cm<sup>2</sup>。

另外碳材料改性也可增加催化剂稳定性。Byon等<sup>[81]</sup>通过增强碳的石墨化程度使其具有高比表面积和更多表面官能团, 以提高Fe-N-C催化剂的稳定性。合成过程为 $\text{g-C}_3\text{N}_4$  (双胍胺作为氮源聚合而成),  $\text{FeCl}_3$ 和氧化石墨(GO)混合后在80~100 °C于 $\text{NH}_3/\text{N}_2\text{H}_4$ 气氛中加热, 得到的产物为 $\text{FeCl}_3/\text{g-C}_3\text{N}_4/\text{rGO}$ , 然后在Ar保护下于800 °C碳化2 h得到最终产物Fe-N-rGO, 氧还原活性比Fe-N-C<sub>CB</sub>明显降低, 但在 $\text{H}_2/\text{O}_2$ 电池测试中其稳定性得到大幅度提高。

随着对石墨烯研究的逐步深入, 石墨烯因具有高比

表面积和高导电率也开始用于过渡金属氮化物中。2012年Li等<sup>[82]</sup>以铁盐、g-C<sub>3</sub>N<sub>4</sub>和经化学还原的石墨烯为原料,合成了Fe-N-G,并用于空气-阴极单室微生物燃料电池(MFC),线性伏安扫描展示了良好的氧还原催化活性。相比不经任何处理的初始石墨烯(P-G)催化剂,Fe-N-G的起始电位更正,氧化电流更大,并且Fe-N-G-MFC的最大功率密度高达1149.8 mW/m<sup>2</sup>,约为Pt/C-MFC (561.1 mW/m<sup>2</sup>)的2.1倍,大大高于初始石墨烯为原料的P-G-MFC (109 mW/m<sup>2</sup>)。该研究表明,Fe-N-G非贵金属催化剂比Pt系催化剂更适用于微生物燃料电池。

过渡金属氮化物对氧还原反应具有一定的催化活性,但仍远低于Pt。通过研究催化剂的表面结构和状态、优化催化剂组成(如引入新型碳材料石墨烯)和结构(掺杂氮形成具有活性的官能团)等,有望大大提高此类化合物的催化活性。

### 3.3. 过渡金属氧化物

过渡金属氧化物用作氧还原反应催化剂时,氧化物在酸性介质中不稳定易缓慢分解,因此电解液主要选择碱性溶液。早期Liu等<sup>[83,84]</sup>采用溅射法制备的ZrO<sub>2</sub>, TiO<sub>2</sub>, SnO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Co<sub>3</sub>O<sub>4</sub>等过渡金属氧化物均能在氧还原的电势范围内稳定存在,且对甲醇的氧化无活性,其对氧还原反应的催化活性顺序依次为: ZrO<sub>2-x</sub> > Co<sub>3</sub>O<sub>4-x</sub> > TiO<sub>2-x</sub> > SnO<sub>2-x</sub> > Nb<sub>2</sub>O<sub>5-x</sub>,表明ZrO<sub>2-x</sub>对氧还原反应具有较高的选择性。

钙钛矿型氧化物ABO<sub>3</sub>中稀土元素占据A位,过渡金属占据B位,同时具有电子和离子导电性,晶格中的氧空位使其能够传导离子,因而也越来越多地用作电池用氧还原催化剂。Jin等<sup>[85]</sup>提出钙钛矿型氧化物在燃料电池中的氧还原活性与e<sub>g</sub>和A-B-O型中的B位密切相关。LaCu<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>催化剂在充满饱和O<sub>2</sub>的KOH电解质(0.1 mol/L)中,氧还原反应发生的起始电位约为0.8 V (vs NHE),且该类催化剂中的氧还原反应是4电子转移过程,而对于燃料电池的能量转化效率和输出电压,4电子还原反应机理最有利。同时对LaCu<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>, LaMnO<sub>3</sub>, LaCoO<sub>3</sub>和LaNiO<sub>3</sub>的活性进行测试,发现分别在781(±5), 834(±24), 847(±3)和908(±8) mV (vs RHE)的电位下出现活性电流。上述几种钙钛矿氧化物中,具有较高电位的

也表现出较好的电催化活性,其中LaMnO<sub>3</sub>和LaNiO<sub>3</sub>在碱性介质中的催化活性甚至与Pt/C相当。

钙钛矿型氧化物在碱性环境下对氧还原反应有很好的催化活性,但在酸性环境中稳定性较差,相关的催化活性及催化机理研究较少。其它过渡金属氧化物催化剂成本较低,耐氧化,但导电性能差,且在电解液中不够稳定,导致催化活性降低。

## 4. 结论与展望

燃料电池非铂催化剂经过几十年的研究已经取得一定成果,但仍存在很多问题与不足,如合成困难,催化活性较低,稳定性差等,目前尚不能与传统的Pt基催化剂相比。应用新方法、新技术改进催化剂制备方法,提高活性组分分散度,从而大幅度提高催化活性是燃料电池的一个主要研究方向。基于国内外研究现状,深入系统地研究非铂催化剂还可以从以下几个方面入手。

(1)运用科学的催化剂制备技术,实现催化材料的纳米化、结构化,同时尽量采用低能耗的制备技术,降低成本。随着材料科学的飞速发展,借助新的制备技术和表征手段势必可以更好地解释催化机理,未来将能设计和开发出活性高、化学和电化学稳定性好以及使用寿命长的新型非铂催化剂。

(2)设计新型载体负载的非铂催化剂。载体具备的某些特殊性质可以影响催化剂颗粒的形状、尺寸、空间分布以及载体-金属之间的电荷转移。因此,获得三维结构的负载型催化剂可以使燃料更好地与催化剂接触进行反应,同时抑制催化层活性面积的减少和反应过程中电阻的增大。另外,采用组合多维纳米碳材料作为载体或使用混合型催化剂也是未来发展的趋势,可以为电极催化层中的物料传输和电子、质子的转移提供通道,进一步提高催化剂颗粒利用率。

(3)优化合成条件。材料性能的优劣通常取决于粒度、分散性、形貌以及表面特性等因素,而这些都受合成参数的影响,如反应剂的选择、温度的调控和前体的预处理等。纳米技术的深入研究使合成过程更趋向于低温和可调控,为制备出小粒径、高分散且具有更多活性位的催化剂提供了有力保障。