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REVIEW ARTICLE

The use of macrocyclic compounds as electrocatalysts in fuel cells

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Abstract Macrocyclic compounds such as metallophthalocyanines demonstrated good catalytic activities toward electrochemical reactions. The characteristics of the central cations in metallophthalocyanines significantly influenced their electrocatalytic activities. Addition of conjugated polymers in electrodes improved the electrocatalytic activity by enhancing the electric conductivity. The electrocatalytic activities of macrocyclic compounds could be further improved by heat treatment. The formation of metallic clusters or metal containing organic fragments after pyrolyzing played an important role in improving electrocatalytic activities of macrocyclic compounds. It was considered that macrocyclic compounds might be functioned as a precursor to obtain well-distributed metallic clusters or metal containing organic fragments.

Keywords Macrocyclic compound · Electrocatalyst · Metallophthalocyanine · Polypyrrole · Oxygen reduction reaction · Fuel cell

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be the most promising fuel cell type for mobile applications because they can be operated at near ambient temperatures. Direct methanol fuel cells (DMFCs) are considered to be potential candidates to substitute batteries for portable applications due to their high energy densities. Platinum is known as one of the best catalysts for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in these fuel cells. However, the scarcity of platinum in nature is a big problem for commercial applications of these fuel cells. Furthermore, poor reaction kinetics of ORR leads to higher cathode overpotentials. The development of alternative materials is therefore one of the critical issues for the fuel cell commercialization.

As mentioned by Wang [1], the future development of catalysts for ORR should be oriented to highly efficient and economical catalysts that are non-Pt containing, nanoparticle-based, molecular-level assemblies. Many non-precious metals and compounds have been used as the catalysts for ORR such as Cu [2], Ni [3], TiO_2 [4], vanadium oxides [5], lanthanum manganite [6], iron nitrides [7], Co nitrides [8], Ag [9, 10], and MnO_2 [11–13].

Though it is hard to establish conclusively a preferred ORR path on individual catalysts right now, it is clear that electrocatalysts in fuel cells must have good electric conductivity and catalytic activities toward electrochemical reactions. Considering that some macrocyclic compounds with π-electrons have good electric conductivities comparable to metals as π-electrons can move via overlaps of π-electron cloud, electrochemists have attempted to use these compounds as the eletrocatalysts in fuel cells. Phthalocyanines are typical macrocyclic compounds with alternating nitrogen–carbon atom ring structures as shown in Fig. 1. Phthalocyanines can coordinate hydrogen or metal cations with four isoindole nitrogen atoms. When a phthalocyanine molecule is coordinated with a metal cation to form metallophthalocyanine, so called MN_4 center is generated. Though metallophthalocyanines are generally

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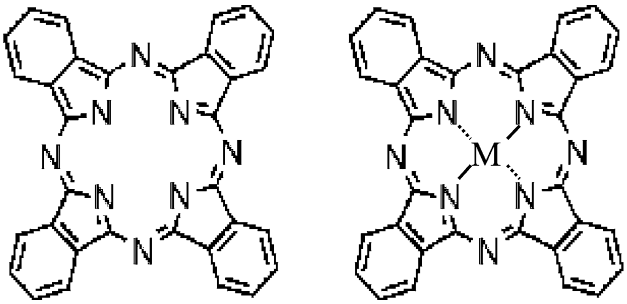


Fig. 1 The structures of phthalocyanine and metallophthalocyanine

studied and developed as dyes, it has been found that many metallophthalocyanines have high electric conductivities. Inabe and Tajima [14] have presented a detailed report about the structures of metallophthalocyanines and their electric conductivities.

Conjugated polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophene, and polyacetylene are another group of macrocyclic compounds. Though some undoped conjugated polymers such as polythiophene and polyacetylene have conductivities of around 10^{-10} to 10^{-8} S cm^{-1} only, the electric conductivities of the ion doped conjugated polymers can reach up to around 10^{-1} S cm^{-1} [15–17]. For example, PANI generally behaves as a semiconductor but it can be adjusted to be highly conductive materials by ion doping. Up to now, the conductivity value as high as 80,000 S cm^{-1} has been achieved from the stretch-oriented polyacetylene. However, polyacetylene is not chemically and thermally stable. In view of environmental stability, facile synthesis, and electric conductivity, polypyrrole is especially promising for commercial applications [18–24].

In this article, metallophthalocyanines and polypyrrole are selected as the examples to discuss the functions of macrocyclic compounds in electrocatalysis. Several synthesis methods of these catalysts are introduced. The heat treatment effects on the catalytic properties of macrocyclic compounds are discussed. The recent achievements of using macrocyclic compounds as the electrode catalysts for fuel cells are summarized.

2 Metallophthalocyanine (MPc)

2.1 MPc synthesis

The most convenient method to prepare MPc is doping selected ions into a metal-free phthalocyanine (Pc). Metal-free phthalocyanines are usually prepared by heating dicyano or diiminoisoindoline precursors in an alkaline solvent with high boiling point [25–30]. The inexpensive phthalic anhydride and phthalimide precursors have been employed for metal-free Pc synthesis by heating a mixture of hexamethyldisilazane, dimethylformamide (DMF), *p*-toluenesulfonic acid, and water at 150 °C [31]. Recently, Luedtke and co-workers [32] suggested a two-step synthesis method to obtain metal-free phthalocyanines by using Zn(II) template. The Zn(II)-templated cyclotetramerization followed by Zn(II) removal provided a high yield route to synthesize various metal-free phthalocyanines.

Zhan et al. [33] suggested a sol–gel method to directly synthesize MPc. Four transitional MPcs (CuPc, CoPc, NiPc, and ZnPc) were successfully synthesized in the silica inorganic matrix by using “an in situ synthesis” technology to encage organic compounds and complexes in sol–gel-derived matrices.

2.2 MPcs as catalysts for fuel cells

2.2.1 As cathode catalysts

The electrocatalytic activities of MPcs depend upon the characteristics of the central cations which act as the active sites. Fe, Co, and Ni phthalocyanines are the most widely studied metallophthalocyanines as the electrocatalysts for ORR since Jasinski discovered the electrocatalytic properties of Co phthalocyanine (CoPc) in 1960s [34]. It was reported that the electrocatalytic activity of CoPc was comparable to those of Pt and Ag as shown in Fig. 2 [35]. In 1974, Randin [36] studied the relative electrochemical activity of several metallophthalocyanines toward ORR. Through correlation of the redox processes on the ligand with the electrochemical activity, it was found that there

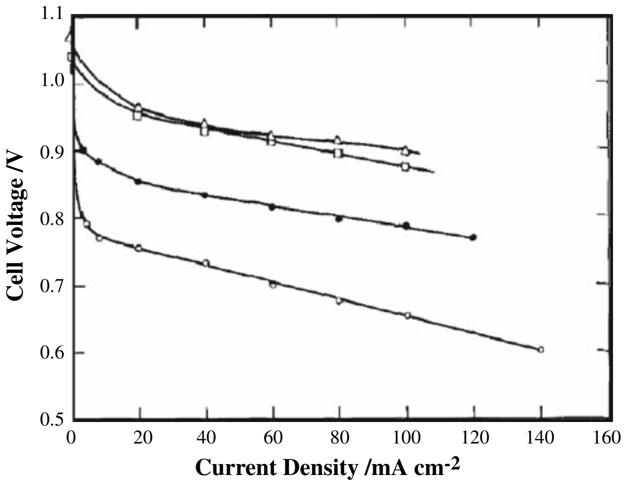


Fig. 2 Performances of H_2/O_2 fuel cells operating at 80 °C with an electrolyte of 35% KOH and a Pt black anode (9 mg cm^{-2}). The cathodes are 9 mg cm^{-2} Pt (*open square*), 40 mg cm^{-2} silver (*open triangle*), 14 mg cm^{-2} CoPc (*filled circle*), and 20 mg cm^{-2} acetylene black (*open circle*) [35]

was a linear relation between redox properties of the metallophthalocyanines and their catalytic activities.

In 1977, Beck [37] suggested a hypothesis of ORR mechanism on MPcs. It was supposed that the central cations with low chemical valence were oxidized when O_2 adsorbed on cations in MPcs, and the molecular O_2 was partially reduced to the superoxide state as shown in following steps:

$$\mathrm{M(II)} + \mathrm{O_2} = [\mathrm{M(III)} - \mathrm{O_2}]^- \tag{1}$$

$$[\mathrm{M(III)} - \mathrm{O_2}]^- + e^- \rightarrow \mathrm{M(II)} + \text{intermediates} \tag{2}$$

The interaction of M(II) center with O_2 reduction involved an oxidation process to M(III). Zagal et al. [38] found that the second step was the potential-determining step based on the studies of ORR kinetics on metallophthalocyanines. The M(III)/M(II) potential was a very important parameter in determining the electrocatalytic activity toward ORR on metallophthalocyanine catalysts. Through correlation of the M(III)/M(II) potential with the catalytic activity as shown in Fig. 3, it was found that the more positive the M(III)/M(II) potential, the higher the activity of MPc [39]. Furthermore, Fe, Mn, and Cr phthalocyanines promoted a four-electron reduction of oxygen whereas ORR on CoPc tended to be a two-electron process. Barendrecht and co-workers [40] found that at high pH, the reduction of O_2 to H_2O_2 on Co-containing chelates was more reversible and independent upon the redox potential; at low pH, the reduction was irreversible. There was a clear correlation between the redox potential of the central cation and the O_2^- reduction behavior.

Zagal and co-workers [41] found that electrocatalytic activities of metallophthalocyanines decreased following the order of Fe > Co > Ni > Cu with exception of Mn, Cr, and Zn after correlating the number of d-electrons of the corresponding metal with the electrocatalytic activity as shown in Fig. 4. Wiesener et al. [42] reported the same tendency except Mn. Zagal and co-workers [38] explained the electrocatalytic properties of these metallophthalocyanines using symmetry and perturbation theory and molecular orbital calculations.

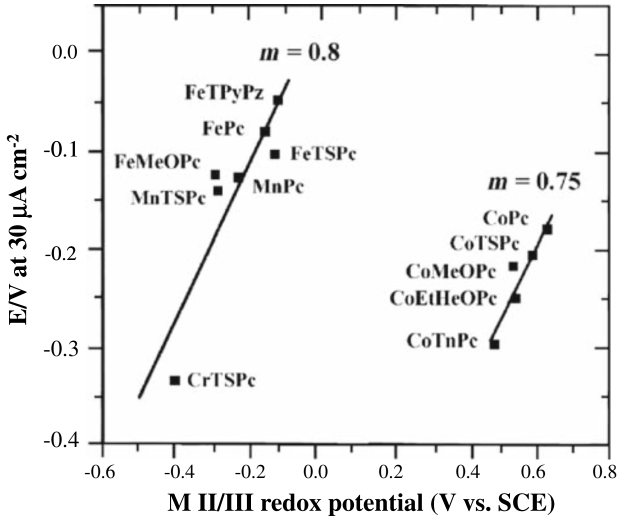


Fig. 3 Plot of log E (at constant current) versus the M(III)/(II) formal potential of the MN_4 macrocyclic for the reduction of oxygen in 0.1 M NaOH [39]

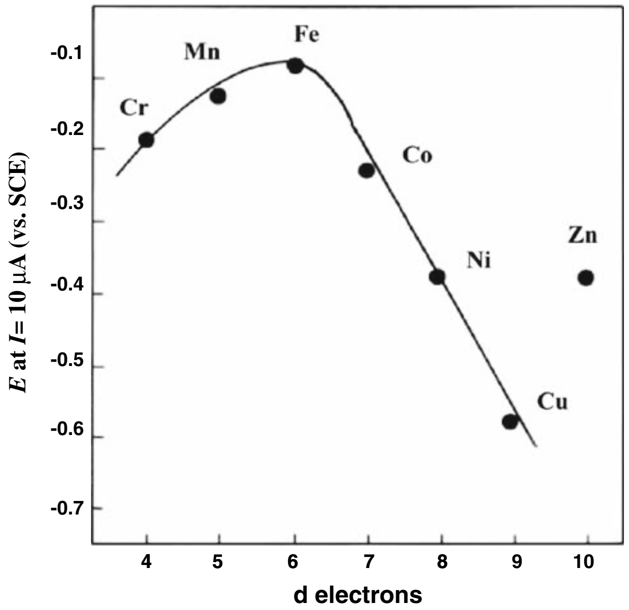


Fig. 4 Volcano plot for the electrocatalytic activity of different M-tetrasulfonated phthalocyanines adsorbed on graphite for O_2 reduction in 0.1-M NaOH, as a function of the number of d-electrons in the metal [41]

Recent researches reveal that CoPc not only exhibits considerable electrocatalyic activity toward ORR, but also demonstrates high tolerance toward fuel crossover in direct fuel cells like DMFC or DBFC [43, 44]. Addition of CoPc in Pt/C cathode improved the methanol tolerance of the cathode in the DMFC [43] because CoPc modified Pt/C demonstrated higher methanol oxidation current than the unmodified Pt/C as shown in Fig. 5. Ma et al. [44] found that CoPc not only exhibited considerable electrocatalytic activity toward ORR in a DBFC, but also demonstrated high resistance against BH_4^- influence on cathode performance. They successfully constructed a fuel cell without using membrane to separate the anolyte (alkaline $NaBH_4$ solution) from the cathode.

FePc is another interesting metallophthalocyanines as the ORR catalyst [45–47]. It was found that the crystal FePc demonstrated better catalytic activity than the amorphous FePc [45]. With increasing the FePc loading on carbon black, the catalytic activity toward ORR on FePc catalyst was increased [46]. The theoretical studies

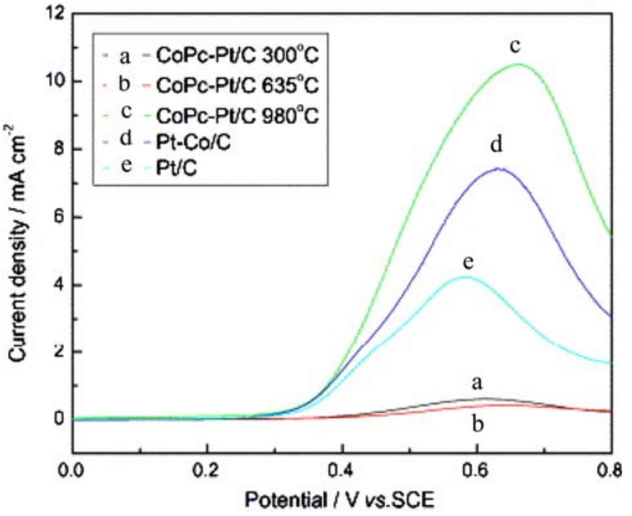


Fig. 5 The polarization of catalysts in 0.5 M H_2SO_4 and 1 M methanol solution. The scanning rate is 5 mV s^{-1} [43]

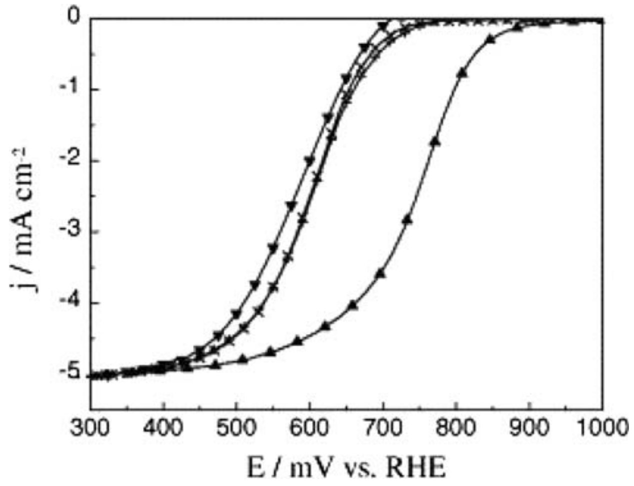


Fig. 6 $j(E)$ polarization curves in O_2-saturated electrolyte (0.5 M H_2SO_4): (*filled triangle*) at a Pt/C catalyst and (*plus*) at a FePc/C catalyst in the absence of methanol, (*inverted filled triangle*) at a Pt/C catalyst and (*times*) at a FePc/C catalyst in the presence of 1.0 M methanol ($T = 20$ °C, $v = 5$ mV s^{-1}, $\Omega = 2{,}500$ rpm) [50]

conducted by Anderson et al. [48] proposed that Fe(II) was the active site for four-electron ORR because H_2O bonded strongly to the Fe(III) site where O_2 adsorption was prevented. On the other hand, calculations showed that –OOH bonded more strongly to Fe(II) than to Fe(III), then subsequent reduction steps had very reversible potentials over both centers (Fe(II) and Fe(III)). Calculations also showed a hydrogen bonding interaction between –(OHOH) and N in the N_4 chelate. This interaction would prevent peroxide from desorbing as a two-electron reduction product. Barendrecht and co-workers [49] confirmed that O_2 was electrochemically reduced to OH^- by the four-electron reduction reaction through the kinetics studies of O_2 reduction on FePc in alkaline medium, but they argued that some HO_2^- would be formed in a narrow potential range.

Like CoPc, FePc also demonstrated a high resistance against fuel crossover in direct fuel cells. Ma et al. [47] found that FePc is a promising cathode catalyst in the DBFC due to its acceptable activity, borohydride tolerance, and stability in alkaline media. A maximal power density of 92 mW cm^{-2} was obtained at room temperature. It was also reported that carbon-supported FePc catalyst was totally insensitive to the presence of methanol toward ORR at low overpotentials as shown in Fig. 6 [50]. However, the infrared spectra showed that FePc degraded due to the substitution of Fe(II) by two protons to form a metal-free phthalocyanine that was known to be inactive for ORR.

2.2.2 *As anode catalysts*

Compared with considerable studies of metallophthalocyanines as the cathode catalysts for ORR, only few research results were reported about the use of metallophthalocyanines as the anode catalysts. Zagal and co-workers [51] studied the electrocatalytic activity of Co phthalocyanines toward hydrazine oxidation reaction. They suggested a N_2H_4 electrooxidation mechanism as follows:

$$N_2H_4 + R_nPcCo(II) = [R_nPcCo(I) - (N_2H_4)^+] \tag{3}$$

$$[R_nPcCo(I) - (N_2H_4)^+] + OH^- \rightarrow R_nPcCo(II) + N_2H_3^\bullet + e^- + H_2O \tag{4}$$

$$N_2H_3^\bullet \rightarrow N_2H_2^\bullet + e^- + H^+ \tag{5}$$

$$N_2H_2^\bullet \rightarrow N_2H^\bullet + e^- + H^+ \tag{6}$$

$$N_2H^\bullet \rightarrow N_2 + e^- + H^+ \tag{7}$$

R_nPcCo represents the different Co phthalocyanines with n substituents R on the periphery of the ligand. The $N_2H_3^\bullet$ radical is electrooxidized in subsequent steps (5)–(7) to give nitrogen as the final oxidation state of N_2H_4.

Ma et al. [52] found that though nickel phthalocyanine-tetrasulfonic acid (NiPcTs) had no eletrocatalytic activity to methanol or CO electrooxidation through the cyclic voltammetry measurements, NiPcTs could enhance the methanol oxidation reaction (MOR) on the NiPcTs modified Pt/C catalyst as NiPcTs promoted electrooxidation of adsorbed CO (CO_{ads}) on the Pt/C catalyst. The enhancement for MOR was also observed when using SnPc modified carbon-supported Pt catalyst as the MOR catalyst [53]. Wu et al. [54] attempted to use CuPc functioning with sulfonic groups to modify Pt catalyst. It was found that the MOR rate and poison tolerance of Pt catalyst could be significantly improved with the CuTsPc modification.

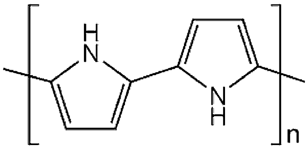


Fig. 7 The structure of polypyrrole

3 Polypyrrole (PPy)

Polypyrrole is a chemical compound formed from a number of connected pyrrole ring structures as shown in Fig. 7. In 1963, Weiss and co-workers [55, 56] found that oxidized iodine-doped PPy possessed high electric conductivity. They explained the effects of iodine doping on conductivity, the conductivity type (n or p), and electron spin resonance of polypyrrole. Due to its favorable electronic properties, environmental stability and fast redox switching, PPy has found many applications in batteries, electronic devices, functional electrodes, electrochromic devices, as well as optical switching devices and sensors [57].

3.1 PPy preparation

PPy is usually prepared by wet chemical methods. Plasma polymerization [58], chemical vapor deposition (CVD) [59], and metal mediated electrochemical methods [60] are also available to obtain electronically conductive polypyrrole.

In general, chemical processes are simpler to bulk PPy production. Chemical synthesis of PPy involves an oxidative polymerization route in which Fe^{3+}, Ag^{+}, Cu^{2+}, or I_2, Br_2, AsF_5 are used as oxidants [61–64]. It was reported that highly conductive PPy powders with good quality could be obtained when using Fe^{3+} as the oxidant. The conductivity of PPy prepared in the presence of anionic surfactant was higher than that of PPy prepared without using anionic surfactant [65]. Kudoh et al. [66] found that the sulfonic surfactant could be selectively incorporated into PPy as a dopant to improve the conductivity. When PPy was synthesized with a solution containing sulfonic surfactant and *p*-nitrophenol (*p*NPh), the obtained PPy demonstrated an enhanced conductivity and good anti-degradation capability.

Besides metallic ions with high chemical valence as the oxidants for PPy synthesis, Toshima and co-workers [67] used molecular oxygen as the oxidant to prepare PPy. After that, they found that Fe(III) catalyst together with molecular oxygen could be used to catalytically polymerize pyrrole to prepare PPy [68]. Dias and co-workers [69] suggested the use of hydrogen peroxide as the oxidant to synthesize PPy under catalysis of Fe^{3+} in an acidified aqueous medium. It was found that this route could produce PPy with high quality in a very good yield. The electric conductivity could reach up to 1 S cm^{-1}.

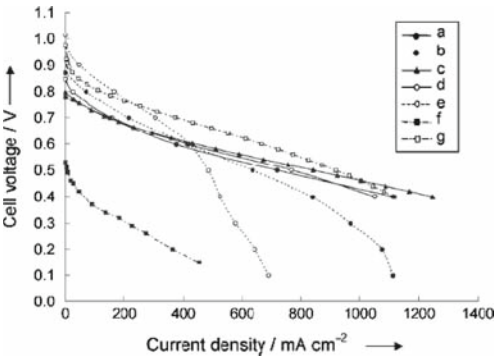
The electrochemical synthesis is a convenient method to prepare PPy nanowires and PPy films. Kim et al. [70] successfully prepared PPy nanowires through the electrochemical polymerization method by using Al_2O_3 nanoporous templates. Mokrane et al. [71] reported that well-adhering PPy films and Ge-doped PPy films could be obtained by anodic oxidation of pyrrole in acidic nitrate solutions.

3.2 PPy composite as the catalyst for fuel cells

Singh et al. [72] successfully prepared electronically conductive composite electrodes: G(graphite)/PPy/PPy($LaNiO_3$)/PPy on graphite for ORR by a sequential electrodeposition method. It was found that the electric conductivity of the composite electrode remained practically constant under the cathodic polarization condition. The electrocatalytic activity of $LaNiO_3$ toward ORR could be significantly improved by PPy modification. Bashyam and Zelenay [73] prepared the carbon-supported Co-incorporated PPy catalyst (Co-PPy-C composite) as the catalyst for ORR in the PEMFC. It was found that the synthesized Co-PPy-C composite demonstrated a high ORR activity without any noticeable loss in performance over long operating time. A power density of 80 mW cm^{-2} was achieved with Co loading of 6.0×10^{-2} mg cm^{-2} at operation temperature of 80 °C.

Yuasa et al. [74] and Qin et al. [75] reported that Co-PPy-C can be used as the electrocatalysts in alkaline medium. Co-PPy-C catalysts demonstrated fairly good electrocatalytic activity for the four-electron reduction of O_2, and good performance stability [74, 75]. It was reported that a maximum power density of 65 mW cm^{-2} was achieved at ambient conditions by the DBFC [75]. In the fuel cell using alkaline hydrazine solution as the fuel, the cell power density had reached up to 500 mW cm^{-2} at 80 °C as shown in Fig. 8 [76]. Li and co-workers [77] found that the PPy modified carbon-supported cobalt hydroxide ($Co(OH)_2$-PPy-C) catalyst showed a smaller electrochemical polarization than the $Co(OH)_2$-C catalyst because PPy modification improved the electric conductivity of the electrode. It was found that $Co(OH)_2$-PPy-C had good short-term durability as the electrode catalysts in the DBFC as shown in Fig. 9 [77]. A maximum power density of 83 mW cm^{-2} was achieved at 0.6 V under ambient conditions.

PPy can be used to modify not only the cathode catalysts but also the anode catalysts. Rajesh et al. [78] reported that the Pt deposited on PPy nanotubes demonstrated good activity and performance stability. It was found that methanol could be electrooxidized on the synthesized catalyst with high performance and stability though the Pt loading was decreased. Feng et al. [79] prepared micro-electrodes mediated by polypyrrole/Nafion composite film. The PPy/



Cell configuration

	Anode	Cathode	Electrolyte
a	Ni	Ag/C	Anion A
b	Ni	Ag/C	Anion B
c	Ni	Co-PPY-C	Anion A
d	Co	Ag/C	Anion A
e	Co	Ag/C	Anion B
f	PtRu/C	Ag/C	Nafion
g	Pt/C	Ag/C	Nafion

Fig. 8 Current–voltage performance of direct fuel PEFCs (cell temperature: 80 °C). Hydrazine was dissolved (0.67 M) in 1 M KOH aqueous solution and supplied at 2 mL min^{-1}. (*a*–*e*) Hydrazine (+20 kPa), (*f*) methanol (+100 kPa), (*g*) hydrogen (+20 kPa) [76]

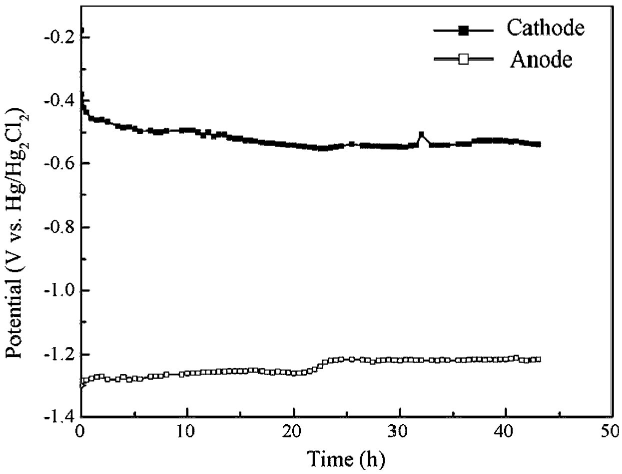


Fig. 9 Polarization stabilities of the anode and cathode of Co(OH)$_2$-PPY-C at a current density of 50 mA cm^{-2} under ambient conditions. Cathode: Co(OH)$_2$-PPY-C loading is 10 mg cm^{-2}, dry O_2 at a flow rate of 150 mL min^{-1} (1 atm.). Anode: Co(OH)$_2$-PPY-C loading is 10 mg cm^{-2}, 5 wt% of NaBH$_4$, 10 wt% of NaOH solution at a fuel flow rate of 10 mL min^{-1}. Membrane: N117 [77]

Nafion composite film could provide good electron and proton conductivity so that electrochemical reaction area and catalyst utilization were increased. The corresponding Si-based micro membrane–electrode-assembly demonstrated good cell polarization characteristics. A power density of 23.4 mW cm^{-2} was achieved at ambient conditions.

4 Other macrocyclic compounds

It was reported that Fe tetramethoxyphenyl porphyrin (FeTMPP) could be used as a cathode catalyst for the DMFC and H_2/O_2 fuel cells in acid medium [80, 81]. FeTMPP also showed reasonably high activity toward ORR, high borohydride tolerance (low activity for borohydride oxidation) and acceptable performance stability in the DBFC [82]. MoTMPP had a similar effect on the improvement of the CO tolerance in the PEMFC [83].

In general, MN$_4$ macrocyclics are poor catalysts for methanol oxidation so that methanol has little influence on ORR at cathodes in the DMFC. Lamy and co-workers [84] studied the catalytic activity of carbon-supported Co-tetraazaannulene (CoTAA) embedded in a cast Nafion film. It was found that its activity for ORR is not affected by the presence of methanol.

Like PPy, PANI functions as an electric conductor. It was reported that Pt dispersed in a piece of PANI film was a better catalyst than bulk platinum for methanol electro-oxidation [85]. The enhanced electrocatalytic activity may be brought by the homogeneous dispersion of Pt particles in the PANI film matrix, and the synergistic effects between the dispersed Pt particles and the PANI film. Santhosh et al. [86] prepared gold nanoparticles dispersed onto a PANI-grafted multi-wall carbon nanotube (MWNT-g-PANI) matrix through an electrochemical process. The results showed that Au nanoparticles dispersed into PANI-grafted MWNTs exhibited enhanced electrocatalytic activities for methanol oxidation, high resistance to CO poisoning, better oxidation kinetics, and thus good performance at elevated temperatures.

5 Heat treatment

Macrocyclic compounds are pyrolyzed when heating to higher temperatures. It is known that heat treatment changes the characteristics of macrocyclic compounds and alters particle size, morphology, active sites. These changes then significantly influence the electrocatalytic activity. The pyrolysis temperature is one of the most critical factors in affecting the electrocatalytic activity. It was found that FePc would convert from α-FePc phase to β-FePc phase after being heat treated at 450 °C. The α-phase displayed an overpotential toward ORR 100 mV lower than the β-phase [87]. If the catalyst was heated to higher temperatures, metallic particles would be formed and growth of metallic particles would occur. The bulk N content decreased with increasing the pyrolysis temperature but no loss of metal element occurred [88]. Maldonado et al. [89] reported that pyrolysis of FePc on nickel substrates could produce carbon nanofiber existing in aligned bundles. The electrodes made from pyrolyzed FePc demonstrated significant electrocatalytic activity in aqueous KNO_3 solutions at neutral to basic pH for the reduction of O_2 to HO_2^-. They considered that the disorder in the graphite fibers and the presence of exposed edge plane defects and remained nitrogen were important factors for enhancing electrocatalysis toward ORR.

Fabjan [90] and Seeliger [91] reported that carbon-supported polypyrrole layers impregnated with a transition metal salt solution gave enhanced electrocatalytic properties after heat treatment. It was found that a metal salt, a nitrogen donor and a carbon support were required to prepare active catalysts. Bouwkamp-Wijnoltz et al. [8] pointed out that the active sites formed by reaction of the metal salt, nitrogen donor and carbon support were the same as those formed during heat treatment of a cobalt porphyrin on carbon. In both cases, a so called CoN_4 site might be formed and acted as the electrocatalytic site. Artyushkova et al. [92] studied the effect of heat treatment on the partial decomposition of the porphyrin macrocycle ring. It was found that pyrolysized electrocatalysts obtained from cobalt porphyrins such as CoTMPP or cobalt tetraphenyl porphyrin (CoTPP) would create a nano-composite of highly dispersed pyropolymer with some remaining N (x)-centers inserting into a graphite-like matrix after heat treatment. Some cobalt was distributed as Co^{2+} associating with N_4-centers. The remaining cobalt existed as crystallites of metallic Co. A thin layer of CoO was coated on these metallic cobalt phases. The structure of the employed precursor would strongly influence the chemical structure of the pyrolyzed product. The TPP-based catalysts demonstrated a higher degree of graphitization. However, TMPP-derived electrocatalysts consisted of a higher content of nitrogen in pyrrolic form as a part of the pyropolymer catalyst matrix.

Weng et al. [93] studied the electrocatalytic activities of carbon-supported CoPc catalysts pyrolysized at different temperatures through ToF-SIMS analysis coupled with XPS and TEM. The most active CoPc/C catalyst for ORR was obtained after pyrolysis at 600 °C under an inert atmosphere for 2 h [94]. Detailed studies [95, 96] showed that the SIMS intensities of Co^+ and all other Co-containing organic fragments decreased with increasing pyrolysis temperature. The formation of Co metal and/or Co-containing fragments was responsible for catalytic activity enhancement in the temperature range of 600–700 °C. Ladouceur et al. [95] investigated the influence of pyrolysis temperature on the electrocatalysis of CoPc from 300 to 1,150 °C. It was found that the best catalysts for ORR can be obtained when CoPc was pyrolyzed at a temperature ranging from 700 to 950 °C. For the pyrolyzed catalyst, the increase in activity compared with that of the unpyrolyzed material was related to the decomposition of the phthalocyanine ring and the formation of small metallic Co particles. After pyrolyzing the carbon-supported CoPc catalyst, no direct correlation between the N content and the activity for O_2 reduction was found. It was considered that CoPc might provide a route to scatter metallic Co clusters on the carbon substrate, whereas this could hardly be achieved by the conventional catalyst preparation method. Alves et al. [96] also confirmed that the maximal electrocatalytic property was obtained by heat treating CoPc at 850 °C due to the formation of tiny metallic cobalt during the heat treatment. The smaller cobalt clusters were formed, the higher the activity could be obtained. XANES measurements confirmed that CoN_4 centers and nitrogen atoms were no longer detected after the heat treatment.

Zhang et al. [97] prepared ORR catalysts through heat treatment of carbon-supported cobalt triethylenetetramine chelate in an inert atmosphere. For a H_2–O_2 fuel cell system, the maximum output power density reached 162 mW cm^{-2} at 25 °C with non-humidified reaction gases as shown in Fig. 10. It was found that the nano-metallic face-centered cubic (fcc) α-Co phase was embedded in the graphitic carbon after pyrolysis.

It is worth mentioning that heat treatment is also effective to transition metal cyanide complexes on carbon [98]. It was found that the cyanide structure was decomposed when heating over 500 °C and oxidation states of cobalt and iron were close to metallic ones. Two types of nitrogen bonding existed in the pyrolyzed samples. The combination of cobalt and iron incorporated at neighboring sites provided a catalytic activity comparable to the

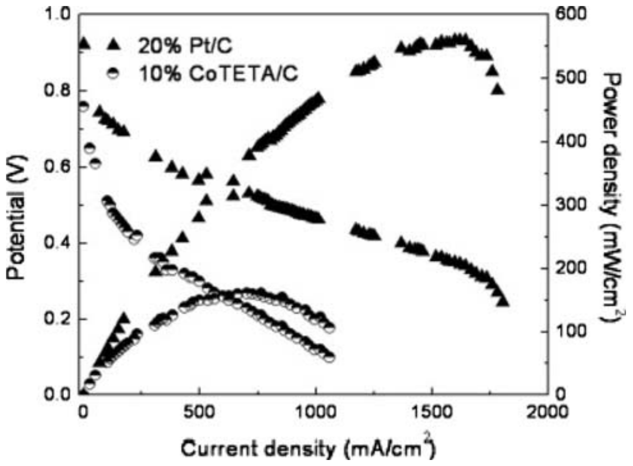


Fig. 10 Electrochemical performance of H_2–O_2 PEMFCs based on a CoTETA/C catalyst. Operation conditions: $T_{cell} = 25$ °C. Flow rates of hydrogen and oxygen are at 200 and 250 mL min^{-1}. Anode and cathode reaction gases are not humidified [97]

platinum black catalyst for ORR. The catalytic activity of the prepared sample was not affected by the presence of methanol in the electrolytes over a wide range of pH.

6 Conclusions

The earlier studies about macrocyclic compounds as electrocatalysts were limited in fundamental researches such as cyclic voltammetry. Many research works were focused on nitrogen containing macrocyclic compounds. It is considered that MN_4 sites in metallophthalocyanines of macrocyclic compounds are the active centers for electrochemical reactions. π-conjugated polymers such as PPy and PANI are usually used as a conductive material to enhance the electrocatalytic activity of the electrocatalysts such as Co and $Co(OH)_2$ in fuel cells. However, there are few reports related to the π-conjugated polymer itself as the electrocatalyst.

The reported results indicate that macrocyclic compounds or their modified catalysts are very promising candidates to substitute Pt as the electrocatalysts for fuel cells. It is worth mentioning that these catalysts not only exhibit considerable electrocatalytic properties for ORR, but also demonstrate a high resistance against fuel crossover in fuel cells.

Heat treatment is an effective method to improve the electrocatalytic activities of macrocyclic compounds or macrocyclic compound modified catalysts. The pyrolysis temperature is one of the critical factors affecting the ORR activity. Though the mechanism of the ORR activity improvement through heat treatment is still not clear, it is considered that the formation of metallic clusters or metal containing organic fragments (CoN_4 site) plays an important role in enhancing the ORR activity. Macrocyclic compounds may be functioned as a precursor to provide a method to obtain well-distributed metallic clusters or metal containing organic fragments which act as the catalytic sites.

In spite of these good results obtained with macrocyclic compounds whose electrocatalytic activities are comparable to Pt, rather few studies have paid their attention on the long-term performance stability for fuel cell applications.

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