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Review

# PEM fuel cell electrocatalysts based on transition metal macrocyclic compounds

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## Contents

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## ABSTRACT

This paper provides a comprehensive overview of the current state of development of transition metal macrocyclic (TMM) complex-based electrocatalysts used in oxygen reduction reactions (ORRs) in polymer electrolyte membrane fuel cells (PEMFCs).

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*Abbreviations:* APFP, (p-aminophenyl)-5,10,15,20(pentafluorophenyl)-porphyrin; CV, cyclic voltammetry; CNT, carbon nanotube; CoPP(s), Cobalt porphyrin(s); DCM, dichloromethane; DMSO, dimethylsulfoxide; DFT, density functional theory; DPX, 4,5-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]-9,9-dimethylxanthene; DWCNT, double-walled CNT; ERGO, electrochemical reduced graphene oxide; EDX, energy dispersive X-ray (spectroscope); FePP(s), iron porphyrin(s); GCE, glassy carbon electrode; GO, graphene oxide; LSV, linear sweep voltammetry; MCV, mesoporous carbon vesicle; MPP, 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine; MWCNT(s), multi-walled CNT(s); NHE, normal hydrogen electrode; RDE, rotating disk electrode; RGO, reduced graphene oxide; RRDE, rotating ring-disk electrode; OMC, ordered mesoporous carbon; ORR, oxygen reduction reaction; PANI, polyaniline; PBE, Perdew–Burke–Ernzerhof; PEMFC(s), polymer electrolyte membrane fuel cell(s); Pc, phthalocyanine; PP, porphyrin; Py, pyridine; RDE, rotating disk electrode; RGO, reduced graphene oxide; SEM, scanning electron microscope; SWCNT(s), single-walled CNT(s); TAA, tetraaxaammlene; TBAP, tetrabutylammonium perchlorate; TFMSA, trifluoromethanesulfonic acid; TM, transition metal; TMM, transition metal macrocyclic (ligand); TMPc(s), transition metal phthalocyanine(s), also including MnPc(s), FePc(s), CoPc(s), NiPc(s), and CuPc(s); TMPP, tetramethoxyphenylporphyrin; TMPyP, meso-tetra(N-methyl-4-pyridyl) porphine chloride; TPFC, 5,10,15-tris(pentafluorophenyl) corrole; TPP, 5,10,15,20-tetraphenylporphyrin; TSPc, tetrasulfophthalocyanine; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

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Up to date performances of carbon material-supported TMM catalysts, including both ORR activity rates and stabilities are, discussed. The effects of different types and natures of metals, macrocyclic ligands, ligand substitutions, catalyst supporting materials, electrode preparation, and various acid/alkaline solutions are thoroughly analyzed and reviewed based on the published literature. The ORR mechanisms facilitated by these TMM catalysts are discussed from both a theoretical and experimental observation point of view. Required improvements in ORR activity, stability and commercial viability in order for TMM complex-based electrocatalysts to be utilized in PEMFCs are identified. Potential research directions to overcome current challenges are also suggested to facilitate future efforts in this area.

## 1. Introduction

Fuel cells, particularly polymer electrolyte membrane fuel cells (PEMFCs), are recognized as highly desirable energy-conversion devices and power sources for many applications – including automobiles and backup power. PEMFCs attractiveness stems from their high energy/power densities, high energy efficiency, and low/zero emissions. However, both an insufficient life-time and high initial cost are identified as the major challenges hindering their commercialization. These two challenges are both closely related to the low stability and high cost of electrocatalysts used for PEMFC cathode oxygen reduction reaction (ORR) and anode fuel (hydrogen or small fuels such as methanol, formic acid, and ethanol) oxidation reaction [1,2]. In the current state of technology, the most practical electrocatalysts for PEMFCs are Pt-based materials which are not only rare but also very expensive. To reduce catalyst cost, two strategies have been explored during the last three decades. One is to reduce the Pt loading, and the other is to replace Pt-based catalysts with non-noble metal catalysts [3–7]. Among the non-noble metal catalysts explored [8], transition metal macrocyclic (TMM) complexes and their pyrolyzed materials have attracted the most attention worldwide for PEMFC applications [9]. Since Jasinski found cobalt phthalocyanine (Pc) as a catalyst for ORR in 1964 [10], a large number of studies on ORR catalyzed by TMM complexes have been reported, including several review articles [11–18] and monographs [19,20]. Due to the rapid progress in this area, a comprehensive overview on recent achievements and issues related to TMM catalysts for ORR, was felt to be timely to facilitate future research and development planning.

Generally, TMM complexes can catalyze ORRs through three major pathways: (1) a two-electron transfer pathway to produce $H_2O_2$; (2) a four-electron transfer pathway to produce $H_2O$; and (3) a mixed pathway of two- and four-electron transfers to produce mixed $H_2O_2$ and $H_2O$ [21]. In rare cases, TMM complexes can also catalyze a one-electron $O_2$ reduction, producing superoxide ions [22]. The four-electron pathway to produce $H_2O$ is the most desirable in electrochemical devices such as fuel cells and metal-air batteries because it can avoid the production of $H_2O_2$ which degrades catalysts through chemical attack.

Regarding the electrochemical reactions during ORR, as described by Zagal et al. [23], both the two-electron and four-electron transfer ORR processes in aqueous solution can be expressed as follows:

Two-electron reduction pathway:

$$\text{In acidic}: O_2 + H_2O + 2e^- \rightarrow 2H_2O_2, \quad E_0 = 0.682\,\text{V(vs.NHE)} \qquad (1)$$

(NHE : normalhydrogenelectrode)

$$\text{In alkaline}: O_2 + H_2O + 2e^- \rightarrow HO_2^-, \quad E_0 = 0.065\,\text{V(vs.NHE)} \qquad (2)$$

Direct four-electron reduction pathway:

$$\text{In acidic}: O_2 + 4H^+ + 4e^- \rightarrow 2H_2O, \quad E_0 = 1.229\,\text{V(vs.NHE)} \qquad (3)$$

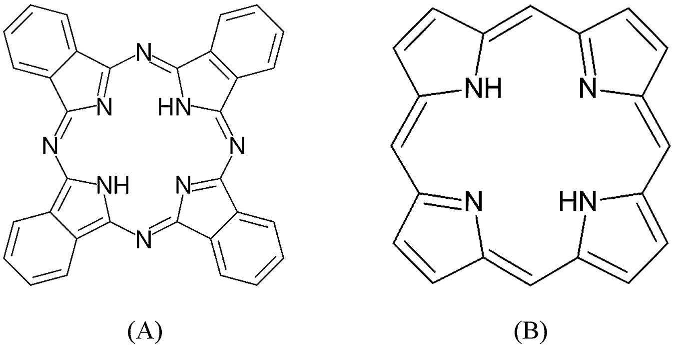

**Fig. 1.** Structural formula of phthalocyanine (Pc, A) and porphyrin (PP, B).

$$\text{In alkaline}: O_2 + 4H_2O + 4e^- \rightarrow 4OH^-, \quad E_0 = 0.401\,\text{V(vs.NHE)} \qquad (4)$$

Actually, for almost all ORR mechanisms catalyzed by TMM complexes, there are no pure two-electron or four-electron pathways. All mechanisms seem to be the mixed two- and four-electron pathways with either two-electrons or four-electrons dominating the pathway. For example, for the two-electron pathway described above by Reactions (1) and (2), the $H_2O_2$ formed could be further electrochemically reduced through Reactions (5) and (6) and chemically decomposed through Reaction (7):

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O, \quad E_0 = 1.77\,\text{V(vs.NHE)} \qquad (5)$$

$$HO_2^- + H_2O + 2e^- \rightarrow 2OH^-, \quad E_0 = 0.867\,\text{V(vs.NHE)} \qquad (6)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (7)$$

Normally, transition metals (TMs) refer to the elements within groups 3–12 in the periodic table of elements. These elements have incomplete penultimate electron shells, and tend to exhibit more than one valence when forming complexes. For forming TMM catalysts for use in ORRs, the following non-noble TMs, involving Fe and Co [12,15,24–30], Ti(O) [31], V [30], Man [32], Ni [25,30,33,34], Cu [30,35,36], Zn [30], and Mo [37] are identified as the main metals in the literature.

Regarding the complex ligands, Pc, porphyrin (PP), and their derivatives are two large classes of macrocyclic ligands which have been well explored, as shown in (Fig. 1) [15]. It can be seen four nitrogen atoms ($N_4$) are the chelating group to coordinate the central metal ion for the TMM complex formation. For a given central ion, the order of ORR activity catalyzed by those TMM complexes is strongly affected by the nature and the electron density of the ligand systems. Beside nitrogen chelating groups, other groups containing oxygen and sulfur have also been observed to form TMM complexes which show ORR activity. For example, Alt et al. [38] tested $N_4$ complexes (tetraarylporphyrins, dibenzotetraazaannulenes, and Pcs as ligands), $N_2O_2$ complexes (Pfeiffer complexes),