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Review

# Metalloporphyrins and related metallomacrocycles as electrocatalysts for use in polymer electrolyte fuel cells and water electrolyzers

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ABSTRACT

Metal complexes of $N_4$-macrocycles such as porphyrins and phthalocyanines have been studied for several decades as alternatives to Pt catalysts in polymer electrolyte fuel cells (PEFCs) and polymer electrolyte membrane (PEM) water electrolyzers. This review mainly describes the recent development of these catalysts for use in anode and cathode of PEFCs and PEM water electrolyzers. Performance of the developed catalysts and strategies of the development are summarized. This review aimed to discuss the advantages and disadvantages of the metallomacrocycle-based catalysts compared to conventional Pt electrocatalysts, and to emphasize their functions that the Pt catalyst does not have.

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## 1. Introduction

### 1.1. Non-PGM electrocatalysts use in polymer electrolyte fuel cells (PEFC) and water electrolyzers

Fuel cells and water electrolyzers are important technologies for addressing global concerns about the environment and energy. Fuel cells achieve the highly efficient generation of electricity based on the electro-oxidation of fuels (mainly $H_2$), and water electrolyzers can generate $H_2$ under the application of electricity. If $H_2$ can be generated from renewable energy sources such as wind or sunlight, the combination of fuel cells and water electrolyzers may lead to the realization of a zero-emission society. These two technologies could help to reduce $CO_2$ emissions and save energy. Especially, polymer electrolyte membrane (PEM) technology has a wide variety of applications since it works at low temperatures (<100 °C) and can be used in a start-stop manner. Polymer electrolyte fuel cells (PEFCs) can be used in vehicles and stationary applications, and a PEM electrolyzer can realize high-throughput $H_2$ production with a compact size.

These devices can contribute to the reduction of $CO_2$ emission only if they can be made highly efficient. Unfortunately, some electrochemical reactions in these devices are sluggish at low temperatures (<100 °C); they need significant overpotentials. For example, the cathode reaction ($O_2$ reduction reaction, ORR) of PEFCs and the anode reaction ($O_2$ evolution reaction, OER) of PEM electrolyzer require a large overpotential. Such large overpotentials prevent highly efficient energy conversion.

Electrocatalysts that significantly reduce overpotentials are needed to attain high efficiency. Platinum group metal (PGM)-based electrocatalysts have been used for this purpose since they have high stability and high activity in various electrochemical reactions. The superiority of Pt catalysts is evidenced by the realization of PEFCs that use Pt electrocatalysts in both the anode and cathode. A stationary PEFC system (so-called ENE-FARM) was commercialized in 2009, and fuel cell vehicles (FCV) powered by a PEFC were put on the market in 2014. PGM catalysts are also used at both the anode and cathode in the PEM type water electrolyzers to realize a high rate of $H_2$ generation per volume.

However, PGM electrocatalysts are not perfect, and they have several drawbacks. First, the cost and scarcity of PGM limit the widespread application of PEFCs and PEM-type water electrolyzers, which use a large amount of Pt catalysts to drive a sluggish ORR in PEFCs and OER in PEM electrolyzers. Second, while Pt catalysts are very active for the electro-oxidation of $H_2$, they are not particularly active for the oxidation of other fuels such as alcohols, sugars, and ammonia. This limits the fuels that can be used in PEFCs. Third, the high reactivity of Pt catalysts means that they have little selectivity for various electrochemical reactions. Pt catalysts sometimes cause undesirable reactions. Finally, Pt catalysts are easily poisoned by a wide variety of compounds, including CO, $H_2S$, and $NH_3$. Hence, fuels have to be extremely purified for use in PEFCs.

The disadvantages of Pt catalysts have prevented the wide spread of PEFCs and PEM electrolyzers, and this has encouraged researchers in a wide range of fields to develop alternative electrocatalysts. Metallocomplex-based electrocatalysts are some of the most promising non-Pt catalysts in terms of activity, cost and suitability for mass production. Among them, transition metal complexes of $N_4$-macrocycles such as porphyrins and phthalocyanines have been most intensively studied regarding their use in fuel cells. Since the first report by Jasinski [1], there has been a tremendous amount of researches on the ORR activity of metallomacrocycles [2–16]. The following two sections explain the reason why metallocomplexes (or metallomacrocycles) have attracted such interest as alternative catalysts.

### 1.2. Pros and cons of metallocomplex-based catalysts

Metallocomplex-based electrocatalysts have several advantages compared to Pt-based conventional electrocatalysts as follows:

(1) *Low cost of metal:* In metallocomplex-based electrocatalysts, the active site is formed by a single atom. Thus, the use of noble metals can be minimized. When a metal atom is a non-noble element, it can cost much less than the Pt-based electrocatalysts. Limitations due to the scarcity of PGMs are counteracted.
(2) *New reactivity:* The electronic states of metallocomplex-based electrocatalysts are totally different from those of Pt-based electrocatalysts. Thus, they can catalyze interesting electro-oxidation/reduction reactions that cannot be catalyzed by Pt-based electrocatalysts.
(3) *Tuning of catalysts:* In metallocomplex-based catalysts, the electronic state of the metal center can be modulated by the ligand structure. The environment around the reactants adsorbed on the central metal can be tuned by the ligand design. The possibility of fine tuning of the catalyst is an important property that is not available with Pt catalysts.
(4) *High selectivity*: Metallocomplex-based electrocatalysts may be more selective than Pt-based catalysts. Pt catalysts can catalyze a wide variety of reactions, and hence they exhibit low selectivity. This low selectivity sometimes leads to a loss of energy. For example, crossover methanol is oxidized on cathode Pt catalysts and decreases cathode potentials in direct methanol fuel cells (DMFCs). Metallocomplex-based materials have been investigated as methanol-tolerant cathode catalysts [13].

While metallocomplex-based electrocatalysts have several advantages, some significant disadvantages have prevented the wider application:

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