



Molecular catalysis of the oxygen reduction reaction by iron porphyrin catalysts tethered into Nafion layers: An electrochemical study in solution and a membrane-electrode-assembly study in fuel cells

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HIGHLIGHTS

- ▶ There exists ionic interaction between sulfonic groups of Nafion and FeTMPyP.
- ▶ The half wave potential value ($E_{1/2}$) for FeTMPyP was positively shifted by modifying the electrode with Nafion.
- ▶ Fuel cell molecular catalysis system has been demonstrated to be working based on a FeTMPyP + Nafion ionomer-coated cathode.

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ABSTRACT

This study was motivated by the need for improved understanding of the kinetics and transport phenomena in a homogeneous catalyst system for the oxygen reduction reaction (ORR). Direct interaction between the sulfonic groups of Nafion and an Fe(III) meso-tetra(*N*-methyl-4-pyridyl) porphine chloride (Fe(III)TMPyP) compound was observed using FTIR and *in situ* UV–Vis spectroelectrochemical characterizations. A positive shift of the half wave potential value ($E_{1/2}$) for ORR on the iron porphyrin catalyst (Fe(III)TMPyP) was observed upon addition of a specific quantity of Nafion ionomer on a glassy carbon working electrode, indicating not only a faster charge transfer rate but also the role of protonation in the oxygen reduction reaction (ORR) process. A membrane electrode assembly (MEA) was made as a sandwich of a Pt-coated anode, a Nafion® 212 membrane, and a Fe(III)TMPyP + Nafion ionomer-coated cathode. This three-dimensional catalysis system has been demonstrated to be working in a H₂/O₂ proton exchange membrane (PEM) fuel cell test.

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1. Introduction

Widespread commercialization of proton-exchange-membrane fuel cells (PEMFCs) is dependent on its component costs and the attainment of an optimum balance between performance and durability [1,2]. In particular, the use of platinum-based electrocatalysts remains a major issue for commercial introduction due to the scarcity of platinum and price pressures due to increasing demand [3,4]. Another serious catalyst-related problem is the voltage loss resulting from sluggish kinetics at the oxygen reduction electrode. Overpotentials as large as several hundred mV, which result from poor oxygen-reduction reaction (ORR) kinetics on carbon-supported Pt catalysts, limit the rate of energy

conversion in PEMFCs [5]. The energy associated with this voltage loss is converted to heat, which must be removed through a complex heat management system that causes particular difficulties for transportation uses where the presently available radiators are inadequate.

There is, therefore, strong motivation to examine alternative, less-expensive, non-platinum catalysts that may actually perform better than platinum. Currently available non-platinum group metal (PGM) electrocatalysts can be broadly classified into pyrolyzed metal macrocycles with metal-N_x reaction centers [6–8], first-row transition metal-based chalcogenides [9–13], and electron-conducting polymer-based structures [14–16]. The so-called “acid stability” criterion has so far necessitated the transition metal reactive sites to be safely ensconced within a protective shell provided by ligands, chalcogens, etc., to prevent them from dissociation and dissolution. Non-noble transition metal-based

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