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Effects of Redox Mediators on the Catalytic Activity of Iron Porphyrins towards Oxygen Reduction in Acidic Media

Qinggong He,^[a] Gang Wu,^[b] Ke Liu,^[c] Samson Khene,^[d] Qing Li,^[b] Tawanda Mugadza,^[e] Elise Deunf,^[f] Tebello Nyokong,^[d] and Shaowei W. Chen^{*,[c]}

The effects of different redox mediators on the oxygen reduction reaction (ORR) catalyzed by an iron porphyrin complex, iron(III) *meso*-tetra(*N*-methyl-4-pyridyl)porphine chloride [Fe^{III}TMPyP], in 0.1 M triflic acid were investigated by cyclic voltammetry (CV) and spectroelectrochemistry in conjunction with density functional theory (DFT) calculations. The formal potentials of the Fe^{III}TMPyP catalyst and the redox mediators, as well as the half-wave potentials for the ORR, were determined by CV in the absence and presence of oxygen in acidic solutions. UV/Vis spectroscopic and spectroelectrochemical

studies confirmed that only the 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)diammonium salt (C₁₈H₂₄N₆O₆S₄) showed effective interactions with Fe^{III}TMPyP during the ORR. DFT calculations suggested strong interaction between Fe^{III}TMPyP and the C₁₈H₂₄N₆O₆S₄ redox mediator. The redox mediator caused lengthening of the dioxygen iron bond, which thus suggested easier dioxygen reduction. Consistent results were observed in electrochemical impedance spectroscopic measurements for which the electron-transfer kinetics were also evaluated.

1. Introduction

The recent surge of interest in non-noble-metal porphyrin and phthalocyanine catalysts has been prompted by their potential to replace Pt as cathodic catalysts in polymer electrolyte membrane fuel cells (PEMFCs).^[1–3] However, to realize the apparent benefits of the metal–N-coordinated catalysts in high-power fuel cells, advances in catalyst design and synthesis are required to produce catalysts with high turnover rates,^[4] and methods of incorporating molecular catalysts into membrane electrode assemblies must be developed. With these advances, the site density can be increased to levels that support high

current densities. One approach is to build a 3D, molecular polymer redox layer on the electrode surfaces.^[5] The polymer redox layer includes a molecular catalyst, and this structure results in full access to all species (electrons, protons, and substrates) with increased reaction rates. In our previous studies,^[1,5,6] we proposed a polymer redox film having a non-noble-metal complex impregnated with Nafion as a new cathode catalyst layer for PEMFCs. In particular, a non-noble-metal catalyst (metal porphyrins) binds with the sulfonic acid sites of Nafion to form a 3D molecular catalyst, and the polymer redox film is attached to the electrode surface.

In the above system, the electrons are transported from the electrode through the catalytic sites, whereas the protons/oxygen atoms migrate along with the hydrophilic domains of Nafion. The water molecules produced by electrochemical reactions move to the polymer surface to form a parasitic liquid water layer. Note that the metal porphyrin complexes are chemically bonded with the sulfonic acid sites of Nafion, and the catalyst is unlikely to migrate. In general, the electron movement is slow among the separate metallic sites, which may be facilitated by the addition of redox mediators with shuttling motions among the active catalytic sites.

In addition to the intrinsic activity of the catalysts for the oxygen reduction reaction (ORR), redox mediators (RMs) also play a crucial role in effective charge transfer.^[7] As such, it is important to understand the kinetics of the ORR in the proposed 3D molecular catalyst with suitable RMs. Herein, the effects of RMs on the ORR were tested by using cyclic voltammetry in a homogeneous catalytic system by employing a water-soluble metal macrocycle compound (iron porphyrin) in a triflic acid solution to mimic the 3D catalyst layer. Surprisingly, (dimethylaminomethyl)ferrocene did not show any enhancement for

[a] Dr. Q. He

Department of Molecular & Medical Pharmacology
University of California
Los Angeles, CA 90095 (USA)
E-mail: QHe@mednet.ucla.edu

[b] Dr. G. Wu, Dr. Q. Li

Materials Physics and Application Division
Los Alamos National Laboratory
Los Alamos, NM 87545 (USA)

[c] K. Liu, Prof. Dr. S. W. Chen

Department of Chemistry and Biochemistry
University of California
1156 High Street, Santa Cruz, CA 95064 (USA)
E-mail: shaowei@ucsc.edu

[d] Dr. S. Khene, Dr. T. Nyokong

Department of Chemistry, Rhodes University
P.O. Box 94, Grahamstown, 6140 (South Africa)

[e] Dr. T. Mugadza

Department of Chemical Technology
Midlands State University
P. Bag 9055, Gweru (Zimbabwe)

[f] Dr. E. Deunf

Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
1 Cyclotron Road, Berkeley, CA 94720 (USA)