Medium Effects Are as Important as Catalyst Design for Selectivity in Electrocatalytic Oxygen Reduction by Iron−Porphyrin Complexes

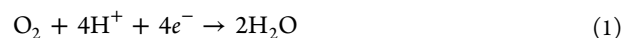Matthew L. Rigsby,[‡] Derek J. Wasylenko,[‡] Michael L. Pegis,[‡,§] and James M. Mayer*[,‡,§]

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S *Supporting Information*

ABSTRACT: Several substituted iron−porphyrin complexes were evaluated for oxygen reduction reaction (ORR) electrocatalysis in different homogeneous and heterogeneous media. The selectivity for four-electron reduction to H_2O versus two-electron reduction to H_2O_2 varies substantially from one medium to another for a given catalyst. In many cases, the influence of the medium in which the catalyst is evaluated has a larger effect on the observed selectivity than the factors attributable to chemical modification of the catalyst. For instance, introduction of potential proton relays has variable effects depending on the catalyst medium. Thus, comparisons of selectivity results from supported and soluble molecular ORR electrocatalysts must be interpreted with caution, as selectivity is a property not only of the catalyst, but also of the larger mesoscale environment beyond the catalyst. Still, in all the direct pairwise comparisons in the same medium, the catalysts with potential proton relays have similar or better selectivity for the preferred $4e^-$ path.

Figure 1. Electrocatalysts used in this study.

The oxygen reduction reaction (ORR) is a critical cathodic half reaction in clean energy technologies such as fuel cells.[1] One of the major challenges of ORR catalysts is achieving high selectivity for the four-electron reduction of O_2 to water (eq 1) versus the two-electron reduction to hydrogen peroxide. The $2e^-$ pathway is deleterious because it results in lower cell voltages and because hydrogen peroxide can damage catalysts and membranes in a device.[2]

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (1)$$

An important goal of ORR research is to develop catalysts that use earth-abundant metals. Molecular catalysts and electrodes derived therefrom have been important research targets in the development of fundamental structure-activity relationships in the design of more effective molecular electrocatalysts.[3] The well-defined nature of the molecular complexes should in principle allow optimization of catalyst design to improve selectivity for the four-electron reduction. One strategy for molecular electrocatalysis for such proton/electron transfer reactions has been to employ acidic or basic functionalities (termed "proton relays") in the second coordination sphere of a metal ion. This approach has been principally explored with electrocatalysts for the hydrogenase reaction, $2H^+ + 2e^- \rightleftharpoons H_2$.[4] Biochemical O_2 reduction pathways

are known to be strongly affected by hydrogen bonding and proton delivery, especially in heme enzymes.[5] This has stimulated the development of many porphyrin and related model systems for O_2 binding, activation, and reduction.[5a,6]

This study compares ORR catalysis by five iron(III) (*meso*-tetra-arylporphyrin) chloride complexes (Figure 1) both in solution and confined at an electrode surface using different methods. We have recently reported a kinetic and mechanistic study of the tetraphenylporphyrin catalyst, abbreviated **Ph**.[7] Previously, we compared the two- and four-carboxyphenyl derivatives (**2-CO₂H** and **4-CO₂H**) in MeCN with [H-DMF][OTf] as the acid[8] and compared the two- and four-pyridyl-substituted analogs (**2-Py** and **4-Py**) in aqueous HCl or triflic acid.[9] In both cases, the catalyst with the proton relay in the 2-position, pointed toward the iron center, displayed higher selectivity for the four-electron ORR pathway relative to the four-substituted isomers. Those studies and the ones reported here determined the ORR selectivity primarily using rotating ring-disk voltammetry (RRDV). This was confirmed by H_2O_2 titration for the **Ph** catalyst[7] and indirectly by spectroelectrochemistry for the **2-CO₂H** catalyst.[8]

Comparisons among these electrocatalysts, and throughout the molecular ORR electrocatalysis literature, are complicated by the variety of conditions used. Our prior studies of the **2/4-CO₂H** and **2/4-Py** catalysts required different solvent systems because of the differing solubilities of the porphyrins.[8,9] Here we follow the more common approach to the study of molecular ORR electrocatalysts as insoluble films on an electrode in aqueous acid.[10] We have examined the ORR selectivity of the five Fe porphyrin catalysts in Figure 1 confined to electrode surfaces using three different techniques. Our results demonstrate that the ORR selectivity is strongly

influenced by factors other than the structure of the catalyst including the method of attachment to the electrode.

The Fe porphyrin complexes were immobilized on carbon electrodes using three methods commonly employed in the electrocatalysis literature: (i) a 1 mM solution of catalyst in 0.5% Nafion dropcast onto a glassy carbon (GC) working electrode (**Nafion** conditions); (ii) an ink of 1 mM catalyst in 0.5% Nafion with 2.5 mg/mL Vulcan carbon additive dropcast on GC (**Nafion/Carbon** conditions); and (iii) catalysts physisorbed on edge-plane pyrolytic graphite (EPPG) electrodes (**EPPG** conditions).

Electrodes were first evaluated in the three heterogeneous conditions with the parent tetraphenyl−porphyrin complex **Ph**. We use a notation to identify both the catalyst and its conditions, for example, **Ph-Nafion** indicates the **Ph** complex in **Nafion** conditions. Electrodes with **Ph-Nafion**, **Ph-Nafion/Carbon**, and **Ph-EPPG** exhibited strong catalytic currents on cathodic polarization in 0.1 M aqueous $HClO_4$ under 1 atm O_2. Much lower currents were seen with no catalyst under O_2 or with catalyst under N_2 (Figures S1 and S2 in the Supporting Information). The fact that large currents are observed only under complete ORR conditions (catalyst + O_2 + acid) demonstrates adhesion of the catalysts to the electrode surfaces and that ORR catalysis is the major component of the observed current.

ORR selectivity was determined by RRDV using a rotation rate of 900 rpm and a 0.1 M aqueous $HClO_4$ solution under 1 atm O_2. In these experiments, the functionalized disk electrode was scanned cathodically, while the Pt ring was held at 1300 mV versus NHE to oxidize any H_2O_2 formed.[11] Selectivity measurements were performed in triplicate using freshly prepared electrodes. Representative RRDVs are shown in Figure 2, with the ring currents scaled five-fold for clarity.

Analysis of the disc and ring currents (see Supporting Information) shows that the amount of H_2O_2 detected was 51% from **Ph-Nafion**, 27% from **Ph-Nafion/Carbon**, and 58% from **Ph-EPPG** (Table 1). This variation in selectivity does not simply correlate with the nature of the electrode film. For example, different selectivity was found for the two samples with Nafion, which should have higher local proton concentrations than the EPPG catalyst.[12] The differences in selectivity are not due to differences in the Nafion concentration, as the %H_2O_2 is the same for **Ph-Nafion/Carbon** inks containing 0.25−1% Nafion (Figure S3 and Table S1 in the Supporting Information). Both the **Ph-Nafion/Carbon** and **Ph-EPPG** catalysts have oxidizable carbon surrounding the catalyst that could conceivably intercept some of the H_2O_2 generated, but this similarity does not lead to similar observed selectivity.

The **Py** and **CO_2H** complexes were also evaluated in **Nafion**, **Nafion/Carbon**, and **EPPG** conditions. The results of these experiments, summarized in Table 1 and Figure 3, do not easily reveal a clear trend. In general, the **EPPG** conditions display the poorest selectivity (highest H_2O_2), though for **4-CO_2H**, this trend does not hold. In general, **Nafion/Carbon** displays better selectivity than **Nafion** alone, though in some cases (**2-Py** and **4-Py**), the two conditions are indistinguishable within error. The same molecular catalyst in different conditions shows differently shaped voltammograms (Figures S1−S7), and there are no obvious correlations between the observed ORR selectivity and the catalytic peak currents or onset potentials (Tables S2 and S3, Figures S8 and S9).
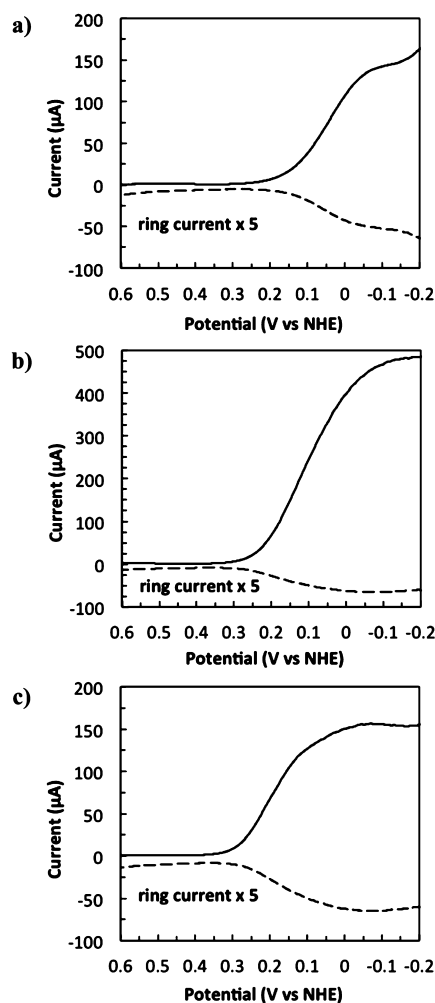

Figure 2. Rotating ring-disk voltammograms of heterogenized **Ph** complex in 0.1 aqueous M $HClO_4$, under 1 atm O_2, with a 900 rpm rotation rate. The disk electrode (solid line) was scanned cathodically at 20 mV/s, while the ring electrode (dashed line, ring current expanded five-fold for clarity) was held at 1300 mV versus NHE. (a) **Ph-Nafion**; (b) **Ph-Nafion/Carbon**; (c) **Ph-EPPG**.

Table 1. %H_2O_2 for ORR Electrocatalysis[a]

catalyst	homogeneous	Nafion	Nafion/Carbon	EPPG
Ph	15[b]	51 (2)	27 (2)	58 (5)
2-Py	~0[c]	25 (6)	20 (3)	51 (5)
4-Py	15[c]	28 (6)	36 (7)	56 (8)
2-CO_2H	<2[d]/ 6(3)[e]	32 (4)	18 (2)	35 (6)
4-CO_2H	9[d] / 11(5)[e]	56 (1)	36 (3)	43 (4)

[a]Values are %H_2O_2 at the ring electrode based on the observed currents (cf., Figure 2) and the experimentally determined collection efficiency. Values in parentheses are one standard deviation estimated from repeated experiments by a single investigator. Experiments with nominally equivalent procedures by a different investigator showed the same qualitative behavior but were not always in quantitative agreement. [b]Labels b−e indicate conditions of homogeneous RRDV electrocatalysis: 0.2 mM complex, DMF with 0.1 M [$^nBu_4N$][PF_6], 1 atm O_2, 20 mM [H-DMF$^+$][OTf$^-$] (see Supporting Information); [c]Aqueous 0.5 M KCl, 0.25 M HCl (ref 9); [d]99:1 MeCN:H_2O with 0.1 M [$^nBu_4N$][PF_6], 18 mM [H−DMF$^+$][OTf$^-$] (ref 8). [e]Same as b conditions with 0.5 mM catalyst.

A key question is how the complexes with the designed proton relays in the 2-position perform versus their
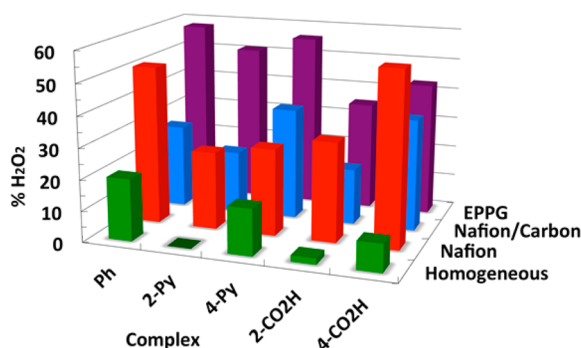
Figure 3. Selectivity of ORR catalysts in various environments. Table 1 gives the data and homogeneous conditions: DMF for **Ph**, aqueous HCl for **2/4-Py**, and MeCN for **2/4-CO₂H**.

corresponding 4-substituted isomers, **2-Py** and **2-CO₂H** versus **4-Py** and **4-CO₂H**. In the nine comparisons in Table 1, the catalyst with positioned relays has the higher $4e^-/4H^+$ selectivity in five cases, and the other four are indistinguishable within 2σ error. There is no example where the trend is reversed and the 4-isomer displays better selectivity. This includes the homogeneous cases (which are soluble and well-behaved only under limited conditions, see Supporting Information). Thus, the relays do appear to increase the selectivity for the $4e^-$ pathway under both heterogeneous and homogeneous conditions.

The magnitude of the selectivity enhancement for catalysts with proton relays is highly dependent on the preparation method for the heterogeneous catalysts. Measured differences range from significant (e.g., **Py** complexes in **Nafion/Carbon**) to indistinguishable (e.g., **Py** complexes in plain **Nafion** or adsorbed to **EPPG**). The conditions chosen for a particular study will thus greatly affect the conclusions of the resulting work. On the basis of these results, we broadly urge caution when interpreting selectivity trends of electrocatalysts. General conclusions must be tested across multiple immobilization methods and electrocatalysis conditions.

The results reported here contradict a common implied assumption in this field, including previously by our group, that the molecular catalyst is the primary determinant of the selectivity and activity of electrocatalysts using metal complexes. Our results indicate that the nature of the catalyst film on a carbon electrode, **Nafion** versus **Nafion/Carbon** versus **EPPG**, has an effect as large as changing the structure of the molecular catalyst. While large effects of preparation procedures and supports are commonplace for traditional solid-state ORR electrocatalysts,[13] one of the selling points of the study of molecular electrocatalysis is that they are well-defined. This study complements a recent report of the effects of different nanocarbons on directly adsorbed phthalocyanine and porphyrin ORR catalysts[14] and the discussion in a recent review of phthalocyanine electrocatalysts.[3b] These results show that organization of the surrounding medium beyond the metal complex, at the mesoscale, has a substantial role in catalysis. This is true even for catalysts with potential proton relays, which were designed to in part control the second coordination sphere. These conclusions create challenges for future catalyst design and perhaps opportunities as well.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Additional experimental details including electrode preparation, electrochemical methods, and voltammetry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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