

V.P.7 Cathode Catalysis in Hydrogen/Oxygen Fuel Cells: Mechanism, New Materials, and Characterization

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Objectives

The objective of this work is to develop an understanding of mechanisms of the Oxygen Reduction Reaction (ORR) and to use this understanding to develop new, non-precious metal containing catalysts for this reaction. A particular focus is to mimic the active site of laccase, a protein that performs near thermodynamic four electron reduction of oxygen to water.

Technical Barriers

The slow kinetics of the ORR have long been identified as a major impediment to the development of PEM fuel cells. Consequences of these slow kinetics include a substantial reduction in the thermodynamic efficiency of fuel cells and the requirement for considerable precious metal usage in practical implementations. Our work is directed to designing new materials that will exhibit low overpotentials without the use of expensive precious metal catalyst.

Abstract, Progress Report and Future Directions

Electrocatalysis of the oxygen reduction reaction (ORR) is currently of widespread interest due to its application in fuel cell cathodes.³ Slow ORR reaction kinetics significantly impact the efficiency of fuel cells, resulting in cell potentials well below (ca. 0.35 V)⁴ the reversible potential for oxygen reduction of 1.229 V vs. the reversible hydrogen electrode (RHE). These lower potentials substantially degrade fuel cell thermodynamic efficiency which obviate fuel cell use. The catalyst for the ORR is usually based on Pt or another precious metal, such as Pd. The costs associated with these

materials can be prohibitive. Thus, there is a search for non-precious metal ORR catalysts.

The focus of our research is to understand the mechanisms of the oxygen reduction reaction (ORR) on different electrode surfaces and then use that understanding to develop new catalysts which feature the use of materials other than Pt or other precious metals.

Substantial previous work from our group strongly suggests that the four electron reduction of oxygen in the electrochemical environment proceeds according to the so-called series mechanism in which dioxygen binds to the catalyst surface and then through a series of coupled proton electron transfers is reduced to the peroxide level. Coupling between two metal atoms then leads to spontaneous decomposition of the peroxide to form two metal hydroxides, as shown in Figure 1.² These hydroxides are then reduced, forming water in acid. This understanding leads us to expect that new catalysts exhibiting four electron ORR activity will feature at least two metal centers. Interestingly, the active site in the protein laccase, which exhibits four electron reduction of water at overpotentials substantially less than that found on Pt⁵ features three Cu atoms bound in close proximity to each other.⁶

The efficacy of laccase led us to wonder if Cu coordination complexes/polymers composed of Cu^{II} coordinated with bridging azole-type ligands, such as the 3,5-diamino-1,2,4-triazole (Hdartz) ligand (Figure 2),⁷ and with other weakly coordinated ligands (such as

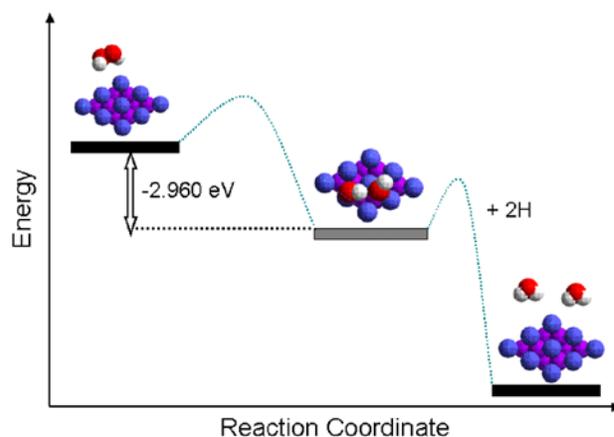


FIGURE 1. Proposed hydrogen peroxide reduction mechanism on the Cu(111) surface. The blue, purple, red, and white balls represent Cu surface atoms, bulk Cu atoms, O, and H atoms, respectively.²

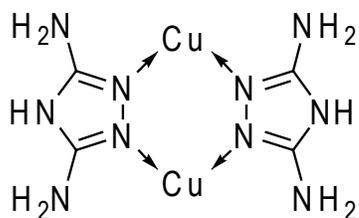


FIGURE 2. Schematic of the Hdartz/Cu interaction showing Cu dimer formation.¹

water, sulphate etc.) might provide stability in addition to multi-Cu sites that could potentially bind and activate O_2 . We developed a method to immobilize insoluble transition metal complexes on Vulcan and other carbons in order to evaluate their activity toward the ORR.¹ Figure 3 shows the activity of the coordination complex formed between Cu and Hdartz in neutral solutions. The figure shows that the onset of four electron ORR activity occurs at potentials significantly more positive than that afforded by the bare carbon. We found that both the Cu metal and the Hdartz ligand were necessary for ORR activity. Figure 4 shows the variation of the onset potential for ORR activity from electrodes modified by Cu and Hdartz. The figure shows that while the onset potential of the complex is low in acid, it increases as a function of pH and is quite high (850 mV vs. RHE) in basic electrolytes.

The structure of the Cu/Hdartz complex shows that Cu forms a dimer coordinated by two of the three heterocyclic nitrogens of the triazole moiety. We thought that suitable modification of the Hdartz ligand at the 4 position might afford a more positive onset

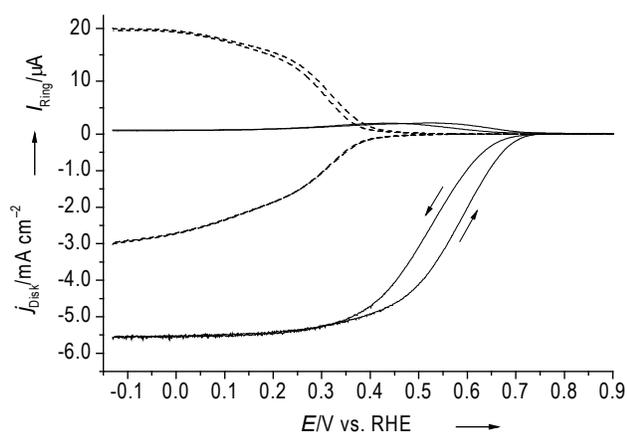


FIGURE 3. Reduction of O_2 at a rotating Pt ring-glassy carbon disk electrode supporting Cu(Hdartz)/Vulcan (solid line) or unmodified Vulcan XC-72 (dashed line) at 1600 rpm in 0.1 M $NaClO_4$ + 0.04 M Britton-Robinson Buffer (pH 7.0) saturated with O_2 . Disk potential scanned at 5 mV/s; ring potential constant at 1.2 V.¹

potential relative to the unmodified Hdartz ligand. The best derivative so far characterized in our group exhibits an onset potential some 150 mV more positive than that reported for the Cu/Hdartz

The performance of the Cu/Hdartz catalyst in basic electrolyte appeared good enough that we thought to compare it with Pt. Figure 5 shows a comparison of the maximum power density achieved by four different catalysts in the alkaline (pH 14) electrochemical environment. The figure shows that while Pt particles on C are still more active than any other catalyst examined here, the Cu/Hdartz sample is second most active, and considerably better than Ag; a material previously used in alkaline fuel cell applications. The comparison with Pt is more broadly made in Figure 6, which compares the peak power generated per metal atom. The Figure shows that the Cu/Hdartz sample is considerably better than Pt on a per metal atom basis. We are presently evaluating the stability of the Cu catalyst in both the alkaline and acidic environments. A full suite of synthetic and computational approaches is coupled to this project.

Future directions involve further exploration of the Cu dimer and trimer motifs for their efficacy in the ORR. Modification of the Cu catalyst we've developed through the agency of ligand synthesis allows for modification of properties and correlation of reactivity with structure.

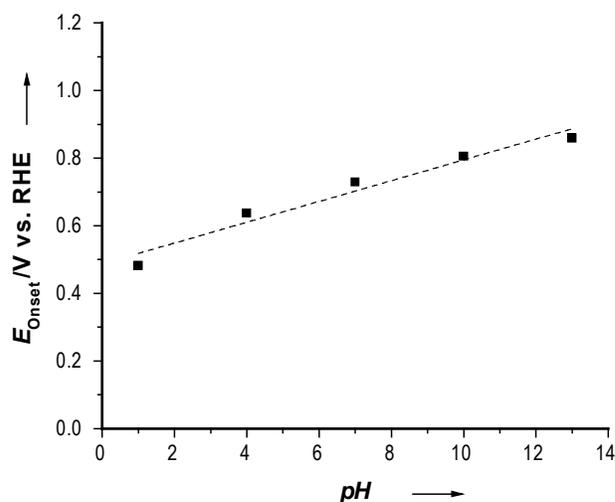


FIGURE 4. Potentials at which the onset of O_2 reduction occurs at electrodes modified with Cu(Hdartz) in electrolytes of varying pH and a linear fit (31 ± 4 mV per pH unit slope and 0.49 ± 0.03 V y-intercept). Electrodes were rotated at 1600 rpm in 0.1 M $HClO_4$; 0.1 M $NaClO_4$ + 0.04 M Britton-Robinson Buffers (pH 4, 7, 10); or 0.1 N $NaOH$ saturated with O_2 . Potential scanned at 5 mV/s. Onset potential chosen as the potential at which the current density reaches $-5 \mu A cm^{-2}$ which is ca. the most positive potential at which a non-zero current can be visually resolved on a full scale voltammogram.¹

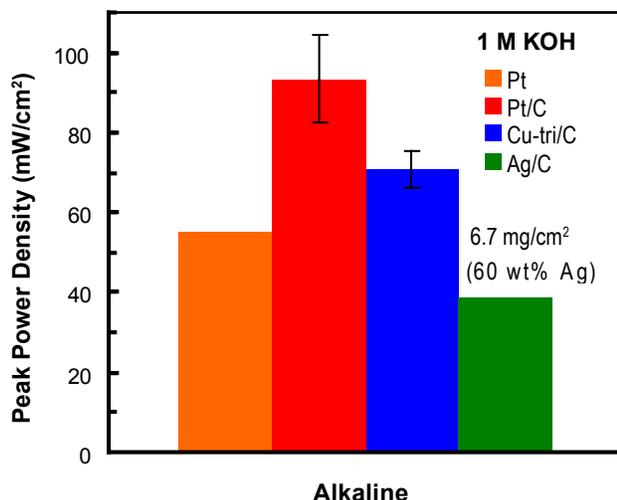


FIGURE 5. Comparison of peak power density from four different catalysts evaluated in this project. The Pt/C loading is 2 mg/cm².

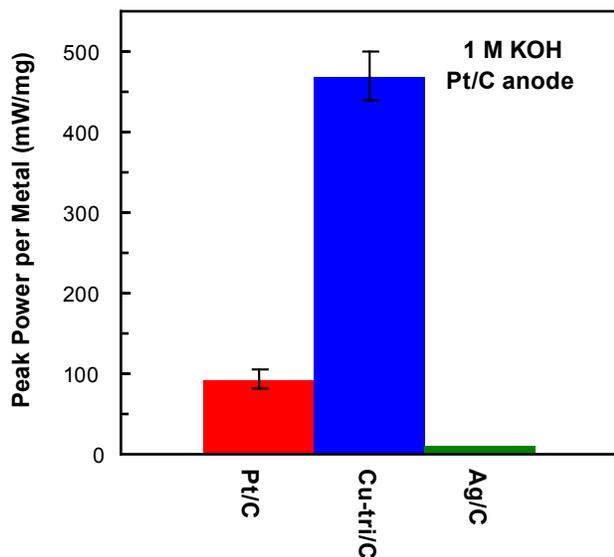


FIGURE 6. Comparison of peak power densities per metal atom for three different ORR catalysts.

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