

Electrocatalysis with Discrete Transition Metal Complexes

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Sponsor: Global Climate and Energy Project

Objective: Our project aims (1) to develop molecular electrocatalysts that can oxidize a variety of organic substrates and reduce molecular oxygen at low-temperature (2) to develop a method for site-isolated immobilization of the electrocatalysts on inexpensive, oxidatively-robust, high-surface-area carbon electrodes.

Background: The reactivity of molecular electrocatalysts can be tailored to a much higher extent than the currently available noble metal nanoparticle electrocatalysts. Design and synthesis of transition metal complexes capable of reversibly electrocatalyze oxidation of hydrocarbon fuels can also be used to generate liquid fuel when electricity is plentiful. Carbon electrodes with covalently immobilized electrocatalysts that can oxidize fuels and reduce oxygen will be used to build Polymer-Electrolyte-Membrane (PEM) fuel cells (Figure 1).

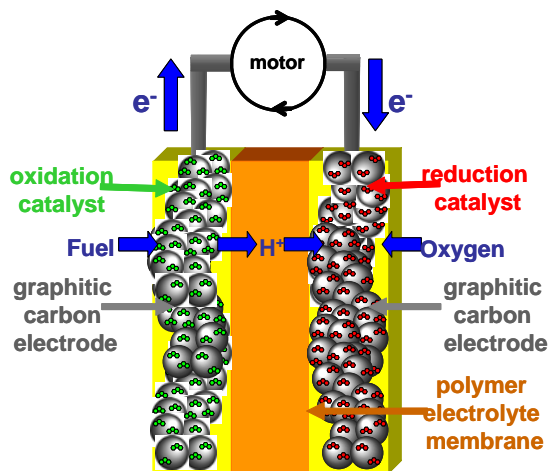


Figure 1: A schematic of PEM fuel cell with molecular catalyst modified electrodes

Approach: The project is divided into three parts focusing on 1) design and synthesis of palladium based molecular catalysts for oxidation of methanol and other hydrocarbons 2) design and synthesis of copper based molecular catalysts for reduction of oxygen 3) developing methods to covalently immobilize molecular catalysts on carbon electrodes in a site-isolated fashion.

1) Hydrocarbon oxidation:

In the pursuit of a low temperature hydrocarbon fuel cell, we have investigated several transition metal complexes for catalytic alcohol oxidation. The palladium complex **1** showed very fast initial rates (>0.04 turnovers \cdot s $^{-1}$) for aerobic alcohol oxidation at room temperature. However, the palladium complex also facilitated C-H activation and oxidation of the benzylic position of our neocuproine ligand, generating the corresponding benzoic acid complex **2**. This process while interesting, inhibits our catalytic cycle. Several methods have been pursued to

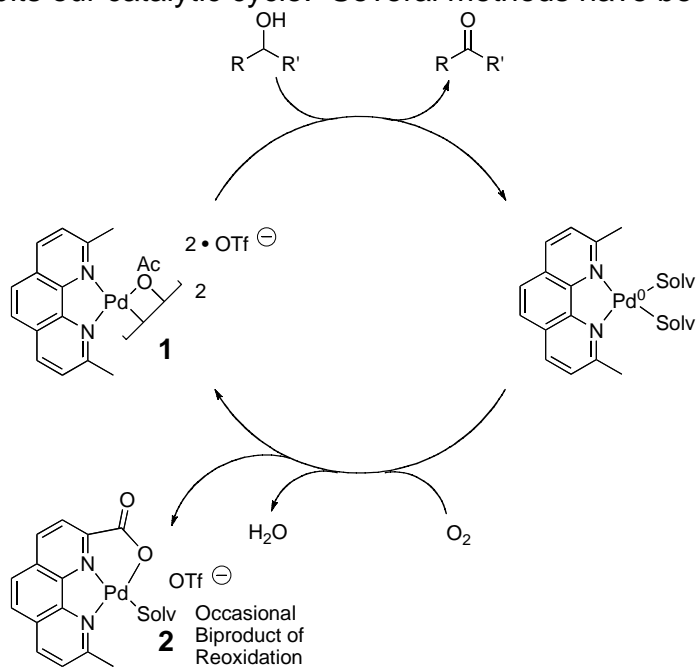


Figure 2: Catalytic scheme for alcohol oxidation

bypass this pathway, including the use of different terminal oxidants and ligands. The use of benzoquinone prolongs the life of the catalyst but also inhibits the catalytic cycle. Additionally, *tert*-butyl peroxide is a competent catalyst only at higher temperature. It is our hope that covalent attachment to an electrode will provide the ideal terminal oxidant, bypassing the formation of **2**, and extending the lifetime of our catalyst.

2) Oxygen reduction: Copper complexes of 1,10-phenanthroline (phen) derivatives have been shown to catalyze the four-electron reduction of O₂ to H₂O when adsorbed onto graphite surfaces.¹ Our initial work has involved the systematic modification of these copper complexes to study the effects of the ligand environment on the redox potential and rate of electrocatalytic O₂-reduction (Figure 3). We have shown that the magnitude of the overpotential of O₂-reduction (the potential energy lost in the reaction) decreased to -600 mV overpotential with turnover rates of 2.5 O₂ molecules per Cu-catalyst per second by altering the ligand environment of the phen-based copper catalysts. However, there is a potential limit at ~ -540 mV beyond which there is no expected catalytic behavior for mono-nuclear complexes of this type. Future work will focus on the

exploration of dinuclear copper systems which will operate with similar turnover rates closer to the thermodynamic potential of O₂-reduction.

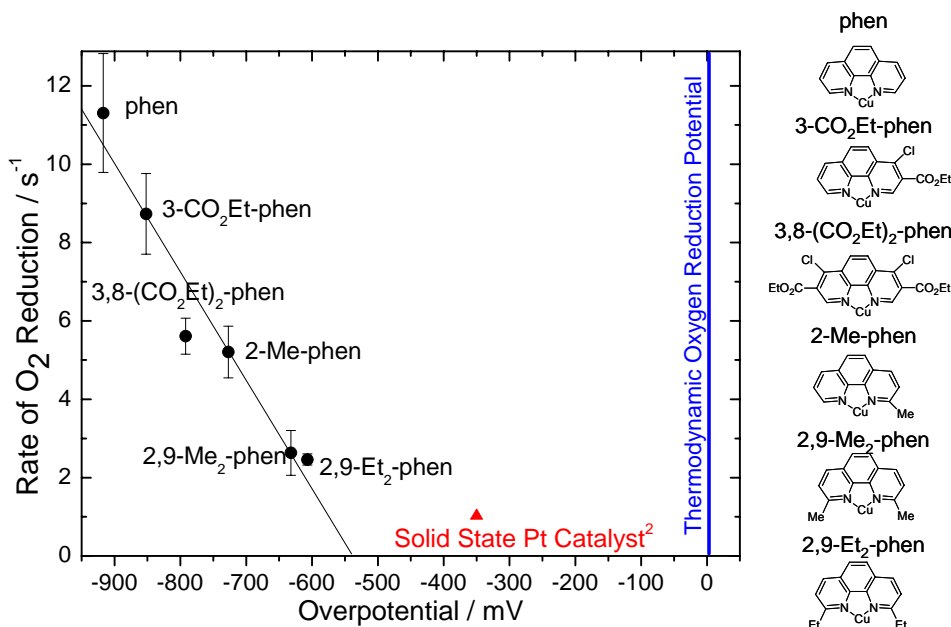


Figure 3: Data showing the overpotential values observed for various Cu-phen complexes for electrocatalytic reduction of oxygen

Reference:

1. Lei, Y.; Anson, F. C. *Inorg. Chem.* **1994**, *33*, 5003-5009.; Zhang, J.; Anson, F. C. *Electrochim. Acta* **1993**, *38*, 2423-2429
2. Ralph, T. R.; Hogarth, M. P. *Platinum Metal Reviews* **2002**, *46*, 3-14.

3) Surface-modification of carbon electrodes: Aromatic nitration is identified as a method to introduce site-isolated nitro groups on carbon surface. Conversion of nitro groups into amine groups can be used to link to carbonyl chloride terminated molecular catalysts as shown in Figure 4. Nitro groups coupled to aromatic rings have a deactivating effect for further nitration and are

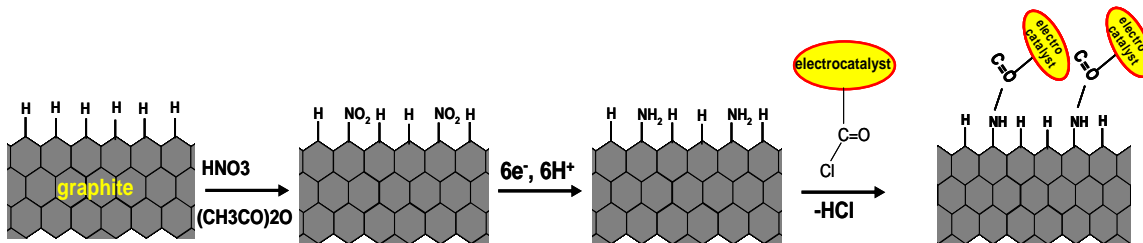


Figure 4; A schematic showing nitration and subsequent modification of electrocatalysts at the graphitic edges

expected to lead to site-isolated introduction of nitro groups. Initial studies have shown that nitro groups with a coverage of up to 1×10^{14} molecules/cm² can be obtained on carbon surfaces similar to glassy carbon. The nitro groups have been successfully reduced to amines by chemical methods. Further work on optimizing the coverage of nitro groups and covalent immobilization of electrocatalysts are underway.

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