Efficient Interconversion of Chemical and Electrical Energy: Electrocatalysis with Discrete Transition Metal Complexes

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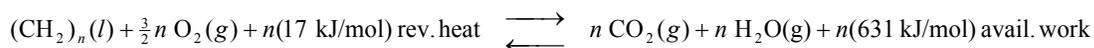Xavier G. Ottenwaelder, Postdoctoral Researcher, Chemistry

Introduction

This project aims to develop efficient electrocatalysts for ambient-temperature direct-hydrocarbon fuel cells. While the efficient catalysis of dihydrogen (H_2) oxidation in fuel cells is well established, the challenges of making, transporting and storing H_2 motivate the development of efficient catalysts for the oxidation of hydrocarbons. Developing an efficient fuel cell to use the established hydrocarbon fuels is an important investment for reducing carbon dioxide (CO_2) emissions and improving the efficiency of energy utilization. Moreover, a hydrocarbon fuel cell would also provide a more efficient way to use CO_2-neutral fuels such as biofuels or synthetic fuels from solar energy. Finally, even in the H_2 fuel cell, the catalysis of dioxygen (O_2) reduction remains a severe problem, with the majority of the waste heat caused by poor catalysis of this reaction. We are exploring transition metal complexes immobilized on carbon electrodes as novel catalysts for both hydrocarbon oxidation and O_2 reduction. Specifically, various configurations of late transition metals in multi-metallic complexes are being investigated for their potential as electrooxidation catalysts, and biologically inspired mono- and multi-metallic copper complexes are being examined as electroreduction catalysts.

Background

Hydrocarbon Fuel Cells

Highly efficient direct hydrocarbon fuel cells would offer the greatest possible combination of energy and space efficiency for mobile applications. The energy density of long-chain hydrocarbons stored in inexpensive tanks at ambient temperature and pressure is 8 kWh/L, twice that of methanol and much better than any practical H_2 storage system[1]. If high catalytic efficiency can be obtained at low overpotentials with relatively inexpensive catalysts, then the advantageous characteristics of the fuel and the overall reaction would allow hydrocarbon fuel cells to produce significant savings in CO_2 emission per useful unit of work and per unit of capital investment.

The complete oxidation of long-chain alkanes by O_2 is described by the following approximate thermochemical equation:

$$(CH_2)_n(l) + \tfrac{3}{2}n\,O_2(g) + n(17\text{ kJ/mol})\text{ rev. heat} \underset{\longleftarrow}{\longrightarrow} n\,CO_2(g) + n\,H_2O(g) + n(631\text{ kJ/mol})\text{ avail. work}$$

In this cell, six electrons must be transferred from anode to cathode for each CH_2 group oxidized. Thus the work available is up to 105 kJ per mole of electrons, i.e. a reversible cell voltage of 1.09 V.

Electrocatalysts

Even with the recent progress made in H_2 and direct methanol fuel cells, operating voltages at reasonable current densities are still far below the reversible voltages. At least one third of the energy in a H_2 polymer-electrolyte-membrane (PEM) fuel cell, and significantly more in a direct methanol cell, is wasted as irreversible heat generated in the electrocatalytic steps[2]. The resulting heat must unfortunately then be removed from the fuel cell across a relatively small temperature gradient at significant capital and operating expense. The dominant approach to electrocatalysis to date has been empirical and oriented toward traditional solid-state catalysts dispersed in porous electrodes. Such work, while showing the quickest incremental advances, is unlikely to lead to the kind of deep understanding and precise tailoring of the reactivity required to bring the operating voltages significantly closer to the reversible values. A recent review of previous efforts to find alternative electrocatalysts highlights the need for a sustained and focused effort in this regard[3]. Intimate contact of hydrocarbon or O_2 with metal atoms is required for efficient electrocatalysis, but neither is effective at displacing other ligands from metal atoms. Thus, a good catalyst must have open coordination sites for hydrocarbon or O_2 binding.

In the first year of this project, we have explored various ligands that maintain open coordination sites around individual copper and palladium atoms. We have also initiated synthetic work to create even better catalysts by precisely positioning two or more metal atoms. We have also developed a new method to attach metal complexes covalently to graphite electrodes in order to immobilize the complexes and prevent their aggregation under catalytic conditions.

Results

Understanding Mononuclear Cu Electrocatalysts for O_2 Reduction

We have extended Anson's study of the rapid 4-electron reduction of O_2 catalyzed by a Cu(I) complex of 2,9-dimethylphenanthroline (Me$_2$-phen) adsorbed on edge-plane graphite (EPG)[4,5]. Many new derivatives of phenanthroline (phen) and other bidentate aromatic amines have been obtained from commercial sources or synthesized to search for systematic trends in O_2 reduction (Figure 1). These copper-binding ligands were adsorbed onto the EPG surface and the surface exposed to a copper(II) nitrate solution. Figure 1 reports the reversible Cu(II) reduction potential for each complex relative to the reversible potential for O_2 reduction to H_2O. Also shown are the potentials of the peak due to O_2 reduction if the complex is electrocatalytic; this is a measure of the overpotential needed to drive O_2 reduction at a reasonable rate. Finally, for a number of the electrocatalytic complexes, the pseudo-first order rate constant for the reduction of O_2 from air by the Cu(I) form of the complex is reported.

Substituents adjacent to the coordinating nitrogens in the bidentate ligand lead to significantly less negative Cu(II) reduction potentials. The most obvious example of this trend is the decreasingly negative potential from phen (-915 mV) to Me-phen (-725 mV) to Me$_2$-phen (-630 mV). We infer that this positive shift is due to the substituents interfering with the coordination of other ligands to the Cu(II). Poor coordination opposite the nitrogens of the bidentate ligand is expected to destabilize Cu(II) relative to Cu(I), thus causing the observed shift. The potentials of the peaks due to O_2 reduction track the Cu(II) reduction potentials up to a point, but then decrease dramatically when

the Cu(II) reduction potential is within about 600 mV of the reversible potential for the reduction of O_2 to H_2O (e.g. Bu_2-phen). Presumably, the reaction of the Cu(I) complex with O_2 is insufficiently favorable at that point and much more negative potentials are needed to effect reduction of O_2, leading to the divergence of the two potentials. Another trend in the data is that electron-withdrawing substituents tend to make the Cu(II) complexes easier to reduce. The most obvious example of this trend is the decreasingly negative Cu(II) reduction potential from phen (-915 mV) to Br-phen (-850 mV) to Br_2-phen (-805 mV). Both the effect of substituents adjacent to the nitrogens and the effect of electron-withdrawing substituents are combined in Me_2NO_2-phen, which exhibits a Cu(II) reduction potential of -545 mV. At this potential, however, the reaction with O_2 again becomes uncoupled from the Cu(II) reduction.
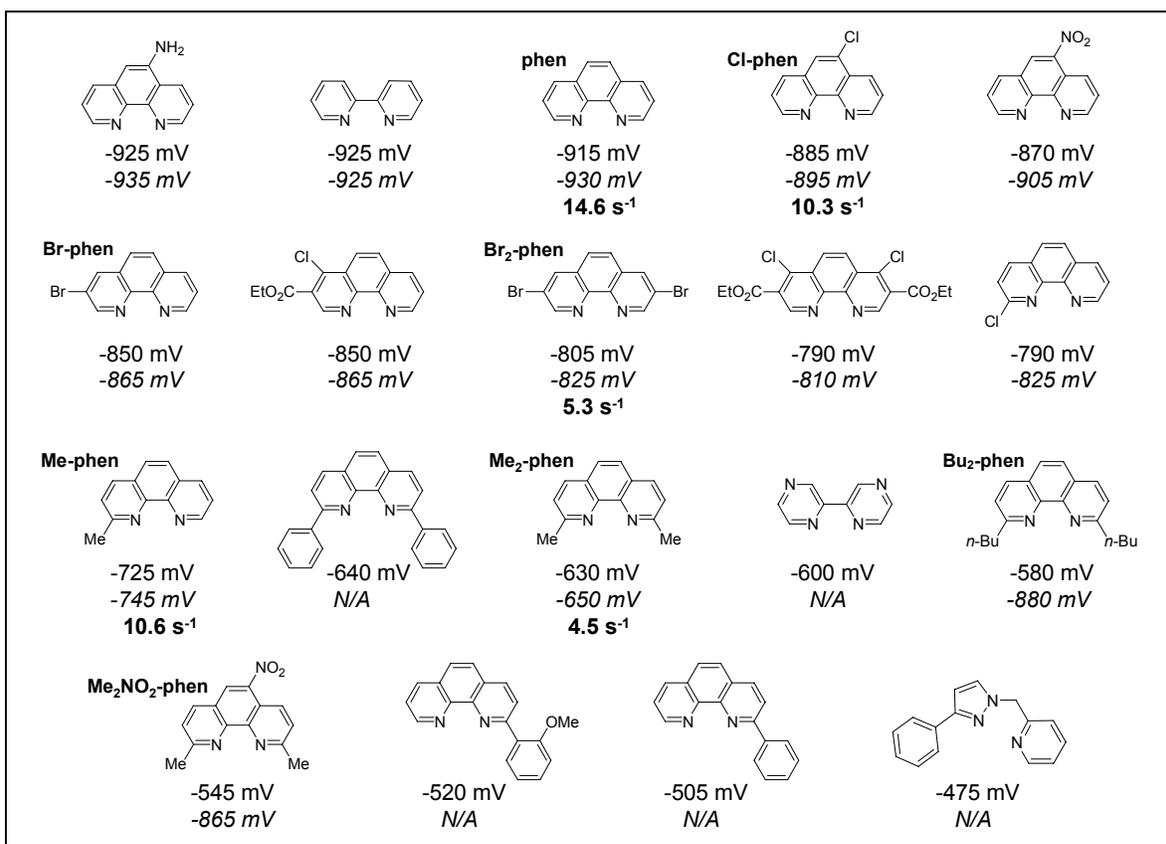
Figure 1: Ligands investigated on an EPG electrode with copper. For each ligand, the first value reports the potential of the Cu(II) reduction as compared to the reversible reduction of O_2 at pH 5 (+930 mV vs NHE). The second value (italics) is the approximate peak potential of the electrocatalytic reduction of O_2. N/A indicates that no electrocatalytic peak was observed. The third value (bold) is the rate of electrocatalysis in O_2 per copper per second for selected complexes saturated with air. All data was taken at 25°C in 0.04 M acetate buffer (pH 5) with 0.1 M $NaClO_4$.

When the peak of O_2 reduction peak tracks the Cu(II) reduction potential, the rate of O_2 binding to the catalyst is believed to be rate-determining. The rates shown in Figure 1 decreases slightly with decreasingly negative Cu(II) reduction potential before the reaction ceases abruptly above about -600mV. For example, the rate constant drops from

14.6 O_2 molecules per copper center per second under one atmosphere of air with phen to 4.5 O_2 molecules per copper per second with Me_2-phen. For comparison, Pt-based nanoparticulate catalysts reduce only about 0.25 O_2 molecules per platinum atom per second in operating H_2 fuel cells.[6] Unfortunately, even the best of these copper-based catalysts has an overpotential of -650 mV, which is not competitive with the overpotential of ca. -350 mV for Pt-based nanoparticle catalysts.[6] We are now finishing up this initial study of mono-copper complexes with a careful study of the role of anions in the O_2 electroreduction process. We find that the acetate anion plays a central role in both the Cu(II) reduction and the O_2 reduction.

We infer from this work that mononuclear copper complexes must be fairly strong reducing agents (reduction potential < -600 mV relative to the reversible potential of O_2 reduction to H_2O) in order to simultaneously reduce O_2 to the superoxide anion (O_2^-), bind it and then allow it to be protonated and further reduced to H_2O:

$$LCu(II) + e^- (< -600 \text{ mV vs } O_2/H_2O) \rightarrow LCu(I) + O_2 \rightarrow LCu(II)O_2^- \rightarrow \text{further reduction}$$

As a result, we conclude that mononuclear copper catalysts are poor candidates for an efficient O_2-reduction catalyst at low overpotentials. Going forward, we will build on our understanding of these mononuclear species to explore the reactivity of complexes with two and three copper atoms that more closely mimic the structure of the enzyme laccase, which has a trinuclear copper site known to effect the 4-electron reduction of O_2 at potentials very close to the reversible potential[7,8].

A Novel Mononuclear Pd Catalyst for C-H Oxidation

We have found a new species that effects rapid oxidation of the C-H bond in methanol and other alcohols at room temperature, an unusual transformation under such mild conditions[8] and a useful starting point for understanding how to activate C-H bonds near room temperature. Figure 2 shows the structure of the crystallized compound, an acetate-bridged palladium dimer. In solution, however, the dimer is in equilibrium with the monomer, $(Me_2$-phen)Pd(O_2CCH_3)(CF_3SO_3), with a dissociation constant of 7 mM. We believe that the monomer is the active species and attribute its high level of reactivity to (1) the weakly coordinating triflate counterion, which provides an accessible coordination site for the alcohol, and (2) the ability of the coordinating acetate counterion to serve as a base in the intramolecular deprotonation of the coordinated alcohol to give the alkoxide. This fairly simple compound provides a good point of reference for future catalyst design.
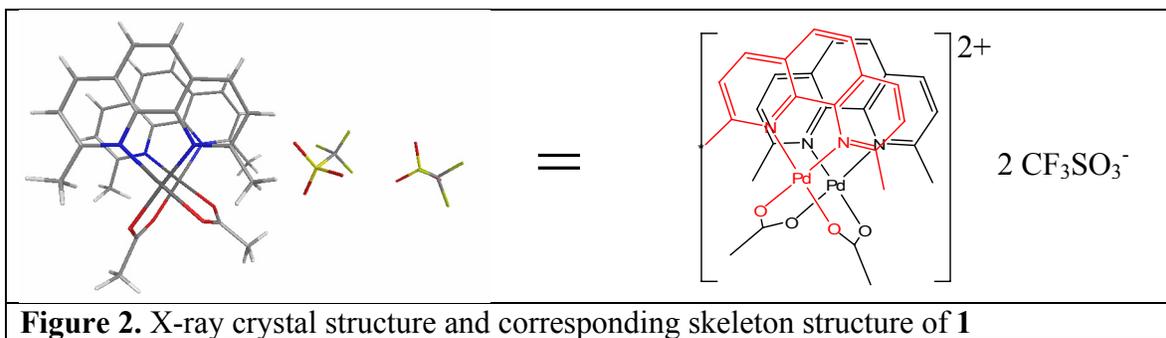

Figure 2. X-ray crystal structure and corresponding skeleton structure of **1**

Oxidation of 2-heptanol with this catalyst and either air or iodobenzene diacetate as terminal chemical oxidants reveal turnover frequencies at room temperature (> 0.03s^{-1})

approaching those required in a fuel cell. However, the rate of oxidation decreases rapidly as the products of the reaction accumulate. We have shown that both hydrogen peroxide, formed in the oxidation by air, and also acetic acid, formed in the oxidation by iodobenzene diacetate, inhibit the catalyst. We are now investigating the electrocatalytic oxidation of alcohols with the catalyst immobilized in various ways on graphite electrodes. In the absence of the reduced products of chemical oxidants, we hope to avoid inhibition of the reaction. Because mobile palladium complexes adsorbed on surfaces can irreversibly form metallic palladium in the presence of reducing agents like methanol, we are focusing particular attention on the novel method described below for covalently coupling metal complexes to carbon electrodes so they cannot aggregate.

Developing Binuclear Oxidation Catalysts

In a parallel effort, we are investigating binuclear species utilizing a second metal such at ruthenium to facilitate proton transfer during oxidation of hydrocarbons. To this end, we have prepared a family of pyrazole-based ligands that position two metal centers in close proximity (Figure 3). We have prepared an intermediate, mononuclear Ru complex (Figure 4) and efforts to synthesize the Ru/Pd complex are underway.

| **Figure 3**: Proposed binuclear complexes | **Figure 4**: Mononuclear Ru complex |
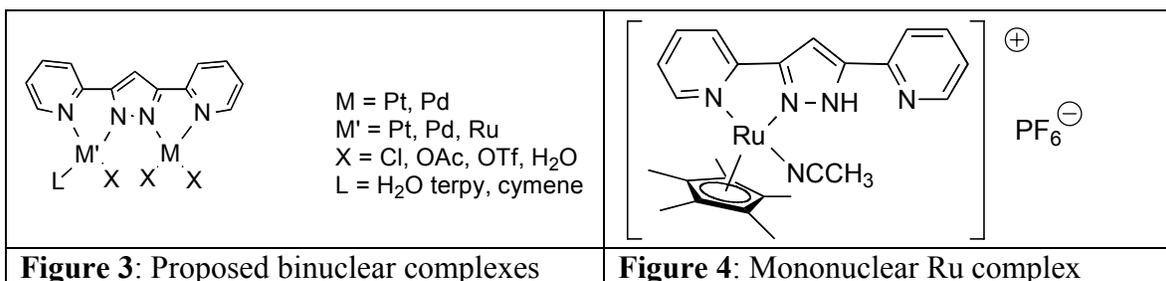
Covalent Attachment of Metal Complexes to Carbon Electrodes

The physisorption of discrete transition metal complexes to edge-plane graphite has provided a convenient starting point for our electrocatalytic studies. However, covalent coupling of the metal complexes to graphite surfaces provides more robust surface immobilization and ensures that individual complexes are held apart so that they do not aggregate. Uncontrolled aggregation of metal complexes often results in bridging ligands occupying the coordination sites that we wish to keep open for binding the reactant (O_2 or the hydrocarbon). We have recently developed a versatile method to covalently attach acetylene-terminated species to modified carbon surfaces. Terminal acetylene groups are relatively easily installed at the periphery of many aromatic ligands such as phen and so provide a nearly universal point of attachment to metal complexes. Figure 5 shows the electrochemical response obtained on a carbon surface before and after covalent coupling to the simple electroactive species ethynylferrocene. The inset in Figure 5 shows the linear dependence of the electrochemical peak current on the scan rate expected for a surface immobilized species. Also as expected for a surface immobilized species, rinsing the surface with various solvents does not alter the electrochemical response. The area under the electrochemical peaks indicates that the coverage is about one attached species per 5 nm^2. A similar coverage is obtained by x-ray photoelectron spectroscopy for a fluorine-containing species coupled to the surface. This is a useful coverage for isolating electrocatalysts one from another and is in the range that would be needed on the carbon electrodes used in PEM fuel cells. We are now preparing acetylene-terminated

phenanthrolines for initial electrocatalysis studies of metal complexes covalently attached to carbon electrodes.
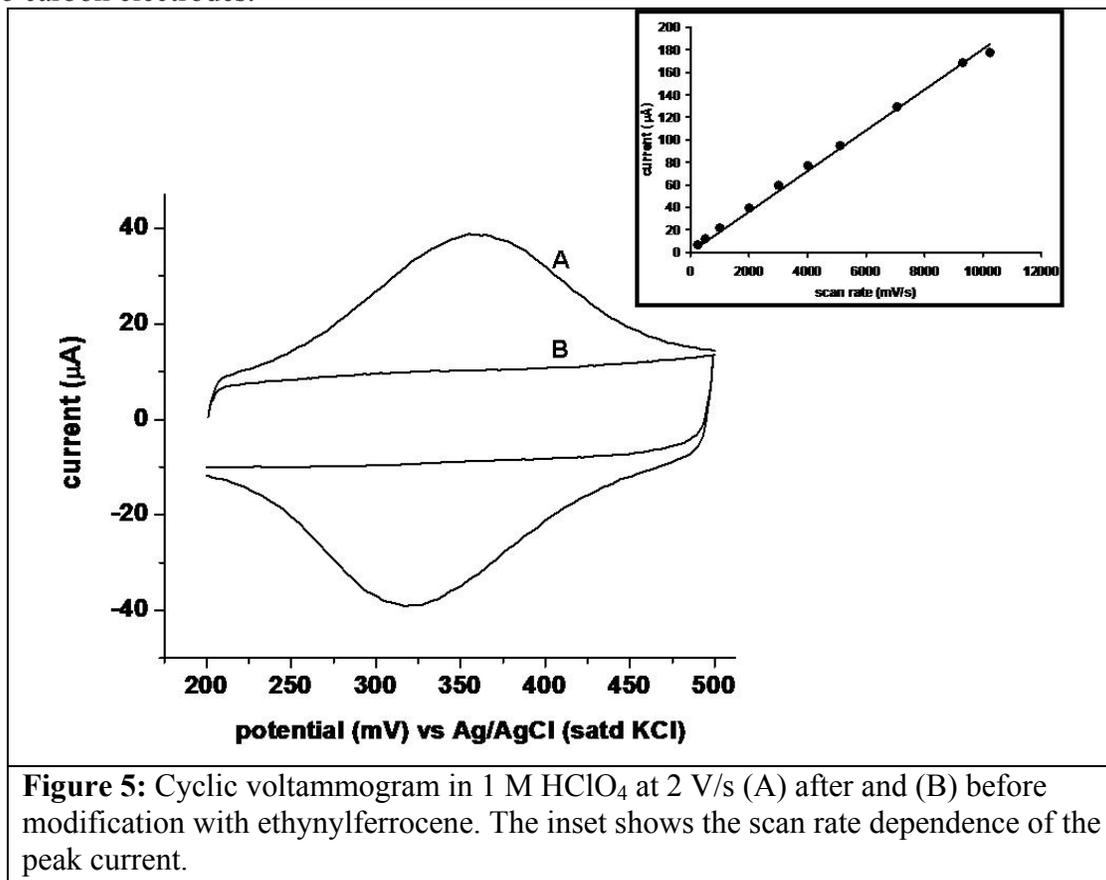
Figure 5: Cyclic voltammogram in 1 M HClO$_4$ at 2 V/s (A) after and (B) before modification with ethynylferrocene. The inset shows the scan rate dependence of the peak current.

Progress

To date, we have examined mononuclear metal complexes for both O$_2$ reduction and C-H oxidation, have developed synthetic methods to make binuclear complexes and have developed a general purpose method for the covalent immobilization of discrete transition metal complexes onto carbon electrodes. These advances give us an experimental base for exploring the structural features of discrete transition metal complexes that determine the electrochemical potential and rate at which O$_2$ can be reduced and hydrocarbons oxidized.

Future Plans

We will now explore bimetallic copper complexes for the reduction of O$_2$. Bridging coordination by O$_2$ between two copper sites held at an appropriate distance is expected to allow O$_2$ to bind to sites at much less negative Cu(II) reduction potentials than in the mononuclear case. One possible mechanism is:

LCu(II)__Cu(II)L + e$^-$ (> -600 mV vs O$_2$/H$_2$O) → LCu(I)__Cu(II)L + O$_2$
         → LCu(II)O$_2^-$Cu(II)L → further red'n

We will be applying the newly develop covalent coupling method to immobilize palladium mononuclear and binuclear complexes on carbon electrodes to determine the potentials at which C-H bonds can be oxidized.

Publications

none yet

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