

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

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Introduction

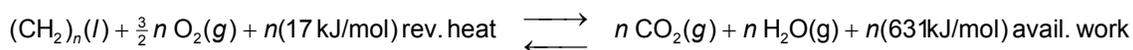
This project aims to develop efficient electrocatalysts for ambient-temperature direct-hydrocarbon fuel cells. While the efficient catalysis of the oxidation of hydrogen in fuel cells is well established, the challenges of making, transporting and storing hydrogen motivate the development of efficient catalysts for the oxidation of long-chain hydrocarbons, which are arguably the best fuels for mobile applications. Developing a more efficient way to use the well-known hydrocarbon fuels is an important investment for the overall reduction of carbon dioxide emissions and improvement in the efficiency of energy utilization. Moreover, in the long term, there are several prospective sources of renewable hydrocarbon fuels that would result in no net carbon emission. Finally, even in the hydrogen fuel cell, the catalysis of oxygen reduction remains a severe problem, with the majority of the waste heat from the hydrogen fuel cell due to poor catalysis of this reaction. We are exploring transition metal complexes adsorbed to carbon electrodes as novel catalysts for both hydrocarbon oxidation and oxygen reduction. Specifically, various configurations of late transition metals in multi-metallic catalyst 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 8kWh/L, twice that of methanol and much better than any practical hydrogen storage system¹. 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 carbon dioxide emission per useful unit of work and per unit of capital investment.

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



In a fuel cell, six electrons must be transferred from anode to cathode for each CH₂ group oxidized. Thus the work available is up to 105 kJ per mole of electrons or 1.09eV per electron, i.e. a reversible cell voltage of 1.09V.

Electrocatalysts

Even with the recent progress made in hydrogen 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 hydrogen polymer-electrolyte-membrane (PEM) fuel cell and significantly more than that in a direct methanol cell is wasted as irreversible heat generated in the electrocatalytic steps². 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 heterogeneous catalysts comprised of solid-state materials dispersed within the porous electrodes. Such work, while likely to show the quickest incremental advances, is unlikely to lead to the kind of deeper understanding and precise tailoring of the required reactivity that would be 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 more sustained and focused effort in this regard³.

Of all previous work, Anson's extensive work on O₂-electrocatalysis with various [Cu(R-phen)₂]²⁺ complexes (R-phen = derivatives of 1,10-phenanthroline)⁴ adsorbed on graphite electrodes best sets the stage for our research on novel electrocatalysts for both the oxidation and reduction reactions (Figure 1). Anson's use of oxidatively robust heterocyclic aromatic ligands that adsorb tenaciously on graphitic surfaces is well matched to the type of electrode and electrolyte used in current PEM-type fuel cells.

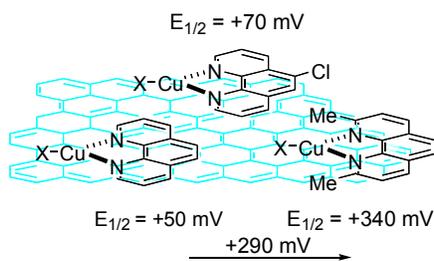


Figure 1: Cu(II)/Cu(I) potentials for various phen-based O₂-electrocatalysts on graphite.

More specifically, Anson's work provides significant insights into the development of an efficient O₂-electrocatalyst based on a discrete copper complex. Anson showed that direct adsorption of [Cu(II)(2,9-dimethyl-1,10-phenanthroline)₂]²⁺ complex leads to a very active O₂-electrocatalyst that retains only one of the phen ligands. The reduced form of the original adsorbed complex with both phen ligands is inactive suggesting that direct O₂ access to an open Cu(I) coordination site is essential for high O₂-electrocatalytic behavior. The current is limited by the rate of formation of the Cu(I)-O₂ complex (1s⁻¹ per open Cu site). The potential necessary for O₂-electrocatalysis matches the reduction potential of the open form of the adsorbed copper complex (+340 mV versus NHE, pH

5). Surprisingly, the reduction proceeds directly to two water molecules without any loss of H₂O₂ even though there is evidence for only one Cu atom per site. While the N-Cu bonds in these complexes are not sufficiently stable against protonation in the strongly acidic electrolyte of a conventional PEM cell, it is known that other metals are stable in such complexes and we believe that with modified ligands even copper may be sufficiently stable. In any case, Anson's basic strategy of using aromatic heterocyclic ligands adsorbed on carbon electrodes is a useful starting point for engineering useful catalysts for PEM-type cells.

Precedents From Biological and Homogeneous Catalysis

While Anson's work provides our starting point for development of novel electrocatalysts, several families of redox enzymes, illustrate how efficient coordination complexes of transition metal ions can be as catalysts for the reactions required in a hydrocarbon fuel cell⁵. Laccase, which very effectively reduces dioxygen using coordinated copper ions, provides a particularly striking example. The enzyme has a trinuclear copper active site and a 12 Å distant single copper center that serves as a transfer site for electrons from substrates to dioxygen in the trinuclear cluster. Rapid binding and 4e⁻ reduction of O₂ requires that all the copper centers are first reduced to Cu(I) and each provides 1e⁻ in the reduction process (Cu(I)→Cu(II)). Laccase from certain organisms reduces oxygen sufficiently rapidly and at sufficiently positive potential that Heller has made a fuel cell cathode for the reduction of oxygen that operates with only 70mV of overpotential – many times less than the best platinum-based fuel cell cathodes at the same current density⁶. A second protein that provides key insights into the efficient reduction of O₂ by copper is hemocyanin, the O₂-transport protein of arthropods and mollusks. These proteins reversibly bind O₂ through a side-on peroxide-level intermediate between two copper ions. As this process is reversible at ambient temperatures and represents an initial 2e⁻ reduction of O₂, it suggests a possible initial step of an efficient 4e⁻ reduction of O₂.

Ambient temperature hydrocarbon oxidation is of course well preceded in biology by fat metabolism which proceeds by cleavage of the hydrocarbon chains into two-carbon fragments (acetic acid derivatives). These two carbon fragments are then converted to CO₂ and reducing equivalents, whose favorable reaction with dioxygen drives the phosphorylation of adenosine diphosphate to adenosine triphosphate, which is the primary energy carrier of biological systems. Though elegant and in parts suggestive of mechanisms that might be useful in a fuel cell, we hope to avoid much of the complexity of the biological oxidation of hydrocarbons by use of monometallic and bimetallic complexes of late transition metal ions, notably palladium, platinum and ruthenium. These have been explored in recent years as homogeneous catalysts for hydrocarbon activation. A number of Pt(II) and Pd(II) complexes ligated by planar bipyrimidine and phenanthroline ligands (Figure 2) have been shown to be stable in strong acid media and to catalyze the oxidation of methane with sulfuric acid and the oxidation of alcohols with O₂⁷⁻⁹. Periana has demonstrated that the bipyrimidyl complexes I are active catalysts for the conversion of methane to methylbisulfate in sulfuric acid. Herrmann reported that Pd complexes of the chelating N-heterocyclic carbene ligands III are stable in strongly acidic media and catalyze the oxidation of methane with potassium peroxodisulfate. Solution

studies of complexes I-III provide good evidence that they can mediate key steps in alkane oxidation. As shown by Anson⁴, such aromatic heterocyclic ligands are expected to adsorb tenaciously to graphitic carbon electrodes.

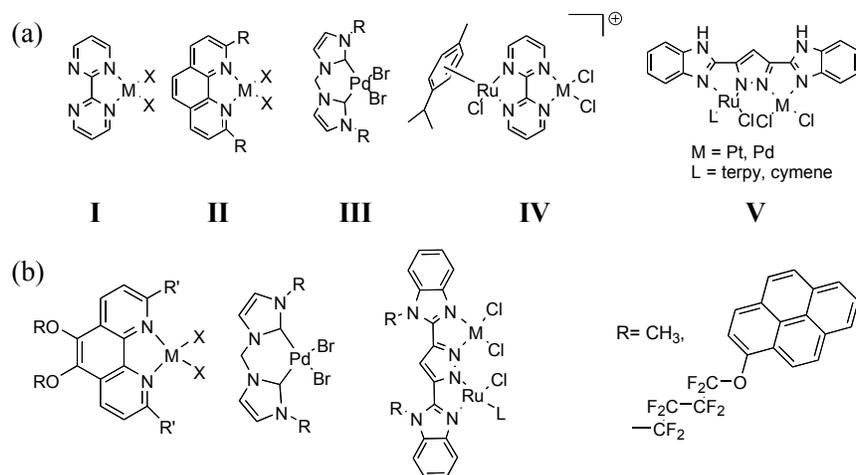


Figure 2 (a) Representative complexes to be absorbed on graphite electrodes
(b) Proposed π -stacking modifiers to enhance absorption to graphite electrodes.

Two intriguing reports provide a starting point for our initial efforts in electrocatalytic C-C activation. One is Sen's observations of the oxidative cleavage of butane in trifluoroacetic acid with either RhCl_3 or bimetallic $\text{PdCl}_2 / \text{CuCl}_2$ catalysts in the presence of carbon monoxide and water (Figure 3)¹⁰. Sen observed an interesting influence of CuCl_2 co-catalysts on the selectivity: in the presence of CuCl_2 , he observed a high selectivity for oxidation of the alkanes to the alcohols; in the absence of CuCl_2 this system oxidized methane to formic acid and ultimately to CO_2 . An intriguing observation of Sen was that for the C-C cleavage reactions, the presence of a CO co-reductant was required.

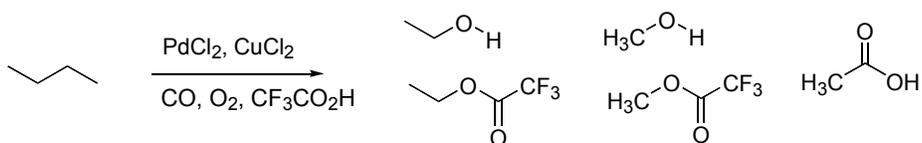


Figure 3. Sen's oxidative cleavage of butane.

The second intriguing report is Henry's report of the carbonylative cleavage of ketones by $\text{PdCl}_2 / \text{CuCl}_2$ catalysts (Figure 4)¹¹. An initial addition of CO to the enol form of the ketone allows C-C cleavage by the reverse of the Claisen condensation (Figure 4). If preceded by an oxidative C-H activation step this mode of reaction could provide a route to the cleavage of unactivated long-chain hydrocarbons to form two smaller and chemically more reactive carboxylic acids.

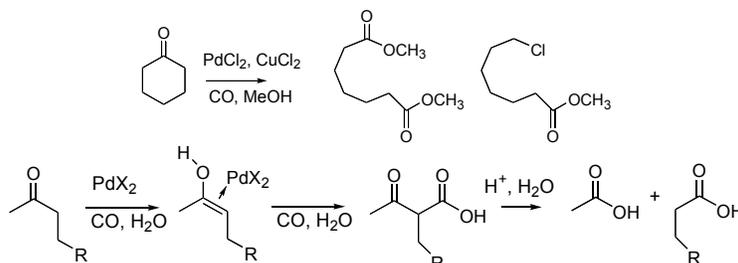


Figure 4. Henry's carbonylation of ketones followed by retro-Claisen condensation.

Results

Our immediate research plan involves five parallel and complementary efforts involving the graduate students and postdoc who have recently joined the project. The efforts are: (1) the synthesis and electrochemical evaluation for oxygen reduction of mononuclear Cu complexes with substituted phenanthrolines (Charles McCrory and Xavier Ottenwaelder), (2) theoretic studies on oxygen binding and activation by Cu(I) complexes (Charles McCrory), (3) the synthesis and electrochemical evaluation for alcohol oxidation of mononuclear Pd complexes (Nick Conley and Charles McCrory), (4) theoretical studies on CO oxidation by Pd(II) complexes (Nick Conley), (5) the synthesis and evaluation of novel ligands for the preparation of bimolecular Pd complexes. Initial technical progress in these efforts has been made as described below.

McCrory has successfully reproducing the Anson observations⁴ of dioxygen reduction in air saturated aqueous electrolyte. Figures 5 and 6 show the cyclic voltammetry and steady-state rotating disk electrode voltammetry of the dimethylphenanthroline-copper complex, Cu(DMP) that McCrory has recently obtained. These results provide an important validation both of the literature reports and of our methods and approach. Ottenwaelder and McCrory are now synthesizing and electrochemically characterizing several other substituted phenanthrolines in order to dissect the origin of the promising 4-electron reduction of dioxygen seen with Cu(DMP).

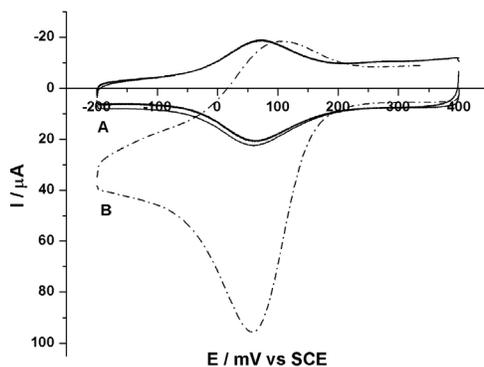


Figure 5: Cyclic voltammetry of Cu(DMP) adsorbed from aqueous solution: (A) in 0.15 M acetate buffer at pH 5 with 0.1 M NaClO_4 under N_2 ; (B) in the same solution as (A) but air saturated.
Scan rate = 100 mV s^{-1} .

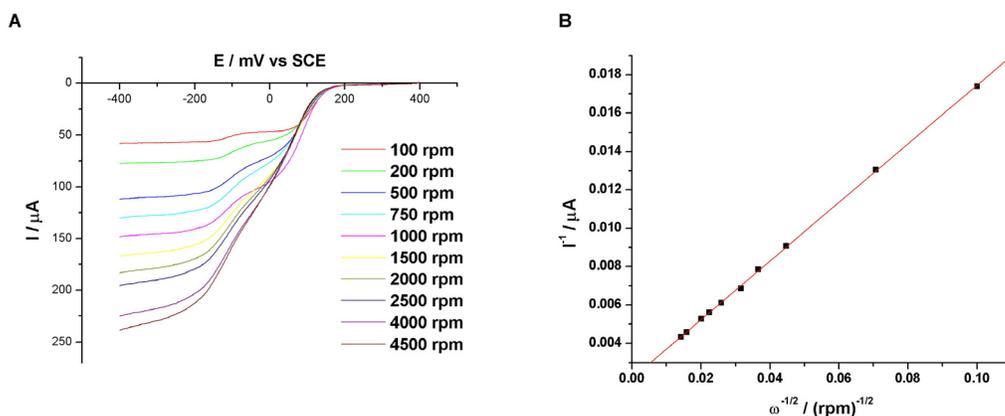


Figure 6: Kinetic analysis of the electrocatalytic reduction of O_2 by adsorbed Cu(DMP). (A) Current-potential curves for the reduction of $\sim 0.26 \text{ mM O}_2$ by $5 \times 10^{-9} \text{ mol/cm}^2$ of Cu(DMP) adsorbed on an edge plane pyrolytic graphite electrode rotating disk electrode (scan rate = 20 mV/s). (B) Koutecky-Levich plot of the (plateau current) $^{-1}$ from (A) vs the (rotation rate) $^{-1/2}$ of the electrode.

It is thought that the rate-limiting step in this catalytic reduction of oxygen by phenanthroline-based copper catalysts adsorbed onto graphite is the binding of O_2 . To better understand this reactivity, McCrory has begun density functional theory simulations to help understand the reduction potential of the bound O_2 species. To date, he has compared the oxygen adducts of the Cu(I) complexes two distinct isomers of dimethyl phenanthroline, the isomer used in the above studies, Cu-2,9-(DMP) $^+$, and an isomer with the methyl groups positioned outside the active site for oxygen binding, Cu-4,7-(DMP) $^+$. All calculations were done using the Gaussian 03 suite of programs. Density functional theory was used for all calculations using the unrestricted hybrid 3-parameter Becke exchange functional and the Lee-Yang-Parr correlation functional (UB3LYP). The 6-31G(d) basis set of orbitals was used for each atom. The two structures both involve dioxygen and the phenanthroline ligand coordinated in a square-planar type geometry. However, the energies of the two isomers are different, reflecting the steric crowding in the 2,9 isomer. The difference in energy of the complexes of the 2,9 and 4,7 isomer is 3.848 kcal/mol, or 0.1668 eV. This energy difference is one portion of the overall energy profile we plan to construct for to help understand the role of the ligand in promoting effective oxygen reduction.



Figure 7: Optimized Geometry of Cu(I)-2,9-dimethyl-1,10-phenanthroline bound with O_2 .



Figure 8: Optimized Geometry of Cu(I)-4,7-dimethyl-1,10-phenanthroline bound with O₂.

Conley and McCrory's initial work on oxidation catalysts has targeted a variety of (Me₂phen)Pd complexes in both the Pd(0) and Pd(II) oxidation state. The complex (phen)Pd(OAc)₂ was characterized in solution and preliminary experiments were carried out on its redox behavior on both edge-plain graphite and glassy carbon electrodes. We have also prepared the peroxo complex (2,9-DMP)PdO₂. Initial attempts to prepare the known Pd(0) complex (2,9-DMP)Pd(dba) (dba = dibenzylidene acetone) were unsuccessful due to its rapid reaction with air to generate the peroxo complex (2,9-DMO)PdO₂.

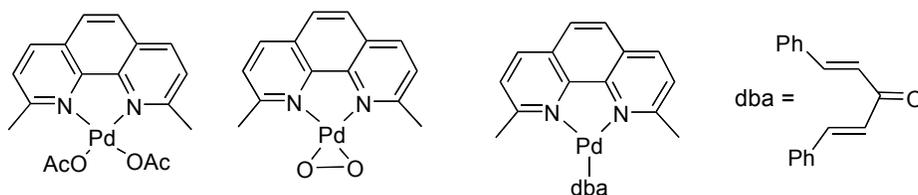


Figure 9. Mononuclear Pd complexes.

Conley found that attempts to mimic a literature method to homogeneously oxidized alcohols with dioxygen and (2,9-DMP)Pd(OAc)₂ as a catalyst¹² failed because the catalyst decomposed quickly to palladium black. We believe the problem was the lower concentration of oxygen in the 1 atmosphere of air used by Conley versus the 30 atm used in the literature report. Conley then attempted the same oxidation using a stoichiometric amount of ferrocenium hexafluorophosphate as the terminal oxidant. Under these conditions, 2-heptanol was efficiently converted to 2-heptanone. Quantitative GC studies are currently underway to determine the turnover frequency for the catalyst under these conditions. The next step will be to adsorb the catalyst on a graphite electrode to provide the oxidation needed to quickly return the palladium to its higher oxidation state with out need for a solution phase oxidant.

Because CO is likely to be the penultimate product of hydrocarbon oxidation, a strategy for the oxidation of CO at reasonably low potentials (optimally 0 – 0.2 V) is

critical to the successful design of electrooxidation catalysts for hydrocarbon fuel cells. To this end, we have begun computational studies on the known compound $\text{phen}(\text{Pd})(\text{C}(\text{O})\text{CH}_3)(\text{CO})^+$ to assess the level of validity of the simulation method. All calculations were performed using Gaussian 03W at the B3LYP level of theory using the LANL2DZ basis set for Pd and both 6-31G(d,p) and 6-311G(3df,2pd) basis sets for C, N, O, and H. The optimized geometry obtained using the latter basis set is shown in Figure 10.

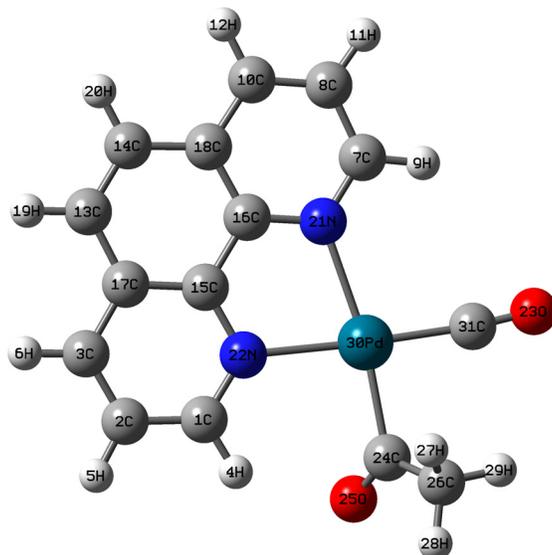


Figure 10. Optimized geometry of $\text{phen}(\text{Pd})(\text{C}(\text{O})\text{CH}_3)(\text{CO})^+$.

Good agreement was obtained between the experimental and theoretical bond lengths and angles, with the N22-Pd30-C24-C26 dihedral angle being the only exception. To assess the significance of this discrepancy, the potential energy surface associated with this degree of freedom was explored. The energy difference between the acyl geometry in the crystal structure and the optimized structure was found to be less than 1 kcal/mol, which is smaller than the uncertainty associated with the method. Thus, to within that accuracy, these results suggest that the simulation method is appropriate for the study of this system. Future work will focus on the activation barrier associated with the nucleophilic attack of H_2O on the carbon of the coordinated CO of this complex.

Progress

The primary progress of this project to date is the recruiting and initial technical setup and calibration of the research efforts of the students and postdocs. An energetic and capable group has now been assembled and is beginning to synthesize useful model compounds and collect meaningful data. The group has developed a healthy climate of collaboration and discussion which we anticipate will lead to exciting innovations in the details of our program plan.

Future Plans

Now that the technical expertise is in place, we plan that the next year will be marked by an exploration of both the reduction of oxygen and the oxidation of simple hydrocarbons, alcohols, acids and carbon monoxide at many different complexes. We

look forward to beginning to untangle the many possible reaction paths and assemble viable strategies for the key catalytic steps required in hydrocarbon fuel cells.

Publications

none yet

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