The Electron Economy: Oxidation Catalysis for Energy Management

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Abstract

The objective of this project is to develop efficient electrocatalysts for the oxidation of chemical fuels. The energy-efficient removal of high free energy electrons stored in chemical fuels is a key chemical step in energy conversion devices such as fuel cells. The efficient interconversion of stored chemical energy to useful work is critical to an efficient electron economy. Our highly collaborative team focused on three complementary objectives: (1) the preparation and characterization of families of electrode surfaces modified with a wide variety of molecular species in a "plug-and-play" experimental protocol, (2) the attachment of metal complexes to the modified electrode surfaces to harvest the electrons from the oxidation of alcohols and other fuels, to investigate the injection of electrons into terminal oxidants such as O_2 and (3) the synthesis and characterization of new classes of molecular electrocatalysts targeted at fast rates of oxidation at low overpotentials.

We have pioneered a versatile method for functionalizing a variety of graphitic and metal oxide electrodes. Functionalization of electrode surfaces with azide, followed by coupling of an ethyne-labeled electroactive metal complex with the surface generates molecular electrocatalysts covalently bonded to the electrode surface. These covalently-attached molecular complexes are stable to high numbers of electrochemical cycles and metal complexes can be prepared and modified on surfaces containing supported ligands. These advances have been coupled to developments in molecular catalysis to generate two new families of supported alcohol oxidation electrocatalysts based on Ruthenium complexes. As part of our efforts to develop fast oxidation catalysts as potential electrocatalysts, we have discovered a new family of Pd complexes for the the oxidation of diols and polyols such as glycerol, a versatile feedstock derived from renewable bio-mass.

Introduction

The objective of this project is to develop new classes of supported molecular electrocatalysts for the efficient removal of electrons from chemical bonds. The energy efficient removal of high free energy electrons stored in chemical fuels is a key step in all energy technologies. Specific objectives are to develop electrocatalysts for the electrocatalytic oxidation of alcohols and to illuminate the fundamental chemical and electrochemical steps required for the selective and energy-efficient oxidative conversion of hydrocarbon fuels.

Background

Direct alcohol fuel cells are attractive energy conversion technologies due to the higher gravimetric and volumetric energy density of liquid alcohol fuels relative to hydrogen. Our objective is to develop an experimental platform to identify new classes of electrooxidation catalysts for methanol and other chemical fuels. Our approach is to investigate molecular electrocatalysts supported on electrode surfaces[1] to illuminate the key chemical steps involved in the extraction of electrons and protons from chemical fuels. The development of molecular catalysts grafted onto electrode surfaces[2-4] is an active and promising area of research for electrocatalytic energy conversion.[5] Electrooxidation catalysts based on PtRu alloys and other nanoparticle noble metal catalysts are known, but the poisoning of these electrodes by CO (a partial oxidation product) leads to high overpotentials to oxidize methanol to CO_2.[6-8] During the past year, Bianchini reported a direct alcohol fuel cell based on a supported molecular Rh catalyst that exhibited power densities of 24 mWcm^{-2} at high potentials (0.65V vs. RHE).[9] While the power density and the longevity of these catalysts was lower than that of the best Pd nanoparticle electrodes, the ability to tune the catalyst and illuminate the mechanism of electrooxidation illustrate the power of this approach.[9]

Results

The 'Click" Reaction for Electrode Modification.

The team has pioneered methods[10,11] to attach molecular electrocatalysts to carbon electrodes, metal oxide electrodes[12,13], and gold electrodes using the Cu(I)-catalyzed azide-alkyne coupling (CuAAC) reaction[14,15] of a surface-bonded azide to an ethyne-functionalized ligand. This reaction is an example of a "click" reaction, so named for its convenience, selectivity and quantitative yield.[16] This reaction provides a versatile synthetic strategy to generate electrode surfaces that can be combined with a variety of electroactive metal complexes.[10] Figure 1 illustrates the general methodology for graphitic carbon and for indium-tin oxide (ITO). The three electrode materials that we have selected provide complementary properties. Glassy carbon presents graphitic surface sites and is convenient for electroanalytical characterization of electrode reactions. It is representative of the wide range of inexpensive carbon-based electrode materials, including the carbon black inks typically used in polymer-electrolyte fuel cells. Carbon surfaces are stable at moderately positive potentials and are highly resistant to acid or base hydrolysis or thermal treatments. ITO is representative of a broad range of metal-oxide electrodes and is completely stable to oxidation, but less so to extreme hydrolytic conditions. Gold coated with a self-assembled azidoalkane or

azidoaryl thiol monolayer provides the best understood electrode on which a high level of control of surface-attached species is possible, making it an excellent platform for mechanistic studies under moderate conditions. However, it is the least stable to extremes of potential, electrolyte or temperature. We employ each electrode system as needed to address key issues in electrocatalysis.

The team has advanced the azide-modification and subsequent "click" reaction on each of these three types of electrode surfaces. The original azide-modification of carbon[10] was conducted in an organic solvent under ambient conditions. We have now developed an azide modification process using the vapor of IN_3 under strictly anaerobic and anhydrous conditions immediately following reductive heat-treatment of the carbon. We have applied the process to a variety of carbon surfaces including flat glassy carbon electrodes and the carbon black (Vulcan XC-72R) used in PEM fuel cells.[17] We have developed two complementary approaches to the azide modification of metal oxide electrodes. The first employs the vapor deposition of trimethoxy azidoalkylsilanes under conditions of controlled humidity. The second employs the chemisorptions of azidophenylphosphonic acid from refluxing ethanol. Both methods have been applied to indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) electrodes.[18]   We have continued to advance our understanding of the optimal conditions for rapid and clean "click" reaction on electrode surfaces, identifying and studying the oxygen sensitivity of the reaction on different substrates and developing the use of metallic copper in electrical contact with the electrode to gently reduce a Cu(II) precatalyst at the electrode surface to the active Cu(I) catalyst.
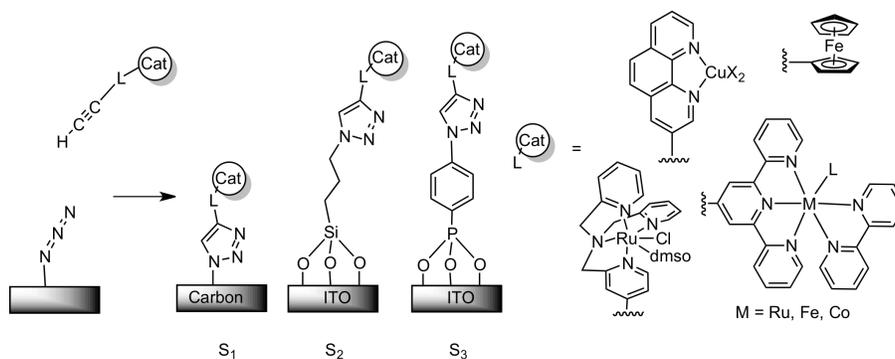

Figure 1. Covalently attached complexes to glassy carbon and metal-oxide electrodes

A. Novel Coordination Chemistry of Immobilized Iron Complexes.   The flexibility of the surface functionalization chemistry is demonstrated by the ability to bind complexes to electrodes and to modify the coordination chemistry of individual sites with ligand substitution reactions. Using these methods, we have prepared supported complexes of both coordinatively saturated Fe(tpy)$_2$ (tpy = terpyridine) and the Fe(tpy)(bpy)L (bpy = bipyridine, L = labile ligand). The latter complex is readily identified by its distinct redox potential 0.2 V negative of the surface Fe(tpy)$_2$ redox potential (Figure. 2).
 This octahedral complex has five coordination sites occupied by polypyridyl ligands, and shows the feasibility of preparing a Fe complex with a sixth coordination site available

for exchange with surrounding species, a key ability for generating high-valent Fe oxidants at surface-immobilized polypyridyl species. Because there is a strong driving force toward forming coordinatively saturated Fe(bpy)$_3$ or Fe(tpy)$_2$ complexes in solution, the stability of the Fe(tpy)(bpy) complex is enabled uniquely by our surface immobilization strategy. We further confirmed the presence of bpy in the ligand sphere of observing the expected variation in reduction potentials when preparing a series of surface bpy complexes with substituted bipyridines.
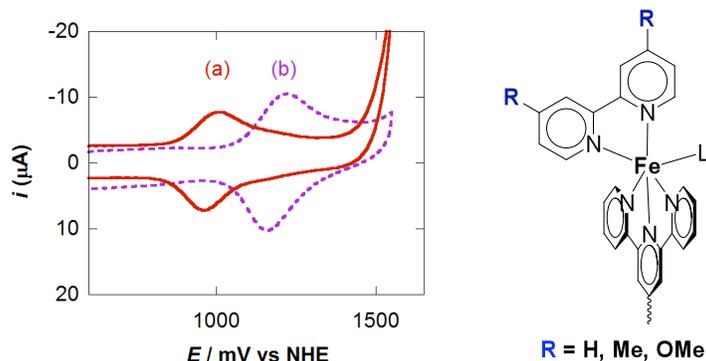

Figure 2. Voltammograms of surface-immobilized complexes: (a) Fe(tpy)(bpy)L; (b) Fe(tpy)$_2$.

B. Stability of Immobilized Complexes. As immobilized oxidation catalyst systems must be stable at potentials higher than the catalyst's redox potential, we have investigated the stability of ethynylated Fe and Ru polypyridyl complexes by monitoring the redox wave remaining after poising the electrode at high potential.
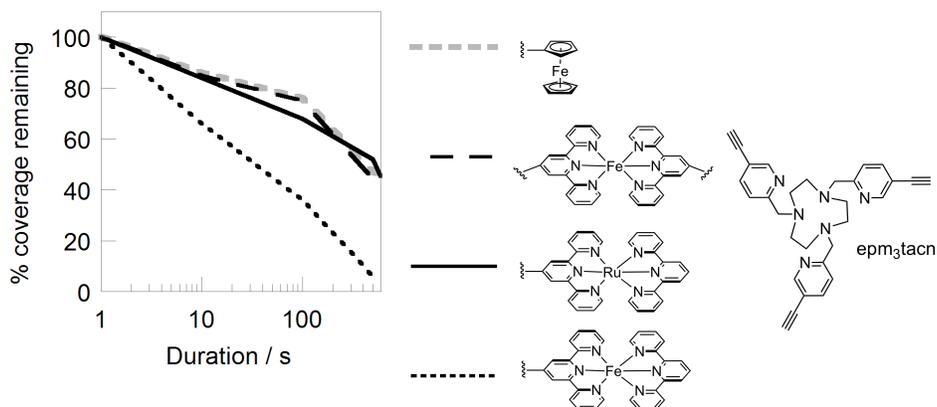

Figure 3: Stability of metal complexes covalently immobilized on ITO at high electrode potential.

At +1.46 V vs NHE, the Fe(tpy)(tpy) complex disappears from the surface after only 500s. We infer that the decay is due to loss of tpy ligand from the Fe(III) metal center. In contrast, three complexes showing higher stability demonstrate that ligand charge, more points of attachment, and kinetic inertness of the metal center all enhance stability of the immobilized complex at high potential. To exploit these design principles, we

have synthesized the new ligand epm$_3$tacn and immobilized its Fe complex (Figure 3). This hexadentate complex with three potential sites of surface attachment is a maximally stable limiting case, and we are currently evaluating its stability at high potentials.

Electrocatalysis with Supported Metal complexes.

   A. Oxygen Reduction with supported Cu complexes. Covalent attachment of complexes to electrodes not only allows access to stable complexes, but can also provide mechanistic insight into transient intermediates in catalytic cycles. In a study of the electrocatalytic reduction of dioxygen, we have varied the coverage of surface-attached Cu phenanthroline complexes on glassy carbon.[19] At low coverages, where all Cu phenanthroline complexes are isolated, only two-electron reduction of dioxygen to hydrogen peroxide occurs.   At high coverage, four-electron reduction to water is the primary product. This coverage dependence provides strong support that a binuclear complex (Figure 4) is the key intermediate in the 4-electron reduction of dioxygen to water.   We are now extending these studies to other electrodes, other complexes and other cases in which binuclear species may be key intermediates for efficient electrocatalysis.
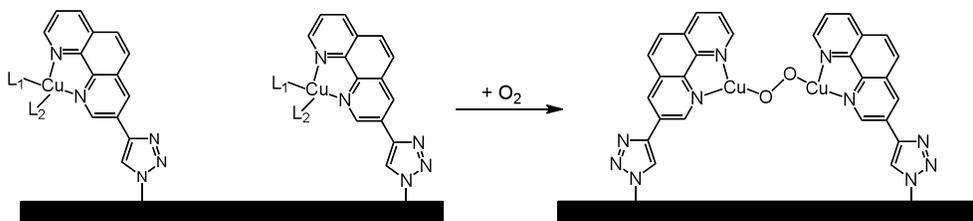

Figure 4. Proposed formation of a binuclear copper complex with O$_2$ that is the key intermediate in the 4-electron reduction of dioygen to water.

   B. Electrocatalytic Oxidation of Alcohols with Immobilized Ruthenium Complexes. Ruthenium oxo complexes have been demonstrated to be versatile oxidation catalysts using either oxo-transfer or one-electron outer-sphere reagents.[20]   The Ru complex [Ru(TPA)(DMSO)(Cl)]•PF$_6$, which is a competent oxidation catalyst for both alcohols and alkanes,[21] was modified with an ethynyl group[22] to enable its immobilization onto azide-modified indium/tin-oxide (ITO) and glassy-carbon (GC) electrode surfaces. Cyclic voltammetry (CV) of this complex in aqueous conditions exhibits a Ru(II)/Ru(III) reversible oxidation at a potential of E^0 = 1.15 V vs. NHE. The immobilized GC-TPA-Ru species exhibits no catalytic activity for electrocatalytic oxidation of alcohols, but it can be partially activated for catalysis under specific copper "click" reaction conditions or exposure to light. On glassy carbon surfaces activation of Ru TPA complex under "click" conditions leads to the highest catalytic activity for the oxidization of primary and benzyl alcohols in pH 7 phosphate buffer solution with an onset of catalysis around 600 mV vs. NHE (Figure 5). This onset of catalysis shows a dependence on pH which is typical of ruthenium aquo complexes. The measured catalytic activity is very sensitive to specific "click" reaction conditions used for activation. Activation by light exposure has

also been demonstrated to activate ruthenium complex but activation is in competition with loss of ruthenium from the surface.
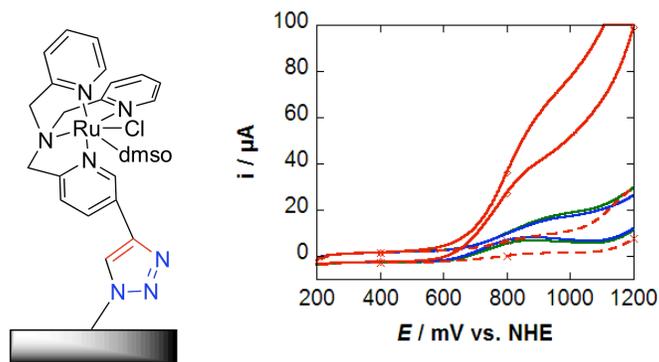

Figure 5: Electrocatalytic oxidation of alcohols by a GC-TPA-Ru Species (a) CV (10 mV/s, pH 7 phosphate buffer) of catalytic oxidization of 0.1 M benzyl alcohol (solid red), 0.1 M isopropanol (solid blue), 0.1 M methanol (solid red), ITO-TPA-Ru complex background (dashed red)

Molecular ruthenium transfer hydrogenation catalysts[23-25] provide attractive candidates for reversible alcohol electroxidation. In a typical transfer hydrogenation, an alcohol is oxidized and a ketone functions as the hydrogen acceptor. The approximate thermoneutrality of these reactions suggests that the catalysts mediating these transformations are operating close to their reversible redox potentials. We have investigated several homogeneous transfer hydrogenation catalysts for the electro-oxidation of alcohols.
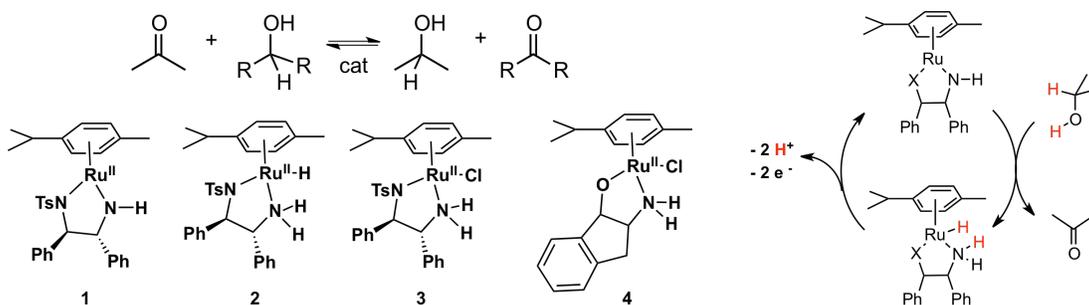

Figure 6: Homogeneous Ruthenium transfer hydrogenation catalysts (left). Proposed mechanism for electrocatalytic alcohol oxidation (right).

Complexes **1**, **2** and **4** were shown to be active electrocatalysts for the electrooxidation of methanol and isopropanol, when physisorbed on edge-plane graphite (EPG) electrodes in aqueous solution. Representative data is shown in Figure 7 for the electrocatalytic oxidation of methanol with amino alcohol complex **4**. Amino alcohol complex **4** adsorbed onto EPG in a 1.23 M methanol solution exhibits an onset of electrocatalytic current at approximately 560 mV vs. NHE (Figure 7).
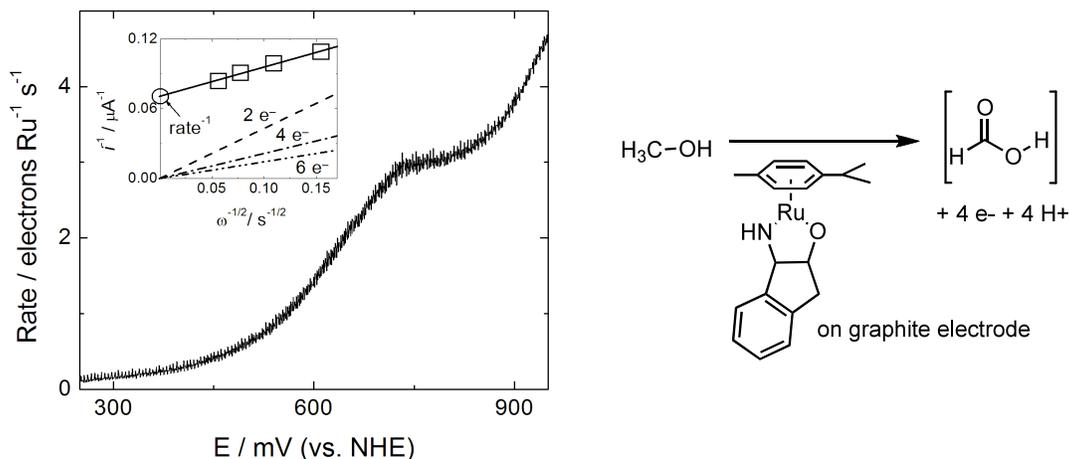
Figure 7: Methanol oxidation catalyzed by an immobilized Ru catalyst on edge-plane graphite (1M NaClO$_4$, 0.1M Phosphate buffer, pH 11.5). The slope of the Koutecky-Levich plot matches that of a theoretical 4 electron oxidation of methanol (insert).[26]

Koutecky-Levich analysis[26] for the oxidation of methanol by **4** at 750 mV vs. NHE yields a current density of 76.4 μA/cm^2, indicative of a rate of approximately 4 electrons/second at 750 mV (coverage = 1.7 x 10^{14} molecules/cm^2). The plot of the inverse currents are parallel to the inverse Levich current calculated with n=4 (Figure 7, inset), suggesting that the adsorbed complex catalyzes a 4-electron oxidation of methanol, generating either formate or carbon monoxide.

Electrocatalytic oxidation of isopropanol by amino alcohol complex **4** reveal an onset of electrocatalytic current at approximately 500 mV vs. NHE, approx. 60 mV more positive than that for methanol. Koutecky Levich analysis is consistent with a 2-electron oxidation of isopropanol with a current density of 430 μA/cm^2, or a rate of approximately 17 electrons/second at 750 mV vs. NHE, considerably higher than that observed for methanol.

The electrocatalytic oxidation of isopropanol occurs with diamide complex **1** adsorbed onto EPG at pH=11.5, albeit at higher potential(ca. 650 mV vs. NHE) for **1** than **4** and at a slower rate (6.5 vs. 17 electrons/second for **1** and **4**, respectively). The lower electrocatalytic activity of **1**(current density=100 μA/cm^2) relative to **4** is consistent with their solution behavior, as **1** exhibits a lower rate of transfer hydrogenation of acetophenone (CH$_3$CO(C$_6$H$_5$)) than **4** (18 vs. 113 moles isopropanol/(mol Ru•hr)).

Selective Oxidation of Polyols: Oxidation of Glycerol to Dihydroxyacetone
As part of our efforts to develop fast oxidation catalysts as potential electrocatalysts, we have developed a new family of Pd complexes for the oxidation of diols and polyols. Mechanistic studies of methanol oxidation with the molecular Pd catalyst [neocuproinePd(OAc)]$_2$[OTf]$_2$ (OTf = trifluoromethylsulfonate) revealed that the oxidation of methanol to methyl formate occurs selectively without the formation of

carbon monoxide,[27] providing an alternate pathway to mechanisms that lead to poisoning on metal electrode methanol oxidation catalysts.   These catalysts are also remarkably selective for polyol oxidation. Oxidation of glycerol with 5 mol% [neocuproinePd(OAc)]$_2$[OTf]$_2$ at room temperature in CH_3CN with air as a terminal oxidant affords a 97% yield of dihydroxyacetone (DHA) in 2 hours.[28] In DMSO, the reaction is complete in 15 min, which corresponds to a turnover frequency of 240 h^{-1}. The selectivity for dihydroxyacetone is remarkably high. In dry CH_3CN, approximately 5% glyceraldehyde is generated along with dihydroxyacetone; in CH_3CN/H_2O or wet DMSO no glyceraldehyde can be detected and the selectivity for DHA is >97%. Glycerol is a major biproduct of bio-diesel manufacturing;[29] this catalyst system is the first example of the selective oxidation of this readily available feedstock to dihydroxyacetone,[29] a commodity product currently used in the cosmetics and the fine chemical industry. Dihydroxyacetone is industrially produced from the microbial oxidation of glycerol;[30] our results demonstrate that high selectivity for DHA is possible with appropriately designed transition metal catalysts.

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