

# **The Electron Economy: Oxidation Catalysis for Energy Management**

## **Investigators**

Robert M. Waymouth, Professor, Chemistry  
Christopher E. D. Chidsey, Associate Professor, Chemistry  
T. Daniel P. Stack, Associate Professor, Chemistry  
Charles C. L. McCrory, Graduate Student, Chemistry  
Kristen Brownell, Graduate Student, Chemistry  
Eric J. Stenebjerg, Graduate Student, Chemistry  
David M. Pearson, Graduate Student, Chemistry  
Matthew A. Pellow, Graduate Student, Chemistry  
Jonathan Prange, Graduate Student, Chemistry  
Vadim R Ziatdinov, Postdoctoral Researcher, Chemistry  
Andrew Thomas, Postdoctoral Researcher, Chemistry  
Ali Hosseini, Postdoctoral Researcher, Chemistry  
Anthony DeCrisci, Postdoctoral Researcher, Chemistry

## **Abstract**

The energy-efficient removal of high free energy electrons stored in chemical fuels is a key chemical step in an efficient electron economy. The objective of this project is to develop efficient electrocatalysts for the oxidation of chemical fuels. We have developed a versatile method for functionalizing a variety of carbonaceous and metal oxide electrodes utilizing a new method pioneered by the team. Functionalization of electrode surfaces with azide, followed by coupling of an alkyne-labeled electroactive metal complex with the surface generates molecular electrocatalysts covalently bonded to the electrode surface. These advances have been coupled to developments in molecular catalysis to generate two new families of supported alcohol oxidation electrocatalysts based on Ruthenium complexes.

## **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**

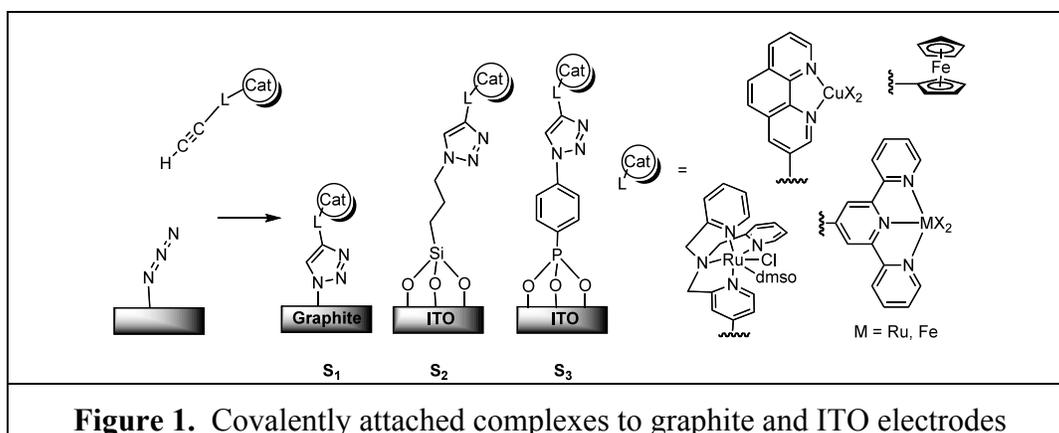
Currently, the most efficient electrooxidation catalysts that operate at fast rates and low overpotentials are Pt catalysts for hydrogen oxidation. Electrooxidation for more energy-

dense liquid fuels (alcohols, hydrocarbons) are plagued by high overpotentials and/or low current densities that result in low energy efficiency.[1] For methanol, the most effective electrocatalysts are PtRu alloys, but the poisoning of these electrodes by CO (a partial oxidation product) leads to high overpotentials to oxidize methanol to CO<sub>2</sub>. [1,2] 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[3] 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[4-6] is an active and promising area of research for electrocatalytic energy conversion[7] and has proven a powerful approach for the design of electrocatalysts for water oxidation[7,8] and alcohol oxidation.[9]

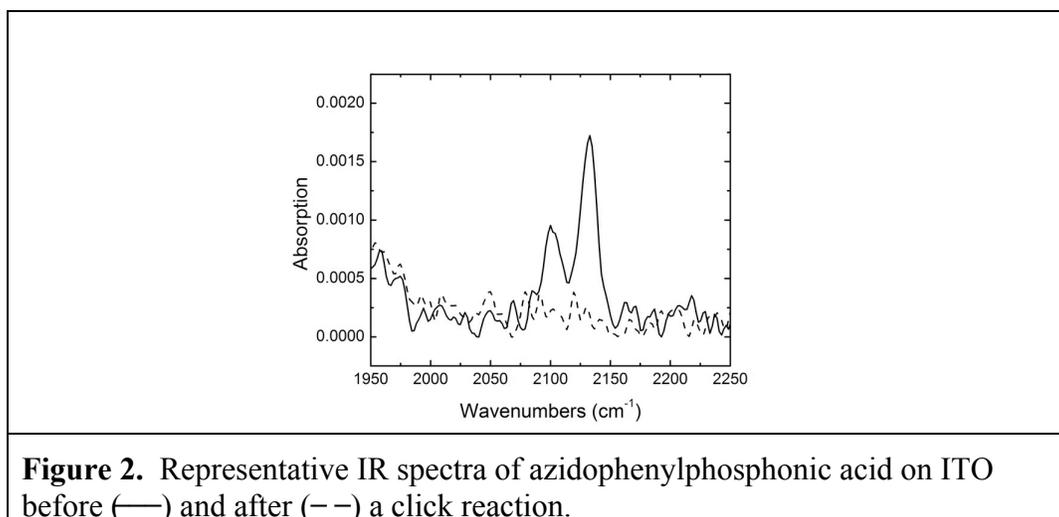
## Results

Our highly collaborative team is 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 and to understand the mechanisms of catalysis by surface-attached molecular species, and (3) the synthesis and characterization of new classes of molecular electrocatalysts targeted at fast rates of oxidation at low overpotentials.

*The 'Click' Reaction for Electrode Modification.* We have adapted our previously developed methods[10,11] to attach molecular electrocatalysts to glassy carbon electrodes, indium-tin-oxide (ITO) electrodes[12,13], and gold electrodes utilizing catalytic 3+2 cycloaddition reactions of surface-bonded azides to alkyne-functionalized ligands ("click" chemistry).[14] This simple and efficient coupling 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 graphite and ITO. The three electrode materials that we have selected provide complementary properties. Glassy carbon is convenient for electroanalytical characterization of electrode reactions and 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 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.

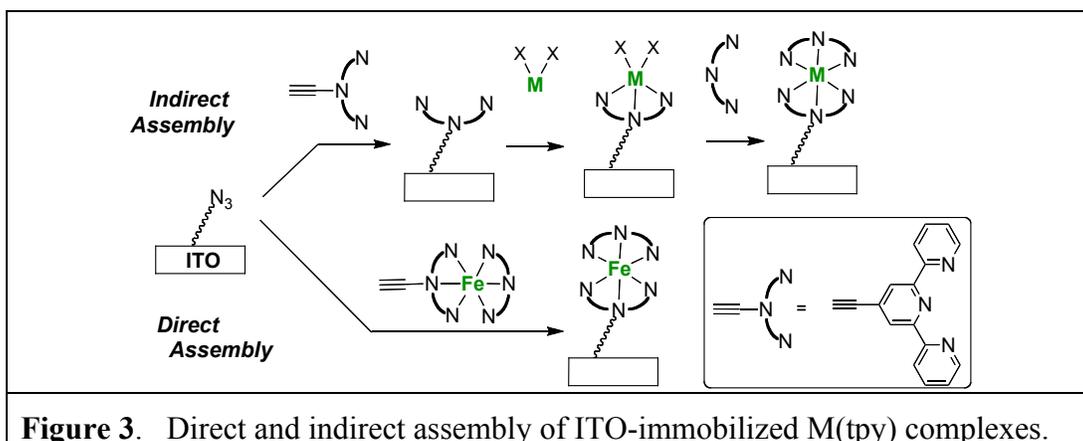


We have developed a series of methods to characterize modified electrode surfaces. As is typical of surface science, a combination of methods is required. This past year we have demonstrated an important new tool: reflection-absorption infrared spectroscopy from ITO surfaces. This is a particularly sensitive, convenient and inexpensive way to monitor the surface azides and their reactions. Figure 2 provides an example where the disappearance of the surface bound azide can be used to monitor the progress of the reaction. The IR absorption can be calibrated by electrochemical measurement of the number of electroactive species coupled to the azides.

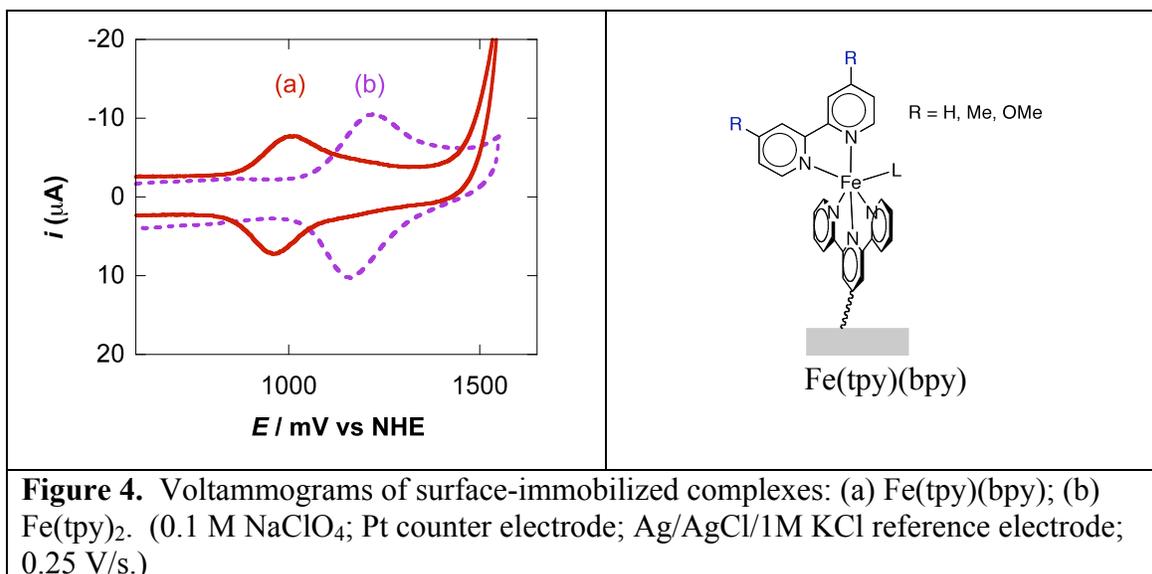


*Metal Complexes Attached to Electrode Surfaces.* In parallel with our investigations of the electrode surface modification chemistry, we have developed a flexible and modular method for introducing reactive metal species onto the modified electrode surfaces. A key advance was the development of a modular method for introducing ligands onto electrode surfaces that can then be combined with a variety of different metals.

For instance, terpyridine (tpy) is a versatile supporting ligand for oxidation catalysis.[15,16] The direct attachment of an iron containing two tpy ligands  $[\text{Fe}(\text{tpy})(\text{tpy}-\text{C}\equiv\text{CH})](\text{OS}(\text{O})_2\text{CF}_3)_2$  can be quantified readily by its electrochemical signature (Figs. 3 and 4). We showed that the same surface complex assembles in an indirect, stepwise synthetic procedure by first attaching the ligand and subsequently adding a solution of the iron tpy (Fig 3). We extended this method to generate a surface-immobilized  $\text{Co}(\text{tpy})_2$  complex, demonstrating the generality of this procedure.



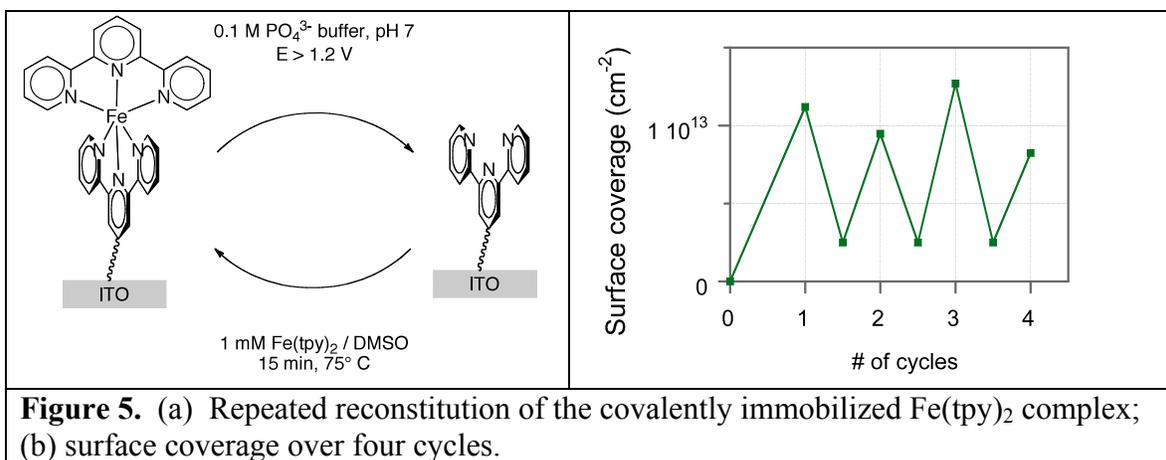
We have extended the preparation of terpyridine surface complexes to a new surface complex containing both terpyridine (tpy) and bipyridine (bpy), identified by its distinct redox potential 0.2 V negative of the surface  $\text{Fe}(\text{tpy})_2$  redox potential (Fig. 4).



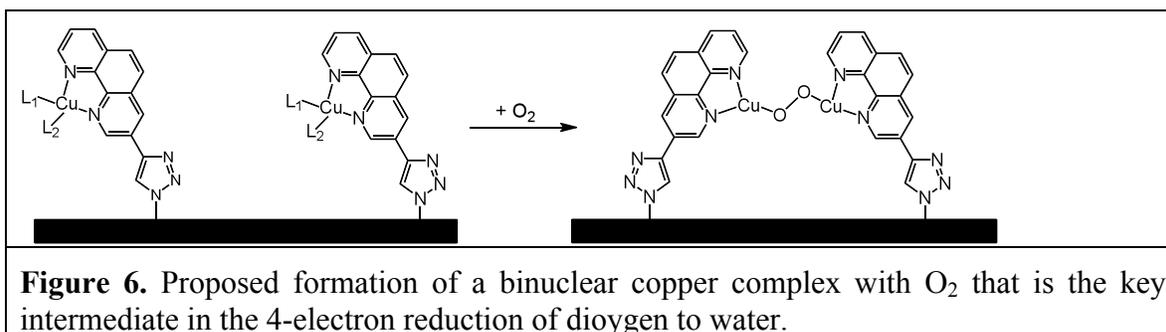
This octahedral complex has five coordination sites occupied by polypyridyl ligands, and shows the feasibility of preparing a Fe complex with a sixth coordination site available for exchange with surrounding species, a key attribute for inner-sphere chemistry. Because a strong driving force exists toward forming coordinatively saturated

Fe(bpy)<sub>3</sub> or Fe(tpy)<sub>2</sub> complexes in solution, the stability of the Fe(tpy)(bpy) complex is enabled uniquely by the surface immobilization strategy. We further confirmed the presence of the bpy in the ligand sphere by the preparing a series of surface bpy complexes with substituted bipyridines (proton, methyl and methoxy substituents). This series shows the expected range of reduction potentials due to the increasingly electron-donating character of the bpy ligands across this series.

We have also confirmed the stability of the covalently immobilized tpy linker through cyclic depletion and reconstitution of the immobilized Fe(tpy)<sub>2</sub> complex (Fig. 5).



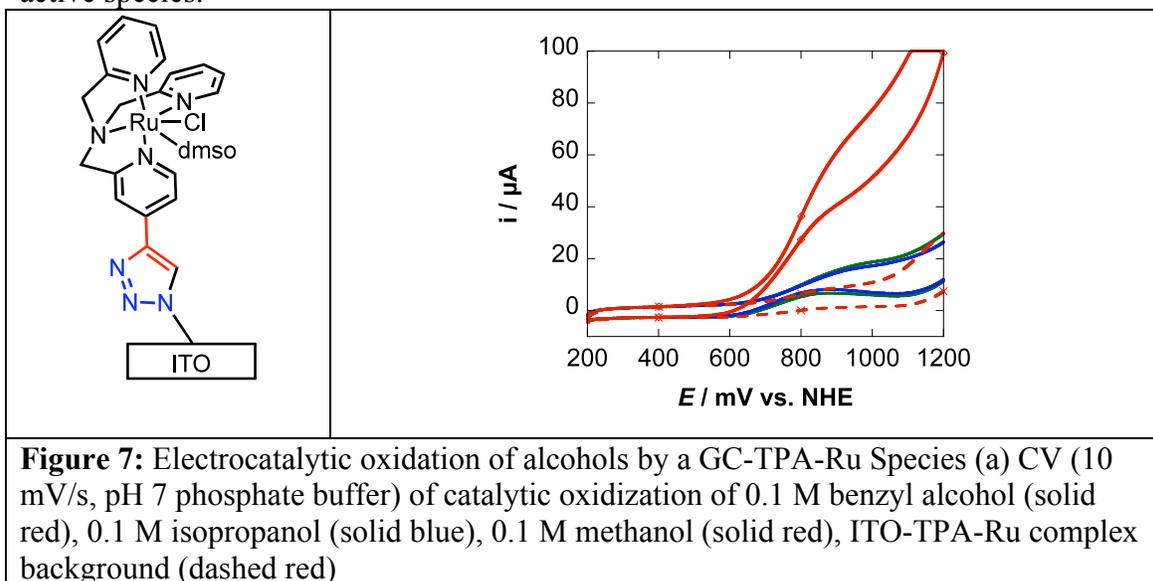
Covalent attachment of complexes to electrodes not only allows access to stable complexes, but can also provide mechanistic insight into transient intermediates in catalytic cycles. In a study of the electrocatalytic reduction of dioxygen, we have varied the coverage of surface-attached Cu phenanthroline complexes on glassy carbon. 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 led us to propose that a binuclear complex (Figure 6) 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.



*Electrocatalytic Oxidation of Alcohols with Immobilized Ruthenium Complexes.* Armed with this battery of electrode surface modification procedures, in the last grant period we have used these methods to generate surface-supported molecular species as electrocatalysts for alcohol oxidation. Our initial investigations have focused on two families of Ru complexes, which are active oxidation catalysts in solution when combined with added oxidants. A key objective is to identify those catalysts that can mediate electrochemical oxidations in which the electrode mediates the removal of electrons rather than a molecular oxidant such as O<sub>2</sub>.

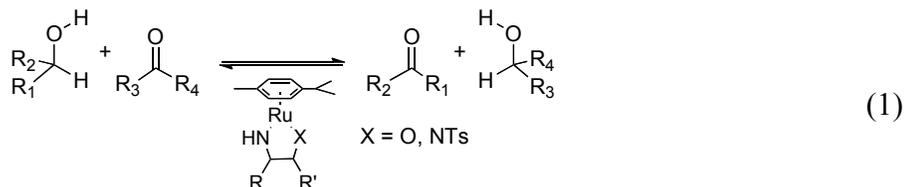
Ruthenium oxo complexes have been demonstrated to be versatile oxidation catalysts using either oxo-transfer or one-electron outer-sphere reagents.[17] The Ru complex [Ru(TPA)(DMSO)(Cl)]•PF<sub>6</sub>, which is a competent pre-catalyst for both alcohols and alkanes,[18,19] was modified with an ethynyl group[20] to enable its immobilization onto ITO and GC azide modified electrode surfaces. Cyclic voltammetry (CV) of this complex in acetonitrile solution exhibits a Ru(II)/Ru(III) reversible oxidation at a potential of E<sup>0</sup> = 970 mV vs. NHE. Electrocatalytic oxidation of alcohols with the ITO and GC surface immobilized Ru complex shows no catalytic activity.

The GC immobilized complex can be activated for catalysis by exposure to light or basic conditions to form an active catalytic complex. Catalysis is seen in a pH 7 phosphate buffer solution for methanol, isopropanol, and benzyl alcohol with an onset of catalysis around 750 mV vs. NHE (Figure 3). The immobilized active catalyst shows a dependence on pH that is typical of ruthenium aquo complexes. Although not yet optimized, this system exhibits some of the highest turnover numbers known for the electrocatalytic oxidation of benzyl alcohol.[9] Further studies will probe the identity of this Ru TPA active species.



The second class of Ru oxidation catalysts that we have targeted is based on a family of molecular catalysts known to mediate the transfer hydrogenation of alcohols and ketones.[21] In transfer hydrogenation, an alcohol is oxidized and a ketone is reduced (Equation 1). Equilibrium is reached rapidly in the presence of these Ru catalysts. From

these facts, we propose that these catalysts will mediate the electro-oxidation of alcohols to ketones at low overpotential.



We have found that edge-plane graphite electrodes with these Ru complexes physically adsorbed to their surfaces electro-oxidize methanol and isopropanol with rates on the order of 1 turnover per metal atom per second, but at high overpotentials (~1.1-1.2 V). We concluded that these catalysts are transforming into ruthenium-oxide species, which are responsible for the alcohol oxidation observed. Homogeneous solution measurements indicated that the initial rate of transfer hydrogenation with alcohols is slow, limiting our ability to observe electrocatalysis at lower potentials. Solution phase cyclic voltametry of these complexes at higher Ru concentrations (~1 mM) in neat isopropanol show an onset of oxidation at 300 mV, illustrating the potential of these complexes to mediate electrocatalytic oxidation of alcohols at low potentials.

## Progress

Progress in this year includes new strategies for generating and characterizing electrodes functionalized with molecular electrocatalysts. Our progress further includes the development of unique metal complexes on the electrodes and mechanistic insights into their catalytic function. Finally, we are expanding the types of catalysts and mechanisms for electrocatalysis by developing new electrocatalysts that can be attached to electrode surfaces. Ultimately, these new developments could have a significant impact on greenhouse gas emissions by maximizing the useable energy that could be derived from chemical fuels per unit mass of CO<sub>2</sub> generated.

## Future Plans

We will continue our study of the formation of metal complexes on different electrode surfaces with a particular focus on the mechanisms of catalytic reactions. We will also continue our exploration of new mechanisms to accelerate the oxidation of alcohols and other fuels including the transfer hydrogenation catalysts, the formation of binuclear intermediates and structures that facilitate proton-coupled electron transfer.

We have prepared highly active Ru transfer hydrogenation catalysts[22] and are currently investigating their electrocatalytic behavior for alcohol oxidation.

## Publications

1. Pearson, D. M.; Waymouth, R. M. "Mechanistic Studies of the Oxidative Dehydrogenation of Methanol using a Cationic Pd Complex" *Organometallics*, **2009**, 28, 3896-3900.

## References

1. Liu, H. S., Song, C. J., Zhang, L., Zhang, J. J., Wang, H. J., and Wilkinson, D. P., A review of anode catalysis in the direct methanol fuel cell, *Journal of Power Sources*, 155, 95-110, 2006.
2. Iwasita, T., Hoster, H., John-Anacker, A., Lin, W. F., and Vielstich, W., Methanol oxidation on PtRu electrodes. Influence of surface structure and Pt-Ru atom distribution, *Langmuir*, 16, 522-529, 2000.
3. Cheung, K. C., Wong, W. L., Ma, D. L., Lai, T. S., and Wong, K. Y., Transition metal complexes as electrocatalysts - Development and applications in electro-oxidation reactions, *Coord. Chem. Rev.*, 251, 2367-2385, 2007.
4. Zhong, Y. L., Ng, W., Yang, J. X., and Loh, K. P., Electrostatically Self-Assembled Polyoxometalates on Molecular-Dye-Functionalized Diamond, *J. Am. Chem. Soc.*, 131, 18293-18298, 2009.
5. Malmos, K., Dong, M. D., Pillai, S., Kingshott, P., Besenbacher, F., Pedersen, S. U., and Daasbjerg, K., Using a Hydrazone-Protected Benzenediazonium Salt to Introduce a Near-Monolayer of Benzaldehyde on Glassy Carbon Surfaces, *J. Am. Chem. Soc.*, 131, 4928-4936, 2009.
6. Decreau, R. A., Collman, J. P., and Hosseini, A., Electrochemical applications. How click chemistry brought biomimetic models to the next level: electrocatalysis under controlled rate of electron transfer, *Chem. Soc. Rev.*, 39, 1291-1301, 2010.
7. Chen, Z. F., Concepcion, J. J., Jurss, J. W., and Meyer, T. J., Single-Site, Catalytic Water Oxidation on Oxide Surfaces, *J. Am. Chem. Soc.*, 131, 15580+, 2009.
8. Concepcion, J. J., Jurss, J. W., Brennaman, M. K., Hoertz, P. G., Patrocino, A. O. T., Iha, N. Y. M., Templeton, J. L., and Meyer, T. J., Making Oxygen with Ruthenium Complexes, *Acc. Chem. Res.*, 42, 1954-1965, 2009.
9. Hornstein, B. J., Dattelbaum, D. M., Schoonover, J. R., and Meyer, T. J., Reactivity of an adsorbed Ru(VI)-oxo complex: Oxidation of benzyl alcohol, *Inorg. Chem.*, 46, 8139-8145, 2007.
10. Devadoss, A., and Chidsey, C. E. D., Azide-modified graphitic surfaces for covalent attachment of alkyne-terminated molecules by "click" chemistry, *J. Am. Chem. Soc.*, 129, 5370-5371, 2007.
11. Collman, J. P., Hosseini, A., Eberspacher, T. A., and Chidsey, C. E. D., Selective Anodic Desorption for Assembly of Different Thiol Monolayers on the Individual Electrodes of an Array, *Langmuir*, 25, 6517-6521, 2009.
12. Fattakhova-Rohfing, D., Brezesinski, T., Rathousky, J., Feldhoff, A., Oekermann, T., Wark, M., and Smarsly, B., Transparent conducting films of indium tin oxide with 3D mesopore architecture, *Advanced Materials*, 18, 2980-2986, 2006.
13. Pohl, A., and Dunn, B., Mesoporous indium tin oxide (ITO) films, *Thin Solid Films*, 515, 790-792, 2006.
14. Kolb, H. C., Finn, M. G., and Sharpless, K. B., Click chemistry: Diverse chemical function from a few good reactions, *Angew. Chem., Int. Ed.*, 40, 2004, 2001.
15. Limburg, J., Vrettos, J. S., Liable-Sands, L. M., Rheingold, A. L., Crabtree, R. H., and Brudvig, G. W., A functional model for O-O bond formation by the O<sub>2</sub>-evolving complex in photosystem II, *Science*, 283, 1524-1527, 1999.
16. Liu, F., Concepcion, J. J., Jurss, J. W., Cardolaccia, T., Templeton, J. L., and Meyer, T. J., Mechanisms of water oxidation from the blue dimer to photosystem II, *Inorg. Chem.*, 47, 1727-1752, 2008.

17. Meyer, T. J., and Huynh, M. H. V., The remarkable reactivity of high oxidation state ruthenium and osmium polypyridyl complexes, *Inorg. Chem.*, 42, 8140-8160, 2003.
18. Yamaguchi, M., Kousaka, H., Izawa, S., Ichii, Y., Kumano, T., Masui, D., and Yamagishi, T., Syntheses, characterization, and catalytic ability in alkane oxygenation of chloro(dimethyl sulfoxide)ruthenium(II) complexes with tris(2-pyridylmethyl)amine and its derivatives, *Inorg. Chem.*, 45, 8342-8354, 2006.
19. Hirai, Y., Kojima, T., Mizutani, Y., Shiota, Y., Yoshizawa, K., and Fukuzumi, S., Ruthenium-catalyzed selective and efficient oxygenation of hydrocarbons with water as an oxygen source, *Angew. Chem., Int. Ed.*, 47, 5772-5776, 2008.
20. Nakazawa, J., and Stack, T. D. P., Controlled Loadings in a Mesoporous Material: Click-on Silica, *J. Am. Chem. Soc.*, 130, 14360-14365, 2008.
21. Ikariya, T., and Blacker, A. J., Asymmetric transfer hydrogenation of ketones with bifunctional transition metal-based molecular, *Acc. Chem. Res.*, 40, 1300-1308, 2007.
22. Baratta, W., Bosco, M., Chelucci, G., Del Zotto, A., Siega, K., Toniutti, M., Zangrando, E., and Rigo, P., Terdentate RuX(CNN)(PP) (X = Cl, H, OR) complexes: Synthesis, properties, and catalytic activity in fast transfer hydrogenation, *Organometallics*, 25, 4611-4620, 2006.

## Contacts

Bob Waymouth, waymouth@stanford.edu

Chris Chidsey, chidsey@stanford.edu

Dan Stack, stack@stanford.edu

Kristen Brownell, krbrowne@stanford.edu

Eric J. Stenohjem, esten@stanford.edu

David M. Pearson, nitrene@stanford.edu

Matthew A. Pellow, mpellow@stanford.edu

Jonathan Prange, jprange@stanford.edu

Vadim R Ziatdinov, vadimius@stanford.edu

Andrew Thomas, amt@stanford.edu

Ali Hosseini, alih2@stanford.edu

Anthony DeCrisci, decrisci@stanford.edu