
Nanoscale Building Blocks for Multi-Electron Electrocatalysis

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Objectives

The goal of this research project is to develop a fundamental understanding of multielectron electrochemical reactions such as the $4e^-$ reduction of oxygen to water involving coupled electron transfer and atom transfer processes. Our approach to electrocatalysis utilizes the attachment of molecules that are selective for the reaction of interest in homogeneous solution to nanotextured conducting supports. Redox active electron donors or acceptors such as the cyclopentadienylironcarbonyl tetramer, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu_3\text{-CO})]_4$, that are capable of providing the multiple electron oxidizing or reducing equivalents at the required potential for near thermodynamic reversibility will mediate electron transfer between the support and the active catalyst sites such as binuclear cobalt porphyrin complexes. The kinetics and the reactivity of these supramolecular assemblies are being studied both experimentally and computationally, and we are conducting *in situ* XANES-electrochemistry experiments to determine the oxidation state of the electron antenna and the metal ion in the active site.

Technical Barriers

The design of electrodes to efficiently carry out processes in which atom transfer accompanies electron transfer, such as the $4e^-$ reduction of oxygen to water, is a fundamental problem in electrochemistry. This research program will provide the fundamental basis for the development of electrocatalysts with lower overpotential for oxygen reduction.

Progress Report

A molecular level understanding of multielectron electrochemical reactions that involve coupled electron transfer and atom transfer reactions will allow the design and preparation of new, efficient electrocatalysts for energy utilization and storage. The overpotential for the reduction of oxygen in fuel cells at a useful operating current density is too high because of the slow electrochemical kinetics of oxygen reduction caused by the build-up of intermediate oxidation states of oxygen. Our approach to the design of electrocatalysts is the attachment of molecules that are selective for the reaction of interest in homogeneous solution to conducting supports. In this approach redox active electron donors or acceptors that can provide the multiple electron oxidizing or reducing equivalents at the required potential for near thermodynamic reversibility are also attached to the active site. These electron transfer catalysts will react with the conducting support with a higher exchange current density than the substrate binding site, and these catalysts will determine the electrode potential. We will use this approach to design "molecular electrodes" that are capable of carrying out multi-electron electrochemical reactions involving atom transfer in a more energy efficient manner. Fundamental theoretical and experimental scientific research is needed to understand both the reactivity of supramolecular or nanoscale assemblies that are capable of effecting selective chemical transformations driven by electrical energy and the methodology to construct these assemblies at the required density. The focus of work in this program falls within the following themes:

- preparation, characterization, and reactivity of active catalysts based on metalloporphyrin binding sites and organometallic electron exchange catalysts
- theoretical description of electron transfer coupled with atom transfer leading to the design of electrocatalysts
- *in situ* characterization of active electrocatalysts using X-ray spectroscopy (XANES and EXAFS)
- electrochemistry of nanostructured conducting carbon supports

Initial progress has been made in studies of monomeric cobalt porphyrins and linked cofacial biscobalt porphyrin dimers adsorbed on carbon by *in situ* electrochemistry-X-ray spectroscopy. EXAFS of the adsorbed catalyst gives information about the coordination site around the Co center, while the XANES band edge contains information about the oxidation state of the active site. Several new cell designs for conducting *in situ* electrochemistry-X-ray

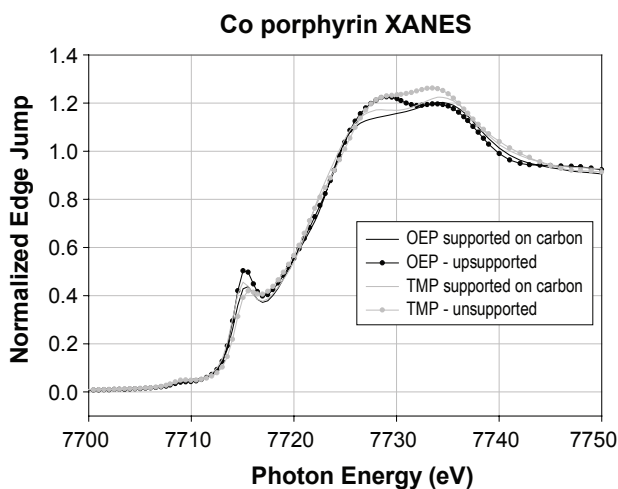


FIGURE 1. XANES of CoOEP and CoTMP Undiluted and Sorbed on Carbon

spectroscopy by detection of X-ray emission have been constructed and tested at the NSLS at Brookhaven National Laboratory. The XANES and EXAFS of several cobalt porphyrins that catalyze the 4e reduction of oxygen when sorbed on graphite electrodes [1] are under investigation. The XANES of a number of Fe and Co compounds were examined to determine the influence of the ligand environment as well as the oxidation state on the band edge and to determine the conditions under which changes in the band edge are a good measure of oxidation state. The band edge of iron cyclopentadienyl compounds was observed to vary little with oxidation state. The XANES of a number of Co porphyrins were examined and a combination of pre-edge features and band edge appears to be a measure of oxidation state. Figure 1 indicates that the XANES of monomeric cobalt(II) tetramethylporphyrin (CoTMP) and cobalt(II) octaethylporphyrin (CoOEP) are independent of whether the complex is adsorbed on a carbon support. A cofacial bridged cobalt porphyrin dimer (Pacman complex) [2] which was reported to catalyze the 4e- reduction of oxygen was prepared and characterized by solution electrochemistry and spectroscopy. The EXAFS of cobalt tetraphenylporphyrin (CoTPP) and CoOEP were measured and the results compared with the predictions from known crystal structures. A comparison of experimental and fitted data for CoOEP is shown in Figure 2.

The reaction chemistry of the cyclopentadienyl iron carbonyl tetramer ($[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu_3\text{-CO})_4]$) is under investigation as an electron exchange catalyst. The rate of electron exchange of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\mu_3\text{-CO})_4]^{+/0}$ couple will be measured, and development of chemical reactions to attach the iron tetramer to the meso positions of porphyrin (either directly or with a bridging phenyl group) is in progress. The Co(II) complex of this

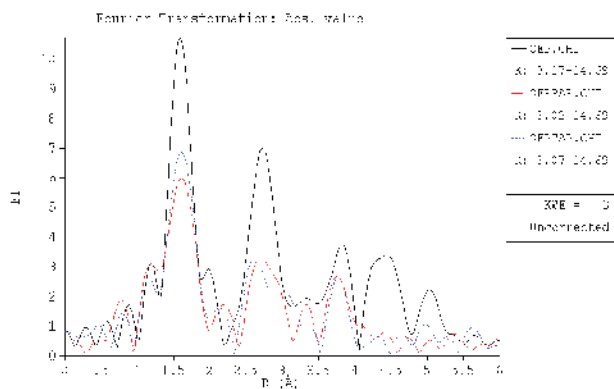
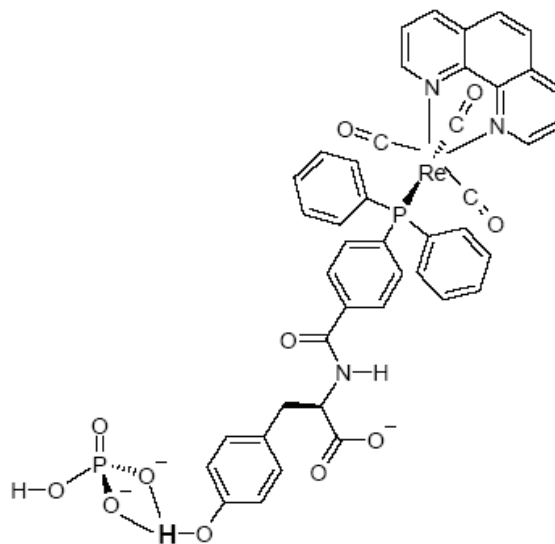


FIGURE 2. Experimental and Theoretical Fourier Transform for CoOEP Sorbed on Carbon and Undiluted

species will be tested for catalysis of the four electron reduction of oxygen to water in comparison to an analogous ferrocene-substituted porphyrin.

We have performed theoretical studies of proton-coupled electron transfer (PCET) in the rhenium(I) polypyridyl system shown in Figure 3. These calculations are based on the experiments of Reece and Nocera [3]. In these experiments, photoexcitation of the complex leads to a metal-to-ligand charge transfer (MLCT) excited state of the rhenium complex. This photoexcitation induces an electron transfer from the tyrosine to the MLCT excited state of the rhenium complex and a concurrent proton transfer from the tyrosine to the HPO_4^{2-} phosphate buffer or, alternatively, to a water molecule. The pH dependence of the rate for this PCET reaction has been measured experimentally. We applied our multistate continuum theory to this PCET reaction and calculated the pH dependence of the rate. Our objective was to determine if the proton is transferred to the phosphate buffer or



to a water molecule. Comparison of the theoretical and experimental results indicates that the proton is transferred to the phosphate buffer. These calculations also provide insight into the detailed mechanism of this PCET reaction.

Future Directions

Experiments have been designed and theoretical studies planned to provide a molecular level understanding of multielectron electrochemical reactions that involve coupled electron transfer and atom transfer reactions. Our objective is to design and study “molecular electrodes” that are capable of carrying out multi-electron electrochemical reactions involving atom transfer in a more energy efficient manner. These supramolecular catalyst assemblies will be attached to nanotextured conducting carbon supports for demonstrating the four-electron electrochemical reduction of oxygen. A theoretical description of electron transfer coupled with atom transfer is expected to lead to the design of electrocatalysts. *In situ* characterization of the catalysts using XANES and EXAFS in concert with electrochemical measurements will assist in validation of models. Our anticipated research accomplishments include the following:

- Improved synthesis of the iron tetramer $[\text{CpFe}(\mu_3\text{-CO})_4]$ and improved attachment synthetic methods so the iron tetramer can be attached to a variety of oxygen binding sites and to the surface of carbon electrodes.
- The kinetics of the reduction of oxygen by cofacial bridged cobalt porphyrin dimers (Pacman complexes) and Co porphyrin complexes with appended proton transfer sites (Hangman complexes) with different electron acceptors will be studied by stopped-flow kinetic spectroscopy.
- Preparation of cobalt porphyrin complexes with appended electron acceptors and the kinetics of the reduction of oxygen in solution and at electrode surfaces will be measured to quantify the four-electron reduction pathway.
- Preparation of chemically modified nanostructured carbon supports and combined electrochemistry-XANES and EXAFS experiments.
- A theoretical understanding of the redox potential at which the four-electron reduction of oxygen proceeds at a convenient rate where oxygen and proton transfer accompany electron transfer.

References

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