

Center for Molecular Electrocatalysis (CME)
EFRC Director: R. Morris Bullock
Lead Institution: Pacific Northwest National Laboratory
Class: 2009 – 2022

Mission Statement: To establish the fundamental principles needed for efficient interconversion of electrical energy and chemical bonds through precise control of electron and proton transfers.

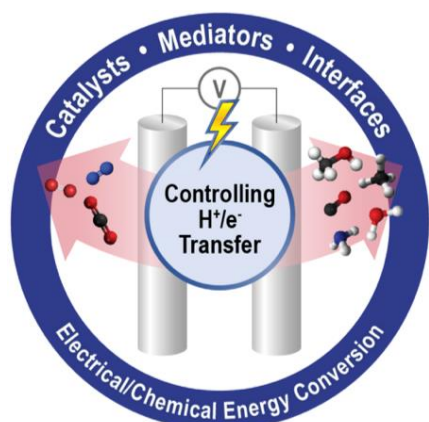


Figure 1. Efficient electrocatalysts require precise control of movement of protons and electrons.

We will pioneer a system-level approach to improve catalyst performance by simultaneously targeting three integrated goals: (1) *transcending scaling relationships*, (2) *enhancing catalysis using mediators*, and (3) *achieving molecular control of interfaces* (Fig. 2). The broad scope of these efforts will be addressed through closely coupled experimental and computational studies, grounded in thermochemical analysis and novel theoretical approaches.

Energy production in the United States is evolving rapidly, with growing contributions from wind and solar. The increasing generation of intermittent and off-peak electricity requires reliable energy storage (Fig. 1). Chemical bonds are ideal for energy storage because of the high energy density of chemical fuels, as well as the large scale at which fuels can be stored. Revolutionary solutions to this challenge require transformative fundamental discoveries in electrocatalysis and interfacial reactivity to achieve energy-efficient interconversion of electrical and chemical energy.

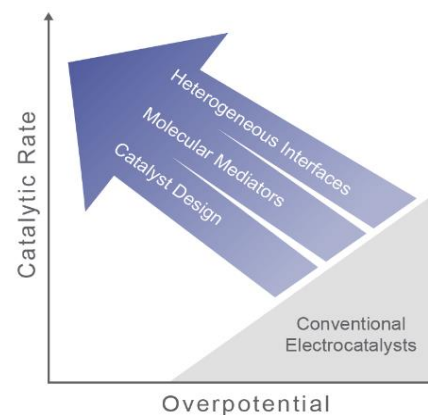


Figure 2. CME seeks to improve the rates, energy efficiencies, and selectivities through the design of catalyst systems that surpass the limitations suggested by conventional correlations between these parameters.

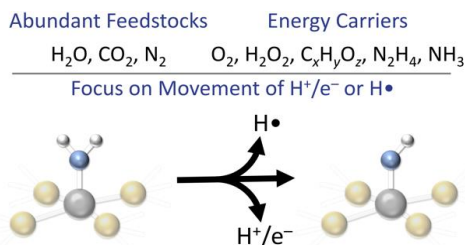


Figure 3. By focusing on the thermodynamics and kinetics of the movement of protons/electrons, CME will develop the principles needed to design catalysts with unprecedented performance.

The **Catalyst Design** research thrust seeks to transcend the limitations of conventional linear free-energy correlations between rate, overpotential, and selectivity by controlling the thermodynamics of proton-coupled electron transfer (PCET) reactions. (Fig. 3). We will show how the mechanistic characterization of catalytic reactions reveals not one, but multiple scaling relationships. Our work will contribute to the strategic design of new catalyst systems with dramatically improved performance. The **Molecular Mediators** research thrust will establish that electron-proton transfer mediators (EPTMs) provide an effective way to achieve “redox communication” between an electrode and a molecular or heterogeneous catalyst in bulk solution (Fig. 4). This use of EPTMs as “soluble electrodes” greatly expands the scope of electrode-driven

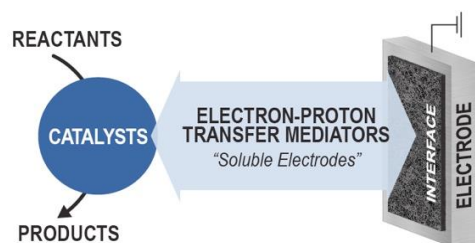


Figure 4. Mediated catalyst design is an emerging concept that will improve system performance by delivering H^+/e^- away from the electrode.

redox processes and provides the basis for dramatic improvements in the rates and/or overpotentials of these reactions. We intend to enhance electrocatalyst performance through cooperativity with tailored EPTMs and mediated electrocatalyst systems. The **Heterogeneous**

Interfaces research thrust will address the challenge of controlling e^-/H^+ transfer steps at heterogeneous interfaces, achieving control through insights from molecular reactivity (Fig. 5). PCET at the surface of electrodes and heterogeneous catalysts is a crucial basic science frontier underlying diverse electrochemical energy transduction reactions. Our cross-cutting **theoretical and computational activities** are aimed at understanding quantitative design principles for efficient control of proton and electron movement. These computational efforts will guide the exploration and optimization of the complex free energy landscape of catalytic processes. Methodological developments will have potential impact beyond the research topics directly addressed in our work, advancing computational capabilities for electrochemical PCET and atomistic modeling of electrochemical processes at interfaces.

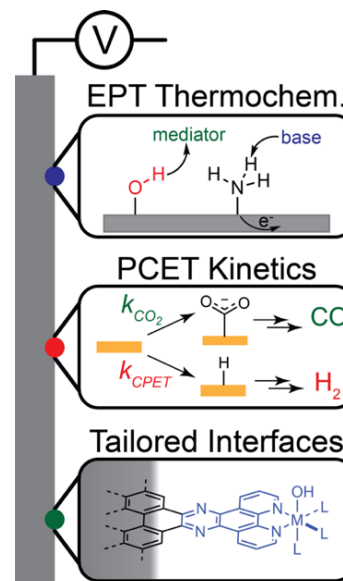


Figure 5. CME uses a molecular approach to tailor interface reactivity.

Fundamental principles developed through the proposed research will impact a range of scientific disciplines, as the bond-forming and bond-breaking reactions studied are applicable to many key questions in energy science. We envision a future energy landscape that has been radically transformed from the familiar long-standing practices, in which fuels will be produced at ambient temperature using electrocatalysts, starting from abundant molecules such as nitrogen, carbon dioxide, and water. The chemical energy in N-H or C-H bonds will be converted directly to electricity using fuel cells based on earth-abundant metals, obtaining high energy efficiency.

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