Center for Molecular Electrocatalysis (CME)
EFRC Director: Morris Bullock
Lead Institution: Pacific Northwest National Laboratory (PNNL)
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***Mission Statement**: To understand and design molecular electrocatalysts for conversions between electrical energy and chemical energy.*

Electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels, or the reverse, converting chemical energy to electrical energy, will play a critical role in future energy storage and energy delivery systems. Electrocatalytic processes involving multi-proton and multi-electron redox reactions are pervasive in energy science, and are critical for sustainable, carbon-neutral energy. The Center for Molecular Electrocatalysis addresses fundamental challenges in understanding how molecular electrocatalysts function, and uses this knowledge to rationally design new classes of molecular electrocatalysts for important energy storage and utilization reactions. Closely coupled experimental and theoretical studies include catalyst design and synthesis, mechanistic investigations, electrochemical and spectroscopic characterization, determination and control of thermochemical parameters for metal complexes, and evaluation of catalytic activity.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \qquad (1)$$

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \qquad (2)$$

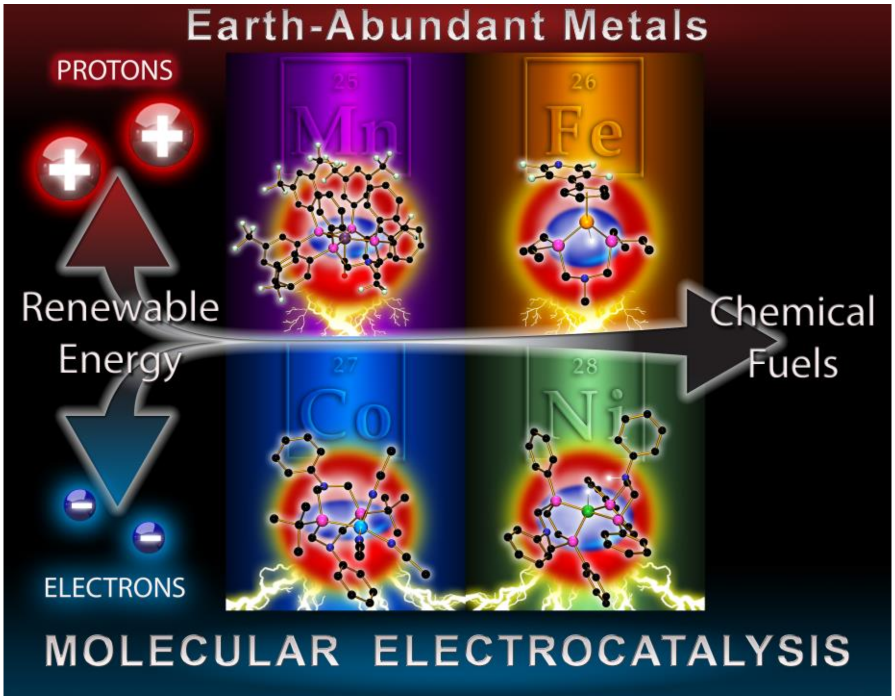
$$N_2 + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_3 \qquad (3)$$

Electrocatalytic reactions studied range from two-proton, two-electron processes to six-proton, six-electron reactions. A unique approach in this Center is a focus on the delivery of protons to (or from) the active site of molecular catalysts.

The prevalence in energy science of reactions that require controlled movement of protons and electrons suggests an immense scope for the methods to precisely control the delivery and removal of protons.

The reduction of protons derived from water to form hydrogen is shown in eq. 1 (forward direction). The reverse process, the oxidation of H_2, is the reaction used in hydrogen fuel cells to convert the chemical energy in the H-H bond to electricity. The four-electron reduction of O_2 to form water, (eq. 2, forward direction), is critical for fuel cells, providing the reductive half-reaction to balance the oxidative half-reaction of H_2. The reduction of nitrogen to ammonia stores energy in N-H bonds, and use of NH_3 in fuel cells converts the chemical energy of the N-H bonds to electrical energy by oxidation of NH_3.

Molecular catalysts offer a remarkable degree of structural control – and therefore the precise probing of relationships between catalyst structure and activity – that are much more difficult for heterogeneous catalysts and enzymes. *We seek to further develop this knowledge of structure-activity relationships.* The two-, four-, and six-*electron* redox processes in eqs. 1-3 for H_2, O_2, and N_2, are also two-, four-, and six-*proton* processes. Facile and controlled movement of both electrons *and* protons from solution to substrates bound at the active metal site is essential for these electrocatalytic reactions. Proton transfers must be very carefully controlled to obtain optimal rates and efficiency of molecular electrocatalysts. The generality of proton transfer processes in most fuel generation and utilization reactions makes understanding these processes at a fundamental level of enormous importance.



Proton relays are functional groups that play a crucial role in the delivery of protons to (or from) the active site of catalysts. They have been shown to play an important role in hydrogenase enzymes, the oxygen-evolving complex, and other biological systems.

Primary goals of the Center for Molecular Electrocatalysis are to:

- Develop an understanding of the fundamental principles that form the basis for designing catalysts with unprecedented activity and efficiency, with a focus on relaying H^+ and e^-.
- Improve catalyst design by predicting and controlling thermodynamic and kinetic features of catalysts, including their first, second, and outer coordination spheres.
- Understand and control mesoscale solvent organization to improve proton delivery.
- Implement and evaluate the impact of coupling proton and electron transfers as a design principle for electrocatalysis, including the use of concerted electron-proton transfer and chemical mediators.
- Advance the computational methodology needed to design new catalysts, toward accelerated discovery by modern computational approaches

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