

EFRC: THE CENTER FOR MOLECULAR ELECTROCATALYSIS (CME)

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AWARDS: \$22.5M (August 2009 – July 2014); \$14.0M (August 2014 – July 2018)

WEBSITES: <http://science.energy.gov/bes/efrc/centers/EFRC/>; <http://efrc.pnnl.gov/>

TEAM: Pacific Northwest National Lab (Lead): Morris Bullock (Director), Aaron Appel, Simone Raugai, Michael Mock, Eric Wiedner, Molly O'Hagan; **Yale University:** James Mayer; **University of Illinois:** Sharon Hammes-Schiffer; **University of Wisconsin-Madison:** Shannon Stahl

SCIENTIFIC MISSION AND APPROACH

The vision of the Center for Molecular Electrocatalysis (CME) is to develop a fundamental understanding of proton transfer reactions that will lead to transformational changes in our ability to design molecular electrocatalysts for the interconversion of electricity and fuels. The objective is to *understand, predict, and control* the intramolecular and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes including the production of H₂, the oxidation of H₂, the reduction of O₂, and the reduction of N₂. The central hypothesis is that *fast and efficient catalysis* for these reactions *requires control of proton movement over multiple length scales that vary by orders of magnitude*. Through a tightly integrated experimental and theoretical strategy, the CME is identifying the molecular and mesoscale principles required for control of both proton transfer and electron transfer reactions to rationally design fast, efficient molecular electrocatalysts. Three subtasks of the CME efforts are:

- **Production of H₂ and Oxidation of H₂:** Representing the simplest reactions, with only 2 H⁺ and 2 e⁻, the production and oxidation of H₂ are critical for solar fuels production and utilization.
- **Reduction of O₂:** The 4 H⁺ and 4 e⁻ reduction of O₂ to H₂O is the essential reaction in the reductive side of a fuel cell, and represents a substantial increase in complexity relative to H₂.
- **Reduction of N₂ and Oxidation of NH₃:** The reduction of N₂ and oxidation of NH₃ are the most complex of these transformations, involving 6 H⁺ and 6 e⁻, and provide the basis for global food production and a potential energy storage cycle based on nitrogen.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Designed the first molecular electrocatalysts that produce H₂ at a rate (>100,000 s⁻¹) faster than the natural hydrogenase enzyme, albeit at a higher overpotential (lower efficiency). This achievement was only possible through an unprecedented mechanistic understanding and tuning of individual steps of the reaction pathway.
- Designed electrocatalysts for oxidation of H₂ based on iron, an earth-abundant metal that is far less expensive than platinum that is commonly used in fuel cells.
- Designed iron complexes that are very fast electrocatalysts for reduction of oxygen, including the fastest known molecular electrocatalysts. Provided critical understanding of the relationship between rate and overpotential.
- Achieved the lowest overpotential to date for electrochemical O₂ reduction reaction (ORR) with a molecular catalyst system, using cooperative metal-free redox shuttles to mediate chemical and electrochemical reactions. This use of electron- and electron-proton-transfer mediators in molecular electrocatalysis introduces an important new strategy to enhance the energy efficiency and rates of electrochemical reactions.
- First successful example using chromium complexes in the reduction of nitrogen to ammonia, using chromium complexes with specialized polyphosphine ligands.



CME research, from left: Formation of the H-H bond in molecular electrocatalysts involves a transition state that combines H^+ and H ; Chromium has been identified in N_2 reduction studies as offering reactivity unique reactivity compared to molybdenum or tungsten; Control of proton movement is critical in H_2 , O_2 and N_2 reactions; Computational analysis of energetics leads to an understanding of many possible pathways for production of H_2 ; Catalytic oxidation of H_2 can occur by different mechanisms, depending on whether the proton or electron is removed first.

IMPACT

- Control of electron transfers has been studied in energy conversion reactions for decades. Addition or removal of protons are key features, yet few catalysts are designed with the recognition of the critical role of proton movement. The pivotal role of pendant amines functioning as proton relays, pioneered by the CME, has been recognized as a key design principle by many research groups worldwide, using ligands designed in the CME.
- The Hydrogen Catalysis Team (including 12 scientists from the CME) was recognized by the 2015 [ACS Catalysis Lectureship for the Advancement of Catalytic Science](#), marking the first time the lectureship was awarded to a team.
- Used accurate experimental and computational thermodynamic approaches to explore competitive reaction pathways, proving a rational basis for catalyst design that has been adopted by other research groups.
- Many research groups have adopted improved techniques developed in the CME for determining overpotentials (a measure of energy efficiency) for transformations of H_2 , O_2 , CO_2 , and N_2 .
- New computational methodology for calculating the reorganization energy, a key parameter required to calculate the rate, for electron transfer and proton-coupled electron transfer in electrochemical systems, was developed and made freely available to the public by porting to the GAMESS electronic structure program.
- The use of molecular mediators for the O_2 reduction reaction was the subject of a patent application at UW-Madison, where researchers received supplemental funding through the [WARF Accelerator Program](#) to promote commercialization.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, CME had published 122 peer-reviewed publications cited over 4,100 times and filed 1 US patent application. A selection of highly cited papers are:

- Helm, M. L.; Stewart, M. P.; Bullock, R. M.; Rakowski DuBois, M.; DuBois, D. L., A Synthetic Nickel Electrocatalyst with a Turnover Frequency Above $100,000\text{ s}^{-1}$ for H_2 Production. *Science* **333**, 863-866, DOI: [10.1126/science.1205864](https://doi.org/10.1126/science.1205864) (2011). [**423 citations**]
- Warren, J. J.; Tronic, T. A.; Mayer, J. M., Thermochemistry of Proton-Coupled Electron Transfer Reagents and its Implications. *Chemical Reviews* **110**, 6961-7001, DOI: [10.1021/cr100085k](https://doi.org/10.1021/cr100085k) (2010). [**386 citations**]
- Kilgore, U.; et al. $Ni(P^{Ph_2}N^{C_6H_4X_2})_2(BF_4)_2$ Complexes as Electrocatalysts for H_2 Production: Effect of Substituents, Acids, and Water on Catalytic Rates. *Journal of the American Chemical Society* **133**, 5861-5872, DOI: [10.1021/ja109755f](https://doi.org/10.1021/ja109755f) (2011). [**181 citations**]
- DuBois, D. L.; Bullock, R. M., Molecular Electrocatalysts for the Oxidation of Hydrogen and the Production of Hydrogen – The Role of Pendant Amines as Proton Relays. *European Journal of Inorganic Chemistry*, 1017-1027, DOI: [10.1002/ejic.201001081](https://doi.org/10.1002/ejic.201001081) (2011). [**125 citations**]