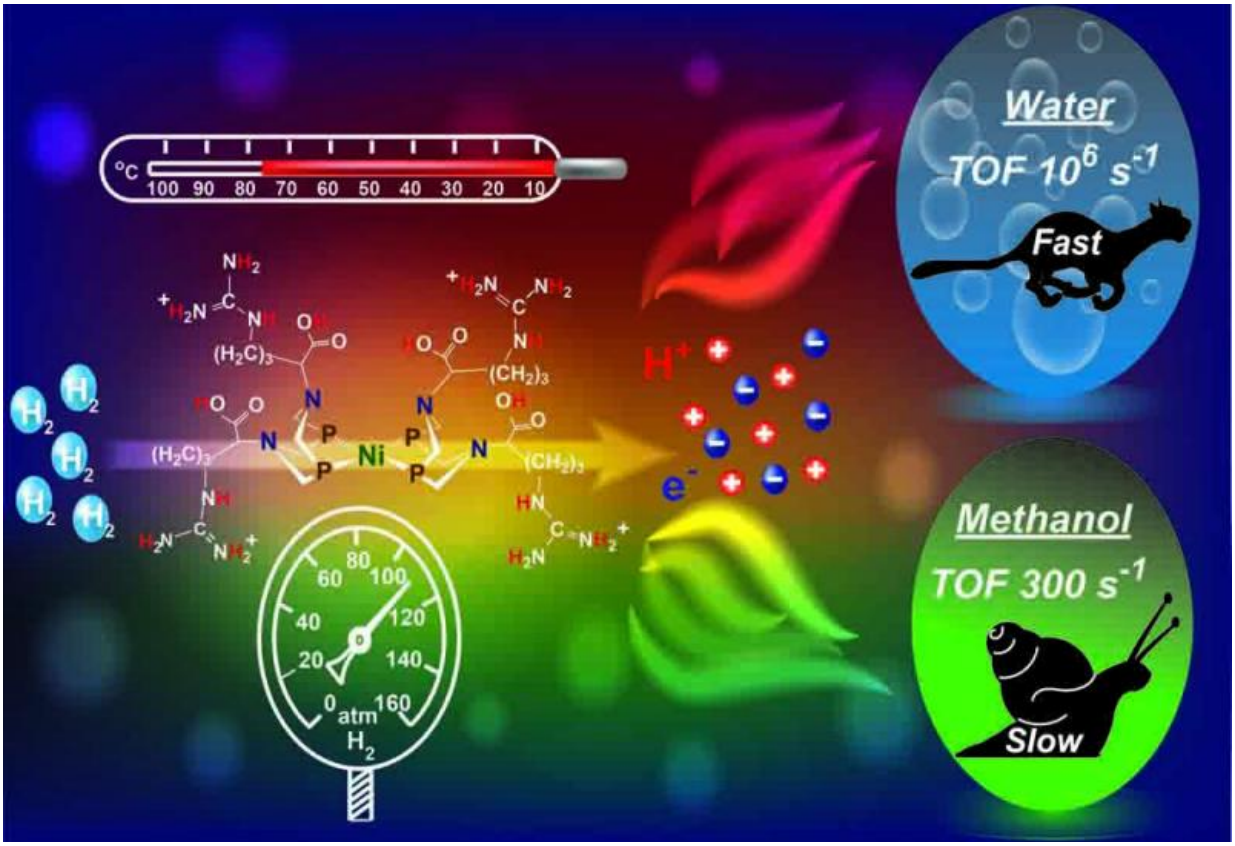
Lessons from nature inspire breakthrough in catalyzing electricity from renewable energy

June 3 2016



A new catalyst developed by PNNL researchers actually performs best in water and at temperatures and acidities remarkably similar to conditions found in fuel cells. Their paper was first made available online and has since inspired cover art for a future 2016 issue of Dalton Transactions. Credit: Pacific Northwest National Laboratory

Efficiently releasing stored chemical energy harnessed from renewable sources remains one of the great scientific challenges facing the catalysis research community. Meanwhile, Mother Nature performs this transformation with ease using abundant metal-containing enzymes as catalysts. So far, lack of an inexpensive and stable catalyst has limited widespread, economical use of hydrogen fuel cells (HFCs). But thanks to a recent breakthrough at Pacific Northwest National Laboratory (PNNL), that may change.

Researchers at PNNL have demonstrated that stored renewable energy can be interconverted efficiently and inexpensively by mimicking enzymatic catalysts used in biological processes. Enzymes consist of an active site-a metal where the reaction happens with connections to the rest of the protein-and a protein scaffold surrounding the active site. That PNNL research team, led by Dr. Wendy Shaw, predicted that many parts of the protein scaffold play critical roles in catalytic activity and efficiency instead of only the active site. This protein scaffold is known as the outer coordination sphere (OCS). It controls the reactivity of the active site by controlling the movement of substrates during catalysis.

Shaw and her research group have shown that adding a simple, amino acid OCS around an artificial nickel-based catalyst has unparalleled improvement in performance. The researchers' new catalyst actually performs best in water and at temperatures and acidities remarkably similar to conditions found in fuel cells.

"Overall, our research shows that proper bridging of synthetic catalysts and features from natural enzymes can help us develop novel sets of materials that can have activity far beyond any natural enzymes," said Shaw. "They also perform better under demanding conditions."

Enzymes are large protein molecules found in nature that catalyze reactions quickly and efficiently. They are ubiquitous in all niches of the

biosphere, and their roles are clearly evident in reactions that fuel the natural world, such as photosynthesis and respiration. In nature, hydrogen (H2) molecules store energy and release it as needed with the aid of hydrogenase enzymes. The basic reaction catalyzed by the hydrogenases is the interconversion of H2 molecules and protons and electrons ($H_2 \Leftrightarrow 2H^+ + 2e^-$).

Although Shaw and her team drew inspiration from hydrogenases, these enzymes are difficult to produce in large quantities. They also perform only under a narrow set of conditions, making them challenging to use in energy applications. But molecular electrocatalysts-inspired by the same natural enzymes-can overcome deficiencies and provide alternatives.

Some of the best and most-studied molecular catalysts for H2 activation contain an enzyme-inspired active site. They are a series of nickel-based catalysts developed at the Center for Molecular Electrocatalysis, an Energy Frontier Research Center at PNNL. To understand the role of the protein scaffold in enzymes, Shaw's team incorporated an enzyme-like OCS to these well-studied catalysts.

Interestingly, including just a single amino acid in the OCS induces water solubility for the catalyst. Solubility makes a catalyst more versatile and active under a range of conditions. It also allows researchers to explore speed and efficiency, including changes in solvent, pressure, and temperature. The researchers found that the best conditions for operating the catalyst were strongly acidic (pH = 0) and hot (72° C)—remarkably similar to the operating environment within HFCs.

Shaw and her PNNL research team assumed they could improve catalytic reactivity. But they were surprised and excited to learn to what degree.

"Our hypothesis was that we could include enzyme-inspired features, such as amino acids, tactically around the synthetic complex and improve its catalytic reactivity," said Shaw. "What really surprised us was how just changing the solvent from water to methanol while using the same temperature and pressure resulted in reactivity almost 4 orders of magnitude slower and with significantly less efficiency," added Shaw.

Their results imply that interactions with the solvent, even similar solvents such as methanol and water, have a very large influence in controlling reactivity. Differences in reactivity as a function of solvent will help to unravel how these complexes operate so efficiently under some conditions.

Electrochemistry and nuclear magnetic resonance (NMR) spectroscopy were the two primary techniques used during this study. Cyclic voltammetry allowed researchers to measure catalytic rates and energy efficiency (overpotential). The team used NMR to probe the structure of the molecule. Computational studies were used to quantify the solvent's role in catalytic reactivity.

Shaw's team and international collaborators will seek similar activity at lower H_2 pressure and evaluate long-term stability of their catalyst. They hope to test it in a real fuel-cell setup. Such testing could pave the way for the development of fuel cells based on inexpensive metals that could replace platinum-based fuel cells currently in use. This advancement holds tremendous potential for inexpensively interconverting energy. It could lead to an inexpensive, environmentally friendly, energy-harvesting procedure for use across the globe.

More information: Arnab Dutta et al. Optimizing conditions for utilization of an Hoxidation catalyst with outer coordination sphere functionalities, *Dalton Trans.* (2016). DOI: 10.1039/C6DT00280C

Provided by Pacific Northwest National Laboratory