

IV.F.9 Combinatorial Development of Water Splitting Catalysts Based on the Oxygen Evolving Complex of Photosystem II

Neal Woodbury (Primary Contact), Trevor Thornton, James Allen, JoAnn Williams
The Biodesign Institute, Arizona State University
1001 S. McAllister Ave.
Tempe, AZ 85287-5201
Phone: (480) 965-3294; Fax: (480) 727-0396; E-mail: Nwoodbury@asu.edu

DOE Technology Development Manager: Matt Kauffman
Phone: (202) 586-5824; Fax: (202) 586-9811; E-mail: Matthew.Kauffman@ee.doe.gov

DOE Project Officer: Carolyn Elam
Phone: (303) 275-4953; Fax: (303) 275-4788; E-mail: Carolyn.Elam@go.doe.gov

Contract Number: DE-FG36-05GO15016

Start Date: July 1, 2005

Projected End Date: June 30, 2009

Objectives

- Develop a high-throughput ($>10^4$) system for the synthesis of potential metal-binding peptide catalysts of the water splitting reaction directly on an array of electrodes.
- Quantify the baseline catalysis rate of the system.
- Through iterative rounds of synthesis and analysis, improve the efficiency of catalysis (decrease the observed overpotential for the system) by 15% in each of three years.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- G. Capital Costs
- H. System Efficiency

Technical Targets

Improved catalytic performance for electrolysis:

- This project has the goal of generating new, more efficient and more cost-effective catalysts for hydrogen production via electrolysis. Specifically, this work will be applied towards meeting the total cell efficiency target of 76% by 2010.

Approach

The attractiveness of hydrogen as an energy storage material arises from the fact that it can be oxidized to water with release of energy and then recovered from water with the input of energy while generating no environmentally detrimental side products. This is particularly appealing as a way of storing electrical energy produced from renewable energy sources such as wind, hydroelectric, solar and biomass. Direct conversion of

water to molecular hydrogen and oxygen via electrolysis followed by regeneration of electrical power in a hydrogen fuel cell would be, in principle, an ideal mechanism for the generation and utilization of hydrogen. However, a number of problems still remain to be solved. One of these stems from the fact that the conversion of water to hydrogen via electrolysis using conventional metal electrodes involves a substantial activation energy, necessitating that the reaction be driven by a considerably higher potential than simple thermodynamics would demand. This overpotential represents a significant energy loss during conversion, impacting the economic practicality of using hydrogen as a fuel in this way.

The biggest part of this overpotential comes from the water splitting reaction at the oxygen evolving electrode (the anode). This is because of the multi-electron nature of the reaction and the high-energy, partially oxidized intermediates that must be formed in order to generate molecular oxygen and protons from water. Fortunately, nature has developed a catalyst, the oxygen evolving complex (OEC) of photosystem II, that works with almost no overpotential for this reaction. The OEC contains four manganese atoms that have a structure and chemical environment defined by the surrounding protein. The manganese cluster is directly involved in the redox process and stabilizes the highly reactive intermediates in the oxidation of water. In recent years, a considerable amount has been learned about the characteristics of this complex, including both the redox properties of the manganese atoms at various stages during the four-electron oxidation of water and the structure of the surrounding protein at low resolution.

A novel combinatorial biochemical approach will be used to develop manganese-binding peptides for modification of the surface of the electrolysis anode used during hydrogen production. The design of these peptides will include features of the OEC and of a model system developed at Arizona State University in which bacterial reaction centers lacking the OEC have been modified to bind and oxidize manganese. The approach involves the light-mediated production of large libraries of manganese-binding peptides using a process similar to that employed in the photolithographic generation of DNA chips (Affymetrix). Each member of the library will be attached to a different microelectrode on a fabricated surface. The current/voltage characteristics of each electrode will be measured in series, looking for the peptide/Mn complexes that result in the lowest overpotential for water splitting. These peptide sequences will then be used as the initial guesses for a subsequent round of molecular evolution, etc. Note that once the peptide-based catalysts are developed in this way, the same types of combinatorial approaches can be used to introduce non-natural chemical features into the peptides, increasing their resistance to degradation by naturally occurring enzymes and other chemical processes. In principle, similar techniques could also be used to develop catalysts for the hydrogen evolving cathode (e.g., using hydrogenase as a model) or for the electrodes in hydrogen fuel cells.

Accomplishments

- None to Date - project just initiated.