Towards Light-Driven Water Oxidation Under Neutral Conditions Using a Co-Phosphate Catalytic Film

Ben Sherman*, Mike Hambourger, Chris Madden, Michael Vaughn, Devens Gust, Ana L. Moore, Thomas A. Moore

Center for Bioenergy and Photosynthesis, and Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604

The development of renewable, carbon-neutral energy sources is one of the most fundamental challenges facing human societies. Many environmentally benign energy resources exist (i.e. solar, wind, hydro, geothermal, tidal, etc). However, the inability to efficiently store this clean energy precludes widespread use. Looking to nature, sunlight is the primary energy source for the majority of life on our planet. Primary production, via photosynthetic organisms, converts incident sunlight to stored chemical energy (i.e. a fuel). The oxidation of this 'solar' fuel provides a release of energy, powering both life and human societies. In particular, oxygenic photosynthesis uses sunlight to drive water oxidation at the Oxygen Evolving Complex (OEC) of photosystem II, with the electrons derived from this process ultimately fixing carbon dioxide into a reduced chemical fuel.

Water oxidation could play an equally important role in technological energy conversion systems, provided that low–cost, Earth-abundant catalysts can be developed. Recently, a catalyst with these desirable properties has been reported (*Science* **2008** *321*:1072) in which an amorphous, electrodeposited cobalt – phosphate film achieves water oxidation at modest overpotentials. This catalyst has been initially demonstrated using electrochemically generated 'holes' to drive water oxidation. In principle the requisite voltage could be supplied by any number of renewable energy systems, making possible the production of carbon-neutral fuels when coupled to an appropriate cathodic catalyst.

In our own work, we endeavor to directly link this water oxidation catalyst to photochemically-generated oxidizing equivalents. One approach involves a photochemical cell in which sunlight excites a dye, adsorbed to a semiconductor electrode surface. Photoinduced electron transfers results in electron injection into the *n*-type semiconductor, with 'holes' being transferred in the opposite direction, towards the anodic solution. We will present results describing our efforts to form the cobalt – phosphate catalyst by light excitation, or to form the catalyst electrochemically followed by light-driven catalytic turnover. Our current studies focus on finding an optimal dye for activating the catalyst and the best method of preparing the electrode to ensure proper communication between dye, catalyst, and electrode surface. Ultimately, we would like to produce a photochemical cell where the electrons generated from the splitting of water to O_2 and protons are passed to the cathode where they reduce protons to H_2.

* bdsherma@asu.edu