

## Artificial photosynthesis and the bio-mimetic production of hydrogen

R.J. Pace, R. Stranger and S. Petrie, Department of Chemistry, College of Science, ANU, Canberra, ACT 0200, Australia.

Natural photosynthesis results in the photo-chemical conversion of visible light quanta into high energy chemical species. Many reactions in the overall process occur with efficiencies unmatched by man-made catalytic systems and operate close to the thermodynamic limit. Such key steps include:

- the electro-chemical splitting of water into H<sup>+</sup> and molecular Oxygen
- the capture and conversion of Carbon Dioxide into energy rich substances (*i.e.*, foods)
- the primary conversion of sunlight into electro-chemical energy.

Although whole photosynthetic organisms can be genetically manipulated to directly produce molecular hydrogen, the process at present has very low quantum efficiency, in part because of fundamental incompatibilities between oxygenase and hydrogenase enzymes operating in close proximity. However oxygenic photosynthesis has 'solved' the most chemically demanding reaction in the electrolytic decomposition of water into H<sub>2</sub> and O<sub>2</sub>, vs the anodic oxidation of water (or OH<sup>-</sup>) to molecular oxygen and protons. The Mn containing water splitting catalytic site in photosystem II (PSII) performs this reaction at close to thermodynamically limiting efficiency (< 0.2 V over-voltage), at a high turnover rate (~10<sup>3</sup> s<sup>-1</sup>), under mild external pH and in the presence of significant concentrations of environmentally common anions, such as Cl<sup>-</sup>. A bio-mimetic electrolysis system based on the natural PSII catalytic site would have substantial thermodynamic and kinetic advantage.

The PS II oxygen evolving complex (OEC) contains 4 Mn and 1 Ca in a compact, exchange coupled cluster. While full structural detail of the site is yet to be resolved, most of the protein ligands, which define the cluster geometry, are located in a very small region near the C terminus of the D1 polypeptide of the PSII reaction centre. This suggests that functioning catalytic site analogs may be assembled from small model peptides or other synthetic constructs. Proposals for such a structures have been made and some existing Mn complex OEC models show promise of useful catalytic function. (for details, see Pace, 2005).

Recently computational chemistry has been employed to explore possible intermediate structures and catalytic pathways to water oxidation which the Mn cluster might utilise (Petre *et al.*, 2007). This approach shows great promise and reveals aspects of the system essentially inaccessible by other techniques. These and other results allow the possibilities of a practical, fully bio-mimetic cathodic water oxidiser to be assessed.

Pace R. (2005) in *Artificial Photosynthesis: From Basic Biology to Industrial Application*. Collings AF & Critchley C. eds. Wiley-VCH, Weinheim, Ch 2.

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