

Recent progress in the photolysis of water*

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It is now generally accepted that the photolysis of water into its elements by sunlight is potentially one of the most attractive routes to solar energy storage; furthermore, the process has been achieved, in some degree, in several laboratories. However, no really complete, efficient and practical system can yet be envisaged even on a laboratory scale, and I shall review the present status of the problem.

Given that visible light absorbers must be used, that efficiencies (in sunlight) should exceed 10% and that the materials must be stable over long periods of time, there are still many possible contenders. These include photovoltaic cells and electrolysis ("two-wire systems"), photoelectrochemical cells ("one-wire systems"), photochemical diodes (heterogeneous wireless systems), homogeneous photochemical systems and photosynthesis *in vivo* or using membranes *in vitro*, as well as many systems intermediate between these prototypes. The photochemist, whilst learning what he can from *in vivo* photosynthesis and from semiconductor physics, is mainly occupied with the intermediate area, and most progress is being made with wireless photochemical systems incorporating heterogeneous catalysts.

Although platinum and ruthenium dioxide have long been known to electrochemists as electrode catalysts for hydrogen and oxygen evolution respectively, it is their use, particularly by Lehn and Gratzel, in colloidal or particulate form as catalysts in otherwise homogeneous photochemical reactions which has provided the biggest step towards the solution of the electron accumulation problem. There are also the encouraging results of Shafirovich *et al.* which indicate that homogeneous catalysis (*e.g.* by cobalt ions) remains a possibility.

Dr. Harriman and his group (Jim Darwent, Marie-Claude Richoux, Philip Walters and Andrew Mills) at the Royal Institution have recently carried out quantitative studies of the yields and their optimization in both the photoreduction and the photooxidation of water. We conclude that porphyrins and phthalocyanines have most advantages as sensitizers and the photophysical properties of a range of these compounds have been determined. The optimum quantum efficiency ($\frac{1}{2}\text{H}_2$) of water reduction so far achieved is 60% using green light. Water oxidation is less efficient and less reproducible and the best efficiency so far achieved is 12% ($\frac{1}{4}\text{O}_2$) with a colloidal ruthenium dioxide catalyst and 8% with a homogeneous solution of cobalt(II) sulphate as catalyst.

Apart from improvements in these efficiencies of photooxidation in particular, the outstanding problem which remains is the coupling together of the re-

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ductive and oxidative cycles through a reversible redox couple, since all the above systems used sacrificial donors or acceptors. The options include reversion to an electrode system or simultaneous hydrogen and oxygen evolution at a particulate photochemical diode. The latter route is unlikely to be practical. The only alternative to wired electron transport is electrolyte transport in a flow system involving localized catalysts. The advantages and difficulties of these alternatives should be discussed.

Photosensitized electron transfer reactions in organized interfacial systems

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The separation of photoproducts formed in photosensitized electron transfer reactions is essential for efficient energy conversion and storage. The organization of the components involved in the photoinduced process in interfacial systems leads to efficient compartmentalization of the products. Several interfacial systems, *e.g.* lipid bilayer membranes (vesicles), water-in-oil microemulsions and a solid SiO_2 colloidal interface, were designed to accomplish this goal.

An electron transfer across a lipid bilayer membrane leading to the separation of the photoproducts at opposite sides of the membrane is facilitated by establishing a transmembrane potential and organizing the cotransport of cations with specific carriers.

Colloidal SiO_2 particles provide a charged interface that interacts with charged photoproducts. By designing a system that results in oppositely charged photoproducts, a retardation of recombination by the charged interface can be produced. The photosensitized reduction of a neutral acceptor by positively charged sensitizers is described. The reactions are substantially enhanced in the SiO_2 colloid compared with in the homogeneous phase. The effect of the SiO_2 interface is attributed to a high surface potential that results in the separation of the intermediate photoproducts. The quantum yields of the photosensitized reactions are correlated with the interfacial surface potential, and the electrical effects of other charged interfaces such as micelles are compared with those of SiO_2 .

The possible utilization of the energy stored in the stabilized photoproducts in further chemical reactions is discussed. Special attention is given to the photodecomposition of water.