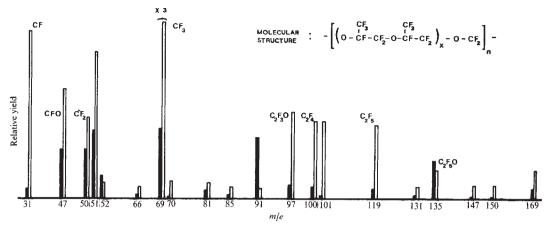
Fig. 1 Mass spectra of: black columns, atmosphere above the vapour stream pump at a chamber pressure of 2.5×10^{-6} torr; white columns, 'Fomblin' components admitted from source at 190° C and with chamber pressure of 2×10^{-6} torr.



on oxygen linkage of fluorocarbon groups; we have found that they can be used in vacuum pumps without the attendant polymerization problems. An earlier study¹ has shown that a high molecular weight (~6,500 a.m.u.) perfluoropolyether fluid has lubricating properties suitable for use in rotary pumps. The work indicated that a similar fluid of greater volatility (molecular weight ~3,000 a.m.u.) should be suitable for use in vapour stream pumps and here we give conclusive evidence of its value for this purpose. The fluids, known as 'Fomblin', are prepared for us by Montecatini Edison S.p.A. (see ref. 2).

The fluid to be tested was used in a vapour pump, Edwards EO4 5 inch diameter aperture, connected to a stainless steel chamber of 28 l. capacity. A rotary pump with a nominal speed of 35 l./min and charged with 'Fomblin' backed the vapour pump. The chevron baffle mounted in the vapour pump inlet was uncooled to ensure a high backstreaming level. The pressure measured by an ion gauge was 10^{-6} torr and the fluid was in use for a total of 1,500 h. We fitted an Edwards mass spectrometer (3 inch radius 60° magnetic sector field) with its unprotected (nude) ion source in the chamber, so that fragmentation spectra could be recorded for the vacuum atmosphere and vapour from the parent fluid injected close to the ion source.

Fig. 1 shows comparative spectra from a sample of unused 'Fomblin' evaporated from a side oven at 190° C and the backstreaming vapour from the vapour pump after 600 h use. Possible compositions of the molecular fragments are also given in Fig. 1. Mass spectra were generally measured up to an m/e ratio of 260, but the yield of fragments above 170 was small and we have not included them. Although the relative abundancies differ, the similarity between the molecular fragments in the two spectra suggests to us that they both arise chiefly by electron impact within the ion source of the mass spectrometer.

Further extensive tests were made by bombarding metal and glass slides with electrons for 1 h, first, in the presence only of backstreaming vapour from the pump, and second, with the fluid spread on the target. The electrons had an energy of 1 keV and a current of 0.5 mA was recorded with a target area of 25 cm². Occasionally, we could detect signs of polymer formation on the target but this was not unexpected because the gas analysis showed traces of hydrocarbons in the system from previous use of the pump with conventional fluids. But, as these impurities disappeared, so did the formation of polymers. The mass spectrometer study showed that electron impact will fragment the perfluoropolyether molecule, so we conclude that neither the parent molecule nor its fragments can be polymerized by electron bombardment either in the liquid or the adsorbed state.

We note that if a mass spectrometer with a nude source, as used in these experiments, had been operated at room temperature in the saturated vapour of any of the hydrocarbon or silicone pump fluids, then serious contamination and failure of the ion source would have ensued within a few hours.

The nude ion source of the instrument was operated in the saturated vapour of the fluid for 50 h and for a further 100 h in backstreaming components from the pump without deterioration in its performance.

Because the fluid can be used in rotary mechanical and vapour stream pumps it could prove valuable for pumping systems on electron microscopes and ion beam accelerators where secondary electrons abound. It will be necessary to ensure that molecular fragments of the fluid are not reactive with specimens or vacuum materials.

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Received February 3; revised March 24, 1972.

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Electrochemical Photolysis of Water at a Semiconductor Electrode

ALTHOUGH the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potential difference of more than 1.23 V is necessary between one electrode, at which the anodic processes occur, and the other, where cathodic reactions take place. This potential difference is equivalent to the energy of radiation with a wavelength of approximately 1,000 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light. Here we describe a novel type of photo-electrochemical cell which decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled. First, oxygen evolution occurs at a potential more negative than that at which hydrogen evolution occurs in normal conditions; second, hydrogen evolution occurs at a potential more positive than that at which oxygen evolution occurs in normal conditions; third, the potential for oxygen evolution is made more negative and that for hydrogen evolution is made more positive, until the former is more negative than the latter.

Current-voltage curves of a semiconducting n-type TiO₂

electrode have been measured with a static potentiometer in the dark and under irradiation with light² (Fig. 1). Anodic current which is proportional to the intensity of light begins to flow for wavelengths shorter than 415 nm, that is 3.0 eV, which corresponds to the band gap of TiO2. The current reaches saturation at potentials positive relative to a saturated calomel electrode (SCE). These facts suggest that the anodic reaction is related to the formation of holes in the valence band by light excitation. Oxygen evolution was confirmed by several means of analytical measurements^{3,4}. Oxygen evolution occurs at -0.5 V (SCE) in an aqueous electrolyte of pH 4.7; this is more negative than the standard potential. We have termed such behaviour "photosensitized electrolytic oxidation" (ref. 2). When halogen ions were introduced in the electrolyte, they were also oxidized through the suggested mechanism of photosensitized electrolytic oxidation. also occurred with other types of n-type semiconductor such as ZnO and CdS (ref. 5). We believe therefore that the oxygen evolution reaction on the TiO2 electrode under irradiation belongs to the first category described above.

We then constructed an electrochemical cell in which a TiO₂ electrode was connected with a platinum black electrode through an external load (Fig. 2). When the surface of the TiO₂ electrode was irradiated, current flowed from the platinum electrode to the TiO₂ electrode through the external circuit. The direction of the current reveals that the oxidation reaction (oxygen evolution) occurs at the TiO₂ electrode and reduction (hydrogen evolution) at the platinum black electrode.

We suggest that water can be decomposed by visible light into oxygen and hydrogen, without the application of any external voltage, according to the following schemes:

$$TiO_2 + 2 hv \rightarrow 2 e^- + 2 p^+$$
 (1) (excitation of TiO_2 by light)

$$2 p^{+} + H_2O \rightarrow \frac{1}{2} O_2 + 2 H^{+}$$
(at the TiO₂ electrode) (2)

$$2 e^{-} + 2 H^{+} \rightarrow H_{2}$$
 (3) (at the platinum electrode)

The overall reaction is

$$H_2O + 2 hv \rightarrow \frac{1}{2} O_2 + H_2$$
 (4)

The starting potential of the oxidation reaction at the TiO₂ electrode corresponds almost exactly to the flatband potential which is constant in the electrolyte solution of a given pH. To

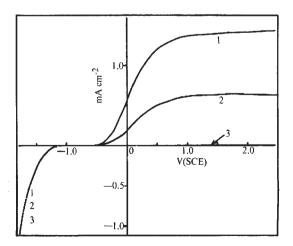


Fig. 1 Current-voltage curves for TiO_2 n-type semiconductor. A single crystal wafer of n-type TiO_2 (rutile) was used after treatment at 700° C at $10^{-4} \sim 10^{-5}$ torr for roughly 4 h to increase the conductivity of the crystal. This wafer was approximately according to the crystal. ately 1.5 mm thick and the exposed (001) surface area was approximately 1.0 cm². Indium was evaporated on to one side of the surface to ensure ohmic contact and a copper lead wire was connected on the indium layer with silver paste. All other surfaces were sealed by epoxy resin.

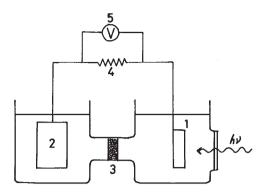


Fig. 2 Electrochemical cell in which the TiO₂ electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm².

increase the efficiency of the decomposition process, more reducible species, for example, dissolved oxygen or Fe3+ ions, must be added in the compartment of the platinum electrode. When Fe3+ ions were added, the current produced under irradiation increased. Currents of a few mA flowed when the TiO₂ electrode (surface area ~1 cm²) was irradiated by a 500 W xenon lamp; we estimate the quantum efficiency in this case to be approximately 0.1. The e.m.f. of the cell was measured to be up to 0.5 V.

It is possible that the hydrogen evolution reaction shifts towards more positive potential than normal when suitable p-type semiconductor electrodes are irradiated, in the same way that photosensitized oxygen evolution occurs with n-type semiconductor electrodes. If such a p-type semiconductor electrode is used instead of the platinum electrode, electrochemical photolysis of water may occur more effectively.

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Received September 13, 1971; final revision April 24, 1972.

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BIOLOGICAL SCIENCES

One and Two-dimensional Structure of Alpha-Helix and Beta-Sheet Forms of Poly(L-Alanine) shown by Specific Heat Measurements at Low Temperatures (1.5–20 K)

HOMOPOLYPEPTIDES provide good model systems for various aspects of proteins^{1,2}. Recent advances in high polymer and solid state physics have enabled the vibrational aspects of the simpler homopolypeptides to be treated as normal-but complicated—polymers by the theoretical techniques of lattice dynamics based on the experimental methods of neutron, infrared and Raman spectroscopy. Basically, however, these latter methods examine the optical vibrational modes of a system, that is, those modes which are of energy higher than, for example, 70 cm⁻¹. The important lower-energy modes are