

# Hydrogen Production under Sunlight with an Electrochemical Photocell

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the Li amalgam case. Similar behavior of potential drift in nonaqueous cells was observed in PC (1, 21), DMSO (22, 23), DMF (24), and N-MF (25). True cell potentials were obtained by extrapolating to zero time in formamide (26, 27). The general agreement with the previous reliable data justifies the extrapolation procedure in the present work.

In conclusion, this fragmentary study establishes the feasibility of using propylene carbonate for thermodynamic measurements of the alkali metal amalgams.

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# Hydrogen Production under Sunlight with an **Electrochemical Photocell**

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An electrochemical photocell has been reported (1) which consists of titanium dioxide (rutile type) single crystal as an anode, and platinum as a cathode. The photocell works under irradiation with light, leading to oxygen evolution on the anode and hydrogen evolution on the cathode. Quantum efficiencies of the cell increases with an increase in the alkaline concentration in the titanium dioxide anode compartment and in the acidic concentration in the cathode compartment (2). However, the use of polycrystal or amorphous titanium dioxide in place of its single crystal is desired from the practical standpoint of realizing a large scale electrochemical photocell.

Key words: hydrogen production, electrochemical photocell, titanium oxide film

Among the various methods of forming oxide film on metal, the following three methods were studied in the present work: (i) electrochemical formation of oxide film on metal; (ii) thermal formation of oxide film in an electric furnace; and (iii) thermal formation of oxide film by simple heating.

Electrochemical formation of oxide film on titanium metal.-Formation of anodic oxide film on titanium was carried out potentiostatically or galvanostatically. The electrolyte solutions used were basic (1.0M NaOH) or acidic (0.5M H<sub>2</sub>SO<sub>4</sub>). Photoelectrochemical behavior of the oxide film electrodes was investigated using a 500W xenon lamp. Maximum photocurrent under anodic polarization of the oxide electrodes was about one-tenth of that on the single crystal rutile

Thermal formation of oxide film by means of an electric furnace.—Oxide films were thermally formed on the titanium metal plates at various temperatures



Fig. 1. Current-potential curves under irradiation in relation to the temperature of heating of 5 min. (1) Ti metal, \*(2) 1200°C, (3) 1300°C, (4) 1400°C, (5) rutile single crystal.



Fig. 2. The geometric arrangement of the electrochemical photocell. (1) Anodes coated with titanium dioxide film, (2) platinum black cathodes, (3) agar salt bridges, (4) gas burettes, (5) ammeter. Anolyte: 1M NaoH, catholyte  $= 0.5M H_2SO_4$ .

in an electric furnace to which oxygen was supplied. The anodic photocurrents obtained with these oxide film electrodes were nearly the same as those films formed electrochemically. On the other hand, when a reducing atmosphere was maintained during the oxide formation in the electric furnace, the anodic photocurrents slightly increased. In the case of  $TiO_2$  single crystal, photoelectrochemical behavior depends on the degree of the reduction treatment, because its electric conductivity related to the amount of the oxygen vacancies in the crystal may govern the probability of the recombination between the electrons and holes created by the irradiation with light (3). Further detailed investigations will be reported elsewhere.

Thermal formation of oxide by a gas burner.--A plate of titanium was heated in a fire of town gas. Oxide could be easily formed on titanium metal. Temperature of fire on Meker burner or Bunsen burner was varied between 1100° and 1400°C. Thickness of the formed oxide film seemed greater than those formed by electrochemical oxidation or thermal oxidation in the electric furnace. Anodic photocurrents on these oxide electrodes were nearly as large as those obtained with the single crystal rutile electrode. Figure 1 shows current-potential curves in 1M NaOH in relation to the temperature of heating for 5 min. These high photocurrents might be due to both the thickness of the oxide being enough to absorb the incident light quanta and the low resistivity of films. The crystal structure of the oxide was found by x-ray diffraction analysis to be the rutile type. Observation of the surface by an electron microscope revealed that the oxide was not a perfect crystalline structure. In the present experiments, the titanium oxide films formed in a flame temperature between 1300° and 1350°C for several minutes showed good photoelectrochemical behavior.



Fig. 3. Hydrogen evolution by the electrochemical photocell under the sunlight. ○: Total amount of hydrogen evolution, ●: hourly evolution.

Hydrogen production under the sunlight.—As described above, the titanium oxide electrodes made by these three methods showed different photoelectrochemical behavior, even when they were irradiated with the light of the same intensity. These differences are probably due to the electric conductivity of the oxide films, and partly to the thickness of the films.

It is possible to prepare, by a simple heating, titanium dioxide film on titanium metal plate which shows pronounced photoelectrochemical activity. The anodes studied were prepared by heating the titanium metal with a surface area of 85 imes 100 mm with nine Bunsen burners. Figure 2 shows the geometric arrangement of the electrochemical photocell using twenty anodes coated with titanium dioxide film. The cell consisted of five platinum cathode and titanium dioxide anode units in which four anode plates of the above dimension were connected in parallel. The cell contained alkaline solution in the anodic compartments and acidic solution in the cathodic compartments. Separation between the anodes and cathodes was made with an agar salt bridge saturated with potassium chloride. In this arrangement, a potential drop through the solution or the salt bridge was not found. The total anodic surface area (Fig. 2) was about 0.17 m<sup>2</sup>. Figure 3 shows the relationship between the operation time and the volume of the hydrogen collected under irradiation with the sunlight on a clear summer day. The intensity of the sunlight measured by means of Toshiba Photocell Illuminometer SPI-1 was about 110,000 lux from 11 A.M. to 2 P.M. We collected 1.1 liter per day using this photocell (6.6 liters of  $H_2$  per m<sup>2</sup> of titanium dioxide).

The combustion heat of this hydrogen is calculated to be 20 kcal/m<sup>2</sup> per day. The mean incident energy of the sunlight at the surface of the earth in Japan was reported (4) to be about 3000 kcal/m<sup>2</sup>. As we measured the characteristics of the photocell in August, the incident energy of the sunlight might be larger than the mean one. The energy conversion efficiency of the photocell to the total sunlight energy is estimated to be more than 0.4%. As the energy ratio of the sensitive region of the titanium dioxide against the over-all spectral region of the sunlight may be below 10%, the quantum efficiency in the intrinsic absorption region becomes much larger.

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## Intricate-Pattern ECM on Ferrous Alloys

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In the electronics industry, the necessary circuit components are fabricated from various metals supported on a variety of substrates by generating the required, highly intricate patterns in the metal through a photomechanical method known as pattern etch machining (1-5). In a parallel development, another metal removing process known as electrochemical machining (ECM) (6,7) has been investigated and evaluated which is based on controlled, high rate, anodic corrosion reactions. The ECM process can be used in a number of operations including plunge cutting, sizing, finishing, deburring and electrochemical grinding; but perhaps, the greatest advantage of this process is its speed in a replication application. This report describes the details of this ECM method and some of the underlying electrochemistry involved.

#### Experimental

The ECM fixture is composed of the cathode tool, the anode work piece, and all cell housing parts which are required to obtain a proper and uniform flow of electrolyte between the electrodes. In Fig. 1, the assembled fixture used in pattern ECM is shown; whereas in Fig. 2, a cross-sectional view of the fixture assembly is given. Essentially, the fixture consists of two machined blocks of brass separated from one another by an insulating layer of epoxy plastic. In operation, the two halves of the fixture were held together with insulated "C"-clamps and made leak-proof with an "O"-ring.

The cathode.—The top half of the fixture (50 mm  $\times$  150 mm  $\times$  20 mm) serves as the cathode. Two cross-hatched patterns (19 mm  $\times$  31.75 mm) of 12.6 lines/cm

• Electrochemical Society Active Member. Key words: ECM, ferrous alloys, pattern ECM, NaClO<sub>3</sub> electrolyte. (32 lines/in.) were etched to a depth of 0.13 mm in the flat ground face of the brass block by a photomechanical method. Next, a layer of epoxy (2 mm

Fig. 1. The fixture for pattern ECM with anode holder and anode sample panel at left and machined cathode at right.