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Formation of Hydrogen Gas with an Electrochemical Photo-cell

Akira Fujishima, Koichi Kohayakawa, and Kenichi Honda*
Department of Applied Chemistry, Kanagawa University, Rokkakubashi, Yokohama 221
**Institute of Industrial Science, The University of Tokyo, Roppongi, Tokyo 106*

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Synopsis. In an electrochemical photo-cell the use of a basic electrolyte solution in the TiO_2 electrode compartment and an acidic one in the Pt cathode compartment can produce a high yield of hydrogen gas.

In a previous paper[1] we reported on an electrochemical photo-cell which consists of a titanium dioxide single crystal semiconductor as an anode, platinum black as a cathode and water as the electrochemically active species. The cell works only under irradiation on the TiO_2 electrode, generating oxygen gas at the surface of the semiconductor and hydrogen on the platinum cathode (Fig. 1). Since the forbidden gap width of TiO_2 is 3.0 eV, the effective wavelength of the irradiated light is restricted to 413 nm or less. The photo-cell produces hydrogen, which can be a source of a "clean energy", through the decomposition of water by means of solar energy.

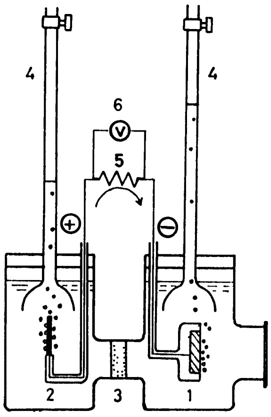

Fig. 1. Schematic diagram of electrochemical photo-cell. 1: TiO_2 electrode, 2: Platinum electrode, 3: Diaphragm (agar salt bridge), 4: Gas burette, 5: External resistance, 6: Voltmeter.

In order to increase the electro-motive force of the cell (and consequently the amount of hydrogen generated), the potential for hydrogen evolution at the cathode should be made more positive, and that for oxygen evolution at the anode more negative. The former can be attained by increasing the proton concentration, the latter by increasing the pH value of the solution, as supported by the fact that the flatband potential of TiO_2 electrode varies linearly with the pH of the solution, with the slope of *ca.* $-60\ \mathrm{mV}/\Delta\mathrm{pH}$.[2] The use of an alkaline solution in the TiO_2 electrode compartment and an acidic solution in the Pt cathode compartment thus brings about a higher e.m.f. of the photo-cell.

Since the potential difference at the semiconductor-electrolyte interface falls normally within the space charge region at the surface of the semiconductor, the increase in the e.m.f. leads to an enhancement of the separation efficiency for electron-hole pairs created by the irradiation in the space charge region. Under irradiation of monochromatic light (380 nm), a quantum efficiency as high as 0.3 or more is attained when the pH value of the anode compartment is higher and that of the cathode compartment is lower; it does not exceed 0.01 in the case of a common neutral electrolyte (*e.g.*, KCl) solution.

In the present study, a wafer of single crystal TiO_2, 1.5 mm in thickness and 1.0 cm^2 in area, treated under a reducing atmosphere before use, was employed. Its donor density calculated from the slope of the Mott-Schottky plot[3] was *ca.* $2.5 \times 10^{17}\ \mathrm{cm}^{-3}$. The (001) face of the crystal was exposed to the electrolyte solution. A 500 W xenon lamp was used as a light source. With the use of a colored glass filter (Toshiba Kasei VV40 filter), the number of the incident quanta per second per square centimeter at the surface of the TiO_2 electrode was measured by means of the chemical actinometry using a potassium ferrioxalate system,[4] and found to be *ca.* 2×10^{17}. A platinum black electrode having the surface area of 1.0 cm^2 served as a cathode.

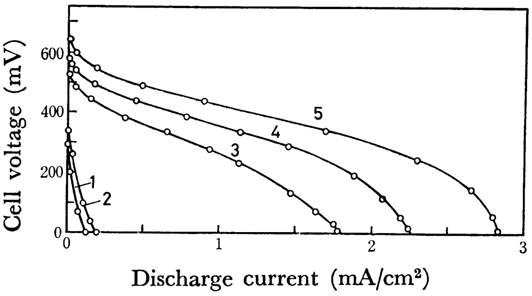

Fig. 2. Relation between the cell voltage and the discharge current.

TiO_2 anode compartment	Pt cathode compartment
1: 1 M NaOH,	1 M NaOH
2: 1 M NaOH,	1 M Na_2SO_4
3: 1 M NaOH,	0.005 M H_2SO_4
4: 1 M NaOH,	0.05 M H_2SO_4
5: 1 M NaOH,	0.5 M H_2SO_4

Figure 2 shows the relations between the cell voltage and the discharge current under irradiation, as a function of the composition of the anodic and cathodic electrolyte solutions. The curves were obtained by adjusting the external resistance. The maximum efficiency was attained by a combination of strong basic and strong acidic solutions (curve 5) as expected, the open-circuited cell voltage being *ca.* 0.64 V. The amounts of hydrogen and oxygen evolved were proportional to the intensity of light and the surface area

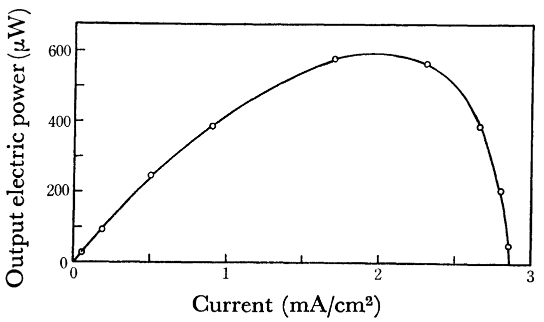

Fig. 3. Relation between the electric power output at the external resistance and the cell current.
The solutions are 1 M NaOH in the TiO_2 anode compartment and 0.5 M H_2SO_4 in the platinum black cathode compartment, respectively. The number of quanta per second per square centimeter: 2×10^{17}.

of the TiO_2 electrode, when the cross section of the incident light flux was sufficiently large as compared with the surface area of TiO_2. The rate of generation of hydrogen amounted to *ca.* 1.1 ml/hr when the cell was short-circuited, indicating the current efficiency of about 100%.

Figure 3 shows the relationship between the cell current and the output electric power at the external resistance (calculated from curve 5, Fig. 2). The apparent over-all internal resistance of the cell is estimated to be about 140 Ω from the slope of curve 5. The maximum output electric power was obtained using an external resistance of 140 Ω, as predicted by a simple theory. The quantity appearing on the abscissa in Fig. 3, *i.e.*, the current density, can be interpreted as representing the amount of hydrogen evolved, since these two quantities are proportional to each other. We see that a fairly large amount of hydrogen is obtained when the maximum output power is attained.

The fact that, when the acidic and basic solutions are used in each compartment, the electro-motive force arising from the concentration difference of hydrogen ions is involved in the cell voltage should be taken into consideration. The electro-motive force is estimated to be *ca.* 0.77 V for a pH difference of 13. In view of the theoretical decomposition voltage of water of *ca.* 1.23 V and the practical one of more than 1.6 V and the heat of combustion of hydrogen (68 kcal/mol), the observed results support the effectiveness of the combined utilization of acid-base electrolyte solutions. The liquid junction potential was actually lower than 0.05 V since a salt bridge consisting of agar containing KCl was used. Use of an ion-exchange membrane of low resistance and long durability could increase the efficiency of hydrogen evolution.

Since the electrode reactions are $4OH^- + 4p^+ \rightarrow O_2 + 2H_2O$ at the TiO_2 electrode, and $4H^+ + 4e^- \rightarrow 2H_2$ at the Pt electrode, after a long run the solution in the TiO_2 compartment will become less alkaline, and that in the Pt compartment less acid.

References

1) A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).

2) A. Fujishima, A. Sakamoto, and K. Honda, *Seisan Kenkyu*, **21**, 450 (1969).

3) J. F. Dewald, *J. Phys. Chem. Solids*, **14**, 155 (1960).

4) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. Ser. A*, **235**, 518 (1956).