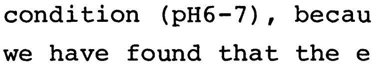
CHEMISTRY LETTERS, pp. 137-140, 1979. Published by the Chemical Society of Japan

CONVERSION AND STORAGE OF LIGHT ENERGY. EVOLUTION OF HYDROGEN IN NEUTRAL AQUEOUS SOLUTION BY A CATALYTIC ELECTRODE PROCESS

Tomoji KAWAI, Katsumi TANIMURA, and Tadayoshi SAKATA
Institute for Molecular Science, Okazaki 444

Hydrogen was evolved from water by the photoelectrochemical reduction of methylviologen (MV^{2+}) and the catalytic electron transfer from reduced $MV^{+\cdot}$ to H^+ in neutral aqueous solution. Taking advantage of this process, reduction of water into H_2 by using a Zinc-tetraphenylporphine (ZnTPP) photoelectrode is suggested.

From the view point of solar energy conversion, the photoanodic oxidation of water into oxygen by using an inorganic semiconductor (TiO_2, $SrTiO_3$, Fe_2O_3 etc) has been well investigated.1)~ 4) Photocathodic hydrogen evolution, however, has been studied on only a few materials, such as p-Gap,5) although this reaction is also very important for the splitting of water. This paper deals with the production of hydrogen by an electrode process and also by a photoelectrode process in neutral aqueous solution.

The noncorrosive electrode reaction is essentially a catalytic process, so that the reaction rate is expressed not only by the electrode potential and the redox potential of the electrolyte, but also by the interaction between the molecules and the electrode, which results in the overpotential for the reaction. Although platinum or palladium was often used as a cathode for hydrogen evolution because the catalytic activity to produce hydrogen is relatively high compared with Au or Hg,6) a small number of H^+ in the solution reduces the rate of H_2 production in the neutral aqueous solution. Desplat7) has reported that a diffusion limit was easily seen in the anodic photooxidation of OH^- by TiO_2. In order to enhance the efficiency of the evolution of oxygen and hydrogen, an acid and a base were often added to the photocell1) for the reason mentioned above and because the flat band potential of the semicondoctor is changed by this procedure. In this case, however, the neutralization energy should be taken into consideration for calculating the efficiency of the light energy conversion. In this paper we report that the addition of methyl-viologen  (H_3C-N^+…$^+N-CH_3$, MV^{2+}) in neutral aqueous solution as a catalyst (an electron carrier), whose redox potential (-0.44 V) is a little more negative than that of H^+/H_2, enables us to enhance H_2 evolution by the electrode process even around the neutral condition (pH6-7), because of, what we will call here "the kinetic reason". Furthemore, we have found that the excited ZnTPP can reduce methylviologen. The combination of these findings with the above process demonstrates the possibility of H_2 evolution by ZnTPP/metal photoelectrode.

We have constructured several types of photoelectrochemical cells as follows;

1) photocell I for the reduction of MV^{2+}; $MV^{2+} + e \longrightarrow MV^{+\cdot}$

----[TiO_2 | 0.2N NaOH || phosphate buffer (pH6), MV^{2+} (10^{-2}mol/l) | metal]

metal = Pt, Au etc

2) photocell II for the study of the reaction; $MV^{+\cdot} + H^{+} \xrightarrow{Pt/Al_2O_3} 1/2\ H_2 + MV^{2+\cdot}$

Small catalyst particles of Pt/Al_2O_3 or Pd/Al_2O_3 (5 weight %, Engelhardt Co Ltd) were added to the photocell I to drive the above reaction.

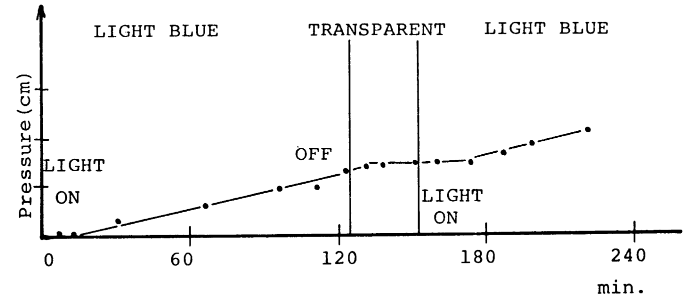
3) photocell III for the reaction of $MV^{2+} \xrightarrow{h\nu,\ ZnTPP} MV^{+\cdot}$

----[ZnTPP/Pt | 0.1N KCl, MV^{2+} || $FeSO_4$ (10^{-3}mol/l) |Pt] ||: glass filter No. 4

The construction of the photoelectrochemical glass cell was basically the same as described previously[8)] except for the following points. All the photocells were evacuated in order to exclude the ambient gasses such as oxygen, and to measure precisely the pressure of the produced gas. The amount of the produced hydrogen was measured by a water manometer. ZnTPP was evaporated in vacuo on a metal substrate. The thickness of the ZnTPP was monitored by a Sloan thickness meter (DTM200). The electrode surface was illuminated by a 500 W Xe lamp.

The illumination of the TiO_2 in the photocell I resulted in the production of oxygen at the TiO_2 surface and the reduction of methylviologen ($MV^{2+} \longrightarrow MV^{+\cdot}$) at the counter electrode, where no hydrogen evolution was observed. The color of the solution changed completely to dark blue in about 10 minutes because of the absorption of $MV^{+\cdot}$ at 630 nm.[9)] The standard redox potential of $MV^{2+}/MV^{+\cdot}$ (-0.44 V) is more negative than that of H^{+}/H_2 (0.0 V at pH0 and -0.414 at pH7). Accordingly, the reaction $2OH^{-} + 2MV^{2+} \xrightarrow{h\nu} H_2O + 1/2\ O_2 + 2MV^{+\cdot}$ ($\Delta G^{\circ} = 1.68$ eV), converts and stores a light energy into a chemical energy. The rate of the reduction of MV^{2+} did not depend on the substrate metal used, such as Pt or Au . The rate depended on the concentration of MV^{2+} and the potential of the electrode. This phenomenon should be compared with the remarkable dependency on the kind of metal for H_2 evolution from reduction of H^{+}.[6)] When the solution does not contain MV^{2+}, the photocurrent of the cell (counter electrode: Pt or Au) was negligibly small (less than 7μ A), which means that hydrogen evolution was very small at the cathode in this condition (with methylviologen: photocurrent of the order of 100μ A). The photoelectrochemical cell with TiO_2 anode and Pt cathode does not work efficiently in alkaline aqueous solution, because the potential of the platinum[10)] can not reach the potential for H_2

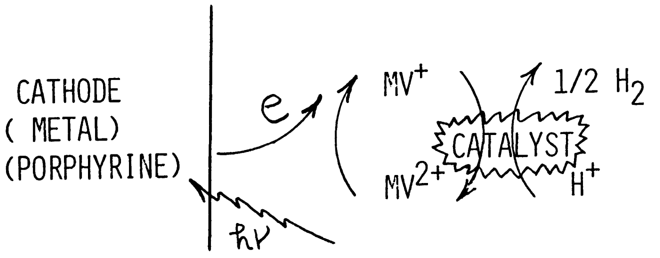
Figure 1



Pressure of the evolved hydrogen at the cathode of photocell II. The color of the solution changed from light blue into transparent when light was off.

evolution (-1.07 V vs SCE) ($2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$). On the other hand, when H^+ is reduced directly into H_2 in neutral aqueous solution, then the number of protons is so small that the rate of H_2 evolution is slow and furthermore the ability to form H_2 depends strongly on the electrode material.6) The redox potential of $MV^{2+}/MV^{+\cdot}$ (-0.44 V) is more negative than H_2/H^+ (0.0 V at pH0 and -0.414 V at pH7), so that H_2 evolution is energetically possible by using $MV^{+\cdot}$. This can be actualized when we choose an appropriate catalyst for the reaction; without the catalyst the rate constant for $MV^{+\cdot} + H^+ \longrightarrow MV^{2+} + 1/2\ H_2$ is very small. Hydrogenase is known to be one of the good catalysts for this reaction.11) Here we chose Pt/Al_2O_3 or Pd/Al_2O_3 powder as the catalyst. When the color of the solution had become dark blue, these powders were added to the solution, and hydrogen was vigorously evolved. The combination of these processes, which we refer to as photocell II, resulted in H_2 evolution as shown in Figure 1. The color of the solution of this photocell during the illumination remained light blue, which means that the amount of reduced $MV^{+\cdot}$ was in a stationary condition. When the illumination of TiO_2 was stopped, then the hydrogen evolution stopped and the solution became transparent simultaneously. The schematic mechanism of the reaction is shown in Figure 2. The methylviologen used in this system can be regarded as the catalyst for the transportation of the electron and the light energy.

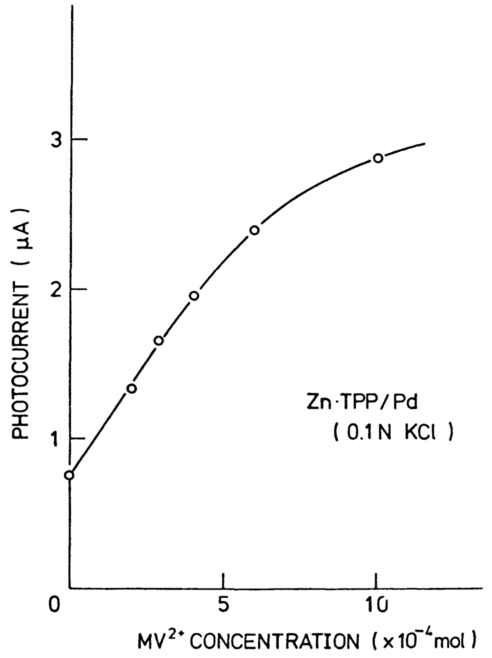
Figure 2



We have found that a thin film (100-1000 A) of zinc-tetraphenylporphine (ZnTPP) formed on metals such as Pt or Au could reduce MV^{2+} with the illumination of this electrode by visible light (435 nm: Soret Band, 550 nm: Q Band). The photocell III was used for this experiment. The photocurrent of this ZnTPP/metal electrode produced after the addition of the electron acceptor (MV^{2+}) into the solution was measured as a probe of the reduction of MV^{2+} (Figure 3). A substrate metal having a large work function such as Pt or Au can reduce MV^{2+} well compared with an electrode made of base metals such as Al or Zn. The detailed mechanism of the photocurrent generation has been described elsewhere.8)

Figure 3

Dependence of photocurrent of ZnTPP/Pd photoelectrode on the amount of methylviologen(MV^{2+})



This phenomenon shows that the electron was transferred from the excited ZnTPP to the MV^{2+} in the solution. The rate of the reduction depends linearly on the concentration of MV^{2+} in the region less than 10^{-3} mol of MV^{2+} (Figure 3). Although the intensity of the photocurrent was relatively small (of the order of 10^{-6} A), the combination of this photoelectrode with the above process indicates that H_2 evolution occurs by a photoelectrode process of organic materials as shown schematically in Figure 2. In the biological system of chlorophyll, photosystems II and I yield oxygen molecules and carbohydrates respectively. Here we can regard the ZnTPP photoelectrode as a model of photosystem I, in the same sense that the TiO_2 anode has been regarded as that of photosystem II.

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(Received October 6, 1978)