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Photochemical Charging of a Silver Electrode Fixed at a Titanium Dioxide Surface

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Synopsis. A regenerative half cell presented here: $TiO_2(Ag)$–Ag^+ can be photochemically charged by irradiation of the TiO_2 surface with sunlight. Electrical energy is extracted from it by connection through the load with a suitable half cell which has a more positive electrode potential than Ag–Ag^+.

The quantum yield of the photoreduction of silver ion (Ag^+) at the surface of both TiO_2 and ZnO by means of 365 nm light is more than 0.1 under suitable conditions.[1] We are interested in an application of the deposited silver at a semiconductor surface to anodic material of galvanic cells. In this paper, we have tried to use a $TiO_2(Ag)$ electrode as a silver metal electrode. If we construct a half cell:$TiO_2(Ag)$–Ag^+ and combine it with another half cell:Pt–X^+/X couple, in which the standard electrode potential of the X^+/X couple is more positive than Ag^+/Ag, we can indeed withdraw electrical energy from such a cell. Zaromb *et al.* have previously described a cyclic photogalvanic silver halide cell from an analogous viewpoint.[2] Hodes *et al.* have investigated the photoelectrochemical storage cell by making use of CdSe.[3]

TiO_2 powder labelled TITONE R-310 made by Sakai Kagaku Co., Ltd., Osaka was molded and sintered at 1300 °C in air for 2 h, to obtain a plate of TiO_2 sinter, *ca.* 2 mm in thickness and 1 cm^2 in surface area. The electrical resistance of the sinter was higher than 1 MΩ in the dark. An indium layer was then evaporated on one face of the sinter and a copper wire was soldered to it. The TiO_2 sinter thus treated was immersed in a 0.1 M† $AgNO_3$ solution and irradiated by sunlight for 30 min. As a result, silver was deposited on the surface of the TiO_2. Since the electrical resistance between the deposited silver on the surface and the copper wire was only a few ohms, it was confirmed that the silver on the surface is in direct contact with the indium layer. After the TiO_2 sinter was washed with distilled water, a copper wire was inserted into a glass tube and the indium layer and TiO_2 surface were covered with an epoxy resin except for the face which is to be exposed to an electrolyte solution (*ca.* 0.77 cm^2). The $TiO_2(Ag)$ electrode thus formed (Fig. 1) was immersed in the electrolyte solution containing 0.1 M $AgNO_3$ plus 1 M KNO_3.

The electrode potential of a $TiO_2(Ag)$–Ag^+ half cell was +0.60 V *versus* saturated KCl–Ag/AgCl electrode. It is in accord with a known value for a Ag–Ag^+ half cell. In order to withdraw electrical energy from such a half cell, we have combined it with another half cell:Pt–Ce^{4+}/Ce^{3+} through a salt bridge containing KNO_3 (Fig. 1). The electrolyte solution of the latter cell comprised 0.05 M $Ce_2(SO_4)_3$, 0.05 M $Ce(SO_4)_2$ and 1 M KNO_3. Current-voltage characteristics of the test cell assembled in this manner: $TiO_2(Ag)$, $Ag^+||Ce^{4+}/Ce^{3+}$, Pt were examined at 25 °C in the dark. The discharge current was measured by the voltage across a resistance box with a switch closed, which was recorded on a recorder EPR-100A (Toa Electronics Co., Ltd.,). A similar measurement of the reference cell having a silver metal electrode (*ca.* 6 cm^2 in surface area) was carried out for comparison. The relation between the discharge current and the output voltage is given in Fig. 2. The open-circuit voltage and the

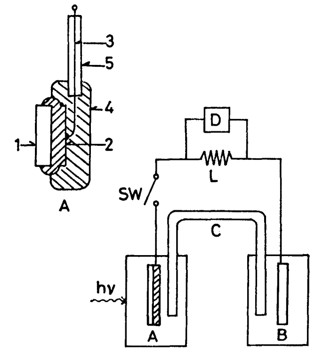

Fig. 1. Schematic representation of a galvanic cell. A: $TiO_2(Ag)$–Ag^+ half cell, B: Pt–Ce^{4+}/Ce^{3+} half cell, C: salt bridge, D: recorder, L: resistance box, SW: switch, 1: TiO_2 sinter, 2: indium layer, 3: copper wire, 4: epoxy resin, 5: glass tube.

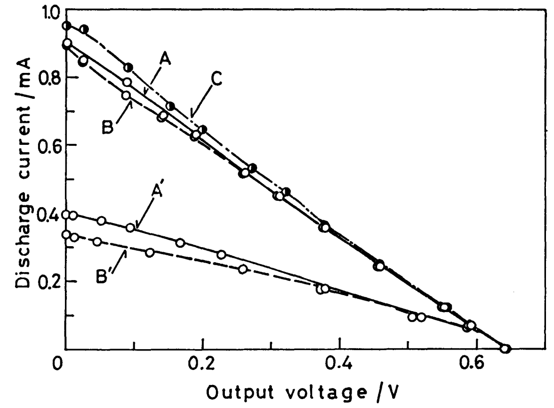

Fig. 2. The current-voltage characteristics for cells; $TiO_2(Ag)$, $Ag^+||Ce^{4+}/Ce^{3+}$ couple, Pt and Ag, $Ag^+||Ce^{4+}/Ce^{3+}$ couple, Pt.
A: After first charging, A′: after first discharge, B: after second charging, B′: after second discharge, C: reference cell.

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† 1 M = 1 mol dm^{-3}.

short-circuit current were 0.64 V and 0.9 mA for the test cell and 0.64 V and 0.95 mA for the reference cell, respectively. Although the observed open-circuit voltage was somewhat less than the difference of the standard electrode potentials of Ag^+/Ag (0.80 V *vs.* NHE) and Ce^{4+}/Ce^{3+} (1.61 V) couples, current-voltage characteristics of these two cells were practically equal. Thus, we may state that the $TiO_2(Ag)$ electrode possesses similar electrochemical properties to a silver metal electrode.

Discharge of the test cell was continued through a 30Ω load resistance. It is observed, as indicated in Fig. 3, the discharge current was decreased with the discharge time, but a current of about 0.3 mA was obtained after 15 min. The current-voltage characteristics of the cell at this stage were somewhat degenerated as seen in Fig. 2. The electrical resistance between the TiO_2 surface and the copper wire amounted to *ca.* 500Ω. We then opened the switch and placed the $TiO_2(Ag)$–Ag^+ half cell under sunlight for 30 min. The electrical resistance decreased again to a few ohms. The characteristics of the recharged cell are given in Figs. 2 and 3. As is indicated, the efficiency in the photochemical charging of the $TiO_2(Ag)$–Ag^+ half cell is very high. Cycles of photochemical charging and discharge were repeated more than ten times. It is found that the characteristics of the cell are similar to those of the first discharge and the efficiency of recharging is not lowered by such cycles. As we are interested only in an application of deposited silver, we have paid little attention to the regeneration of the Pt–Ce^{4+}/Ce^{3+} half cell in this work.

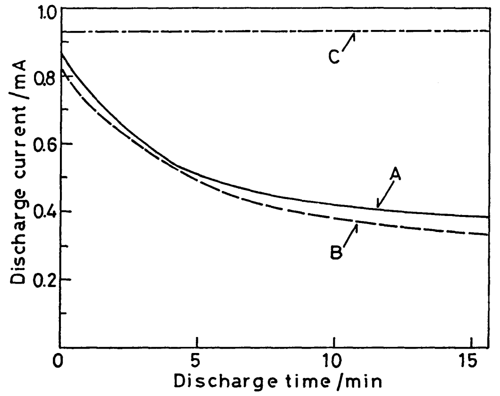
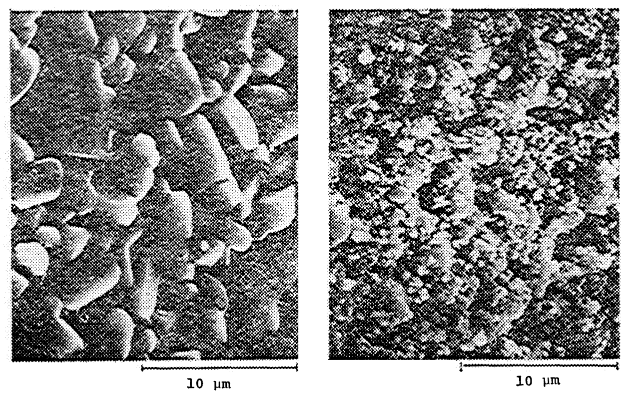


Fig. 3. Relation between discharge current and discharge time.
A: After first charging, B: after second charging, C: reference cell.



(A) (B)

Fig. 4. Scanning electron micrographs of TiO_2 surface before (A) and after (B) charging.

It seems that the lower electrical resistance of the $TiO_2(Ag)$ electrode after charging implies a whole electrode surface covered with deposited silver. Observation of the electrode surface with a scanning electron microscope JSM-T20S (Nippon Denshi Co., Ltd.,) confirms this (Fig. 4). According to a procedure reported previously,$^{1)}$ the amount of photoreduced silver at the TiO_2 surface in the $TiO_2(Ag)$–Ag^+ half cell was determined for varying the irradiation time with 365 nm light from a 500 W Xenon lamp. The number of photons incident on the TiO_2 surface was 3×10^{13} cm^{-2} s^{-1}. The quantum yield of the silver deposition (amount of photoreduced silver/number of incident photon) was *ca.* 0.9. Thus the conversion efficiency of the 365 nm light to the reduced silver is very high. It would seem that silver deposited at the surface restricts the penetration of the incident light into the TiO_2 layer and causes a decrease of the rate of silver deposition. Indeed, such a filter effect may ultimately restrict the amount of silver deposition, which determines the maximum amount of silver storage per electrode surface. However, we have observed elsewhere that deposited silver does not influence the rate of silver deposition even when it increases to a considerable extent.$^{1)}$

Another important aspect of this cell is that at the time of photochemical charging, the metal deposition is carried out without transporting the charge carriers (electrons and holes) into the TiO_2 bulk. Therefore, we can make use of various semiconductors provided only that they can reduce metal ions under illumination of sunlight. Moreover, at the time of discharge, the current flows from the deposited metal directly to the lead wire without passing through the semiconductor bulk and therefore, its bulk resistance does not affect the internal resistance of the cell. Provided we can establish successful electrochemical properties and photochemical charging, as well as relatively large quantum yield of silver deposition, the $TiO_2(Ag)$–Ag^+ half cell may be useful in the field of solar energy conversion.

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