1640 © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54, 1640—1644 (1981)* [Vol. 54, No. 6

Energy Conversion and Storage in Solid-state Photogalvanic Cells

Hiroshi Hada,* Kazuchiyo Takaoka, Masahiko Saikawa, and Yoshiro Yonezawa

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

(Received November 22, 1980)

The solid-state photogalvanic cells involving photochemically deposited metals as active materials are presented. As these cells have many excellent features as compared with usual photogalvanic cells in which both the cathodic and anodic materials are dissolved in solution, they will promise a novel storage system for the conversion of solar energy to electrical energy. A typical two-compartment cell: TiO_2, aqueous $Ce(SO_4)_2$–$Ce_2(SO_4)_3$||aqueous $AgNO_3$, Pt could be charged by the irradiation of 300—400 nm light on TiO_2. The deposited silver on a platinum black storage electrode has almost the same electrochemical properties as the silver metal electrode and is capable of recharging after a nearly complete discharge.

Although good efficiencies in solar energy conversion have been achieved with solid-state devices, especially with a *pn*-junction solar cell, energy conversion of light in electrochemical cells based on the photovoltaic effect at the semiconductor-liquid interface has still attracted considerable attention.[1,2] Fujishima and Honda have shown that water photolysis occurs in a photoelectrochemical cell using TiO_2 as a photosensitive electrode, together with taking out the electrical energy through an external load (photoelectrolysis cell).[3] When a suitable redox couple is dissolved in the electrolyte solution, the chemistry occurring in the cell having a n-type semiconductor electrode can be represented by the two half-cell reactions: oxidation of the reduced form at the photoelectrode and reduction of the oxidized form at the dark electrode, respectively. Light energy is thus converted to electrical energy with no net chemical changes in the whole cell (photovoltaic cell).[4] Since Becquerel first discovered the photogalvanic effect,[5] a number of papers on the subject appeared in the scientific literature.[6–8] However, the energy conversion efficiency in the conventional photogalvanic cells which make use of the photochemically generated species in an electrolyte solution as active materials is not so high due mostly to wasteful recombination reactions. The photoelectrolysis cell of Fujishima and Honda can produce hydrogen and oxygen from water, which are both useful active materials of the fuel cell. On the practical aspect, it seems to be most convenient to store the light energy as solid-state active materials at the electrode surface. We want to call such cells as solid-state photogalvanic cell in a sense that light energy is stored in solid state and *in situ* before taking out electrical energy at any time. We expect that these cells will show more excellent properties of the conversion and storage of light energy than the conventional photogalvanic cells because of their relatively compact size and ease to prevent wasteful reactions of active materials. There have been only few reports on such cells until now. Zaromb *et al.* proposed the cyclic photogalvanic silver halide cells: Pt, Ag–AgX, aqueous FeX_3–FeX_2, Pt (X=Cl, Br).[9] Recently, Hodes *et al.* have investigated the photoelectrochemical storage cell: CdSe; S/S^{2-} couple, Ag_2S–Ag.[10]

We have investigated the photoreduction of Ag^+ at the surface of either ZnO or TiO_2 by means of 365 nm light which belongs to the fundamental absorption band of them and observed that the quantum yield of the reaction is about 10^{-1} and that general feature of the reaction is elucidable by a local cell model.[11] While ZnO suffers irreversible decomposition by positive holes in the course of the reaction, TiO_2 is fairly stable and decomposes water into oxygen. Therefore, the photochemical reaction at TiO_2 surface may be regarded as conversion of light energy to the chemical energies represented by Ag^+/Ag couple (0.80 V *vs.* NHE) and $O_2,H^+/H_2O$ couple (1.23 V at pH=1). If we construct a photocell so as to separate the photochemical reaction at TiO_2 surface; an anodic reaction at TiO_2 photoelectrode (O_2 evolution) and a cathodic reaction (Ag deposition) at a storage electrode, we can indeed store the light energy *in situ* as active materials of the galvanic cell ready to convert to electrical energy any time. Cyclic discharge and photoelectrochemical recharging of the cell are easily accessible by switching the TiO_2 electrode to an inert counter electrode and *vice versa*. One of the merits of this cell is a decreased internal resistance as the electrodes are not made of non-metallic materials such as AgX and Ag_2S which were used by Zaromb *et al.* and Hodes *et al.*, respectively. If we make use of anion specific membrane to separate the solutions of two half cells, we can employ various combinations of cathodic and anodic materials. The present study is aimed at a preliminary examination of the possibility of various solid-state photogalvanic cells by using TiO_2 as a photoelectrode.

Experimental

TiO_2 film electrode was prepared by heating a plate of titanium in a fire of town gas at about 1600 K for 300 s according to Fujishima *et al.*[12] Titanium oxide of *ca.* 2 μm in thickness and more than 10 cm^2 area could be easily formed on titanium metal. Photoelectrochemical behavior of the oxide film electrode was somewhat inferior to TiO_2 single crystal electrode. The maximum photocurrent of the former electrode in UV-region was less than the latter one. An experimental cell is schematically indicated in Fig. 1. A storage electrode (A) and a counter electrode(C) are both made of platinum black disc. Anion specific membrane ACH-45T (Tokuyama Soda Co. Ltd.) separated the solutions of two half cells. A TiO_2 electrode (P) was connected with A-electrode directly or through an external load under photoelectrochemical charging, and then exchanged to C-electrode on discharge by two switch terminals. The electrolyte solution in the compartment of P- and C-electrodes consisted of aqueous solutions of KNO_3 plus HNO_3, Ce^{4+}/Ce^{3+} couple, or Fe^{3+}/Fe^{2+} couple.

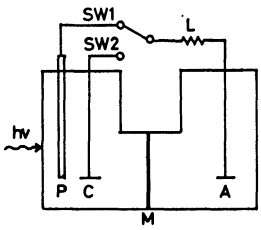

Fig. 1. Schematic representation of the solid-state photogalvanic cell with three electrodes.
P: TiO_2 electrode, A: Pt–Pt electrode (5.5 cm^2), C: Pt–Pt electrode (1.0 cm^2), M: Anion specific membrane, L: External load composed of variable resistance box, SW1, SW2: switches.

That in the A-electrode compartment ordinarily comprised KNO_3 plus either Ag^+ or Cu^{2+}. When we examined an applicability of AgCl/Ag, Cl^- couples as a storage electrode, AgCl electrode of *ca.* 0.1 cm^2 area was prepared according to Zaromb *et al.*[9] All potentials given in this paper are measured *versus* a normal hydrogen electrode (NHE).

As the light source, a high pressure 500-W mercury lamp (Ushio Denki Co. Ltd.) was used in combination with an interference filter UV-D2 (Toshiba Co. Ltd.) and water filter to select 300—400 nm light. The number of photons incident on the cell was 1.9×10^{17} cm^{-2} s^{-1} according to the trioxalatoferrate(III) actinometry.[13] Photoelectrochemical charging was achieved by irradiating on about 3 cm^2 area of TiO_2 electrode through the electrolyte solution. The photocurrent was measured by the voltage across a resistance box, which was recorded on an electrometer TR-84M (Takeda Riken Co. Ltd.) or a recorder EPR-100A (Toa Electronics Co. Ltd.). The current-voltage characteristics of the cells before and after charging were determined in a similar manner at 298 K in the darkness. The amounts of electricity passed through the circuit on the photoelectrochemical charging and discharge were obtained by the integration of the current monitored continuously as the voltage across a constant resistance. The amount of silver atoms deposited on a storage electrode was determined with an aid of a Jarrel-Ash AA-780 atomic absorption spectrophotometer. The optical density measurement of the solutions containing Ce^{4+}/Ce^{3+} couple has been carried out by using a MPS-5000 spectrophotometer (Shimadzu Seisakusho Co. Ltd.). All solutions were prepared from reagent grade chemicals purchased from Nakarai Chemicals Co. Ltd.

Results

Possibility of Solid-state Photogalvanic Cell. We have searched for a possibility of several combination of active materials which can be charged photoelectrochemically. With a reference of our former study on the photoreduction of Ag^+ at the semiconductor surface,[11] we at first examined the solid-state photogalvanic cell involving oxygen and silver as active materials: TiO_2, $HNO_3||Ag^+$, Pt (cell I). The electrolyte solutions comprised 1 M HNO_3 plus 1 M KNO_3 for a compartment of TiO_2 electrode and 1 M $AgNO_3$ plus 1 M KNO_3 for a compartment of the storage electrode, respectively. Figure 2 shows the curve of photocurrent against photovoltage in light. Photocurrent flowed from a storage electrode to TiO_2 electrode. The net electrochemical reactions will be as follows:

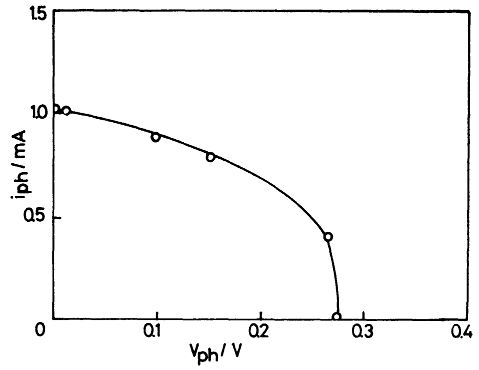

Fig. 2. Curve of photocurrent, i_{ph}, against photovoltage, V_{ph}, for the TiO_2 photocell: TiO_2, $HNO_3||Ag^+$, Pt.

$$TiO_2 + h\nu \longrightarrow e^- + p^+ \quad (1)$$

$$Ag^+ + e^- \longrightarrow Ag \quad (2)$$

$$2H_2O + 4p^+ \longrightarrow 4H^+ + O_2, \quad (3)$$

where e^- and p^+ denote an electron and positive hole, respectively. The photocurrent under a short-circuit condition was *ca.* 1 mA, which corresponds to an apparent quantum efficiency of about 1% (The number of electrons passed per s divided by the number of incident photons for 300—400 nm region per s). The open-circuit photovoltage was about 0.28 V. After illuminating the cell for 7200 s (the electricity flowed was 7.2 C), the discharge current from the counter electrode to the storage electrode was measured. The current-voltage curve of this cell was compared with that of a reference cell having a silver metal electrode of nearly equal surface area (Fig. 3). Except for somewhat smaller short-circuit current, the current-voltage characteristics of the photogalvanic cell is not so inferior to the reference cell. Furthermore, we could hardly take out electrical energy from the cell either before the charging or after a nearly complete discharge. Therefore, we confirmed that this cell can be photoelectrochemically charged and that the contribution of a different hydrogen ion concentrations in the two cell compartments will be negligible.

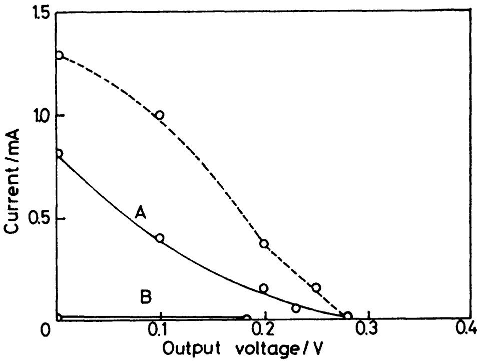

Fig. 3. The current-voltage characteristics for cells; Pt, $HNO_3||Ag^+$, Pt, ○—○, and Pt, $HNO_3||Ag^+$, Ag, ○···○. A: After charging, B: after nearly complete discharge.

In order to employ an active material more positive than $O_2,H^+/H_2O$ couple, we next examined a photogalvanic cell: TiO_2, Ce^{4+}/Ce^{3+} couple $||Ag^+$, Pt (cell II). The electrolyte solutions comprised 5×10^{-2} M $Ce_2(SO_4)_3$, 0.1 M $Ce(SO_4)_2$ plus 1 M HNO_3 for a compartment of P-electrode and 0.1 M $AgNO_3$ plus 1 M KNO_3 for A-electrode, respectively. The current flowed from a storage electrode to TiO_2 on irradiation. Silver atom was deposited at platinum black according to Eq. 2. Positive hole at the TiO_2 can oxidize Ce^{3+} according to Frank and Bard.[14] After illuminating the cell for 3600 s

$$Ce^{3+} + p^+ \longrightarrow Ce^{4+} \qquad (4)$$

(2.6 C), the current-voltage curve of the cell was measured and compared with that of a reference cell having the same silver electrode as mentioned before (Fig. 4). Two cells show almost the same features. The open-circuit voltage nearly coincides with a difference of the standard electrode potentials of Ag^+/Ag and Ce^{4+}/Ce^{3+} (1.61 V) couples.

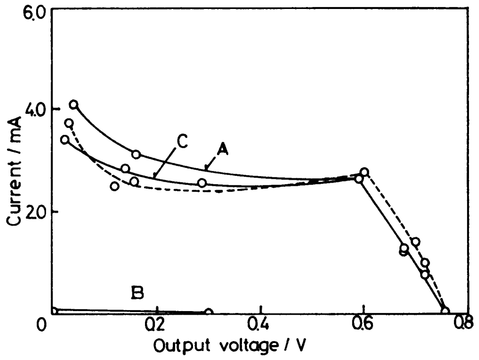

Fig. 4. The current-voltage characteristics for cells; Pt, Ce^{4+}/Ce^{3+} couple$||Ag^+$, Pt, ○—○, and Pt, Ce^{4+}/Ce^{3+} couple$||Ag^+$, Ag, ○···○.
A: After charging, B: after nearly complete discharge, C: after recharging.

With an aim to employ an active material more negative than Ag^+/Ag couple, we constructed a cell: TiO_2, Fe^{3+}/Fe^{2+} couple $||Cu^{2+}$, Pt (cell III). Electrolyte solutions comprised 1.0×10^{-2} M $FeSO_4$ plus 1.09 M KNO_3 for P-electrode and 2.5×10^{-2} M $CuSO_4$ plus 1.1 M KNO_3 for A-electrode, respectively. This cell was capable of photoelectrochemical charging in agreement with an induction from the former work of Wrighton *et al.*[15] We charged the cell for 6600 s (2.3 C)

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad (5)$$

$$Fe^{2+} + p^+ \longrightarrow Fe^{3+} \qquad (6)$$

and then measured the current-voltage curve. Figure 5 gives a comparison of a deposited copper electrode with copper metal electrode of 2.2 cm² area. The current-voltage curves of the two cells resembled each other but the open-circuit voltage of them was somewhat smaller than the difference of the standard electrode potentials of Cu^{2+}/Cu (0.34 V) and Fe^{3+}/Fe^{2+} (0.77 V) couples.

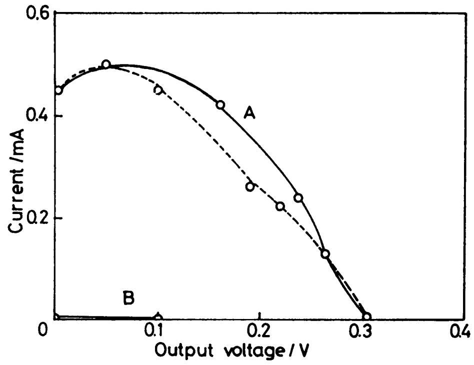

Fig. 5. The current-voltage characteristics for cells; Pt, Fe^{3+}/Fe^{2+} couple$||Cu^{2+}$, Pt, ○—○, and Pt, Fe^{3+}/Fe^{2+} couple$||Cu^{2+}$, Cu, ○···○.
A: After charging, B: after nearly complete discharge.

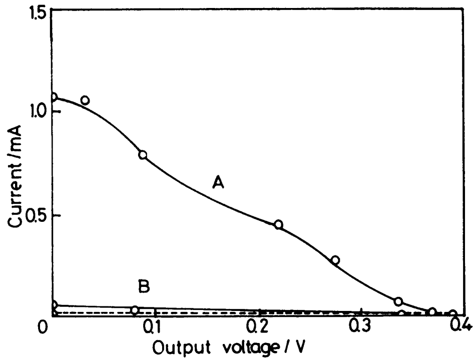

Fig. 6. The current-voltage characteristics for cells; Pt, Fe^{3+}/Fe^{2+} couple$||KCl$, AgCl, Pt, ○—○, and Pt, Fe^{3+}/Fe^{2+} couple$||KCl$, Ag/AgCl, ○···○.
A: After charging, B: after nearly complete discharge.

We finally intended to employ a $AgCl/Ag,Cl^-$ couple (0.22 V) and constructed a cell: TiO_2, Fe^{3+}/Fe^{2+} couple $||KCl$, AgCl,Pt (cell IV) with a reference of the former study of Zaromb *et al.*[9] The electrolyte solutions contained 1.0×10^{-2} M $FeCl_2$ plus 0.2 M KCl for P-electrode and only 0.2 M KCl for A-electrode, respectively. Irradiation of TiO_2 extended the photocurrent to induce cathodic decomposition of AgCl:

$$AgCl + e^- \longrightarrow Ag + Cl^- \qquad (7)$$

accompanied with reaction (6). After illumination for 4200 s (0.21 C), we measured the current-voltage characteristics. Figure 6 gives a comparison of the Ag/AgCl electrode established in this manner with a commercial Ag/AgCl reference electrode HS-305D (Toa Electronics Co. Ltd.). The current-voltage curve of the former cell seems to be superior to the latter, although a direct comparison of the discharge current may be difficult because of a different surface area of them.

Energy Storage in the Cell II Using Ce^{4+}/Ce^{3+} Redox Couple. In order to obtain a most convincing proof of the true photoelectrochemical charging with a typical photogalvanic cell, we illuminated the cell II for varying irradiation time over a 110 Ω resistance. The electrolyte solution of the compartment of A-electrode was the same as in Fig. 4 throughout this item. That of a TiO_2 compartment contained 5×10^{-3} M $Ce_2(SO_4)_3$, 0.6 M HNO_3 plus 0.5 M KNO_3. The magnitude of silver atom deposited at the A-electrode was compared with the net charge stored which was determined by integrating the total photocurrent on irradiation (Fig. 7). A linear plot obtained is in agreement with the charging reaction of Eq. 2. It is observed that the greater part

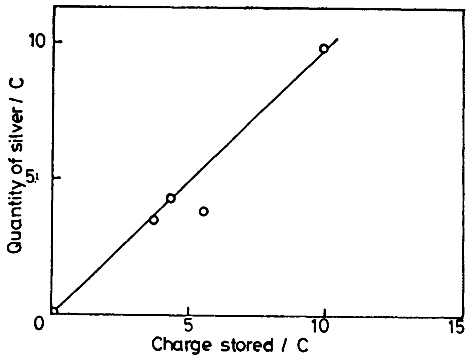

Fig. 7. Relation between the net charge stored in and the quantity of silver deposited on a Pt–Pt electrode for a cell: Pt, Ce^{4+}/Ce^{3+} couple||Ag^+, Pt.

of the photocurrent was consumed for the silver reduction at the A-electrode, because a slope of the straight line in this Figure is 0.94. The apparent quantum efficiency of silver deposition was about 1%. The power efficiency of this cell for 300—400 nm light was roughly estimated from the product of the apparent quantum efficiency of charging current and the ratio of energy level difference of Ag^+/Ag and Ce^{4+}/Ce^{3+} couples (0.81 eV) to the band-gap energy of TiO_2 (3.05 eV). It was about 0.3%. We next tried to detect an increase of Ce^{4+} in the TiO_2 compartment. The concentration of Ce^{4+} was determined spectrophotometrically by measuring the optical density at 375 nm corresponding to the absorption tail of this ion. The solutions in the cell were the same as those in Fig. 7. Ce^{4+} initially increased with time and then reached some stationary value after a prolonged irradiation. For example, the amount of oxidized Ce^{3+} corresponded initially to 98% of the net charge at 3.7 C charging but only to 22% after 10 C charging.

The relation between the charge stored on illumination and withdrawn in the darkness was examined by using two electrolyte solutions in the TiO_2 compartment, either the same as in Fig. 4 or 2.5×10^{-3} M $Ce_2(SO_4)_3$, 0.6 M HNO_3 plus 0.5 M KNO_3. It is observed that although a discharge current over a 1 kΩ resistance had initially a constant value of *ca.* 0.7 mA, it then successively decreased without stirring of a Ce^{4+}/Ce^{3+} half cell by a suitable stirrer. Such tendency was more evident for the cell containing smaller initial concentration of this couple. Figure 8 gives a plot between the net charge stored and withdrawn determined by integrating the total current before an above-mentioned fall-off region of the discharge current. From the slope, it is found that *ca.* 18% of the charge stored could be withdrawn as a nearly constant discharge current from cell A even without stirring. Furthermore, even from cell B which had smaller initial Ce^{4+}/Ce^{3+} concentration than cell A, up to 78% of the charge stored could be extracted only with a stirring by a magnetic stirrer.

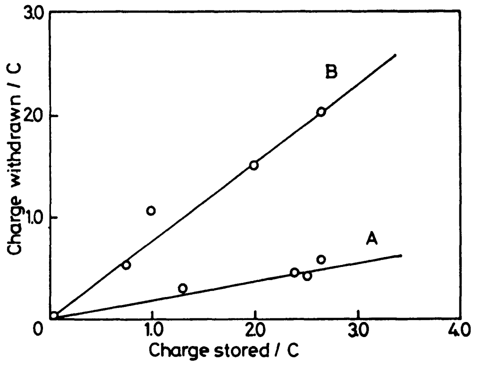

Fig. 8. Dependence of the net charge withdrawn on the charge stored in the two different Pt, Ce^{4+}/Ce^{3+} couple|| Ag^+, Pt cells.
A: 5×10^{-2} M $Ce_2(SO_4)_3+0.1$ M $Ce(SO_4)_2$ without stirring, B: 2.5×10^{-3} M $Ce_2(SO_4)_3$ with stirring.

We finally confirmed that the cell with the same electrolyte solution as in Fig. 4 could be recharged by many times after nearly complete discharge. A typical result is included in the same Figure.

Discussion

Photoelectrochemical charging of the solid-state photogalvanic cells having a TiO_2 photoelectrode was achieved with four different storage modes. According to an energetic consideration, it seems to be promising at sight to employ a combination of active materials: those which have as negative electrode potentials as the conduction-band edge and those which have as positive electrode potentials as the valence-band edge of the surface of the photoelectrode. In this respect, Ag^+/Ag–Ce^{4+}/Ce^{3+} combination is superior to Ag^+/Ag–O_2,H^+/H_2O one. Moreover, Cu^{2+}/Cu–Fe^{3+}/Fe^{2+} and $AgCl/Ag$,Cl^-–Fe^{3+}/Fe^{2+} combinations may also treasure up some possibilities. However, H_2 evolution at the cathode and O_2 evolution at the anode during photoelectrochemical charging strongly limit the choice of arbitrary redox couples in aqueous solution. A decreased charging current, as expected from a local cell consideration, may give an additional criterion for the choice.

So far as our experiments, solid-state photogalvanic cell of type II seems to be most excellent with regard to the short-circuit current and open-circuit voltage. Moreover, almost all the photocurrent could be stored as deposited silver. In the darkness, an active material Ce^{4+} could be stored over a long time at the open-circuit condition, because thermal reduction of Ce^{4+} by water is rather slow at room temperature.[16] In this respect, Ce^{4+}/Ce^{3+} couple seems to be superior to, say, Co^{3+}/Co^{2+} one, as Co^{3+} is reduced by water in the darkness.[17] Indeed, there are several problems to be solved with this cell. The power efficiency of the cell seems to be not so large at present. However, it will be due mostly to the reduced quantum efficiency of anodic photocurrent of TiO_2 film electrode employed here. So that, we may expect a considerable improvement if we operate a refined electrode under an optimum condition. Appearance of a stationary concentration of Ce^{4+} with irradiation time suggests an existence of competition processes of the formation and disappearance of this ion. It may be due at least in part to both the bulk photochemical reactions of Ce^{4+} and Ce^{3+} even in 300—400 nm region[18,19] and to the filter effect of incident light on TiO_2 by Ce^{4+}. The effect of stirring of Ce^{3+},Ce^{4+}/Pt half cell in Fig. 8 suggests that discharge current will be limited by some reasons at this part of the photogalvanic cell. To overcome these difficulties, several efforts are undertaken at present.

In the silver halide cell of Zaromb *et al.*,[9] the energy of light absorbed by, say, AgCl was converted to the chemical energy by the following reaction:

$$AgCl + Fe^{2+} \longrightarrow Ag + Cl^- + Fe^{3+}. \qquad (8)$$

A serious drawback of this cell was that it could operate satisfactorily only in light because there exist several self-discharge reactions in the darkness. With regard to this, cell IV may be an extension of their cell.

Though TiO_2 electrode is photochemically stable, spectral response of it is mostly in the ultraviolet. With regard to this point, the photoelectrochemical storage cell of Hodes *et al.*[10] using CdSe photoelectrode seems to be superior to ours. However, as CdSe suffers the irreversible decomposition reaction unless operated in the alkaline solution containing a suitable redox couple such as S/S^{2-}, the choice of active materials stable in alkaline solution will inevitably be reduced in consequence. Apart from an application of some other photoelectrode having smaller band-gap energy, the design of the solid-state photogalvanic cells which are capable of *in situ* storage of both anodic and cathodic materials is under way.

References

1) "Semiconductor Liquid Junction Solar Cells," ed by A. Heller Electrochemical Society, Princeton, New Jersey (1977).
2) A. Nozik, *Ann. Rev. Phys. Chem.*, **29**, 189—222 (1978).
3) A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
4) H. Gerischer, *J. Electroanal. Chem. Interfacial Electrochem.*, **58**, 263 (1975).
5) E. Becquerel, *C. R. Acad. Sci.*, **9**, 561 (1839).
6) E. Rabinowitch ,*J. Chem. Phys.*, **8**, 551, 560 (1940).
7) A. W. Copeland, O. D. Black, and A. B. Garrett, *Chem. Rev.*, **31**, 117 (1942).
8) T. Sakata, Y. Suda, J. Tanaka, and H. Tsubomura, *J. Phys. Chem.*, **81**, 537 (1977); Y. Suda, Y. Shimoura, T. Sakata, and H. Tsubomura, *ibid.*, **82**, 268 (1978); H. Tsubomura, Y. Shimoura, and S. Fujiwara, *ibid.*, **83**, 2103 (1979).
9) S. Zaromb, M. E. Lasser, and F. Kalhammer, *J. Electrochem. Soc.*, **108**, 42 (1961).
10) G. Hodes, J. Manassen, and D. Cahen, *Nature*, **261**, 403 (1976); J. Manassen, G. Hodes, and D. Cahen, *J. Electrochem. Soc.*, **124**, 532 (1977).
11) H. Hada, H. Tanemura, and Y. Yonezawa, *Bull. Chem. Soc. Jpn.*, **51**, 3154 (1978).
12) A. Fujishima, K. Kohayakawa, and K. Honda, *J. Electrochem. Soc.*, **122**, 1487 (1975).
13) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
14) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 4667 (1977).
15) M. S. Wrighton, P. T. Wolczanski, and A. B. Ellis, *J. Solid State Chem.*, **22**, 17 (1977).
16) D. Grant, *J. Inorg. Nucl. Chem.*, **26**, 337 (1964).
17) M. E. Gerstner, *J. Electrochem. Soc.*, **126**, 944 (1979).
18) L. J. Heidt and A. F. Mcmillan, *Science*, **117**, 75 (1953); *J. Am. Chem. Soc.*, **76**, 2135 (1954).
19) R. J. Marcus, *Science*, **123**, 399 (1956).