# An Investigation of the Power Characteristics in Heterogeneous Electrochemical Photovoltaic Cells for Solar-energy Utilization

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A heterogeneous electrochemical photovoltaic cell was constructed using the system of cadmium sulfide(CdS)/sulfides reducing agents//oxidizing agents/platinum. The output power characteristics were investigated focusing upon the redox potentials of the oxidizing agents in the cathodic half-cell and then discussed from the point of view of the solution-electrode junction. Though this type of cell intrinsically has a negative free energy for redox reactions of redox agents in an anodic and a cathodic compartment, it has a characteristic point that a larger open-circuit output than the intrinsical electromotive force determined by a redox couple was obtainable in operation under illumination. For example, in the CdS/$S^{2-}$/S//$Fe^{2+/3+}$/Pt system we found the open-circuit photovoltage of *ca.* 2.0 V, which is *ca.* 83% of a band gap (2.4 eV) of CdS. These measurements showed that a larger open-circuit photovoltage was obtained, though, of course, it was smaller than the band-gap energy of CdS, when the oxidizing agent of the more positive redox potential was dissolved in the cathodic compartment.

The conception of solar-energy conversion to chemical energy and/or electrical energy has been actualized by the use of such electrochemical photocells as photoelectrolytic cells[1—8] and regenerative photovoltaic cells.[9—11] As these photocells have a Schottky-type junction of a semiconductor/solution interface, photoinduced electron-hole pairs are separated by the electric field in the space-charge layer and react with redox agents in an electrolyte solution. For the efficient conversion of solar energy, much information has been presented on the reactions at semiconductor electrodes under illumination.[12] The stabilization of a photoelectrode with a small bandgap is a key problem and is attained by the competitive reaction of redox agents in an electrolyte solution.[12—16] For a regenerative photovoltaic cell after it has been stabilized by a strong reducing agent, its output photovoltage was small with respect to the bandgap value of the semiconductor employed. In order to obtain good output-power characteristics in a regenerative photovoltaic cell, a variety of combinations of semiconductors and solution species have been employed and then discussed, focusing upon the solar-conversion efficiency.[17—19]

Cadmium sulfide (CdS) is a promising material because its bandgap (2.4 eV) is suitable for the conversion of solar light and because its flatband potential ($E_{\mathrm{fb}}$) is sufficiently negative, in particular in a sulfide solution.[14,20—22] However, the output voltage of the regenerative photovoltaic cell constituted by the single compartment of the CdS/redox species/Pt system is limited to about 600 mV,[18] as determined by the potential difference between the flatband potential of CdS and the reduction potential of the oxidized species. When the low value of the photovoltage is compared with the CdS bandgap of 2.4 eV, one can understand that it limits the electric-output power efficiency.

In order to increase the electric-output power, it may be advantageous to employ a photovoltaic cell constructed by two separated half cells: CdS/sulfide solution//oxidizing solution/Pt. In this case, such a cell can be expected to overcome the photovoltage limitation (*ca.* 600 mV) by means of the positive reduction potentials of the oxidizing agent dissolved in the cathodic compartment, while stabilizing the CdS photoanode by means of the sulfide solution. The evaluation of the power characteristics of such systems is the subject of the present study.

## Experimental

The cadmium sulfide electrode was an n-type single crystal (Teikoku Tsushin Kogyo Co., Ltd.) with a resistivity of 0.26 Ω·cm and a carrier density of $8\times10^{16}$ $\mathrm{cm}^{-3}$ (as determined by the company). The irradiated face (001) had an area of 0.85 $\mathrm{cm}^2$. This face was polished by alumina powder and etched in concentrated HCl for 10 s. Ohmic contact for a copper wire was made by means of indium and silver paste, and the electrode was isolated on a glass rod by means of epoxy resin. As a cathode, platinum foil (1.7 $\mathrm{cm}^2$) was used. Before the experiment, the platinum electrode was treated with concentrated $HNO_3$. The solution for stabilizing CdS was 0.5 M $Na_2S$+0.1 M NaOH (M=mol/$\mathrm{cm}^3$). The aqueous solutions in the cathode compartment were as follows: (1) 0.1 M NaOH+0.5 M $Na_2S$+0.01 M S; (2) 0.2 M $Na_2SO_4$; (3) 0.5 M $K_3Fe(CN)_6$; (4) 0.5 M $Fe(NO_3)_3$; (5) 0.5 M KI +0.1 M $I_2$+0.2 M $Na_2SO_4$. All the chemicals used were reagent-grade. The light source was a 500-W Xe lamp (Ushio Electric UXL Type). The incident light was filtered by means of a UV-D2 (Toshiba Kasei) glass filter, which lets the wavelengths of 300—400 nm pass through and which has a peak transmittance of 80% for the wavelength of 360—370 nm. The power output characteristics were measured by using a compensated electrometer (Kowa Electronics VM-208) and an ammeter (Nikko Keisoku NZ-1). The anode and cathode compartments were separated with an agar-agar salt bridge containing saturated KCl.

## Results and Discussion

Figure 1 shows the current-potential curves at the illuminated CdS electrode and at the platinum electrode obtained under potentiostatic conditions. The anodic photocurrent (Curve 1) appears at a potential more positive than −1.13 V *vs.* NHE at the CdS photoelectrode in the electrolyte solution containing sulfide ions. When the platinum counter electrode is set in an electrolyte solution containing oxidizing agents ($K_3Fe(CN)_6$), the cathodic current appears at the

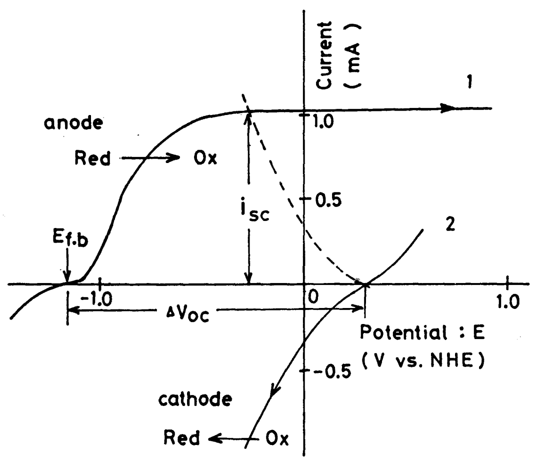


Fig. 1. Current-potential curves at a CdS photoanode and a platinum cathode.
Solid line 1: at CdS in 0.5 M $Na_2S$+0.1 M NaOH+0.01 M S aqueous solution, solid line 2: at Pt in 0.5 M $K_3Fe(CN)_6$+0.2 M $Na_2SO_4$ aqueous solution, dashed line: rewriting of a negative part of a solid line 2 with absolute values

potential of *ca.* 0.37 V *vs.* NHE. This cathodic onset potential is more positive than the onset potential of the cathodic current which appears at the Pt electrode in the solution containing sulfides. Considering the limitation of the open-circuit photovoltage determined by the potential difference between anodic and cathodic onset potentials, one can see that the larger electric-output power will be obtained when the cathode is set in the solution with the stronger oxidizing agent.

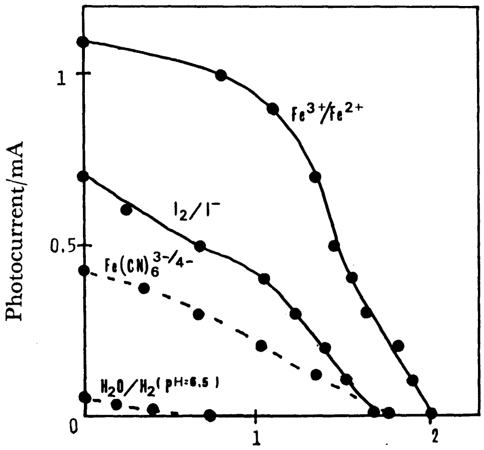


Fig 2. Output power characteristics (current-voltage curves) in heterogeneous photovoltaic cells of CdS/0.5 M+0.1 M NaOH/0.5 M oxidizing agent/Pt systems. Oxidizing agents: 1, $H_2O$ (pH=6.5); 2, $K_3Fe(CN)_6$; 3, $I_3^-$; 4, $Fe_2(SO_4)_3$.

In Fig. 2 we present some output power characteristics for [a CdS/0.5 M $Na_2S$+0.01 M S+0.1 M NaOH aqueous solution//solution containing oxidizing agents/Pt] photovoltaic cell. The actual output power was in the order of $Fe^{3+} > I_2(I_3^-) > Fe(CN)_6^{3-} > H_2O$, so the maximum of the open-circuit photovoltage was about 2.0 V, which was *ca.* 83% of the bandgap (2.4 eV) of CdS. This suggests that the output power increases with the more positive shift of the redox potential of an oxidizing agent.

We examined the open-circuit output voltages in the dark and under illumination when various oxidizing agents were introduced in the solution. The results are shown as functions of their redox potentials in Fig. 3.

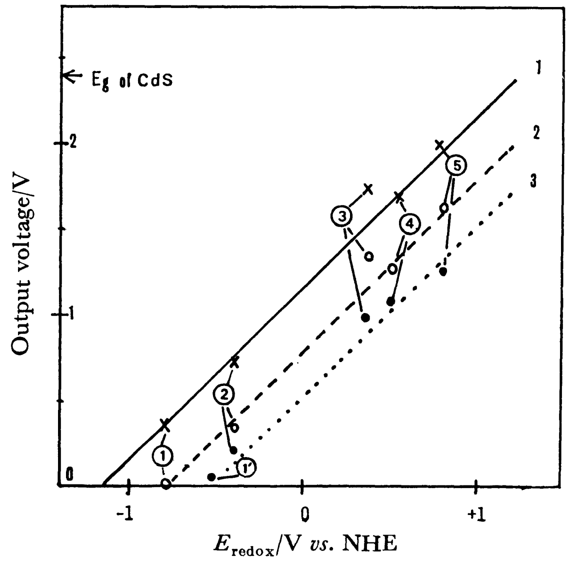


Fig. 3. Open-circuit voltage in heterogeneous photovoltaic cells as a function of the redox potentials of oxidizing agents in cathodic compartments.[25]
1: $H_2O/H_2$ (pH=13.5), 1′: $S^{2-}/S_2^{2-}$, 2: $H_2O/H_2$ (pH =6.5), 3: $Fe(CN)_6^{3-/4-}$, 4: $I_2/I^-$, 5: $Fe^{3+/2+}$.
×, Solid line 1; output photovoltage between CdS and Pt, ○, dashed line 2; output voltage (dark) between CdS and Pt ●, dotted line 3; output voltage between Pt and Pt.

The dashed line 2 represents the output voltages in dark conditions, its slope is *ca.* 1.0. The intersection of this line with the abscissa is at the potential of −0.8 V *vs.* NHE, which is close to the water reduction potential (hydrogen evolution) at this pH value (13.5). The solid line 1 represents the output voltages obtained under irradiation. The value of its slope is also 1.0, and the intersection of the line with the abscissa is at the potential of −1.16 V *vs.* NHE, corresponding to the flatband potential of the CdS electrode under these conditions. As for the flatband potential ($E_{fb}$), Minoura *et al.*[20] have reported $E_{fb} \fallingdotseq -1.13$ V *vs.* NHE for a 0.1 M $Na_2S$+1 M $Na_2SO_4$ solution, Ginley and Butler[21] have reported $E_{fb} \fallingdotseq -1.05$ V *vs.* NHE for a 0.9 M $Na_2S$+0.05 M KOH solution, while we ourselves[22] have presented $E_{fb} \fallingdotseq -1.09$ V *vs.* NHE for a 0.1 M $Na_2S$+0.2 M $Na_2SO_4$ solution. The dotted line 3 in Fig. 3 represents the relation between the open-circuit output voltage and the redox potentials of the oxidizing agents when we employed the Pt electrode instead of the CdS electrode in the anodic compartment (pH=13.5). The intersection of this line with the abscissa is at the potential ($E_{redox,1} = -0.52$ V *vs.*

NHE) of a $S^{2-}/S$ system.

The open-circuit output voltage ($\Delta V_{oc}$) of the electrochemical photovoltaic cell arises from the difference between the flatband potential of the semiconductor photoanode and the redox potential ($E_{redox,2}$) of an oxidizing agent ($O_x$) at a cathode:

$$\Delta V_{oc} = |E_{fb} - E_{redox,2}| \qquad (1)$$

$$2S^{2-} \longrightarrow S_2^{2-} + 2e^- \text{ (at an anode)} \qquad (2)$$

$$O_x + ne^- \longrightarrow \text{Red (at a cathode)} \qquad (3)$$

Some investigations have also reported as the output characteristics in the electrochemical photovoltaic cell determined using a CdS electrode, as are shown in Table 1. The upper four electrochemical photovoltaic cells are composed of a single compartment with a redox couple, so they are regenerative. The last two electrochemical photovoltaic cells are similar to ours and are not regenerative. From the data in Fig. 3 and Table 1, we can conclude that the relation (Eq. 1) is applicable to the output voltage in the electrochemical photovoltaic cell.

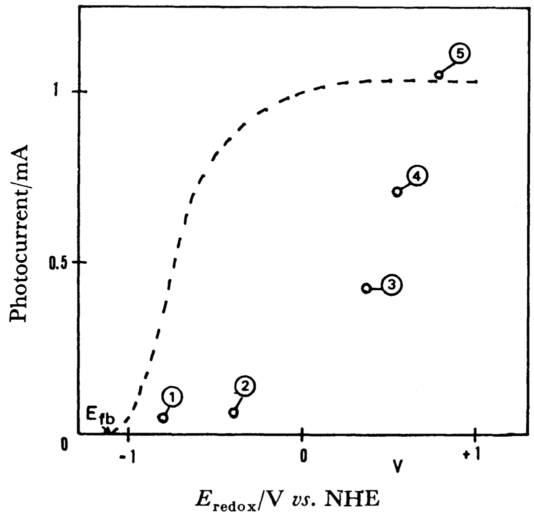


Fig. 4. Short-circuit currents in heterogeneous photovoltaic cells as a function of the redox potentials of oxidizing agents in cathodic compartments.[25] A dashed line shows a current-potential curve of a CdS photoanode. All numbers are the same as those in Fig. 3.

Figure 4 shows the short-circuit output currents as functions of the redox potentials of oxidizing agents dissolved in the cathodic compartment. The dashed curve represented the anodic photocurrent at a CdS electrode obtained under potentiostatic conditions. The currents actually obtained are smaller than the CdS anodic photocurrent observed under the potentiostatic conditions. The difference in photocurrents between the value from this dashed curve and that from the experimental results may come from polarization losses in an operation. Therefore, if the redox couples in the cathodic half-cell are infinitely reversible, and also if all losses in the semiconductor bulk and surface can be neglected, these plots will lie on the ideal dashed curve. The fact that the losses diminish with an increase in the redox potential can be explained the fact that the increase in the cell electromotive force advantageously affects the polarization characteristics of both electrode reactions. It can be assumed that the limited photocurrent determined by the light absorption of CdS can be obtained in this cell when an oxidizing agent with a redox potential more positive than a $Fe^{2+/3+}$ couple is dissolved in the cathodic compartment.

Figure 5 shows the output power in the electrochemical photovoltaic cells as functions of the redox potentials of the oxidizing agents. The dashed line represents the maximum output power ($P_{max}$) obtainable for a particular redox system, it is calculated by the following procedure:

$$P_{max} = i[E_F](E_{redox} - E_F) \qquad (4)$$

where $E_F$ denotes the semiconductor Fermi level, *i.e.*, the electrode potential in an operation; $E_{redox}$, the redox potential of an oxidizing agent in a cathodic compartment; and $i[E_F]$, the output current determined from the photocurrent at the potential of $E_F$. Figure 6 explains the calculation procedure of $P_{max}$ schematically, where the magnitude of the current is determined by means of the polarization of CdS. The output power observed is plotted in Fig. 5 and is reflected in the

TABLE 1. VARIOUS ELECTROCHEMICAL PHOTOVOLTAIC CELLS USING CdS

| Workers | No. | | $\Delta V$exp | $U_{fb} - E_{redox}$[a)] | Ref. |
|---|---|---|---|---|---|
| Gerischer and Gobrecht | 1 | $\mathrm{CdS/Fe(CN)_6^{3-/4-}/Pt}$ | 0.97 | 0.99 | 6 |
| | 2 | $\mathrm{CdS}\Big/\begin{matrix}\mathrm{S_2O_3^{2-}}\\\mathrm{S_4O_6^{2-}}\end{matrix}\Big/\mathrm{Pt}$ | 0.82 | 0.85 | 6 |
| Heller, Chang, and Miller | 3 | $\mathrm{CdS}\Big/\begin{matrix}\mathrm{Na_2S}\\\mathrm{NaOH}\end{matrix}\Big/\mathrm{C}$ | 0.60 | 0.59 | 10 |
| Minoura, Tsuiki, and Oki | 4 | $\mathrm{CdS}\Big/\begin{matrix}\mathrm{Na_2S}\\\mathrm{Na_2SO_3}\end{matrix}\Big/\mathrm{Pt}$ | 0.38 | 0.38 | 16 |
| | 5 | $\mathrm{CdS}\Big/\begin{matrix}\mathrm{Na_2S}\\\mathrm{Na_2SO_3}\end{matrix}\Big/\begin{matrix}\mathrm{Na_2SO_4}\\\mathrm{pH=7}\end{matrix}\Big/\mathrm{Pt}$ | 0.78 | 0.74 | 16 |
| | 6 | $\mathrm{CdS}\Big/\begin{matrix}\mathrm{Na_2S}\\\mathrm{Na_2SO_3}\end{matrix}\Big/\begin{matrix}\mathrm{Na_2SO_4}\\\mathrm{pH=1}\end{matrix}\Big/\mathrm{Pt}$ | 1.15 | 1.10 | 16 |

a) The potentials ($E_{redox}$) of various oxidizing agents were calculated by consulting Ref. 23.

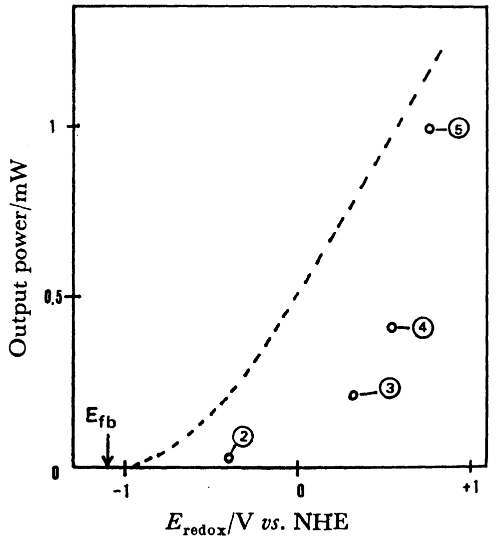


Fig. 5. Maximum electric output power in heterogeneous photovoltaic cells as a function of the redox potential of oxidizing agents in cathodic compartments.[25] Dashed line was calculated by Eq. 4. All numbers are same in Fig. 3.

characteristics shown in Fig. 4. The calculated power, $P_{\max}$, increases with the variation in the redox potential and will be saturated at the potentials near the valence-band potential (*ca.* 1.4 V *vs.* NHE) of CdS.

In conclusion, we have shown the power characteristics in the heterogeneous electrochemical photovoltaic cell. This type of photovoltaic cell has two kinds of redox systems. Sulfides as a reducing agent shift the flatband potential of CdS and are oxidized at the CdS photoanode. Oxidizing agents are reduced at the Pt electrode. The characteristic point is that a large open-circuit voltage is obtainable with respect to the bandgap (2.4 V) of CdS. For the elucidation of the

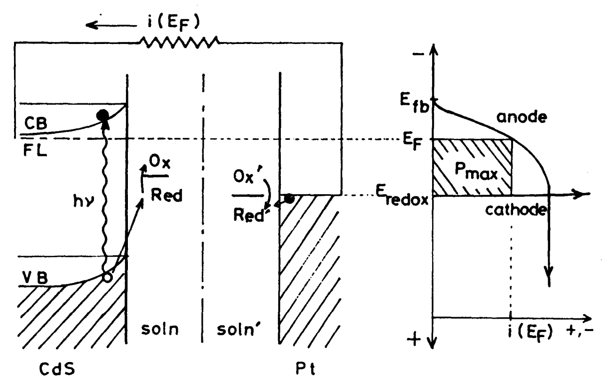
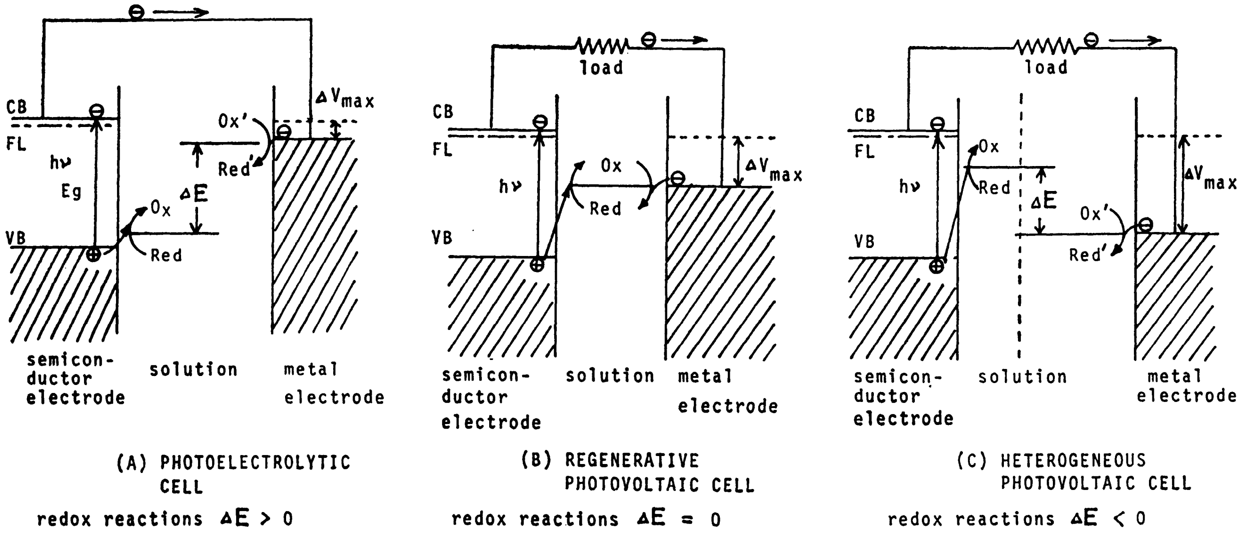


Fig. 6. Schematic explanation for calculation of $P_{\max}$ according to Eq. 4.

heterogeneous photovoltaic cell, we show in Fig. 7 a schematic illustration of the potential variations in the solution-electrode junctions in comparison with other types of electrochemical photocells. We can classify the electrochemical photocells into three types from the point of view of the difference ($\Delta E$) in redox potentials at an anode and a cathode:

$$\Delta E = E_{\text{redox},1} - E_{\text{redox},2} \tag{5}$$

First, when the value of $\Delta E$ is positive, the electrochemical photocell works as a photoelectrolytic cell which can convert the light energy to chemical and/or electrical energy and also store the chemical energy. Second, when the value of $\Delta E$ is zero, it works as a regenerative photovoltaic cell which can convert the light energy only to electrical energy. Third, when the value of $\Delta E$ is negative, it works as a heterogeneous photovoltaic cell which can convert both the light and the chemical energy to electrical energy and which can generally give the largest output photovoltage of these three electrochemical photocells.



(A) PHOTOELECTROLYTIC CELL
redox reactions ΔE > 0

(B) REGENERATIVE PHOTOVOLTAIC CELL
redox reactions ΔE = 0

(C) HETEROGENEOUS PHOTOVOLTAIC CELL
redox reactions ΔE < 0

Fig. 7. Schematic illustrations of the semiconductor electrode-solution junctions for three typesof electrochemical photocells.

(A) Photoelectrolytic cell (Refs. 4, 6, 7, 8), free energy of a redox reaction is positive.

(B) Regenerative photovoltaic cell (Refs. 7—11), free energy of a redox reaction is zero.

(C) Heterogeneous photovoltaic cell (this study), free energy of a redox reaction is negative.

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