The Investigation of Energy Efficiency of the ZnO Semiconductor Photoelectrode by Photothermal Measurement

Yasuhisa Maeda, Akira Fujishima,* and Kenichi Honda
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received March 11, 1982)

The energy efficiency of a polycrystalline ZnO photoanode in an electrolyte solution containing redox agents was investigated by measuring the temperature change of the electrode surface. The results of photothermal measurements show that the energy efficiency depends on the kind of redox agents used. Reducing agents with more positive potentials gave larger energy efficiencies, but the potential must be negative enough to decrease ZnO dissolution.

A number of photoelectrochemical cells using semiconductor electrodes have been reported for the photodecomposition of water and the conversion of solar energy into electricity.[1–17] The energy conversion and quantum efficiencies of photoelectrochemical cells are needed for effective utilization of solar energy. However, during the course of a photoelectrochemical reaction only a portion of the photons absorbed by the semiconductor can be utilized by the electrode reaction, while the remaining portion is converted to heat. Thus, photothermal measurements of a semiconductor electrode during the course of electrolysis can be used to determine the energy efficiency (*i.e.* the ratio of the chemical or electrical power output to the radiant power input).

We have developed a new method to determine the quantum efficiency and the energy efficiency by measuring the temperature change of the surface of a semiconductor electrode with a thermistor.[18–21] When a semiconductor is illuminated with a pulse of monochromatic light having a photon energy E and an average absorbed intensity I for a period of time t, the relationship between the temperature change and the applied potential is represented by Eq. 1, which applies in a limited photocurrent region

$$E\frac{\Delta T}{\Delta T^\circ} = \frac{Q_{\mathrm{s.c.}} + T\Delta S}{It} + \eta e(V - V_{\mathrm{FB}}), \tag{1}$$

where ΔT is the temperature change of the semiconductor surface with an applied potential V (*vs.* a reference electrode), ΔT° is the temperature change of the semiconductor surface for an open circuit, ΔS is the entropy change of the semiconductor electrode reaction, $Q_{\mathrm{s.c.}}$ is the heat evolved in the semiconductor due to radiationless processes, η is the quantum efficiency of the photoelectrode reaction, and V_{FB} is the flatband potential (*vs.* a reference electrode).

Under constant illumination conditions, *i.e.* $EIt=$ constant, a plot of $E(\Delta T/\Delta T^\circ)$ *vs.* $(V-V_{\mathrm{FB}})$ yields a straight line, whose slope is the quantum efficiency, η and whose intercept gives the quantity $(Q_{\mathrm{s.c.}}+T\Delta S)/It$ and also $E(\Delta T/\Delta T^\circ)$ when $V=V_{\mathrm{FB}}$.

The energy conversion efficiency, therefore, can be obtained when we know the value of the entropy change $T\Delta S$ associated with the electrode reaction.

In previous papers,[18–21] we investigated only the quantum efficiency of photoelectrode reactions from the slope of the linear plot of $E(\Delta T/\Delta T^\circ)$ *vs.* $(V-V_{\mathrm{FB}})$, but we had not made a detailed analysis of the energy efficiency.

In this paper, during the course of photoelectrochemical reactions at a ZnO polycrystalline electrode in an electrolyte solution containing redox agents, we determined both the quantum and energy efficiencies. The significance of the intercept and the value of energy efficiency are discussed from the point of view of redox potential.

Experimental

The semiconductor electrode used was a sintered polycrystalline ZnO prepared by pressing reagent-grade ZnO powder at a pressure of 150 kgf/cm²[†] and then heating at 1300 °C for 3 h in air. After making an ohmic contact with an In–Ga alloy, a copper wire was attached with silver epoxy resin. All surfaces except one were covered with epoxy resin. The exposed polycrystalline face of ZnO was etched in concentrated HCl for 10 s, and then washed with water. The procedure for the photothermal measurement was described in previous papers.[18–21] A platinum electrode was used as the counter electrode and a saturated calomel electrode (SCE) was the reference electrode. A potentiostat (Nikko Keisoku) was used to control the potential of the ZnO electrode with respect to SCE. The supporting electrolyte was 0.2 M Na_2SO_4 (1 M=1 mol dm^{-3}) and all the redox agents used were of reagent-grade.

Results and Discussion

Figure 1 shows the plots of $E(\Delta T/\Delta T^\circ)$ *vs.* V during the course of photoelectrochemical reactions of the ZnO polycrystalline electrode in the electrolyte solution containing one of four different kinds of reducing agents. The electrode was irradiated for 10 s with monochromatic light provided by a 340 nm interference filter. The values of $E(\Delta T/\Delta T^\circ)$ were different for each reducing agent at a given potential. The slopes of the linear plots of $E\ \Delta T/\Delta T^\circ$ *vs.* V, *i.e.* the quantum efficiencies of the photoelectrode reactions, were 0.90 for each reducing agent except S^{2-} for which the slope was 0.80. In the case of S^{2-} the smaller value might be due to the optical absorption of sulfur generated by the oxidation of sulfur ion at the electrode/electrolyte interface. The values obtained by extrapolating the linear portion of $E(\Delta T/\Delta T^\circ)$ *vs.* V to the flatband potentials which were obtained from the onset potentials of the photocurrents depended on the kind of reducing agent. The onset potential was the lowest potential at which a photo-

---

[†] 1 kgf=9.80665 N.

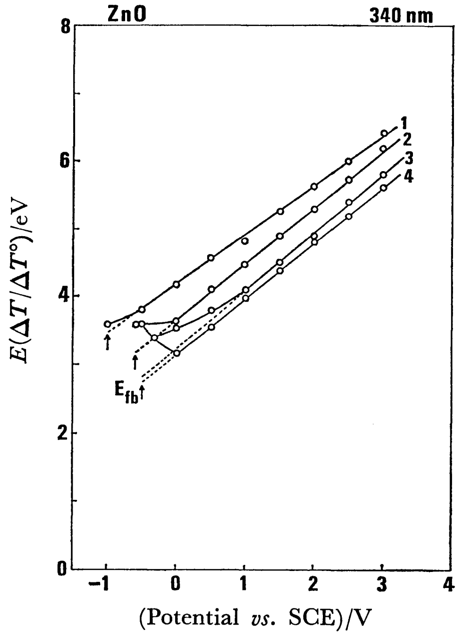

Fig. 1. Normalized temperature change *vs.* potential of a ZnO polycrystal electrode.
Curve 1: 0.5 M Na_2S, curve 2: 0.5 M $Na_2S_2O_3$, curve 3: 0.5 M H_2Q, curve 4: 0.5 M KBr in 0.2 M Na_2SO_4.

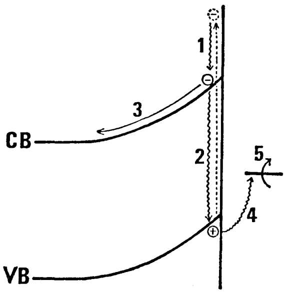

Fig. 2. The state of heat generating during the course of photoelectrode reaction.

current was measurable. As shown in Fig. 1, the onset potentials in the case of S^{2-}, $S_2O_3^{2-}$, H_2Q, and Br^- were −1.0, −0.60, −0.50, and −0.50 V *vs.* SCE, respectively. That of S^{2-} was more negative relative to others because of the higher pH value of this electrolyte.

The heat generated during the course of the photoelectrode reaction consists of five components evolved in the processes shown in Fig. 2, namely (1) radiationless transition within the conduction band (*i.e.* when the photon energy absorbed is in excess of the band gap energy), (2) electron-hole recombination, (3) electron transport from the surface to the bulk through the space charge layer in the conduction band, (4) charge transfer reaction between the hole in the valence band and the redox species in the electrolyte solution, and (5) entropy change of the redox reaction. The Joule heat in the solution due to the current flow is very small and can be neglected.

When one photon with energy E is absorbed by the electrode surface, the photoelectrochemical reaction proceeds with a quantum efficiency η at an applied electrode potential V, and the heat generated by the five processes discussed above are as follows: (1) $E-E_g$ (E_g: the band gap of the semiconductor), (2) $E_g(1-\eta)$ (if the semiconductor is not a fluorescent or phosphorescent material), (3) $\eta e(V-V_{FB})$, (4) $\eta(E_v-E_R)$ (E_R: redox potential, E_v: energy position of the valence band), and (5) $\eta T\Delta S$.

In the supporting Na_2SO_4 electrolyte solution, the photoelectrode reaction results in the dissolution of the ZnO electrode,[22)]

$$ZnO + 2p^+ \longrightarrow Zn^{2+} + \frac{1}{2}O_2.$$

However, when electrolyte solution contains a redox agent, the oxidation of the reducing agent and the dissolution reaction proceed competitively. It is probable that $\eta e(E_v-E_R)$ and $T\Delta S$ represent the heat due to these two photoelectrode reactions. Therefore, by using the competitive oxidation ratio[23)] of a reducing agent $\alpha(0\leqq\alpha\leqq1)$ and the five types of heat losses, Eq. 1 can be as follows;

$$\begin{aligned} ITE(\Delta T/\Delta T°) &= (E-E_g) + E_g(1-\eta) + \eta\alpha(E_v-E_R) \\ &\quad + \eta(1-\alpha)(E_v-E_D) + \eta\alpha T\Delta S \\ &\quad + \eta(1-\alpha)T\Delta S' + \eta e(V-V_{FB}), \end{aligned} \tag{2}$$

where E_D is the decomposition potential of ZnO (the value thermodynamically calculated[24)] is +0.65 V *vs.* SCE), ΔS is the entropy change of the oxidation reaction of a reducing agent, and $\Delta S'$ is the entropy change of the dissolution reaction of ZnO.

From the measurement of reaction heat (Peltier heat) by using a platinum electrode,[25)] the values of $T\Delta S$ for the redox reaction employed were found to be a fairly small fraction of $E(\Delta T/\Delta T°)$. For example, the Peltier heat for the oxidation of S^{2-} and H_2Q was below one fifth of that for the oxidation of $Fe(CN)_6^{4-}$ which was the biggest value, 0.4 eV, we observed. However, it was difficult to determine the accurate value of the Peltier heat for each electrode reaction by a metal electrode. Therefore, we could not say the exact values for the Peltier heat, but we thought that $T\Delta S$ and $T\Delta S'$ in these cases might be negligible.

When the quantum efficiencies of photoelectrode reactions are the same in different electrolyte solutions, the value of the intercept at the flatband potential,

$$\begin{aligned} Q &= (E-E_g) + E_g(1-\eta) \\ &\quad + \eta\alpha(E_v-E_R) + (1-\alpha)(E_v-E_D), \end{aligned} \tag{3}$$

is expected to depend on the competition ratio α, and the redox potential E_R. Q was plotted against redox potential in Fig. 3 for H_2Q, $S_2O_3^{2-}$, SO_3^{2-}, and S^{2-} all which have more negative redox potentials than the decomposition potential of ZnO, 0.65 V *vs.* SCE. As shown in this figure, Q was smaller as the redox potential was more positive. The nearly linear relationship between the redox potential and Q is evident. The slope of this line $\eta\alpha$ is about 0.85, a value almost the same as the quantum efficiency in each electrolyte solution which was 0.90. Therefore the competitive ratio was close to 1, and we conclude that the main photoelectrode reactions in these solutions are as follows:

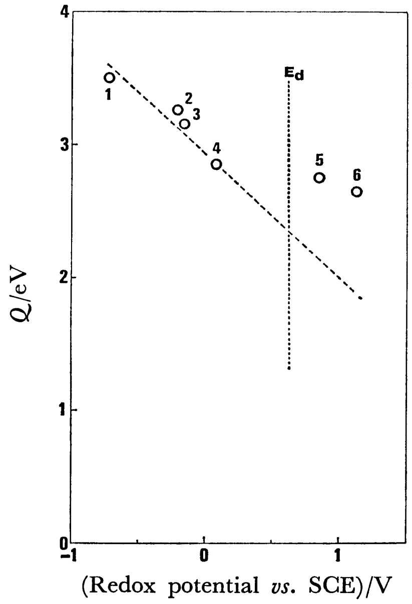

Fig. 3. Relationship between Q and redox potential. No. 1: 0.5 M Na_2S, No. 2: 0.5 Na_2SO_3, No. 3: 0.5 M $Na_2S_2O_3$, No. 4: 0.5 M H_2Q, No. 5: 0.5 M KBr, No. 6: 0.5 M KCl in 0.2 M Na_2SO_4.

$$H_2Q + 2p^+ \longrightarrow Q + 2H^+$$
$$2S_2O_3^{2-} + 2p^+ \longrightarrow S_4O_6^{2-},$$
$$2SO_3^{2-} + 2p^+ \longrightarrow S_2O_6^{2-},$$
$$S^{2-} + 2p^+ \longrightarrow S.$$

In case of Br^- and Cl^- which have a more positive oxidation potential than the decomposition potential of ZnO, +0.65 V *vs.* SCE, Q was smaller as the redox potential was more positive, but the degree of the decrease in Q was smaller in comparison to that for H_2Q, $S_2O_3^{2-}$, SO_3^{2-}, and S^{2-} which have more negative redox potentials. This suggests that the competitive ratios of Cl^- and Br^- are small, and that in these solutions the dissolution reaction of ZnO is faster than the oxidation of Cl^- and Br^-. In this figure, it is evident that Q depends on the competition ratio and redox potential of the reducing agents.

From the point of view of thermodynamics[24,26]) a reducing agent with a redox potential more negative than the decomposition potential of a semiconductor can decrease photoelectrocorrosion of the semiconductor. In fact using the rotating ring-disk electrode technique, we reported that a reducing agent with a more negative redox potential has a larger competition ratio and can better stabilize the ZnO electrode.[27]) The present measurements confirm this relationship for the stabilization of the ZnO electrode.

The electrochemical photocell in which a photosemiconductor works with a counter electrode in a redox couple solution is called as the regenerative photocell. In the photocell absorbed light energy is converted to electrical energy. The ideal maximum energy conversion efficiency ϕ_v is represented as follows,

$$\phi_v = \frac{|E_{FB}-E_R|}{E} \times 100\ (\%), \tag{4}$$

where E_{FB} is the flatband potential, E is absorbed light energy. $|E_{FB}-E_R|$ means the maximum photovoltage in the regenerative cell.

Table 1. Energy efficiencies for the photooxidation of each reducing agent on ZnO polycrystal electrode

Redox agent	(E_r *vs.* SCE)/V	Q/eV	ϕ_T/%	ϕ_v/%
S^{2-}	−0.72	3.50	2.8	7.9
SO_3^{2-}	−0.22	3.25	10.8	10.7
$S_2O_3^{2-}$	−0.16	3.15	12.5	12.2
H_2Q	+0.08	2.85	20.8	16.1

$$\phi_T = \frac{3.6-Q}{3.6} \times 100\ (\%),\quad \phi_v = \frac{|E_{FB}-E_r|}{3.6} \times 100\ (\%)$$

On the other hand, from the photothermal data the energy conversion efficiency ϕ_T can be obtained by using the value of Q,

$$\phi_T = \frac{E-Q}{E} \times 100\ (\%). \tag{5}$$

The energy efficiencies for the reducing agents S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, and H_2Q under irradiation of monochromatic light 340 nm (3.6 eV) were given from the values of Q as shown in Table 1.

The meaning of ϕ_T can be considered as follows. When the competitive oxidation ratio α is 1.0, the value of Q is expressed from Eq. 3 as below,

$$Q = \eta(E_v - E_R) + E - E_g\eta. \tag{6}$$

Therefore

$$\frac{E-Q}{E} = \frac{\eta\{E_g-(E_v-F_R)\}}{E}. \tag{7}$$

Since $|E_g - E_v|$ equals almost to the flatband potential, the next equation is given,

$$\frac{E-Q}{E} = \frac{\eta|E_{FB}-E_R|}{E}. \tag{8}$$

Therefore, from Eq. 8 the energy efficiency ϕ_T can be derived as the product of the quantum efficiency (which is obtained from the slope of the photothermal measurement) and the maximum photovoltage under monochromatic light irradiation. In the case of ZnO, the value of quantum efficiency is near 1, so ϕ_T is expected to equal to ϕ_v. In Table 1 energy efficiencies ϕ_v are also shown.

The values of ϕ_T and ϕ_v are similar in the case of each reducing agent. It was ascertained that a reducing agent with a more positive redox potential gave larger energy efficiency.

We conclude that the photothermal measurement technique provides information on the energy efficiency and the stabilization of a semiconductor electrode by redox agents.

References

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

2) T. Ohnishi, Y. Nakato, and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.,* **79,** 523 (1975).

3) J. H. Carey and B. G. Oliver, *Nature,* **259,** 554 (1976).

4) M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abrahamson, and D. S. Ginley, *J. Am. Chem. Soc.,* **98,** 2774 (1976).

5) H. Gerischer and J. Gobrecht, *Ber. Bunsenges. Phys. Chem.*, **80**, 1635 (1976).

6) A. B. Ellis, S. W. Kaiser, and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 6855 (1976).

7) D. Laser and A. J. Bard, *J. Electrochem. Soc.* **123**, 1027 (1976).

8) A. B. Ellis, S. W. Kaiser, J. M. Bolts, and M. S. Wrighton, *J. Am. Chem. Soc.*, **99**, 2839 (1977).

9) A. B. Ellis, J. M. Bolts, S. W. Kaiser, and M. S. Wrighton, *J. Am. Chem. Soc.*, **99**, 2848 (1977).

10) A. Heller, K. C. Chang, and B. Miller, *J. Am. Chem. Soc.*, **100**, 684 (1978).

11) R. N. Noufi, P. K. Kohl, and A. J. Bard, *J. Electrochem. Soc.*, **125**, 375 (1978).

12) H. Tributsch, *Ber. Bunsenges. Phys. Chem.*, **82**, 169 (1978).

13) B. A. Parkinson, A. Heller, and B. Miller, *J. Electrochem. Soc.*, **126**, 954 (1979).

14) P. A. Kohl and A. J. Bard, *J. Electrochem. Soc.*, **126**, 603 (1979).

15) R. N. Noufi, D. Tench, and L. F. Warren, *J. Electrochem. Soc.*, **127**, 2709 (1980).

16) L. F. Schneemeyer and M. S. Wrighton, *J. Am. Chem. Soc.*, **102**, 6964 (1980).

17) H. S. White, F. F. Fan, and A. J. Bard, *J. Electrochem. Soc.*, **128**, 1045 (1981).

18) A. Fujishima, Y. Maeda, K. Honda, G. H. Brilmyer, and A. J. Bard, *J. Electrochem. Soc.*, **127**, 840 (1980).

19) Y. Maeda, A. Fujishima, and K. Honda, *Chem. Lett.*, **1980**, 271.

20) A. Fujishima, Y. Maeda, and K. Honda, *Bull. Chem. Soc. Jpn.*, **53**, 2735 (1980).

21) Y. Maeda, A. Fujishima, and K. Honda, *Nippon Kagaku Kaishi*, **1981**, 349.

22) H. Gerischer, *J. Electrochem. Soc.*, **113**, 1174 (1966).

23) T. Inoue, T. Watanabe, A. Fujishima, K. Honda, and K. Kohayakawa, *J. Electrochem. Soc.*, **124**, 719 (1977).

24) H. Gerischer, *J. Electrochem. Soc.*, **82**, 133 (1977).

25) R. Tamamushi, *J. Electroanal. Chem. Interfacial Electrochem.*, **45**, 500 (1973); **65**, 263 (1975).

26) A. J. Bard and M. S. Wrighton, *J. Electrochem. Soc.*, **124**, 1706 (1977).

27) T. Inoue, A. Fujishima, and K. Honda, *Bull. Chem. Soc. Jpn.*, **52**, 3217 (1979).