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# The Correlation between Photo-electrochemical Cell Reactions and Photocatalytic Reactions on Illuminated Rutile

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Photocatalytic reductions of $MnO_4^-$, $Cr_2O_7^{2-}$, and $Fe^{3+}$ on illuminated rutile were demonstrated. The suitability of a method to analyze the reduction process of the photocatalytic reaction was discussed. It was concluded that a high utilization of light energy could not be expected for photocatalytic reactions because both bands of the semiconductor participated in the reaction. In such a case, the development of the photocatalytic process into a photoelectrochemical cell has a great advantage from the point of view of energy utilization.

Recently, electrochemical reactions on semiconductor electrodes have been investigated extensively.[1-3] The "Photo-sensitized electrolytic reaction" on an illuminated semiconductor electrode is one of the most interesting features of semiconductor electrochemistry.[4] Fujishima and Honda reported a photo-electrochemical cell with a decomposition of water,[5,6] and the cells of this type have been investigated intensively.[7-9] On the other hand, photocatalytic reactions on illuminated semiconductor catalysts seem to be another feature of the "photo-sensitized electrolytic reaction."[10,11] Some attempts have been made to analyze a photocatalytic reaction on an illuminated semiconductor catalyst by electrochemical methods.[11]

It has been reported that electrochemical measurements based on the local cell process are useful for analyses of the reaction rates and mechanisms of the reduction of Methylene Blue[12] and quinones[13] dissolved in methanol on illuminated rutile catalysts. The local cells of these reactions were found to be composed of the "photo-sensitized electrolytic oxidation" and the cathode process of a reaction which obeys usual thermodynamics.[10]

When the local cell is established on an illuminated semiconductor catalyst, a photo-electrochemical cell can be constructed in which the cell reaction is composed of the two individual reactions. This idea was successfuly demonstrated in a previous paper.[10]

It is well known that water is oxidized to oxygen on an illuminated rutile anode in the following way:[4-7]

$$2H_2O + 4p^+ \longrightarrow O_2 + 4H^+, \qquad (1)$$

where $p^+$ denotes a positive hole in the valence band of rutile. If one chooses an oxidizing agent whose redox-potential is more noble than the potential at which the oxidation of water commences on an illuminated rutile electrode, then one can easily construct a photo-electrochemical cell by using a rutile anode and a Pt cathode. The performance of the cell will be different depending on the redox-potentials of the oxidizing agents chosen so long as the anode process is not heavily disturbed by the existence of the oxidizing agent, which may cause a partial cathodic current.

If the Pt cathode is taken out from the cell, and the rutile electrode is illuminated at the open-circuit condition, then a local cell must be established on the illuminated rutile surface with the same reaction as that in the photo-electrochemical cell. The reaction in this case may be termed a photocatalytic reaction, as in the cases of the reduction of Methylene Blue[12] and quinones[13] on illuminated rutile in methanol solutions. It is quite natural to expect, however, that the reaction behavior will be different between the photo-electrochemical cell and the photocatalytic process.

The purpose of this paper is to present the difference in the behavior between the two kind of reactions by using several kinds of oxidizing agents.

## Experimental

A commercial single crystal of rutile (1×1×0.2 cm) was used as the electrode material. It was reduced in an argon atmosphere at 800 °C for 2 h. Before being mounted in a glass tube with epoxy resin, the rutile was etched in a concd $H_2SO_4$ solution containing the same weight of $(NH_4)_2SO_4$ at 240 °C for 0.5 h. The (100) face was chosen as the electrode surface. Its carrier concentration ($N_D$), as estimated from Mott-Shottky plots in the dark, was about $10^{19}/cm^3$. Before measurements, the rutile electrode was dipped in a concd $HNO_3$ solution for 2 min, washed with de-ionized water for about 0.5 h, and then dried by hot air. A Pt electrode (1×1 cm) as the cathode of a photo-electrochemical cell and rutile powder as the catalyst were prepared in a manner described previously.[13]

The solution used in this study was 0.5 mol $dm^{-3}$ $H_2SO_4$ containing an oxidizing agent. The oixdizing agents chosen were $KMnO_4$, $K_2Cr_2O_7$, and $Fe_2(SO_4)_3$. The water used as the solvent was distilled twice, and the $H_2SO_4$ solution was pre-electrolyzed for 48 h. All the chemicals were of a guaranteed reagent grade. Nitrogen gas was bubbled into the solution during all the electrochemical and chemical experiments.

A 500 W ultra-high pressure Hg arc lamp (Ushio Electric, Inc.; model UI-501) was used as the light source. The light of wavelengths shorter than 350 nm was cut off by setting a convex glass lens in front of the quartz window of the measurement cell. In the case of the experiment using the $KMnO_4$ solution, a $CoSO_4$-solution filter was set in front of the cell to prevent the photo-excitation of $MnO_4^-$.[14]

Polarization curves were obtained in a steady-state condition by means of a potentiostat (Hokuto Denko Co.; model ps-500B). The potentials were measured against the SCE. The concentration of chemical species in the solution was determined by means of absorptiometry. A Hitachi 124 spectrophotometer was used for this purpose.

The other details such as the purification of the gas, the construction of the measurement cell, and the procedure for the chemical analysis, have been described before.[13]

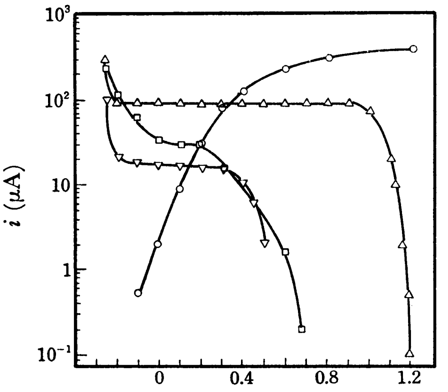

Fig. 1. Polarization curves of the illuminated rutile and the Pt electrodes in 0.5 mol dm$^{-3}$ $H_2SO_4$ solution with and without $5\times10^{-4}$ mol dm$^{-3}$ of the oxidizing agent. (○) Anodic curve at rutile without the oxidizing agent, and cathodic curves at Pt with (△) $KMnO_4$, (□) $K_2Cr_2O_7$, and (▽) $Fe_2(SO_4)_3$.

## Results and Discussion

*Photo-electrochemical Cells.* Figure 1 shows the polarization curves of the photo-electrochemical cells of

$$\text{rutile}|0.5\ \text{mol dm}^{-3}\ H_2SO_4\,\vdots\,\text{Ox},\ 0.5\ \text{mol dm}^{-3}\ H_2SO_4|\text{Pt},$$

where Ox denotes the oxidizing agent. This figure suggests that if the cell of

$$\text{rutile}|\text{Ox},\ 0.5\ \text{mol dm}^{-3}\ H_2SO_4|\text{Pt}$$

works ideally, the cell reaction is composed of the oxidation of water and the reduction of the oxidizing agent. The term "ideally" means that the partial cathodic reduction of Ox and the oxidation of the product formed at the Pt cathode are negligible at the rutile electrode. The establishment of this ideal condition was confirmed, at least in the cases of the reduction of $MnO_4^-$ to $MnO_2$ and of $Cr_2O_7^{2-}$ to $Cr^{3+}$, by analyzing the concentration of the oxidizing agent in the cell as a function of the quantity of electricity drawn under short-circuited conditions.

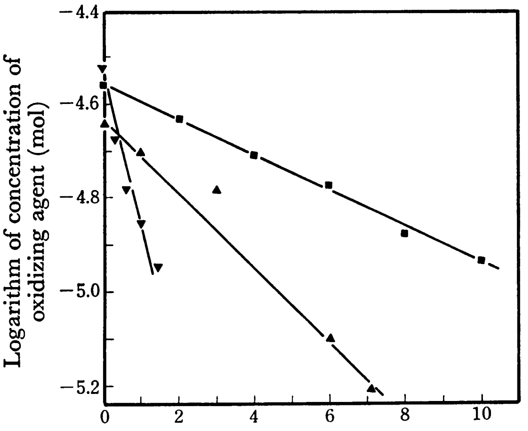

Fig. 2. Change of the concentration of oxidizing agents in 0.5 mol dm$^{-3}$ $H_2SO_4$ with the reaction time on the illuminated rutile powder catalyst. The solutions containing (▼) $Fe^{3+}$, (■) $1/2Cr_2O_7^{2-}$, and (▲) $MnO_4^-$, respectively.

*Chemical Analysis of Photocatalytic Reactions.* When a rutile powder catalyst was suspended in a 0.5 mol dm$^{-3}$ $H_2SO_4$ solution (50 cm$^3$) containing an oxidizing agent, the concentration of the oxidizing agent was decreased by illumination. The results are shown in Fig. 2.

The solutions retained their original absorbance when they were illuminated without the rutile catalyst for 20 h. By the reaction, the solution containing $KMnO_4$ produced a brown precipitate and the purple solution turned light yellow. The other solutions became transparent, and no deposit was detected on the catalyst. Accordingly, the cathode processes of the photocatalytic reactions are the reductions of $MnO_4^-$, $Cr_2O_7^{2-}$, and $Fe^{3+}$ to $MnO_2$, $Cr^{3+}$, and $Fe^{2+}$ respectively. On the other hand, the anodic process is the oxidation of water.[4–7] These results suggest that illuminated rutile worked effectively as a catalyst, causing the same reaction as in the photo-electrochemical cell.

The reaction in Fig. 2 seems to be first-order with respect to the oxidizing agent chosen, since linear relations were established between the logarithm of the concentration of the oxidizing agent and the reaction time. The rate constant calculated from the slopes of the lines are summarized in Table 1.

TABLE 1. REACTION RATES DETERMINED BY ELECTROCHEMICAL ANALYSIS AND REACTION RATE CONSTANTS DETERMINED BY CHEMICAL ANALYSIS

| Solution | $K_2Cr_2O_7$ | $KMnO_4$ | $Fe_2(SO_4)_3$ |
|---|---|---|---|
| Electrochemical analysis (μA) | 0.26 | 0.73 | 2.2 |
| Chemical analysis ($\times10^{-4}$, l/s) | 1.1 | 1.5 | 6.0 |

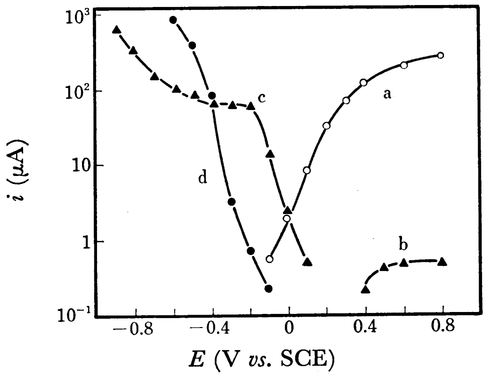

Fig. 3. Polarization curves of the rutile electrode in 0.5 mol dm$^{-3}$ $H_2SO_4$ solution with and without $5\times10^{-4}$ mol dm$^{-3}$ $KMnO_4$. (a): Anodic curve without $KMnO_4$ under illumination, (b): anodic curve with $KMnO_4$ in the dark, (c): cathodic curve with $KMnO_4$ in the dark, (d): cathodic curve without $KMnO_4$ in the dark.

*Electrochemical Analysis of Photocatalytic Reactions.* Figure 3 shows the polarization curves of the rutile electrode in 0.5 mol dm$^{-3}$ $H_2SO_4$ solutions with and without $5\times10^{-4}$ mol dm$^{-3}$ $KMnO_4$. The anodic curve (a), obtained under illumination in a solution without $KMnO_4$, is the same as the curve at the rutile anode in

Fig. 1, and indicates the anodic oxidation of water by positive holes.4–7) This curve was little affected by the presence of $KMnO_4$ in the solution. On the other hand, it can be noticed, from a comparison of the two cathodic curves (c) and (d), that the cathodic current was distinctly increased by addition of $KMnO_4$ to the solution. This increase in the cathodic current may be ascribed to the participation of the reduction of $KMnO_4$ to $MnO_2$. The magnitude of the current in the presence of the oxidizing agent was by far larger than that in the absence of it. This means that the polarization curve of the oxidizing agent was eventually the same as curve (c). The stagnation of the cathodic current in curve (c) under a relatively high cathodic polarization is attributable to the deposition of $MnO_2$ onto the rutile surface. The cathodic process is based on the conduction-band electrons, since the cathodic current increased exponentially with an increase in the cathodic polarization.1–3)

Similar results were obtained for the solutions with the other oxidizing agents. The reduction curves of these oxidizing agents are summarized in Fig. 4, together with the oxidation curve of water.

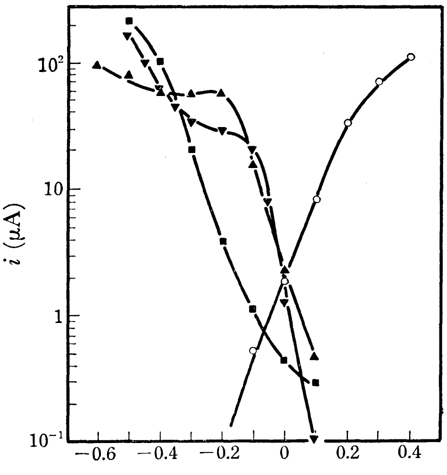

Fig. 4. Polarization curves of the rutile electrode in 0.5 mol $dm^{-3}$ $H_2SO_4$ solution with and without the oxidizing agent. (○) Anodic curve without the oxidizing agent under illumination. Cathodic curves with $5\times10^{-4}$ mol $dm^{-3}$ (▲) $KMnO_4$, and $2.5\times10^{-4}$ mol $dm^{-3}$ (▼) $Fe_2(SO_4)_3$ and (■) $K_2Cr_2O_7$ in the dark.

When the cathodic polarization curves obtained in the dark are not changed by the illumination, the rate of the catalytic reaction on illuminated rutile can be estimated as the current value at the intersection point of the anodic and the cathodic curves in Fig. 4; this procedure is widely adopted in the estimation of the corrosion rates of metals.15) The illumination has a negligible influence on the cathodic polarization curves when the electron concentration at the rutile surface is almost unchanged by the illumination. Therefore, it is necessary to discuss whether or not such a condition is fulfilled in the present study.

The electron concentration at equilibrium in the rutile electrode at room temperature ($n_0$) was about $10^{19}/cm^3$, as stated in the experimental section. The concentration of excited electrons by the illumination ($n^*$) is given as a function of the distance $x$ from the illuminated surface by16)

$$\mathrm{d}n^*(x)/\mathrm{d}t = \alpha f' \exp(-\alpha x) - \mathrm{d}i/\mathrm{d}x - n^*(x)/\tau,$$
$$i = -D\mathrm{d}n^*(x)/\mathrm{d}x \tag{2}$$

where $\alpha$, $f'$, $\tau$, and $D$ denote the absorption coefficient of rutile, the numbers of incident photons per $cm^2$ per second on the crystal, the lifetime of the carrier in rutile, and the diffusion constant of the carrier in rutile respectively. In a steady state, Eq. 2 becomes

$$\alpha f' \exp(-\alpha x) + D\mathrm{d}^2 n^*(x)/\mathrm{d}x^2 - n^*(x)/\tau = 0 \tag{3}$$

since $\mathrm{d}n^*(x)/\mathrm{d}t=0$.16) By applying the conditions that $n^*(x)$ becomes 0 when $x$ is infinitely large, and that carriers which diffuse to the surface can escape from the crystal to cause the current to flow, that is, $i=-D\{\mathrm{d}n^*(x)/\mathrm{d}x\}_{x\to0}=n^*(x\to0)$, Eq. 3 gives the following equation:

$$n^*(x) = \alpha f'\tau\{\exp(-\alpha x)\}/(1-D\tau\alpha^2)$$
$$+ K\exp\{-x/(D\tau)^{1/2}\}$$
$$K = \alpha f'\tau^{3/2}(D\alpha-1)/\{(D\alpha^2\tau-1)(D^{1/2}-\tau^{1/2})\} \tag{4}$$

$\alpha$ is judged to be $10^3/cm$ for the light of 400 nm,17,18) which gives the maximum photo-response at the rutile electrode.19,20) $\tau$ has been reported to be $5\times10^{-6}$ s and almost independent of the applied electric field and temperature.21) If a value of 1 $cm^2/V$ s is chosen as the electron mobility,22,23) then we can obtain $3\times10^{-2}$ $cm^2/s$ for $D$ from the well-known Einstein relation.24)

The quantum yield of the "photo-sensitized electrolytic oxidation" of water is dependent on the wavelength and $N_D$, and is around $0.3\pm0.2$ in an rutile anode having $10^{19}$ carriers/$cm^3$ at 2 V *vs.* SCE for the light of 400 nm.19) If it is assumed that the numbers of holes reached at the electrode surface per second are a 0.1 fraction of that of the incident photons, we can get a rough measure of $f'$ from a knowledge of the saturated photo-current. We use here the smallest value of the quantum yield, 0.1, because we have to estimate the upper limit of $n^*$. In the present study, the saturated hole current at 2 V *vs.* SCE in a 0.5 mol $dm^{-3}$ $H_2SO_4$ solution was 875 μA/$cm^2$. Accordingly, $f'$ was estimated to be less than $10^{17}/cm^2$ s.

In order to get information on the concentration of photo-generated electrons at the surface, Eq. 4 was simplified with the condition of $x\to0$:

$$n^*(x\to0) = \alpha f'\tau/(1-D\tau\alpha^2) + K. \tag{4'}$$

By substituting the just-estimated values into Eq. 4′, $n^*(x\to0)$ was determined to be smaller than $10^{15}/cm^3$.

Now it is possible to get information on the relative measure of the numbers of photo-generated electrons at the surface of rutile to those of electrons at equilibrium in the dark. The electron concentration at the surface of the electrode $n_s$ in the dark is given by Eq. 5:25)

$$n_s = n_0 \exp\{-e(E-E_{fb})/kT\} \tag{5}$$

where $E$ and $E_{fb}$ are the electrode potential and the flat-band potential of rutile respectively. The $E_{fb}$ of rutile in a 0.5 mol $dm^{-3}$ $H_2SO_4$ solution was reported to be −0.1 V *vs.* SCE.26) A similar argument can also be applied to $n^*(x\to0)$ when the effect of the band bending is taken into consideration for $n^*(x \to 0)$. Anyway, comparing the value of $n_s$ with that of $n^*(x \to 0)$, $n^*(x \to 0)$ is too small to give a distinct change in the numbers of electrons at the rutile surface.

It may also be valuable to discuss the effect of the photovoltage on cathodic polarization curves obtained in the dark. A depletion layer is formed when an $n$-type semiconductor electrode such as rutile is placed in contact with a solution containing a chemical species which has a more noble redox-potential than $E_{\mathrm{fb}}$. By illumination, the degree of the band bending is reduced, and this effect causes the so-called photovoltage.[27] According to Gerischer, the electron-energy level in the semiconductor is changed by illumination by the magnitude of the photovoltage, and the change is equal to $\mathrm{e}(E_{\mathrm{F}}^* - E_{\mathrm{F}})$ eV, where $E_{\mathrm{F}}^*$ and $E_{\mathrm{F}}$ denote the Fermi levels of the semiconductor under illumination and in the dark respectively. By the illumination, the electrode potential is shifted toward a cathodic direction by the magnitude of the change in the band bending. If the illuminated electrode is polarized anodically by $|E_{\mathrm{F}}^* - E_{\mathrm{F}}|$, the electrode potential is brought back to the same value as before illumination, and simultaneously the band bending also returns to the same situation as before illumination. It is concluded from this discussion that the same band situation is realized at rutile electrodes both with and without illumination if the electrodes are polarized at the same potential.

It is, therefore, believed that the reduction curves obtained in the dark in Fig. 4 represent the behavior of the reduction of the oxidizing agents on the illuminated rutile catalyst.

It is, then, possible to determine the rates of the photocatalytic reactions as the current values of the intersection points in Fig. 4.[12,13] In the cases of $\mathrm{MnO_4^-}$ and $\mathrm{Cr_2O_7^{2-}}$, three and six Faradays are needed to produce 1 mol of $\mathrm{MnO_2}$ and 2 mol of $\mathrm{Cr^{3+}}$ respectively. One-third of the current values at the intersection points in Fig. 4 thus correspond to the reaction rates for these systems. The reaction rates estimated from the electrochemical measurements are summarized in Table 1, together with the reaction rate constants determined by the chemical analysis described above.

The rutile powder catalyst used in the chemical analysis had an unidentified $N_{\mathrm{D}}$ and various crystal planes exposed to the solution. On the other hand, the electrochemical analysis was performed on the single crystal which had a fixed $N_{\mathrm{D}}$ and crystal plane. Nevertheless, the results in Table 1 show that the reaction rates determined by the two kinds of methods had a similar tendency in their relative magnitudes. The important influence of $N_{\mathrm{D}}$ on the rate of the photoelectrochemical reaction was theoretically predicted[27] and was also experimentally found on the photoelectrolytic decomposition of water at rutile anodes and GaP cathodes.[19] However, the ambiguity of $N_{\mathrm{D}}$ does not cause any serious problem in the qualitative comparison of the reaction rates determined by the two kinds of methods, because the dimensions of the reaction rates are completely different between the two kinds of methods, and the same powder catalyst was used in the series of the experiments, by which the effect of $N_{\mathrm{D}}$ was fixed in various systems of the photocatalytic reactions.

The value of the reaction rates on the illuminated rutile catalyst is determined by the feasibility of electron exchange between the semiconductor and the species in the solution, as has been discussed in a previous paper in the case of quinones dissolved in methanol.[13] The feasibility is determined by the positions of the energy levels of the band edges of semiconductor relative to the electron-energy levels of the chemical species, which are distributed with a specified rearrangement energy.[2,3] Accordingly, the difference in the reaction rates of the oxidizing agents in Table 1 seems to be due to this factor. No detailed discussion of the difference in the reactivity could be done, however, since we have no data on the rearrangement energy of $\mathrm{MnO_4^-}$ and $\mathrm{Cr_2O_7^{2-}}$, which are reduced by three-step processes.

*Difference in the Behavior of the Cathodic Polarization Curves between Photo-electrochemical Cells and Photocatalytic Reactions.* It can be noticed by comparing Figs. 1 and 4 that the main difference lies in the cathodic polarization behavior of the oxidizing agents.

The cathodic curves on the rutile electrode given in Fig. 4 commenced at almost the same potential of 0.1 V *vs.* SCE. This means that the overpotential was different depending on the kind of oxidizing agent. In the case of a semiconductor electrode, an externally applied potential causes a change in the band bending in the semiconductor.[1-3] When the semiconductor electrode is polarized at potentials anodic to $E_{\mathrm{fb}}$, the bands bend up toward the surface.[1-3] Consequently, the cathodic current should be controlled by this energy barrier, and it shoud eventually be independent of the redox-potentials of the oxidizing agents used as long as the cathodic process is affected only by the electron density at the semiconductor surface. The validity of this view has already been reported in connection with ZnO.[25] In that case, the potential barrier to bringing the cathodic current flow of an order of 0.1 $\mu\mathrm{A/cm^2}$ was 0.6 eV at most.[25] Therefore, the cathodic polarization curves in Fig. 4 are judged to be reasonable, since the $E_{\mathrm{fb}}$ values of rutile in 0.5 mol dm$^{-3}$ $\mathrm{H_2SO_4}$ has been reported to be $-0.1$ V *vs.* SCE.[26]

On the other hand, the polarization of the rutile electrode at a potential cathodic to $E_{\mathrm{fb}}$ causes an energy barrier for the positive holes reaching the electrode surface in the same manner as electrons for the anodic process.[1-3]

When both electrons and positive holes transfer from the electrode to the chemical species in the solution, as is the case in the present photocatalytic reaction, the flat-band condition will be feasible for the transfer of both carriers. The potential where the reaction proceeds reflects this situation and is located around $E_{\mathrm{fb}}$, as Fig. 4 shows. Under these conditions, the quantum yield of the reaction should be quite low, since electron-hole recombination predominates,[19,27,28] and the reaction rate is low, as is shown in Fig. 4. Therefore, it can be confirmed in the present study that a good utilization of light energy can not be expected for a photocatalyst where both bands participate in the reaction.

In the case of photo-electrochemical cells using the illuminated rutile anode and metal cathode, it is necessary to take the energy barrier into consideration only for positive holes in the anode. When the energy bands bend up enough to accelerate positive holes effectively to the semiconductor surface, a larger reaction rate can be expected than that of the photocatalytic reaction.

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