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Hole Transfer Rates at Illuminated α-Fe_2O_3 Electrodes. Rate Declining in Highly Exothermic Reactions and Hole Transfer via Surface States

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Deactivation of photogenerated holes was effectively suppressed on thin film α-Fe_2O_3 photoanodes with reducing agents having E^0_{redox} of ca. 0.4 V vs. NHE. This suggested that the reaction rate decreases in highly exothermic reactions and that the hole transfer takes place via surface states.

A number of studies have been carried out so far on reaction kinetics of interfacial charge transfer at illuminated semiconductor electrodes. However, measurements of the interfacial reaction rates seem not satisfactory.[1)] This is mainly because transient behavior of photopotential and photocurrents associated with pulsed and/or step illumination are usually governed by the charge transport in the semiconductor electrode and not by the charge transfer across the interface.[2)] This difficulty can be partly avoided by using special reactions (e.g., current doubling reactions)[3)] or by employing competition reactions.[4-7)] For instance, Frese recently suggested that stabilization efficiency shows the Marcus-Gerischer reactivity pattern[8)] on n-CdSe by using iron-based complexes.[7)] We discuss here a competition between deactivation of the photogenerated holes and the interfacial hole transfer at polycrystalline α-Fe_2O_3[9)] using a set of reducing agents to see a relation between the hole transfer rates and electron acceptor levels in solution.

A thin film α-Fe_2O_3 was deposited onto SnO_2-coated glass by the spray pyrolysis method.[2)] The thin film electrode was attached to an electrochemical cell as a window (surface area 3 cm^2) and was irradiated from the glass side.[2)] A platinum wire served as a counter electrode, and a reference electrode (Ag/AgCl) was connected to the cell with an agar bridge. The light source used was an Ar-ion laser (wavelength 488 nm); the laser beam was chopped with an acousto-optic modulator. The transient behavior of the photocurrents was monitored with a potentiostat, and was recorded using a transient memory. The solution was continuously stirred with a magnetic stirrer. The aqueous solution used contained 0.1 mol/dm^3 of Na_2SO_4 as a supporting electrolyte and one of the following reducing agents; $Na_2S_2O_3$, Na_2SO_3, $K_4Fe(CN)_6$, hydroquinone (H_2Q), KI, KBr, and KCl. These reagents were used because they were employed in Refs. 4-6.

The photocurrent started to flow at rather positive electrode potentials (ca.

0.5 V vs. Ag/AgCl in the absence of reducing agents), and a dark current flowed at E>1.1 V vs. Ag/AgCl. This shows that the polycrystalline film Fe_2O_3 electrode contains a lot of defects.[2,9] Figure 1 shows transient behavior of photocurrents in the presence of H_2Q with different concentrations. The photocurrent immediately appeared when the irradiation started, and quickly decreased from the initial value (j_i) to a steady state value (j_s). In addition, a spike-like cathodic dark current was observed when the irradiation was interrupted. These transient photocurrents have been attributed to the recombination between the photogenerated holes located at the electrode surface and the electrons in the conduction band.[9]

The ratio j_s/j_i represents how extensively the charge recombination is suppressed. Figure 2 shows the values of j_s/j_i as a function of standard redox potential (E^0_{redox}) of the reducing agents at different electrode potentials. The concentration of the reducing agents was 10^{-2} mol/dm^3. It is apparent that j_s/j_i takes a large values for reducing agents having E^0_{redox} of ca. 0.4 V vs. NHE, and that the plots show a definite decrease in j_s/j_i at E^0_{redox}<0.3 V vs. NHE. Similar results have been obtained by our group and others for competition reactions on CdS (peak position is < 0 V vs. NHE),[4] on ZnO (peak at ca. 0.6 V vs. NHE),[5] on TiO_2 (peak at ca. 0.6 V vs. NHE),[6] and on CdSe (peak at ca. -0.25 V vs. NHE).[7] Note that CdS, ZnO, TiO_2, and Fe_2O_3 gave different peak positions although the same reducing agents were used.

We can calculate ratios between the interfacial hole transfer rate (k_h) and the electron-hole recombination rate (k_r) from the data in Fig. 2 using the following relations.[9]

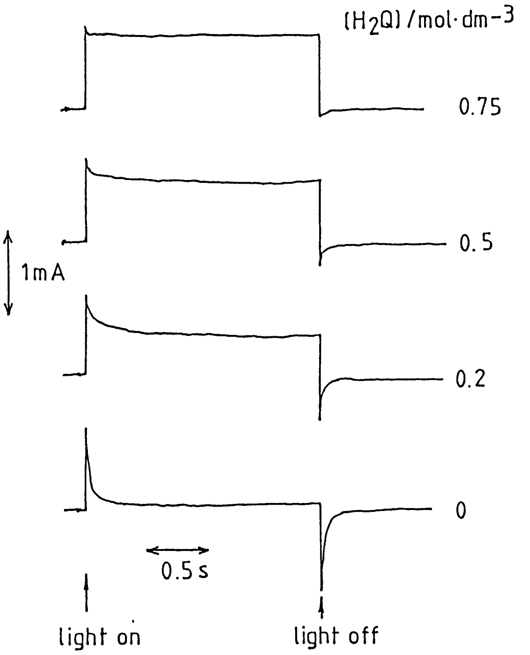


Fig. 1.
Transient behavior of photocurrents in the presence of H2Q with different concentrations. E=1.0 V vs. Ag/AgCl.

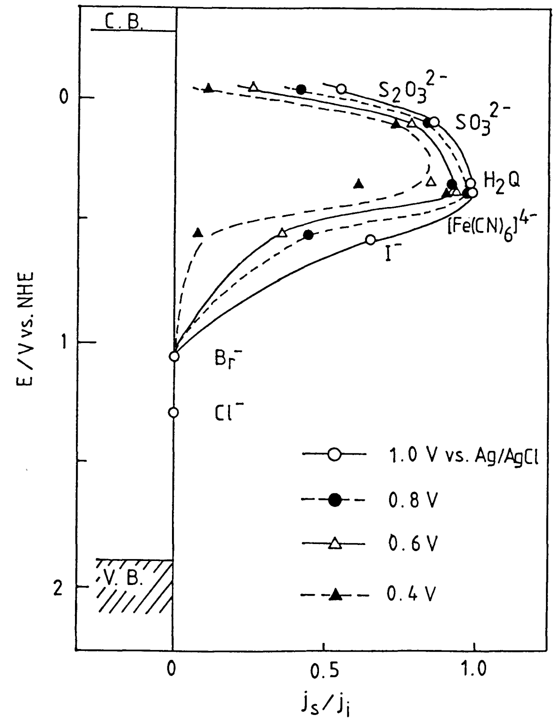


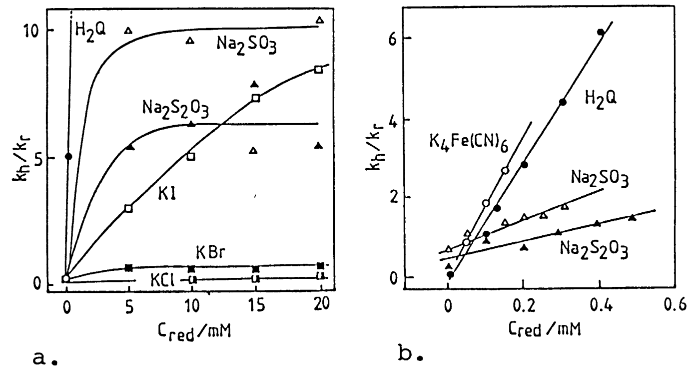
Fig. 2.
The values of j_s/j_i as a function of standard redox potential of the reducing agents at different electrode potentials.

$$k_h/k_r = j_s \;/\; (j_i - j_s) \qquad (1)$$

$$k_h = k_s C_{red} + k_w \qquad (2)$$

Here, k_s denotes a rate constant of the reaction between the holes and a reducing agent, and k_w a reaction rate for water. It should be noted that k_r is a function of the electrode potential, and is not affected by the addition of the reducing agents. The values of k_h/k_r are plotted against C_{red} in Fig. 3. Slopes of these plots should correspond to k_s/k_r according to Eqs. 1 and 2. The values of k_s/k_r thus obtained from Fig. 3b are shown in Fig. 5 as a function of E^0_{redox}. In addition, we have found that k_h/k_r is proportional to C_{red} only for small C_{red}'s. This is presumably due to adsorption of the electroactive species onto the Fe_2O_3 surface. In fact, the dark currents observed at E>1.1 V vs. Ag/AgCl showed saturation behavior as shown in Fig. 4. This is markedkly different from the behavior of dark currents at SnO_2 electrodes, where currents were linear to C_{red} up to $C_{red} = 2\text{x}10^{-2}$ mol/dm^3 for all the reagent tested here. We should therefore use an adsorbed amount of the reducing agent C^s_{red} instead of C_{red} to obtain k_s/k_r. Since it was difficult to obtain absolute values of C^s_{red}, we employed the values of the dark currents at higher C_{red}'s in Fig. 4 considering that the dark current at large overpotential is a measure of C^s_{red} for the adsorbed species. Thus, values of k_s/k_r can be obtained in an arbitrary unit. Also this result is shown in Fig. 5. The qualitative feature did not change after the correction based on C^s_{red}; that is, the peak is considerably sharp and takes a maximum value at ca. 0.4 V vs. NHE.

The present result most likely shows that the hole transfer reaction at the illuminated Fe_2O_3 electrodes follows the Marcus-Gerischer reactivity pattern[8] or similar relations proposed for "abnormal region" reactions;[10] both the theories[8,11] predicted the rate declining in highly exothermic reactions. A poss-



a. b.

Fig. 3.
The ratiobetween the interfacial hole transfer rate (k_h) and the electron-hole recombination rate (k_r) plotted against Cred.
a: high [C_{red}], b: low [C_{red}].

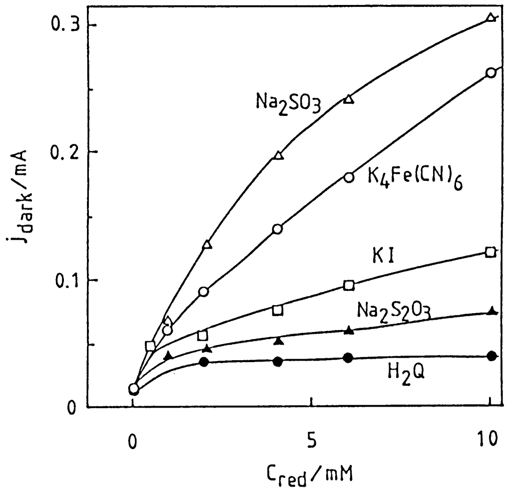


Fig. 4.
Dark currents monitored at 1.1 V vs. Ag/AgCl for different reducing agents.

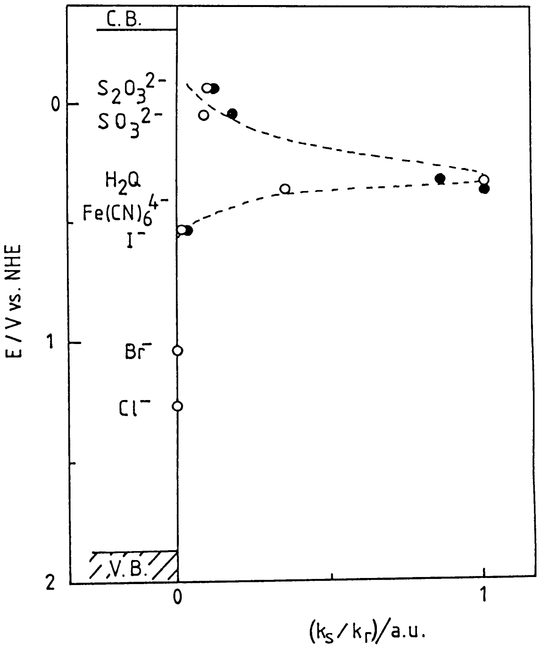


Fig. 5.
Hole transfer rates k_s plotted against E^0_{redox}. ●:k_s based on C_{red} in bulk, ○:k_s based on C^s_{red}.

ible contribution of vibrational excited states proposed in Ref. 10 is interesting, but the number of the reducing agents tested is not sufficiently large in the present study and in the experiments of Refs. 4-7. A further investigation is needed for detailed understanding of this type of reactions.

Moreover, it should be noted that the peak in Fig. 5 is ca. 1.5 V negative from the valence band edge of Fe_2O_3. This probably means that the holes relax to surface states prior to the reaction with reducing agents because the value 1.5 eV is large enough in comparison with a typical value of reorganization energy, e.g., 0.72 eV for $Fe(CN)^{3-/4-}$ couple.[7)] This is in contrast with the conclusion of Pajkossy, who suggested that hole transfer takes place directly from the valence band of Fe_2O_3.[9)] However, his analysis was incomplete since not all possible paths were taken into account. In fact, his results can be explained by considering two kinds of surface states. The detail will be presented elsewhere. As a summary, the present technique can provide good information on the reaction dinamics at photoelectrodes although the choice of the reducing agent tested is not sufficient at this stage.

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