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# Mechanism of the Current Doubling Effect. I. The ZnO Photoanode in Aqueous Solution of Sodium Formate

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Current doubling mechanism of the photoanodic reaction of sodium formate at the ZnO electrode is re-examined. Quantitative analysis of the reaction products revealed that ZnO electrode corroded during the current doubling reaction, which has not been previously reported. However, zinc ions were formed with about 50% of current efficiency. Carbon dioxide, instead of oxygen, was formed during the reaction. These experimental observations strongly suggested mechanism proposed by earlier workers were incorrect. A new mechanism is proposed.

The anodic photoreaction of a ZnO electrode in an inert electrolyte solution is known[1,2] as a dissolution reaction ($ZnO+2p^+ \rightarrow Zn^{2+}+1/2O_2$), in which the current efficiencies of $Zn^{2+}$ dissolution and oxygen evolution are each 100%.

However, when formic acid, aldehydes or alcohols are added to the electrolyte solution, Morrison *et al.*[3-6] found that the anodic photocurrent of a ZnO single crystal doubled, and they proposed a current doubling mechanism. Subsequently, similar effects were reported on other semiconductor electrodes. Gerischer *et al.* observed[7,8] current doubling behavior on a single crystal CdS electrode when aldehydes or alcohols were added to the electrolyte. Tamura *et al.*[9,10] found that the photooxidation current for a $TiO_2$ single crystal electrode increased with the addition of alcohols. Bard *et al.*[11-15] studied the oxidation of acetate ions, both on an irradiated $TiO_2$ electrode and on $TiO_2$ powders, and they named the reaction the Photo-Kolbe Reaction. Using irradiated p-type GaP electrode, Memming showed[16,17] that $S_2O_8{}^{2-}$, $H_2O_2$, or *p*-benzoquinone were current-doubling agents under cathodic polarization.

According to the mechanism proposed by Morrison *et al.*,[3-6] holes formed by photoirradiation of an n-type semiconductor react with a current doubling agent R to give $R^+$, which then donates an electron to the conduction band and becomes $R^{2+}$. In this case, the dissolution reaction of ZnO is suppressed.

However, our preliminary study[18] with the ZnO electrode shows that while typical current doubling agents such as formate ion or ethyl alcohol made the photoanodic current increase, oxygen evolution could not be observed and zinc ions were detected in the electrolyte solution after photoelectrolysis. The quantity of zinc ions dissolved was almost equivalent to the quantity of holes flowing to the ZnO surface. These facts indicate that the current doubling effect may not always follow Morrison's mechanism.

In this paper we re-examine the mechanism of current doubling. Using a polycrystalline ZnO electrode and $HCOO^-$ as the current doubling agent, we present quantitative data on the magnitude of photocurrent, the amount of zinc ions dissolved, and the amount of oxygen and $CO_2$ formed.

## Experimental

*Polycrystalline ZnO Electrode.* A polycrystalline ZnO pellet was made by pressing the powder (reagent grade) with a pressure of 0.5 t/cm$^2$ and then heating it for 3 h at 1300 °C in air.[19] Its diameter was 17 mm and the thickness about 2 mm. After an ohmic contact was made with an In-Ga alloy, a lead wire was connected with Silver Epoxy, and then all surfaces except one were covered with an epoxy resin.

*Electrochemical Reaction on Illuminated Polycrystalline ZnO Electrode.* Current-potential and photocurrent-time behavior of the ZnO electrode were measured with a potentiostat (Nikko Keisoku NPG 301), with a saturated calomel electrode as the reference electrode and platinum as the counter electrode. Irradiation was carried out with the light from a 500 W high pressure mercury lamp with a quartz lens and a filter (Toshiba Kasei UVD2) to pass wavelengths around 360±30 nm. The electrolyte contained $Na_2SO_4$ or $KNO_3$, and HCOONa was employed as a current doubling agent. A potassium nitrate agar salt bridge separated the cell compartments containing the ZnO and the Pt electrodes. All chemicals. were reagent grade. The experimental setup is shown in Fig. 1.

To elucidate the reaction mechanism, quantitative analyses of the products ($Zn^{2+}$, $O_2$, $H_2O_2$, and $CO_2$), which could be predicted by the photoanodic reactions on the ZnO electrode, were carried out, as follows: $Zn^{2+}$ ions, which were formed as the result of photoanodic reaction of ZnO electrode, were quantitatively analysed photometrically[20] using the absorp-

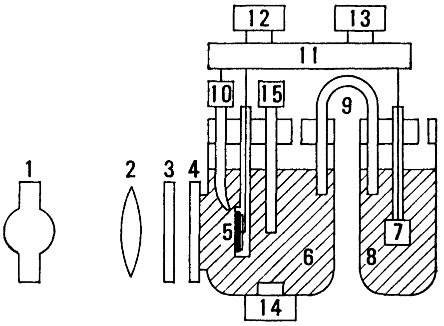

Fig. 1. Experimental setup.
1: 500W high pressure Hg lamp, 2: lens, 3: filter, 4: optical window, 5: sintered ZnO electrode, 6: electrolyte, 7: Pt electrode, 8: electrolyte, 9: salt bridge, 10: SCE, 11: potentiostat, 12: potential sweeper, 13: recorder, 14: stirrer, 15: $O_2$ detector.

tion peak ($\lambda$=570 nm) of complex between $Zn^{2+}$ and Xylenol Orange at pH 6.0. The amount of dissolved oxygen was measured with an oxygen meter (Ishikawa Seisakusho DG) and a gas-chromatography (Ohkura Denki). The amount of $CO_2$ formed after photoelectrolysis was determined by making the electrolyte solution pH 12 with highly purified NaOH, then adding an aqueous $BaCl_2$ solution, and finally weighing the $BaCO_3$. For this measurement we used $KNO_3$ as the electrolyte. Hydrogen peroxide was quantitatively analyzed with permanganate.[21]

## Results

The current-potential curves obtained using a polycrystalline ZnO electrode were almost the same as those obtained previously using a single crystal ZnO, as shown in Fig. 2. With addition of formate ions to the supporting electrolyte solution, a saturated photoanodic current increased.

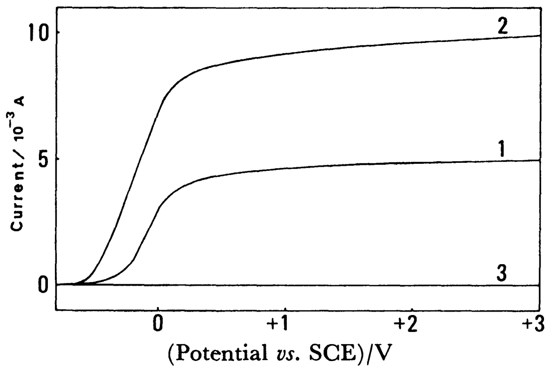

Fig. 2. The current-potential curves of a polycrystalline photoanode.
1: 0.4 M $KNO_3$, 2: 0.4 M HCOONa+0.4 M $KNO_3$ (1 M=1 mol $dm^{-3}$), 3: in dark.

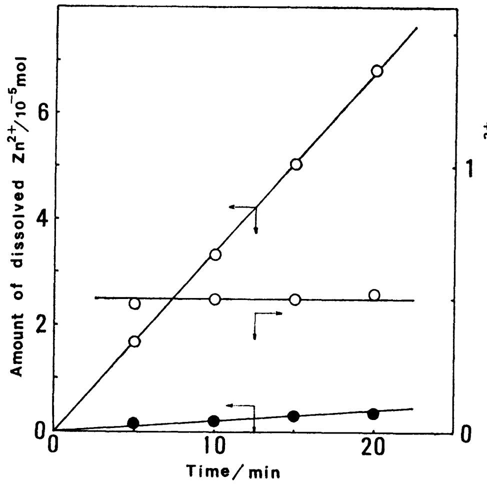

Fig. 3. Amounts of dissolved $Zn^{2+}$ and current efficiency of $Zn^{2+}$ against time.
Electrolyte solution: 0.4 M HCOONa +0.4 M $KNO_3$, ●: in dark, ○: under irradiation (density of photocurrent: 17.5 mA $cm^{-2}$).

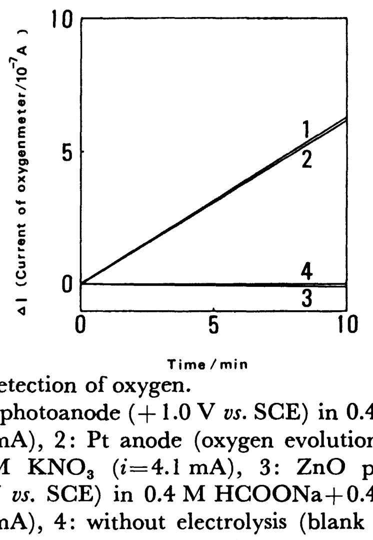

Fig. 4. Detection of oxygen.
1: ZnO photoanode (+1.0 V *vs.* SCE) in 0.4 M $KNO_3$ ($i$=4.1 mA), 2: Pt anode (oxygen evolution reaction) in 0.4 M $KNO_3$ ($i$=4.1 mA), 3: ZnO photoanode (+1.0 V *vs.* SCE) in 0.4 M HCOONa+0.4 M $KNO_3$ ($i$=7.8 mA), 4: without electrolysis (blank test; $i$=0) $\Delta I$ is in proportion to the dissolved oxygen.

Table 1 shows the results of photocurrent densities, current efficiencies of $Zn^{2+}$, oxygen, $H_2O_2$, and $CO_2$ formation. With addition of HCOONa, photocurrent increased up to almost twice. However, the amounts of dissolved $Zn^{2+}$ were almost the same, that was, the current efficiencies of dissolution of $Zn^{2+}$ were the half. Figure 3 shows amounts of dissolved $Zn^{2+}$ and current efficiencies of $Zn^{2+}$ against time. At any irradiation time current efficiencies were almost the half. This indicates that $Zn^{2+}$ ions were dissolved in the equivalent quantity of the numbers of the holes formed in the valence band by the light excitation. It means that under irradiation of the constant intensity of light, the rates of dissolution of $Zn^{2+}$ were almost the same with

TABLE 1. QUANTITATIVE ANALYSES OF PRODUCTS ON A POLYCRYSTALLINE ZnO PHOTOANODE

| Reactants | Photocurrent density / mA $cm^{-2}$ | The amount of $Zn^{2+}$ ions dissolved in 150 ml anolyte for 10 min / $10^{-5}$ M | Current efficiencies | | | | |
|---|---|---|---|---|---|---|---|
| | | | $Zn_2^+$ | $O_2$[a] (1) | $O_2$[a] (2) | $H_2O_2$ | $CO_2$ |
| | 4.62 | 2.91 | 1.03 | 1.02 | 0.91 | 0.0 | 0.00 |
| 0.01 M HCOONa | 5.94 | 2.44 | 0.67 | | 0.67 | | 0.37 |
| 0.1 M HCOONa | 8.78 | 2.69 | 0.50 | 0.00 | 0.00 | 0.0 | 0.51 |
| 0.4 M HCOONa | 9.14 | 2.79 | 0.50 | 0.00 | 0.00 | | 0.55 |
| 0.4 M NaI | 3.42 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.00 |

Supporting electrolyte: 0.4 M $KNO_3$, Applied potential: + 1.0 V *vs.* SCE, Irradiation wavelength: 360±30 nm.
a) (1): By the oxygen meter, (2): by gas chromatography.

and without the presence of HCOONa, even photocurrent increased with it. On the other hand, with addition of concentrated HCOONa increase of oxygen was not observed, as shown in Table 1. The results of the quantitative analysis of dissolved oxygen versus time are shown in Fig. 4. The quantity of oxygen produced versus time upon irradiating the ZnO in 0.4 M $KNO_3$ and with a photocurrent $i=4.1\times10^{-3}$ A/cm$^2$ is shown in Curve 1. About the same oxygen versus time relationship was obtained without irradiation by substituting the ZnO electrode with a Pt electrode and with an oxidation current of $4.1\times10^{-3}$ A/cm$^2$ (Curve 2). The latter conditions correspond to electrolysis of water. With the addition of HCOONa the photocurrent increased, and at a high enough concentration ($>10^{-2}$ M) the photocurrent was almost double the value obtained with the inert electrolyte alone. This addition of HCOONa decreased the rate of oxygen during photolysis to essentially zero as shown in Curve 3. Finally, a blank run was made without electrolysis but with irradiation of the ZnO electrode in an electrolyte, with or without HCOONa, and the results show essentially a zero oxygen evolution rate (Curve 4).

Formation of $H_2O_2$, which was reported by Hauffe and Range[22] during the photooxidation of ZnO electrode, was not detected with and without HCOONa, as shown in Table 1.

The amount of the formation of $CO_2$ was almost the half compared with the charge flowed, but nearly close to that calculated by the charge based on the increased part of photocurrent in the presence of HCOONa.

As shown in the last column in Table 1, we analyzed the products when iodide ions were added to the electrolyte solution. The photocurrent decreased to less than the value only in the supporting electrolyte, because iodine formed absorbed light quanta. Both current efficiencies of $Zn^{2+}$ dissolved and $CO_2$ formation became to zero, and also increase of $O_2$ dissolved was not detected. The behavior can easily be understood[6] that holes formed in the valence band reacted preferentially with $I^-$ ions, resulting in suppression of dissolution ZnO.

## Discussion

According to Morrison's current doubling mechanism,[3-6] the holes formed by irradiation of a semiconductor react with $HCOO^-$, to give $H^{\cdot}$ and $CO_2$;

$$HCOO^- + p^+ \longrightarrow H^{\cdot} + CO_2. \qquad (1)$$

The $H^{\cdot}$ formed as an intermediate donates an electron to the conduction band:

$$H^{\cdot} \longrightarrow H^+ + e^-. \qquad (2)$$

Therefore, the net current doubling reaction is

$$HCOO^- + p^+ \longrightarrow H^+ + CO_2 + e^-. \qquad (3)$$

Recently, Harbour and Hair,[23] using the spin trapping technique, detected $COO^{\bar{\cdot}}$ as an intermediate of the photocatalytic reaction occurring on ZnO powder irradiated in an aqueous solution containing formate or oxalate ions. They proposed a new mechanism in which $COO^{\bar{\cdot}}$ donated an electron to the conduction band as follows,

$$HCOO^- + p^+ \longrightarrow H^+ + COO^{\bar{\cdot}} \qquad (4)$$

$$COO^{\bar{\cdot}} \longrightarrow CO_2 + e^-. \qquad (5)$$

In this case the net reaction is the same as Eq. 3.

The above mechanisms assume that ZnO is not photooxidized to $Zn^{2+}$. However, the results in Table 1 show that we observed $Zn^{2+}$ in the electrolyte solution after photoirradiation when the photocurrents was increased, even in the presence of $HCOO^-$. When $HCOO^-$ was present, the current efficiency of $Zn^{2+}$ formation was about 0.5, but the current efficiency would be almost 1.0 if we used the same value of photocurrent observed without $HCOO^-$ addition.

Can we explain these facts from the Morrison's mechanism? One possibility is that the $H^+$ formed by Eq. 3 reacts chemically with the ZnO,

$$ZnO + 2H^+ \longrightarrow Zn^{2+}(aq) + H_2O. \qquad (6)$$

However, it may be very difficult for $H^+$ formed on the ZnO surface to attack the ZnO lattice. In an alternative and more probable mechanism, an intermediate oxygen species, O*, which is assumed to be one of the intermediates of the simple dissolution reaction of ZnO, reacts with $HCOO^-$ to produce an active $^{\cdot}COO^-$ radical;

$$ZnO + 2p^+ \longrightarrow Zn^{2+} + O^* \qquad (7)$$

$$O^* + 2HCOO^- \longrightarrow 2COO^{\bar{\cdot}} + H_2O. \qquad (8)$$

Then, $COO^{\bar{\cdot}}$ can donate an electron to the conduction band, as in Eq. 5,

$$2COO^{\bar{\cdot}} \longrightarrow 2CO_2 + 2e^-. \qquad (9)$$

By combining Eqs. 7, 8, and 9 we obtain the net reaction,

$$\begin{aligned} &ZnO + 2p^+ + 2HCOO^- \\ &\qquad \longrightarrow Zn^{2+} + H_2O + 2CO_2 + 2e^-. \end{aligned} \qquad (10)$$

The experimental results shown in Table 1, *e.q.* the current efficiencies of the products $Zn^{2+}$, $O_2$, and $CO_2$, can be explained if Eq. 10 is valid for the current doubling effect. For example, with HCOONa present in solution, the current efficiencies for $Zn^{2+}$ and $CO_2$ are observed to be almost 0.5, in accordance with the stoichiometry of Eq. 10.

## Conclusion

Mechanism of current doubling reaction of formate ion was re-examined by using a polycrystalline ZnO photoanode. From the quantitative analyses of the products of the current doubling reaction, a new mechanism is proposed;

$$\begin{aligned} &ZnO + 2p^+ + 2HCOO^- \\ &\qquad \longrightarrow Zn^{2+} + H_2O + 2CO_2 + 2e^-. \end{aligned}$$

The ZnO electrode corrodes during the current doubling reaction.

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