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Photo-effects of Metal Oxide Electrode. I. Photoelectrochemical Processes on a Silver–Silver Oxide Electrode and the Influence of Ethylene Glycol

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The influence of light excitation on the anodic oxidation of a silver electrode in alkaline solutions has been studied. The experimental results have shown that, in addition to the formation of Ag(II) species by a reaction of Ag(I) species with photo-generated holes, illumination in the Ag_2O formation region causes the photogeneration of Ag(I) species at the metal/oxide interface. In the presence of ethylene glycol, the so-called current doubling phenomenon was found. This phenomenon has been interpreted in terms of a mechanism involving a catalytic reaction of the glycol with the photogenerated Ag(II) species, and not by a mechanism involving the oxidation of glycol by the photo-generated holes.

A silver–silver oxide electrode is very useful as a cathode in batteries with a high energy-to-mass ratio; hence, to date, the anodic behavior of silver in alkaline solutions has been extensively studied.[1)] Also, the use of silver–silver oxide electrode in organic synthesis has received considerable attention[2)] because silver oxides are known to react selectively with certain organic groups.[3)]

In recent years, some work has been done on the photoeffects of silver–silver oxide electrodes.[4–7)] Illumination definitely increases an anodic current in the Ag_2O formation region; the increment is generally accepted to be a photocurrent due to light absorption by an Ag_2O layer. There is, however, some disagreement concerning what kind of product is formed by light excitation. For example, Göhr and Breitenstein[4)] explained the production of the photocurrent by assuming a photo-decomposition of Ag_2O into oxygen and silver, which is reoxidized either to Ag_2O or directly to AgO, depending on the electrode potential adjusted, whereas Memming *et al.*[5)] suggested that light absorption by an Ag_2O layer leads to an anodic oxidation to AgO by the interaction of the photo-generated holes in the Ag_2O with Ag_2O. Perkins *et al.*[6)] proposed that, in addition to the oxidation of interstitial Ag^+ to Ag^{2+}, which acts as a catalytic center for AgO formation, illumination enhances the rate of the primary Ag^+-formation process at the metal/oxide interface, resulting in a substantial increase in the Ag_2O formation.

In order to obtain more information about the photoelectrochemical process in the anodic oxidation of silver in alkaline solutions, the present work was performed. Furthermore, the influence of ethylene glycol on the electrode process was examined. Ethylene glycol was selected because it has a relatively high reactivity for a reaction with AgO and is virtually inactive for Ag_2O.[8)]

Experimental

The working electrode was made from a wire of silver (purity> 99.99%) in the form of a disk (5 mm dia.) surrounded by a Teflon sheath. The reference electrode, against which all the potentials in the present paper are quoted, was Hg/HgO in 1 M KOH, and it was separated from the working electrode by a Luggin capillary. The electrolyte solutions were prepared from extra-pure-grade potassium hydroxide and water, twice distilled from deionized stock. Extra-pure-grade ethylene glycol was used without further purification.

The silver electrode was polished by means of a fine emery paper (number 0/8), cleaned in acetone and distilled water, and washed with a 1 M KOH solution. In addition, the electrode was subjected to the repeating of the potential cycle over the potential of from 0.0 to 0.8 V, with a sweep rate of 2.9 mV/s, in a 1 M KOH solution in the dark, using a potentiostat in conjunction with a linear sweep generator. After several cycles (in most cases, 6 times) the electrode was introduced into another cell filled with the solution to be studied, and then cyclic voltammograms were recorded on a x-y recorder. Simple H-shaped cells with a quartz window, which allowed the illumination of the working electrode, were used.

Coulomb-potential curves, which were measured simultaneously with the cyclic voltammograms, were displayed on a x-y recorder by means of a device constructed in our laboratory. From these curves, the amounts of charge for each peak were obtained.

In the experiments on the photo-effects, a 500 W Xenon arc lamp UXL-500D (Ushio Electric Inc.), which was enclosed in a lamp housing and powered by a dc power supply, was used as the light source. A fairly homogeneous and

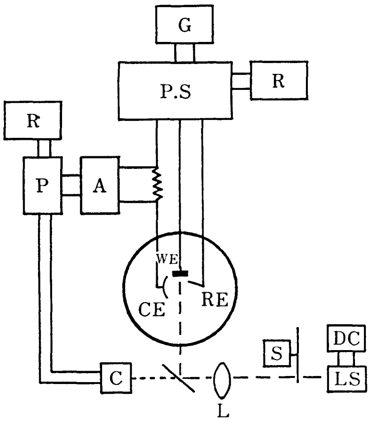

Fig. 1. Block diagram of experimental setup.
G: Function generator, PS: potentiostat, R: x-y recorder, P: prebox for a.c. Voltage measurement, A: differential amplifier, C: photo-cell, S: rotated sector, LS: Xenon lamp house, DC: d.c. power supply, L: lens, WE: working electrode, CE: counter electrode, RE: reference electrode.

horizontal beam was focussed on the working electrode by means of appropriate quartz lenses. For measuring photocurrents, as is shown in Fig. 1, the light was chopped with a rotated sector (35 Hz), and the resulting photocurrent was amplified and displayed on a x-y recorder, in which the dark current is eliminated. The procedure for the determination of the relative intensity of the light was described previously.[9]

The additional amount of silver oxides produced by illumination was determined as follows. Silver oxides formed under illumination in the Ag_2O formation region were dissolved into a 1 M ammonium acetate solution, and then the amount of silver ion in the solution was determined by means of atomic absorption spectrometry. The same measurements were carried out in the dark. The difference in the amount of silver ions between under illumination and in the dark was taken as equivalent to the amount of oxides produced by light excitation. The charges consumed during the formation of the silver oxides were measured by means of a Coulomb meter CLM-2A (Hokuto Denko Corp.). The composition of the oxides produced by light excitation was estimated on the basis of the data obtained above.

All measurements were carried out at ambient temperatures (25±2 °C). Oxygen was removed from solution by bubbling with nitrogen before every measurement.

Results and Discussion

Photo-effects on Oxidation to Silver Oxides in 1 M KOH. A potentiodynamic voltammogram for a silver electrode in an alkaline solution exhibits two major anodic and two major cathodic peaks corresponding to the formation and reduction of Ag_2O and AgO. A typical voltammogram run in 1 M KOH with the sweep rate of 2.9 mV/s is shown in Fig. 2, which also illustrates the effect of light during one cyclic sweep. Figure 2 definitely shows that, in addition to the increase in the magnitude of all the peaks, illumination causes the threshold potential for the commencement of AgO formation to shift to a more negative potential. This potential shift may be interpreted in terms of an overvoltage effect in the formation of AgO as well as in terms of the explanation by Parkins *et al.*;[6] *i. e.*, the overvoltage for the AgO formation is reduced by the Ag(II) species generated photoelectrochemically in the Ag_2O formation region, so that the cathodic shift occurs. The existence of such photo-generated Ag(II) species may be easily proved, as will be shown later.

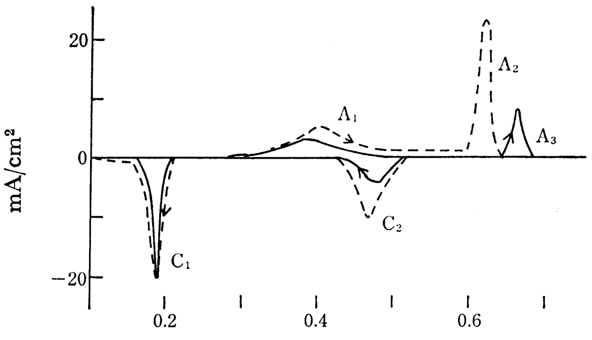

Fig. 2. Potentiodynamic current/potential profile for formation and reduction of oxides at a silver electrode in 1 M KOH. Sweep rate: 2.9 mV/s, ——: in the dark, ----: under illumination.

The potential dependence of a photocurrent was examined by using the chopped light described in a previous section. The general shape of the photocurrent-potential curve for 1 M KOH was the same as that reported by Memming *et al.*[5] The influence of the light intensity on the photocurrent is demonstrated in Fig. 3-a. Figure 3-b presents the ordinary current-potential curve measured simultaneously with Curve A in Fig. 3-a. In spite of the fact that both Ag_2O and AgO films exhibit *n*-type semiconducting behavior,[10] the anodic photocurrent arose only over the range of potentials at which the Ag_2O film exists, but did not appear at more positive potentials than the end of the AgO formation region. The maximum anodic photocurrent increased linearly with the light intensity of the illumination. In the cathodic direction of the potential sweep, photocurrents of different signs were observed in the region between the reduction peaks of AgO and Ag_2O. Such cathodic photocurrents have been examined in detail by Perkins *et al.*[6]

The charges consumed for each peak in Fig. 2 are presented in Table 1. It was found that the ratio of the total cathodic charge to the total anodic one was substantially unity, even under the illumination, indicating that the dissolution of reaction products into the alkaline solution may be neglected during one cycle of the potential. Furthermore, as can be seen from Table 1, the charge for the A_1 peak was increased by

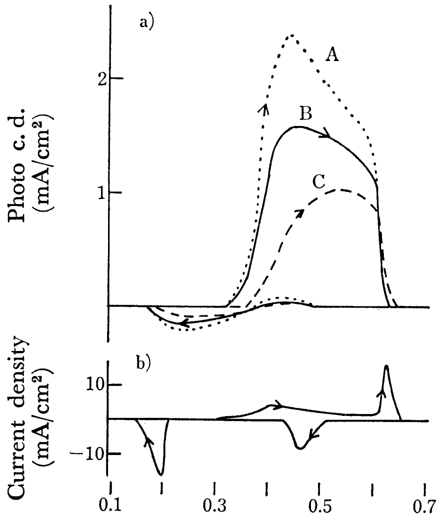

Fig. 3. (a) Photocurrent *vs.* electrode potential for a silver electrode in 1 M KOH (Dark current is eliminated). (b) Current *vs.* electrode potential measured simultaniously with the curve A in (a). Sweep rate: 2.9 mV/s, A, B, and C: light intensity of 110, 64.7, and 32.8 (a.u.), respectively.

Table 1. The amount of charge for each peak in Fig. 1 (mC/cm²)

	A_1	A_2	A_3	C_2	C_1	Total anodic charge	Total cathodic charge
Dark	103	67	0	47	125	170	168
Light	178	128	6	123	186	312	309

about 70% by the illumination, and the charge for A_2 peak under the illumination was larger by about 20% than the charge for the A_1 peak in the dark. From these facts it is clear that, in addition to the formation of Ag(II) species, illumination in the Ag_2O formation region causes a substantial increase in the formation of Ag(I) species at the metal/oxide interface. Therefore, the anodic photocurrent must be due to the photo-generation of both Ag(I) and Ag(II) species.

Composition of Photo-generated Products. In order to determine whether the photo-generated species in the Ag_2O formation region is mainly the Ag(I) or the Ag(II) species, the increment in silver species upon illumination and the corresponding charge were determined as follows. The pretreated electrode was subjected to the potential sweep from 0.0 to 0.575 V at the sweep rate of 2.9 mV/s under illumination. Immediately after the circuit had been opened, the electrode was taken out from the cell and then dipped in a 1 M ammonium acetate solution to remove from the silver substrate the silver oxides which were produced during the potential sweep. The analysis of the silver species in the acetate solution was made by atomic absorption spectrometry. The potential of 0.575 V corresponds to a less positive potential than that at which the electrochemical formation of AgO begins to appear. The anodic charge consumed during this potential sweep was simultaneously determined by means of a Coulomb meter. Blank runs in the dark were carried out as well. The results thus obtained are presented in Table 2. It was found that the illumination during the anodic sweep (0.0—0.575 V) causes the amount of silver ions to increase considerably, as well as the anodic charge. The current efficiency[11] for the additional amount of silver oxides formed by the illumination was 61%. If the photo-associated reaction were only the formation of Ag(II) species from Ag(I) species, the current efficiency for the additional amount of silver oxides would be zero. On the other hand, if only the formation of Ag(I) species from the silver substrate had arisen, the current efficiency of 100% would be obtained. No such results were obtained in this experiment. Accordingly, these experimental results also indicate that the photo-generated species are both Ag(I) and Ag(II) species.

The Ag(II)/Ag(I) ratio on the silver oxides produced only by the light excitation was estimated to be 1.8. This value was calculated on the basis of the current efficiency of 61% and by assuming that the anodic photocurrent arises according the following scheme:

$$\mathrm{Ag/Ag_2O} \xrightarrow{h\nu} \mathrm{Ag(I)/Ag_2O} + \mathrm{e}, \qquad (1)$$

$$\mathrm{Ag(I)\ and\ Ag_2O} \xrightarrow{h\nu} \mathrm{Ag(II)\ species} + \mathrm{e}. \qquad (2)$$

That is,

$$E_{\mathrm{eff}} = \frac{q_1}{q_1+q_2}\cdot 100. \qquad (3)$$

In the case of $E_{\mathrm{eff}} > 50\%$

$$\frac{\mathrm{Ag(II)}}{\mathrm{Ag(I)}} = \frac{q_2}{q_1-q_2}. \qquad (4)$$

From Eqs. 3 and 4, we obtain

$$\frac{\mathrm{Ag(II)}}{\mathrm{Ag(I)}} = \frac{100-E_{\mathrm{eff}}}{2E_{\mathrm{eff}}-100} = 1.8,$$

where q_1 and q_2 are the charges consumed in Eqs. 1 and 2 respectively.

TABLE 2. THE COMPOSITION OF SILVER OXIDES PRODUCED BY LIGHT EXCITATION DURING THE ANODIC POTENTIAL SWEEP FROM 0.0 TO 0.575 V

	Q_a[a] (mC/cm²)	M_{Ag}[b] (10^{-3}mmol/cm²)	Current efficiency (%)	Ag(II)/Ag(I) ratio
Dark	103	1.06	99	
Light	176	1.52	83	
Difference between light and dark	73	0.46	61[c]	1.8

a) Q_a: the charge consumed during the anodic sweep. b) M_{Ag}: the amount of silver ion, determined by means of atomic absorption spectrometry. c) See Ref. 11.

From Table 1 and 2, it is clear that illumination causes the efficiency for the conversion of Ag_2O and AgO to increase. That is, the conversion was about 65% in the dark, whereas under illumination it was estimated to be almost 100%.[12] One may easily understand such a photo-effect by assuming that the photo-generated Ag(II) species, which act as nuclei for the AgO formation, exist widely within the Ag_2O film.

In further experiments, the effect of the time interval of illumination on the composition of the silver oxides was examined by the above method except for the procedures of illumination and polarization. An Ag_2O film was produced by the anodic potential sweep from 0.0 to 0.5 V (sweep rate, 2.9 mV/s), and then the electrode potential was stepped up to 0.45 V, at which no AgO is electrochemically formed. After the current had decreased to a very low value, the electrode was illuminated for a given period. Immediately afterward, the electrode was taken out from the cell and was worked up according to the above procedure. The charges consumed before and during illumination were measured by means of a Coulomb meter at the same time. In addition, the charges necessary for the reduction of the silver oxides formed under the above conditions were separately determined by sweeping back

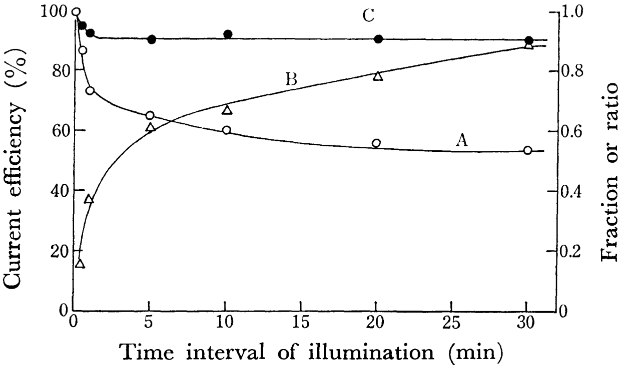

Fig. 4. Effect of illumination time on the current efficiency (curve A), the fraction of Ag(II) in the oxides (curve B), and the ratio of cathodic charge to anodic charge (curve C) about the silver oxides produced by illumination.

from 0.45 to −0.1 V as soon as the light was extinguished. Figure 4 illustrates the effect of the illumination time on the current efficiency for the photo-generated oxides (Curve A), on the fraction[13] of Ag(II) in the oxides (Curve B), and the ratio of the anodic charge consumed only during the illumination and the cathodic charge necessary for the reduction of the photo-generated oxides (Curve C). The current efficiency and the fraction of Ag(II) species varied, as is shown in Fig. 4, as the time interval of illumination increased. That is, the ratio of Ag(II)/Ag(I) increased with an increase in the time interval of illumination. On the other hand, the anodic charges, increased by the light excitation, were always somewhat larger than the corresponding cathodic charges. This fact indicates that only a small part of the anodic photocurrent was used for the photo-decomposition of Ag_2O into silver and oxygen. Therefore, the photo-decomposition of Ag_2O postulated by Göhr *et al.*[4] is not considered to be the main origin of the photocurrent.

If the photo-generation of Ag(II) species is due only to the photoelectrochemical oxidation of interstitial Ag^+, as was proposed by Perkins *et al.*,[6] or if the anodic photocurrent is due only to the formation of AgO, as was reported by Memming *et al.*,[5] the results obtained in the present experiments can not be interpreted. Our conclusion is that the anodic photocurrents are due to the formation of both Ag(I) and Ag(II) species according to Eqs. 1 and 2. In addition, it must be noted that a small part of the anodic photocurrent is used for the evolution of oxygen.

Influence of Ethylene Glycol on the Photo-effects. Figure 5 shows the influence of ethylene glycol on the photocurrent during a cyclic potential sweep of silver in 1 M KOH. The addition of the glycol to the base electrolyte caused the anodic photocurrent to increase considerably. The relation between the photocurrent and the glycol concentration is presented in Fig. 6 as plots of i_p/i_a *vs.* log C, where i_p and i_a imply the maximum photocurrent (peak value) in the presence and absence of the glycol respectively, and C, the bulk concentration of the glycol. The value of i_p/i_a increased with an increase in the glycol concentration and reached a factor of two. Such a current doubling phenomenon had previously been found at a zinc oxide single-crystal electrode by Morrison and Freund.[14] They interpreted it by means of the following two-step mechanism:

$$R + h^+ \longrightarrow R^+, \tag{5}$$

$$R^+ \xrightarrow{\qquad} R^{2+} + e, \tag{6}$$

where h^+ is a photo-generated hole in the crystal; R, a current-doubling agent; R^+, a radical-type species, and e, an electron. However, it seems that current-doubling phenomenon in the silver oxide electrode system can not be interpreted by the mechanism indicated above, but rather by a alternative mechanism, as will be shown below.

Figure 7 shows typical voltammograms for the silver electrode in a 1 M KOH solution containing 0.2 M ethylene glycol in the dark and under illumination. In the presence of glycol, a specific anodic peak (Peak A_4) was observed between the AgO formation and its reduction peaks under a cathodic sweep. The values in both cases, light and dark, increased linearly with an increase in the glycol concentration. The illumination increased the peak value. The appearance of such a peak can be explained by the catalytic mechanism proposed by Sasaki and Toshima,[15] in which a reaction of alcohols with AgO leads to the formation of Ag_2O (or Ag), which is then electrochemically oxidized to AgO. The question arises, however, of why such a catalytic reaction does not easily occur in the AgO formation region under an anodic sweep. This question might be answered by assuming the competitive adsorption of glycol and OH^-; *i.e.*, with an increase in the anode potential, the surface concentration of glycol decreases, whereas that of OH increases.

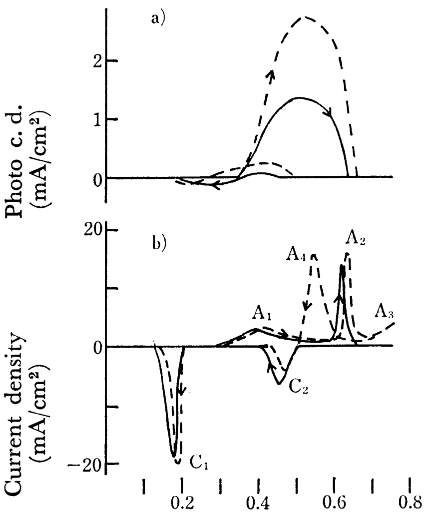

Fig. 5. (a) Influence of ethylene glycol on the photocurrent. (b) Current *vs.* electrode potential measured simultanously with the curve in (a). Sweep rate: 2.9 mV/s, ——: 1 M KOH, ----: 1 M KOH +0.2 M ethylene glycol.

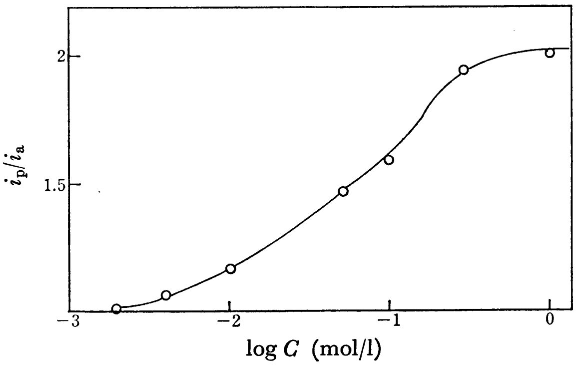

Fig. 6. Maxmum photocurrent *vs.* concentration of ethylene glycol. i_a and i_p: the maxmum photocurrent in the absence and presence of the glycol, respectively, C: the bulk concentration of the glycol.

As can be seen from a comparison of Figs. 2 and 7, the anodic current in the region (A_3) between the AgO formation peak and the oxygen evolution was increased by the addition of glycol, and it was further increased by the illumination. We have no idea, however, how to explain such an increase at the A_3 peak.

The amounts of charge for each peak in Fig. 7 are

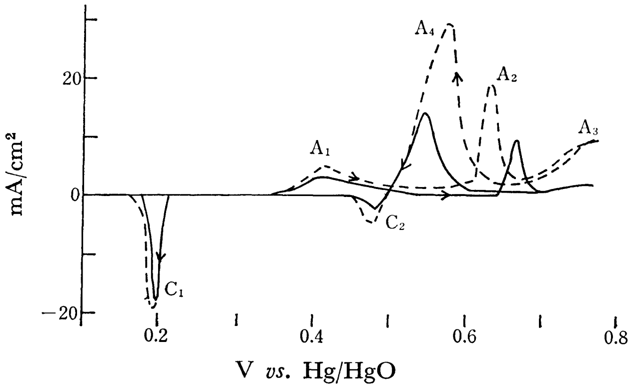

Fig. 7. Potentiodynamic voltammograms for a silver electrode in 1 M KOH +0.2 M ethylene glycol. ——: in the dark, ----: under illumination, sweep rate: 2.9 mV/s.

listed in Table 3. The illumination considerably increased the charges for all peaks. It should be noted that, in spite of the fact that the photocurrent does not arise in the region of either A_3 or A_4 as is shown in Fig. 5, the amounts of charge for these peaks (A_3 and A_4) increased remarkably under the illumination. The remarkable increase in the specific anodic current (A_4) by the illumination is considered to be due to an increase in the surface roughness of the electrode, although the variation in the roughness was not directly examined by means of a microscope. The increase in the surface roughness mainly occurs in the Ag_2O formation region. This idea came from such observations as: (i) When an upper limit of a potential cycle was set at the end of the A_2 peak, when the illumination was limited to the Ag_2O formation region, or when one cyclic voltammogram was run in the solution containing the glycol under illumination, and the next cyclic one was recorded in the dark, little change in the amount of charge for the A_4 peak was observed. (ii) In the presence of glycol, illumination rather decreased both the amount of silver oxides, which formed during the anodic sweep from 0.0 to 0.575 V, and the corresponding cathodic charge, although the anodic charge for the Ag_2O formation region was considerably increased by illumination.

If the anodic photocurrent observed in the present study had arisen according to a mechanism similar to that proposed by Morrison and Freund,[14] the increase in the surface roughness by the light excitation would not occur. Therefore, an alternative mechanism for the current-doubling phenomenon should be proposed in the case of the present electrode system. For example, the following catalytic mechanism are considered: (i) Ethylene glycol reacts with the photo-generated AgO to give a radical intermediate to inject an electron into the electrode. In this case, the AgO is reduced to Ag_2O, which is also oxidized to AgO according to Eq. 7; *i. e.*,

$$Ag_2O + h^+ \longrightarrow AgO, \quad (7)$$
$$AgO + Glycol \longrightarrow Ag_2O + Intermediate, \quad (8)$$
$$Intermediate \longrightarrow Aldehyde + e, \quad (9)$$

or (ii) similarly, the reaction of glycol with the AgO results in the formation of aldehyde and Ag, followed by the electrochemical reoxidation of the latter to Ag_2O, which is then oxidized by the photo-generated hole; *i. e.*,

$$Ag_2O + h^+ \longrightarrow AgO, \quad (7)$$
$$AgO + Glycol \longrightarrow Ag + Aldehyde, \quad (10)$$
$$Ag \longrightarrow Ag_2O + e. \quad (11)$$

Such chemical decomposition and photochemical reformation of AgO is repeated on the electrode surface, and this causes the surface roughness of the electrode to increase.

TABLE 3. THE AMOUNT OF CHARGE FOR EACH PEAK IN Fig. 7 (mC/cm²)

	A_1	A_2	A_3	A_4	C_2	C_1	Total anodic charge	Total cathodic charge
Dark	108	79	75	246	23	119	508	142
Light	223	175	451	619	35	129	1468	168

Consequently, the current-doubling phenomenon at the silver oxide electrode may be interpreted by either mechanism indicated above, and not by a mechanism involving a reaction of glycol with the photo-generated hole.

References

1) B. V. Tilak, R. S. Perkins, H. A. Kozlowska, and B. E. Conway, *Electrochim. Acta*, **17**, 1447 (1972), and references therein.

2) N. A. Hampson, J. B. Lee, and K. I. MacDonald, *Electrochim. Acta*, **17**, 921 (1972).

3) J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962).

4) H. Göhr and A. Breitenstein, *Electrochim. Acta*, **13**, 1377 (1968).

5) R. Memming, F. Mollers, and G. Neumann, *J. Electrochem. Soc.*, **117**, 451 (1970).

6) R. S. Perkins, B. V. Tilak, B. E. Conway, and H. A. Kozlowska, *Electrochim. Acta*, **17**, 1471 (1972).

7) V. I. Veselovsky, T. I. Borisova, A. A. Jakovleva, and S. O. Izidinov, *Electrochim. Acta*, **10**, 325 (1965).

8) S. Toshima, H. Sasaki, and K. Itaya, *Denki Kagaku*, **40**, 234 (1972).

9) T. Shimizu, A. Kunugi, and S. Nagaura, *Denki Kagaku*, **44**, 187 (1976).

10) M. J. Dignam, H. M. Barret, and G. D. Nagy, *Can. J. Chem.*, **47**, 4253 (1969).

11) The current efficiency, E_{eff} was defined by: $E_{eff} = (M_1 - M_D)F/(Q_L - Q_D) \cdot 100(\%)$, where M and Q are the amount (mol) of silver ion formed and the charge (coulomb) consumed during the anodic sweep (0.0−0.575 V) respectively; the subscripts L and D indicate under illumination and in the dark respectively, and F is Faraday's constant.

12) The additional charge for the A_1 peak by the illumination $= (Q_{A_1})_L - (Q_{A_1})_D = 178 - 103 = 75$ mC/cm², and the fraction of Ag(I) in the oxide produced by the illumination $= 1 - [Ag(II)/Ag(I)]/[Ag(II)/Ag(I) + 1] = 1 - 1.8/(1.8 + 1) = 0.36$. Therefore, the charge corresponding to the amount of Ag(I) species produced by illumination $= 75 \times 0.36 = 27$ mC/cm². Thus, the charge corresponding to the total amounts of Ag(I) species produced in the A_1 region $= 103 + 27 = 130$ mC/cm². Consequently, the electrochemical conversion of Ag(I) to Ag(II) $= (128/130) \times 100 = 98\%$.

13) The fraction of Ag(II) in the oxides $= [Ag(II)/Ag(I)]/[Ag(II)/Ag(I) + 1]$.

14) S. R. Morrison and T. Freund, *Electrochim. Acta*, **13**, 1343 (1968).

15) H. Sasaki and S. Toshima, *Electrochim. Acta*, **20**, 201 (1975).