Effect of Oxidation Temperature on Photo-catalytic Properties of Stainless Steel Coated by Copper Oxide

Motoaki MORITA,^{1)*} Kengo KISHIHARA,¹⁾ Shinichi MOTODA,¹⁾ Norimitsu KOGA²⁾ and Tadashi SHINOHARA³⁾

1) Tokyo University of Marine Science and Technology, 2-1-6 Etchujima, Koto-Ku, Tokyo, 135-8533 Japan.

2) Yokohama National University, 79-5 Tokiwadai, Hodogaya-Ku, Yokohama, 240-8501 Japan.

3) National Institute for Materials Science, 1-2-1 Sengen, Tsukuba-shi, Ibaraki, 305-0047 Japan.

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Copper oxide (Cu-oxide) electrodes were produced by the vacuum deposition of pure copper on a stainless steel substrate, followed by oxidation in air between 150 and 550°C. The potentials and durability of the Cu-oxide electrodes under xenon light irradiation were evaluated, and the effects of the microstructure on the electrode performance were discussed. The photocatalytic effect of a p-type semiconductor in a Cu-oxide electrode was confirmed for all treatment temperatures. Electrodes oxidized at 150°C showed a very weak photocatalytic effect because the main phase of the thin film comprised amorphous Cu. The potentials of the electrodes oxidized at 450 and 550°C shifted to more than 230 mV (SCE) after light irradiation but they immediately decreased to 100 mV (SCE) due to the self-corrosion (photo-corrosion) of CuO. The electrodes oxidized at 250 and 350°C retained their photocatalytic activities at irradiation time of more than 24 h. The initial potentials of the electrodes oxidized at 250 and 350°C are 100 mV (SCE) and 280 mV (SCE), respectively. The potential of the electrode oxidized at 250°C increased with time because Cu₂O, which was the initial main phase of the electrode, was oxidized to CuO by a surface reaction during irradiation. In the electrode oxidized at 350°C, the photo-excited electrons and the photo-generated holes hardly reacted with the electrode surface by the interactions between the Cu-oxide film and the passive film of stainless steel substrate. The electrode exhibited the best performance in terms of potential and durability during the light irradiation.

KEY WORDS: photocathode; photo-corrosion; cuprous oxide; cupric oxide; p-p junction; passive film.

1. Introduction

Wet solar cells using seawater as an electrolyte have been reported as a method to generate solar power directly using marine environments.^{1–4)} The advantage of generating power in this manner is that using seawater as an electrolyte means that the cell walls are not required to contain the electrolyte, and thus the vast area of the ocean may be utilized. However, it is unrealistic to use expensive electrode materials over such large areas; therefore, low-cost, high-performance electrode materials are needed. A great deal of research and development has been performed using titanium dioxide (TiO₂) as a photocatalytic anode with the above characteristics.⁴⁾ However, there are not many studies of the cathodes that constitute these cells. For example, stainless steel is superior in cost effectiveness and corrosion resistance as a cathode electrode, but it is not often used because of its low catalytic activity. One effective utilization of a stainless steel in electrodes is to use it as substrate on which a p-type semiconductor is deposited. The metal oxides used in p-type semiconductors include copper (I, II) oxide (Cu₂O and CuO), nickel (II) oxide (NiO), and

cobalt (II) oxide (CoO). In particular, Cu₂O and CuO are easy to obtain and can produce a layer. For example, the high-temperature oxidation of a pure Cu film can produce an oxide film with photocatalytic activity at a low cost. In previous studies, the electrical properties and photoelectrical ones of the oxide film on a glass and Cu sheet have been reported.^{5–8)} However, the relationship between photopotential and durability of the oxide film is not apparent. In addition, there are few works to report the effect of a substrate on the property of the electrode. In this study, the cathode electrode was produced by the high-temperature oxidation of a pure Cu film that was vacuum vapor-deposited onto stainless steel substrate, and the electrode potential of their electrodes were measured. We elucidated the effect of the oxidation temperature on the photopotential and durability of the Cu-oxide formed on the stainless steel substrate applying to the cathode electrode of the cells.

2. Experimental Method

2.1. Preparation of Cu-oxide Electrodes

2.1.1. Formation of the Vapor-deposited Film

We used Type 329J4L dual-phase stainless steel as the substrate and #40 sandpaper to grind a grid pattern into the substrate. The chemical composition of the Type 329J4L

* Corresponding author: E-mail: morita@kaiyodai.ac.jp
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Table 1. Chemical composition of Type 329J4L stainless steel substrate (mass%).

Type 329J4L	C	Si	Mn	P	S	Ni	Cr	Mo	W	N
	0.025	0.44	0.77	0.027	–	6.34	24.96	3.22	0.14	0.27

stainless steel is shown in **Table 1**. Pure Cu was vacuum vapor-deposited onto the stainless steel substrate under the following conditions: vacuum = 0.4×10^{-3} Pa, current = 40 A, and voltage = 1.3 V. The thickness of the vapor-deposited Cu film was about 0.3 μm .

2.1.2. Oxidation Treatment of the Vapor-deposited Film

A heat treatment was performed in open air using a muffle furnace, and then the vapor-deposited pure Cu film was oxidized. The heat treatment was performed at temperatures of 150, 250, 350, 450, and 550°C. The temperatures were maintained for intervals of 30 min, and then samples were air-cooled. These electrodes are referred to as Cu-oxide electrodes.

2.2. Irradiation Testing to Measure the Photopotential

Figure 1 is a schematic diagram of a photopotential measuring device. A saturated calomel electrode (SCE) was used as the reference electrode (RE), and the working electrode (WE) was a Cu-oxide electrode. We use the abbreviated unit of mV to represent the potential with respect to the SCE (mV(SCE)). Artificial seawater was used as the electrolyte in this cell module. To prevent a change of the refractive index from affecting the electrode properties, the vertical incident light on the electrode surface initially passed through a quartz glass window. The distance between sample and the quartz glass is 3 mm. The standard light source was a 150 W xenon lamp with a wavelength range of 250 to 800 nm, and the intensity of the light exiting the quartz glass window was 105 W/m². The electrode was kept in dark conditions for three min in the artificial seawater, irradiated with the xenon lamp, and then the potential was measured for 24 h.

2.3. Microstructure of the Oxidized Vapor-deposited Film

The electrode surface was examined using images from an optical camera. In addition, we used a scanning electron microscope (SEM)/energy-dispersive X-ray spectroscopy (EDS) to analyze the microstructure of the Cu-oxide electrode surfaces. The phases of the main components of the vapor-deposited film were identified using an X-ray diffraction (XRD) apparatus.

3. Results and Discussion

3.1. Photocatalytic Properties of the Electrodes

Figure 2(a) shows the changes of the electrode potential before and after light irradiation in the 24 h irradiation testing. For all the electrodes, the potential ennobled immediately after light irradiation. Especially, the Cu-oxide electrodes with the oxidation temperatures between 350°C and 550°C rapidly ennobled. The ennobled potentials of the electrodes with oxidation temperatures above 250°C were 100 mV or higher after light irradiation compared to

Fig. 1. Schematic representation of the experimental apparatus for measuring the electrode potential.

Fig. 2. Time variation of the electrode potentials for the electrodes which are oxidized at 150, 250, 350, 450, and 550°C (a) before and after light irradiation, and during (b) the first 30 min and (c) 24 h in the 24 h irradiation testing.

the value in the dark. The potential immediately after light irradiation tended to be more ennobled for electrodes treated at higher oxidation temperatures.

The potentials of the electrodes treated at the oxidation temperatures of 150, 250, and 350°C stabilized within 30 min of irradiation (**Fig. 2(b)**), and their values after 30 min were –30, 120, and 280 mV, respectively. The electrode potentials with the oxidation temperatures of 450 and 550°C decreased with time during the 30 min irradiation. For each electrode, the potential at an irradiation time of 24 h was different from that at 30 min (**Fig. 2(c)**). The potential of the electrodes with an oxidation temperature

Fig. 3. X-ray diffraction profiles of the oxidized electrodes (a) before and (b) after the 24 h of Xe light irradiation.

of 150°C showed a significant ennoblement after 5 h, and stabilized at 100 mV after 12 h. The potential of the electrodes with an oxidation temperature of 250°C ennobled significantly up to 15 h, and the trend continued to a lesser degree, reaching 230 mV at 24 h. The photopotential of the electrodes oxidized at 350°C gradually decreased up to an irradiation time of 6 h, and then gradually became ennobled. The potential at 24 h was 260 mV. The potential of the electrodes with an oxidation temperature of 450°C continued to decrease following light irradiation, reaching 110 mV after 24 h. The potential of the electrodes with an oxidation temperature of 550°C decreased significantly initially, but started to ennobel after 30 min. The potential at 24 h was about 90 mV. The potentials of the electrodes with oxidation temperatures of 250 and 350°C were 200 mV or higher, and those with oxidation temperatures of 150, 450, and 550°C were about 100 mV.

3.2. Time Variations of the Microstructures in the Electrodes

3.2.1. Phase Identification of the Electrodes Prior to the Irradiation Test

Figure 3(a) shows the XRD profile of each electrode prior to the test. For all the electrodes, both ferrite phase (α -Fe) diffraction peaks and austenitic phase (γ -Fe) ones were detected. The stainless steel substrate (Type 329J4L) is comprised with their phases, and X-ray was transmitted through to the substrate. The diffraction peaks of austenitic phase in Type 329J4L are almost the same with those of crystalline Cu. In this study, the diffraction peaks of the Cu-oxide electrode with all the same temperatures at ferrite stainless steel (Type 430) were also measured, and their results ensured no crystalline Cu in the Cu-oxide film before light irradiation. The diffraction peak of Cu_2O was observed for the electrodes oxidized at 250°C. The diffraction peaks of CuO , was detected for the electrodes with oxidation temperatures of 350, 450, and 550°C. At an oxidation temperature of 150°C, the diffraction peaks of the Cu species (such as pure Cu, Cu_2O , and CuO) were not detected. The XRD results for the substrate, as-vapor-deposited material, and the material heat-treated at 250°C are shown in Fig. 4. In earlier studies, amorphous films were sometimes observed when metal films were formed through vacuum vapor-deposition,^{9,10)} and sometimes the XRD profile background values would increase.¹¹⁾ Pure Cu diffraction peak was not observed in the as-vapor-deposited material, but its background intensity was higher than that for the substrate.

Fig. 4. X-ray diffraction profiles of the Type 329J4L stainless steel substrate, the as-vapor-deposited electrode, and its oxidized one at 250°C.

Therefore, the as-vapor-deposited pure Cu was amorphous, and the main component of the surface film treated at an oxidation temperature of 150°C was amorphous Cu. The background intensity for the electrodes with an oxidation temperature of 250°C was lower than that of the as-deposited material, and showed a clear diffraction peak of Cu_2O . Therefore, the heat treatment at 250°C oxidized the amorphous Cu on the electrode to Cu_2O . The background values in all the heat-treated electrodes were higher than that of the untreated substrate, and thus, it is likely that the non-oxidized amorphous Cu remained in the film on all Cu-oxide electrodes.

The main phase that constitutes the vapor-deposited film on the electrodes with an oxidation temperature of 150°C was amorphous Cu, that on the electrodes with an oxidation temperature 250°C was Cu_2O , while those of 350, 450, and 550°C were CuO .

3.2.2. Effect of the Surface Microstructure on the Photocatalysis under Light Irradiation

The electrodes produced at an oxidation temperature of 150°C exhibited no remarkable ennoblement after light irradiation (Fig. 2(a)). The vapor-deposited pure copper film did not become oxidized at this temperature. A significant photocatalytic effect was not expected because the main component was amorphous Cu. Electrodes with oxidation temperatures of 250°C or higher became clearly ennobled after light irradiation. The potential of the electrodes with an oxidation temperature of 250°C was 100 mV immediately

Fig. 5. Optical images of the Cu-oxide electrode surfaces before and after the 24 h irradiation testing. Arrows show the visually observed pits.

after light irradiation. The potentials of the electrodes with oxidation temperatures of 350, 450, and 550°C were around 200 mV, higher than that of the electrode oxidized at 250°C. The main component of the electrodes with oxidation temperatures of 250°C was Cu_2O , those of 350°C and higher were CuO (Fig. 3(a)). The electrode potentials immediately after light irradiation correlated with the microstructures of the electrodes.

3.2.3 Changes of the Electrode Surface Morphology

Figure 5 shows optical images of the various electrode surfaces before and after the 24 h irradiation testing. The electrodes with an oxidation temperature of 150°C appeared red. Cu_2O peaks and CuO ones were not detected in the XRD analysis (Fig. 3(a)). A small amount of copper oxide substance may exist in the film because the electrode had a slight photocatalytic effect (Fig. 2(a)). The surfaces of the electrodes with oxidation temperatures of 250, 350, 450, and 550°C presented the interference color, especially at 250°C. The interference colors of the electrodes with oxidation temperatures of 350, 450, and 550°C contained a black tinge.

After 24 h irradiation testing, there was a slight visible surface change for the electrodes with oxidation temperatures of 250 and 350°C; however, there was a significant change in those oxidized at 150, 450, and 550°C. Some metallic luster was observed on the surface treated at 150°C, while those treated at 450 and 550°C presented an interference color with reddish brown spots.

Figure 6 shows the secondary electron (SE) images of the electrode surfaces before the 24 h irradiation testing. There were grains whose sizes increased with increasing oxidation temperature. The approximate grains sizes on the electrode surfaces with oxidation temperatures of 150, 250–450, and 500°C were 10, 30–40, and 100 nm, respectively. The electrode surfaces with oxidation temperatures of 350, 450, and 550°C were porous with a significant surface relief. The surface conditions of the Cu-oxide electrodes after an irradiation time of 24 h are shown in **Fig. 7**. The grains disappeared for the electrodes with oxidation temperatures of 150, 450, and 550°C; the corresponding surface morphology also significantly changed. On the electrode surfaces

Fig. 6. Secondary electron images of the Cu-oxide electrode surfaces at (a) 150°C, (b) 250°C, (c) 350°C, (d) 450°C, and (e) 550°C before the 24 h irradiation testing.

oxidized at 250 and 350°C, there was a slight change of the microstructural surface itself. These results are consistent with the observations from the optical images (Fig. 5). We will discuss the factors associated with these time variations in the following section.

3.3. Factors Associated with Time Variations of the Electrode Potential

3.3.1. Electrodes with an Oxidation Temperature of 150°C

The potential of the electrodes with an oxidation temperature of 150°C for the 24 h irradiation was 100 mV, which was also the free corrosion potential of the Type 329J4L stainless steel. After the 24 h irradiation testing, there was a metallic luster on the surface of the electrodes (Fig. 5).

Fig. 7. Secondary electron images of the Cu-oxide electrode surfaces at (a) 150°C, (b) 250°C, (c) 350°C, (d) 450°C, and (e) 550°C after the 24 h irradiation testing.

Fig. 8. Backscattered images of the electrodes oxidized at 150°C (a) before and (b) after the 24 h irradiation testing.

We analyzed the area with the metallic luster using SEM/EDS and confirmed the exposure of stainless steel substrate (Fig. 8). The vapor-deposited film on the electrodes dissolved after the 24 h irradiation. In addition, the results of the XRD analysis of the electrodes after testing showed a Cu_2O peak (Fig. 3(b)). Cu_2O is formed by the corrosion of Cu.¹²⁾ Therefore, the potential ennoblement of the electrodes with an oxidation temperature of 150°C occurred with time due to the corrosion of amorphous Cu that exposed the stainless steel substrate (whose potential was presented). In galvanic series in seawater, the electrode potential for a stainless steel is more noble than that for Cu,¹³⁾ and Cu had a lower potential than stainless steel. Amorphous Cu might have dissolved during the test due to bimetallic corrosion with the Type 329J4L stainless steel substrate.

3.3.2. Electrodes with an Oxidation Temperature of 250°C

The potential of the electrodes with an oxidation temperature of 250°C was 100 mV immediately after light irradiation, and it was ennobled up to 200 mV during the 24 h irradiation (Fig. 2). There was no significant difference of the surface microstructure before or after the irradiation test (Fig. 5), although the main component of the electrode

Fig. 9. Time variation of the electrode potentials for the Cu-oxide electrodes oxidized at 250°C for 15 min, 30 min, 1 h, 3 h, 6 h, and 24 h.

surfaces changed from Cu_2O to CuO (Fig. 3(b)). Therefore, after the 24 h irradiation, the potential of 230 mV was caused by the photocatalytic effect of CuO. In these electrodes, the main component (Cu_2O) was oxidized to CuO, ennobling the electrode potential. To verify this phenomenon, we prepared electrodes with accelerated oxidation from Cu_2O to CuO by controlling heat treatment time, and evaluated the time variations of their electrode potentials (Fig. 9). The potentials of the electrodes that were heat-treated for ≥ 1 hour were ennobled to about 150 mV immediately after light irradiation, while those of electrodes with ≤ 30 min of heat treatment was lower. However, the potentials of the latter electrodes became more ennobled with time; after the irradiation time of 12 h, the potentials became similar to that of the electrode heat-treated for 1 h. The ennobling of the potential up to 12 h was caused by the photocatalytic effect of Cu_2O or CuO.

3.3.3. Electrodes with an Oxidation Temperature of 350°C

The potential of the electrodes with oxidation temperatures of 350°C decreased with time up to 12 h, and then stabilized (Fig. 2(c)). No change was observed in the optical images of the electrode surfaces (Fig. 5), and the grains appeared to have dissolved (Figs. 6 and 7). The XRD profile of the electrode after the 24 h irradiation testing showed CuO and Cu_2O peaks (Fig. 3). It seemed that the amorphous Cu in the deposited film was corroded, and Cu_2O was formed during the 24 h irradiation.

3.3.4. Electrodes with Oxidation Temperatures of 450 and 550°C

Grains found prior to the 24 h irradiation testing were no longer observed on the surfaces of the electrodes at oxidation temperatures of 450 and 550°C after the 24 h irradiation (Figs. 6 and 7). Immediately after light irradiation, the potential rapidly ennobled to 200 mV and higher, but then rapidly decreased. It appears that the photocorroded due to its own photocatalytic effect. We analyzed the pits area shown in Fig. 5. A clear contrast was observed in the BSE image near the pits, and SEM/EDS analysis confirmed that the iron concentration. The pits in the optical images was the pitting corrosion of stainless steel substrate. When the

Fig. 10. Optical image of the surface on the Cu-oxide electrode with the oxidation temperature of 550°C after the 24 h non-irradiation testing. Arrows show some observed pits.

electrodes immersed under the condition of non-irradiation, only the pitting of stainless steel occurred (**Fig. 10**). Therefore, CuO results from the photocorrosion under the light irradiation, while the pitting may result from the structural defects of oxide film formed on the electrode with the oxidation temperature of 450 and 550°C.

3.4. Optical Responsivity

The electrodes with an oxidation temperature of 350°C had a more ennobled potential and were more stable than the other heat-treated electrodes (**Fig. 2(c)**). They also showed little change in the surface microstructure before and after the 24 h irradiation testing and had a higher durability (**Figs. 5–7**). Therefore, they demonstrated the best performance in terms of the potential and durability among the prepared electrodes. The 72 h irradiation testing was performed using these optimal electrodes, and the results are shown in **Fig. 11(a)**. Ennobling continued from 12 h until the end of testing, and the potential reached 280 mV. There was no significant change in the electrode surface morphology before or after the 24 h irradiation test. We also alternated the irradiation and darkness every hour using the present electrodes, and evaluated their photocatalytic effect and optical responsivity (**Fig. 11(b)**). The potential ennobled immediately upon light irradiation; within 10 min of light exposure, it reached a maximum value that was higher than that of the same electrode immersed for 72 h. The ennobled potential decreased with time, reaching the pre-irradiation value within 1 h of the light cut-off, although the photocatalytic effect was still observed at this point. The potential of the electrode prepared at an oxidation temperature 350°C followed the same pattern as that of the light irradiation.

3.5. Semiconductor Properties of the Passive Film Formed on Type 329J4L Stainless Steel

The time variation of the electrode potentials of the stainless steel substrates varying the oxidation temperatures between 150 and 550°C were measured (**Fig. 12**). Immediately after light irradiation, the substrates with the oxidation temperatures between 150 and 350°C exhibited the n-type semiconductor property, while those with the oxidation temperatures of 450 and 550°C exhibited p-type semiconductor property. The oxide state was identified by XPS analysis. The main oxides of passive film on Type 329J4L were iron oxide and chromium oxide. **Figure 13** shows XPS Spectra of Fe 2p_{3/2} and Cr 2p_{3/2} on Type 329J4L with the oxidation temperatures of 250 and 550°C. When the oxidation temperature increased, the amount of iron oxide decreased and that of chromium oxide increased. After background subtraction, the XPS results were separated into contribu-

Fig. 11. Time variation of the potential of the electrodes oxidized at 350°C for 72 h (a), and on-off photoresponsivity of the electrode potential after 72 h of irradiation (b).

Fig. 12. Time variation of electrode potentials of the stainless steel substrates oxidized at 150, 250, 350, 450, and 550°C during 30 min.

tions of the different oxidation states by referring the XPS spectra of the oxides and hydroxides of iron^{14–21)} and chromium.^{21–27)} The most amount of oxide at the electrode with the oxidation temperature of 250°C and 550°C was Fe₃O₄ and Cr₂O₃, respectively. The main oxides of passive film in the austenitic stainless steel (Type 304) with the oxidation temperature at 350°C²⁸⁾ are Fe₂O₃ and Cr₂O₃, and it agrees with those of passive film formed on type 329J4L. Fe₂O₃ is n-type semiconductor^{28,29)} and Cr₂O₃ is p-type one.^{28,30)} The types of semiconductor depend on the main oxide of the passive film. Therefore, the main oxides of the passive films with the oxidation temperatures between 150 and 350°C are Fe₂O₃, and those with the oxidation temperatures of 450 and 550°C are Cr₂O₃.

3.6. Surface Reactions of the Electrode during Light Irradiation

The surface reactions of Cu₂O semiconductor in aqueous³¹⁾ can be expressed as

In general p-type Cu₂O/substrate electrodes in aqueous, the photo-excited electrons reduce Cu₂O to Cu.³²⁾ In the Cu-oxide electrode with the oxidation temperature of 250°C, however, Cu₂O was oxidized to CuO (**Fig. 3**): the

Fig. 13. XPS spectra of Fe 2p_{3/2} and Cr 2p_{3/2} of the passive film formed on Type 329J4L stainless steel with the oxidation temperatures of 250°C and 550°C. (a)–(d) presents XPS spectra of (a) Fe 2p_{3/2} at 250°C, (b) Fe 2p_{3/2} at 550°C, (c) Cr 2p_{3/2} at 250°C, and (d) Cr 2p_{3/2} at 550°C, respectively.

photo-generated holes transferred into electrolyte, and the photo-generated holes oxidized Cu₂O to CuO. The oxides on the substrate effect on the film. Some photo-generated holes must transfer to the substrate side because the photo potential ennobled immediately upon light irradiation. It suggested that copper oxide substance except Cu₂O is also included in the Cu-oxide electrode with the oxidation temperature of 250°C. By double sweep cyclic voltammetry method (DSCV method),^{33,34} CuO and Cu(OH)₂ in the Cu-oxide film were actually detected. The CuO contributes the potential ennoblement immediately after light irradiation. In the Cu-oxide electrodes with the oxidation temperatures of 450 and 550°C, photo-corrosion occurred. Based on the oxidation reaction of photo-corrosion by photo-generated holes,³⁵ the surface decomposition of CuO can be expressed as Eq. (3):

The photo-generated holes transferred into the electrolyte. In the Cu-oxide electrode with the oxidation temperature of 350°C, whose semiconductor property of the passive film is different with those with 450 and 550°C, CuO did not decompose. The band structure changes by the oxide thin-film on substrate.³² The interactions between the Cu-oxide film and the passive film of stainless steel substrate affected on potential and durability during the light irradiation. In present study, it is clarified made the existence of interaction between Cu-oxide film and the passive film of stainless steel substrate clear, but an analysis of band structure diagram based on this experiment is necessary in the future. The photo-excited electrons may decompose CuO to Cu.

The reaction in Eq. (4) was not occur because the behav-

ior of electrode potential was stable in the electrode with the oxidation temperature of 350°C. Therefore, the electrons oxidized water, and its surface reaction³¹⁾ can be expressed as:

The electrodes oxidized at 350°C exhibited the highest the durability because the photo-excited electrons and photo-generated holes hardly reacted with the substance of electrode surface by the interactions between the Cu-oxide film and the passive film of stainless steel substrate.

4. Conclusions

We have produced Cu-oxide electrodes by the high-temperature oxidation of pure Cu that was vacuum vapor-deposited on stainless steel (Type 329J4L). The potentials and durability of these electrodes under light irradiation were evaluated, and the effect of electrode microstructure on the potential and durability were elucidated.

(1) The main phase of the vapor-deposited film on the electrodes with an oxidation temperature of 150°C was amorphous Cu, the main phase at 250°C was Cu₂O, and that at 350, 450, and 550°C was CuO.

(2) The passive film of the stainless steel substrates with the oxidation temperature between 150 and 350°C showed the n-type semiconductor property, instead those with the oxidation temperatures of 450 and 550°C were p-type semiconductor.

(3) In the electrodes oxidized at 250°C, the potential became more ennobled with time as Cu₂O was oxidized to form CuO, although the potential ennobling immediately after light irradiation was relatively low.

(4) The potential of the electrodes with an oxidation temperature of 350°C stabilized with the highest ennoblement.

ment. The electrode surface morphology showed little change during the 24 h irradiation.

(5) Immediately after light irradiation, the potential of the electrodes with CuO was more ennobled compared to that of the electrodes with Cu₂O. Stronger potential ennobling was observed at higher oxidation temperatures. In the electrodes with an oxidation temperature of 450°C or higher, the potentials decreased immediately after irradiation due to the self-corrosion (photo-corrosion) of CuO, and to the pitting corrosion of the stainless steel substrate with the passive film of p-type semiconductor.

(6) In the Cu-oxide electrodes prepared at an oxidation temperature of 350°C, the photo-excited electrons and photo-generated holes hardly reacted with the substance of electrode surface by the interactions between the Cu-oxide film and the passive film of stainless steel substrate. The electrode exhibited the highest performance from the viewpoint of the potential and durability under light irradiation.

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