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SURFACE CHARACTERIZATION OF CU ELECTRODES IN ELECTROCHEMICAL REDUCTION OF CO₂ BY CORE LEVEL X-RAY PHOTOELECTRON SPECTROSCOPY AND VALENCE LEVEL PHOTOELECTRON EMISSION MEASUREMENT

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ABSTRACT

To obtain the relation in the electrochemical reduction of CO₂ in aqueous KHCO₃ solution between an activity for the product and the nature of Cu electrode, the electrode surface was characterized by using two methods: X-ray photoelectron spectroscopy (XPS) and photoelectron emission (PE) measurement. Electrolyses were performed with Cu electrodes pretreated in several ways. The distribution of the products changed drastically with electrolysis time and the pretreatment method. The features in XPS spectra were closely connected with the product distribution. The oxide film at the electrode surface was gradually reduced to bare Cu metal with electrolysis time, resulting in a variation of the product distribution. PE was measured by varying the wavelength of incident light at several temperatures. The dependence of PE on the measurement temperature changed greatly before and after electrolysis.

INTRODUCTION

The products on the electrochemical reduction of CO₂ depend remarkably on the electrode metal^{1,2)}. Although the same elemental metal was used, it has also been reported that the product distribution varies because of slight differences in electrolytic conditions such as temperature, pressure, the concentration of electrolyte, stirring, and the electrode preparation method^{3,4)}.

In the preparation of electrodes, various procedures have been used to prepare the electrode surface to lead to the reduction of CO₂ with high reproducibility. They include

the removal of the native oxide film by chemical etching, degreasing by an organic solvent, production of a mirror finish by mechanical and electrolytic polishing (anodization), and electrolytic cleaning by applying a cathodic current. However, it is usually impossible to eliminate any oxides and contaminants at the surface perfectly. Metallic Cu is said to be the only electrocatalyst for effective production of hydrocarbons in the electrochemical reduction of CO₂¹⁾. It has two stable oxides (Cu₂O and CuO) and the oxidation states are alterable, depending on the surroundings. And metallic Cu is also very likely to be contaminated with organic com-

pounds because of their high affinity⁵). However, little is known about how the oxides and the contaminants on the electrode participate in the reaction mechanism and the electrocatalytic activity.

In this paper, we report that the product distribution is greatly influenced by the pretreatment method even under the same electrolytic conditions. In addition, we present some information on the chemical structure of the electrode surface required to form the desirable product effectively. Moreover the correlation between the product distribution and the ease of PE from electrode surface will be discussed.

EXPERIMENTAL

Preparation of working electrode

Polycrystalline copper sheets (Nilaco, purity >99.9%, thickness 0.2mm, size 10 × 10mm²) were used for working electrode. The sheets cleaned ultrasonically in acetone for 40 min, followed by drying in a vacuum, called untreated, and then two pretreatments were carried out. The electrodes used are summarized in Table 1. The electrolytic pretreatment (Table 1, Electrode III) was expected to reduce organic contaminants by both electro-

chemical reduction and mechanical cleaning by H₂ bubbles produced vigorously at the pretreatment potential. This pretreatment time to be most effective in the reduction of CO₂ was adopted.

Electrolysis

Aqueous carbonate solutions of 0.1 M were prepared from KHCO₃ (Wako Pure Chemical Industries, reagent grade) and distilled deionized water. A cell with two-compartments for the working and counter electrodes was used. These compartments were separated by a cation exchange membrane (Nafion® 117). A Pt sheet (20 × 20 × 0.1mm³) was used as a counter electrode (anode). A saturated calomel electrode (SCE) was used as the reference. Before each run, the fresh carbonate solutions were introduced into each compartment (100mL) and then the solution of the solution of the working compartment was purged with and saturated with CO₂ gas (Takachiho, purity 99.99%) by vigorous bubbling for 90min. After saturation, the pH of the solution was approximately 6.8.

All electrolyses were carried out at room temperature and at several potentials of the working electrode controlled by a potentiostat (Hokutoh Denko HA-501). During electrolyses, the catholyte was bubbled continuously by CO₂ gas at a flow rate of 2.5 mL/min and was magnetically stirred. The data used in this paper were obtained at an electrode potential of -1.9V vs. SCE.

Product analysis

Effluent gases from the cell were sampled periodically with a gas syringe and analyzed by gas chromatographs (Shimadzu GC-8A),

Table 1 Pretreatment of Cu working electrodes

Electrode	Pretreatment
I	Untreated
II	Oxidized in air at 200°C for 30 min
III	Electrolytically cleaned by sweeping potential back and forth 30 times between 0 and -3.0 V vs. SCE at the rate of 0.1 V/min

equipped with thermal conductivity detectors. 3m stainless-steel columns packed with a Molecular sieve 5A and with a Porapak QS were employed at 60°C with Ar and He carrier gases at a flow rate of 25mL/min. For liquid products in the solution, the latter column was also employed at 110°C. The results of the product analysis in this paper represent the average values of the data collected repeatedly under the same electrolytic conditions.

Characterization of the electrode surfaces

XPS spectra of working electrodes before and after electrolysis were taken with a Shimadzu ESCA 750 spectrometer using $MgK\alpha X$ -ray radiation. The measurements were conducted at a pressure of $\leq 10^{-8}$ Torr. The electrode was taken out of the electrolyte solution immediately before and after each electrolysis, rinsed in distilled deionized water for 20 s, dried in a vacuum, and then transferred into spectrometer within 15 min in all.

PE measurement apparatus is shown in Fig. 1. The voltage of an electron counter was set at 1400V. Q gas [He(95-97% + iso C_4H_{10})] was used as a counter gas. A 94V potential relative to the grounded grid of the counter was applied to accelerate and collect

the electrons emitted from the sample. A spot of $4mm^2$ on the sample was illuminated with the light. PE intensity(count/mim) was measured by varying the wave length of the light from 300 to 170 nm at the scan rate of 20 nm/min. We call the emission intensity vs. the wave length "a PE spectrum" and the number of emitted electrons in a PE spectrum "a PE total count". For one sample of a Cu electrode before or after electrolysis, PE spectra were taken repeatedly at different temperatures, which were changed successively between 25 and 350°C in a round cycle of heating and colling.

Here it should be noted that the electrode before electrolysis were prepared by holding in the electrolyte solution at open circuit during bubbling with CO_2 for 90 min as in the usual procedure for electrolysis.

RESULT AND DISCUSSION

Product analysis

Gaseous products, CH_4 , C_2H_4 , CO and H_2 were detected in every cell effluent in addition to the CO_2 bubbled into and passed through the catholyte. On the other hand, there was no amount of detectable products soluble in the catholyte even after 10h of electrolysis. The yield of the gaseous products was monitored as a function of electrolysis time, and was converted into the relative ratio of the electric charge, which would have been used for each product formation. In other words, the ratio was calculated from the yield by assuming that each product was formed directly from CO_2 and then the following number of electrons were consumed : 2 electrons per-molecule CO, 8 electrons per molecule CH_4 , 12 electrons per molecule C_2H_4 , and

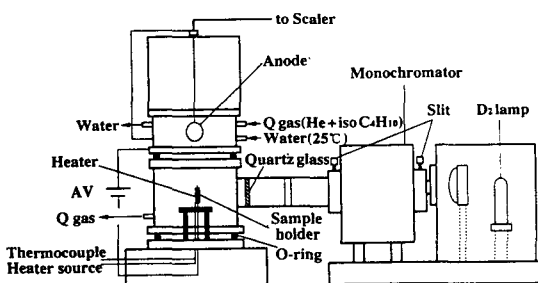


Fig. 1 Apparatus for photoelectron emission(PE) measurement.

2 electrons per molecule H₂. If any other products are negligible, then the ratio is regarded as the value corresponding to the faradaic efficiency (FE). We call the ratio "the production ratio of gas", and use this as a criterion for the efficiency of gas formation.

Figure 2 shows the dependence of the production ratio on electrolysis time for Electrode I. The time profile of CH₄ exhibits a rapid rise at the initial stage of electrolysis, reaching a peak at 1 h. This peak value is approximately 30%, followed by a slow decay to 11% at 5h. The ratio of CO drastically increases from nearly zero at the start of electrolysis to about 50% at 5h. The ratio of H₂ has a rapid fall at the early stage of electrolysis and then reaches a level of about 30% after 2 h. Figure 3 shows the results for Electrode II. A large amount of H₂ is produced preferentially over the whole electrolysis time, while the ratio of CO remains considerably low.

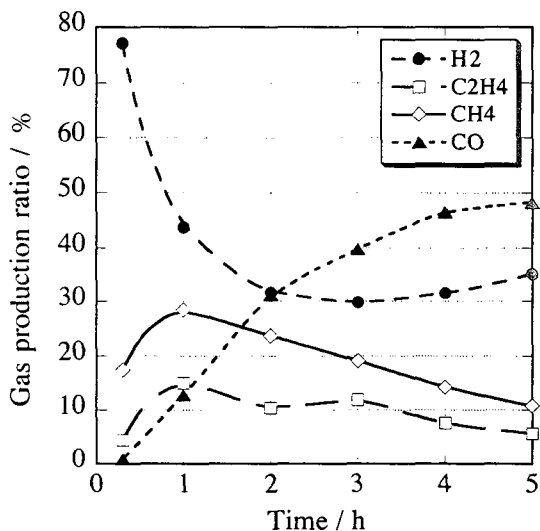


Fig. 2 Plots of the production ratio of gases vs. electrolysis time for CO₂ reduction at Electrode I in KHCO₃ aq..

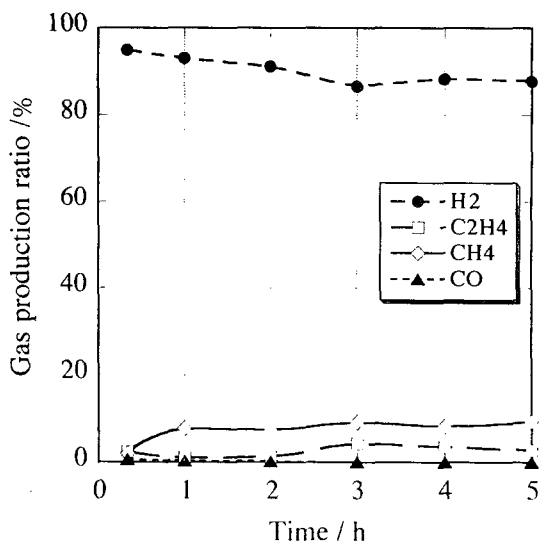


Fig. 3 Plots of the production ratio of gases vs. electrolysis time for CO₂ reduction at Electrode II in KHCO₃ aq..

Figure 4 shows the results for Electrode III. The rate of increasing in the ratio of CO becomes markedly lower than that of Electrode I. On the other hand, the ratio of CH₄ is significantly greater than that for Electrode I over the whole range of time.

XPS analysis

Figure 5 shows the XPS spectra of Electrode II before and after electrolysis. Before electrolysis [Fig. 5(a)] the whole surface is covered with a mixed film of CuO and Cu₂O as shown by two features: satellite peaks located at 5–10 eV above the principal Cu 2p_{3/2} line (933 eV) in the Cu 2p spectrum and a peak at about 337 eV in the x-ray-induced Auger Cu_{LMM} spectrum⁶. After electrolysis [Fig. 5(b)], a new shoulder peak assigned to metallic Cu appears at about 335 eV in the Cu_{LMM} spectrum⁶. This suggests that the surface oxide is unstable and is reduced electrochemically. The O 1s spectra before and after

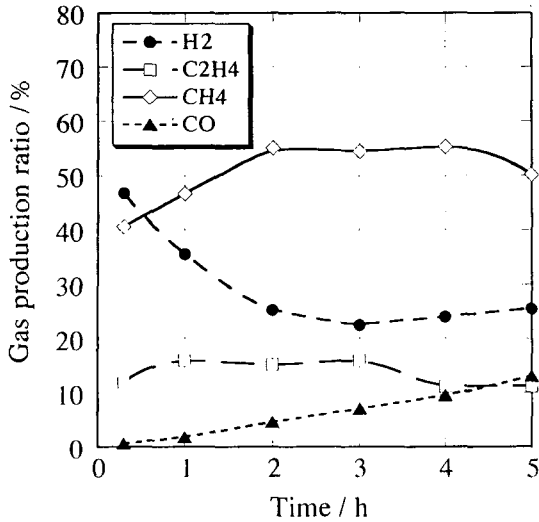


Fig. 4 Plots of the production ratio of gases vs. electrolysis time for CO₂ reduction at Electrode III in KHCO₃

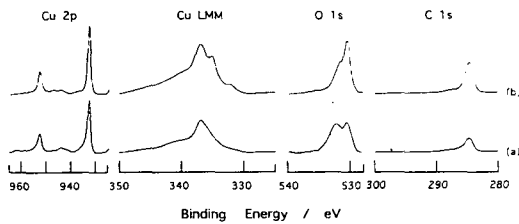


Fig. 5 XPS spectra for Electrode II for CO₂ reduction : (a) before electrolysis, (b) after electrolysis for 5h.

electrolysis consist of two components at lower and higher binding energies. The former appearing at about 530 eV is identified to be oxide oxygen [CuO (529.7 eV) and Cu₂O (530.6 eV)] and the latter at about 532 eV to be adsorbed oxygen (532.5 eV)⁷. A comparison of both O1s spectra shows that adsorbed oxygen decreases remarkably after electrolysis.

Figure 6 shows the spectra of Electrode I for various periods of electrolysis. The peak derived from metallic Cu in the Cu_{LMM} spectra is always present. It develops greatly after 1

h of electrolysis, followed by a gradual increase in the intensity with electrolysis time. We also found that this peak becomes still higher at longer time of electrolysis. These facts suggests that the native oxide film is rapidly reduced to a certain extent at the initial stage of electrolysis, and is then gradually reduced, a surface with more metallic character being exposed. The increase in CO production with electrolysis time can be related to the gradual disappearing of Cu oxide at the electrode surface. On the other hand, the Cu_{LMM} spectrum before electrolysis [Fig. 6 (a)] is very similar to that of Electrode II after electrolysis [Fig. 5(b)]. At the initial stage of electrolysis for Electrode I and over the whole time for Electrode II, H₂ is produced in remarkable great amounts. This reveals that the surface covered with Cu oxide largely favors H₂ production, but not CO production.

Figure 7 shows the XPS spectra of Electrode III. From the Cu_{LMM} spectra before electrolysis for Electrode III [Fig. 7(a)] and for Electrode I [Fig. 6(a)] it can be seen that the native oxide film is reduced in parts by the pretreatment. Contrary to our expectation, quantitative analysis showed that the

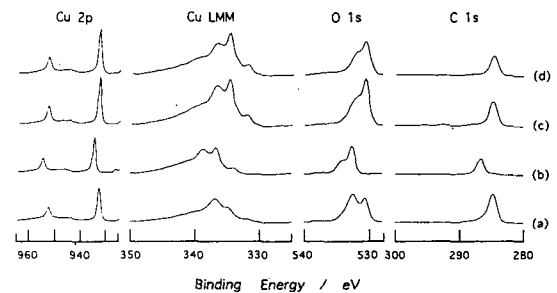


Fig. 6 Variation of XPS spectra for Electrode I with electrolysis time for CO₂ reduction : (a) 0h, (b) 1h, (c) 3h, (d) 5h

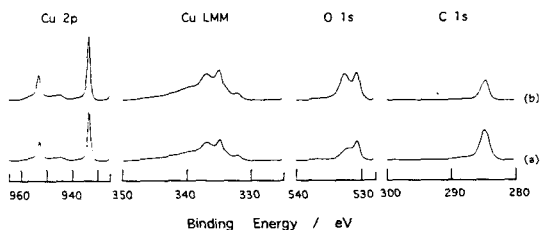


Fig. 7 XPS spectra for Electrode III for CO₂ reduction: (a) before electrolysis, (b) after electrolysis for 5h.

pretreatment did not so much decrease the amount of carbon. After electrolysis, there is no further increase of metallic Cu in the Cu_{LMM} spectrum, in contrast to the result for Electrode I. This implies that the pretreatment yields an oxide film resistant to electrochemical reduction under a negative bias. In the O1s spectrum after the O1s spectrum after electrolysis (Fig. 7(b)), the peak assigned to adsorbed oxygen increases to a level comparable to the peak of oxide oxygen. This trend contrasts with the fact that adsorbed oxygen decreases after electrolysis for Electrodes I and II (Fig. 5 and 6). These observations suggest that CH₄ is produced on the surface with both Cu oxide and metallic Cu, having a high affinity for adsorbed oxygen.

PE

Figure 8 shows the PE spectra of Electrode I before and after 40 min of electrolysis [(a) and (b)] at room temperature. The threshold values, that is, the minimum Photon energies necessary for PE of both are substantially the same. PE intensity is, however, apparently higher before electrolysis than that after electrolysis.

Regarding the lowering of PE intensity, we observed at Electrode I that the current decreased with electrolysis time. At the initial of electrolysis, which may be taken as the corresponding to (a), the electrode surface

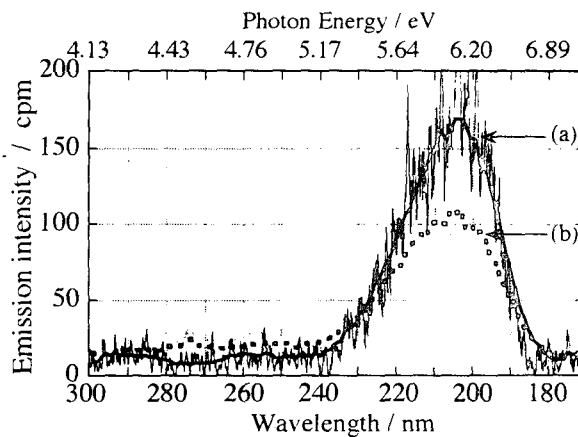


Fig. 8 PE spectra of Electrode I before and after electrolysis; (a) before electrolysis, (b) after electrolysis.

gave preferential H₂ production. For Electrode II, which also gave remarkable H₂ production, PE intensity was as high as that for (a). This threshold is inconsistent with that for (a). At the electrolysis period of (b), the surface came to have an activity for hydrocarbon production. Therefore it is possible that the product distribution is related to PE intensity. PE intensity may be connected with the supply of electron from the surface during electrolysis. Then, this may influence the adsorption of intermediate species like atomic hydrogen.

Figure 9 shows the dependence of the PE total count on temperature for Electrode I before electrolysis. In this experiment, the area illuminated with the light was 6mm². A remarkable feature is that for the temperature-elevation the total count maximum with a markedly increased level at 250°C. This trend was more pronounced for Electrode I without dipping in the electrolyte solution. On the other hand, such behavior was not observed for the Electrode I after electrolysis, that is, the total count was independent of

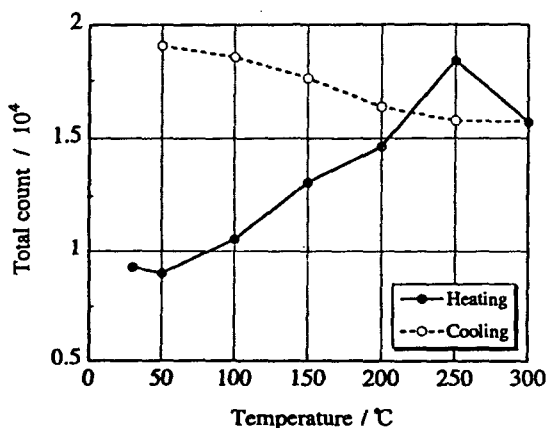


Fig. 9 Relation between the total count for Electrode I before electrolysis and the measurement temperature.

temperature. We have a very great difficulty to explain the cause for the maximum PE observed at 250°C. Such maximum was usually observed for metallic Cu samples, but not for air-oxidized one above 200°C. We believe that the low total count at low temperature for metallic Cu samples is responsible for adsorbed oxygen and we also know that the maximum at 250°C is accompanied with some changes in the oxidation state of Cu, depending on the stability of the surface with adsorbed oxygen in the measuring system. Accordingly, the result for Electrode I after electrolysis may be related that the surface after electrolysis is likely to be oxidized even at relatively low temperature during PE measurement because of its high activity for oxidation. The ease of oxidation can be presumed by XPS analysis at room temperature to a certain extent.

CONCLUSION

The product distribution for an untreated electrode in the electrochemical reduction of CO₂ varied greatly with an increase of elec-

trolysis time: the ratio for CO markedly increased. On the other hand, the electrolytically pretreated electrodes exhibited only a slight change with time and gave a large production of hydrocarbon. As for the former electrode, a gradual increase of metallic Cu was observed at the surface. For the latter, the ratio of Cu oxide to metallic Cu always remained nearly unchanged. In addition, the electrode surface covered with Cu oxide produced plenty of H₂.

Moreover it was found that the dependence of PE on temperature changed greatly before and after electrolysis. This may be related to the change of the product distribution for the electrode, too.

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