—Communication—

Effect of the Micro-crystallite Structures of Cu-Sn and Cu-Zn Alloys on Electroreduction of CO₂

Akihiro KATO, Masami SHIBATA and Masahiro WATANABE*

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1. INTRODUCTION

It has long been recognized that accumulation of CO₂ from fossil sources, together with a low efficiency of energy conversion, causes a serious degradation of the global environment. This gives an impetus to develop efficient systems for fossil energy conversion and also to study various artificial processes for fixation of CO₂. An electrochemical reduction is one approach for fixation, and has a potential to reduce CO₂ both selectively and reversibly in the future by electric power producing no CO₂ emission or by solar energy with a photo-electrochemical process. Many studies have been carried out on the electrochemical reduction of CO₂ at various elemental metal electrodes, where selective reduction was found, e.g., formic acid on Hg and Pb, CO on Ag and Au,^{1,2)} methane or ethane on Cu,²⁾ and hydrocarbons on various transition metals.³⁾ All these reactions on elemental metals require a large overpotential, i.e., they are not reversible. Due to the CO₂ problems resulting from the large consumption of fossil sources with a low conversion efficiency, reversibility is essential for the electrochemical reduction of CO₂ as well as for selectivity of the reduction products. We have worked on alloy electrocatalysts for CO₂ reduction, which can satisfy either or both of these requirements.⁴⁾ This paper will report on the importance of micro-crystallite structures for the reversibility or the selectivity of the reduction reaction.

2. EXPERIMENTAL

Electrodes of Cu-Sn and Cu-Zn alloys or the elemental metals were prepared on gold flag electrodes (2.25 cm²) by electroplating from conventional plating baths containing dissolved copper and/or tin or zinc chlorides. The alloy compositions were controlled by changing the ratios of the chlorides contained in the baths and/or the current densities at a constant plating tempera-

ture.⁵⁾ The electrode surfaces were protected from formation of oxides or dissolution of the components by blanketing with hydrogen gas during the replacement of electrolyte, washing the surfaces, and then saturating the electrolyte with CO₂ gas. Potentiostatic electrolysis was performed on the CO₂ saturated 0.05M KHCO₃ aqueous solution at 2°C. Analyses of the products in both the gas and liquid phases were carried out using a gas chromatograph and a liquid chromatograph, or with a steam gas chromatograph. After the electrolyses experiments, analyses of alloy compositions were carried out using an ICP method, and of the crystallite structures by using an X-ray diffraction method.

3. RESULTS AND DISCUSSION

Relationships of the current efficiency or selectivity for the reduction products from CO₂, to the reduction potential on Cu-Sn alloy electrodes, prepared from a pyrophosphate bath and a cyanide bath, are shown in Fig. 1. In spite of their similar gross compositions, i.e., Cu/Sn = 57/43 and 50/50 in the atomic ratio, the main products were formic acid at the former and CO at the latter. The potentials for detectable formation of formic acid and CO were ca. -0.5V vs. SHE for the former, which is close to the thermodynamically reversible

Fig. 1. Effect of the electroplating pyrophosphate (○, △) and cyanide (●, ▲) baths on the current efficiencies for CO (○, ●) and HCOOH (△, ▲) formation.

Faculty of Engineering, Yamanashi University,
Takeda 4, Kofu 400

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potential for formation. That for the latter is -1.0V, exhibiting a much larger overpotential. X-ray diffraction analyses showed that the differences in the catalytic behaviour can be attributed to the differences in the micro-crystallite structure of the alloys, namely; the alloy from the phosphate bath consists of a mixture of crystallites of Cu, Sn and Cu_5Sn_5 inter-metallic compound; but the alloy from cyanide bath consists of $\text{Cu}_{5.6}\text{Sn}$, Cu_3Sn and a non-detectable phase corresponding to the balance of the gross composition and the composition of the detected alloy phases. Neither an elemental Cu nor Sn electrode is selective and reversible for the formation of formic acid and CO as is shown in Fig.2. The results suggest that the presence of the both dissimilar atoms in neighboring sites, particularly in the atomic ratio such as $\text{Cu}/\text{Sn} = 1/1$, is important to the selective and reversible formation on the alloy.

Figure 2 shows the relationship between the current efficiency for the reduction products at -1.25V vs. SHE and the composition of Cu-Sn alloys prepared from cyanide baths. The addition of 15 atomic % of Sn to Cu improves the current efficiency for CO and shows a maximum of 70%, which is much higher than that of elemental Cu, but shows no noticeable effect on formic acid formation. The crystallite structures detected by X-ray diffraction are shown in the same figure. It is clear that the solid solution of (Cu+Sn) or $\text{Cu}_{5.6}\text{Sn}$, of which compositions are close to the gross one of the electrode, plays an important role in the selective formation of CO, but requires a relatively large overpotential.

Figure 3 shows the relationship between the current efficiency for the reduction products at -1.50V vs. SHE and the composition of Cu-Zn alloys prepared from cyanide baths. It was found that a maximum current efficiency of 85% can be obtained at $\text{Zn}/(\text{Cu}+\text{Zn}) = 0.59$ by a cooperative

Fig. 2. Effect of Cu-Sn alloy compositions on the current efficiencies for CO(●) and HCOOH (▲) formation. A: (Cu+Sn) solid solution + $\text{Cu}_{5.6}\text{Sn}$, B: $\text{Cu}_{5.6}\text{Sn}$ + Cu_3Sn , C: Cu_6Sn_5 + Sn

action between Cu and Zn atoms for CO formation, but only with a diluting action for formic acid formation. The crystallite structures detected by X-ray diffraction are shown in the same figure. The crystallites structure of CuZn appeared in both of B and C regions, but that of Cu_5Zn_8 appeared only in region B. The ratios of the diffraction peak heights of Cu_5Zn_8 and CuZn_2 were 1.5/1 and 16/1 at the alloy gross compositions of $\text{Zn}/(\text{Cu}+\text{Zn}) = 0.50$ and 0.59, respectively. It is clear, therefore, that the Cu_5Zn_8 crystallines are the most active for the CO formation, although they require a large overpotential.

In summary, the results described here clearly show that the gross composition of alloys is not important but the combination of alloy components and the composition of the micro-crystallines are most important. In this way, the evaluation of electrocatalytic activity and the discussion on electrocatalysis at well-defined alloy surfaces become significantly important.

Fig. 3. Effect of Cu-Zn alloy compositions on the current efficiencies for CO(●) and HCOOH (▲) formation. A: (Cu+Zn) solid solution, B: Cu_5Zn_8 + CuZn_2 , C: CuZn_2 + Zn

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