

Selective Formation of C₂ Compounds from Electrochemical Reduction of CO₂ at a Series of Copper Single Crystal Electrodes

Yoshio Hori,* Ichiro Takahashi, Osamu Koga, and Nagahiro Hoshi

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Inage-ku, Chiba 263-8522, Japan

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Electrochemical reduction of CO₂ was studied using single-crystal electrodes, Cu(111), Cu(100), Cu(S)-[*n*(100) × (111)], and Cu(S)-[*n*(100) × (110)] at a constant current density 5 mA cm⁻² in 0.1 M KHCO₃ aqueous solution. Copper single crystals were prepared from 99.999% copper metal in graphite crucibles by the Bridgeman method. The crystal orientation was determined by the X-ray back reflection method. The Cu(111) electrode yields mainly CH₄ from CO₂, and the Cu(100) favorably gives C₂H₄. Introduction of (111) steps to Cu(100) basal plane, leading to Cu(S)-[*n*(100) × (111)] orientations, significantly promoted C₂H₄ formation and suppressed CH₄ formation. The selectivity ratio C₂H₄/CH₄ on Cu(711) (*n* = 4) amounted to 14, 2 orders of magnitude higher than that on Cu(111).

Introduction

Electrochemical reduction of carbon dioxide is an excellent candidate for new energy storage processes for utilization of natural energies.¹ Copper electrode can uniquely reduce CO₂ to CH₄, C₂H₄, and alcohols in aqueous electrolytes at ambient temperature, as first reported from our laboratory^{2,3} and later confirmed by many workers.^{4–7} Copper electrode yields a wide variety of hydrocarbons and alcohols from CO₂, but neither ethane nor methanol is produced in this reaction.⁸ The product distribution depends on the temperature, the electrode potential, the electrolyte, and the pretreatment of the electrode surface according to the previous studies.^{3,5,6,8}

A fundamental study using single-crystal electrodes is appropriate to reveal the unique electrocatalytic properties of copper metal. The electrochemical reduction of CO₂ at single-crystal copper electrodes Cu(111), Cu(110), and Cu(100) was studied by Frese.⁹ He indicated that CH₄ formation is favored in the order of Cu(111), Cu(110), and Cu(100). We also published the electrochemical reduction of CO₂ at single-crystal copper electrodes of low index planes.¹⁰ C₂H₄ is formed more favorably than CH₄ on the (100) electrode, and CH₄ is predominantly produced on the (111) surface. CO, intermediately formed in the electrochemical reduction of CO₂,^{5,8,11} is also reduced at copper single-crystal electrodes, with similar product distribution.

Higher selectivity of the reduction product is preferable for any practical application of CO₂ reduction in the future, and formation of C₂H₄ or C₂H₅OH will be more suitable for this purpose. The (100) configuration is favorable for ethylene formation among low index planes as mentioned above. Thus we attempted to modify the (100) surface in order to enhance the selectivity for ethylene formation. The present communication briefly describes the product selectivity of copper single-crystal electrodes Cu(S)-[*n*(100) × (111)] and Cu(S)-[*n*(100) × (110)] in the electrochemical reduction of CO₂; the electrode surface comprises *n* atomic rows of (100) terrace and one atomic height of (111) or (110) step. Introduction of (111) or (110)

step atoms to (100) basal plane significantly enhances the C₂/C₁ selectivity.

Experimental Section

Spherical copper single crystals (10 mm dia.) attached with a copper stick lead were prepared from 99.999% copper metal by the Bridgeman method using a graphite crucible. After orientation of the crystal surface by the X-ray Laue back reflection method within 0.5 degree, the surface of the electrode was polished mechanically to mirror finish with diamond paste down to 0.25 micron, then electrochemically polished for 1 s in mixed concentrated phosphoric acid and sulfuric acid.¹² This procedure removes the stressed surface layer and possible impurities from the electrode surface. The surface maintained mirror finish during the process. Rinsed with 0.1 mM HClO₄ prepared from Merck Suprapur grade chemicals and ultrapure water treated with Milli Q low TOC (Millipore), the electrode was transferred to the Pyrex electrolysis cell with the electrode surface protected by a drop of 0.1 mM HClO₄. The electrode was set in the electrolysis cell according to the hanging meniscus method.

We conducted voltammetric measurements of the copper single-crystal electrodes at 0 °C in CO saturated 0.1 M K₂HPO₄ + 0.1 M KH₂PO₄ (pH 6.8) prior to every electrolysis measurement in order to verify the crystal orientations. The significance of the voltammograms will be discussed later. The potential of zero charge (PZC) was also determined by the differential capacity measurements in 0.01 M KClO₄ solution. A linear correlation was obtained between the PZC and the broken bond density (*d_{bb}*),¹³ verifying that the surfaces of the Cu electrode are correctly oriented. Detailed description of the PZC measurements of the copper single crystals of high index planes will be published elsewhere.

The electrolyte solutions were prepared from superpure grade chemicals (Nacalai Tesque). 0.1 M K₂HPO₄ + 0.1 M KH₂PO₄ was employed for the voltammetric measurements, and 0.1 M KHCO₃ for the electrochemical reduction of CO₂; both electrolyte solutions were purified by pre-electrolysis using a Pt black cathode overnight prior to the measurements.

* Corresponding author. E-mail: hori@tc.chiba-u.ac.jp. Fax: +81 43 290 3382.

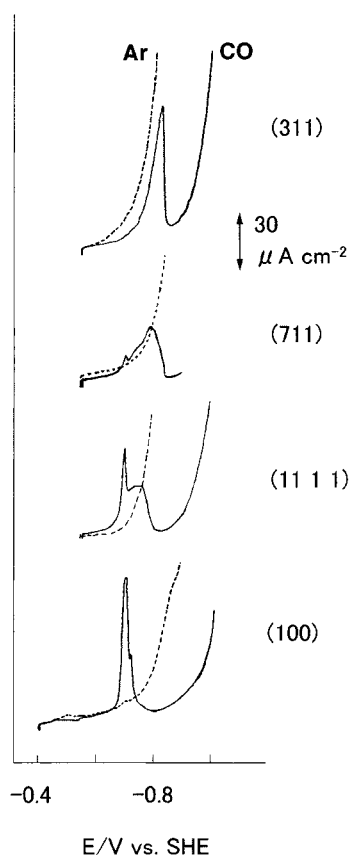


Figure 1. Voltammograms of copper single-crystal electrodes at 0 °C obtained in 0.1 M K_2HPO_4 + 0.1 M KH_2PO_4 (pH 6.8) saturated with CO or argon. Scanning rate: 50 mV s^{-1} .

After voltammetric measurements for the verification of the crystal orientation, we again conducted electrochemical polishing of the single-crystal electrodes. The electrodes were then treated in the identical manner described above, and the electrochemical reduction of CO_2 was carried out. The electrolyses were made at a constant current density of 5 mA cm^{-2} for 1 h with CO_2 gas bubbled through the electrolyte solution continuously. The electrolysis cell was stirred by a magnetic stirrer and thermostated at 18 °C. The gas sample of the effluent CO_2 from the electrolysis cell, taken at every 10 min, was analyzed by gas chromatography. Soluble products were analyzed by an ion chromatograph (Toyo Soda) and a gas chromatograph-mass spectrometer (Shimadzu GCMS-QP5050). CO_2 gas, the purity of which was higher than 99.99%, was passed through an activated copper column and a silica gel column to remove trace amount of gaseous impurities. Other experimental details are referred to in the previous publications.⁸

Results and Discussion

Voltammograms of $\text{Cu(S)}-[n(100) \times (111)]$. We previously reported the charge displacement adsorption of CO at various copper single-crystal electrodes in some electrolyte solutions.^{10,14} Copper single-crystal electrodes display reproducible cyclic voltammograms that correspond to displacement of specifically adsorbed anion by adsorption of CO; the voltammograms are characteristic of the crystal orientations that can be utilized as the fingerprint.

Figure 1 demonstrates the voltammograms of some of the $\text{Cu(S)}-[n(100) \times (111)]$ electrodes employed in the present study. The voltammograms of $\text{Cu}(100)$ ($n = \infty$), reported in our previous paper,^{14c} are presented here for comparison. The $\text{Cu}(100)$ gives a sharp peak at -0.70 V with a small shoulder at -0.72 V. The $\text{Cu}(311)$ ($n = 2$) gives a single peak at -0.83 V. Other two electrodes show the intermediate features between the $\text{Cu}(100)$ and the $\text{Cu}(311)$. With the increase of (111) step atom density or the decrease of n value, the sharp peak at -0.70 V diminishes and the wider peak at -0.72 to -0.77 V grows, as shown in the $\text{Cu}(111)$ ($n = 6$) and the $\text{Cu}(711)$ ($n = 4$). The profile of the voltammograms will be discussed in connection with the surface atom configuration in more detail elsewhere.

Electrochemical Reduction of CO_2 at Copper Single-Crystal Electrodes. The formation rates of the gaseous products remained virtually constant, and “deactivation of copper electrode”, reported by several workers,⁷ was not observed during the electrolysis for 1 h. If the pre-electrolysis is properly conducted to remove impurities contained in any chemical reagent in ppm to sub-ppm level, so-called “deactivation of copper electrode in prolonged electrolysis” does not take place, as pointed out in our previous paper.¹⁵

The product distributions from the electrodes of various crystal orientations are tabulated in Table 1 in terms of the current efficiency together with n value. CH_4 , C_2H_4 and CO were produced as the gaseous products with small amount of H_2 . Acetaldehyde, ethanol, propionaldehyde, allyl alcohol, n -propanol, formic acid, and acetic acid were detected as soluble products in the electrolyte solution. The total current efficiency amounted approximately to 100%. This fact verifies that the major products were accurately analyzed in the present experimental procedures.

Two electrolysis data are given for some crystal orientations for the purpose of comparison. One can see that the reproducibility is good, considering that the reaction takes place at the solid-liquid interface. The shape of the voltammograms, measured after the electrolysis for 1 h, did not change greatly and showed features identical to those before the electrolysis. Thus the crystal orientation remains stable.

TABLE 1: Product Distribution in the Electrochemical Reduction of CO_2 at a Series of Copper Single Crystal Electrodes $\text{Cu(S)}-[n(100) \times (111)]^a$

crystal orientation	$n(100)-(111)$ n	potential V vs SHE	current Efficiency/%													$\text{C}_2\text{H}_4/\text{CH}_4$
			CH_4	C_2H_4	CO	H_2	MeD ^b	EtOH ^b	PrD ^b	AlOH ^b	PrOH ^b	HCOOH	CH_3COOH	C2+ ^c	total	
(100)	∞	-1.39	19.8	40.7	1.9	10.3	1.0	12.8	1.2	0.7	1.6	11.7	2.5	58.0	104.2	2.1
(111)	6	-1.38	15.0	45.3	1.9	13.0	0.8	12.5	1.7	1.6	2.4	6.1	1.7	64.3	102.0	3.0
(911)	5	-1.36	5.4	48.2	0.6	12.4	0.4	17.9	10.5	0.8	1.6	3.2	n.a. ^d	79.4	101.0	8.9
(711)	4	-1.37	6.9	58.5	1.3	13.1	0.4	9.7	0.4	3.9	6.1	3.6	n.a.	79.0	103.9	8.5
(711)	4	-1.34	3.8	51.6	2.1	13.7	0.5	5.7	10.4	1.3	3.4	4.8	n.a.	72.9	97.3	13.6
(511)	3	-1.35	11.0	37.7	2.4	20.3	4.2	8.8	5.1	1.9	3.8	8.0	n.a.	61.5	103.2	3.4
(311)	2	-1.37	35.3	24.4	3.1	15.5	6.2	3.8	2.7	1.0	2.3	12.1	n.a.	40.4	106.4	0.7
(311)	2	-1.37	35.9	23.7	2.8	15.0	0.3	3.7	1.8	0.7	1.9	18.6	0.6	32.1	105.0	0.7
(111)		-1.52	50.5	8.8	4.9	13.1	2.6	5.3	0.0	tr ^e	tr	16.6	1.1	16.7	102.9	0.2

^a Electrolyte solution: 0.1 M KHCO_3 . Current density: 5 mA cm^{-2} . ^b MeD: acetaldehyde, EtOH: ethanol, PrD: propionaldehyde, AlOH: allyl alcohol, PrOH: propanol. ^c C2+ contains all the substances that have more than two carbon atoms except CH_3COOH . ^d n.a.: not analyzed. ^e tr: less than 0.05%.

TABLE 2: Product Distribution in the Electrochemical Reduction of CO₂ at a Series of Copper Single Crystal Electrodes Cu(S)-[*n*(100) × (110)]^a

crystal orientation	<i>n</i> (100)-(110) <i>n</i>	potential V vs SHE	current efficiency/%													C ₂ H ₄ / CH ₄
			CH ₄	C ₂ H ₄	CO	H ₂	MeD ^b	EtOH ^b	PrD ^b	AlOH ^b	PrOH	HCOOH	CH ₃ COOH	C ₂ + ^c	total	
(100)	∞	-1.39	19.8	40.7	1.9	10.3	1.0	12.8	1.2	0.7	1.6	11.7	2.5	58.0	104.2	2.1
(610)	6	-1.37	9.8	44.0	2.7	12.3	1.4	15.7	3.4	1.6	0.0	4.8	3.1	66.1	98.8	4.5
(510)	5	-1.37	5.5	46.4	1.5	11.4	1.2	19.3	1.3	1.0	2.1	10.3	1.6	71.3	101.6	8.4
(310)	3	-1.42	15.3	34.3	1.2	13.9	0.4	19.1	2.9	0.7	0.3	3.6	3.8	57.7	95.5	2.2
(210)	2	-1.52	60.5	11.6	2.6	7.3	0.4	6.6	0.3	0.0	0.3	8.2	1.3	19.2	99.1	0.2

^a Electrolyte solution: 0.1 M KHCO₃, Current density: 5 mA cm⁻² ^b MeD: acetaldehyde, EtOH: ethanol, PrD: propionaldehyde, AlOH: allyl alcohol, PrOH: propanol. ^c C₂+ contains all the substances which have more than two carbon atoms except CH₃COOH.

The product distribution is significantly affected by the crystal orientation. The Cu(111) electrode gives rise to CH₄ formation with the current efficiency as high as nearly 50% at highly negative potential. Ethylene formation on the Cu(111) is less than 10%. Formation of CO is higher than the other crystal orientations. The Cu(111) surface of fcc crystals has the lowest dangling bond density, and the surface is relatively stabilized. Thus CO, intermediately formed in CO₂ reduction, will not strongly interact with (111) and may easily be released from the electrode surface.

C₂H₄ formation gradually increases for *n* down to 4, as shown in Table 1, and again decreases for *n* below 4. The C₂+ value, which contains C₂H₄, ethanol, allyl alcohol, *n*-propanol, acetaldehyde, and propionaldehyde, shows a similar trend with C₂H₄. C₂+ exceeds 70% at *n* 4 to 5. CH₄ formation steeply diminishes simultaneously, taking a minimum at *n* = 4 to 5. The selectivity ratio C₂H₄/CH₄ in terms of the current efficiency reaches 9 to 14 at the Cu(711). This value is 2 at the (100) surface, and 0.2 at the (111) surface. Thus the C₂H₄/CH₄ value ranges 2 orders of magnitude by introduction of the (111) step to the (100) basal plane.

Table 2 shows the results from the series Cu(S)-[*n*(100) × (110)], in which the (100) basal plane is modified by introduction of (110) steps. The features are quite similar to Table 1. C₂H₄ formation once increases and decreases; CH₄ steeply decreases and increases again. The C₂H₄/CH₄ value takes 8 at *n* = 5. Thus the introduction of step atoms into the (100) terrace, regardless of (111) step or (110) step, activates C₂H₄ formation and suppresses CH₄ formation. It is interesting that the crystal orientations composed of 4 to 6 atomic rows of (100) terrace are the most active in ethylene formation.

The electrode potential for Cu(S)-[*n*(100) × (110)] is nearly constant and relatively positive, -1.3 to -1.4 V vs. SHE in comparison with the highly negative potential at Cu(111), whereas the potential for Cu(S)-[*n*(100) × (110)] shifts to the negative value with the increase of step atom density. We are proceeding to reveal the mechanism by which the atomic configuration is related to the electrocatalytic activity of the electrode surface and the reason why C₂+ formation is activated by insertion of step atoms.

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