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Kinetics of Electrochemical Reduction of Carbon Dioxide on a Gold Electrode in Phosphate Buffer Solutions

Hidetomo Noda,# Shoichiro Ikeda,* Akio Yamamoto, ## Hisahiko Einaga, and Kaname Ito

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

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The kinetics of the CO formation by electrochemical reduction of carbon dioxide on a gold electrode investigated in a series of potassium phosphate buffer solutions. CO is the principal product under the above condition. Small amounts of hydrocarbons, such as CH_4, C_2H_4, and C_2H_6, are detected in the solutions of pH 5.2, 6.2, and 6.8. The Tafel slopes of the partial current density for the CO formation, I_{CO}, at different pH are all ca. −120 mV/decade. The reaction mechanism has been proposed on the basis of the relationships between I_{CO} and the electrode potential and between I_{CO} and the reaction order with respect to CO_2, which is ca. 1.

Gold metal is one of the useful catalysts for the formation of carbon dioxide (CO_2) from carbon monoxide (CO) and O_2, and for the decomposition of CO_2.[1—8] The electrochemical oxidation of CO to CO_2 on the Au electrode was first investigated by Roberts and Sawyer in order to determine the concentration of CO in solutions by an electroanalytical method.[9] Later, a few reports concerning the electrooxidation of CO on Au were published.[10—12] Recently, Kita et al. have also examined the anodic oxidation of CO on the Au electrode in acidic and alkaline solutions.[13]

On the other hand, the selective formation of CO from CO_2 on the Au electrode was reported by Hori et al.[14,15] In the previous paper,[16] the authors have confirmed the formation of CO from CO_2 on Au and have indicated that the partial current density for the reaction on Au is higher than that on the other metals. The Au metal is interesting, because it is electrochemically active for the CO oxidation and the CO_2 reduction (i.e. the CO formation). However, a detailed investigation has not been made on the mechanism of the CO formation. Likewise, the knowledge and understanding of the mechanism for the reaction on the Au electrode may lead to insights into the early stage of the hydrocarbon formation reaction from CO_2 which is expected to proceed from CO_2 to the hydrocarbon via CO or CO related species.[17]

In the present paper, the electrochemical reduction (electroreduction) of CO_2 on the Au electrode is studied in potassium phosphate buffer solutions at different pH values (2.5—6.8) with the intention to detect any adsorbate which originates from CO_2. A reaction mechanism will be proposed.

Experimental

A solid Au foil of 99.95% was used as the working electrode. The geometrical area of the electrode was 4.5 cm^2. A Pt foil electrode of 6.0 cm^2 served as a counter electrode. The electrode potential was referred to a silver–silver chloride electrode saturated with KCl. Pretreatment of the working electrode was made as follows; it was polished with alumina powder (particle size: 0.05 μm) and was etched in hot aqua regia for 30 s. Thereafter, the electrode was rinsed with doubly-distilled water.

The electrolytic cell and cyclic gas flow system employed were the same as described in the previous paper.[16] The electrolytic solutions were prepared from appropriate amounts of reagent grade K_3PO_4, K_2HPO_4, KH_2PO_4, and H_3PO_4, and doubly-distilled water. The concentration of phosphate in the aqueous solutions was kept at 0.1 $mol\,dm^{-3}$. The pH values of the solutions were maintained at ca. 2.0, 4.3, 5.2, 6.2, and 6.8 when they were saturated with CO_2, CO, N_2, or He. These solutions were pre-electrolyzed for 12 h with platinized Pt electrodes as the working and counter electrodes at a current density of 40 μA cm^{-2} under a N_2 atmosphere. The reactant gas was purified by passing it through an activated copper column and then through a trap containing the same electrolytic solution. CO_2 gas was diluted with helium gas when necessary.

The potentiometric electrolysis for 40 C and the analysis of the reduction products were carried out in the same manners as described in the previous paper.[16] The anodic stripping voltammetry was carried out using a potentiostat, HA-301 (Hokuto Denko), a function generator, HB-105 (Hokuto Denko), and an X–Y recorder, BW-201 (Rikadenki Kogyo).

#Present address: Chubu Electric Power Company, Inc., Kitasekiyama, Odaka-cho, Midori-ku, Nagoya 459.
##Present address: Wako Research Center, Honda R & D Co., Ltd., 1-4-1, Chuo, Wako-shi 351-01.

Results and Discussion

Interaction between Au and Carbon Dioxide. The interaction between Au and CO_2 was examined by recording variations of the rest potential with time under open circuit conditions. A typical result for the variations in the solution of pH 6.8 is illustrated in Fig. 1. The initial pH of the solution saturated with N_2 was 12.7; the rest potential was ca. −0.08 V. After the electrode potential became stable, the CO_2 gas was added to the solution. The potential gradually moved in the positive direction. Finally, the potential became ca. 0.3 V and the solution pH became ca. 6.8. In the blank solution saturated with N_2 (pH 6.8), the rest potential denoted by the dashed line was stable at ca. 0.3 V. The above findings show that the rest potential depends on only the variations of pH in relation to the CO_2 addition and there exists no or little interaction between Au and CO_2 under open circuit conditions.

As was described in the preceding paper,[16] the Au cathode produces mainly CO, with a smaller amount of $HCOO^-$. Species related to the CO_2 reduction have some interaction with Au under open circuit conditions (cf. Fig. 1). Since the Au cathode is effective for the reduction of CO_2 to CO at the more negative potentials, the interaction between Au and CO_2 may occur as the surface charge density on Au becomes higher than that under open circuit conditions.

pH Dependence of Formation of CO on Au Electrode. Figures 2 and 3 show the faradaic efficiency–potential curves for the formation of CO from CO_2 and H_2 in the buffer solutions (pH 4.3—6.8) on the Au cathode. $HCOO^-$ was not detected. It is apparent from Fig. 2 that the more negative the electrode potential becomes, the larger the faradaic efficiency for the CO formation in the solutions of pH 4.3 and 5.2. The efficiency increases from −1.20 V, passes through a maximum at −1.40 to −1.50 V, and then decreases as the potential moves in the negative direction in solutions of pH 6.2 and 6.8. In addition, there is a tendency that the higher the pH becomes, the larger the maximum efficiency for the CO formation is. The formation of small amounts of hydrocarbons is observed in the so-

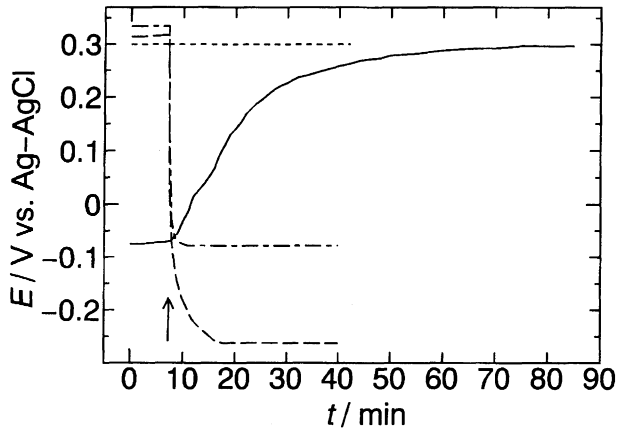


Fig. 1. Variation of the electrode potential with time under the open circuit condition in the 0.1 M (1 M=1 mol dm^{-3}) potassium phosphate buffer solution (pH 6.8) after the addition (arrow in the figure) of CO_2, CO, and 2 mmol $HCOO^-$ into the solution. ---: N_2, —: CO_2, -------: CO, ------: $HCOO^-$.

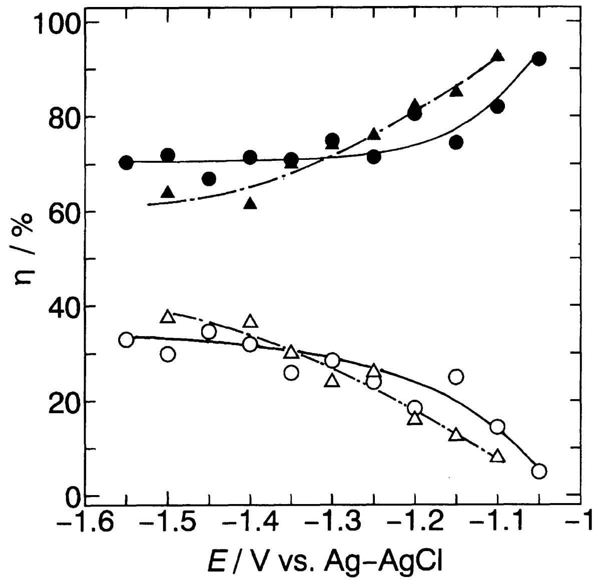


Fig. 2. Faradaic efficiency, η, –potential curves for the formation of CO (○: pH 4.3, △: pH 5.2) and H_2 (●: pH4.3, ▲: pH 5.2) on the Au electrode in the potassium phosphate buffer solutions of pH 4.3 and 5.2. Quantity of electricity passed: 40 C.

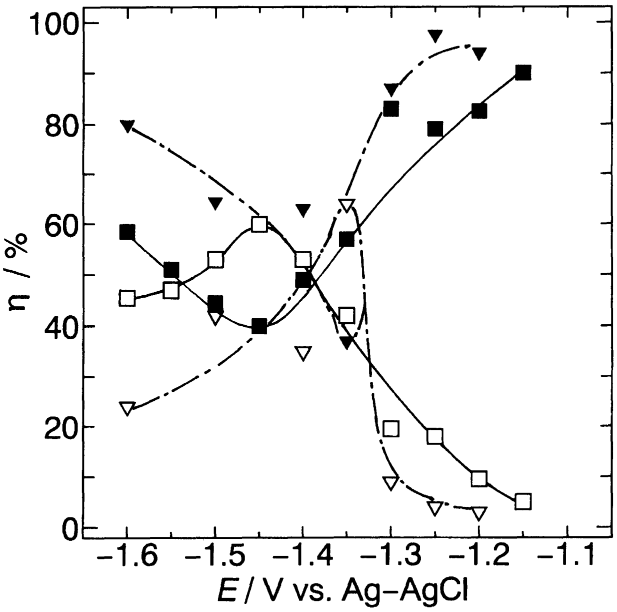


Fig. 3. Faradaic efficiency, η, –potential curves for the formation of CO (□: pH 6.2, ▽: pH 6.8) and H_2 (■: pH 6.2, ▼: pH 6.8) on the Au electrode in the potassium phosphate buffer solutions of pH 6.2 and 6.8. Quantity of electricity passed: 40 C.

lutions of pH 5.2, 6.2, and 6.8. Typical results for the formation of hydrocarbons are listed in Table 1. No hydrocarbon was detected below pH 5.

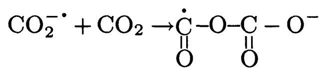
As described above, Au is active for the formation from CO_2 in the aqueous phosphate buffer solutions. On the other hand, in nonaqueous solutions, the CO formation has been observed in the CO_2 reduction on various metal electrodes.[18—20] Saveant et al.[19] have proposed the following mechanisms:

(A) Overall reaction:

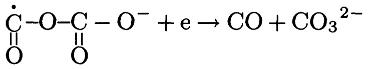
$$2CO_2 + 2e \rightarrow CO + CO_3{}^{2-} \quad (1)$$

and elementary steps:

$$CO_2 + e \rightarrow CO_2^{-\bullet} \quad (2)$$

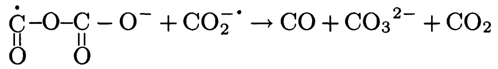


$$CO_2^{-\bullet} + CO_2 \rightarrow \underset{\underset{O}{\|}}{\dot{C}}\text{-O-}\underset{\underset{O}{\|}}{C} - O^- \quad (3)$$



$$\underset{\underset{O}{\|}}{\dot{C}}\text{-O-}\underset{\underset{O}{\|}}{C} - O^- + e \rightarrow CO + CO_3{}^{2-} \quad (4)$$

or



$$\underset{\underset{O}{\|}}{\dot{C}}\text{-O-}\underset{\underset{O}{\|}}{C} - O^- + CO_2^{-\bullet} \rightarrow CO + CO_3{}^{2-} + CO_2 \quad (5)$$

On the other hand, it is necessary to take into account the participation of proton donors in this reaction in the aqueous solutions:

(B) Overall reaction:

$$CO_2 + H^+B^- + 2e \rightarrow CO + OH^- + B^- \quad (6)$$

and elementary steps:

$$CO_2^{-\bullet} + H^+B^- + e \rightarrow CO + OH^- + B^- \quad (7)$$

or

$$CO_2^{-\bullet} + H^+B^- \rightleftharpoons COOH(ads) + B^- \quad (8)$$

$$COOH(ads) + e \rightarrow CO + OH^- \quad (9)$$

or

$$H^+B^- + e \rightarrow H(ads) + B^- \quad (10)$$

$$H(ads) + CO_2 + e \rightarrow CO + OH^- \quad (11)$$

or

$$H(ads) + CO_2^{-\bullet}(ads) \rightarrow CO + OH^- \quad (12)$$

Table 1. Faradaic Efficiencies for the Formation of Hydrocarbons from CO_2 on the Au Electrode in the Potassium Phosphate Buffer Solutions at 298 K

pH of	Potential, E	Faradaic efficiency/%				
solution	V vs. Ag–AgCl	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
5.2	−1.15	0.01	n	n	n	n
	−1.20	0.02	n	n	n	n
	−1.25	n	n	n	n	n
	−1.30	0.04	n	n	n	n
6.2	−1.15	0.30	n	0.14	n	n
	−1.20	0.60	n	0.22	n	0.10
	−1.25	0.30	n	n	n	n
	−1.30	1.19	0.11	n	n	n
	−1.35	0.30	n	0.10	n	n
	−1.40	0.10	n	n	n	n
	−1.45	0.10	n	0.04	n	n
	−1.50	n	n	n	n	n
6.8	−1.20	0.40	0.05	0.18	0.06	0.13
	−1.25	0.73	0.08	0.29	0.09	0.21
	−1.30	0.99	0.10	0.36	0.11	0.24
	−1.35	t	t	t	t	t
	−1.40	0.61	0.06	0.18	0.07	0.10
	−1.50	0.30	0.04	0.09	0.04	0.05
	−1.60	0.03	n	n	n	n

n: not detected, t: trace amount, quantity of electricity passed: 40 C.

Here, the standard potential of the reaction (1) has been reported to be ca. −1.27 V, while that of (6) to be ca. −0.7 V (pH 6.8).[21]

On the basis of the results obtained by the electrolysis (cf. Figs. 2 and 3), the partial current density for the formation of CO, I_{CO}, was estimated from the following equation:

$$I_{CO} = Q\ F_{CO}/(A\ t) \quad (13)$$

where F_{CO} denotes the faradaic efficiency for the formation, t the operation time, Q the quantity of electricity passed, and A the electrode area. The potential dependence for I_{CO} in solutions of different pH is illustrated in Fig. 4. Log I_{CO} is proportional to E in the potential

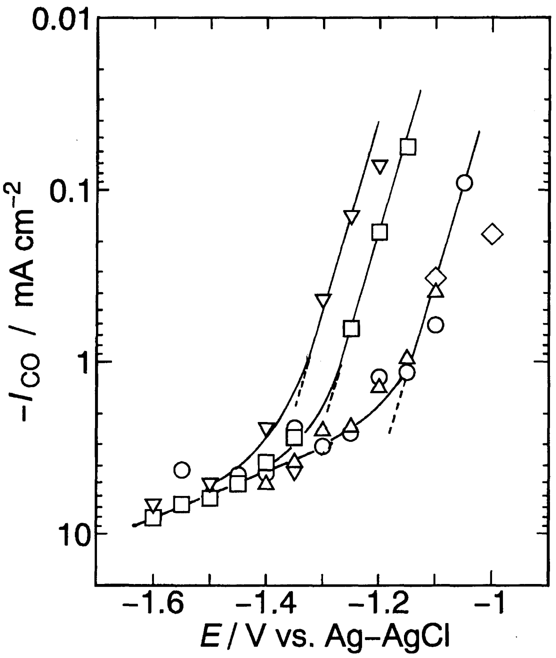


Fig. 4. Relationship between the partial current density for the formation of CO and the electrode potential on the Au electrode in the potassium phosphate buffer solutions at different pH. ◇: pH 2.5, ○: pH 4.3, △: pH 5.2, □: pH 6.2, ▽: pH 6.8.

region of −1.0 to −1.2 V in solutions of pH 2.5, 4.3, and 5.2, in the region of −1.1 to −1.3 V in that of pH 6.2, and in the region of −1.2 to −1.4 V in that of pH 6.8. The relationship can be written as follows:

$$E = \text{const} - (120 \pm 10)\log I_{\text{CO}} \tag{14}$$

Here, the Tafel slope is estimated to be ca. −120 mV/decade.

It is also found that I_{CO} at a constant potential is independent of the solution pH in the solutions of pH 2.5, 4.3, and 5.2, while I_{CO} is dependent on the solution pH in the solutions of pH 6.2 and 6.8. The concentration of the reactant is considered to be unchanged by the solution pH in the range of pH 1 to 7, because the partial current density for the $HCOO^-$ formation on the metal electrodes has been reported to be independent of the solution pH[22—24] and a limiting current of mass transfer observed less than −1.4 V (cf. Fig. 4) is also independent of the solution pH. The pH dependence of I_{CO} in the low overpotential region implies the participation of H^+ in the reaction or a decrease of the activity for the CO formation on Au with variation of pH.

Anodic Stripping Voltammetry of Adsorbates Au from CO_2. If the stable adsorbates which originate from CO_2 cover the Au surface, the reaction rate for the CO formation as well as the H_2 evolution is expected to be suppressed by the adsorbates. Furthermore, the decrease of I_{CO} may be caused by formation of poisonous species when the solution pH becomes high. The production of adsorbate on Au has been reported to occur in the alkaline solutions saturated with CO.[13] Therefore, the oxidation current for poisonous species was followed by means of anodic stripping voltammetry in the buffer solution (pH 6.8). A typical voltammogram after polarization at −1.2 V for 15 min is shown in Fig. 5 (A). Two oxidation peaks are observed in the potential region of −1.2 to +1.2 V. The first peak at ca. +0.1 V may correspond to the oxidation current for the bulk-CO, because a similar peak is observed in the solution saturated with CO as shown in Fig. 5 (B). The second peak at ca. +1.0 V indicates formation of surface oxide on Au. However, no stable adsorbate on Au was detected, because the oxidation current of bulk-CO was large and was seen over a wide potential range.

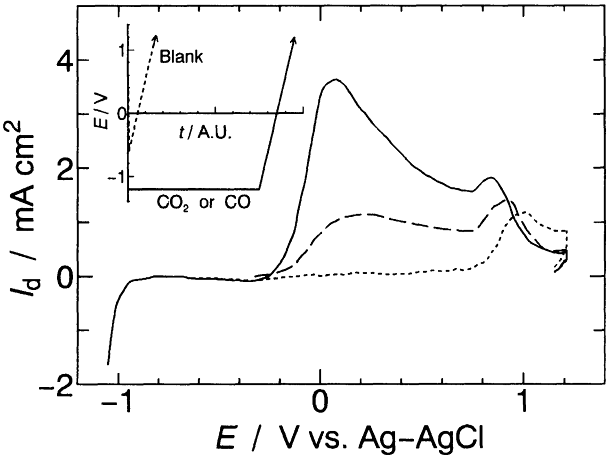


Fig. 5. Voltammograms on the Au electrode in the potassium phosphate buffer solution of pH 6.8 after the polarization at −1.2 V for 15 min: (solid line). Dotted and dashed lines correspond to the voltammograms for the blank and for the CO oxidation on the Au electrode in the buffer solution of the same pH, respectively. Sweep rate: 100 mV s^{-1}. Inserted figure represents the change of the applied potential.

The electrode was polarized at −1.0 V for 15 min in the CO_2 saturated solution (pH 6.8), and then at −0.6 V for another 20 min under N_2 atmosphere. The voltammogram, as shown in Fig. 6 (A), indicates that the oxidation current is detected at a peak potential of ca. +0.45 V. The peak current decreases as pH is lowered below 6.2 and disappears at pH 5.2. It is also found that the peak current, I_{P}, is proportional to the scan rate, v, as shown in Fig. 7. This finding assumes that the peak corresponds to the oxidation current of the adsorbates, analogous to those obtained by the CO adsorption (cf. Fig. 6 (B)). Consequently, I_{CO} and the activity of Au for the reaction decrease with the variation of pH above 5.2, because the adsorbates are formed on Au and behave as poisonous species for the CO formation. Hence, I_{CO} is expected to be independent of

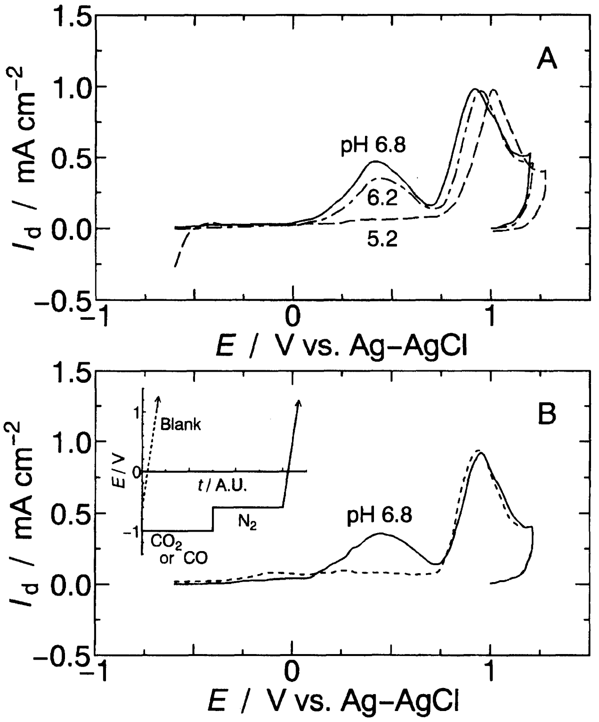


Fig. 6. Anodic stripping voltammograms on the Au electrode for the oxidation of the adsorbates, (A): from CO_2 and (B): from CO and the blank test, after polarization at −1.0 V in the potassium phosphate buffer solutions of different pH. Sweep rate: 100 mV s^{-1}.

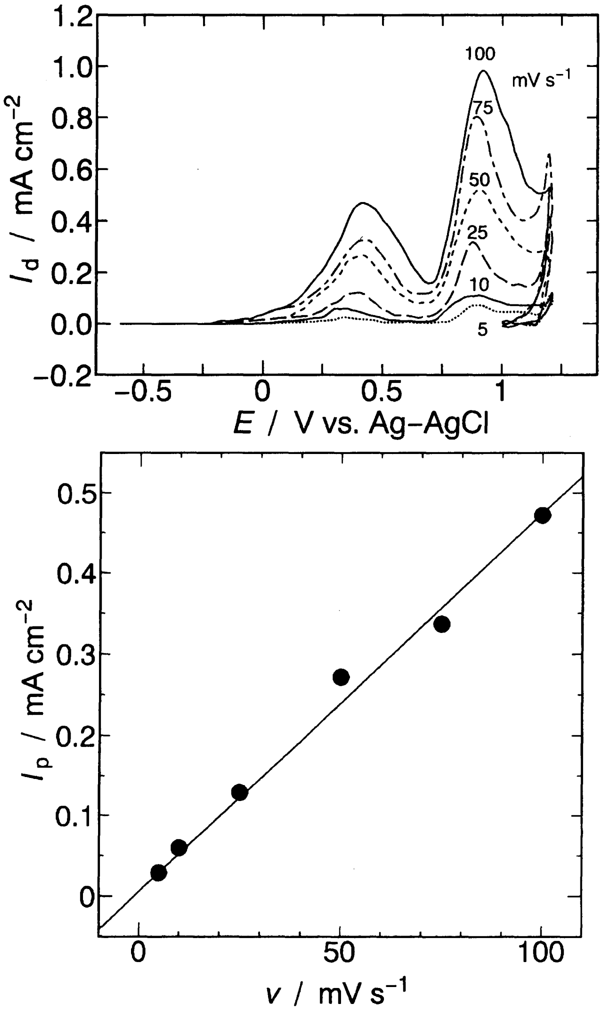


Fig. 7. Anodic stripping voltammograms on the Au electrode at the different sweep rates in the potassium phosphate buffer solution of pH 6.8: (A) (Numbers in the figure represent the sweep rate). The relationship between the peak current for the oxidation of the adsorbates from CO_2 and the sweep rate on the Au electrode: (B).

Table 2. Quantities of Electricity Passed during the Oxidation of the Adsorbates on the Au Electrode in the Potassium Phosphate Buffer Solutions

pH of solution	E_c/V vs. Ag–AgCl	P_{CO_2}/kPa	Q_{OX}/mC
4.3	−1.00	103	0
5.2	−1.00	103	0
6.2	−1.00	103	0.59
6.8	−1.00	103	0.98
6.8	−1.20	103	1.03
6.8	−1.35	103	0.66
6.8	−1.35	56	0.69
6.8	−1.35	42	0.67
6.8	−1.35	26	0.69

Time for the cathodic polarization was 15 min. E_c; the potential for the cathodic polarization, P_{CO_2}; the partial pressure of CO_2, Q_{OX}; the quantity of electricity passed during oxidation of adsorbates.

the solution pH in the solutions of pH 6.2 and 6.8 at a constant potential so long as the adsorbate is absent from the Au surface.

Table 2 shows the dependence of the quantities of electricity passed in the oxidation of the adsorbates, Q_{OX}, on the potential for the cathodic polarization, E_C, and the dependence of these on the CO_2 pressures, P_{CO_2}. It is found that the value of Q_{OX} is similar at the E_C of −1.0 and of −1.2 V. Q_{OX} decreases by one thirds as E_C becomes −1.3 V. On the other hand, Q_{OX} is independent of P_{CO_2}. These findings indicate that the amount of the adsorbate on the Au surface is dependent on the E_C, but independent of P_{CO_2}; i.e., the concentration of intermediate species on the Au surface, which is involved in the formation of the adsorbate, and the concentration of the adsorbate, may determine the amount of the adsorbate and the concentration of the intermediate species on the surface may depend on the electrode potential.

Reaction Order with Respect to Carbon Dioxide. The reaction order with respect to CO_2 was determined in the buffer solutions of pH 4.3 and 6.8 by measuring I_{CO}. Typical results obtained at −1.15 V in the solution of pH 4.3 and at −1.35 V in that of pH 6.8 are shown in Fig. 8 in the form of a $\log I_{CO}$ vs. $\log P_{CO_2}$, where the reaction order, m, is defined as follows:

$$I_{CO} = \text{const}\ P_{CO_2}{}^{m}\ \exp(-FE/\ 2RT) \qquad (15)$$

$$m = (\partial\ \log I_{CO}/\partial\ \log P_{CO_2})_{E,T} \qquad (16)$$

As shown in Fig. 8, the reaction order with respect to CO_2 is estimated to be about unity. Thus, it is ex-

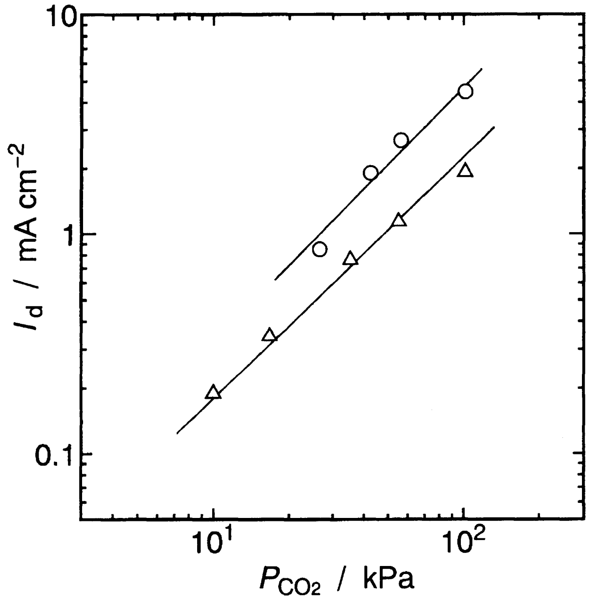


Fig. 8. Relationship between the partial current density for the CO formation and the CO_2 pressure on the Au electrode at the constant potential in the potassium phosphate buffer solutions at 298 K. ○ at −1.35 V and pH 6.8, △: at −1.15 V and pH 4.3.

pected that the formation of CO from CO_2 on the Au electrode is of the first order with respect to CO_2. If the disproportionation reaction represented by the sequence of Eqs. (2)→(3)→(4) or (2)→(3)→(5) is valid, I_{CO} should be proportional to $(P_{CO_2})^{2 \text{ or } 3}$. However, the present results indicate that the reaction is of the first order with respect to CO_2. In addition, the CO formation in this media occurs at the potentials more positive than −1.27 V, which is the standard potential of the reaction (1). Hence, the CO formation on Au proceeds by a mechanism different from those expressed by Eq. 1 to Eq. 5.

Reaction Mechanism for the Formation of Carbon Monoxide from Carbon Dioxide on Au Electrode. As described above, the mechanisms written by Eqs. 1, 2, 3, and 4 and/or Eq. 5 are not valid in the present systems. The proton donor is expected to be involved in this reaction (cf. Eq. 6). However, the Tafel plots (cf. Fig. 4) indicate that the proton donor does not take part in the rate determining step (r.d.s.) in the solution of pH 2.5—5.2. Likewise, in the solution of pH 6.2 and 6.8, I_{CO} at a constant potential should also be independent of the solution pH so long as the adsorbate is not formed on the Au surface, as mentioned before. Therefore, the proton donor may be involved in the fast reactions. There is also a possibility that the proton donor is reduced to activated hydrogen species (H(ads)?) and it reacts with CO_2 (cf. Eqs. 10 and 12). However, the reduction in the initial step of the proton donor can be ruled out, because $CO_2^{-\bullet}$ has been observed on some metal electrodes by spectroscopic techniques[25,26] and the formation of $CO_2^{-\bullet}$ is an acceptable step.[21] Thus, the mechanisms expressed by Eqs. 2 and 7 or Eqs. 2, 8, and 9 are preferable to other mechanisms. The calculated Tafel slope and the reaction order of CO_2 on the reaction Eqs. 2 and 7 and Eqs. 2, 8, and 9 are listed in Table 3, where the Langmuir-type isotherm is assumed for adsorption of $CO_2^{-\bullet}$ with coverage θ.[27] When reaction Eq. 2 is the r.d.s. of Mechanism A or B, the Tafel slope and the reaction order of CO_2 for both mechanisms should be $-2.3\ RT/F$ and unity at $\theta \rightarrow 0$, respectively, and are in agreement with the experimental results. Moreover, the degree of coverage of $CO_2^{-\bullet}$ on some metals has been reported to be less than 0.2 at maximum by measurement with the spectroscopic techniques and impedance methods.[18,22,23,25,26] These facts support the conclusion that the degree of coverage of $CO_2^{-\bullet}$ is low on Au. Thus, it is concluded that the reaction Eq. 2 is the r.d.s. In addition, the rate for the proton transfer reaction from H_2O to $CO_2^{-\bullet}$ has been reported to be rapid; the value of the rate constant was ca. 5.5 $\text{mol}^{-1}\,\text{s}^{-1}$.[25] This also supports a possibility that the CO formation proceeds via reaction Eq. 8. If the proton transfer occurs from the proton donor to $CO_2^{-\bullet}$, the H site of H^+B^- may react with the O site of $CO_2^{-\bullet}$.

Thus, the authors propose the following mechanism for the CO formation on the Au electrode:

$$CO_2 + e \nrightarrow CO_2^{-\bullet}(\text{ads}) \tag{2}$$

$$CO_2^{-\bullet}(\text{ads}) + H^+B^- + e \rightarrow CO + OH^- + B^- \tag{7}$$

or

$$CO_2 + e \nrightarrow CO_2^{-\bullet}(\text{ads}) \tag{2}$$

$$CO_2^{-\bullet}(\text{ads}) + H^+B^- \rightarrow COOH(\text{ads}) + B^- \tag{8}$$

$$COOH(\text{ads}) + e \rightarrow CO + OH^- \tag{9}$$

Conclusion

The results are summarized as follows:

(i) The principal product of the CO_2 reduction on the Au electrode is CO in the potassium phosphate buffer solutions. Small amounts of hydrocarbons, such as CH_4, C_2H_4, and C_2H_6, are detected in the solutions of pH 5.2, 6.2, and 6.8.

(ii) From the relationship of $\log I_{CO}$ vs. E at different pH, the Tafel slopes are ca. −120 mV/decade; I_{CO} at the constant potential decreases with increasing the solution pH above 5.2.

(iii) Formation of the adsorbates on Au similar to species originating from CO is observed in the solutions of pH 6.2 and 6.8.

(iv) The reaction order with respect to CO_2 is ca. 1.

(v) Some reaction mechanisms are proposed: they are represented by Eqs. 2 and 7 or Eqs. 2, 8, and 9.

Table 3. Parameters for the CO Formation in the Electrochemical Reduction of Carbon Dioxide (Theoretical)

Rate-determining step	Eq.	Tafel slope		Reaction order of CO_2	
	No.	$\theta \rightarrow 0$	$\theta \rightarrow 1$	$\theta \rightarrow 0$	$\theta \rightarrow 1$
A $CO_2+e \rightarrow CO_2^{-\bullet}(\text{ads})$	2	$-2/f$	—	1	—
$CO_2^{-\bullet}(\text{ads})+H^+B^-+e \rightarrow CO+OH^-+B^+$	7	$-2/3f$	$-2/f$	1	0
B $CO+e \rightarrow CO_2^{-\bullet}(\text{ads})$	2	$-2/f$	—	1	—
$CO_2^{-\bullet}(\text{ads})+H^+B^- \rightleftarrows COOH\ (\text{ads})$	8	$-1/f$	$-\infty$	1	0
$COOH(\text{ads})+e \rightarrow CO+OH^-$	9	$-2/3f$	$-2/f$	1	0

θ: Coverage of $CO_2^{-\bullet}$(ads), f: F/RT. Transfer coefficient was assumed to be 0.5.

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