

Product Selectivity Affected by Cationic Species in Electrochemical Reduction of CO₂ and CO at a Cu Electrode¹⁾

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Electroreduction of CO₂ and CO was studied with a copper electrode in hydrogencarbonate solutions of various cations. Product selectivity was greatly affected by cationic species as well as HCO₃⁻ concentration. H₂ evolution prevailed over CO₂ reduction in Li⁺ electrolyte, whereas CO₂ reduction was favorable in Na⁺, K⁺, and Cs⁺ solutions. C₂H₄ formation became greater than CH₄ with increase of the cation size, i.e. with sequence of Li⁺, Na⁺, K⁺, Cs⁺. The variation of the product selectivity caused by cationic species is rationalized by the difference of outer Helmholtz plane (OHP) potential. The OHP potential will vary with cationic species in accordance with the degree of specific adsorption. The concentration of H⁺ at the electrode will depend upon the OHP potential, since H⁺ is a charged species. This difference of pH at the electrode will lead to the variation of product selectivity.

Metallic copper is an effective electrocatalyst for reduction of CO and CO₂ to CH₄, C₂H₄, and alcohols as firstly reported by the present authors.^{2–5)} Other investigators also confirmed the formation of hydrocarbons and alcohols at Cu electrodes.^{6–10)} The electroreduction of CO₂ at Cu proceeds with intermediate formation of CO adsorbed on the electrode as reported in the previous paper.^{5,11)} In the course of this study, we found that the product selectivity is significantly affected by cationic species of aqueous electrolyte. The present paper reports the experimental results, discussing the model.

Experimental

A copper electrode (99.999%, 2 cm×2 cm) was electroplished in concentrated phosphoric acid. Aqueous 0.1 M hydrogencarbonate solutions of Li, Na, K, and Cs were employed as the electrolytes, prepared with doubly distilled deionized water. LiHCO₃ and CsHCO₃ solutions were prepared by dissolving the respective carbonate and saturating with CO₂. The solubility of Li₂CO₃ is 1.31 g in 100 g of saturated solution, or 0.18 M at 20 °C.¹²⁾ The upper limit of concentration of LiHCO₃ is thus 0.36 M (1 M=1 mol dm⁻³). The electrolytes were purified by pre-electrolysis with a Pt black cathode. Coulometric measurements were conducted in a three compartment cell in which two anode compartment faced each side of the cathode. The cathode compartment was separated from two anodes with sheets of cation-exchange membrane. Electrolysis was carried out at 18.5 °C

with controlled current densities. The cathode potential was measured with respect to an Ag/AgCl reference electrode, corrected for the IR drop by a potentiostat equipped with a positive feedback electronic circuit. Effluent gas from the cell was analyzed by gas chromatographs. Alcohols and formate ion dissolved in the electrolyte were analyzed by a gas chromatograph and an ion chromatograph after electrolysis. Other experimental details were described elsewhere.¹¹⁾

Results

Some measurements were carried out for 1 h. The concentration of gaseous products remained nearly constant during coulometric measurements. Thus most of the works were conducted for 30 min. Table 1 presents average faradaic efficiencies of products in electroreduction of CO₂ in 0.1 M various hydrogencarbonate solutions with constant current density 5.0 mA cm⁻². The sums of the faradaic efficiencies are close to 100%; the tabulated substances will be the major products of this reaction. H₂ evolution is favorable with the sequence of Li⁺>Na⁺>Cs⁺>K⁺. The faradaic efficiencies of CH₄ and C₂H₄ depend greatly upon cationic species. The highest value of methane formation takes place in Na⁺ electrolyte. C₂H₄ formation is the most favorable in Cs⁺ electrolyte. CH₄/C₂H₄ faradaic efficiency ratio C₁/C₂ increases in the order of Cs⁺<K⁺<Na⁺<Li⁺. C₂H₅OH and *n*-C₃H₇OH are fairly produced in K⁺ and Cs⁺ electrolytes.

Table 1. Current Efficiencies of the Products in Electrochemical Reduction of CO₂ in 0.1 M Hydrogencarbonate Solutions^{a)}

Cation	Potential	Current efficiency/%								C ₁ /C ₂
	V/SHE	CH ₄	C ₂ H ₄	CO	EtOH	PrOH	HCOO ⁻	H ₂	Total	
Li ⁺	-1.45	32.2	5.2	Tr	1.6	Tr	4.7	60.5	104.2	6.19
Na ⁺	-1.45	55.1	12.9	1.0	4.2	0.6	7.0	25.1	105.9	4.27
K ⁺	-1.39	32.0	30.3	0.5	10.9	1.6	8.3	14.5	98.1	1.06
Cs ⁺	-1.38	16.3	30.5	2.4	7.2	4.4	15.8	24.4	101.0	0.534

a) Current density: 5.0 mA cm⁻². Temperature: 18.5 °C. pH value at the electrode is estimated to be 9.5 under the experimental conditions (See text).

Table 2. Current Efficiencies of the Products in Electrochemical Reduction of CO in 0.1 M Hydrogencarbonate Solutions^{a)}

Cation	Potential V/SHE	Current efficiency/%						C ₁ /C ₂
		CH ₄	C ₂ H ₄	EtOH	PrOH	H ₂	Total	
Li ⁺	-1.40	26.0	13.4	0.4	Tr	61.1	100.9	1.94
Na ⁺	-1.43	21.6	15.8	1.4	1.1	59.9	99.6	1.37
K ⁺	-1.37	8.9	25.7	3.1	2.2	54.7	94.6	0.346
Cs ⁺	-1.31	2.0	15.9	1.7	1.3	76.8	97.7	0.126

a) Current density: 1.5 mA cm⁻². Temperature: 18.5°C. pH value at the electrode is estimated to be 9.1 under the experimental conditions.

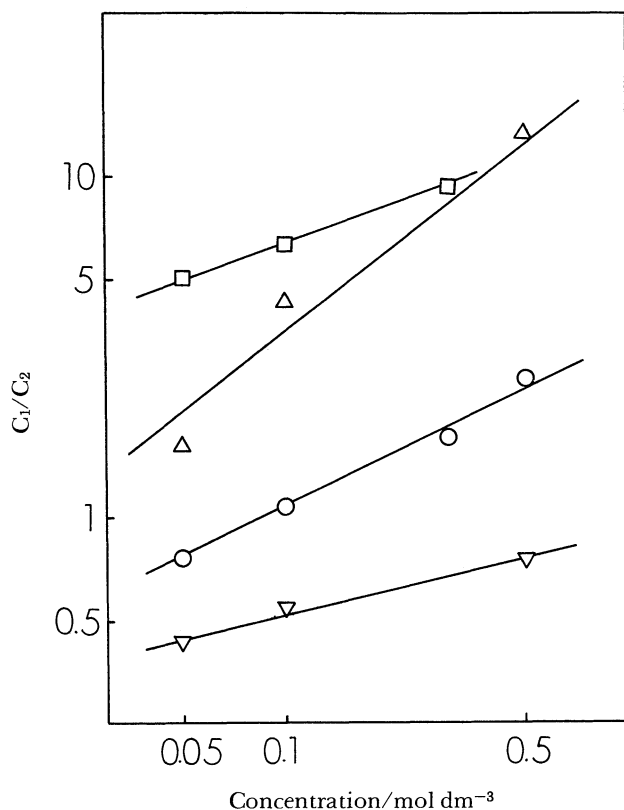


Fig. 1. Variation of the C₁/C₂ in the electroreduction of CO₂ in hydrogencarbonate solutions of various concentration. Current density: 5.0 mA cm⁻². Temperature: 18.5°C. Cationic species; □, Li; △, Na; ○, K; ▽, Cs. Estimated pH values ranged between 8.9 in 0.5 M solution and 10.1 in 0.05 M solution (See text).

CO formation is very low. HCOO⁻ increases in the order of Li⁺<Na⁺<K⁺<Cs⁺. C₂H₆ and CH₃OH were not detected at all.

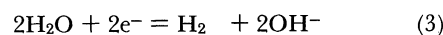
Figure 1 illustrates variation of C₁/C₂ in various electrolytes at the current density 5.0 mA cm⁻². C₁/C₂ rises linearly with logarithm of electrolyte concentration, and falls in the order of Li⁺>Na⁺>K⁺>Cs⁺, identical with the order of cation size. C₂H₄ formation becomes favorable with decrease of HCO₃⁻ concentration and increase of cation size.

Table 2 presents faradaic efficiencies of products in

the electroreduction of CO in 0.1 M hydrogencarbonate solutions at a constant current density 1.5 mA cm⁻². The current efficiency of H₂ formation, not much different with one another, is relatively low in Na⁺ and K⁺ electrolytes, and takes the highest value in Cs⁺ electrolyte. These values are higher than those obtained in CO₂ reduction. The solubility of CO is ca. 1/40 that of CO₂.¹²⁾ The electrolysis current 1.5 mA cm⁻² may exceed the limiting current governed by CO diffusion to the electrode, and the H₂ may be evolved more easily. CH₄, C₂H₄, C₂H₅OH, and *n*-C₃H₇OH are produced in the electroreduction of CO as well. C₁/C₂, ranging to a similar extent with CO₂ reduction, increases with the sequence of Cs⁺<K⁺<Na⁺<Li⁺.

Discussion

Product Selectivity Affected by Concentration of HCO₃⁻. Cathodic reduction of CO₂, CO, and H₂O releases an OH⁻ per one electron.

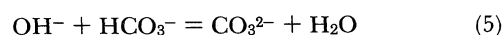


In the case of HCOO⁻ production, one OH⁻ is formed per two electrons.



The rate of OH⁻ formation is thus determined by the current density and the product distribution.

OH⁻ produced at the electrode will be instantaneously neutralized by HCO₃⁻ in the diffusion layer.



In dilute hydrogencarbonate solutions, the transport of HCO₃⁻ may be short of neutralization of OH⁻; pH value will rise in the neighborhood of the electrode. A simple model may clarify the situation. H₂O is reduced to H₂ at a plane electrode in 0.1 M KHCO₃ solution without CO₂. Released OH⁻ reacts with HCO₃⁻, giving CO₃²⁻. pH value can easily be

Table 3. Current Efficiencies of the Products in Electrochemical Reduction of CO₂ in Various Concentration of KCl Solutions^{a)}

Concn M	Potential V/SHE	Current efficiency/%								C ₁ /C ₂
		CH ₄	C ₂ H ₄	EtOH	PrOH	CO	HCOO ⁻	H ₂	Total	
0.05	-1.59	14.2	44.5	18.9	2.7	2.4	7.5	11.3	101.5	0.342
0.1	-1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8	0.241
0.3	-1.49	14.2	40.8	16.0	2.1	2.1	11.3	10.9	97.4	0.348
1.0	-1.42	8.7	42.2	15.5	1.8	3.3	9.6	15.8	96.9	0.206

a) Current density: 5.0 mA cm⁻². Temperature: 18.5°C. The values were obtained at 15 min after the start of electrolysis. pH value at the electrode is estimated to be 10.6 under the experimental conditions.

calculated in this case as a simple steady state diffusion problem. With assumption of the diffusion layer thickness 0.0030 cm, pH at the electrode is ca. 9.1 and 9.7 for the current density of 1.5 and 5.0 mA cm⁻² respectively.¹³⁾ pH at the electrode becomes higher in dilute hydrogencarbonate solution due to low buffer capacity in Eq. 5. The pH values at the electrode during CO reduction will be equal to those calculated in this manner. The details of the procedure were described in the previous paper.¹¹⁾

In CO₂ saturated solution, pH at the electrode may differ from the values obtained by the method described above since OH⁻ will be partially neutralized by CO₂. However, the rate of neutralization of CO₂ by OH⁻ is very low as is well-known.¹⁴⁾ CO₂ will thus be present under non-equilibrium situations at the electrode in spite of high pH value.¹¹⁾ We have strictly treated the diffusion problem accompanied with simultaneous neutralization of CO₂ by CO₃²⁻ (or OH⁻) and the electroreduction of CO₂ in a mathematical procedure. pH values at the electrode surface have been obtained for hydrogencarbonate solutions saturated with CO₂. The procedure and the results were partially reported¹⁵⁾ and the details will be published in near future. The pH values at the electrode calculated in this manner ranged between 8.9 in 0.5 M solution and 10.1 in 0.05 M solution as shown in Fig. 1, Tables 1 and 3. However, the calculation was carried out without taking into consideration of the cation effect described below.

CO₂ is reduced to CH₄ and C₂H₄ with CO intermediately produced. In CO electroreduction, C₂H₄ formation relatively increases with pH of the bulk solution.^{5,11)} It is thus reasonable that C₁/C₂ tends to smaller value in more dilute hydrogencarbonate solution, in which pH becomes higher at the electrode.

Variation of the Potential at Outer Helmholtz Plane with Cationic Species and Its Effects on CO₂ Reduction and Hydrogen Evolution. We previously reported electroreduction of CO₂ to HCOO⁻ at a Hg pool electrode in various hydrogencarbonate solutions, referring to the effect of cationic species.¹⁶⁾ The electrode potential at a constant partial current of HCOO⁻ formation shifts to the positive direction with

the sequence of Li⁺, Na⁺, K⁺. We discussed the results in connection with the variation of potential at the outer Helmholtz plane (OHP) E_2 .

Variation of the product selectivity with cationic species indicated in Tables 1 and 2 can be rationalized in terms of the potential distribution at the electrode surface. If ions are strongly hydrated, they will not be specifically adsorbed on the electrode. The hydration number of Li⁺ is the largest, and that of Cs⁺ is the smallest among alkali metal ions.¹⁷⁾ The potential of zero charge (pzc) of Cu is -0.3 to -0.7 V vs. SHE in neutral electrolytes.¹⁸⁾ The electrode potentials during the electrolysis are far more negative than the pzc, nevertheless there may be some differences with regard to the degree of the cationic adsorptions. The extent of specific adsorption of Li⁺ would be the least on the electrode, and that of Cs⁺ the greatest. Specific adsorption of cation will shift E_2 to the positive direction. Thus, the value of E_2 would be more positive in the sequence of Cs⁺>K⁺>Na⁺>Li⁺.

The cation specific adsorption and its effect on H₂ evolution were partly substantiated by Maznichenko et al.¹⁹⁾ They measured the overvoltages of H⁺ reduction at constant current and discussed the relation with E_2 . The overvoltages measured in mixtures of HCl and alkali halide aqueous solution are greater in the sequence of Cs⁺>K⁺>Na⁺>Li⁺.

The effect of E_2 on the rate of an electrode reaction is twofold, according to Frumkin.²⁰⁾ First, the concentration of the ions at OHP undergoing an electrode reaction is changed as compared to the bulk concentration in the solution. Second, the effective potential difference which determines the charge transfer current density is $|E-E_2|$, where E is the electrode potential. If E_2 become more positive, E at constant current density will naturally be more positive as well. The situations are depicted in Fig. 2. The potential variations in Tables 1 and 2 confirm the validity of this model.

CO₂ is not electrically charged, and the concentration of CO₂ at OHP will not be changed from that of the bulk of the solution, if we neglect the concentration gradient due to transport process. However, H⁺ is positively charged, and the concentration at OHP $[H^+]_s$ will be given as follows.²⁰⁾

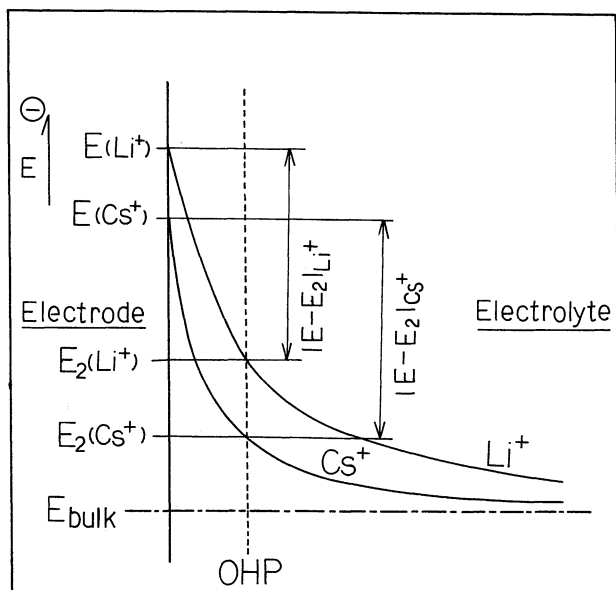


Fig. 2. Potential distribution in the neighborhood of the electrode.

$$[H^+]_s = [H^+] \exp(-FE_2/RT) \quad (6)$$

The more negative E_2 is, the more concentrated H^+ will be. pH at the electrode surface will be lower in the sequence of $Cs^+ > K^+ > Na^+ < Li^+$. During the electrolysis, the rate of OH^- release at the electrode is approximately constant at constant current density. Thus, pH at OHP will be relatively lower in Li^+ solution, and higher in Cs^+ solution. The H_2 evolution will most favorably proceed in Li^+ solution, as is confirmed by Table 1. One would expect that the current efficiency of H_2 would be the least in Cs^+ solution in accordance with the present model. But Cs^+ solution is more advantageous for H_2 evolution than K^+ and Na^+ solutions, especially in the CO electroreduction. The reason is unknown at present.

Ito et al. carried out the electrochemical reduction of CO_2 at an indium electrode in various alkali carbonate solutions.²¹⁾ Alkali carbonate solutions must have been converted to hydrogencarbonate ones since the solutions were saturated with CO_2 . According to their report, the current efficiency of $HCOO^-$ increases in the sequence of $Rb^+ < K^+ < Na^+ < Li^+$. This result does not agree with ours obtained with a Hg pool electrode.¹⁶⁾ The discrepancy may be caused by the difference of experimental conditions such as the preparation and the treatment of the electrode surface. Additionally, CO_2 reduction is sensitive to contamination of the electrode surface, but Ito et al. did not give any remarks to this point. It is impossible to discuss this problem more extensively.

Product Ratio of CH_4 and C_2H_4 . C_1/C_2 significantly decreases with decrease of HCO_3^- concentration (Fig.

1) or increase of pH at the electrode surface; C_2H_4 formation is favorable in high pH conditions. pH at the electrode will be in the order of $Li^+ < Na^+ < K^+ < Cs^+$ as discussed above. Thus C_1/C_2 will decrease in the order of increasing pH at OHP, $Li^+ > Na^+ > K^+ > Cs^+$, as shown in Tables 1, 2 and Fig. 1.

It is remarkable that the variation of cations affects similarly the product distribution of both CO and CO_2 reduction. This fact indicates the validity of the specific adsorption/OHP potential model. It can also confirm the intermediate formation of CO in the course of CO_2 reduction.

According to Tables 1 and 2, C_1/C_2 takes higher values in CO_2 reduction than CO reduction. pH at the electrode is 9.5 in CO_2 reduction at 5.0 mA cm^{-2} , whereas 9.1 in CO reduction at 1.5 mA cm^{-2} .²²⁾ These facts do not appear compatible with the model described above that high pH value leads to low C_1/C_2 . This apparent contradiction may be rationalized as below. The current efficiency of CH_4 exceeds that of C_2H_4 as the electrode potential tends negatively as revealed by the potentiostatic electroreduction of CO_2 in 0.1 M $KHCO_3$ solution.¹¹⁾ Thus C_1/C_2 is enhanced with increase of negative potential. As shown in Tables 1 and 2, the potential in CO_2 reduction is more negative than in CO reduction, C_1/C_2 becoming higher in CO_2 reduction. We undertook identical experiments under potentiostatic conditions. Potentiostatic electrolysis measurements are accompanied with change of the current density during the measurements probably due to the change of surface condition of the electrode. pH at the electrode will vary if the current is not kept constant in accordance with the model of electrogenerated OH^- mentioned above. However, C_1/C_2 value similarly depended on the cationic species as demonstrated in Tables 1 and 2 obtained in constant current electrolyses.

Table 3 shows the results obtained in CO_2 electroreduction in KCl solutions of various concentrations. C_1/C_2 does not vary to a great extent as those in hydrogencarbonate solutions illustrated in Fig. 1. It is evident that the product distribution does not depend upon concentration of cation and anion which do not neutralize OH^- . The invariant C_1/C_2 values in Table 3 may suggest that the amount of specifically adsorbed cations does not depend upon the concentration; the specific adsorption would be saturated at the electrode in 0.1 M KCl solution. It is also remarkable that C_1/C_2 assumes smaller values since pH at the electrode would be much higher in KCl solutions than in $KHCO_3$ ones.

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 - 22) The product distribution of CO₂ reduction may be preferably compared with that of CO reduction at the same current density. However, it is impossible due to the reason below. The CO₂ reduction does not proceed effectively at 1.5 mA cm⁻² with Li⁺ and Cs⁺ electrolytes, yielding only H₂ with slight amount of CH₄ and C₂H₄. CO must be adsorbed at the electrode surface for formation of CH₄ and C₂H₄ from CO₂. Under the conditions of 1.5 mA cm⁻², H₂ evolution preferentially proceeds, and little CO is formed from CO₂ on the Cu electrode surface.
- On the other hand, the solubility of CO in aqueous solution is low, and the current density of 5 mA cm⁻² will be far beyond the limiting current.
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