Product Selectivity Affected by Cationic Species in Electrochemical Reduction of CO_2 and CO at a Cu Electrode[1)]

Akira MURATA and Yoshio HORI*
Department of Applied Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 260
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Electroreduction of CO_2 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 HCO_3^- concentration. H_2 evolution prevailed over CO_2 reduction in Li^+ electrolyte, whereas CO_2 reduction was favorable in Na^+, K^+, and Cs^+ solutions. C_2H_4 formation became greater than CH_4 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 CO_2 to CH_4, C_2H_4, 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 CO_2 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 electropolished 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. $LiHCO_3$ and $CsHCO_3$ solutions were prepared by dissolving the respective carbonate and saturating with CO_2. The solubility of Li_2CO_3 is 1.31 g in 100 g of saturated solution, or 0.18 M at 20 °C.[12)] The upper limit of concentration of $LiHCO_3$ 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 CO_2 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. H_2 evolution is favorable with the sequence of $Li^+ > Na^+ > Cs^+ > K^+$. The faradaic efficiencies of CH_4 and C_2H_4 depend greatly upon cationic species. The highest value of methane formation takes place in Na^+ electrolyte. C_2H_4 formation is the most favorable in Cs^+ electrolyte. CH_4/C_2H_4 faradaic efficiency ratio C_1/C_2 increases in the order of $Cs^+ < K^+ < Na^+ < Li^+$. C_2H_5OH and *n*-C_3H_7OH are fairly produced in K^+ and Cs^+ electrolytes.

Table 1. Current Efficiencies of the Products in Electrochemical Reduction of CO_2 in 0.1 M Hydrogencarbonate Solutions[a)]

Cation	Potential	Current efficiency/%								C_1/C_2
	V/SHE	CH_4	C_2H_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	Current efficiency/%						C_1/C_2
	V/SHE	CH_4	C_2H_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.

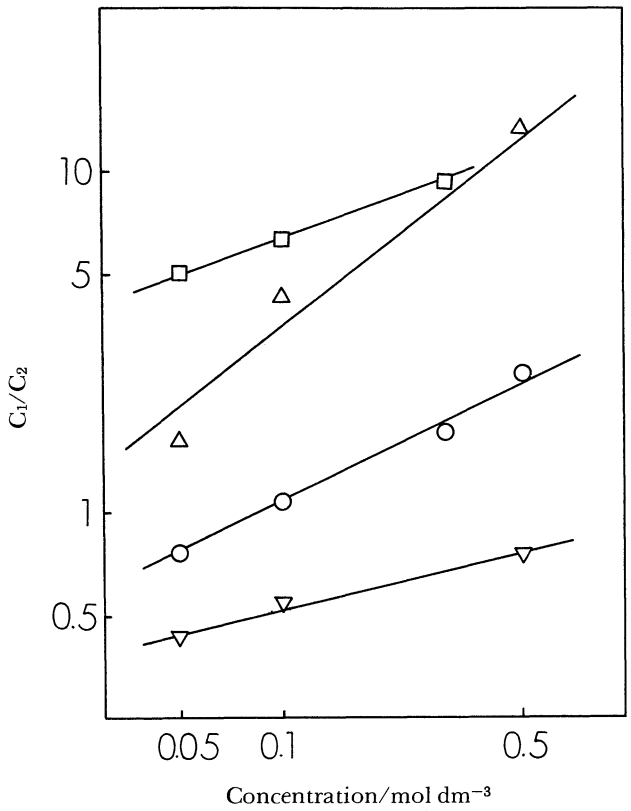

Fig. 1. Variation of the C_1/C_2 in the electroreduction of CO_2 in hydrogencarbonate solutions of various concentration. Current density: 5.0 mA cm^{-2}. Temperature: 18.5 °C. Cationic species; □, Li; △, Na; ○, K; ▽, Cs. Estimated pH values ranged between 8.9 in 0.5 M solution and 10.1 in 0.05 M solution (See text).

CO formation is very low. $HCOO^-$ increases in the order of $Li^+<Na^+<K^+<Cs^+$. C_2H_6 and CH_3OH were not detected at all.

Figure 1 illustrates variation of C_1/C_2 in various electrolytes at the current density 5.0 mA cm^{-2}. C_1/C_2 rises linearly with logarithm of electrolyte concentration, and falls in the order of $Li^+>Na^+>K^+>Cs^+$, identical with the order of cation size. C_2H_4 formation becomes favorable with decrease of HCO_3^- 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 H_2 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 CO_2 reduction. The solubility of CO is ca. 1/40 that of CO_2.[12] The electrolysis current 1.5 mA cm^{-2} may exceed the limiting current governed by CO diffusion to the electrode, and the H_2 may be evolved more easily. CH_4, C_2H_4, C_2H_5OH, and n-C_3H_7OH are produced in the electroreduction of CO as well. C_1/C_2, ranging to a similar extent with CO_2 reduction, increases with the sequence of $Cs^+<K^+<Na^+<Li^+$.

Discussion

Product Selectivity Affected by Concentration of HCO_3^-. Cathodic reduction of CO_2, CO, and H_2O releases an OH^- per one electron.

$$CO_2 + 6H_2O + 8e^- = CH_4 + 8OH^- \quad (1)$$

$$CO + 5H_2O + 6e^- = CH_4 + 6OH^- \quad (2)$$

$$2H_2O + 2e^- = H_2 + 2OH^- \quad (3)$$

In the case of $HCOO^-$ production, one OH^- is formed per two electrons.

$$CO_2 + H_2O + 2e^- = HCOO^- + OH^- \quad (4)$$

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 HCO_3^- in the diffusion layer.

$$OH^- + HCO_3^- = CO_3^{2-} + H_2O \quad (5)$$

In dilute hydrogencarbonate solutions, the transport of HCO_3^- may be short of neutralization of OH^-; pH value will rise in the neighborhood of the electrode. A simple model may clarify the situation. H_2O is reduced to H_2 at a plane electrode in 0.1 M $KHCO_3$ solution without CO_2. Released OH^- reacts with HCO_3^-, giving CO_3^{2-}. pH value can easily be

Table 3. Current Efficiencies of the Products in Electrochemical Reduction of CO_2 in Various Concentration of KCl Solutions[a)]

Concn	Potential	Current efficiency/%								C_1/C_2
M	V/SHE	CH_4	C_2H_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 CO_2 saturated solution, pH at the electrode may differ from the values obtained by the method described above since OH^- will be partially neutralized by CO_2. However, the rate of neutralization of CO_2 by OH^- is very low as is well-known.[14)] CO_2 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 CO_2 by CO_3^{2-} (or OH^-) and the electroreduction of CO_2 in a mathematical procedure. pH values at the electrode surface have been obtained for hydrogencarbonate solutions saturated with CO_2. The procedure and the results were partially reported[15)] 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.

CO_2 is reduced to CH_4 and C_2H_4 with CO intermediately produced. In CO electroreduction, C_2H_4 formation relatively increases with pH of the bulk solution.[5,11)] It is thus reasonable that C_1/C_2 tends to smaller value in more dilute hydrogencarbonate solution, in which pH becomes higher at the electrode.

Variation of the Potential at Outer Helmholz Plane with Cationic Species and Its Effects on CO_2 Reduction and Hydrogen Evolution. We previously reported electroreduction of CO_2 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 Helmholz 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 H_2 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.

CO_2 is not electrically charged, and the concentration of CO_2 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)]

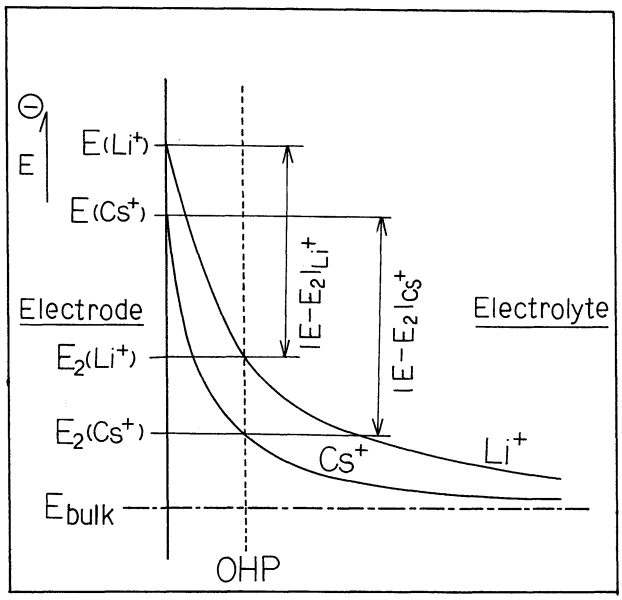

Fig. 2. Potential distribution in the neighborhood of the electrode.

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

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.

References

1) The content of this article was briefly reported by Y. Hori and A. Murata in the 58th Meeting of the Chemical Society of Japan, Kyoto, April 1989, Abstr., No. 2IB38.

2) Y. Hori, K. Kikuchi, and S. Suzuki, *Chem. Lett.*, **1985**, 1685.

3) Y. Hori, K. Kikuchi, A. Murata, and S. Suzuki, *Chem. Lett.*, **1986**, 897.

4) Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, *J. Chem. Soc., Chem. Commun.*, **1988**, 17.

5) Y. Hori, A. Murata, R. Takahashi, and S. Suzuki, *J. Am. Chem. Soc.*, **109**, 5022 (1987).

6) R. L. Cook, R. C. MacDuff, and A. F. Sammels, *J. Electrchem. Soc.*, **134**, 1873 (1987).

7) R. L. Cook, R. C. MacDuff, and A. F. Sammels, *J. Electrochem. Soc.*, **134**, 2375 (1987).

8) J. J. Kim, D. P. Summers, and K. W. Frese, Jr., *J. Electroanal. Chem.*, **245**, 233 (1988).

9) H. Noda, S. Ikeda, Y. Oda, and K. Ito, *Chem. Lett.*, **1989**, 289.

10) D. W. Dewulf, T. Jin, and A. J. Bard, *J. Electrochem. Soc.*, **136**, 1686 (1989).

11) Y. Hori, A. Murata, and R. Takahashi, *J. Chem. Soc., Faraday Trans. 1*, **85**, 2309 (1989).

12) J. A. Dean, "Lange's Handbook of Chemistry," 12th ed, McGraw-Hill, New York (1979).

13) The diffusion layer thickness was assumed to be 0.01 cm as a probable value in the previous paper.[11] In the present experimental conditions, the diffusion layer thickness was estimated to be 0.0030 cm from measurements of limiting current densities of anodic oxidation of $Fe(CN)_6^{4-}$ at a Pt electrode with equivalent hydraulic conditions.

14) B. R. W. Pinsent, L. Pearson, and F. J. W. Roughton, *Trans. Faraday Soc.*, **52**, 1512 (1956).

15) Y. Hori, Y. Yoshinami, and H. Kawarada, 41th Meeting of International Society of Electrochemistry, Praha, August 1990, Abstr., No. Mo.-110.

16) Y. Hori and S. Suzuki, *Bull. Chem. Soc. Jpn.*, **55**, 660 (1982).

17) J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, New York (1970), Vol. 1.

18) G. J. Clark, T. N. Andersen, R. S. Valentine, and H. Eyring, *J. Electrochem. Soc.*, **121**, 618 (1974). Cited from R. S. Perkins, Ph. D. Thesis, University of Utah, U. S. A., 1967.

19) P. Delahay, "Double Layer and Electrode Kinetics," Wiley, London (1965). Maznichenko et al.'s work was relevantly mentioned. Originally, E. A. Maznichenko, B. B. Damaskin, and Z. A. Iofa, *Dokl. Akad. Nauk SSSR*, **138**, 1377 (1961).

20) K. J. Vetter, "Electrochemical Kinetics," Academic Press, New York (1967). Frumkin's theory was relevantly mentioned and discussed. Originally, A. N. Frumkin, *Z. Phys. Chem., Abt. A*, **164**, 121 (1933).

21) K. Ito, T. Murata, and S. Ikeda, *Bull. Nagoya Inst. Techn.*, **27**, 209 (1975).

22) The product distribution of CO_2 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 CO_2 reduction does not proceed effectively at 1.5 mA cm^{-2} with Li^+ and Cs^+ electrolytes, yielding only H_2 with slight amount of CH_4 and C_2H_4. CO must be adsorbed at the electrode surface for formation of CH_4 and C_2H_4 from CO_2. Under the conditions of 1.5 mA cm^{-2}, H_2 evolution preferentially proceeds, and little CO is formed from CO_2 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.