Enhanced Formation of Ethylene and Alcohols at Ambient Temperature and Pressure in Electrochemical Reduction of Carbon Dioxide at a Copper Electrode

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In the electroreduction of CO_2 at a copper cathode in aqueous solution at ambient temperature and pressure the faradaic yield of C_2H_4 amounted to 48%, and appreciable amounts of EtOH and Pr^nOH were formed; the selectivity of the products depends strongly upon the electrolytes.

Electroreduction of CO_2 in $KHCO_3$ aqueous electrolytes yields CH_4 and C_2H_4 at Cu electrodes, as reported previously.[1] We also observed the formation of CH_4, C_2H_4, and alcohols in the electroreduction of CO at Cu electrodes in aqueous solution.[2] We now describe a significantly enhanced formation of ethylene along with production of alcohols in the electroreduction of CO_2 in various aqueous media at ambient temperature and pressure. The selectivity of the products depends strongly upon the electrolytes.

A copper electrode (99.999%, 20 × 20 mm) with a copper

Table 1. Faradaic efficiencies of products from the electroreduction of CO_2 at a Cu electrode at 5 mA cm^{-2} in various solutions at 19 °C.

Electrolyte	Conc./ mol l^{-1}	pH[a]	E/V vs. N.H.E.	Faradaic efficiency/%							
				CH_4	C_2H_4	EtOH	Pr^{n}OH	CO	HCO_2^-	H_2	Total
KCl	0.1	5.9	−1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8
	0.5		−1.39	14.5	38.2	b	b	3.0	17.9	12.5	
	1.5	5.7	−1.36	9.6	40.6	b	b	1.6	31.6	16.3	
KClO$_4$	0.1	5.9	−1.40	10.2	48.1	15.5	4.2	2.4	8.9	6.7	96.0
K$_2$SO$_4$	0.1	5.8	−1.40	12.3	46.0	18.2	4.0	2.1	8.1	8.7	99.4
K$_2$HPO$_4$	0.1	6.5	−1.23	17.0	1.8	0.7	tr	1.3	5.3	72.4	98.5
	0.5	7.0	−1.17	6.6	1.0	0.6	0.0	1.0	4.2	83.3	96.7

[a] pH values were measured for bulk solutions after electrolyses. [b] Not analysed.
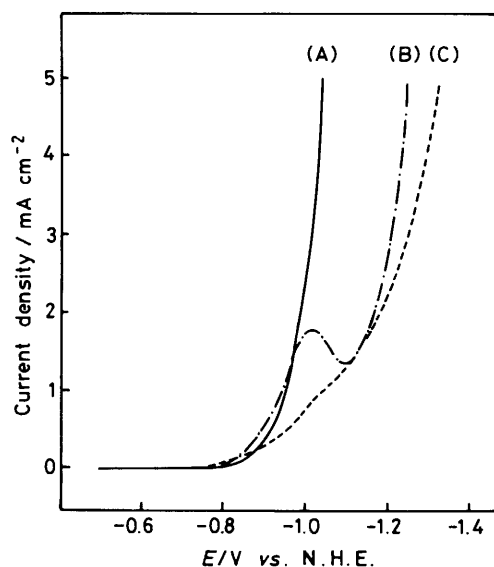

Figure 1. Voltammograms obtained with N_2 and CO_2 saturated solutions. (A): N_2 saturated phosphate buffer solution (0.10 M KH$_2$PO$_4$ + 0.10 M K$_2$HPO$_4$, pH 6.7). (B): CO_2 saturated phosphate buffer solution (initial composition: 0.05 M KH$_2$PO$_4$ + 0.15 M K$_2$HPO$_4$, pH 6.7 after equilibration with saturated CO_2). (C): 0.1 M KHCO$_3$ saturated with CO_2 (pH 6.8).

connecting strip attached was electrolytically polished in phosphoric acid at ambient temperature, and then rinsed with doubly distilled deionized water. The electrolytes were purified by pre-electrolysis with a Pt black cathode under purified N_2 for 20 h. The measurements were conducted in a three compartment cell in which two anode compartments faced each side of the Cu electrode.

Coulometric measurements were conducted with purified CO_2 bubbled into the catholyte (*ca.* 140 ml min^{-1}). The electrolyte (60 ml) was vigorously stirred by a magnetic stirrer during electrolysis. Gaseous products in the effluent gas from the cell and EtOH and Pr^{n}OH in solution were analysed by gas chromatography, at least three columns being used for identification of each product. The formation of CH_4 and C_2H_4 was confirmed by gas chromatography–mass spectrometry. The electrolytes were analysed by an ion chromatograph. Other details were as previously reported.[1]

Figure 1 shows voltammograms obtained for solutions saturated with N_2 and CO_2. The electrolytes for curves A (saturated with N_2) and B (CO_2) were phosphate buffer solutions of pH 6.7 for each. The cathodic current A starts at −0.79 V *vs.* normal hydrogen electrode (N.H.E.) and increases sharply. The onset of B is close to that of A. The

current B has a peak at −1.01 V. Curve C, obtained in 0.1 M KHCO$_3$ saturated with CO_2 (pH 6.8), has a shoulder at −1.02 V.

Coulometric measurements were conducted with constant current density (5 mA cm^{-2}). The gaseous products, CH_4, C_2H_4, and H_2, appeared in the effluent gas after the electrolysis started. Their concentrations remained virtually constant during the electrolysis, *e.g.* in a typical experiment in 0.1 M KHCO$_3$: CH_4 202 p.p.m., C_2H_4 139 p.p.m., and H_2 386 p.p.m. The concentration of CH_4 in blank samples without electrolysis was <0.5 p.p.m. The products in the electrolytes were EtOH, Pr^{n}OH, and HCO_2^-. C_2H_6 and MeOH were not produced. Figure 2 presents the faradaic yields of products at 19 °C in KHCO$_3$ solutions of various concentrations. The electrode potential ranged from −1.28 V *vs.* N.H.E. in 1.5 M KHCO$_3$ to −1.42 V in 0.03 M KHCO$_3$. The faradaic yields were calculated on the basis of the number of electrons required for the formation of one molecule of the products from CO_2 and H_2O: 8 for CH_4, 12 for C_2H_4, 12 for EtOH, 18 for Pr^{n}OH, 2 for CO, 2 for HCO_2^-, and 2 for H_2. The sum of the faradaic yields exceeded 90%. Hence the substances mentioned here are the major products of the reaction. The faradaic yields of C_2H_4 and EtOH are high in dilute electrolyte solutions. CH_4 formation increases with increase of the electrolyte concentration, reaching a maximum, and then decreases. The faradaic yields of HCO_2^- and CO, not shown in Figure 2, do not depend strongly on the electrolyte concentration, *ca.* 10 and 2% respectively. H_2 formation increases with the electrolyte concentration.

Table 1 presents the faradaic yields of some products at 19 °C in various electrolyte solutions. The faradaic yields of C_2H_4 and EtOH are high in KCl, KClO$_4$, and K$_2$SO$_4$ solutions; the trends of the yields in these solutions are close to those in dilute (0.03 M) KHCO$_3$. The sum of the faradaic yields of CH_4 and C_2H_4 are low in K$_2$HPO$_4$ solutions, H_2 formation being prevalent.

The faradaic yield of CO_2 reduction amounts to 90% or more for a total current density of 5 mA cm^{-2} (Figure 2 and Table 1). It is remarkable that hydrocarbons and alcohols are produced in high yields from CO_2 reduction under ambient conditions, although the overvoltages are high [$E°$ (CO_2/CH_4) −0.19 V *vs.* N.H.E., $E°$ (CO_2/C_2H_4) −0.28 V, at pH 6.0 and 25 °C].[3]

Curve B in Figure 1 starts to increase at a potential nearly equal to that for A, passes through a peak (at −1.01 V *vs.* N.H.E.), decreases, and then increases again. A coulometric measurement at a controlled potential of −1.01 V with the phosphate electrolyte for B with CO_2 bubbled showed faradaic yields of 88.7% for H_2, 3.0% for CO, and 1.3% for HCO_2^-; <0.03% for CH_4 and C_2H_4.

We previously reported that the presence of CO markedly inhibits the cathodic hydrogen discharge at a Cu electrode.[2]
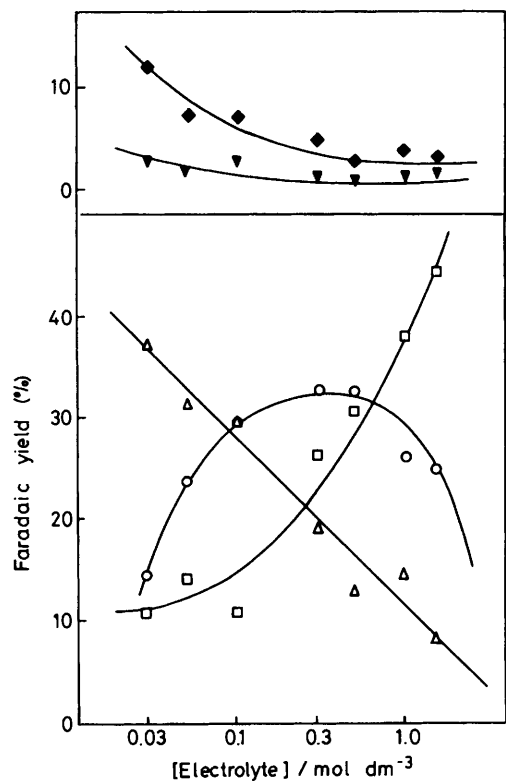
Figure 2. Faradaic yields of the products in the electrochemical reduction of CO_2 at 19 °C in $KHCO_3$ aqueous solutions of various concentrations. Current density 5 mA cm^{-2}. $\triangle$, C_2H_4; O, CH_4; $\square$, H_2; $\blacktriangledown$, Pr^{n}OH; $\blacklozenge$, EtOH.

Anodic oxidation of MeOH, as is well known, is greatly inhibited by some intermediate species formed in the reaction, e.g. CO or another related species adsorbed on the electrode.[4] CO, produced in the reduction of CO_2 at -1.0 V in the present system (curve B), may be adsorbed on the electrode. These adsorbed species would interfere with the cathodic hydrogen discharge. The cathodic current B is thus greatly suppressed at potentials more negative than -1.0 V. The peak height at -1.0 V of curve C is markedly lowered, probably because of

slow proton donation in the hydrolysis of CO_2 (CO_2 + H_2O → H^+ + HCO_3^-).[5]

Hydrocarbons and alcohols will be produced in the reduction of adsorbed intermediate species related to CO at potentials more negative than -1.0 V vs. N.H.E. According to our studies of the electroreduction of CO at Cu electrodes, formation of C_2H_4, EtOH, and Pr^{n}OH is favoured in solutions of high pH.[2] They are preferably produced in the electroreduction of CO_2 in KCl, $KClO_4$, K_2SO_4, and dilute $KHCO_3$ solutions (Table 1). These facts may be explained in terms of a non-equilibrium local region of high pH close to the electrode.

OH^- ions are released at the electrode when hydrocarbons and hydrogen are produced: e.g. CO_2 + $6H_2O$ + $8e^-$ → CH_4 + $8OH^-$. OH^- is instantaneously neutralized by HCO_3^-.[5] However, OH^- release will be much faster than the supply of HCO_3^- to the electrode in dilute $KHCO_3$, KCl, $KClO_4$, and K_2SO_4. The rates of the reaction of CO_2 and OH^- are very low owing to slow hydration of CO_2.[5] CO_2 will thus remain un-neutralized. The pH will consequently rise in the neighbourhood of the electrode in non-equilibrium situations. Hydrogen discharge is prevented under high pH conditions, and the electroreduction of CO_2 will be favoured. In concentrated $KHCO_3$ or phosphate solutions, H_2 formation will advantageously proceed since sufficient HCO_3^- or $H_2PO_4^-$ is present to neutralize OH^- and the pH value is not enhanced at the electrode. Hence, the faradaic yields of CO_2 reduction will be lowered in concentrated $KHCO_3$ solutions.

References

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