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Electrochemical reduction of carbon dioxide in methanol at ambient temperature and pressure

K. OHTA*, M. KAWAMOTO, T. MIZUNO

Department of Chemistry for Materials, Mie University, Mie, Tsu, 514, Japan

D. A. LOWY

The University of Memphis, Department of Chemistry, Campus Box 526060, Memphis, TN 38152-6060, USA

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The electrochemical reduction of carbon dioxide was studied in methanol-based supporting electrolytes on various metal electrodes at ambient temperature and pressure. The ionophore of the catholyte was benzalkonium chloride, $[RN(CH_3)_2CH_2C_6H_5]^+Cl^-$, where $R = C_8$–C_{18}, the chain length being distributed around C_{14}. A divided H-type cell was used, the supporting electrolytes were 10^{-2} mol dm^{-3} benzalkonium chloride in double distilled methanol (catholyte) and a 10^{-1} mol dm^{-3} aqueous $KHCO_3$ solution (anolyte). Nine different, high purity ($>99.5\%$) metal electrodes were used: Ti, Fe, Co, Ni, Pt, Ag, Au, Zn and Sn. Carbon monoxide, methane and ethane were the main organic products. Silver, Au, Zn and Sn cathodes allowed for the best faradaic yields of CO production, the maximum amount of CO (71%, 185 mmol) being formed on the Ag electrode. Methane evolved on each of the nine tested electrodes, with current yields in the range from 0.2 to 3.0%. Ethane and ethylene were produced on the nickel electrode, with low faradaic efficiencies, 0.5 and 0.3%, respectively. No dimerization products were detected. This research can contribute to large-scale manufacturing of useful organic products from a readily available and cheap raw material: CO_2-saturated methanol from industrial absorbers (the Rectisol process).

Keywords: *electroorganic reduction*, *carbon dioxide*, *methanol*, *electrocatalysis*, *benzalkonium chloride*

1. Introduction

Methanol is a better solvent of carbon dioxide than is water (at 25 °C the solubility of CO_2 in methanol is 0.17 mol dm^{-3} vs 0.033 mol dm^{-3} in water). Hence, methanol has been used industrially as a physical absorber of carbon dioxide (the Rectisol process) [1]. Compared to water, methanol is a poor solvent of acidic gases such as SO_x and NO_x. Due to these two properties of methanol, the direct electrochemical reduction of carbon dioxide in methanol-based supporting electrolytes is an advantageous choice, especially when the process is performed under energetically efficient conditions.

The electrochemical reduction of CO_2 in aqueous solution has been extensively studied at ambient temperature and pressure [2, 3]. However, surprisingly few papers deal with the electroreduction of carbon dioxide in methanol [4–10].

In this study the main results are reported on the electrochemical reduction of carbon dioxide using on various metal electrodes in methanol-based supporting electrolyte at ambient temperature and pressure. Based on this work, the large-scale manufacturing of useful organic products from a readily available and cheap raw material, CO_2-saturated methanol from industrial absorbers, may be possible. Expected products include the hydrocarbons methane and ethylene, as well as carbon monoxide. Thus, the synthesis of hydrocarbons by the electrochemical reduction of CO_2 may be of practical interest for fuel production, storage of solar energy, and the production of raw materials for the chemical industry [11].

2. Experimental details

2.1. *Procedures*

Electrochemical reductions of carbon dioxide were performed in a home-made divided H-type cell. An Aldrich 117-type sulfonic ion exchange membrane was used as the diaphragm. The experimental conditions of the electroreduction experiments are listed in Table 1.

The methanol (99.8%, Nacalai Tesque, Inc., Japan) was purified by double distillation (from metallic magnesium). The high purity carbon dioxide (Kawase Sangyou, Inc., Japan) was analysed for the presence of trace impurities, such as low molecular hydrocarbons. Benzalkonium chloride was used as the ionophore in the methanol-based catholyte, at a

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* Author to whom correspondence should be addressed.

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Table 1. Experimental conditions used for the electrochemical reduction of carbon dioxide in methanol-based supporting electrolytes

Cell: H-type
Counter electrode: Pt mesh (100 mesh, ϕ0.07, 50 × 50 mm, 99.98% purity)
Reference electrode: Saturated calomel electrode
Electrolytes: Catholyte: 10^{-2} mol dm^{-3} benzalkonium chloride in methanol; Anolyte: 10^{-1} mol dm^{-3} $KHCO_3$ in water
Carbon dioxide: 99.9999% pure
Potential of the working electrode: from −1.5 to −1.9 V vs SCE
Temperature: 288.0 ± 0.5 K

concentration of 10^{-2} mol dm^{-3}. Benzalkonium chloride (98%, Kanto Chemical Co., Inc., Tokyo, Japan) or alkyl dimethylbenzylammonium chloride, $[RN(CH_3)_2CH_2C_6H_5]Cl$, has $R = C_8$–C_{18}, the distribution of the length of the alkyl chain showing a maximum around C_{14}. The anolyte was a 10^{-1} mol dm^{-3} solution of $KHCO_3$ in water. A discontinuous electroreduction procedure was used: first, carbon dioxide was bubbled into the catholyte for about 3 min at the rate of 40 cm^{-3} min^{-1}, then the CO_2-saturated solution was reduced electrolytically at cathodic polarizations in the range from −1.5 to −1.9 V vs SCE. The faradaic efficiency of the formation of the main products was calculated by assuming a total charge of 30 C passed through the cell when using the Fe, Co, Zn and Au electrodes, and of 50 C when using the Ti, Ni, Pt, Sn and Ag electrodes.

2.2. *Treatment of the electrodes*

A wide variety of metals were used as the cathode material, both *d*-group metals: Ti, Fe, Co, Ni and Pt, and *s*-group metals: Sn, Zn, Ag and Au.

The purity of each metal was greater than 99.5%. Typically, an electrode was of 20 mm × 30 mm with a thickness in the range from 0.01 to 0.1 mm. Mechanical processing of the electrodes involved polishing each surface with successively finer grades of alumina powder (Baikalox emulsion, manufactured by Baikowski International Co.), down to 0.05 mm, followed by the removal of fats with acetone. Titanium, Fe, Sn, Zn, Ag and Au electrodes were chemically conditioned by their immersion in 6.6 mol dm^{-3} nitric acid for 1 min (Ti), in 14.7 mol dm^{-3} phosphoric acid for 5 min (Fe), in 2.9 mol dm^{-3} hydrochloric acid for 1 min (Sn), in 14.7 mol dm^{-3} phosphoric acid for 5 s (Zn), in 6.6 mol dm^{-3} nitric acid for 10 s (Ag), and in 6.6 mol dm^{-3} nitric acid for 1 min (Au). Cobalt, Ni and Pt electrodes were activated electrochemically, at 500 mA for 90 s (Co), at 500 mA for 2 min (Ni) and at 500 mA for 2 min in 14.7 M phosphoric acid (Pt). Following the above treatment, the electrodes were rinsed with both water and ethanol. The platinum sieve anode was cleaned of fat with acetone and then immersed in 18 mol dm^{-3} sulfuric acid for 5 min. Finally, the mesh was rinsed with water and ethanol.

2.3. *Product analysis*

Gaseous products obtained during the electroreduction were analysed by gas chromatography (Yanako G-2800 and GL Science GC-380) on a conventional column (2 m long, i.d. 1.5 mm), filled with either molecular sieves 0.5 nm or Porapak Q. High purity helium was the carrier gas. Those products soluble in the catholyte were analysed by both liquid chromatography (Hitachi L600) and gas chromatography.

3. Results and discussion

3.1. *Cyclic voltammetry*

The electrocatalytic effect exerted by different cathode metals on the electroreduction of CO_2 was investigated using cyclic voltammetry (CV). The electrochemical work station consisted of an HB-111 model potentiostat (Hokuto Denko Ltd, Japan), equipped with an WX1100-model X–Y recorder (Graphtec Inc, Japan). Figure 1 shows the current-potential curves both in CO_2-saturated methanol and N_2-purged methanol. CO_2 reduction is evident on most of the voltammograms recorded in CO_2-saturated methanol. Table 2 lists the onset potentials of the cathodic current, that is, those potential values at which a current density of 0.1 mA cm^{-2} is observed. Potential values recorded in CO_2-saturated methanol were compared to the onset potentials reported by Ortiz *et al.* [12] for a supporting electrolyte formed of 0.1 mol dm^{-1} $NaClO_4$ in methanol. An additional column of the same table contains the onset potentials vs SHE obtained by Hori *et al.* [13] for the electroreduction of CO_2 in aqueous 10^{-1} mol dm^{-3} $KHCO_3$ solution. In this study, the onset potentials recorded in CO_2-saturated methanol did not show a tendency similar either to the values obtained by Ortiz *et al.* [12] or those reported by Hori *et al.* [13]. Both the reduction potential and the onset potential are normally affected by the pH of the catholyte. Even by considering these pH effects, we could not elucidate the reason of the different tendency of the onset potentials recorded and similar values, obtained on Ni, In, Ru, Pt, Sn, Cu and Au, in 10^{-1} mol dm^{-3} $NaClO_4$/methanol, by Ortiz *et al.* [12] or on Cu, Ag, Au, Zn and Pt in 10^{-1} mol dm^{-3} $KHCO_3$ catholyte, by Hori *et al.* [13].

No voltammetric peak was observed in the range from 0 to −2.2 V. The polarization curves recorded on Fe, Co, Sn, Zn, Ag and Au electrodes in CO_2-saturated methanol were shifted to more positive potential values relative to the polarization curves recorded in N_2-purged methanol. However, Ti, Ni and Pt electrodes behaved differently: when the electrolyses were conducted under nitrogen atmosphere, exclusively hydrogen was evolved, no carbon dioxide being reduced. We may conclude that the cathodic currents recorded on Ti, Ni and Pt were due solely to water reduction. Significant cathodic waves were

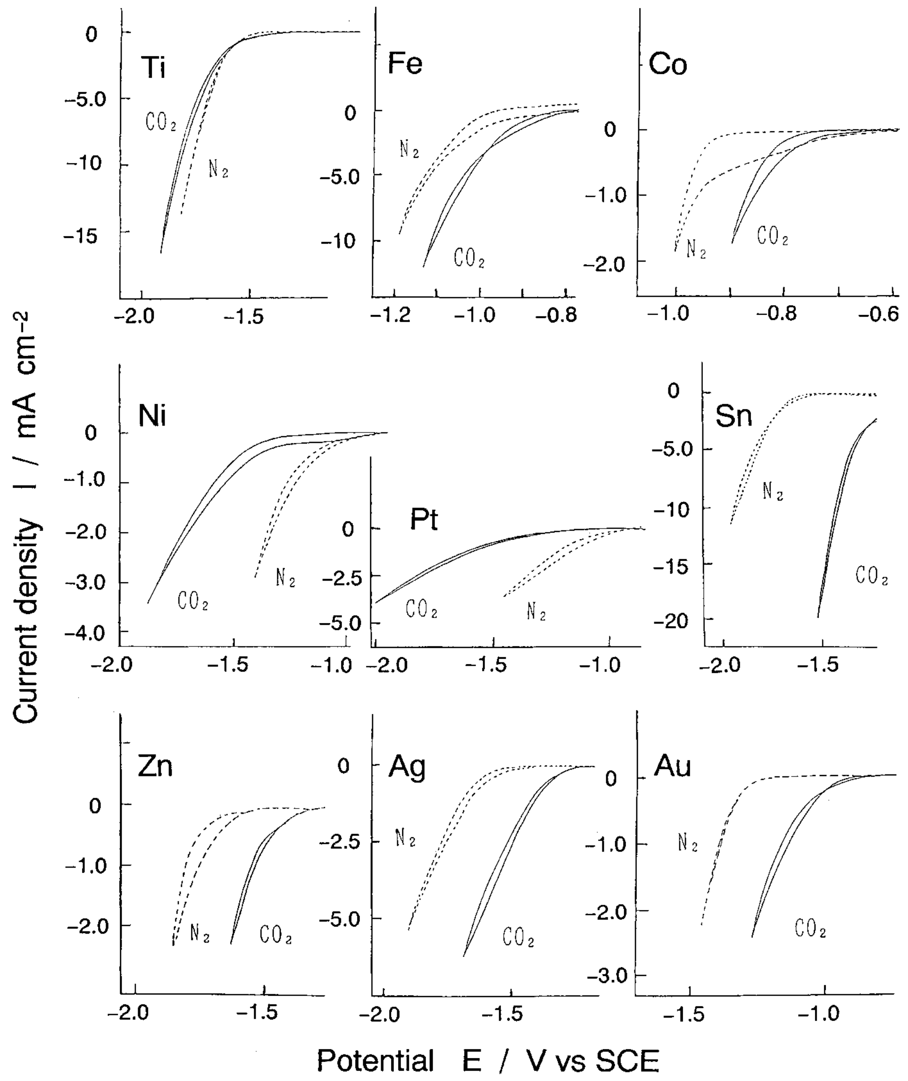


Fig. 1. Cyclic voltammograms. Solid line: under CO_2 atmosphere; broken line: under N_2 atmosphere; catholyte: 10^{-2} mol dm^{-3} benzalkonium chloride in methanol; anolyte: 10^{-1} mol dm^{-3} $KHCO_3$ in water.

obtained with Ti, Fe, Sn and Ag electrodes. The largest cathodic current was observed using a Sn working electrode in CO_2-saturated methanol. With the exception of Ni, all of our metallic electrodes behaved similarly to those used in 10^{-1} mol dm^{-3} $NaClO_4$/methanol catholyte by Ortiz and coworkers [12]. In the same study [12], using a nickel electrode, the cathodic current started increasing at a greater positive potential value in CO_2-saturated catholyte than in N_2-purged methanol. However, in our experiments perfomed in 10^{-2} mol dm^{-3} benzalkonium/methanol supporting electrolyte, the potential was more negative than the potential value in N_2-purged methanol (see Fig. 1). The reason for this reversal of the polarization curves is still being examined.

Table 2. Onset potentials of the cathodic current in CO_2-saturated methanol at various metal electrodes

Electrode voltage/V	*vs SCE*	*vs Ag/Ag$^+$*	*vs SHE*
Ti	-1.6		
Co	-0.75		
Pt	-1.0	-1.30*	-0.35†
Zn	-1.4		-1.2†
Au	-0.9	-1.36*	-0.85†
Fe	-0.9		
Ni	-1.4	-1.42*	-0.72†
Sn	-1.3	-1.40*	-1.1†
Ag	-1.3		-1.2†

*Data from [10]: onset potentials in 10^{-1} mol dm^{-3} $NaClO_4$ solution in methanol.

†Data from [11]: potentials of CO_2 reduction in 10^{-1} mol dm^{-3} aqueous solution of $KHCO_3$.

Once the onset potentials were determined from polarization experiments, we investigated the electrochemical reduction of carbon dioxide in CO_2-saturated methanol at cathodic polarizations exceeding the onset potential. The potentials for each electrode were set in the following ranges: from −1.7 to −1.9 V vs SCE for the Ti electrode, from −1.0 to −1.35 V vs SCE for Fe, from −1.2 to −1.5 V vs SCE for Co, from −1.5 to −1.9 V vs SCE for Ni, from −1.0 to −1.8 V vs SCE for Pt, from −1.4 to −1.6 V vs SCE for Sn, from −1.5 to −1.6 V vs SCE for Zn, from −1.4 to −1.7 V vs SCE for Ag and from −1.0 to −1.2 V vs SCE for the Au electrode.

3.2. *Effect of potential on faradaic efficiency of the products*

The effect of the electrode potential on the faradaic efficiency of products obtained in CO_2 electroreduction is shown in Figs 2–10. Carbon monoxide, methane and ethane were the main products. In aqueous catholytes formic acid was the major product, on Sn, Pb, Zn and Cu electrodes [13], but in methanol solution no formic acid was produced. Under nitrogen atmosphere the electrolysis yielded exclusively hydrogen. A GC–MS study with deuterated methanol catholyte demonstrated that no hydrogen, CO, methane, ethylene and ethane was produced from methanol [4]. Consequently, the above products were produced by the electrochemical reduction of CO_2.

As seen in Fig. 2, when Ti cathodes were used, the most efficient hydrogen and methane production occurred at −1.8 V vs SCE (current yields of 114 and 2.0%, respectively, being achieved). The yields of hydrogen were greater than those predicted by the stoichiometry of the reaction; the only possible explanation of this phenomenon resides in the competing electrolysis of water molecules that cross the membrane from the anode compartment to the cathodic half-cell. On Ti, carbon monoxide formed with approximately constant faradaic efficiency (0.2%) over the entire potential range investigated.

When an iron electrode was used, the best efficiency of methane and hydrogen formation was attained at −1.2 V vs SCE (r_f = 1.7 and 108%, respectively; see Fig. 3). Ethylene was produced with 0.2–0.8% efficiency at potentials from −1.0 to −1.35 V vs SCE. Over the same potential range, traces of carbon monoxide were produced at constant faradaic efficiency ($r_f \approx 0.2\%$).

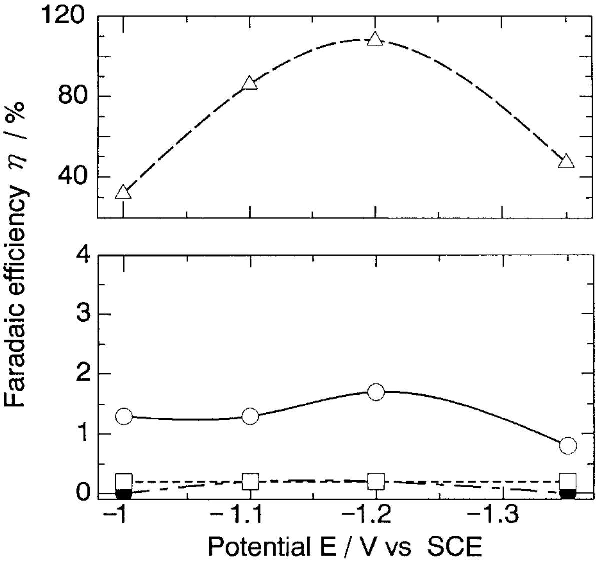


Fig. 3. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Fe electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △; C_2H_4: ●.

On Co electrodes the efficiency of methane formation increased with increasing cathodic polarization, reaching a maximum value of 2.3% at −1.5 V vs SCE. As seen in Fig. 4., hydrogen evolution was almost independent of the potential ($r_f \approx 88\%$).

Figure 5 details the effect of the potential on the electroreduction of CO_2 on Ni electrode. The current efficiency for hydrogen ($r_f \approx 94\%$) was almost constant over the potential range from −1.6 to −1.9 V vs SCE. Methane was produced with r_f = 3.0%, at −1.5 V vs SCE, and r_f = 2.7%, at increased cathodic polarizations (−1.9 V vs SCE), while in the potential range from −1.6 to −1.8 V vs SCE the current yield passed through a minimum of $r_f \approx 1.0\%$. Both

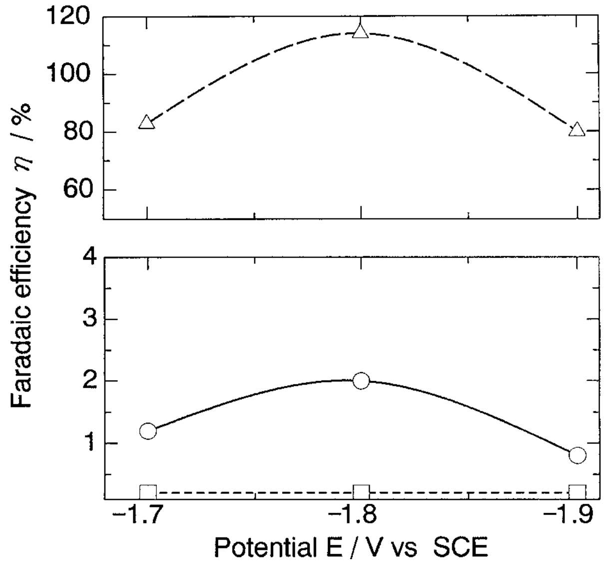


Fig. 2. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Ti electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △.

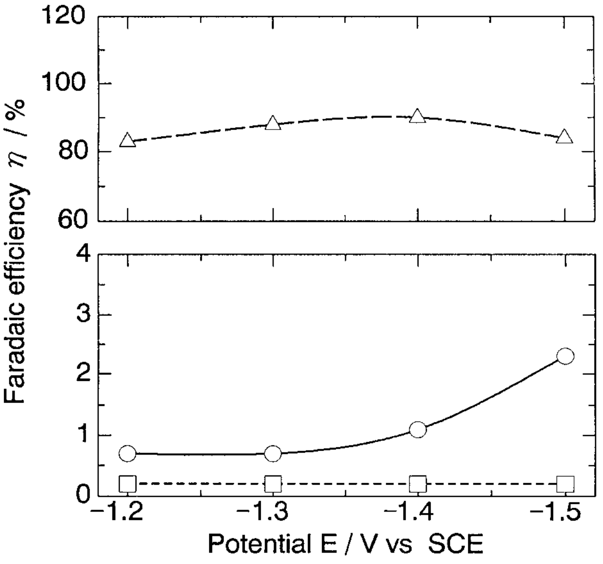


Fig. 4. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Co electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △.

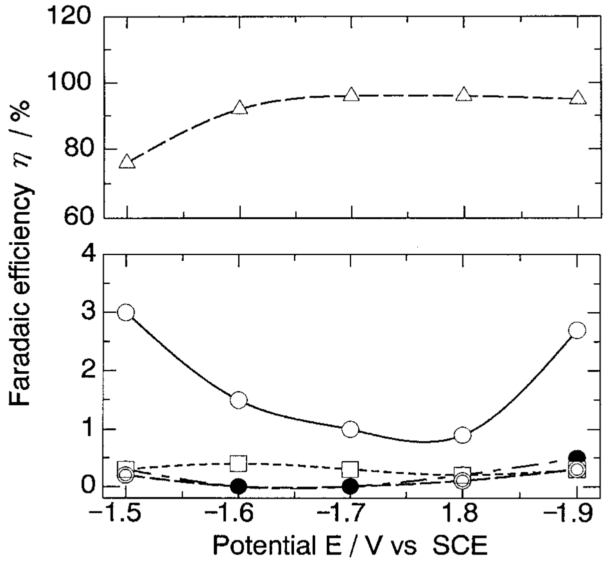


Fig. 5. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Ni electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △; C_2H_4: ●; C_2H_6: ◎.

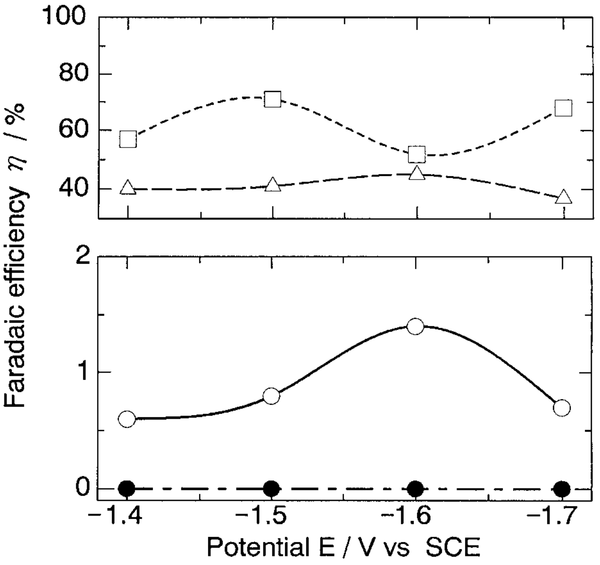


Fig. 7. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Ag electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △; C_2H_4: ●.

ethylene and ethane formed at low faradaic efficiency (r_f = 0.5 and 0.3%, respectively).

Hydrogen was the main electrolysis product on the Pt electrode, even in CO_2-saturated methanol. Hydrogen evolution was enhanced with increasing cathodic polarization (see Fig. 6). Under optimal conditions, a maximum of r_f = 94% was attained. Methane formation was insignificant over the entire potential range ($r_f \approx$ 0.2%).

The potential dependence of r_f for the formation of CO, H_2 and methane on a Ag electrode is shown in Fig. 7. Carbon monoxide was produced with $r_f \approx$ 60% from −1.4 to −1.7 V vs SCE, passing through a maximum of 70% at −1.5 V vs SCE. No potential dependence was observed for hydrogen $r_f \approx$ 40%. The most efficient formation of methane occurred at −1.6 V vs SCE ($r_f \approx$ 1.4%).

On Au electrodes, CO formation was enhanced with cathodic polarization. A maximum current yield of 63% was reached at −1.2 V vs SCE (Fig. 8). The best efficiency for both hydrogen and methane formation (r_f = 16 and 2.4%, respectively) were recorded at −1.0 V vs SCE for H_2 and −1.1 V vs SCE for CH_4.

The influence of the cathodic potential on the products formed on a pure Zn electrode is shown in Fig. 9. Carbon monoxide formed more efficiently at more negative potentials, a maximum r_f of 64% being achieved at −1.6 V vs SCE. By contrast, methane evolution was reduced at more negative polarizations.

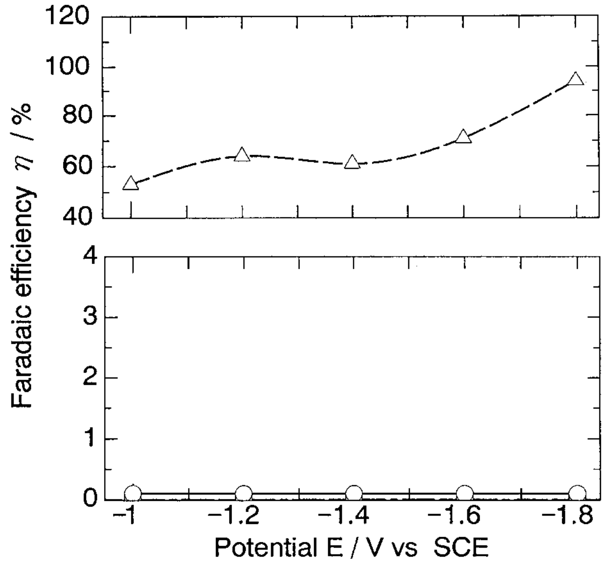


Fig. 6. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Pt electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; H_2: △.

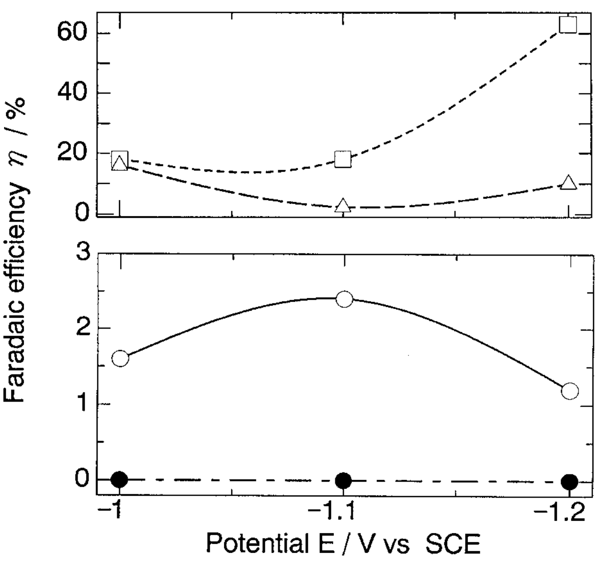


Fig. 8. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Au electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △; C_2H_4: ●.

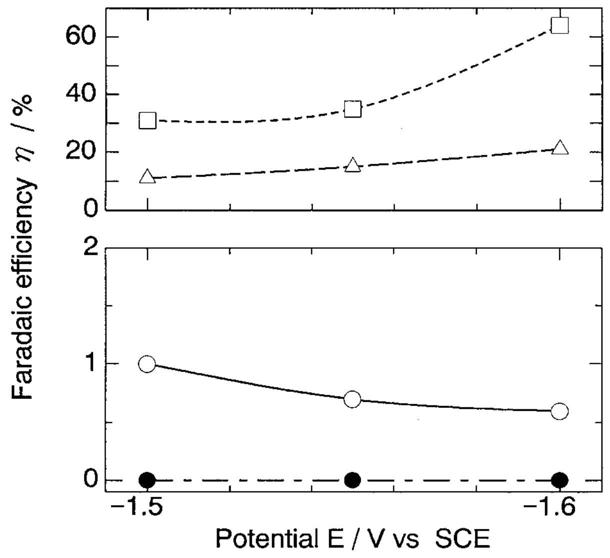


Fig. 9. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Zn electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △; C_2H_4: ●.

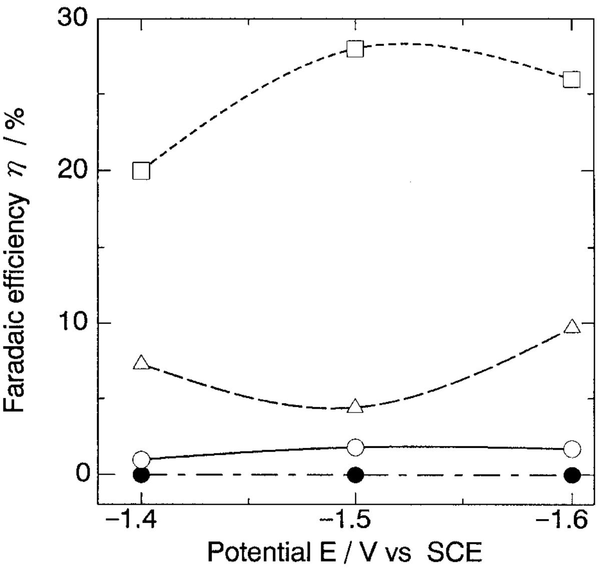


Fig. 10. Faradaic efficiencies for the products by CO_2 electrochemical reduction at Sn electrode in 10^{-2} mol dm^{-3} benzalkonium chloride–methanol catholyte. CH_4: ○; CO: □; H_2: △; C_2H_4: ●.

Only insignificant amounts of methane were produced on the Sn electrode (about 1 mmol, corresponding to approximately 1.5% efficiency; see Fig. 10). Maximum amounts of CO (28%) were detected at −1.5 V vs SCE. Hydrogen formed with a current yield less than 9.7%, over the entire potential range.

3.3. *Effect of the nature of the metallic electrode on faradaic efficiency of products*

Table 3 summarizes the amounts and faradaic efficiencies of the products obtained on various electrodes, under optimized experimental conditions. Methane was produced with a faradaic efficiency in

Table 3. Electrochemical reduction products of carbon dioxide on various metallic electrodes in methanol-based catholyte

Group	*Cathode*	*Charge*†/C	*Potential /V vs SCE*	*Amount*/mmol (*upper*) *Faradaic efficiency*/% (*lower*)					
				CH_4	C_2H_4	C_2H_6	CO	H_2	*Total*
IV	Ti	50	−1.8	1.3	nd	nd	0.5	296	
				2.0			0.2	114	116
VIII	Fe	30	−1.1	0.5	0.1	nd	0.3	133	
				1.3	0.2		0.2	86	88
	Co	30	−1.5	0.9	nd	nd	0.3	130	
				2.3			0.2	84	87
	Ni	50	−1.9	1.8	0.2	0.1	0.8	246	
				2.7	0.5	0.3	0.3	95	99
	Pt	50	−1.8	0.1	nd	nd	nd	243	
				0.2				94	94
I B	Cu*	50	−1.9	0.9	1.4	nd	46	140	
				1.4	3.5		16	54	75
	Ag	50	−1.5	0.5	nd	nd	185	105	
				0.8			71	41	113
	Au	30	−1.2	0.4	nd	nd	98	16	
				1.2			63	10	74
II B	Zn	30	−1.6	0.2	nd	nd	99	33	
				0.6			64	21	86
IV B	Sn	50	−1.5	1.2	nd	nd	72	11	
				1.8			28	4.4	34

† Total charge passed.
* Data from [5].
nd: not detected.

the range from 0.2 to 3.0% (corresponding to amounts of 0.1–2 mmol) on all the nine electrodes. Largest amounts of ethylene (0.1–1.4 mmol) were formed on Group VIII metals (Fe and Ni) and on copper. Ethane was produced on Ni only, with a low faradaic yield: 0.3% (0.1 mmol). According to Hori *et al.* [13], when a copper wire electrode was employed in aqueous 5×10^{-1} mol dm^{-3} $KHCO_3$ solution, ethane formed with $r_f = 38\%$, while r_f recorded on Sn and Ni electrodes was only 0.1–1.2%. In organic solvents, such as propylene carbonate, acetonitrile, dimethylformamide and dimethylsulphoxide, only low concentrations of hydrocarbons were detected [2, 14]. Nevertheless, in recent work carried out on copper electrodes at low temperature (−30 °C), CO_2 dissolved in methanol was reduced to methane, an excellent current efficiency of 42.5% being achieved [7]. One may conclude that methanol is among the most suitable solvents for the preparation of hydrocarbons.

Carbon monoxide is the major reduction product on IB (Ag, Au), II B (Zn) and III B-group metal (Sn) electrodes, with faradaic efficiencies of 71, 63, 64 and 28%, respectively. The maximum amount of CO (185 mmol) was formed on a Ag electrode. Since the solubility of CO_2 in methanol is of 4.6 cm^3/cm^{-3} (205 mmol CO_2 /cm^{-3} methanol) [15], 138 cm^3 (6.16 mmol) of CO_2 at 15 °C dissolve in 30 cm^3 of methanol based supporting electrolyte. From this one can calculate the yield of the process as equal to 3.0%. However, when the electroreduction of CO_2 was performed in aqueous supporting electrolytes, the amount of products are directly proportional to the charge passed [16]. It is expected that the amount of products obtained in methanol-based media should also obey Faraday's law. Upon recirculating the supporting electrolyte through the electrochemical cell, the yield of electroreduction reached 100%. According to literature reports, in the electroreduction performed on silver electrodes in organic solvents, oxalic acid and formic acid were produced in addition to CO [2, 14]. Moreover we were unable to detect oxalic acid and formic acid in the methanol-based catholyte we used. In methanol, CO was produced selectively on IB, IIB and IIIB group metal electrodes. Particularly on Sn, hydrogen evolution was maintained at amounts below 10%. Thus, methanol-based catholytes were more efficient in avoiding hydrogen evolution than most organic solvents and water.

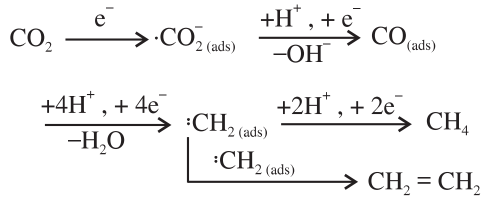
Hydrogen production was significant on IV and VIII group metal electrodes, while the reduction of CO_2 was barely detected. This is in agreement with our observation that with Ti, Ni and Pt electrodes the polarization curves in CO_2-saturated methanol were shifted toward more negative potentials relative to those obtained in N_2-purged methanol. Two exceptions were, however, found: both Fe and Co electrodes had greater positive potentials in CO_2-saturated methanol than in N_2-purged methanol.

The total current yield of the electroreduction products obtained on Fe, Co, Cu, Au, Zn and Sn electrodes did not sum to 100%. The residual current, 12–66%, might be attributed to the formation of methanol from CO_2 and H_2O, as it is not possible to completely avoid the diffusion of water through the membrane from the anode compartment into the cathodic half-cell. Methanol production by the electroreduction of CO_2 in aqueous supporting electrolytes has been previously reported by Frese [17] and Hori *et al.* [13], and reviewed by Jitaru *et al.* [3].

3.4. *Mechanism of electrochemical reduction of carbon dioxide*

The mechanism of the electroreduction of CO_2 in methanol was studied at ambient temperature and pressure. These experimental data and literature reports [2, 3, 5, 13, 14], suggest the pathway by which methane, carbon monoxide and ethylene are formed can be found.

Hydrocarbons are yielded by a series of simultaneous or consecutive electronation/protonation steps, according to the following simplified scheme:



The adsorbed $\cdot CO_2^-$ radical anion formed in the first electronation step undergoes a second electronation/protonation to yield adsorbed CO as the key intermediate. By a succession of four electronation/protonation steps an adsorbed reactive methylene group forms, and this may either stabilize as a methane molecule by a subsequent double electronation/protonation sequence or dimerize to ethylene.

For the formation of carbon monoxide on IB, IIB and IIIB group metal electrodes we assume the usual pathway, one which involves a one-electron reduction followed by the disproportionation of the $\cdot CO_2^-$ radical anions to neutral CO molecules and dinegative carbonate ions:

$$CO_2 \xrightarrow{e^-} \cdot CO^-_{2(ads)} \xrightarrow{+CO_2, +e^-} CO + CO_3^{2-}$$

In conclusion, the main products of the electrochemical reduction of carbon dioxide on Ti, Fe, Co, Ni, Pt, Ag, Au, Zn and Sn electrodes in benzalkonium/methanol solution at ambient temperature and pressure were CO, methane and ethylene. Carbon dioxide was selectively converted to CO on Ag, Au, Zn and Sn electrodes. Methane was produced with current yields in the range from 0.2 to 3.0%. On nickel electrodes, ethane and ethylene were formed at low faradaic efficiency (0.5 and 0.3%, respectively). With methanol being widely used industrially as a

CO_2-absorbent, the procedure reported in this paper may find applications in the conversion of CO_2-saturated methanol into useful products.

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