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Influence of CO_2 partial pressure and the supporting electrolyte cation on the product distribution in CO_2 electroreduction

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This paper reports a study of the influence of CO_2 partial pressure and the cation of the supporting electrolyte on the electrochemical reduction of CO_2 at copper electrodes in aqueous solution at 25° C. Both current efficiency (CE) and the rates of formation of the reduction products diminish linearly with decreasing CO_2 pressure, while evolution of hydrogen increases. The product distribution was greatly influenced by the supporting electrolyte cation. The CE for the formation of C_2H_4 increased with cation in the order $Cs^+ \approx K^+ > Na^+ > Li^+$, apparently in a manner related to the size of the cation radius. The non-metallic cation NH_4^+ allowed only hydrogen evolution with a CE of about 92%.

1. Introduction

The electrochemical reduction of carbon dioxide has received considerable attention in recent years, partly because of the undesirable 'greenhouse' phenomenon believed to be due in part to high concentrations of CO_2 in the atmosphere [1].

A variety of metallic and semiconductor electrodes have been tested for their effectiveness in the reduction of CO_2 to hydrocarbons or other useful materials [2–7]. Thus far the most promising electrode seems to be copper, insofar as hydrocarbons or alcohol products are concerned [4, 5].

Experimental results indicate that the reduction rate of CO_2 and the CE for product formation depends on crystallographic parameters and surface morphology of the electrode [8–10], the temperature [11, 12] and also the concentration and kind of the electrolyte anion [13, 14]. Formation of C_2H_4, EtOH, and *n*-PrOH is favoured in solutions of KCl, K_2SO_4, $KClO_3$ and dilute $KHCO_3$, whereas formation of CH_4 is favoured in 0.5 M $KHCO_3$ [14]. As far as we know no studies have been reported on the influence of the electrolyte cation on the reduction products of CO_2 at copper electrodes.

Pressure effects have been studied by voltametric methods at high hydrogen overvoltage electrodes [15–19]. In certain studies, before 1985, analysis for only HCOOH was carried out because at that time it was thought that HCOOH was the only possible reduction product [16, 17]. Later it was shown that CO and gaseous hydrocarbons were also reduction products of CO_2 [2, 4].

The present study was concerned with effects of CO_2 pressure and the cation of the supporting electrolyte (Li^+, Na^+, K^+, Cs^+ and NH_4^+) on the reduction of CO_2 at a copper electrode.

2. Experimental details

2.1. *Electrode treatment*

High-purity copper foils 99.999% (Alpha Metal) of 1 cm^2 surface area were used for all experiments. These electrodes display crystal orientation in the (2 0 0) plane, as realised by X-ray diffraction. The area ratio given in the literature [20] for the (1 1 1), (2 0 0) and (2 2 0) diffractions in the normal copper lattice is 100 : 46 : 20 respectively. In the foils used in this work the corresponding relation is 6.66 : 100 : 22.7.

The copper foil was washed with warm dichloromethane and was then immersed for 1 h in concentrated HCl for degreasing and removal of metallic surface impurities (Fe and Ni) which result from rolling process. It was anodized in 85% w/w H_3PO_4 at 500 mA cm^{-2} current density for 2 min, in order to obtain a shiny smooth surface, and washed several times with doubly distilled-deionized water. The electrode was then anodised in 0.1 M KCl at 25 mA cm^{-2} for 2 min and washed with water as above.

The roughness factor of this electrode was 3.6. This value was estimated by comparing the currents of the cyclic voltamograms of the V^{3+}/V^{2+} couple, obtained at rough and smooth Cu electrodes with the same geometric area [10].

2.2. *Electrolysis procedure*

Electrolysis was performed in a three-compartment cell placed in a thermostated bath at 25°C, with the copper cathode placed between two platinum foil anodes [4] and the reference electrode (SCE) connected via a Luggin capillary. Separation between anolytes and catholyte compartments was achieved by two Nafion 417 membranes (0.43 mm, H^+ form).

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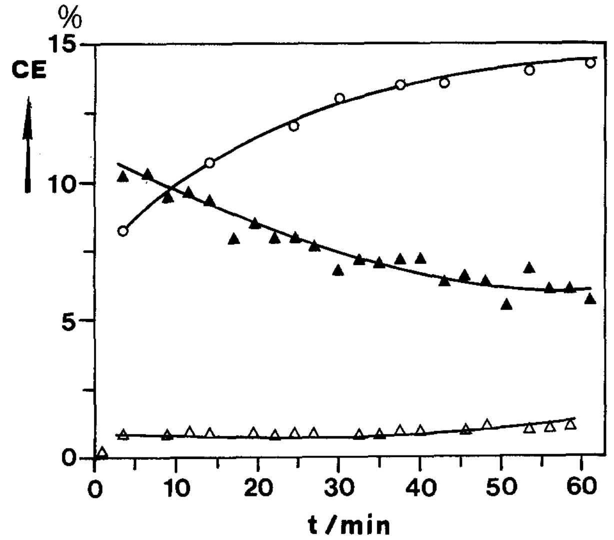

Fig. 1. CE against time for CO_2 reduction products in 0.5 M $KHCO_3$ solution at 25° C, electrode potential −1.65 V/SCE and CO_2 pressure 1 atm. (○) CO, (▲) C_2H_4 and (△) CH_4.

The copper electrode was placed for 5 min in solution previously deaerated with CO_2 for 10 min and was instantly polarised to the required potential. Agitation was provided by a magnetic bar stirrer. A Bank Electronic potentionstat POS 73 was used for all experiments.

Reagent grade chemicals (Aldrich) and doubly distilled-deionized water were used for solution preparation. The lithium bicarbonate solution was prepared by passing CO_2 through lithium carbonate solution, for 6 h. High-purity CO_2 (Air metal) or a controlled mixture of CO_2, Ar was bubbled through the catholyte at a flow rate of 100 ml min^{-1}. The exact mixture composition was determined by GC (gas chromatography).

2.3. *Products analysis*

Hydrocarbons and carbon monoxide analysis (after its passage though a catalytic methanizer) were performed by GC with Porapak QS column and a FID detector. Hydrogen analysis was carried out by TCD detector with argon as carrier gas. The gas sample was injected at 2.5 min intervals via a six-way valve with 750 μL loop. The catholyte solution was analysed by GC in order to test for trace alcohols. The concentration of the formate was determined using a Wescan Ion Analyser 213A and Anion Exclusion 269006 column. The reproducibility of analysis for CO, hydrocarbons, H_2 and HCOOH were 1.8, 1.1, 3 and 1.4%, respectively.

3. Results

3.1. *Pressure effects*

Figure 1 shows the change in CE for the various gaseous products with electrolysis time. It can be seen that the CE for C_2H_4 formation diminishes with electrolysis time to 60% of the initial value after 60 min of electrolysis, while the CE for CO and CH_4 increases.

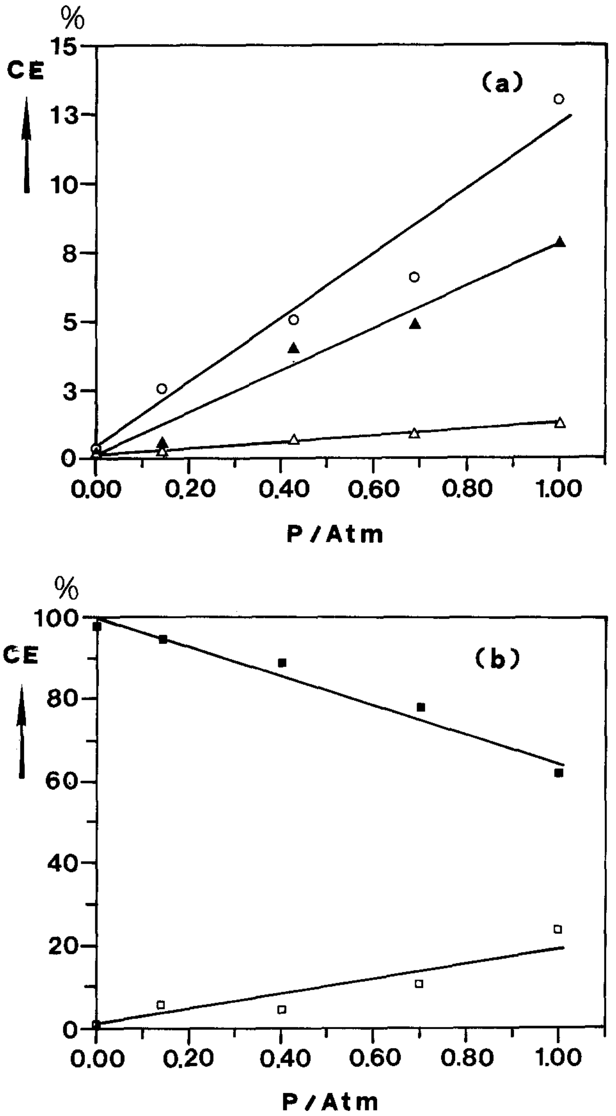

Fig. 2. Mean CE for the products of CO_2 electroreduction against CO_2 partial pressure at a copper electrode in 0.5 M $KHCO_3$ solution at 25° C, electrode potential −1.65 V/SCE and electrolysis time 60 min. (a) ▲: C_2H_4, △: CH_4, ○: CO and (b) ■: H_2, □: HCOOH.

Both the CE for hydrogen evolution and the total current density show a slow increase with electrolysis time. Such effects were also observed previously [10,21].

Pressure effects were studied at −1.65 V vs SCE because the CE fluctuations against time were smaller at this potential than at more negative potentials. Figure 2a and b shows the CE for reduction products with respect to CO_2 partial pressure in 0.5 M $KHCO_3$ solution. The CE for all products decreases linearly with decreasing CO_2 pressure, while the CE for hydrogen increases.

Figure 3 shows that the current density, calculated on the basis of the geometric electrode area, is dependent almost linearly on CO_2 pressure. With no CO_2 addition the current density for CO_2 reduction was not zero. This was attributed to small amounts of CO_2 in the solution due to the equilibrium [22]:

$$HCO_3^- \rightleftharpoons CO_2 + OH^-$$

The reaction order was determined as previously proposed [16, 23] from the slope of log i/log P_{CO_2} curve

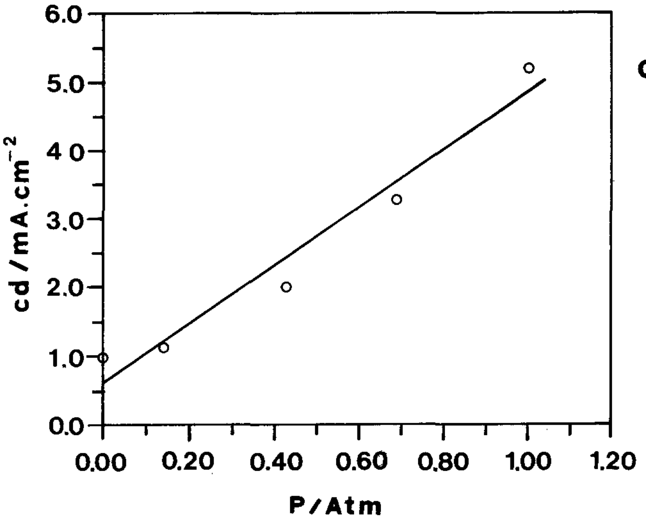

Fig. 3. Apparent current density for CO_2 reduction against partial CO_2 pressure, at electrode potential -1.65 V vs SCE.

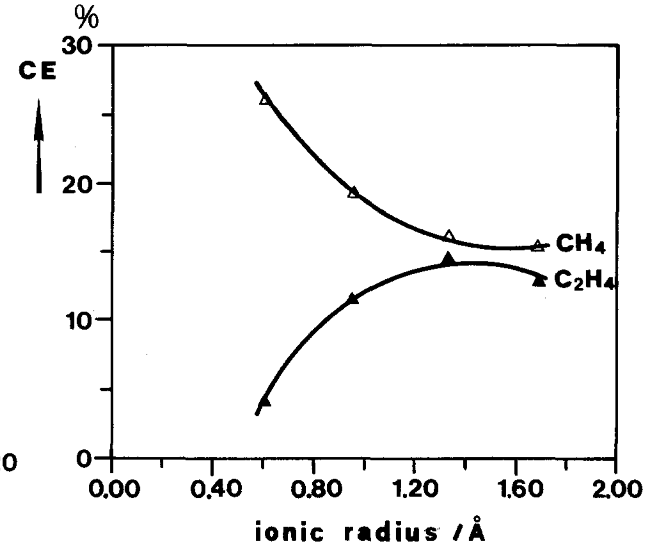

Fig. 4. Mean CE for CH_4 and C_2H_4 production against ionic radius of supporting electrolyte cation at the copper electrode, 25° C, electrode potential -1.85 V vs SCE and electrolysis time 60 min.

and was found to be 1.05. This value is in agreement with literature values at other metallic electrodes [16, 17, 19]. Fischer *et al.* [15] have also observed a linear dependence between CO_2 pressure and CO_2 reduction current density at copper electrodes.

3.2. *Effect of electrolyte cations*

The cations chosen for study were Li^+, Na^+, K^+, Cs^+ and NH_4^+. Electrolyses with solutions containing these ions were performed at -1.8 V vs SCE at 25°C and CO_2 pressure 1 atm. The mean CE values for all reduction products formed in the first 60 min of electrolysis, are listed in Table 1. It can be seen that the distribution of products was significantly influenced by the cation, especially for hydrocarbon formation and hydrogen evolution. The non-metallic NH_4^+ ions almost completely inhibited the formation of organic products in favour of hydrogen production (92% CE).

Figure 4 indicates the observed relationship between CE for hydrocarbon formation and cation radius of the electrolyte. The CE for C_2H_4 formation increased as the radius of the cation increased i.e, $K^+ > Na^+ > Li^+$, whereas the CE for CH_4 was influenced in the opposite order with respect to ionic radius size. It is interesting to note that the CE for C_2H_4 was 3.2 times higher when K^+ was the cation of the supporting electrolyte than in the case of Li^+. Cs^+ with larger ionic radius, gave a small decrease, rather than an increase, in the CE for C_2H_4 formation.

Table 1. Mean CE of products from the electroreduction of CO_2 at Cu electrodes in various solutions at -1.85 V/SCE, 25° C and electrolysis time 60 min.

Electrolyte	*Current efficiency/%*					
	CO	*CH_4*	*C_2H_4*	*H_2*	*HCOOH*	*Total*
$LiHCO_3$ (0.5 M)	2	26	4	68	3	103
$NaHCO_3$ (0.5 M)	3	19	11	62	4	99
$KHCO_3$ (0.5 M)	4	16	14	59	5	98
$CsHCO_3$ (0.5 M)	5	15	13	56	6	95
NH_4HCO_3 (0.5 M)	1	1	–	92	2	96

Similar cation effects were also observed by Eyring *et al.* [16, 17] for HCOOH formation at a mercury electrode. At glassy carbon electrodes, with quaternary ammonium salts as supporting electrolytes, different products were formed [24] and were attributed to special electrical double layer effects.

4. Discussion

The electroreduction of CO_2 is, apparently, a very complex process whose mechanism is not yet fully understood [9, 10, 12]. Most studies have indicated that the first steps in the reduction of CO_2 at high hydrogen overpotential cathodes are [19, 25, 26] as follows:

$$CO_{2_{ads}} + e^- \longrightarrow CO^{\cdot -}_{2_{ads}} \qquad (1)$$

$$CO^{\cdot -}_{2_{ads}} + BH + e^- \longrightarrow HCO^-_{2_{ads}} + B^- \qquad (2)$$

where BH = proton donor.

At pH < 4 the hydrogen ion plays the role of BH, while at pH > 4 water supplies the required protons. The presence of adsorbed $CO_2^{\cdot -}$ and HCO_2^- anion radicals at Hg electrodes was ascertained by electrochemical and spectroscopic techniques [26, 27].

For the reduction of CO_2 at copper electrodes there are no data suggesting such adsorption of $CO_2^{\cdot -}$ and HCO_2^- anion radicals, but some workers [14] propose Reaction 1 as the first step. In that case the strength of adsorption and the degree of surface coverage by $CO_2^{\cdot -}$ should influence the reduction rate and the nature of the reduction products [27, 28].

The reduction rate of CO_2 in the second Tafel region at various moderate and high hydrogen overpotential electrodes was expressed by Vassiliev *et al.*

[19] as:

$$i_1 = k_1 [CO_2]^{\beta} \times \exp\left\{\frac{-S}{2}(E - E_{max})^2 - \frac{\alpha n F}{RT}(E - \psi')\right\} \quad (3)$$

where E is the electrode potential, E_{max} is the potential of maximal adsorption, S represents the adsorption sites and ψ' is the potential value in the plane in which are located the centres of the charges of reacting products in the transition state of the reaction.

The value of β at lead cathodes was found to be 0.9–1, at mercury cathodes 1 and at tin cathodes between 0.6 and 0.8 [19]. The value of β of about 1 in the present work is reasonably close to that of the above literature.

It is known that Li^+ has a higher hydration number than cations with larger radii. This means that the total radius of the hydrated Li^+ cation is larger than those of Na^+, K^+ and Cs^+, resulting in lower ψ' potential value around the Li^+ cation [29]. Equation 3 shows that a decrease in the ψ' potential decreases the CO_2 reduction rate. Decrease of the CO_2^- anion radical adsorption strength leads to an increase in hydrogen adsorption. Therefore, it is speculated that cations with small radii tend to favour hydrogen evolution at the cathode, while those with the larger radii favour CO_2 reduction.

The above remarks are in agreement with the previously observed decrease in CO_2 reduction rate with increase in electrolyte concentration [14], since the ψ' potential decreases.

On the basis of previous studies [9, 10, 30] CO_2 was initially reduced to CO and then to adsorbed CH_2 groups at the copper surface. Consequently, the formation of hydrocarbons from CH_2 groups proceeds as follows:

$$Cu{=}CH_2 + Cu{=}CH_2 \rightarrow CH_2{=}CH_2 + 2Cu \quad (4)$$

$$Cu{=}CH_2 + 2CuH_{ads} \rightarrow CH_4 + 3Cu \quad (5)$$

The conversion of intermediate $Cu{=}CH_2$ to $CH_2{=}CH_2$ does not require the presence of adsorbed hydrogen. Thus this reaction is favoured at lower surface hydrogen coverage, as seems to be the case, when K^+ or Cs^+ are the cations of the supporting electrolyte. The opposite tends to occur when hydrogen adsorption is high, as is the case with Li^+ or Na^+.

The results show that the current efficiency (CE) for hydrocarbon formation in the presence of Cs^+ is about equal or somewhat smaller than in the presence of K^+. The Gibbs free energy (ΔG) for the removal of water molecules from the electrode surface and adsorption of Li^+, Na^+ and K^+ cations is positive, while the corresponding energy change for Cs^+ is negative [29]. This implies that only Cs^+ is capable of spontaneous 'contact adsorption' under the experimental conditions. It is possible that the adsorption of Cs^+ diminishes the available copper electrode area for the adsorption of CO_2 and hence the reduction of CO_2.

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