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Electrochemical reduction of CO_2 at metallic electrodes

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1. INTRODUCTION

The quantities of carbon stored in the form of atmospheric carbon dioxide, CO_2 in the hydrosphere and carbonates in the terrestrial environment, substantially exceed those of fossil fuels. In spite of this, the industrial use of carbon dioxide as a source of chemical carbon is presently limited to preparation of urea and certain carboxylic acids as well as organic carbonates and polycarbonates. However, the situation is expected to change in the future, if effective catalytic systems allowing to activate carbon dioxide will become available. In this connection, the electrochemical reduction of CO_2 , requiring only an additional input of water and electrical energy, appears as an attractive possibility.

For more than 100 years formic acid and formates of alkali metals were considered as the only significant products of the electroreduction of carbon dioxide in aqueous solutions. The highest current efficiencies, exceeding 90 %, were obtained with mercury and with amalgam electrodes [1-5] as well as at gallium, zinc, indium, tin, lead and cadmium [6-8] i.e., at the metals exhibiting high hydrogen overvoltages. It is, however, to be mentioned that under particular conditions (in the solutions containing quaternary ammonium salts) the same metal cathodes produced C_2, C_3 and C_4 carboxylic acids [8]. The only comprehensive study regarding kinetics of CO_2 reduction in aqueous solution has been performed by Eyring et al. [9,10] using a mercury cathode. The proposed mechanism includes two charge transfer steps, eq. 1 and 3, separated by a rapid chemical reaction, eq. 2 .

$$CO_2 + e^- \rightarrow CO_2^{\cdot-}{}_{(ad)} \quad (1)$$

$$CO_2^{\cdot-}{}_{(ad)} + H_2O \rightarrow HCO_{2(ad)} + OH^- \quad (2)$$

$$HCO_{2(ad)} + e^- \rightarrow HCO_2^- \quad (3)$$

The involvement of the radical anion $CO_2^{\cdot-}$ as the reaction intermediate at the mercury electrode has been confirmed by the photoemission measurements [11]. Small amounts of $CO_2^{\cdot-}$ radical anions have also been identified at a lead cathode using modulated reflectance spectroscopy [12]. It is important to recall, in this connection, that both these cathodes exibit high overvoltages for the CO_2 reduction (for the mercury electrode, for example, it exceeds 1V at a current density of 1mA/cm^2). This is consistent with a strongly negative value of the

half-wave potential of the reaction (1) close to -2V versus standard hydrogen electrode (SHE). Other "soft" metal cathodes, particularly indium and tin allow still to obtain formates with high current efficiencies but at lower overvoltages [6,7].

It was the observation by Hori et al. [13-15] that medium hydrogen overvoltage cathodes, gold, silver and copper are able to promote formation of gaseous products of CO_2 electroreduction which has led to a marked regain of interest in this process. These authors have in fact demonstrated that the electrolysis of slightly alkaline solutions containing alkali metal hydrogen carbonates and CO_2, when conducted at gold and silver, leads to the formation of carbon monoxide with faradaic yields attaining 100%. On the other hand, in the case of a copper cathode, the CO_2 reduction continues further to form hydrocarbons-methane and ethylene as well as ethanol. These findings were rather unexpected as, for the long time, carbon monoxide together with oxalic acid had been considered as typical products of CO_2 reduction in non-aqueous solutions [8]. Despite a large number of studies devoted, since more than 10 years, to the reduction of CO_2 at the Au, Ag and Cu cathodes, several important features of this reaction remain still unclear. This concerns, in particular, (i) the nature of the first charge transfer step leading to the subsequent formation of CO and (ii) the reasons of deactivation of the above cathodes occurring during continuous electrolysis runs. The next paragraphs are devoted to the discussion of the most important aspects of the CO_2 reduction at the copper cathode.

2. EXPERIMENTAL

Electrolysis experiments conducted under atmospheric pressure were carried out in a two-compartment, tight Teflon® cell. The cathodic compartment contained ca. 30 cm^3 of electrolyte and was separated from the anodic one by a Nafion® membrane. The cell was equipped with a cyclic gas flow system. Before each electrolysis run, CO_2 supplied from a gas cylinder was passing through catholyte and gas circuit during 2 h to saturate the solution and to fill the system with CO_2. The total volume of the gas enclosed in the system was 185 cm^3 and its circulation rate 12 cm^3 min^{-1}. High purity metals rods (7 mm in diameter, 99,999%) served as cathodes. All electrodes were mechanically polished with 1200 grit polishing paper and 0.3 μm alumina. The copper cathode was in addition subjected to an etching in 10 % HCl for 15 s or, in some cases, to an anodic cleaning in concentrated H_3PO_4. The oxide-modified Cu electrodes were prepared by attaching Cr_2O_3 and ZrO_2 (Merck) powders to the mechanically polished copper surface by means of poly(vinylidenefluoride), PVDF, and annealing at 250°C in air. A suspension of Cr_2O_3 (ZrO_2) in DMF containing dissolved PVDF (typical composition : 1 g oxide and 0.2 g PVDF per 5 cm^3 DMF) was deposited on a cross-section (0.28 cm^2) of Cu rods and dried in ambient air for 20 min before the final annealing. Solutions were prepared from reagent grade chemicals and twice distilled water. If not otherwise indicated, all potentials are given with respect to normal calomel electrode (NCE). In order to eliminate heavy metal contaminants, a constant current pre-electrolysis (25 $\mu A/cm^2$) was usually conducted for at least 48 h, under nitrogen atmosphere, between two platinum electrodes separated by a Nafion® membrane. 99.99% CO_2 was further purified by passing through an activated charcoal filter before being introduced to the cathodic compartment of the cell and to the gas flow system. Electrolysis experiments under increased

pressure of CO_2 were performed in a stainless steel autoclave including a two-compartment electrolysis cell. Analyses of the gaseous as well as solution products of the reaction were carried out on a Hewlett Packard 5890 Model gas chromatograph. The gas was sampled periodically with a gas syringe during the electrolysis, but products in the electrolyte were analysed once electrolysis run was completed. The chromatographic column Porapak HayeSepQ was employed to determine hydrocarbons and the reaction products in the solution, whereas analyses of CO were performed with the Carbosieve S-II column.

3. RESULTS AND DISCUSSION

3.1 CO_2 reduction at copper under atmospheric pressure

The progressive poisoning affecting Au, Ag and Cu cathodes during electroreduction of CO_2 [16-20] renders their behaviour in some ways similar to that of the catalysts employed in the gas phase hydrogenation of CO and CO_2.

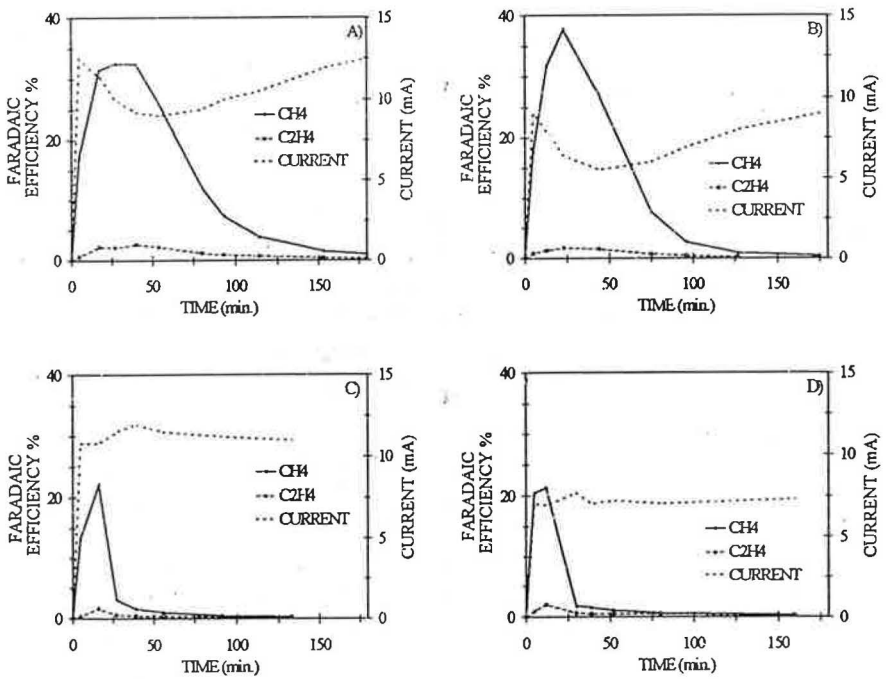

Fig. 1. Temporal evolution of faradaic efficiencies for methane and ethylene and of the cathodic current for CO_2 reduction in 0.5 M $KHCO_3$ at 22°C ; electrode potential, E = -2 V. 99.9 % and 99.999 % copper was used as electrode material, Figs A and C, respectively B and D. Solution was pre-electrolyzed in the case of C and D and without pre-electrolysis for A and B.

This poisoning is less severe for gold, where it results in a decay of the current (at constant controlled potential) without affecting faradaic efficiency of CO formation [18] than in the case of silver for which η (CO) tends to decrease as a function of time [17,21]. The heaviest deactivation is observed for the copper electrode, where CO_2 reduction is virtually stopped after 20-40 min of continuous electrolysis, being replaced by hydrogen evolution [19,20]. This phenemenon is illustrated by a series of curves in Fig. 1. Importantly, the copper electrode behaved in a similar way whether the electrolyte was pre-electrolyzed or not. Moreover, XPS (X-ray induced photo-electron spectroscopic) analysis of the copper samples polarized for 2h at -2V in both kinds of 0.5M $KHCO_3/CO_2$ solutions (ie, with and without pre-electrolysis) revealed only the presence of Cu, O and C signals. In particular, none of the metal elements present in trace amounts in $KHCO_3$ such as, for example, Fe, Zn, Cr, Pb or Cd was detected. The time associated with the deactivation of the cathode was no more influenced by the degree of purity of the copper metal (99.999% vs. 99.9%). It is to be pointed out that the observed poisoning of the Cu electrode affects selectively the CO_2 reduction while, at the same time, the rate of hydrogen evolution tends to increase (cf. variation of the electrolysis current vs. time in Fig. 1. This kind of behaviour can be expected in the case of formation of the elemental carbon [20] or of a layer of organic products [21,22] at the Cu surface. An in situ electrochemical activation method has been demonstrated to act very efficiently against the inhibition of the copper cathode versus the CO_2 reduction. Such a treatment involves a periodic anodic stripping of the nascent poisoning species from the electrode surface by means of a series of 2-3 rapid voltammetric sweeps, repeated every 5-10 min. over the entire electrolysis run [16,19].

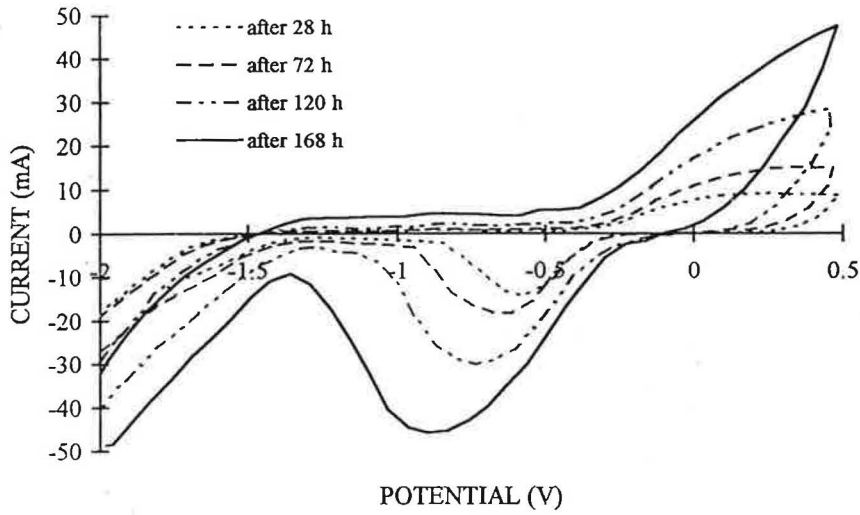

Fig. 2. Cyclic voltammograms (scan rate 5 V/s) representing sequences of the activation treatment of the Cu electrode (0.28 cm^2) performed periodically at different stages of a long-term electrolysis of CO_2 in 0.5 M $KHCO_3$.

The electrode activation requires less than 1 percent of the total electrolysis time (i.e., 2-3 s every 5 or 10 min.) and consumes a negligible extra amount of electrical charge. A typical series of cyclic voltammograms corresponding to the activation sequence is shown in Fig. 2. No features directly associated with the oxidation of the poisoning species are perceptible on any of these voltammograms. An initial increase of the current on the anodic side, connected with the oxidation of the copper surface is followed, during the cathodic sweep, by a large peak due to the reverse process. The increasing area under voltammograms is indicative of a continuous increase in the true surface area of the electrode. Application of such a potential program allows high faradaic efficiencies of CH_4, C_2H_4 and C_2H_5OH to be maintained over long electrolysis runs. Thus, the amount of methane formed at an activated Cu electrode increases considerably along a 24h electrolysis run (cf. Fig. 3).

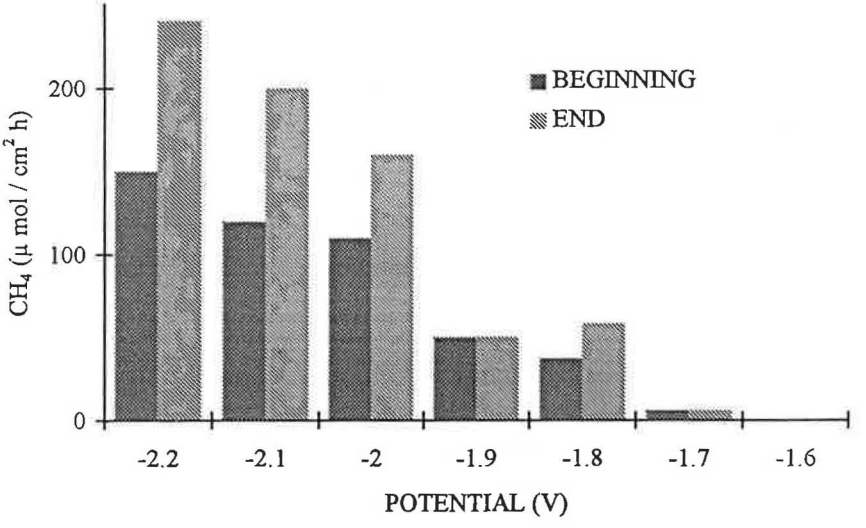

Fig. 3. Methane formation rates recorded at the beginning and after 24h of continuous electrolysis runs performed at increasingly cathodic potentials. Activated Cu electrode, 0.5 M-$KHCO_3/CO_2$ solution, 22°C.

As shown in Fig. 4, no electrode deactivation was observed during a 8-days long continuous electrolysis experiment. While the total rate of hydrocarbon formation remained remarkably constant as electrolyses progressed, an increase of the amount of ethylene accompanied by a decrease of the amount of methane were in general observed. These variations in the product distribution are probably associated with the structural changes occurring at the electrode surface and, in particular, with the increasing presence of $Cu^+_{(s)}$ species [19,23]. Interestingly, experiments performed using Cu electrodes modified with attached oxide (Cr_2O_3,ZrO_2) particles showed a dramatic change in the distribution of the CO_2 reduction products [23]. In fact, under such conditions, ethylene and ethanol are formed in larger amounts than methane (cf. Figs 5 and 6). This is in contrast with the results of electrolyses conducted using a bare Cu cathode, under otherwise identical conditions, where methane remained the major product.

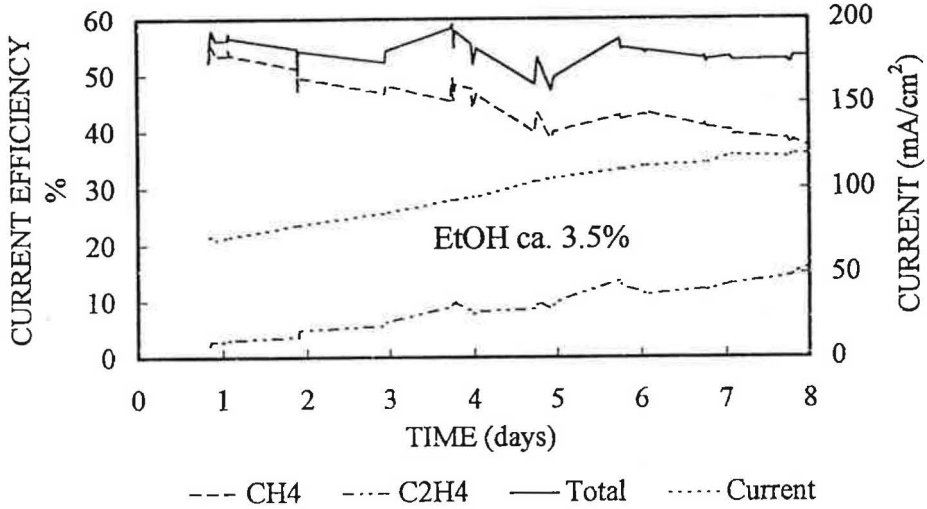

Fig. 4. Faradaic efficiencies of CH_4 and C_2H_4 vs. time for CO_2 reduction at an activated Cu electrode (0.28 cm^2) in 0.5 M $KHCO_3$ at 22°C ; E = -2V. Dotted line shows evolution of the apparent current density during 8 days-long electrolysis run.

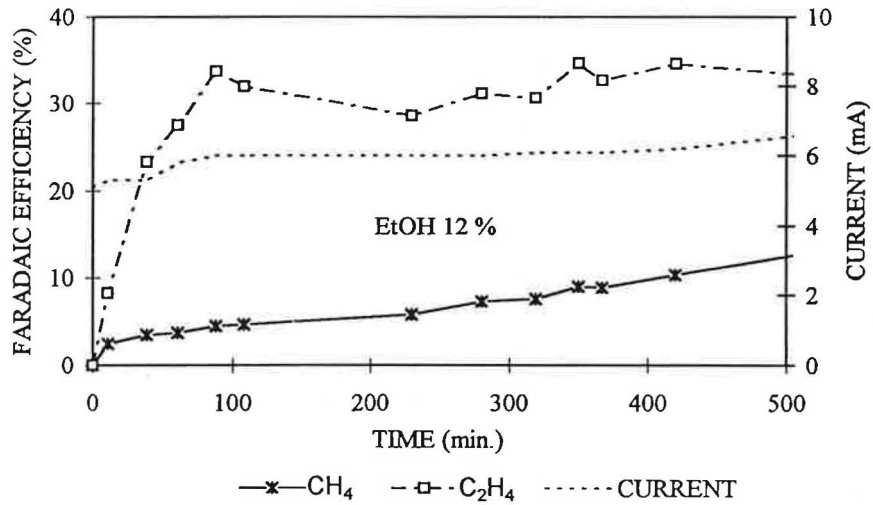

Fig. 5. Faradaic yields for C_2H_4 and CH_4 recorded together with cathodic current during electrolysis of CO_2 at a ZrO_2-modified, periodically activated, Cu electrode (0.28 cm^2) in 0.5 M K_2SO_4 at 5°C ; E = -1.8 V.

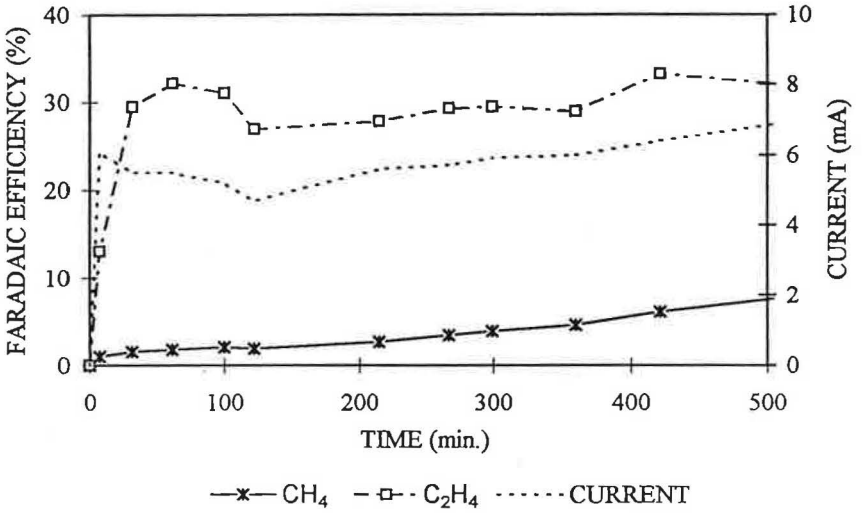

Fig. 6. Behaviour of a Cr_2O_3-modified Cu electrode ; all other features as in Fig. 5.

3.2 CO_2 electrolysis experiments at a copper cathode conducted under increased pressure

Because of a relatively small CO_2 solubility in water under atmospheric pressure (0.033 mol/dm^3 at 15°C), the reduction process meets limitations due to the slow transport of the reactant to the electrode. Such limitations appear clearly for an activated Cu electrode where a continuous increase in the cathodic current during prolonged electrolysis runs (cf. Fig. 4) leads finally to a decrease of the faradaic yield for hydrocarbons. To overcome this problem, several authors conducted electrolysis experiments at elevated CO_2 pressures.

Ito et al. [24] examined the effect of CO_2 pressure up to 20 atm on its reduction at metals displaying high overvoltage for hydrogen evolution : Zn, In, Pb and Sn. They found that the yield of formic acid (the main reaction product at these electrodes) was increased at higher pressures. Nakagawa et al. [25] investigated the CO_2 reduction at pressures up to 60 atm on group VIII metal electrodes : Fe, Co, Ni, Pd and Pt. At ambient pressure these metals yield almost exclusively hydrogen. At the CO_2 pressures of 50 and 60 atm, CO was produced at all the above electrodes with faradaic efficiencies of 62 % for Pd, 37 % for Ni and 34 % for Pt. The same group of researchers investigated the effects of CO_2 pressure, stirring and current density on the reduction product distribution at a Cu electrode [26,27]. They found that in order to obtain high faradaic efficiencies of hydrocarbons, a balance between CO_2 supply and current density should be maintained. If the flux of CO_2 was too high with respect to the current density, CO and HCOOH were the major products. If, on the contrary, CO_2 was in a short supply (too low pressure for a given current or no stirring) water reduction to hydrogen prevailed. It should be stressed that all these results concern short term experiments.

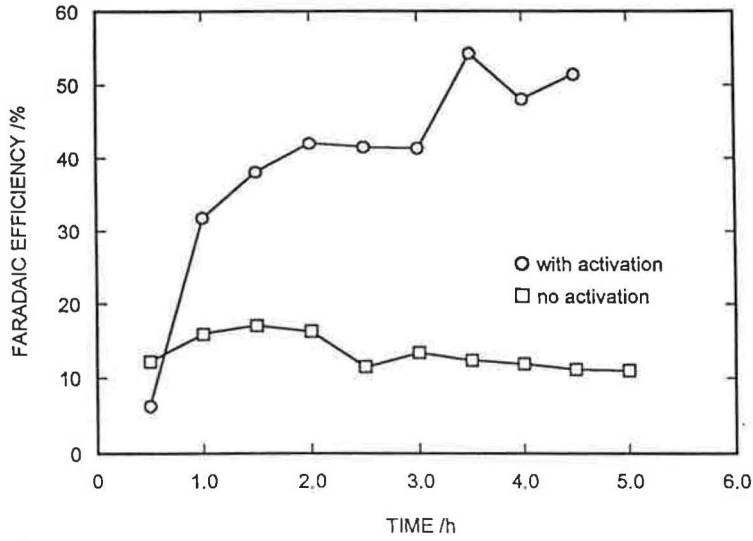

Fig. 7 Faradaic yields of hydrocarbons (CH_4 and C_2H_4) obtained during electrolyses of CO_2 (20 atm) in 0.5 M $KHCO_3$ at an activated, respectively, non-activated copper electrode ; 22°C, E = -2.85 V.

Our work [28] has extended to significantly longer electrolysis periods in order to check whether the Cu cathode undergoes poisoning also under increased pressure conditions. As shown in Fig. 7, the deactivation of copper is, in fact, much slower than under ordinary pressure, even if the amount of produced hydrocarbons remains definitely smaller than at an activated Cu electrode. Typically, the highest faradaic yields of CH_4 and C_2H_4 are reached at more negative potentials than under 1 atm CO_2 pressure (cf. Fig. 8), in spite of a careful compensation for the ohmic drop. However, the cathodic current densities recorded under a 20 atm CO_2 pressure, exceeding 600 mA/cm^2, are almost 6 times larger than those attained during an electrolysis conducted under ordinary pressure.

3.3 Nature of the inhibiting processes at the Cu electrode.

Recent surface enhanced Raman scattering (SERS) measurements, carried out during the reduction of CO_2 on the Cu surface [29], provide some insight into a series of events associated with deactivation of the electrode. These include: (i) the time-dependent decay of the SERS bands corresponding to adsorbed CO paralleled by (ii) the increase of a new band attributed to the formation of a "patina" like species (including copper oxide, hydroxide and carbonate). At this stage, the latter surface compound appears as the most likely poisoning species.

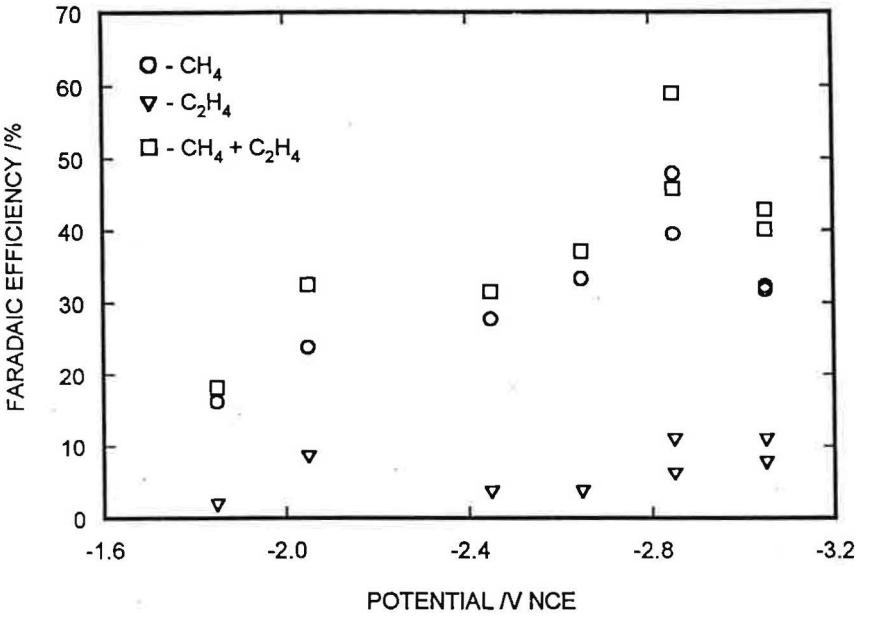

Fig. 8. Effect of the Cu electrode potential upon faradaic yields of hydrocarbons, formed during electrolyses of CO_2 under increased, 20 atm pressure in 0.5 M $KHCO_3$ at 22°C.

On the other hand, the fact that graphitic carbon, visible on the Cu surface at less cathodic potentials (-0.64 V), is readily hydrogenated to CH_x already at -1.54 V rules it out as a possible poison (the formation of a layer of graphitic carbon was evoked by De Wulf et al. [20] as the reason of deactivation of the Cu electrode observed in the course of CO_2 reduction.

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