

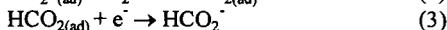
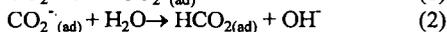
ELECTROREDUCTION OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS AT METAL ELECTRODES

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INTRODUCTION

The quantities of carbon stored in the form of atmospheric carbon dioxide, CO₂ 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 CO₂, 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 either with mercury or with amalgam electrodes [1-5]. The only comprehensive study regarding kinetics of CO₂ reduction in aqueous solution has been performed by Eyring et al. [6,7] using a mercury cathode. The proposed mechanism includes two charge transfer steps, eq. 1 and 3, separated by a rapid chemical reaction, eq. 2.



The involvement of the radical anion CO₂^{·-} as the intermediate of the reduction at the mercury electrode has also been confirmed by the photoemission measurements [8]. Small amounts of CO₂^{·-} radical anions have as well been identified at a lead cathode using modulated reflectance spectroscopy [9]. It is important to mention, in this connection, that both these cathodes exhibit high overvoltages for the CO₂ reduction (for the mercury electrode, for example, it exceeds 1V at a current density of 1mA/cm²). This is consistent with a strangely negative value of the half-wave potential of the reaction



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 [10,11]. As all these metals (i.e., Hg, Pb, In and Sn) exhibit high overvoltages for the reduction of water (hydrogen evolution), it was believed for the long time that this must be the necessary characteristic of every efficient electrocatalyst of CO₂ reduction. It was the observation by Hori et al. [12,13] that medium hydrogen overvoltage cathodes, gold, silver and copper are able to promote formation of gaseous products of CO₂ 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 CO₂, 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 CO₂ reduction continues further to form hydrocarbons-methane and ethylene as well as ethanol. The next paragraphs are devoted to the discussion of the most important features of the CO₂ reduction at these three cathodes (Au, Ag, Cu).

EXPERIMENTAL

All the electrolysis experiments related in the next paragraph were carried out in a two-compartment, tight Teflon® cell. The cathodic compartment contained ca. 30 cm³ 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, CO₂ 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 CO₂. The total volume of the gas enclosed in the system was 185 cm³ and its circulation rate 12 cm³ min⁻¹. High purity metals rods (7 mm in diameter, 99,999%) served as cathodes. Solutions were prepared from reagent grade, chemicals and twice distilled water. In order to eliminate heavy metal contaminants, a constant current preelectrolysis (25 μA/cm²) was usually conducted for a least 48 h, under nitrogen atmosphere, between two platinum electrodes separated by a Nafion® membrane. 99.99% CO₂ 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. 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.

RESULTS AND DISCUSSION

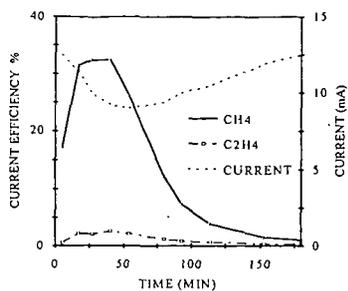
The common feature of the gold, silver and copper cathodes is the occurrence of poisoning during electroreduction of CO₂ [15-18]. This poisoning is less severe for gold, where it results in a decay of the current (at constant controlled potential) without affecting faradaic efficiency of CO formation [17], than in the case of silver for which η (CO) tends to decrease as a function of time [16,20]. The heaviest deactivation is observed for the copper electrode, where CO₂ reduction is virtually stopped after 20-40 min of continuous electrolysis being replaced by hydrogen evolution [18,19]. This problem being mentioned only in few among many papers devoted to this subject [19] it renders difficult any systematic comparison of the results obtained by different authors. In fact, in most cases the described experiments were conducted for very short periods of time corresponding to the passage of about 10C/cm² of the cathode surface. This is just less than the electrolysis duration after which, for example, a severe deactivation of the copper electrode usually starts. This phenomenon is illustrated by a series of curves in Fig. 1. Importantly, the copper electrode behaved in a similar way whether the electrolyte was pre-electrolysed or not. Moreover, XPS (X-ray induced photoelectron spectroscopic) analysis of the copper samples polarized for 2h at -1.72V in both kinds of 0.5M KHCO₃/CO₂ solutions (ie, with and without preelectrolysis) revealed only the presence of Cu, O and C signals. In particular, none of the metal elements present in trace amounts in KHCO₃ such as, for example, Fe, Zn, Cr, Pb or Cd was detected. The time associated with the deactivation of the cathode was no more affected 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 CO₂ 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 [19] or of a layer of organic products [20,21] 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 CO₂ 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 each 5-10 min. over the entire electrolysis run. The electrode activation requires less than

1 percent of the total electrolysis time (i.e., 2-3 s each 5 or 10 min.) and consumes a negligible extra amount of electrical charge (Fig. 2). Application of such a potential program allows high faradaic efficiencies of CH_4 , C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$ to be maintained over long electrolysis runs. As shown in Fig. 3, 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 distributions are probably associated with the structural changes occurring at the electrode surface.

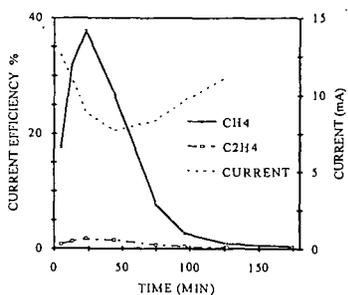
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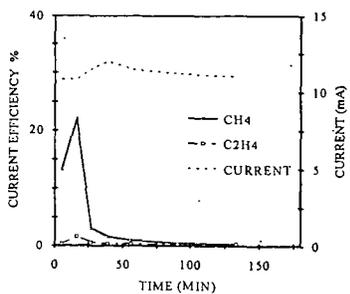
Fig. 1 Changes in the current efficiency of methane and ethylene occurring during first 2 hours of the electroreduction of CO_2 in 0.5M KHCO_3 solution at a copper electrode maintained at a constant potential of -1.72 V (vs. SHE). Temperature 22°C . All copper electrodes etched in a HCl solution [18].



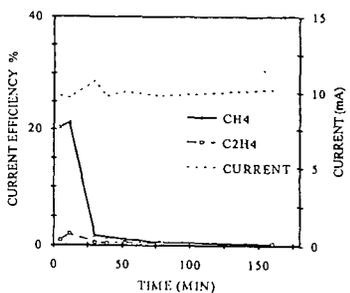
a) 99,9% copper cathode, non-pretreated KHCO_3 solution



b) 99,99% copper cathode, non-pretreated KHCO_3 solution



c) 99,9% copper cathode, pretreated KHCO_3 solution



d) 99,99% copper cathode, pretreated KHCO_3 solution

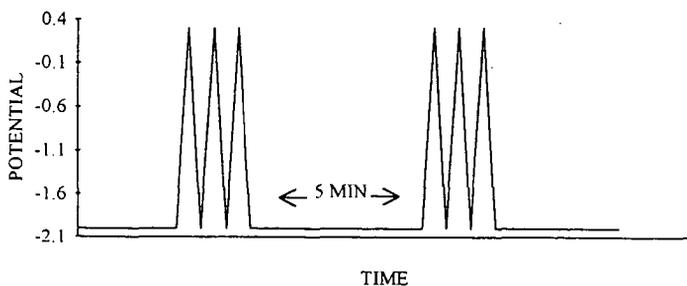


Fig. 2 Schematic representation of the anodic activation treatment (3 successive potential scans at 5 V/s into anodic region) applied to the copper electrode in the course of CO_2 electrolysis.

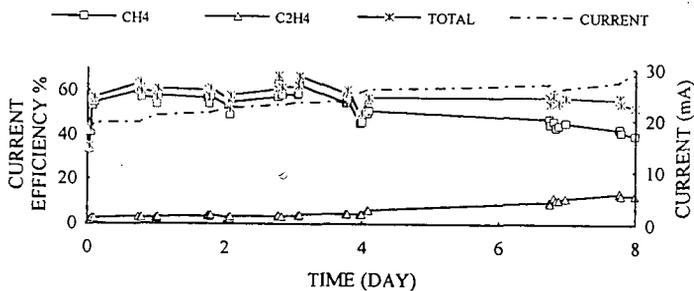


Fig. 3 Results of the 8-days long continuous electrolysis of CO_2 sat. $0.5\text{M K}_2\text{SO}_4$ solution performed at an activated copper electrode (0.28 cm^2) at 22°C . Potential -1.72 V

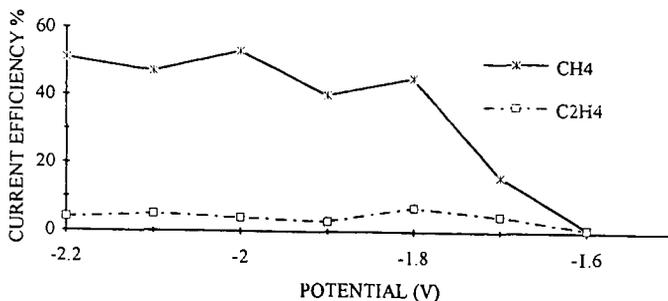


Fig. 4 Steady-state distribution of the CO_2 electrolysis products at the copper electrode as a function of the potential