ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE ON COPPER ALLOY

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Dedicated to Professor Dr. A.J. Arvia on occasion of his 75th Anniversary

Abstract

The electrochemical reduction of CO_2 using Cu-Zn alloy electrodes shows that the mechanical alloying synthesis method is becoming very attractive for the production of Cu-Zn powder alloy with small grain sizes. The reduction was studied in $KHCO_3$ and $NaClO_4$ solutions using carbon paste electrode and painting electrode supported on membrane. The analysis of the reduction products using ex situ and in-situ techniques, gas chromatography (CG) and differential electrochemical mass spectroscopy (DEMS), shows the presence of alcohols and hydrocarbons. Methanol, ethanol, acetone, methane, ethane and ethylene were detected. The products depend on the electrode potential and electrolyte solution. The SEM- EDAX analyses show the relative stability of the Zn-Cu alloys when they are used as catalyst in the carbon dioxide reduction. On the other hand the current-time response to the presence of CO_2 is reproducible and it is possible its application to an amperometric sensor. The Cu-Zn alloy prepared by mechanical alloying seems to be an adequate catalyst for the carbon dioxide reduction.

Resumen

Se estudia la reducción electroquímica de CO_2 sobre electrodos que contienen aleaciones de Cu-Zn preparadas por aleado mecánico. Se utilizan como electrolito soporte soluciones acuosas de $KHCO_3$ y $NaClO_4$. Se prepararon dos tipos de electrodos: electrodo modificado de pasta de carbono y electrodos pintados soportados sobre membrana. El análisis de los productos de reacción obtenidos a diferentes potenciales, fueron analizados por cromatografía gaseosa (CG) y espectroscopia de masa diferencial (DEMS). Se detectaron alcoholes e hidrocarburos: metanol, etanol, acetona, metano, etano y etileno. Los productos de reacción obtenidos dependen del potencial de electrodo y de la solución electrolítica. La aleaciones de Cu-Zn fueron caracterizadas por difracción de rayos X (XRD), microscopía electrónica de barrido (SEM) y análisis de energía dispersiva de rayos X (EDAX). La respuesta corriente-tiempo a potencial constante a la presencia de Dióxido de Carbono es reproducible y muestra que la reacción de reducción de CO_2 sobre electrodos de Cu-Zn puede ser utilizada en un sensor amperométrico.

Introduction

Electrochemical reduction of CO_2 to useful products is an important subject in modern electrochemistry, which will contribute to new energy storage technology in the next generation. It is also a promising approach for reducing the accumulation of CO_2 one of the origins of the global green house effect or acid rain. The capacity of the biosphere has been exceeded an many studies have been realized to overcome this problem but they have not been successful [1-3]

On the other hand, the demand for CO_2 monitoring has increased for controlling environmental, agricultural and biological process. Several procedures for Carbon Dioxide sensing have been studied in order to simplify the commercial available detection systems. They are expensive and are unsuitable for routine detection. Sensing materials have been used including solid electrolytes, oxide ceramics and organic polymers. The composite films consisting of base-type polyaniline and poly(vinil alcohol) was studied by Ogura et al.[4]. As regards the amperometric sensors there is little information. The main problem is the electrochemical reduction of Carbon Dioxide.

The electro-reduction of Carbon Dioxide using various metal electrodes in aqueous and non-aqueous solutions have shown a selective (high faradaic efficiency) reduction yielding, *e.g*., formic acid on Hg, Pb, In, Zn; CO on Ag and Au, methane and ethylene on Cu and some hydrocarbons on various transition metals.[5] However almost all the electrode reactions require a large over-potential for the electro-reduction.

Besides experimental results indicate that the reduction rate of CO_2 and current efficiency for product formation depends of crystallographic parameters and surface morphology of the electrode. [6,7] the temperature, the CO_2 pressure, the concentration and nature of the electrolyte anion. Formation of C_2H_4 is favored in solutions of KCl, $KClO_3$ and dilute $KHCO_3$, whereas formation of CH_4 is favored in 0.5 M $KHCO_3$[8]

Reduction reaction of Carbon Dioxide was performed on modified glassy carbon electrodes [9] applying different potential pulses yield carbon monoxide and methanol as products. The highest value was obtained for methanol in sodium chloride and carbon monoxide in ammonium oxalate. Jitaru et al. in an important review [10] discussed the procedure for the selective preparation for the manufacturing of hydrocarbons and /or alcohols using carbon dioxide as the carbon source. The electro-reduction procedures have been grouped according to both the nature of the cathode (*sp* or *d* group metal electrodes) and the solvent used for the supporting electrolyte. They also informed that copper cathodes are among the most promising options for hydrocarbon manufacturing. The electrochemical reduction of CO_2 on a copper electrode has been extensively investigated [11-13]. A cooper electrode possesses high catalytic activity but the electrode loses its activity for the reduction. The degradation of activity is attributed to the deposition of poisoning species such graphitic carbon, adsorbed organic intermediates or copper oxide. The main products obtained were CO, C_2H_4 and CH_4 using a three – phase interface [14]. Methanol, HCOO-, C_2H_5OH and C_3H_7OH have also informed by other authors [15]

The Zn-Cu and Sn-Cu alloys studied showed the effect of the micro-crystalline structures on the selectivity, reversibility and reactivity for CO or HCOOH production [16].

The catalytic reduction of Carbon Dioxide with atomic hydrogen permeating through palladized Pd sheet electrodes was also performed [17]. Formic acid was detected as a product together with H_2 evolution. The current efficiency depended on the reaction time and current density for palladization.

To reduce carbon dioxide with high selectivity, high-energy efficiency and high reactivity, it is essential to develop novel electro-catalysts. In the present paper, the electrochemical reduction of Carbon Dioxide in alkaline solution of potassium bicarbonate and sodium perchlorate solution is studied using Cu-Zn alloy as catalyst. The purpose is to prepare an electrode with high catalytic activity for optimizing the response of amperometric sensors for detecting Carbon Dioxide.

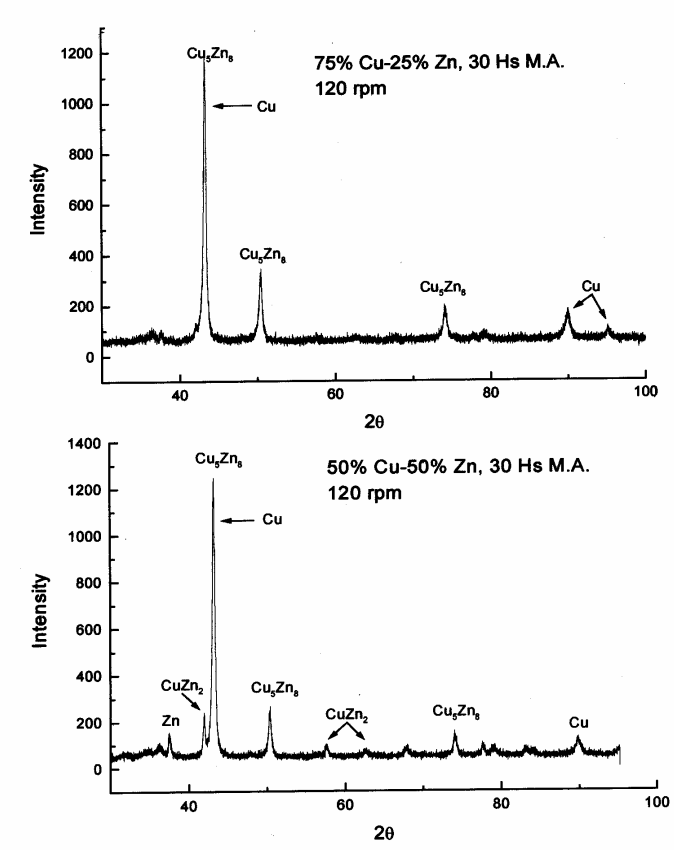

***Figure 1**: XRD patterns for the Cu-Zn alloy prepared by mechanical alloying powder mixture during 30 hs at 120 rpm. a) 75-25 Cu-Zn atom percent. b) 50-50 Cu-Zn atom percent.*

Experimental

The Cu-Zn alloys were prepared by mechanical alloying. This method allows obtaining nano-structural materials. The starting material was mixtures of elemental powders of copper and zinc in atomic relation 75-25 and 50-50 and submitted ball milling at a hardened steel vial at 125 and 200 rpm. The maximum milling time was 50

hs. Samples of the material submitted to different milling times were examined by X-ray Diffraction.

X-ray diffraction spectra were obtained using a Philips diffractometer with a horizontal goniometer. The wavelength chosen for the incident X-ray beam was the CuK line (λ = 154.2 nm) using a Ni filter. The radiation from 40 kV X-ray source running at 30 mA. The scanning range was from $2\theta = 20^{\circ}$ until $2\theta = 100^{\circ}$ and counting time of 5 second per step. The material was oriented such that it rotated by θ with the detector rotating 2θ to ensure that only planes parallel to the surface in the correct orientation for reflection.

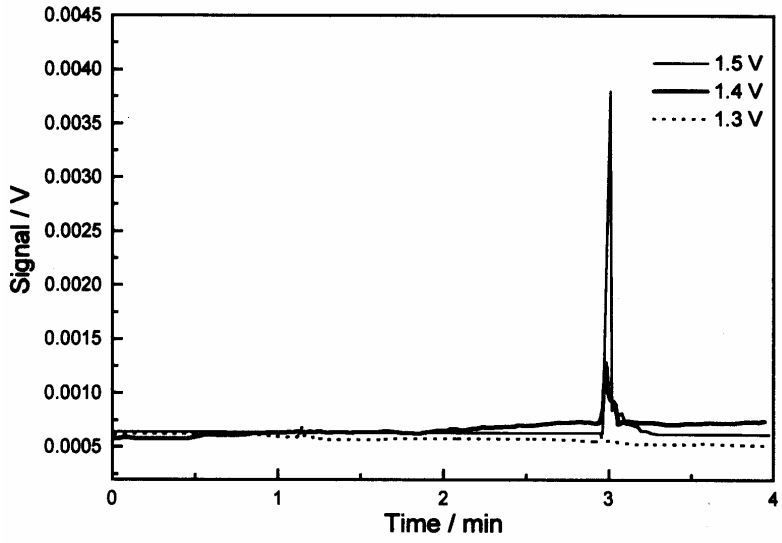

***Figure 2**: Chromatogram obtained from the electrochemical experiments performed at different potential using Cu-Zn (50-50) alloy on a carbon paste electrode.*

Two types of working electrodes were prepared using the Cu-Zn alloy: an electrode of carbon paste modified with metal alloy and the electrode for using on the Differential Electrochemical Mass Spectroscopy (DEMS) measurements.

The electrode of carbon paste was prepared out of a mixture of graphite, carbon powder, the alloy and an agglutinative; the paste was introduced into a teflon cylinder. The platinum sheet was used as counter electrode and the reference electrode was a Hg/Hg_2SO_4 /$SO_4^{=}$ 0.2 M (0,65 V *vs* NHE).

The electrolytic solutions were a 0.5 M $NaClO_4$ and 0.5 M $KHCO_3$ and prepared with pure water (MilliQ/MilliRO). All the experiences were performed at 25,0^{o}C. The electrochemical techniques were cyclic voltammetry and current –time curves at constant potential.

After the electrolysis, the reduction products were analyzed using a KONIK gas chromatograph model HRGC 3000,equipped with DB-1 column (30 m x 0.32 mm x 25μm) and DB-17 column (30 m x 0.25 x 2,5 μm) operating at 50°C. Detection was performed with a flame ionization detector (FID) operating at 250°C; Argon gas was used as carrier and data were processed with Konikrom(KONIK) data system software. GC-MS was performed with HP gas chromatograph model 5890 Series II, equipped with HP-

5 (crosslinked 5% Me-Silicone) column (30 m x 0.32 mm x 25μm) operating at 50°C. Detector temperature was 280°C and the gas carrier was Helium

Differential Electrochemical Mass Spectroscopy (DEMS)

For analysis of volatile products a mass spectrometer was used. The species generated at the electrode evaporate at the pores of the membrane in the vacuum are detected by the mass spectrometer with a time constant of *ca.*1s. This time constant is small enough to allow for selected masses to be recorded in parallel to electrochemical techniques: cyclic voltammograms, current-times curves at constant potential, etc.

Appropriated mass to charge ratios (*m/z*) have to be selected for this purpose. A quadropole mass spectrometer equipped with axial beam ion source and a secondary electron multiplier for the detection of ion was used. The working electrode was prepared by painting a layer onto hydrophobic membrane (Scomat Ltd. Average thickness 60 um, porosity 50%, mean pore size 0,17 um) from a suspension prepared with 200 mg of Cu-Zn alloy, 300 μl of solvent (50.7% athylglykol + 45.9 % toluene + 3.4 % xylol) and 130 μl organic shellac. The membrane acts as the interface between the solution and the vacuum chamber. More details about DEMS technique have been given elsewhere [18-19].

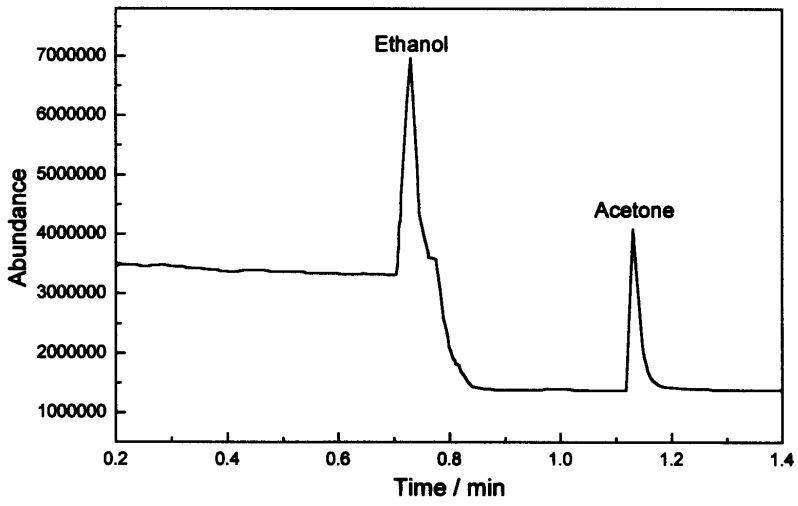

***Figure 3**: Chromatogram obtained with CG/MS techniques.*

All experiments were carried out at room temperature. Solutions were deoxygenated and the electrochemical cell was a cylinder of plexiglass. The morphologies of the alloy powders were characterized with Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis of X-ray (EDAX). They were performed in order to obtain information about the composition of the Cu-Zn alloys. The scanning microscope JSM 6300 was used.

Results and discussion

Figure 1 shows the XRD patterns of alloy powder obtained by mechanical alloying. Figure 1(a) correspond to Zn content of 25 atom percent and 1(b) 50 atom

percent of Zn content. The informed gross composition corresponds to the initial composition of the Cu-Zn powder mixture putted in the ball milling for preparing the alloy. (Figure 9 shows the composition determined from the EDAX spectrum).

Figure 1(a) shows the presence of the inter-metallic compound Cu_5Zn_8 (cubic) [20] and the Cu (one peaks of pure Cu is superimposed with one peak of Cu_5Zn_8). When the Zn content in the alloy increases we can observe the peaks of both the Cu_5Zn_8 compound and Cu and also appears the diffraction peaks assigned to $CuZn_2$ (cubic) [21] and small peaks of Zn (hcp). The XRD patterns obtained by mechanical alloying are slightly different with the patterns of the Cu-Zn alloys prepared by electrodeposition. The $CuZn_2$ compound was observed when the Zn content was 75 atom percent [16].

The alloy was used for preparing the modified carbon paste electrode and painting electrode supported on membrane for DEMS experiments. The electrochemical reduction of carbon dioxide was studied using cyclic voltammograms and current-time curves.

The voltammograms obtained using modified carbon paste electrode in KHCO3 solution showed that the carbon dioxide reduction starts at –1.30 V. The reduction current increases with the carbon dioxide pressure although the reaction occurs together with hydrogen reduction. At higher potential the gas hydrogen produced inside of carbon paste is the cause of loss of electrode stability. This is why it is no possible to study the CO_2 reduction at potential more negative than -1.60 V on carbon paste electrode.

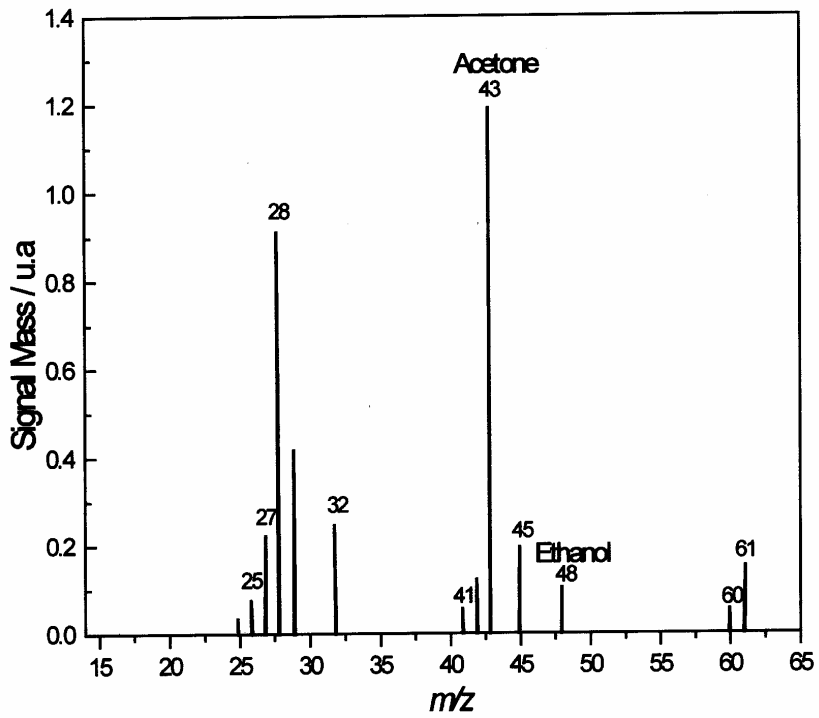

***Figure 4**: Mass signal response of the chromatogram in Figure 3.*

The product analysis obtained at different potential was performed using CG/FID and CG/MS as described in experimental section. The results are in Figures 2-4. Figures 2 show a chromatogram at -1.30 V, -1.40 V and -1.50 V using a FID detector. The analyzed samples give characteristic signals correspond to methanol, ethanol and acetone (retention time 2.81 min., 2.96 min. and 3.15 min respectively). A better separation was obtained using more polar DB-17 column and the signals are higher at -1.50 V. The products were confirmed with CG/MS (Figures 3 and 4).

The current-potential profile using Cu-Zn electrode 50-50 atom percent (painting electrode supported on membrane) in sodium perchlorate solution is shown in Figure 5. The reduction of CO_2 starts approximately at -1.60 V. The corresponding DEMS experiments were performed. Fig 6 shows the mass signal in function of time, for measurements realized as follow: the initial potential (Ei) was fixed at -1.80 V until an stabilized current was obtained. The potential step was applied to –1.50 V during 120 s and after that it was returned to the Ei. A cyclic scan was applied with 0.010 V/s between Ei and -1.20 V. A permanent bubbling of CO_2 was maintained. The mass signal in Figure 6(a) corresponds to the ratio m/z = 15, a fragment of CH_4. Figure 6(b) shows m/z = 26, a fragment of C_2H_2 and Figure 6(c) shows m/z = 30 a fragment of C_2H_6. The intensity of methane (m/z = 15) signal is higher than ethane and ethylene. The experiments were repeated changing the initial potential between -2.00 to 1.50 V. The intensities of the signals increase as Ei is more negative. Ogura et al., in a recent paper, showed the conversion of carbon dioxide to CO, C_2H_4 and CH_4 on a Cu net electrode in acidic solution [14]. On the other hand, measurements selecting ratio m/z =15 were done. The initial potential was fixed between -0.60 V and -1.00 V and a potential step from Ei to -1.50 V was applied. In all of the experiments methane was produced.

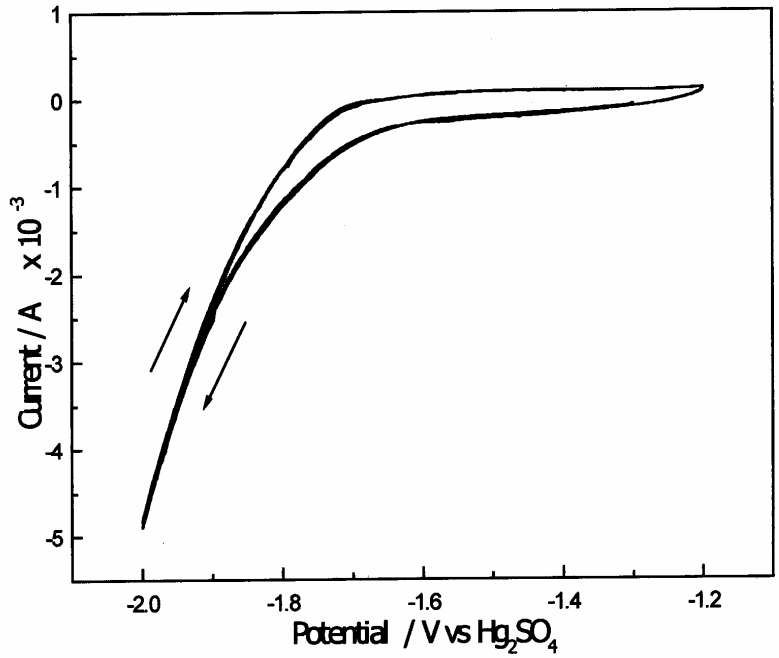

***Figure 5**: Current –potential curves of Cu-Zn (50-50) in 0.5 $NaClO_4$.*

Other experiments were performed using a small flow cell. In this cell, solution change was carried out holding the control of potential on the working electrode. The potential was fixed at -1.90 V, the supporting electrolyte was replaced by sodium perchlorate solution previously saturated with carbon dioxide. Both the current and the m/z = 15 ratio were recorded as a function of time. We can observe the current transient of the carbon dioxide reduction in Figure 7(a) and the mass transient for CH_4 in Figure 7(b).

After 190 s a cyclic scan was applied between -1.90 V to -1.20 V. The current-potential response for the first cycle is in figure 8(a) and the mass signal response (m/z = 15 ratio) is in Figure 8(b). Also the presence of methane is observed.

The preliminary results from DEMS technique show that the major product is methane, but it is no possible to discard the other products in perchlorate solutions.

In order to obtain information about the morphology and composition of the Cu-Zn alloy and the possible changes during the carbon dioxide reduction, SEM and EDAX analyses were performed. Figure 9(a) shows the microphotograph of the 50-50 atomic relation of the Cu-Zn electrode using for the SEM experiments. The particle size is between 50 μm to 200 μm. The energy spectrum obtained by EDAX is shown in Figure 9(b). The calculated composition for the alloy results Cu = 50.7 atom percent and Zn = 49.3 atom percent

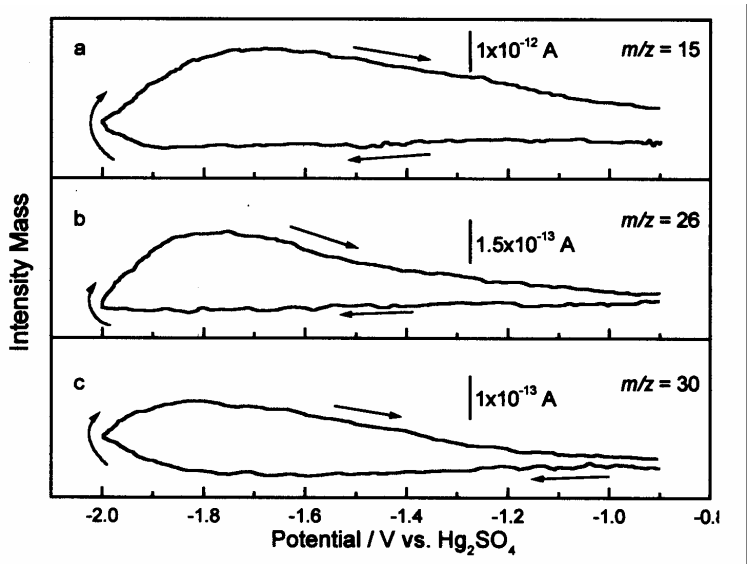

***Figure 6**: Mass signal vs potential at Cu-Zn electrode in 0.5 $NaClO_4$. a) m/z = 15; b) m/z = 26 c) m/z = 30 . Scan rate: 0.010 V/s, Argon purging.*

Figure 10 shows de SEM pictures and EDAX spectrum after using the electrode in the carbon dioxide reduction. There are slight modifications in the morphology and the composition of the Zn-Cu electrode after electrolysis. EDAX analysis shows the composition of alloy is Cu = 48.9 atom percent and Zn = 51.1 atom percent.

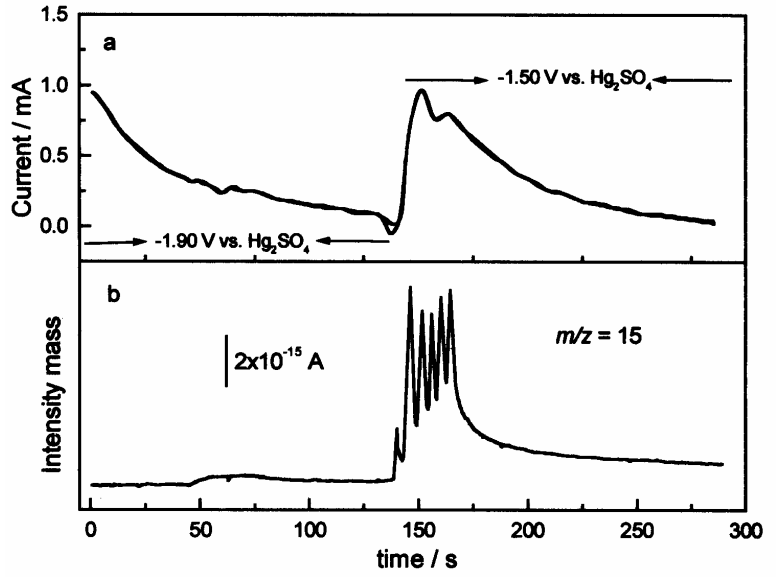

***Figure** 7: Current and mass signal (m/z= 15) vs time at constant potential = -1.90 V.*

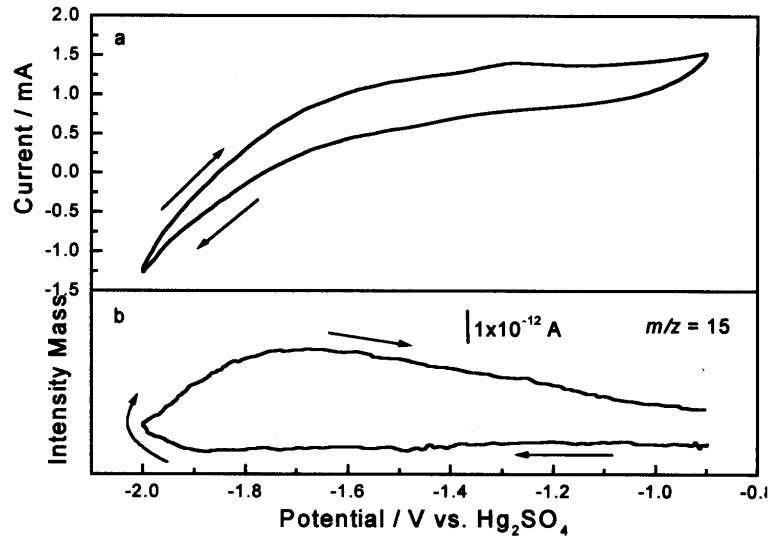

***Figure 8**: Current and mass signal (m/z = 15) vs potential during a potentiodynamic experiments performed 190 s after experiment of figure 7. 1st cycle. Scan rate: 0.010 V/s.*

In order to study the performance of the carbon dioxide reduction for its application to an amperometric sensor, experiments at constant potential were performed.

These experiments were carried out as follow: a constant potential was applied to the working electrode and the current was recorded as a function of time until a good

base line was obtained, then a carbon dioxide was bubbling to the working electrode compartment. The presence of carbon dioxide was detected through the current-time experiments. The current-time response at two constant potential is shown in Figure 11.

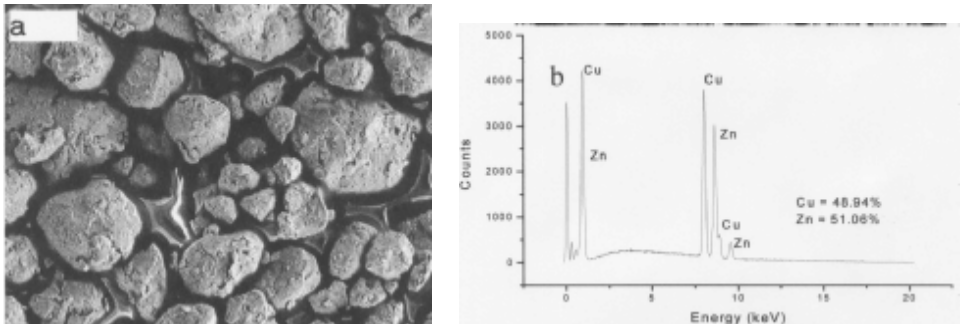

***Figure 9**: SEM-EDAX analyses of Cu-Zn electrode before reduction of carbon dioxide in 0.5 M $NaClO_4$.*

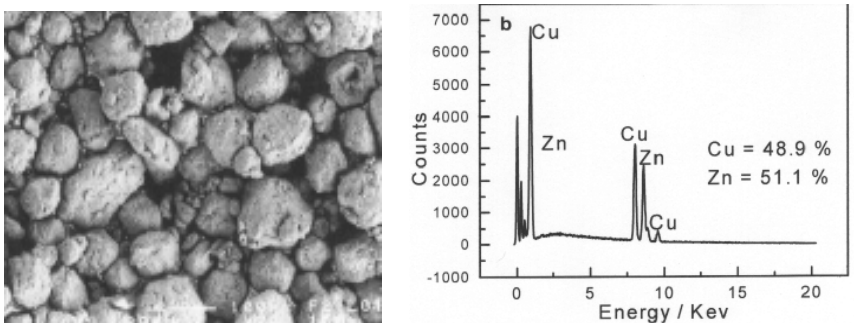

***Figure 10**: SEM-EDAX analyses of Cu-Zn electrode after the reduction of carbon dioxide in 0.5 M $NaClO_4$*

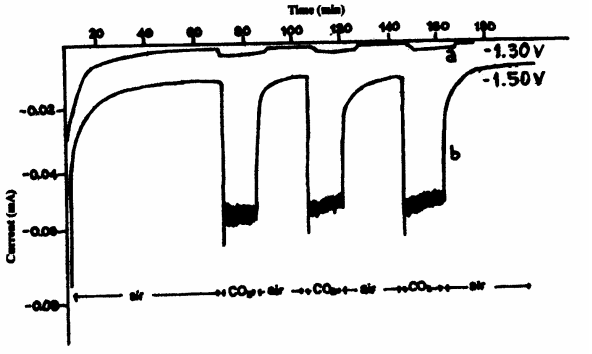

***Figure 11**: Current-time response of the Cu-Zn carbon paste electrode at the CO_2 pressure 0.1 M $KHCO_3$; a) E = - 1.30 V b) E = -1.50 V*

The reduction current increases rapidly till it reaches its maximum where it stabilizes, after that air is bubbled again to reach the base line and carbon dioxide is added once more. The experiments were repeated and the response to the CO2 was reproducible. It is also observed that at the potential of –1,50 V the current is higher than at -1.30 V.

Conclusions

The electrochemical reduction of CO_2 on Cu-Zn alloy electrodes in KHCO3 and $NaClO_4$ solutions shows: The mechanical alloying synthesis method is becoming very attractive for the production of metal alloys. This non-equilibrium method has been proven to be an efficient processing technique to prepare Cu-Zn powder alloy with small grain sizes. In KHCO3 solution and using modified carbon paste electrode the reduction of carbon dioxide was studied in a -1.30 V to -1.60 V potential region. The analysis by *ex- situ* condition shows the presence of alcohols and acetone. In $NaClO_4$ solution and using *in situ* techniques as DEMS the results shows the presence of methane, ethane and ethylene. The reduction products depend on the electrode potential and the electrolyte solution The SEM- EDAX analyses show the relative stability of the Zn-Cu alloys when they are used as catalyst in the carbon dioxide reduction. The current-time response to the presence of CO_2 is reproducible and it is possible its application to an amperometric sensor. The Cu-Zn alloy prepared by mechanical alloying seems to be an adequate catalyst for the carbon dioxide reduction.

Acknowledgements

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