Electrochemical Reduction of Carbon Dioxide

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Introduction Electrochemical reduction of CO2 to useful products is an important subjet in modern chemistry, which will contribute to a new energy storage technology in the next generation. It is also a promising approach for reducing the accumulation of CO2, an origin of the global green house effect or acid rain. The studies on the electroreduction of carbon dioxide using various metal electrodes in aqueous or nonaqueous solutions have shown that selective (high faradaic efficiency) reduction has been performed , 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. [1] . However almost all the electrode reactions requere a large overpotential for the electroreduction. The cinc - cupper and tin-cupper alloys studies showed the effect of the microcrystalline structures on the selectivity , reversibility and the reactivity for CO or HCOOH production [2]. To reduce carbon dioxide with high selectivity, high energy efficiency and high reactivity , it is essencial to develop novel electrocatalysts In the present paper the electrochemical reduction of carbon dioxide in alkaline solution of potassium bicarbonate using Cu-Zn and Cu-Sn alloys as electrode is studied. Experimental An electrode of carbon paste modified with metal alloys of Cu-Zn and Cu-Sn prepared by mechanical alloying is used as a working electrode. The alloys were prepared using a mill with high power balls that allows the obtention of nanostructural materials when is worked with powder mixtures of different metals Powder mixtures of Zinc and Copper were used at different percentages. Sample 1: 25 Sample 2 : 50 Sn-Cu alloy prepared by temperature treatment also was used. The electrochemical cell was a conventional three-compartment glass cell. In the cathodic compartment CO2 is bubbling at a constant flow. The electrolytic solution was a KHCO3 prepared with pure water coming from a Millipore equipment (MilliQ-MilliRo) The electrochemical techniques were cyclic voltametry and current-time curves. After the electrolysis the reduction products were analyzed by gas chromatography ,HPLC and CG/Mass. All the experiences were performed at 25.0C. Results and Discussion The i-E profiles of the voltammograms obtained in the CO2 electrolysis upon different modified carbon paste electrodes show the reaction starts in the zone of -0.80 V up to -1.20 V . The reduction current increases with the CO2 pressure , although a hydrogen reduction current is observed. To determine the potencial in which the reaction of CO2 reduction is favoured, the analysis of the reaction products was performed , using the chromatographic technique in gaseous phase.. For the alloy Zn:Cu ,after maintaining constantly the potential at -0.90 V, -1,00V and -1.10 V , the analyzed samples give characteristical signals of the methanol, ethanol and acetone retention times. The signals being higher at -1,10 V. The products were confirmed with CG/Mass analysis using the same experimental conditions Current-time experiments , at constan potential show before the CO2 aggregate, the reduction current increases rapidly till it reaches its maximun where it stabilizes; this behavior indicates that the response ot the catalyst to the presence of CO2 is quite rapid. It is observed that at the potential of -1.10V it is higher than at -0.80 V. So we suppose that the CO2 reduction reaction would be favoured at this potential. The preliminary results were obtained with a capillary column DB-1 (330 m x0.25 um). A better separation was obtained using more polar fase column. DB-17 (30 mx0.25um) . The chromatogram show the presence of the other products which are studied with CG/Mass. These experiments were performed under ex -situ conditions. In-situ studies are realized with Differential Electrochemical Mass Spectroscopy (DEMS) techniques. The Cu-Zn alloy , prepared in different proportion by mechanical alloy seems to be a good catalyst for the CO2 electroreduction. References 1. V. S. Bagotzky and N. V. Osetrova .Russian Journal of Electrochemical 31,409 (1995). 2. A. Katoh , H. Uchida, M. Shibata and. M. Watanabe . J.Electrochem. Soc., 141 2054(1994)