

A Differential Electrochemical Mass Spectrometry Study for the Investigation of the Electroreduction of Carbon Dioxide on Metal Electrodeposits

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The possibility of reduction of CO₂ to useful products at room temperature electrochemically has stimulated the studies of this reaction for number of years. In general the reduction of CO₂ is conducted on Cu electrodes and methane is one of major product [1]. However, electrodes of noble metals are also studied among other electrocatalysts [2,3]. The interest of the carbon dioxide electroreduction lies on its importance in environmental issue as well as in the significance of the synthesis of small organic molecules in chemistry [4]. Moreover, the electroreduction of CO₂ may also be studied as the reverse electrochemical reaction of a complete oxidation of these simple organic molecules; one of them is methanol, which raises fundamental interest in the fuel cells field. We will present a spectroelectrochemical study of the reduction of carbon dioxide on porous surfaces under conditions where CO₂ can be partially reduced to methane and methanol.

The DEMS technique permit that volatile products to be detected by connecting an electrochemical cell to the mass spectrometer. The products generated at the electrode interface reach the ion source within few 10th of second and therefore mass intensity (mass signal, m/z) can be followed potentiodynamically in parallel with the voltammogram. The reduction of CO₂ on Pt electrode in acidic media occurs concurrently with hydrogen evolution. From the mass signal vs. potential curves we observed an exponential response without hysteresis between the cathodic and anodic scan, indicating that the processes are kinetically controlled. The reaction on Pt is not selective and various products are obtained. The major product is formic acid (m/z=45), which corresponds to the addition of one proton on the carbon and one acidic proton on one of the oxygen of CO₂ molecule. Formic acid fragments have also been detected on a Cu layer deposited on Pt porous surface. The spectroscopic evidence of the formation of the formyl like species at low overpotential indicates that these species may be

the first step or intermediates for the formation of totally reduced form of CO₂ such as MeOH. The latter has been detected by on line Differential Electrochemical Mass Spectroscopy (DEMS). MeOH is present at potential where hydrogen evolution reaction occurs. These results showed for the first time the on-line production of formic acid and MeOH in acidic media. The reaction of carbon dioxide reduction will be compared on Cu layer and Pt surfaces. Adsorbed CO formed, as an intermediate species seems to be present on Cu layer as well.

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