

## Meeting Abstracts

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## Cu-Based Bimetallic Electrocatalysts for CO<sub>2</sub> Electrochemical Conversion to Valuable Chemicals: Study of Product Selective Distribution

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### Abstract

The carbon dioxide emissions contribute largely to the global climate change, and this may lead to serious consequences, such as ice melting at the Earth's poles and the fast-rising of the sea level [1]. The conversion of CO<sub>2</sub> to molecules with higher energy is a possible strategy for fuel and/or chemical reactant production or even energy storage. In this context, different metal electrocatalysts are under investigation, but only copper seems to be effective for generating hydrocarbons, mainly methane (CH<sub>4</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>) [2]. However, further advances are still necessary to increase its product selectivity and stability. Considering this scenario, in this study, the selectivity and stability of copper-based electrocatalysts for the CO<sub>2</sub> electrochemical reduction, in KHCO<sub>3</sub> aqueous electrolyte, was investigated by on-line Differential Electrochemical Mass Spectrometry (DEMS), under different reaction conditions. Polycrystalline bulk copper electrodes (Cu rod of a rotating electrode) produced only CH<sub>4</sub> as the reaction product in the first scan from -0.5 to -2.4 V vs. Ag/AgCl. However, in the subsequent scans, the signal for C<sub>2</sub>H<sub>4</sub> became evident and its magnitude increased, while that for CH<sub>4</sub> decreased. During long-term potentiostatic polarization at -2.0 V, after ca. 1 h, CH<sub>4</sub> was suppressed and only C<sub>2</sub>H<sub>4</sub> was observed, this being stable for more than 7 h. After this period of polarization, XRD analysis revealed the formation of copper hydroxide. When the reaction was conducted on copper oxide, only C<sub>2</sub>H<sub>4</sub> was observed. Although the Cu<sub>2</sub>O phase suffer reduction to metallic copper, as revealed by EXAFS [3], some superficial (and metastable) hydroxides may remain or be sustained by the OH<sup>-</sup> species that are produced during the CO<sub>2</sub> reduction in the aqueous media. The formation of OH<sup>-</sup> may also be responsible for the observed copper hydroxide phase on the surface of the bulk copper electrode, after 7 h of polarization. Interestingly, when the concentration of KHCO<sub>3</sub> was reduced from 0.5 to 0.1 mol L<sup>-1</sup> (reduced buffer capacity) the DEMS signal for C<sub>2</sub>H<sub>4</sub> was increased for all cases, as observed before [4]. These results point out to an important role of the superficial oxides/hydroxides (or high local pH) on the selectivity for C<sub>2</sub>H<sub>4</sub>. Importantly, in addition to the increase in the selectivity, it is noted an increase in the stability of the electrocatalyst when the reaction is totally deviated to the formation of C<sub>2</sub>H<sub>4</sub> [5]. The necessary presence of hydroxides on the copper surface for the C<sub>2</sub>H<sub>4</sub> formation is further confirmed when palladium was co-deposited or alloyed with copper. As palladium induces the hydrogen spillover, copper is already present in the metallic state in the as-prepared material, and remains in the same reduced state even after the CO<sub>2</sub> reduction, as revealed by XRD analyses. This copper-palladium electrocatalyst produced only CH<sub>4</sub> and H<sub>2</sub> (to a higher extent), with no measurable C<sub>2</sub>H<sub>4</sub> signal. The adsorbed hydroxide species (or high local pH) may favor the electron transfer with non-simultaneous proton transfer, which favor pathways of CO – CO coupling species, producing ethylene as the final product [4].

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