

Investigation of copper catalyst degradation with time for CO₂ reduction

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Introduction

Carbon dioxide (CO₂) is a readily available industrial byproduct that can be used to produce useful chemical compounds. Electrochemical reduction is a highly effective method for converting CO₂ to CO, organic acids, low molecular weight hydrocarbons and alcohols. Product distribution from the reduction of CO₂ is highly dependent on the composition, preparation of the catalysts and reduction potential, as such, multiple reduction pathways are observed depending on the catalysts material and the preparation methods. Copper-based catalysts have been found to produce higher molecular weight hydrocarbons, such as ethylene, methanol and ethanol.¹

This project focused on the degradation process that is seen during extended applied potential of such catalysts. Precious work has shown that thorough rinsing of the electrode surface as well as application of oxidative potentials can restore previous catalytic activity with varying degrees of success. The effect of applied potential will be investigated. The means of this degradation as well as these regeneration techniques will be further discussed.

Experimental

A custom build acrylic flow cell used to investigate the products of CO₂ reduction on various copper based catalysts. The cell used a Ag/AgCl (3 M NaCl) reference electrode, a Nafion® divider (Alfa Aesar 0.05mm), and a DSA® counter electrode (De Nora). All electrochemistry was performed on a PAR 236A potentiostat and 1260 Solartron FRA. All catalysts were analyzed in a pre-electrolyzed KHCO₃ (0.1 M) solution saturated with CO₂ at 1 atm. The solution was passed through the cell at a rate on 1 mL/min. The headspace gas were analyzed in real time by flowing the head space gasses (5 mL/min) to a GC(7890A). The gaseous products were detected via mass spectrometry (9475C) as well as thermal conductivity. Aliquots of the electrolyte were collected to be analyzed via Ion chromatography (IC, Dionex 1500) and NMR (Bruker DPS).

Catalyst surfaces were characterized ex situ after the significant change in the product distribution. The catalyst surface was characterized using x-ray photoelectron spectroscopy (XPS, Kratos Axis), scanning electron microscopy, and X-ray diffraction (XRD, Bruker Advance D8).

Results and Discussion

Amongst the gaseous products, a large decrease is observed within the methane and ethylene while an increase was seen within the hydrogen production. While both ethylene and methane decrease over time they do not do so at the same rate indicating that the surface features need to produce each product may be significantly different from one another.

Preliminary XPS data indicates that there no external metal contaminants on the surface but there is some evidence of a change in the carbonaceous species present on the surface. Further data is needed to conclude what contaminants are present. It is possible that the surface morphology has also altered; crystallographic data from XRD will be needed to exclude or confirm this possibility.

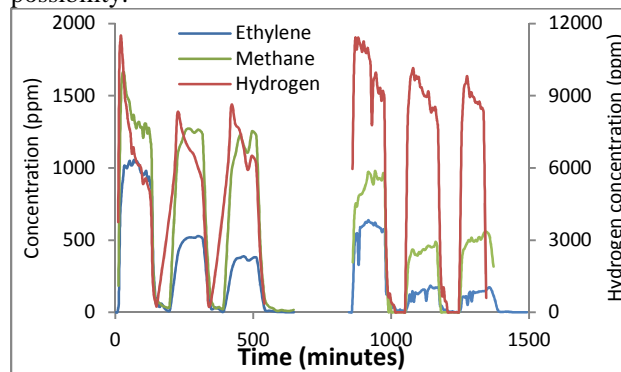


Figure 1: The concentrations of Cu mesh mapped for the course of 2 days. A series of two hour potential holds (-2V) followed by time for the cell to sit at open circuit potential (OCP) for 45 minutes.

References

- Hori, Y.; Wakebe, H.; Tsukamoto, T.; Koga, O. *Electrochim. Acta* 1994, 39,1833