

In Situ Observation of Electrochemical Reduction of CO₂ Using Cuprous and Intermetallic Catalysts

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Electrochemical reduction of CO₂ into more valuable commodities is a potential strategy for reducing the levels of atmospheric CO₂ saturation globally while profitably yielding organic carbon-based products [1, 2]. In order to reduce CO₂ to the more desirable organic products, such as methanol, ethanol, and propanol, it is necessary to stabilize many different intermediates and bind them to the catalytic interface in order to go through the entire reduction pathway. Although there has certainly been a deal of work in homogeneous catalysis of CO₂ reduction [3], the focus of this project is on heterogeneous catalysts and how they interact with the reduction mechanism. Heterogeneous catalysts capable of promoting the electrochemical reduction of CO₂ have been studied a great deal, with many studies extensively examining Cu or Cu-based catalysts. However, electrocatalysts for these reductions are often costly, both in terms of the overpotential required to conduct the electrochemical reduction as well as in terms of the raw costs needed for the materials used. Therefore, it is beneficial to use novel in situ transmission electron microscopy (TEM) electrochemical techniques to image the electrochemical reduction process, observing the surface morphological changes as they happen, in order to design a catalyst capable of producing higher order organic products at decent efficiency.

In this study, we performed electrochemical experiments via in situ TEM liquid cell (Protochips, Fig. 1a) to monitor the electrochemical reduction process and the surface morphological changes. Before the experiment of electrochemical reduction of CO₂, we prepared Cu clusters (see Fig. 1b) on the C/Pt electrode of the e-chip via electrochemical deposition. Cu clusters formed on the working electrodes of the e-chips using cyclic voltammograms conducted from 0.3 to -0.5 V in 0.2M CuSO₄ and 0.05M H₂SO₄ under vacuum ($1-3 \times 10^{-7}$ hPa). The CO₂ reduction was carried out using 0.1M K₂SO₄ (aq.) which was purged with CO₂. For in situ TEM observation of the electrochemical reduction of CO₂, the solution was run for the most part at 1 μl /min, with deionized water being simultaneously run at the same rate through the other port on the TEM holder. The liquid that was flowed through the cell was collected, and then run in a ¹H-NMR, where as can be seen in Fig. 2, resulted in the possible production of methanol, ethanol, and potentially 1-propanol. The successful processing of the electrochemical reduction of CO₂ purged K₂SO₄ across a Cu cluster catalyst informs our understanding of the stability of metallic films under reducing potentials and the overall feasibility of TEM use in electrochemistry. We are now working on intermetallic catalysts such as Ni-Ga thin films to examine the efficiency in the electrochemical reduction of CO₂ and the chemical stability of the catalysts. [4]

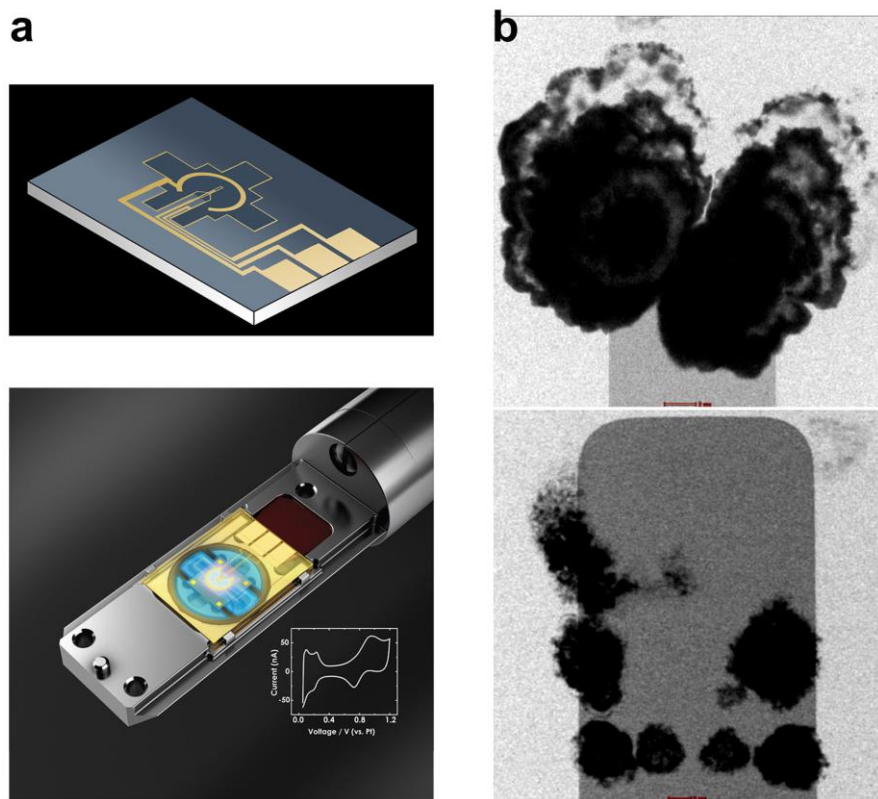


Figure 1. a, Schematics of the setup of in situ liquid cell. b, TEM image of Cu clusters deposited on the working electrode of a Protochip's e-chip under 0.2M CuSO₄ and 0.05M H₂SO₄ flow.

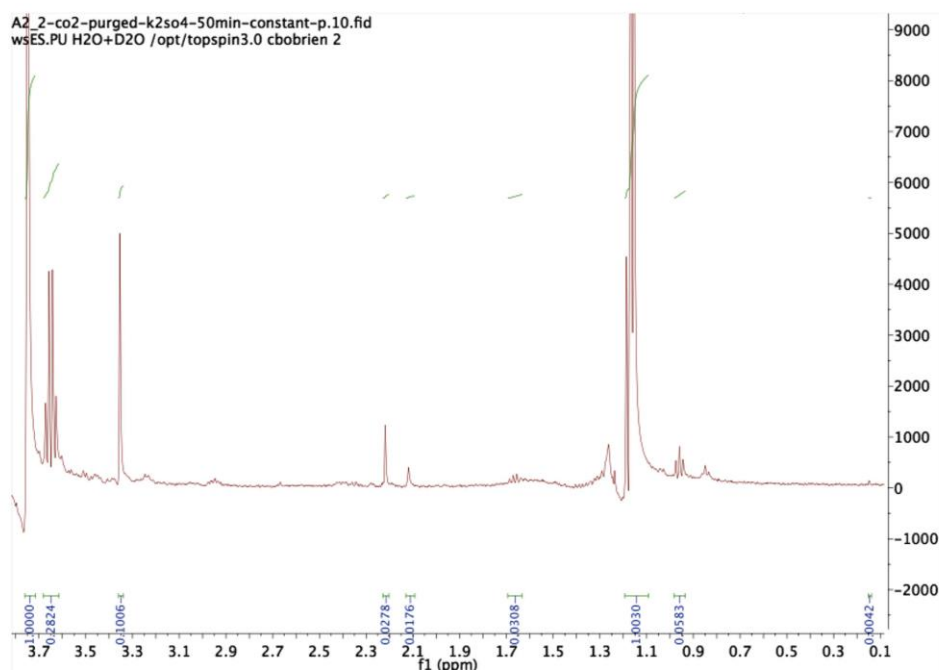


Figure 2. ¹H-NMR of the liquid product collected from an in situ TEM experiment where CO₂ purged 0.1M K₂SO₄ and deionized water were run through the liquid cell, which was cycled from -0.8 to 0.45 V with 80 cycles.

References

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- [4] The authors acknowledge the use of Princeton's Imaging and Analysis Center, which is partially supported by the Princeton Center for Complex Materials, a National Science Foundation (NSF)-MRSEC program (DMR-1420541).