In Situ Observation of Dynamic Changes in Structure and Product Selectivity of Cu-catalysts during Electrochemical CO_2 Reduction

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Electrochemical conversion of carbon dioxide into fuel and chemicals offers a promising way to turn carbon-containing compounds responsible for global climate change into valuable products such as methane, ethylene, and ethanol.[1] For this conversion, flow reactors such as membrane electrode assembly (MEA)-type electrolyzers provide advantages in selectivity and production rates over traditi onal liquid phase reactors.[2] As an electrocatalyst, copper nanoparticles have been widely used with their structural controls since local electronic structure dramatically influences CO_2 reduction reaction (CO_2RR) activity and product selectivity.[3] For example, Cu (100) facet favors ethylene formation whereas the formation of methane or ethanol will be more dominant on the Cu (111) facets, respectively.[4,5] Although the morphology change of the Cu (100) facet has been revealed by in-situ atomic force microscopy (AFM) during the CO_2RR[6], there is little study about what degradation we can see and how this degradation can be affected by contaminants in Cu (111) and (110) surfaces via in-situ AFM. In addition, it has not yet been investigated simultaneously to understand how this degradation affected by contaminants alters product selectivity in the MEA CO_2 electrolyzer.

Here, we will present the concept and preliminary results of our recently started project on the fundamental understanding of degradation mechanism using various in-situ approaches including AFM. We have measured the morphology of Cu (111) and (110) substrates and each substrate showed different surface properties; for example, the Cu (111) is relatively flat with ~0.67 nm of roughness whereas the Cu (110) has ~2.7 nm of roughness. The aim of this study is to understand how the structure of the electrocatalysts evolves under various conditions such as a function of the nature and concentration of the contaminants (eg., NO and SO_2 from 2-200 ppm) and pH of electrolyte (pH: 8 - 13). Dynamic changes in the morphology of each Cu (111) and (110) (e.g., roughened surface, formation of pores, etch pits, and defects) will be monitored via electrochemical AFM. Then, we will analyze how each crystalline structure and the morphological change affected by the contaminants influence activity and product selectivity with the MEA CO_2 electrolyzer. Lastly, in-situ Raman spectroscopy and X-ray photoelectron spectroscopy will be employed to investigate how the morphological change influences the chemical state of the substrates and intermediate. Based on these in-situ measurements, we will gain insight into how the dynamic evolution of copper progresses during CO_2RR and how this dynamic change can influence product selectivity.

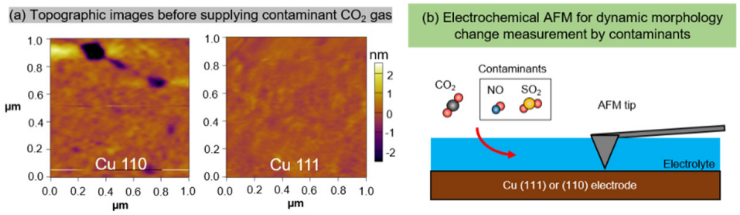

Figure 1. (a) Topographic images of Cu (111) and (110) surfaces before experiment. (b) Illustration of electrochemical AFM approach for dynamic morphology measurement by contaminants during CO_2RR.

1. De Luna, P.*; et al.* What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **2019**, *364*, eaav3506.
2. Lees, E. W.*; et al.* Gas diffusion electrodes and membranes for CO_2 reduction electrolysers. *Nat. Rev. Mater.* **2022**, *7*, 55-64.
3. Birdja, Y. Y.*; et al.* Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels. *Nat. Energy* **2019**, *4*, 732-745.
4. Ting, L. R. L.*; et al.* Enhancing CO_2 Electroreduction to Ethanol on Copper–Silver Composites by Opening an Alternative Catalytic Pathway. *ACS Catalysis* **2020**, *10*, 4059-4069.
5. Schouten, K. J. P.*; et al.* Two Pathways for the Formation of Ethylene in CO Reduction on Single-Crystal Copper Electrodes. *J. Am. Chem. Soc.* **2012**, *134*, 9864-9867.
6. Simon, G. H.*; et al.* Potential-Dependent Morphology of Copper Catalysts During CO_2 Electroreduction Revealed by In Situ Atomic Force Microscopy. *Angew. Chem., Int. Ed.* **2021**, *60*, 2561-2568.