Method Development for Quantification of Activity of Carbon-supported Cu Nanoparticles toward CO_2 Electroreduction

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CO_2 is a green-house gas that can be used for production of useful fuels or fuel cell stocks such as methane or ethane [1]. Electrochemical reduction of carbon dioxide to hydrocarbon fuels is one of emerging technologies, with the advantage of being performed under ambient temperature and pressure. As a technology currently in development, it can benefit from accomplishments in the proton exchange membrane fuel cell (PEMFC) technology. The design principles for CO_2 electrolyzers are similar to those of PEMFCs. Similar to the oxygen reduction reaction (ORR) in PEMFCs, the reaction at the cathode of a CO_2 electrolyzer requires a nanoscale catalyst. Contrary to the ORR, CO_2 electroreduction reaction results in multiple reaction products that are generated both in liquid and gas phase. Due to complexity of the system, no method has yet been developed to evaluate the electrocatalytic activities of nanoscale catalysts for reactions that result in multiple reaction products.

Here we report our results on method development for the evaluation of electrocatalytic activity of carbon-supported Cu catalysts for the CO_2 electroreduction reaction. The method involves a combination of the rotating disk electrode (RDE) technique and online gas chromatography (GC). The sealed RDE cell is designed and it is demonstrated that the reaction products generated on small surface area thin RDE films can be quantified by online GC. Liquid reaction products are separated and identified *ex-situ* by liquid chromatography.

Catalysts were synthesized using two different synthetic routes: 1) a nanocapsule method [2] with $LiEt_3BH$ as the reducing agent in benzyl ether and 2) a hydrazine method where N_2H_4 was a reducing agent. Carbon black and 600J Ketjen black were used as catalyst supports. X-Ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) were used for nanoparticles *ex-situ* analysis. The Cu electrochemical surface area was evaluated using Pb underpotential deposition [3].

The particle size of Cu/C catalysts was determined to be *ca*. 30 nm by XRD analysis. The XRD also showed that Cu was partially oxidized to Cu_2O and CuO prior to use in the cell.

For comparison, CO_2 electroreduction reaction products were characterized for Cu films electrodeposited on glassy carbon RDE tips.

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References

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