

Electrochemical reduction of CO<sub>2</sub> by Cu electrode with aid of annealing effect and pre-electroreduction in different electrolytes

Ping Jiang, Jinli Qiao\*, Jianshe Liu  
College of Environmental Science and Engineering,  
Donghua University, 2999 Ren'min North Road,  
Shanghai 201620, China  
\*qiaojl@dhu.edu.cn

Copper electrode have been reported as the unique metal for CO<sub>2</sub> reduction, for it enables CO to be further reacted to more reduced species<sup>1</sup>. Different types of Cu oxides electrocatalysts have showed high current density in KHCO<sub>3</sub> electrolyte, especially cuprous oxide<sup>2</sup>. However, Cu (I) was reduced at more positive potentials than CO<sub>2</sub> reduction, which leads to deactivation of the electrode.

The activity of modified Cu electrode prepared by different methods exhibited a strong dependence on the specified morphology and predetermined microstructure. For example, it was reported that annealing Cu foil in air at certain temperatures could produce the Cu<sub>2</sub>O film subsequently. The reduced Cu resulting from electroreduction of Cu<sub>2</sub>O film performed favorable energy-efficient of CO<sub>2</sub> reduction and stabled to the deactivation at low overpotential<sup>3</sup>. Based on the above conceptions, in this work, the effects of both annealing temperature and pr-electroreduction in different solution of Cu reduced on electroreduction of CO<sub>2</sub> were investigated.

Pieces Cu foil (99.99%, 10 mm × 10 mm × 0.02 mm) were electropolished in 85% phosphoric acid at 4V for 5 min, which was then annealed in air at 300, 500 and 700 °C for 12 and 6 hours allowing the formation of a Cu oxide layer. Cu electrode was then obtained by further electrochemical reduction of Cu oxide films in 1M H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and NaOH at 2V, respectively. Three different types of Cu electrodes were thus obtained and denoted as Cu-a, Cu-b and Cu-c, where a, b, c indicates H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, NaOH used for electrode fabrications. The kinetics and electrocatalytic activity of the Cu electrodes were measured using cyclic voltammetry (CV) and linear sweep voltammetry (LSV). All these tests were carried out in H-type electrolytic cell consisting of 0.5M KHCO<sub>3</sub> at ambient solution temperature. An Ag/AgCl electrode was used as the reference electrode and a Pt foil was used as the counter electrode.

Figure 1 display the polarization curves for CO<sub>2</sub> reduction on Cu-a, Cu-b and Cu-c electrodes, respectively, which were scanned at 5 mV/s in CO<sub>2</sub>-statured 0.5M KHCO<sub>3</sub> at room temperature. For all three Cu electrodes, the voltages started from -0.3V (for Cu-b) and -0.7 V (for Cu-a and Cu-c) were reduced gradually at initial scan to -0.9 V (for Cu-b) and -1.0 V (for Cu-a and Cu-c), and then reduced sharply to -1.5 V. The Cu-b electrode, ie., Cu-oxides reduced in H<sub>3</sub>PO<sub>4</sub> showed the best catalytic activity if both the onset potential (-0.3 V) and the maximum current density (23.5 mA / cm<sup>2</sup>) are compared.

Almost oxides in surface of electrode were reduced to copper, thus the different performance of the resultant Cu electrode was probably due to the fact that the acid solution for electrode pre-electroreduction plays a

promoting role in the formation of microstructure and active sites.

Reference

1. Lee, Jaeyoung, Tak, Yongsug. *Electrochim. Acta*, **46**(19) 3015-3022(2001)
2. M. Le, M. Ren, Z. Zhang, P. T. Spunger, R. L.Kurtz, J. C. Flake. *J.Electrochem Soc.*, **158**(5) E45-E49 (2011)
3. Christana, W. Li, Matthew W. Kanan. *J. Am. Chem. Soc.* **134**,7231-7234 (2012)

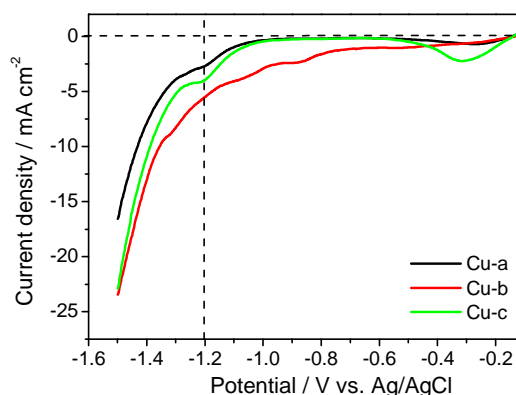


Fig.1 LSV curves of Cu electrodes resulting from reduced Cu oxides in H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, NaOH, donated Cu-a, Cu-b, Cu-c respectively, in CO<sub>2</sub>-statured 0.5M KHCO<sub>3</sub>. Scan rate: 5 mV / s. Cu foil was annealed in air at 300 °C for 12 h.