Catalysts for Electrochemical Reduction of CO_2 to CO

H.R. Molly Jhong and Paul J.A. Kenis

Department of Chemical & Biomolecular Engineering
University of Illinois at Urbana Champaign
600 South Mathews Avenue, Urbana, IL 61801, USA

E-mail: kenis@illinois.edu

Atmospheric carbon dioxide (CO_2) levels are rising globally. This has resulted in various undesired environmental consequences, the most prominent being climate change. If the current increasing trend in atmospheric CO_2 levels is not blunted, a cascade of damaging climate changes could threaten modern civilization. The amounts of CO_2 being produced are so large that multiple approaches need to be implemented simultaneously, including switching from fossil fuel-burning power plants to renewable energy sources, increasing the energy efficiency of buildings, increasing the fuel efficiency of vehicles, and underground carbon capture and sequestration (CCS) to curb the increasing trend in atmospheric CO_2 levels [1-3]. One additional approach to address this grand challenge is the electrochemical reduction of CO_2 into useful chemicals including carbon monoxide (CO), formic acid, methane, and ethylene[5, 6]. Coupled to renewable energy sources such as wind and solar, this process can produce carbon-neutral fuels or commodity chemicals by using CO_2 as the starting material. Furthermore, electrochemical reduction of CO_2 may provide a storage medium for the otherwise wasted excess renewable energy from intermittent sources.

Over the past three decades, efforts have mostly focused on screening different metal catalysts and the various products that can be formed using those metals. Unfortunately, the conversion is often low (<20 mA/cm^2) under ambient conditions and the selectivity for the desired product is also low.[7] For the electrochemical conversion of CO_2 to become economically-feasible, current performance levels of CO_2 electrolyzers need to be improved significantly. Specifically, more active and stable catalysts in combination with optimized electrode and electrolyte formulations are necessary such that the CO_2 electrolyzer can be operated at sufficient conversion (current density >250 mA/cm^2), reasonable energetic efficiency (>60%), and sufficient selectivity for the desired product (>90%).[6]

This paper will report some of our recent efforts to understand and improve catalysts, electrode structure, and operating conditions (Figure 1 top). For example, we have optimized the electrode structure and have recently reported that a catalyst layer with a loading of 0.75 mg/cm^2 of silver nanoparticles deposited via a fully-automated airbrushing method resulted in state-of-the-art cell performance for the electrochemical reduction of CO_2 to CO, namely: 91 mA/cm^2 total current density, 94% Faradaic efficiency to CO, and 46% cell energetic efficiency at a cathode potential of -1.68 V vs. Ag/AgCl (cell potential = -3 V) [4]. Also, we have developed supported catalysts via embedding metal nanoparticles (*e.g.*, Ag, Au) on multiwall carbon nanotubes. This catalyst exhibits a very high partial current density of the desired product, CO, up to 160 mA/cm^2 (Figure 1 bottom), but at a very low gold loading (0.17 mg/cm^2). Furthermore, we have developed metal-free catalysts that exhibit even better performance than the state-of-the-art silver nanoparticles (Figure 1 bottom), which is encouraging as the catalyst cost could be reduced significantly.

In summary, the results of these recent efforts in design, characterization, and testing of catalysts for electrochemical reduction of CO_2 start to approach the aforementioned specified performance metrics needed for an economically viable process.

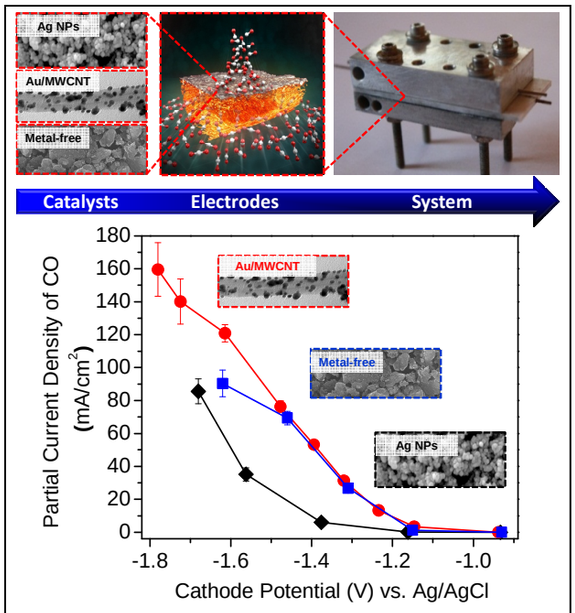

Figure. 1. **Top:** Overview of our recent efforts to understand and improve catalysts, electrode structure, and operating conditions. **Bottom:** Results of the electrochemical reduction of CO_2 to CO using the flow reactor operated with three different high-performance cathode catalysts, *i.e.*, silver nanoparticles (black curve)[4], metal-free catalyst (blue curve), and metal nanoparticles supported on multiwall carbon nanotubes (Au/MWCNT) (red curve).

Acknowledgements

We gratefully acknowledge financial support from UIUC, DOE, and I^{2}CNER, a World Premier Institute at the University of Illinois in the USA and at Kyushu University in Japan.

References

[1] S. Pacala, R. Socolow, *Science* **2004**, *305*, 968.
[2] M. I. Hoffert, *Science* **2010**, *329*, 1292.
[3] S. J. Davis, K. Caldeira, H. D. Matthews, *Science* **2010**, *329*, 1330.
[4] H. R. Jhong, F. R. Brushett, P. J. A. Kenis, *Advanced Energy Materials* **2013**, *3*, 589.
[5] D. T. Whipple, P. J. A. Kenis, *J Phys Chem Lett* **2010**, *1*, 3451.
[6] H. R. Jhong, S. Ma, P. J. A. Kenis, *Current Opinion in Chemical Engineering* **2013**, *in press.*
[7] Y. Hori, H. Wakebe, T. Tsukamoto, O. Koga, *Electrochim Acta* **1994**, *39*, 1833.