

## The Effect of Support Materials on the Electrocatalytic Activity of Ag for the Reduction of CO<sub>2</sub> to CO

Sichao Ma, Yangchun Lan, and Paul J.A. Kenis\*

Department of Chemistry and Chemical & Biomolecular Engineering

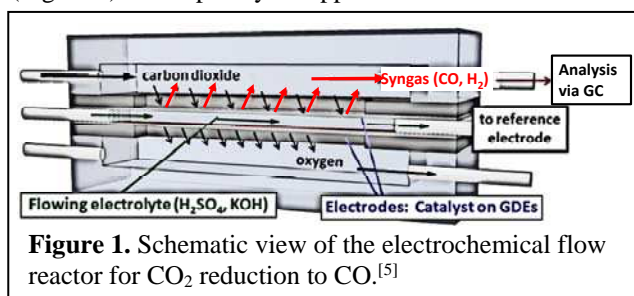
University of Illinois at Urbana-Champaign  
600 S. Mathews Avenue, Urbana, IL 61801, USA

E-mail: [Kenis@illinois.edu](mailto:Kenis@illinois.edu)

Over the last ~200 years, the CO<sub>2</sub> levels in the earth's atmosphere have been rising steadily. This rise has started to lead to a number of undesired climate effects, e.g., global warming, rising sea levels, and more powerful storms. A variety of strategies, such as switching to renewable energy sources, increasing the energy efficiency of buildings, switching to less taxing fuels, e.g. natural gas instead of coal, and underground carbon sequestration need to be employed simultaneously to slow, or better, to stop this rise.<sup>[1]</sup> An additional strategy that can be employed to overcome this daunting challenge is the electrochemical reduction of CO<sub>2</sub> into value added chemicals or their intermediates, such as formic acid, carbon monoxide, hydrocarbons, or alcohols. This process can be driven by the vast amounts of intermittent excess renewable power that is becoming available. This approach provides a means to store intermittent renewable energy and simultaneously recycle CO<sub>2</sub> as an energy carrier, thereby reducing CO<sub>2</sub> accumulation in the atmosphere.<sup>[2]</sup> Furthermore, by utilizing CO<sub>2</sub> as the starting material for chemical production, this process reduces our dependency on fossil fuels.

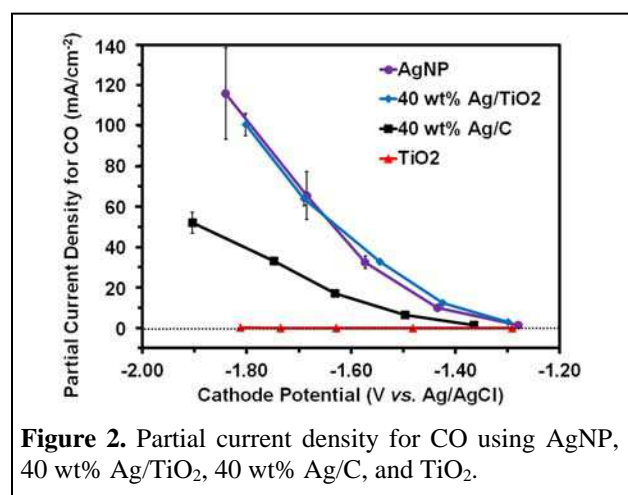
The conversion of CO<sub>2</sub> into CO is attractive due to the versatility of CO (with hydrogen) as a feedstock for the Fischer-Tropsch process, which enables the synthesis of a variety of products including liquid hydrocarbon fuels. However, the viability of the process for the electrochemical reduction of CO<sub>2</sub> to CO is presently limited by the poor energy efficiencies and current densities, mainly caused by the low activity of the catalyst.<sup>[3]</sup> One of the main obstacles to significantly high performance is the high overpotentials due to the formation of the CO<sub>2</sub><sup>•-</sup> intermediate. Significant improvements could be made by finding suitable catalysts and support materials that stabilize this intermediate.

Here, we investigate different support materials for Ag catalysts to improve the reduction of CO<sub>2</sub> to CO. We synthesized and characterized two types of catalysts: Ag supported on TiO<sub>2</sub> (Ag/TiO<sub>2</sub>) and Ag supported on carbon black (Ag/C). Previously, we reported that the activity of Ag catalysts in CO<sub>2</sub> reduction can be improved by decreasing Ag particle size to ~5 nm.<sup>[4]</sup> Here, Ag particles can be immobilized and stabilized as small nanoparticles (<10 nm) on both support materials. Their performance in the electrochemical reduction of CO<sub>2</sub> to CO was compared using an electrochemical flow reactor (Figure 1) developed by Whipple *et al.*<sup>[5]</sup>



**Figure 1.** Schematic view of the electrochemical flow reactor for CO<sub>2</sub> reduction to CO.<sup>[5]</sup>

The 40 wt% Ag/TiO<sub>2</sub> catalyst was more active for CO production than the 40 wt% Ag/C catalyst (Figure 2). Almost two times of the partial current density for CO can be achieved using TiO<sub>2</sub> rather than carbon black as the support material for the Ag particles. The lower performance of the Ag/C catalyst relative to the Ag/TiO<sub>2</sub> catalyst is due to the higher electrode resistance caused by the higher hydrophobicity of the carbon black material. In addition, as confirmed by TEM, most of the Ag particles on carbon black are trapped in deep micropores or recesses, making them less accessible for CO<sub>2</sub> and electrolyte, while Ag particles in the Ag/TiO<sub>2</sub> catalysts are more accessible on the surface of TiO<sub>2</sub>. Furthermore, the 40 wt% Ag/TiO<sub>2</sub> and the Ag nanoparticle (AgNP) catalysts exhibit very similar performance at the same cathode loading. This result indicates that when using Ag/TiO<sub>2</sub> catalyst, the Ag content can be reduced without sacrificing performance, thus improving its commercial viability for CO<sub>2</sub> reduction.



**Figure 2.** Partial current density for CO using AgNP, 40 wt% Ag/TiO<sub>2</sub>, 40 wt% Ag/C, and TiO<sub>2</sub>.

We also studied the effect of Ag loading (5 wt%, 10 wt%, 20 wt%, 40 wt%, and 60 wt%) on performance. The data indicates that with a higher Ag loading, a higher partial current density for CO can be achieved. However, the 60 wt% Ag/TiO<sub>2</sub> catalyst did not follow the above trend. This is probably due to the agglomeration of the Ag particles during the reaction as confirmed by TEM.

In summary, we will show that using TiO<sub>2</sub> as the support material for Ag particles stabilizes Ag particles and leads to better performance compared to carbon black. We also will report on the beneficial role TiO<sub>2</sub> play in the CO<sub>2</sub> electroreduction pathway.

### Acknowledgements

We gratefully acknowledge financial support from UIUC, DOE, and I<sup>2</sup>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*, 968-972.
- [2] D. T. Whipple, P. J. A. Kenis, *J. Phys. Chem. Lett.* **2010**, *1*, 3451-3458.
- [3] H.-R. M. Jhong, S. Ma, P. J. A. Kenis, *Curr. Opin. Chem. Eng.* **2013**, *accepted*.
- [4] A. Salehi-Khojin, H.-R. M. Jhong, B. A. Rosen, W. Zhu, S. Ma, P. J. A. Kenis, R. I. Masel, *J. Phys. Chem. C* **2012**, *117*, 1627-1632.
- [5] D. T. Whipple, E. C. Finke, P. J. A. Kenis, *Electrochem. Solid-State Lett.* **2010**, *13*, B109-B111.