Homogeneous Reactions Limit the Efficiency of Gold Electrodes in CO_2 Electroreduction

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An overlooked factor affecting electrochemical reduction of CO_2 is identified.

Electrochemical reduction of CO_2 is a potential solution of CO_2 recycling and energy storage. Developing better electrocatalysts and improving mass transport of CO_2 using gas diffusion electrodes (GDEs) are widely pursued to achieve high activity and selectivity in CO_2 electroreduction. In this issue of *ACS Central Science*, Nocera, Costentin, and colleagues have identified a previously overlooked homogeneous reaction of CO_2 with OH^- as a factor limiting the rate of CO_2 electroreduction on gold electrodes at high current densities.[1]

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CO_2 electroreduction may lead to many products including alcohols and alkanes. Among these, CO is one of the most valuable because it is a major component of syngas which is used on a large scale to make various carbon-based fuels. Moreover, the gaseous CO is easily separated from the liquid-phase reaction mixture. The state-of-the-art electrocatalyst for CO_2 reduction to CO is Au, which can achieve low overpotentials and high Faradaic efficiency.[2] Significant progress has been made in tailoring the atomic structures of Au's surface for better performance at low overpotentials.[3,4] The current densities are typically
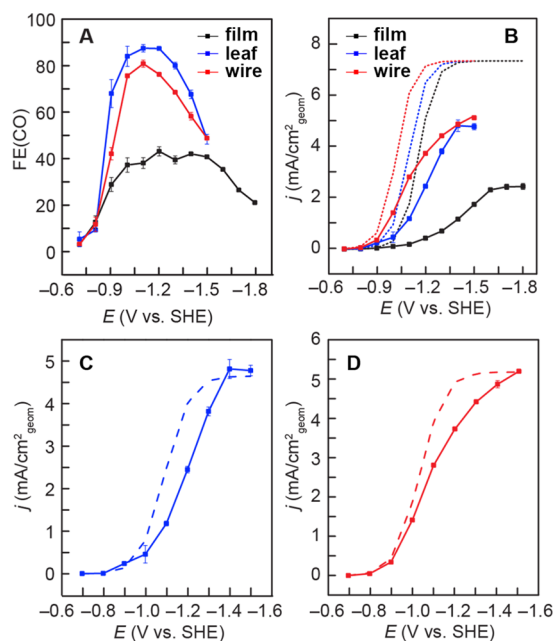

Figure 1. (A) Faradaic efficiency and (B) partial current density of CO production on Au film (black), leaf (blue), and wire (red). Dashed lines in part B show the simulated current density of CO production taking mass transport into account. Comparison of experimental (solid lines) and simulated current density of CO production taking mass transport and homogeneous reactions into account (dashed lines) for (C) Au leaf and (D) Au wire electrodes. Modified and reproduced with permission from ref 1. Copyright 2019 American Chemical Society.

below 10 mA/cm^2 at these potentials. A practical electrolysis device will likely operate at much higher current densities, for instance, at 500–2000 mA/cm^2. Therefore, it is important to understand the behavior of electrodes at relatively high current densities, for example, more than 100 mA/cm^2 on a lab scale. These current densities are obtained at high overpotentials. The activity–potential relationship at high overpotentials, however, is rarely studied. It is assumed that the currents are mainly controlled by electrokinetics and CO_2 mass transport.

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The work published now in *ACS Central Science*[1] studied CO_2 electroreduction on gold surfaces with very different morphologies (planar, leaves, and wires) over a wide range of overpotentials. The authors found that the difference in geometric current densities of these different Au surfaces was due to different electrochemical surface areas. The intrinsic activity of these surfaces was similar. The Faradaic yields of CO formation of these surfaces had a similar bell-shaped dependence in potentials (Figure 1A). The lower efficiency of Au film was due to a higher competing hydrogen evolution reaction (HER). At low overpotentials ($E > -0.85$ V versus SHE), the HER was dominant, and CO formation was limited by a slow 1 e reduction of CO_2.[5] As overpotential was increased, the HER was potential-independent, but the rate of 1 e reduction of CO_2 increased with increasing potentials leading to high Faradaic yields of CO formation. Finally, at high overpotentials a second HER process via bicarbonate direct reduction came into play, and CO_2 reduction leveled off due to CO_2 depletion at the catalyst surface.
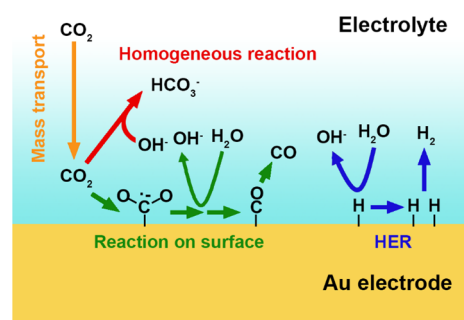
Figure 2. Factors influencing CO_2 electroreduction to CO on Au electrodes.

The authors simulated the activity−potential correlation taking into consideration the electrokinetics of CO_2 reduction and the HER as well as mass transport of CO_2. They found the simulated behaviors deviated significantly from the experimental observations (Figure 1B). Only when they included homogeneous reactions, particularly the reaction of CO_2 with OH^- (Figure 2), could they approximate the experimental data with simulations (Figure 1C,D). The OH^- ions were the side products of both the HER and

CO_2 reduction. Their reaction with CO_2 decreased the concentration of CO_2 at the electrode, limiting the current densities. Thus, the study identified a previously overlooked factor that limits the performance of CO_2 electroreduction at high current densities.

To improve the mass transport of CO_2 dissolved in liquid electrolyte for supporting high current densities, GDEs where the mass transport of CO_2 benefits from gas−electrolyte−electrode three-phase interfaces are being developed by various researchers.[6,7] The authors suggested that the homogeneous reactions put a constraint in the effectiveness of GDEs. They reasoned that CO_2 dissolved in the solution was the active reactant when using GDEs, with a maximum concentration of 0.038 M at 298 K. The homogeneous reactions will still substantially deplete the concentration of CO_2 at the GDEs at high current densities. Their simulation suggested that a thickness of less than a few μm is required to maintain a maximum CO_2 concentration at the entire catalyst layer. Moreover, the rapid homogeneous reaction of CO_2 with OH^- in alkaline medium would lead to a CO_2 penetration layer of only about 1 μm, which would be the upper limit of the thickness of the catalyst layer. The formation of CO_3^{2-} byproduct in alkaline medium also reduces the carbon efficiency and increases the cost of CO_2 electroreduction in alkaline medium.

This study revealed an important mechanistic element for the understanding of the kinetics of CO_2 electroreduction over a wide range of overpotentials, especially at high overpotentials which are required to achieve technology-relevant current densities. Future kinetic models should consider homogeneous reactions of CO_2. How general the implications are, however, remains to be explored. Numerous reports indicate the intrinsic activity and selectivity in CO_2 electroreduction on Au can be tuned by creating defects and strains[8] or by exposing different facets.[9] Indeed some Au catalysts, for example, the oxide-derived Au (Au-OD),[2] seem to have higher intrinsic activity than the Au electrodes examined in this study. The minimum current density and overpotential where homogeneous reactions start to significantly limit the reaction rate should in principle increase with increasing intrinsic activity. Thus, developing more active catalysts remains a valid strategy to achieve high current densities. Finally, in terms of concentration control, one might ask whether GDEs can be engineered, for example, by mesostructuring, to minimize the contact of CO_2 with the electrolyte before reacting at the three-phase interface to alleviate the homogeneous reaction of CO_2 with OH^-.

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REFERENCES

(1) Zhang, B. A.; Ozel, T.; Elias, J. S.; Costentin, C.; Nocera, D. G. Interplay of Homogeneous Reactions, Mass Transport and Kinetics in Determining Selectivity of the Reduction of CO_2 on Gold Electrodes. *ACS Central Science* **2019**, in press.

(2) Chen, Y. H.; Li, C. W.; Kanan, M. W. Aqueous CO_2 Reduction at Very Low Overpotential on Oxide-Derived Au Nanoparticles. *J. Am. Chem. Soc.* **2012**, *134* (49), 19969−19972.

(3) Zhu, W.; Zhang, Y.-J.; Zhang, H.; Lv, H.; Li, Q.; Michalsky, R.; Peterson, A. A.; Sun, S. Active and Selective Conversion of CO_2 to CO on Ultrathin Au Nanowires. *J. Am. Chem. Soc.* **2014**, *136* (46), 16132−16135.

(4) Liu, M.; Pang, Y.; Zhang, B.; De Luna, P.; Voznyy, O.; Xu, J.; Zheng, X.; Dinh, C. T.; Fan, F.; Cao, C.; de Arquer, F. P. G.; Safaei, T. S.; Mepham, A.; Klinkova, A.; Kumacheva, E.; Filleter, T.; Sinton, D.; Kelley, S. O.; Sargent, E. H. Enhanced electrocatalytic CO_2 reduction via field-induced reagent concentration. *Nature* **2016**, *537*, 382.

(5) Wuttig, A.; Yoon, Y.; Ryu, J.; Surendranath, Y. Bicarbonate Is Not a General Acid in Au-Catalyzed CO_2 Electroreduction. *J. Am. Chem. Soc.* **2017**, *139* (47), 17109−17113.

(6) Weekes, D. M.; Salvatore, D. A.; Reyes, A.; Huang, A.; Berlinguette, C. P. Electrolytic CO_2 Reduction in a Flow Cell. *Acc. Chem. Res.* **2018**, *51* (4), 910−918.

(7) Verma, S.; Hamasaki, Y.; Kim, C.; Huang, W.; Lu, S.; Jhong, H.-R. M.; Gewirth, A. A.; Fujigaya, T.; Nakashima, N.; Kenis, P. J. A. Insights into the Low Overpotential Electroreduction of CO_2 to CO on a Supported Gold Catalyst in an Alkaline Flow Electrolyzer. *ACS Energy Lett.* **2018**, *3* (1), 193−198.

(8) Mariano, R. G.; McKelvey, K.; White, H. S.; Kanan, M. W. Selective increase in CO_2 electroreduction activity at grain-boundary surface terminations. *Science* **2017**, *358* (6367), 1187−1192.

(9) Back, S.; Yeom, M. S.; Jung, Y. Active Sites of Au and Ag Nanoparticle Catalysts for CO_2 Electroreduction to CO. *ACS Catal.* **2015**, *5* (9), 5089−5096.