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Preview

Well-Defined Model CO_2 Electroreduction Catalyst

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In this issue of *Chem*, Veenstra et al. combine an advanced catalyst fabrication and computational simulations to reveal how the local reaction environment affects the selectivity of CO_2 electroreduction on Cu. The model microstructured catalyst with a well-defined architecture provides an ideal platform for fundamental investigation of the structure-property correlation.

The CO_2 electrolysis technology shows great potential to produce a range of carbon-based fuels and chemicals by using greenhouse gas CO_2 as the carbon feedstock.[1] Much effort has been devoted to improving the performance of Cu catalysts in electrocatalytic CO_2 reduction reaction (eCO_2RR) because of its unique capability of C–C bond formation.[2] The most common strategy is to tune the material properties of Cu catalysts, such as morphology, porosity, crystal facet, oxidation state, strain, grain boundary, and composition,[3] whereas much less attention is dedicated to optimizing the local chemical environment near or on the catalyst surface, such as surface intermediate coverage, local pH, regulation of reactant and product diffusion at interfaces, and local electric field,[4,5] which could strongly affect the catalyst selectivity. A quantitative understanding of the correlation between the local reaction conditions and the eCO_2RR product selectivity is important but fundamentally challenging, largely due to the intertwined nature of numerous parameters and the ill-defined structure of the electrodes. As illustrated in Figure 1A, typical gas diffusion electrodes (GDEs) that are often used in CO_2 electrolyzers to achieve high current densities (> 100 mA cm^{-2}) have a complex nature in structure.[6] Nanostructured catalyst particles are mixed with ionomers, deposited on a porous gas diffusion layer, and partially immersed in a liquid electrolyte or pressed against an ion-conducting polymer membrane, making it nearly impossible to conduct quantitative measurements and precise modeling of local reaction environment. In this regard, model catalysts with a well-defined, simplified structure become an ideal platform to gain fundamental insights in eCO_2RR (Figure 1B).

In this issue of *Chem*, Veenstra et al. use an ultra-short pulsed (USP) laser-ablation technique to fabricate a set of microstructured CuO electrodes with a regular distribution of conical cavities (Figure 1B).[7] The circular laser beam, in which small energy input per pulse allows for the sub-micrometer resolution and the rapid processing, creates conical cavities on Cu foils with different depths but same diameter and pitch. Because the electrode geometry restricts the diffusion of reactant(s) and product(s), the local chemical environment can be manipulated in the model catalyst by precisely controlling the depth of the cavities. Moreover, the simple well-defined electrode architecture enables computational modeling and quantitative study of the local reaction environment, which are usually difficult for complex catalyst systems. The authors estimate the local pH and CO_2 concentration by using the advanced computational simulation, capturing various phenomena that affect the concentration and the flux of OH^-, CO_2, HCO_3^-, and CO_3^{2-} species in the electrolyte, including eCO_2RR and hydrogen evolution reaction, chemical equilibria of the carbonate species, local buffer effect of the hydrolysis of the cations, and diffusion. The computational modeling effort is crucial to revealing how the Cu selectivity is correlated with the local reaction conditions, because the environment near the catalyst surface might deviate substantially from the bulk. This also motivates the development of advanced operando and *in situ* characterization techniques to measure local pH and CO_2 concentrations near the catalyst surface under reaction conditions. For instance, there have been attempts to determine the local pH by using *in-situ*-attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) by correlating the amount of carbonate species measured near the catalyst surface with the local pH.[8]

Veenstra et al. further generate a series of selectivity maps with the estimated local pH and CO_2 concentration. The maps exhibit clear patterns for eCO_2RR products with respect to applied potential, local pH, and CO_2 concentration on the Cu catalyst, revealing novel insights such as the existence of two reaction pathways for propanol. The presence of two reaction mechanisms for propanol has not been explored in previous literatures, and the selectivity patterns suggest that ethylene might be a key intermediate for the formation of propanol. Furthermore, ethylene and ethanol patterns match closely with one another, indicating that ethylene and ethanol might share similar reaction

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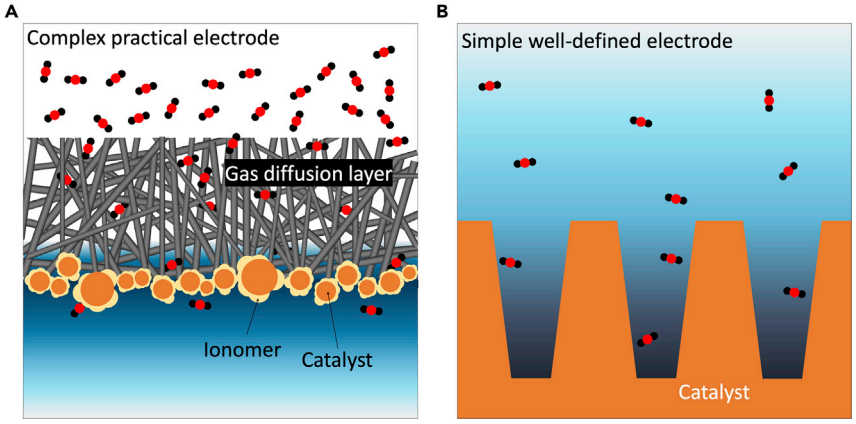

Figure 1. eCO_2RR System with Different Levels of Complexity

Schematics of (A) a complex practical electrode that uses gas diffusion electrode and (B) a simple, well-defined electrode in a conventional aqueous system. The simple, well-defined structure offers an ideal platform for fundamental studies in eCO_2RR.

pathways, which is in agreement with a previous study by Jiao and co-workers.[9] The lack of dependency of acetate on ethanol also suggests that Cannizzaro-type reaction is not the dominant pathway for ethanol production.[10] The correlation between the local reaction environment and the product selectivity revealed by these maps is highly valuable for further studies to explain the unaccounted reaction pathways and their dependencies on the local reaction environments, such as pH, surrounding solvent, and surface coverage of H, CO_2, and CO. Moreover, the selectivity maps successfully predict the eCO_2RR selectivity at different operating conditions (e.g., stirring rate and the choice of electrolyte), providing useful guidance for rational design of efficient electrode-electrolyte interfaces in practical but more complex electrodes, such as GDEs.

Controlling the local chemical environment in the practical electrodes requires further research efforts to address the additional complexity. For instance, the gas diffusion layer in a typical GDE plays a vital role in facilitating the mass transport of gaseous reactants and products across the electrolyte-electrode interface. The hydrophobicity, porosity, and thickness of the gas diffusion layer are all important parameters that could substantially affect the pH and CO_2 concentration near the catalyst surface. The ionomer layer on the catalyst particle surface and the properties of the ion-conducting polymer membrane (e.g., anionic or cationic, structure, and functional groups) also have strong influences on ion transport and local chemical environment. Furthermore, when the electrodes operate at practical current densities (> 100 mA cm^{-2}), a large amount of gas bubbles is formed at the catalyst surface that disrupts the electrolyte-electrode interface and creates another level of complexity. Existing tools are insufficient to provide accurate measurements and predictions of the chemical environment near/on the catalyst surface, and therefore, new characterization techniques and advanced computational simulations are needed to capture the additional complexity in the practical electrodes.

This preview discusses the work by Veenstra et al., in which the experimental and computational efforts are combined to elucidate how the local reaction environment influences the eCO_2RR selectivity of the Cu catalyst. The simplicity of Cu electrodes with a well-defined architecture enables a quantitative prediction of the selectivity of Cu catalyst in eCO_2RR.

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