Modeling and parametric study of transport processes in a gas diffusion electrode for CO_2 reduction

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Introduction

Achieving climate goals requires innovative solutions to reduce CO_2 emissions. One promising approach is the electrochemical conversion of CO_2 into value-added products such as CO, hydrocarbons, and alcohols, which serve as platform chemicals for industrial processes, fuels, or energy storage solutions [1]. A challenge in electrolysis cell design is the limited solubility of CO_2 in water [2], which reduces its availability at the reaction sites. Gas diffusion electrodes (GDEs) address this issue by facilitating CO_2 diffusion to the catalyst surface. A GDE is a complex multiphase system comprising solid, liquid, and gas phases. Electron transport occurs through the solid phase, which also contains the catalytically active material for CO_2 reduction. The liquid phase ensures charge balance via ionic transport, while the gas phase supplies the gaseous reactants, thereby shortening the diffusion path of CO_2 through the liquid phase. Knowledge-based GDE design requires advanced models of the micro- and macrokinetic processes within and between the involved phases.

Modeling approach

A 2D cylindrical pore model is developed to resolve transport processes in the multiphase pore structure and the associated interfacial reaction phenomena in GDEs.

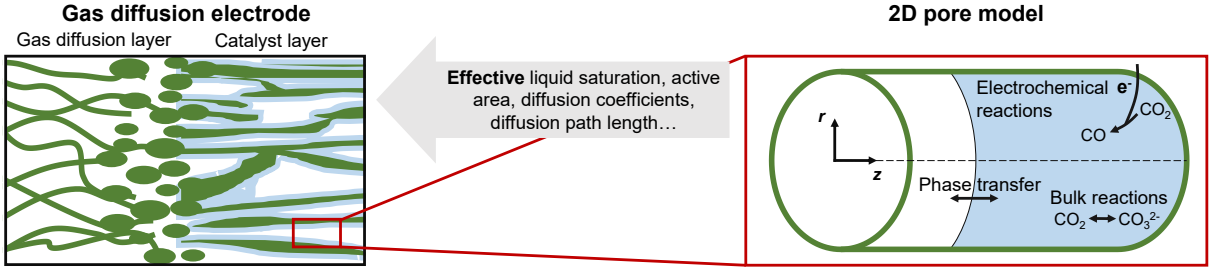

Figure 1: *Schematic structure of the 2D pore model and its upscaling to a macroscopic GDE model.*

The model enables the calculation of the degree of pore flooding as a function of the capillary pressure. Furthermore, the model accounts for mass and charge transfer across phases, including H_2 and CO evolution, as well as homogeneous electrolyte reactions.

Results

The pore-scale simulations quantify how capillary force-controlled interface positioning alters transport pathways within an individual GDE pore. Increasing liquid saturation shifts the dominant diffusion resistance from the gas phase to the liquid phase, reducing the reactant concentration at the catalyst interface. This limits attainable current densities at a given overpotential and promotes transport-limited operation, increasing concentration overpotentials and potentially decreasing Faradaic efficiency toward CO_2 reduction in favor of hydrogen evolution. Conversely, limited flooding preserves efficient gas phase transport, maintaining higher reactant concentrations. However, reduced liquid saturation also decreases the wetted catalyst surface area, lowering the effective number of active reaction sites and shifting operation toward kinetic limitation. The simulations therefore indicate an optimal saturation window balancing reactant supply and electrochemically active area, resulting in improved Faradaic efficiency and reduced cell voltage. Overall, the model demonstrates how pore geometry, wettability, and operating pressure determine both transport limitations and the electrochemically active area. It translates microstructural characteristics into performance-relevant quantities at the cell level.

Conclusion and Outlook

The developed pore model provides a mechanistic description of capillary force-driven phase distribution and its impact on mass transport in gas diffusion electrodes. The modular formulation further allows the integration of electrochemical kinetics and potential distributions, forming a basis for multiscale modeling of CO_2 electroreduction in GDE systems. By resolving local transport resistances, the framework enables the derivation of effective parameters for larger-scale electrode models, establishing a physically consistent multiscale model.

References

[1] B. Belsa, L. Xia, F.P. García de Arquer, *ACS Energy Lett.*, 2024, 9, 4293–4305.

[2] W. M. Haynes, D.R. Lide, T. J. Bruno, CRC handbook of chemistry and physics, 2014-2015, 95.