

Hierarchical multiscale analysis of CO₂ electroreduction at high current densities : The onset of transport limitations

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Significance and Relevance

This work provides an explanation of the experimentally observed CO₂ electrolyzer underperformance at high current densities in a gas-diffusion electrode (GDE) based cells using a hierarchical multiscale modeling approach. The low-dimensional model is developed using highly accurate physicsbased effective property correlations obtained through high-dimensional simulations and is rigorously validated with experimental CO, H₂ formation rates at different cathodic overpotentials . Our analysis reveals that at high current densities, the diffusional resistances of the GDE strongly influence the experimentally observed reaction rates, thus demonstrating the need to carefully consider such limitations when performing kinetic studies and benchmarking the GDE-based reactor performance.

Preferred and 2nd choice for the topic: Advanced process with electrocatalysis and plasma utilization, Multiscale modeling and advanced simulation aspects Preferred presentation: Oral / Short Oral

Introduction and Motivations

Low-temperature electrochemical CO_2 reduction offers a lucrative route for re-utilizing the emitted CO_2 towards the production of base chemicals using renewable electricity¹. However, for commercial adoption, the electrolyzer needs to operate at high current densities using gas diffusion electrodes (GDEs) as an effective medium for transporting the gaseous reactants/ products to the catalyst layer at the interface between the cathode and the electrolyte². At these current densities, the observed reaction rates may deviate from the intrinsic kinetics due to the presence of ohmic and transport resistances originating from the underlying multiphase interfaces in the geometry³. This work untangles this complex interplay between charge, mass transport and kinetic processes using a hierarchically refined one-dimensional continuum model for the GDE-assisted CO_2 electroreduction. Our low-dimensional model uses physics-based effective property correlations, derived from high-dimensional simulations of the GDE geometry and ensures a high degree of accuracy in terms of the model predictions. The provided analysis provides potential routes for future reactor design strategies for CO2 electrolyzers towards industrial-scale performance.

Materials and Methods

A one-dimensional multi-region, multiphase reactor-scale model for GDE-assisted CO_2 electroreduction is developed. The model resolves the gas phase diffusion of the reactant, product species, solid phase charge transport through the GDE and couples them with a spatially resolved thin catalyst layer model using flux continuity. The catalyst layer is modeled as a one-dimensional heterogeneous reaction-diffusion system which accounts for the reactant-product dissolution in an aqueous electrolyte and their subsequent participation in homogeneous liquid phase buffer reactions and catalytic charge-transfer reactions. To keep the present analysis tangible, two-electron charge transfer reactions are only considered, i.e. the formation of CO and H₂, using silver catalyst.

Results and Discussion

In the Fig. 1(a), the experimental CO current density (circular, square and triangular markers) are plotted with respect to the cathodic potential *vs. RHE* in the cathodic chamber^{4,5}. It can be seen that our model is able to faithfully reproduce the experimental current density data over the range of applied voltages. The current density profile based on intrinsic kinetics without any transfer resistance



is also shown (blue dashed curve) to indicate that as the applied voltage is increased, the experimentally obtained current density profile deviates considerably from the intrinsic kinetics, indicating the possible onset of transport limitations. Our model is able to accurately predict this onset and follow the experimentally observed CO current density. In order to explain this behavior, the model-predicted mean reactant/ product concentrations in the catalyst layer at different cathodic potentials are analyzed. Our analysis shows that as the cathodic potential is increased, the gaseous product build-up in the catalyst layer causes the partial pressure of the reactant to decrease, pushing down the CO₂ saturation concentration at the gas-liquid interface. This in turn, lowers the quantity of CO₂ reaching the electrolyte-submerged catalyst layer and consequently, the reaction rates.



Figure 1. Profiles of (a) average catalyst layer current density, (b) Damkohler equivalents in the GDE, catalyst layer and electrolyte dissolution, overlapped on logarithmic CO current densities, with respect to the cathodic potential *vs. RHE*

To locate the origin of the transport resistance appearing in the cathodic chamber of the electroreduction process (transport in the GDE/ catalyst layer/ bulk reactions), dimensionless quantities characterizing the different transport and kinetic processes are further analyzed. Fig. 1(b) shows the profiles of the Damkohler equivalents for the mass transport through the GDE, the catalyst layer and liquid electrolyte, over-imposed on the CO current density-voltage plot (logarithmic scale). In the entire range of voltage studied, our model suggests that the transport of liquid phase CO₂ from the bulk to catalyst surface offers minimal resistance due to the large surface area and small diffusion path length. However, around -0.85V vs. RHE, where the experimental/ model-predicted current density (blue curve) starts to deviate from the intrinsic kinetics (red curve), the gas phase mass transfer resistances start to play a role, reducing the supply of reactant to the catalytic active sites. In fact, the Damkohler equivalent in the GDE is observed to be higher than the catalyst layer due to its significant thickness in comparison to the catalyst layer. Thus, the developed multiregion continuum model is able to explain the experimentally observed CO₂ electrolyzer under-performance at high current densities and demonstrates the importance of considering the transport resistances in the GDE at high current densities, when measuring reaction rates. Hence, our model provides a useful tool for analyzing and optimizing the reactor design for improved performance at industrially relevant scales.

References

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