Elucidating the interplay of transport processes, buffer and charge transfer kinetics in CO_2 electroreduction in Gas Diffusion Electrodes through hierarchical multiscale analysis

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Highlights

- Virtual reconstruction and characterization of gas diffusion electrode are carried out
- Computational fluid dynamics is used to derive effective property correlations
- Our hierarchical analysis reveals the state-of-the-art reactor-scale model prediction discrepancies.

1. Introduction

Low-temperature electrochemical reduction of CO_2 offers a lucrative route for re-utilizing the emitted CO_2 for the production of base chemicals using renewable energy [1]. The gas diffusion electrode (GDE) has shown promise in advancing the CO_2 electroreduction technology towards industrial adoption by overcoming the limitation of CO_2 solubility in aqueous electrolytes. However, a detailed fundamental understanding is currently needed regarding how the GDE meso-structural geometry impacts the transport of reactants (products) to (from) the active sites in the catalyst layer at the electrode-electrolyte interface [2]. This becomes crucial at high current densities, where mass transport resistances starts to impact the intrinsic reaction rates. Reactor-scale modeling can be a very useful tool in deciphering this interplay, also providing holistic insights into the interconnectivity between various process parameters. However, such models often rely on simplifying assumptions regarding the underlying meso-structural geometry [3,4]. These simplifications manifest themselves in the form of semi-empirical/empirical porous media correlations, which are then used to close the governing equations of the system. In this work, we address this knowledge gap by applying a hierarchical multiscale modeling approach [5]. In this approach, we computationally reconstruct an accurate virtual GDE porous geometry and perform Computational Fluid Dynamics (CFD) simulations on them to extract detailed engineering effective property correlations. Then the derived correlations are inserted in a multi-region multiphase reactor-scale model that we have developed for the GDE-assisted CO_2 electroreduction. The hierarchical methodology enables us to understand the mutual interactions between the various phenomena, increasing the fundamental understanding and clarifying potential routes for future improvements.

2. Methods

First, a virtual representation of the GDE meso-structural geometry is reconstructed using open-source CAD software. The geometry consists of randomly distributed carbon fibers stacked on top of each other, creating the mesh matrix of the carbon paper material. The binder material, holding the fibers together, is computationally generated using image processing algorithms. Next, morphological characterization of the geometry, in terms of the porosity (sectional/ bulk) and pore size distribution, is carried out using image analysis tools. CFD simulations for species diffusion and current conduction are carried out next on the generated geometries using finite-volume based in-house solver catalyticFOAM. A multi-region multiphase reactor-scale model of the GDE-assisted CO_2 electroreduction is developed next, where the CFD-derived correlations are plugged in and the effect of transport and ohmic resistances on intrinsic charge transfer kinetics are analyzed.

3. Results and discussion

Figure 1(a) shows a sample of the virtually reconstructed GDE geometry highlighting the carbon fibers bonded together by the resinous binder material. A detailed morphological characterization is carried out by comparing the sectional porosity and pore size distribution (Figure 1(b)) with experimental data from SEM, tomographic scans, showing good agreement. Next, engineering correlations for the effective conductivity/ diffusivity are developed by performing three-dimensional CFD simulations on the generated geometries, shown in Figure 1(c). Our correlational analysis reveals that generic empirical correlations such as Bruggeman, overpredict the transport processes in the GDE, as they underpredict the tortuosity inside its asymmetric fibrous geometry. Following the hierarchical approach, a reactive reactor-scale model is developed for the analysis of the process performance at high current densities.

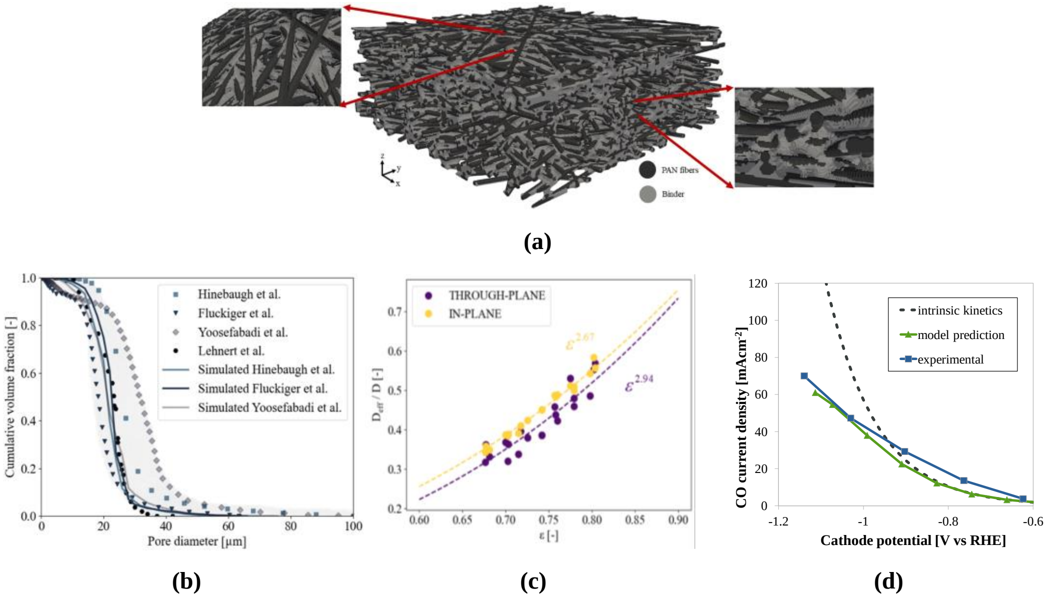

Figure 1. (a) Virtually reconstructed GDE carbon paper (b) Cumulative pore size distribution of reconstructed GDE (c) CFD based correlations for effective diffusivity vs. porosity, (d) CO current density profile vs. voltage [vs. RHE].

As shown in Figure 1(d), the model is able to reproduce the experimental behavior even at high cathodic potentials where significant deviation from chemical regime occurs. Our analysis reveals that as the applied voltage is increased, the charge transfer resistance offered by the solid skeleton of the GDE determines the potential reaching the catalyst layer, determining the net driving force for the charge transfer reactions. The GDE pore space starts to offer partial mass transfer resistance for reactant supply/product removal, and in turn, results in lowering the partial pressure of the gas phase primary reactant in the catalyst layer and the corresponding CO_2 saturation concentration near the catalytic active sites, thus lowering the obtained CO current density. Our work thus shows that the GDE structure plays a critical role in determining the product yield, selectivity at industrially-relevant high current densities .

4. Conclusions

In this work, the hierarchical approach is employed to fundamentally investigate the interplay between transport properties and kinetics in GDE-assisted CO_2 electroreduction. Detailed CFD simulations are used to developed engineering correlations that are then plugged into a reactor-scale model for the GDE-assisted CO_2 electroreduction. Our framework accurately reproduces experimental data. Moreover, the simulations reveal the impact that transport properties have at industrially-relevant conditions providing fundamental guidelines to optimizing the GDE design for the CO_2 electroreduction process.

References

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Keywords
Hierarchical multiscale modeling; CO_2 electrolysis, Gas diffusion electrodes, Computational fluid dynamics.