Modeling of a membrane electrode assembly for the electrochemical reduction of CO_2 to CO

Luzie Klöckner[1], Kevinjeorjios Pellumbi[2], Dominik Rudolf[1], Kai junge Puring[2], Ulf-Peter Apfel[2,3], Marion Börnhorst[1], Hannsjörg Freund[1]

[1]TU Dortmund University, Institute of Reaction Engineering and Catalysis, 44227 Dortmund, Germany

[2]Fraunhofer Institute for Environmental, Safety and Energy Technology, UMSICHT, 46047 Oberhausen, Germany

[3]Ruhr University Bochum, Chair of Inorganic Chemistry I, Technical Electrochemistry - Activation of small molecules, 44801 Bochum, Germany

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 reaction sites. Gas diffusion electrodes (GDEs) in membrane electrode assemblies (MEAs) address this issue by facilitating CO_2 diffusion to the catalyst surface. An MEA is a complex multiphase system whose efficiency significantly depends on the interactions between membrane, catalyst layers and transport layers. Adapting the cell design to industrial processes requires an understanding and advanced models of the micro- and macrokinetic processes in MEAs.

Modeling approach

A 1D model for a GDE in a Half-MEA that considers mass and charge transfer across gas, liquid, and solid phases, accounting for H_2 and CO evolution at the cathode, O_2 evolution at the anode, and homogeneous reactions in the $KHCO_3$ electrolyte is used.

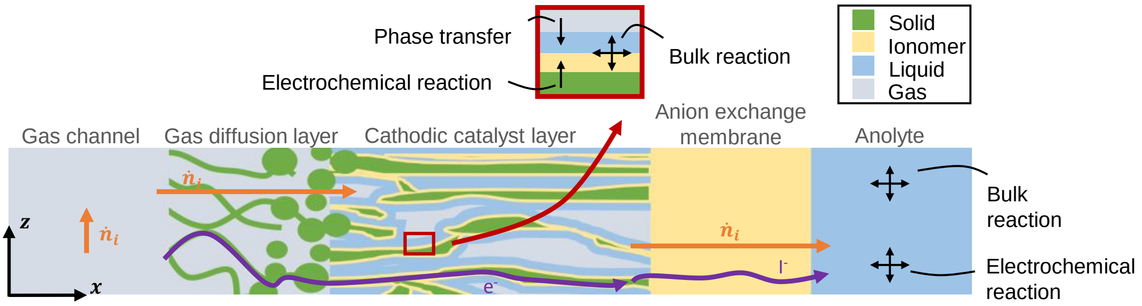

Figure 1: Schematic structure of the 1D model including mass and charge transport in each domain.

The model is validated using experimental data from an electrolysis cell at Fraunhofer UMSICHT [3] at current densities between 1000 and 5000 A m^{-2} and applied for sensitivity analysis of reaction kinetics and liquid saturation in catalyst pores.

Results

The model results of the Faraday efficiency, the conversion of CO_2 and the selectivity to CO as a function of the total current density agree qualitatively and quantitatively with results from the literature model by Weng et al. [4]. Kinetic parameters were taken from this literature model [4]. A comparison of the model results with the results obtained in the experiments at Fraunhofer UMSICHT reveals qualitative differences. While the model predicts an increase in CO Faraday efficiency with rising current density, experiments show a decrease, consistent with findings from experimental studies in the literature [5]. The deviations between simulation and experimental data are attributed to the model's high sensitivity to kinetic parameters, which require adjustment to match experimental trends. In addition to the kinetic parameters, there are a number of other performance-critical parameters, such as the liquid saturation in the pores of the GDE, which are yet unknown. The model developed thus highlights the general problem of *a posteriori* parameter adjustment in the literature models. Investigation of the concentration profiles shows pH differences between the anolyte, the anion exchange membrane and the liquid film on the cathodic catalyst layer and the effects of the pH value on CO_2 loss via the membrane.

Conclusion

The developed GDE model explains individual physical phenomena and reproduces existing experimental correlations. Detailed investigations of liquid saturation and reaction kinetics are required for a quantitative MEA model. A validated model of an MEA will enable a deeper understanding of electrochemical reactions and transport phenomena as well as the optimization of design and operating parameters of electrochemical cells.

References

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