Sensitivity Analysis of One-Dimensional Multiphysics Simulation of CO_2 Electrolysis Cell

Harry Dunne[1], Weiming Liu[1], Mohammad Reza Ghaani[1], Kim McKelvey[2], Stephen Dooley*,[1]

[1]*School of Physics, Trinity College Dublin, Ireland*
[2] *MacDiarmid Institute for Advanced Materials and Nanotechnology and School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington 6012, New Zealand*

**Corresponding author: Stephen.dooley@tcd.ie*

Highlights

- In this work we construct a 1-D simulation of an electrochemical cell for CO_2 reduction.
- We then perform a sensitivity analysis of all input parameters to the simulation, which has not been presented before in the literature. CO partial current density (i_{CO}) is significantly affected by each input parameter of the simulation, and is most sensitive to electrochemical kinetic parameters i_0 and α, with a 1% change in α resulting in up to 6% change in i_{CO}.
- This indicates that infidelity between experiment and simulation is likely, and thus caution should be practiced when comparing experimental results to simulation results. Further, we show that the large range of conditions simulated in literature helps to explain the large variance in i_0 and α_c reported in literature.
- The results of this paper demonstrate the potential of sensitivity analysis methods to quickly optimise aspect of cell performance (CO_2 utilisation, Faradaic efficiency, etc.).

1. Introduction

The field of electrochemical CO_2 reduction is concerned with converting CO_2 to value-added products by means of electrochemical reactions. The operation of a CO_2 electrolysis cell is complex, so to aid with this problem, simulations of CO_2 electrolysers are built to provide insight that experiment cannot bui [1]. One key challenge in building a multiphysics simulation of a CO_2 electrolysis cell is sourcing the input parameters. Often parameters are taken from work done in different experimental conditions and/or by different groups. This may lead to 'infidelity' in the simulation, where the output of the simulation will not accurately describe experimental observations. Further, many of the input parameters commonly used may be inaccurate, since the values reported in literature are highly variable, and they are difficult to measure experimentally. The effects of inaccurate or unsuitable parameters on the output of multiphysics simulations is not well known. In this work we aim to investigate the effects of each input parameter on the current density of the CO_2 reduction reaction, by means of a sensitivity analysis to a typical multiphysics simulation of a CO_2 electrolysis cell.

2. Methods

A multiphysics simulation is constructed which accounts for electrochemical reactions, solution phase reactions, solvation of $CO_{2(g)}$ to $CO_{2(aq)}$, transport of gaseous species ($CO_{2(g)}$, $H_{2(g)}$, $CO_{(g)}$, $N_{2(g)}$) and solution phase species ($CO_{2(aq)}$, $H_2O_{(aq)}$, $H^+_{(aq)}$, $OH^-_{(aq)}$, $HCO_3^-{}_{(aq)}$, $CO_3^{2-}{}_{(aq)}$, $K^+_{(aq)}$), and transport of electrons in the solid phase weng [1] [2]. Equations describing mass balance and current balance are used alongside the Nernst-Planck equations for transport of species. These equations are populated with defined input parameters and solved using COMSOL Multiphysics v6.0.

3. Results and discussion

This work shows that at any condition, the current density of the CO_2 reduction reaction (i_{CO}) is highly sensitive to the kinetic parameters of all electrochemical reactions (i_0, α). Therefore, one should choose i_0/α which reflect the conditions being simulated, and which faithfully describe one's experimental output. If using a multiphysics simulation to attempt to extract i_0/α for ones experimental setup, then the simulation should be used in combination with quantum mechanical (QM) simulation, since multiphysics simulations approximate the CO_2 reduction reaction as a single step. The large range in reported i_0/α values in literature are further explained high sensitivity of i_{CO} to i_0/α. There is large

variance in input parameters used, resulting in a large variance in polarization curves, thus a large variance in fitted parameters.

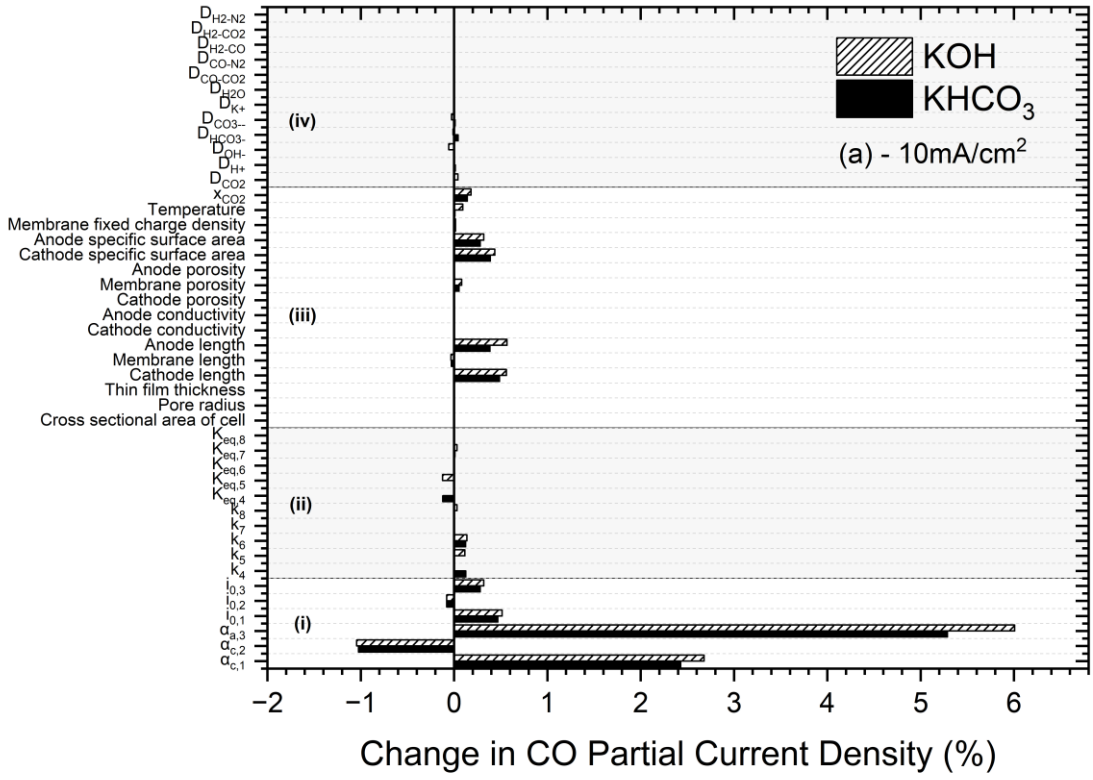

Figure 1. The sensitivity of the multiphysics simulation to each input parameter, for the KOH and $KHCO_3$ cases (a) at 10mA/cm^2. The sensitivity is defined as the percentage change in the CO partial current density (i_{CO}) with a 1% increase in the given parameter. Parameters are divided into categories i) electrochemical kinetic parameters, ii) solution phase kinetic parameters, iii) physical parameters, and iv) diffusion coefficients.

4. Conclusions

The sensitivity analysis presented shows that kinetic parameters i_0 and α are the most important factors affecting i_{CO}. This suggests that to increase i_{CO}, future work should be directed at improving catalyst performance, as is currently the case in CO_2 reduction space. The large variance in reported kinetic parameters, of both solution phase and electrochemical reactions, suggests that work should be done to determine them more precisely in the typical conditions of cell operation. The nature of the reaction network in such a cell means that all species concentrations are strongly linked, and thus errors are likely to propagate and result in infidelity in the simulation. The sensitivity analysis methodology presented here can also be employed to optimise cell performance, by giving the most important parameter with respect to any performance metric other than i_{CO}, such as Faradaic efficiency, energy efficiency, CO_2 utilisation, etc.

References

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Keywords
CO_2 reduction; electrochemistry; multiphysics simulation; COMSOL.