

Ice-Crystallization Kinetics During Cold-start of a Proton-Exchange-Membrane Fuel Cell

T. J. Dursch,^{1,2} J. F. Liu,¹ G. J. Trigub,¹ C. J. Radke,^{1,3}
A. Z. Weber²

¹Chemical and Biomolecular Engineering Department,
University of California, Berkeley, CA 94720

²Environmental Energy Technology Division, Lawrence
Berkeley National Laboratory, Berkeley, CA 94720

³Earth Sciences Division, Lawrence Berkeley National
Laboratory, Berkeley, CA 94720

Proton-exchange-membrane fuel cells (PEMFCs) reduce oxygen to water in the cathode catalyst layer (cCL). Under subfreezing conditions, water solidifies and hinders access of oxygen to the catalytic sites in the cCL, severely inhibiting cell performance and potentially causing cell failure. Elucidation of the kinetics of ice formation within PEMFC-porous media is, therefore, critical to successful cell startup and high performance at low temperatures. In previous work¹⁻³, we measure and predict ice-crystallization rates in the gas-diffusion layer (GDL) and cCL. In this study, we implement our newly-developed ice-crystallization kinetic expressions in a simplified 1-D transient PEMFC cold-start model. To investigate the importance of ice-crystallization kinetics, we compare ice saturations and cell-failure times predicted using our kinetic rate expression to that predicted using a thermodynamic-based approach.⁴ From this comparison, we identify conditions under which including ice-crystallization kinetics is critical and elucidate the impact of freezing kinetics on low-temperature PEMFC operation.

Figure 1 illustrates the simplified 1-D geometry for the PEMFC. Dashed lines indicate the spatial domain used in the present work (i.e., only the cCL and GDL). Symbols a and c denote the anode and cathode, respectively. Coupled equations (ice, liquid, and gas mass balances and an energy balance) are solved numerically in Matlab R2010a using finite differencing and a Crank-Nicholson scheme to resolve nonlinearity. Ice saturations and cell-failure times are predicted as functions of environmental temperature, current density, and overall heat transfer coefficient. Preliminary results demonstrate that for both the kinetic-based and thermodynamic-based models, cell-failure time decreases with both decreasing environmental temperature and increasing current density. In both cases, ice saturations are significantly higher in the cCL than the GDL at low environmental temperatures (e.g., -20 °C) when freezing times are short. As environmental temperature increases increasing freezing times, product water migrates to the GDL, resulting in an increase in cell-failure time.

Both the kinetic and thermodynamic-based models show agreement with isothermal PEMFC cold-start experiments⁵ at low environmental temperatures. However, the cold-start model reveals that only the kinetic-based approach shows agreement with cold-start experiments at higher environmental temperatures (e.g., greater than -7 °C). Consequently, the simplified PEMFC cold-start model illustrates that ice-crystallization kinetics are critical when induction/freezing times are long (i.e.,

high external temperatures, greater than -7 °C, and/or low overall heat transfer coefficients).

Acknowledgement

This work was funded by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Fuel Cell Technologies, of the U. S. Department of Energy under contract number DE-AC02-05CH11231.

References

1. T.J. Dursch et al., *Langmuir* **2012**, 28, 1222-1234.
2. T.J. Dursch et al., *Int. J. Heat and Mass Trans.* **2013**, 60, 450-458.
3. T.J. Dursch et al., *ECS Transactions* **2013**, 50, 429-435.
4. R. J. Balliet and J. Newman, *J. Electrochem. Soc.* **2011**, 158, B927-B938.
5. K. Tajiri et al., *J. Power Sources* **2007**, 165, 279-286.

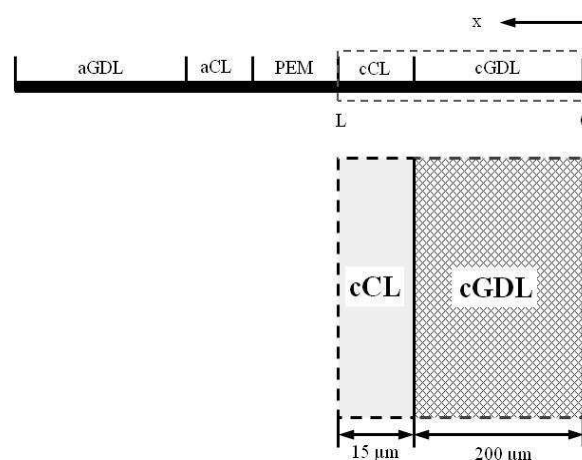


Figure 1. Schematic for the 1-D PEMFC cold-start geometry. Dashed lines represent the modeling domain. a and c label the anode and cathode, respectively.