V.G.12 Sub-Freezing Start-Up of a Fuel Cell

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Objectives

- To understand fundamental aspects of the start-up process at sub-freezing conditions and to identify the key mechanisms that
  - Limit rapid start-up
  - Lead to failure
- To study the effect of different start-up and shutdown protocols on the fuel cell durability and performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(D) Thermal, Air and Water Management
(J) Startup Time/Transient Operation

Technical Targets

This project is conducting fundamental studies of fuel cell operation at low and subzero temperatures. Understanding of the factors that limit a fast start-up and the failure mechanisms will be applied to meet the following DOE 2010 targets:

- Start-up time: 30 s to 90% rated power at -20°C ambient conditions
- Survivability: -40°C

Accomplishments

- 3D model simulations suggest that ice may start to form under the bipolar plate and spread towards the flow channel rather than first starting downstream and progressively moving to the inlet of the fuel cell.
- Numerical analysis showed that parameters such as thin gas diffusion layers, thin membranes and interdigitated- or cascade-flow field designs improve water removal from the cathode.
- A fuel cell test apparatus capable of operating between -40° to 100°C has been completed. Initial testing at low temperatures, but above freezing, indicates that a high stoichiometry of air is needed to avoid flooding of the cell.

Introduction

The primary objective of this work is to achieve a fundamental understanding of, and to identify the technical barriers to, the material integrity and operational stability of automotive polymer electrolyte fuel cells (PEFCs) during repeated startup, operation, and shutdown at sub-freezing ambient temperatures. In particular, using a combination of experimental and modeling activities, we aim to develop and validate a detailed model of the startup of a PEFC under sub-freezing ambient temperatures down to -40ºC. To refine and improve upon existing developed models, there is a need to determine thermodynamic and transport properties of polymer electrolyte membranes and the state and distribution of water in them under a variety of operating conditions. This data is crucial to enable the development of a first-principles model that can correlate transport properties with the initial water conditions, and temperature from –40ºC to 80ºC. Such a detailed understanding is necessary for the successful development of the cold-start fuel cell model and to explore alternative start-up (and shutdown) strategies.

Approach

The overall approach is a combination of mathematical modeling and experiments for model verification. Initially, numerical simulations are used to qualitatively identify mechanisms of water transport and to guide relevant experimental conditions. Along with modeling efforts, experiments are undertaken at subzero temperatures to validate and incorporate correct phenomena into the models.

Results

At temperatures below the freezing point, there is a delicate balance between how much current can be drawn to heat the cell/stack as fast as possible and accumulation of liquid water. At these low temperatures, the product water vapor condenses and may freeze on the electrochemically active surface area or even at the GDL thus effectively blocking the reaction and transport of reactants. An excessive air stoichiometry is thus needed below 0°C to avoid saturation of water (and hence ice formation) because of the limited capacity of the air to hold water vapor. At -10°C, for example, the water vapor pressure is only 0.0028 atm., and to avoid saturation at this temperature, an air stoichiometry of at least 148 is needed.

Hishinuma et al. [1] investigated the start-up of a single cell below freezing conditions. Depending on the temperature, the authors observed that the cell potential quickly decreased above a certain threshold value of the current density. At -10°C and using dry gases, the voltage started to decrease as a function of time at a constant current density of 15 mA/cm^2 even with an air stoichiometry of 225.

Initially, we conducted a series of simulations to delineate the effects of operation at subfreezing conditions on water transport and eventual ice formation. The scenario for comparison was based on the parameters in the work of Hishinuma et al. [1] at -10°C using a current density of 15 mA/cm^2 (the case where voltage decayed with time under the assumption of ice formation). Assuming negligible axial gradients in the channel of the fuel cell, Figure 1 shows the dimensionless water concentration profile (relative humidity) at the cathode side. This figure shows a worst case scenario where no water produced at the cathode is transported to the anode side. The idealized case (perfectly mixed reactor) predicts a relative humidity of 60% which is the water concentration at the flow channel. However, saturation of water at the catalyst layer may be possible due to a concentration gradient as a result of diffusion resistance in the GDL, especially with very thick GDLs. In practice, however, since the inlet hydrogen feed is dry, water transport from cathode to anode will likely occur to some extent. Since water transport through the membrane can play an important role in the interpretation of Figure 1, the back flux of water from cathode to anode was investigated in more detail by varying the membrane water diffusivity and membrane thickness.

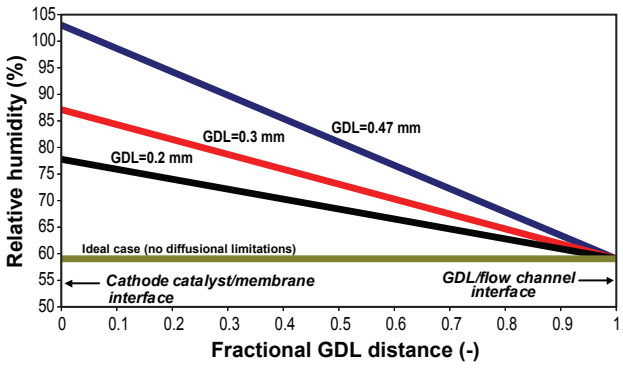

FIGURE 1. Effect of GDL thickness on water removal from the cathode electrode layer. Air flow rate 6.33 SLPM (stoichiometry of 225), i=15 mA/cm^2, T=-10°C, porosity=0.4.

Figure 2, shows the dimensionless water flux, α, from the cathode to the anode side as functions of water diffusivity, D_m, and the membrane thickness. Water flux to the anode can indeed become small in the case of very thick membranes or when the diffusivity is low. The membrane thickness used in the work of Hishinuma et al. [1] was, however, only 30 μm thick. Typical diffusivity values at 30°C are in the range between 10^{-10}-10^{-9} m^2/s [2]. At subfreezing conditions, there is very little data available for those constants. However, Cappodonia et al. [3], experimentally estimated diffusivity values for a few typical membranes at temperatures below freezing. At -20°C, where some form of a phase change in the water content of the membrane was observed, a low value (order of 10^{-11}) of the diffusivity constant was measured. Even with such low diffusivity values, the thin membrane allows for significant water content to be transported to the anode. Including transport of water to the anode side, no water saturation is predicted even with the thickest GDL in Figure 1. Yet, according to experimental results [1], the voltage decayed over a short period of time due to the hypothesis of ice formation blocking the electrochemically active area.

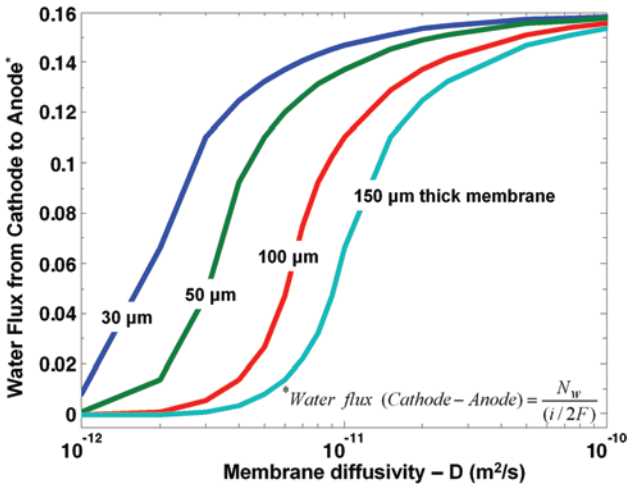

FIGURE 2. Effect of water transport through the polymer membrane as a function of membrane thickness and diffusivity values. Current density held constant at 15 mA/cm^2. Air-flow rate=6.33 SLPM, hydrogen flow-rate=0.79 SLPM.

The numerical effort was further extended to a 2D model in order to investigate axial variation of water and possible saturation near the exit of the fuel cell. Figure 3 shows the results using a 2D model for the water concentration combining anode, cathode and membrane equations. In those calculations, as much as 75% of the water produced at the cathode at the inlet crosses over to the anode but decreases to 10% at the exit as anode water content increases. Due to the increased water flux to the anode, the maximum water concentration (relative humidity) is only 80% at the exit of the fuel cell. However, a further extension of the transport model into 3D revealed that saturation of water (and hence ice formation) may be possible. Again, the same parameters as in previous numerical cases (15 mA/cm^2, T=-10°C) were used to compare the results. Figure 4 shows a cross-section plot of the symmetry plane of the exit of a single channel. The water concentration (relative humidity) is now very high under the bipolar plate. Product water formed under the bipolar plate has a longer distance to be transported out to the flow channel while water formed under the flow channel has a shorter way to be transported out from the GDL. A 2D model is hence not an accurate representation of serpentine flow geometry since it only accounts for the shortest possible diffusion path through the GDL (parallel plate geometry). Consequently, with the increased diffusion path under the bipolar plate, water will likely saturate under the bipolar plate and freeze. Hence, ice formation may probably progress under the bipolar plate and outwards to the flow channel.

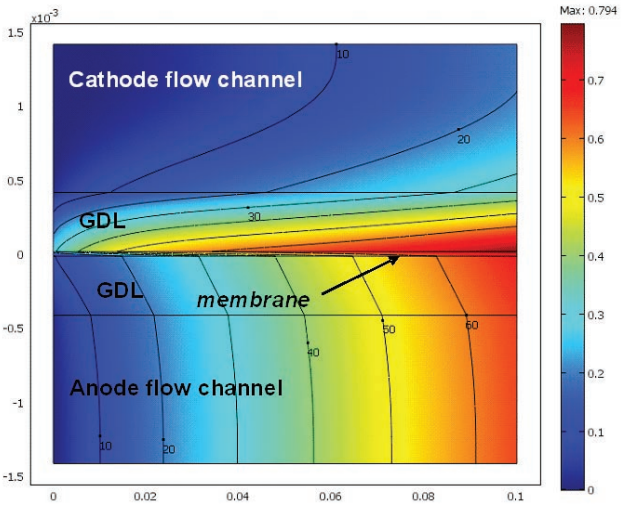

FIGURE 3. Water concentration profiles (relative humidity) in a single fuel cell channel using a 2D model. 15 mA/cm^2, T=-10°C, Air=6.33 SLPM, H_2=0.79 SLPM. Color and contour lines denote relative humidity. Length scale (x,y) is in meters.

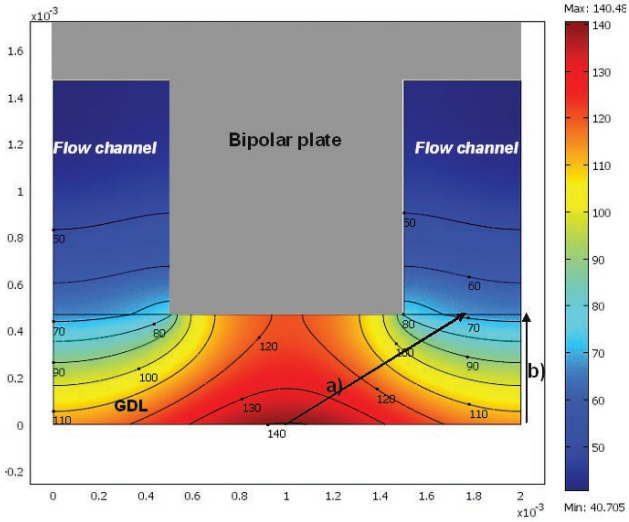

FIGURE 4. Water concentration profiles (relative humidity) in the cathode channel using a 3D model. Flux of water through membrane is 15%. Parameters: i=15 mA/cm^2, T=-10°C, Air=6.33 SLPM, color and contour lines denote relative humidity. a) long diffusion path to flow channel, b) short diffusion path to flow channel. Length scale (x,y) is in meters.

Besides transport phenomena, alternate fuel cell designs may be more effective in improving the transport of water out from the GDL and catalyst layer. The typical designs of serpentine or straight channel flow-field designs depend on diffusion through the GDL for transport of reactants and products from the catalyst-flow channel interface. In case of interdigitated- or cascade-flow field designs, gas flow is forced through the GDL and transport of reactants and products occur by forced convection. Figure 5 shows the schematic representation of the interdigitated flow-field. Performing this calculation using the same base case as in previous figures (15 mA/cm^2, T=-10°C), the results in Figure 5 show that water is effectively removed without reaching saturation at the catalyst interfaces (no water transport through the membrane was assumed as a worst case scenario. Indeed, the exit water concentration (relative humidity) is close to that predicted with an idealized model. However, as always, there is a trade-off. When flow is forced through the GDL, pressure drop increases sharply. The point, however, is that a large number of factors can be important in the study of cold-start behavior for PEM fuel cells where membrane, GDL and flow-field are just a few examples. Experimental tests have been started, initially above freezing temperatures, in order to collect data for model development and validation.

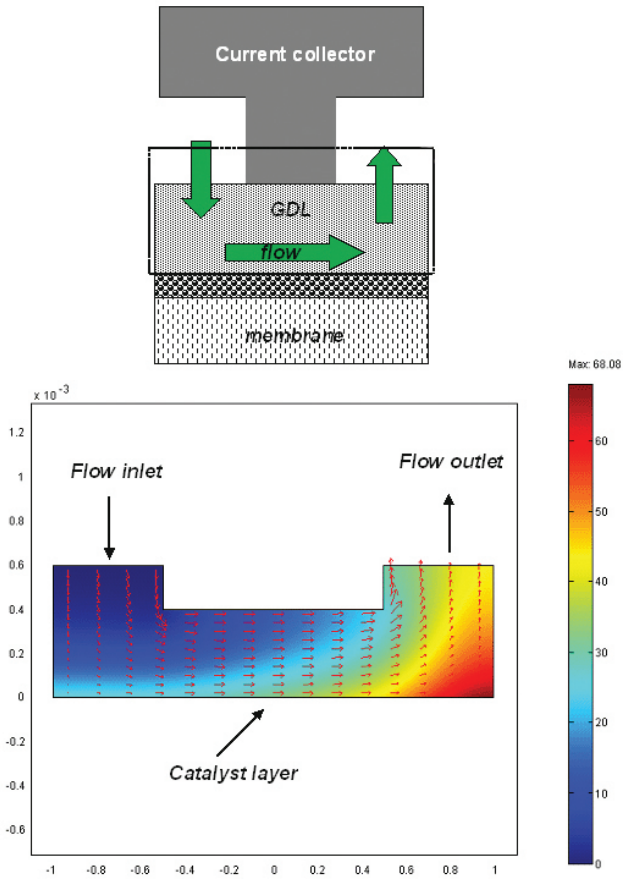

FIGURE 5. Effect of interdigitated flow field on water saturation. Air flow rate 6.33 SLPM (stoichiometry of 224), i=15 mA/cm^2, T=-10°C, GDL porosity=0.4. (α=0, no flux through membrane). Arrows denote flow field direction.

Conclusions and Future Directions

The results from a 3D model showed that water produced under the bipolar plate has a longer path to the flow channel; hence, the concentration at that point will be higher, well above the saturation point. Ice may start to form under the bipolar plate and spread towards the flow channel rather than first starting downstream and progressively moving to the inlet of the fuel cell. Transport parameters such as GDL thickness and membrane thickness may be important to study experimentally when generating data for model validation. Furthermore, flow-field designs may also have a great impact on water removal.

Future work will focus on developing a transient model that includes phase-change of water and experimental verification of the models from -20°C using a single cell test apparatus. Experiments to investigate the effect of different shutdown protocols will be carried out.

References

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