Models for Predicting MEA Water Content During Fuel Cell Operation and After Shutdown

R. Bradean, H. Haas, A. Desousa, R. Rahmani,
K. Fong, K. Eggen , D. Ayotte, A. Roett and A. Huang
Ballard Power Systems, 4343 North Fraser Way, Burnaby, BC, V5J 5J9, Canada

Abstract

Effective fuel cell operation requires the optimization of the water content of the membrane electrode assembly (MEA) such that to meet targets for performance, freeze start, durability and reliability. In this work we present models for predicting the MEA water content, which are used to provide input into the design of operating strategies of fuel cell stacks at Ballard Power Systems. The measurements of MEA water content during steady state fuel cell operation, stack purging after shutdown, or natural cooling after shutdown are in good agreement with the model results.

Introduction

The international demand for new energy resources has recently stimulated the fuel cell research worldwide and the commercialization of fuel cell products is now in sight in several industries. In the automotive industry, for example, most of the largest manufacturing companies have tested fuel cell vehicle fleets and gathered crucial information for the improvements at the vehicle level. In parallel, fuel cell research has significantly advanced resulting in improvements of several aspects of fuel cell operation, such as performance, startup from subzero temperatures, lifetime and reliability.

Liquid water transport in fuel cells was identified as a very important process for effective fuel cell operation by many researchers. Too much water in fuel cells can prevent reactants reaching the catalyst layers, whereas insufficient humidification of the membrane can affect the protons transport across the membrane. This critical water balance can also affect fuel cell startup from subzero temperatures as well as lifetime and reliability.

Many studies in the literature investigate various transport processes in fuel cells with the objective of developing understanding on the parameters that affect MEA water content and its effect on fuel cell operation. Most of this work is performed on modeling the water content in separate MEA components during fuel cell operation, such as Springer [1] and Weber and Newman [2] for membranes, and Bradean et al. [3] and Wang et al. [4] for gas diffusion electrodes. However, some recent CFD models also couple the MEA components in a unit cell model, see Berning and Djilali [5] and Mazumder and Cole [6]. Although these models develop a general understanding of the two-phase flow transport in the MEA, they are not validated to the level of making accurate quantitative predictions.

In this paper we present models for accurately predicting the MEA water content during several stages of a possible operating cycle of a fuel cell stack. Models were developed for fuel cell operation during steady state operation, for purging after shutdown and natural cooling after shutdown. These models use some simplification assumptions and empirical correlations, but they were extensively validated with experimental data at Ballard Power Systems.

MEA Water Content During Steady State Operation

To model the MEA water content during operation we first take into consideration some empirical observations. Thus, the experiments performed to measure the MEA water content at Ballard showed that if the gas in the channels is water vapor saturated, the MEA water content is almost constant when other operating conditions are varied. In this situation the membrane is water saturated, whereas the water content in the cathode gas diffusion electrode (GDE) has a value significantly below that of water saturated electrode. This value of GDE water content measured in experiments is an input into the model. If the gas in the channels is (significantly) under saturated with water vapor then the membrane is partially humidified and the cathode GDE is dry. In all situations the anode GDE water content was found to be very small.

Consider a straight channel design PEM fuel cell operated using steady state conditions. To calculate the MEA water content along the channel we use a 1+1 dimensional model along the channel and normal to the MEA described schematically in Figure 1. We model the 1D water transport across the MEA as follows: water production at cathode catalyst (interface between membrane and cathode GDE in Figure 1), water diffusion across cathode GDE, membrane and anode GDE and electro-osmotic drag in the membrane. This model is coupled with a 1D water transport model by convection along the anode and cathode channels. The MEA water content is calculated as the sum of the membrane and cathode GDE water contents (we assume that the anode GDE is dry). The membrane water content is obtained from the membrane transport model whereas the cathode GDE water content is assumed to be either zero if the cathode catalyst is below 100% relative humidity or the value measured in experiments otherwise.

The model results for the MEA water content distribution in steady state operation as well as measurement data for model validation are presented in Figures 2 and 3 for the co-flow (oxidant, fuel and coolant flows all in the same direction) and counter-flow (oxidant and coolant flows opposite to fuel flow) configurations, respectively. The fuel cell operating conditions used in the model and experiment are water vapor under saturated at the oxidant and fuel inlets. Figures 2 and 3 show that the model and the experimental results are in reasonable good agreement and that the model predicts the length of the dryer MEA regions near fuel cell inlets with reasonable accuracy. The good agreement between model and experiment is maintained when operating conditions such as inlet flow rates and dew points, coolant inlet temperature and coolant temperature increase are varied. This model has been extensively used at Ballard for the design of appropriate operating strategies to target a “desired” MEA water content distribution during fuel cell operation.

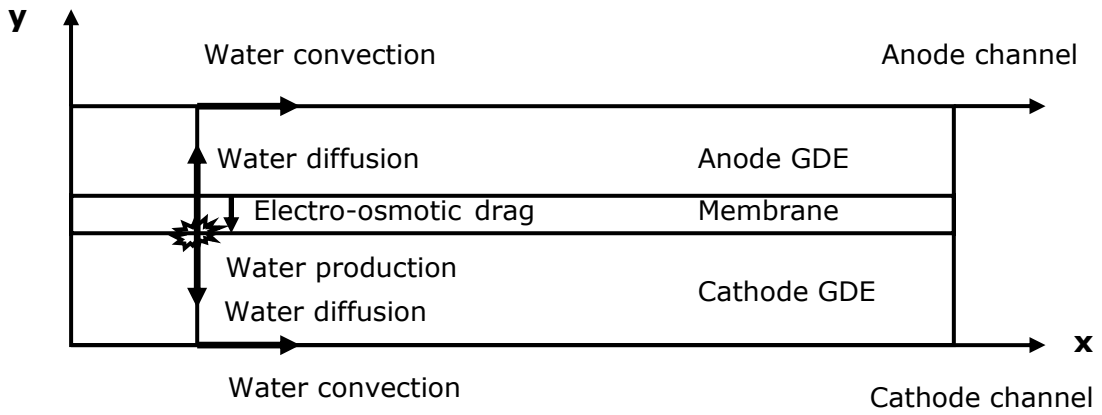

Figure 1. A schematic of the unit cell 1+1 dimensional model and domain.

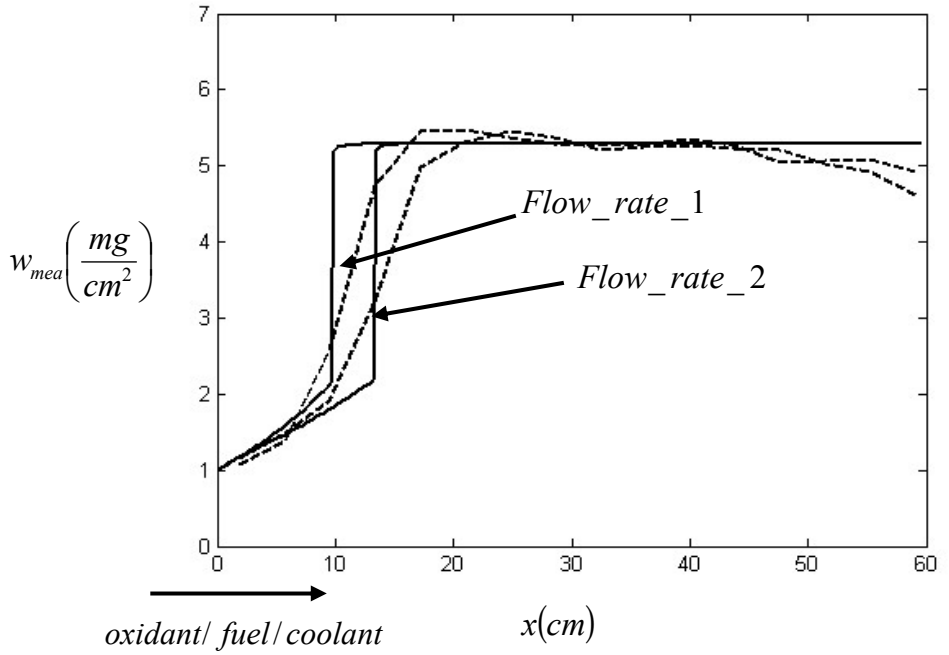

Figure 2. The MEA water content as a function of the distance along the channel obtained from the model (continuous line) and experiment (dashed line) using two oxidant flow rates. Operating conditions: 0.1 A/cm^2 current density, 60^0C coolant inlet temperature, 1^0C coolant temperature increase and 53^0C and 59^0C fuel and oxidant dew points.

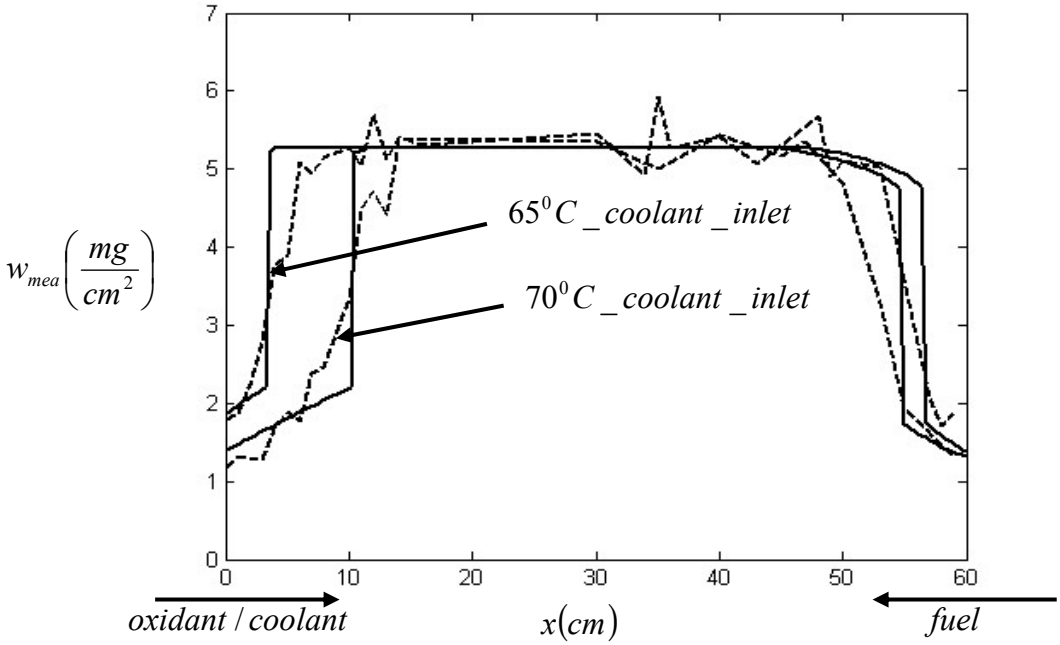

Figure 3. The MEA water content as a function of the distance along the channel obtained from the model (continuous line) and experiment (dashed line) using two coolant inlet temperatures. Operating conditions: 0.33 A/cm^2 current density, 7^0C coolant temperature increase and 57^0C and 61^0C fuel and oxidant dew points.

MEA Water Content During Purging After Shutdown

The MEA water removal during purging after shutdown is investigated as an evaporative mechanism in this study. Mechanical water removal from the MEA is an unlikely mechanism since the GDE and the membrane are porous media with very small pores and would require an extremely large pressure drop across. For realistic fuel cell pressure drops the flow in the GDE (the MEA component with largest pores) is in the Darcy regime with the pore Reynolds number much smaller than 1. In this situation the mechanical water removal should be negligible.

Consider a fuel cell with straight channels operating in a counter flow configuration, which is shut down. Since most of the MEA water present during operation is in the cathode GDE and the membrane, the purge is only performed on the cathode side. The evaporative mechanism of water removal from the MEA considered in this paper is assumed to be the following: water evaporation in the MEA, then water diffusion to the channel, and then water convection along the channel. This mechanism of water removal is investigated using a 1+1 dimensional model along the channel and normal to the membrane as described in Figure 4. It is assumed that the evaporation is not a limiting factor for water removal from the MEA and that there is 100% relative humidity in the MEA where the water evaporates. Also, based on experimental observations we assume that there is no water removal from the MEA at any location where the water content decreases below a specified small value.

In the present model the amount of water in the MEA is treated as a reservoir from which water is removed as the purge time increases. The time scales for diffusion across the MEA and convection along the channel are much smaller than the time scale for water removal from the MEA. Therefore, the models for vapor diffusion through the MEA and convection along the cathode channel are assumed to be steady (we neglect the time derivatives) and the only time dependence of the model is in the MEA water removal.

Figures 5 and 6 present the MEA water content distribution obtained from the model and the experiments after purging the cathode side of the fuel cell with dry air. The initial MEA water content measured after the fuel cell shutdown from counter-flow operation was fitted for model input. The model and experimental results are found to be in good agreement when varying several purge parameters such as air flow rate, purge time and fuel cell temperature. Figures 2 and 3 also confirm that the MEA water removal mechanism is dominated by evaporation and as a result the most sensitive parameter of the purge is the fuel cell temperature. Therefore, to remove the same amount of water from the MEA using the same air flow rate we need to purge for hours at $10-30^0C$ instead of seconds or minutes at $60-80^0C$. This model has been extensively used at Ballard for the design of various shutdown strategies to achieve the "desired" MEA water content for a subsequent start up.

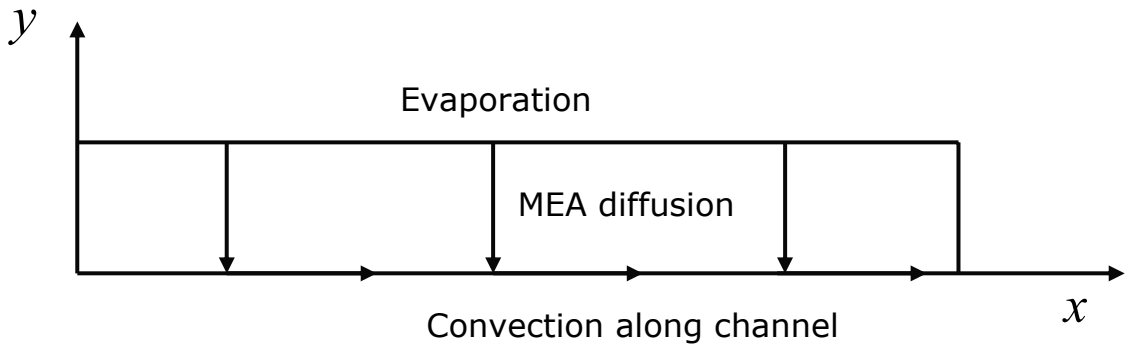

Figure 4. A schematic of the unit cell 1+1 dimensional purge model

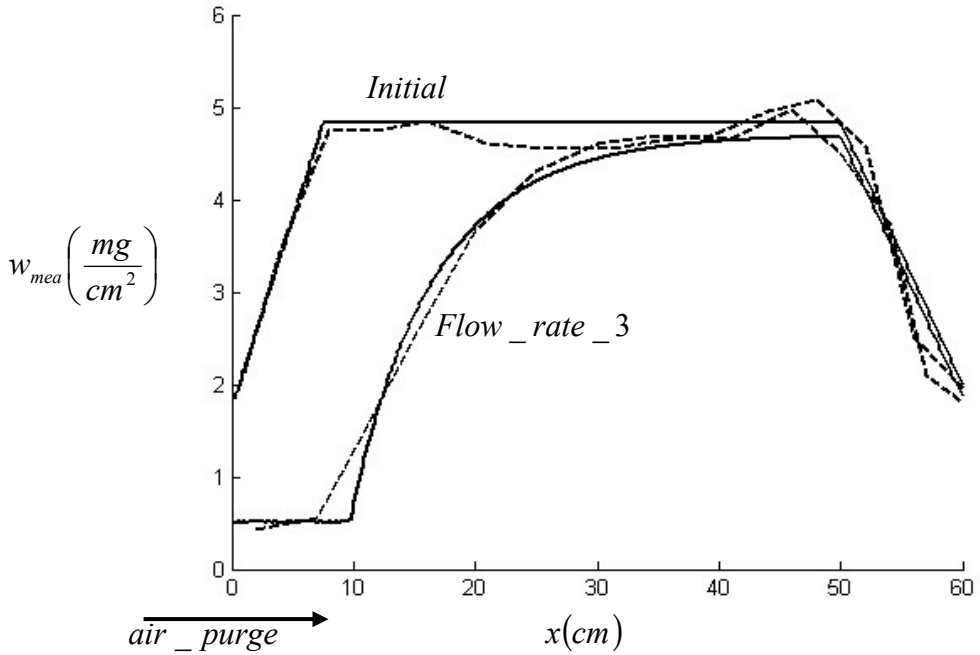

Figure 5. The MEA water content as a function of the distance along the channel obtained from the model (continuous line) and experiment (dashed line) after a dry air purge for 30 seconds of a fuel cell at a temperature of $80^0 C$.

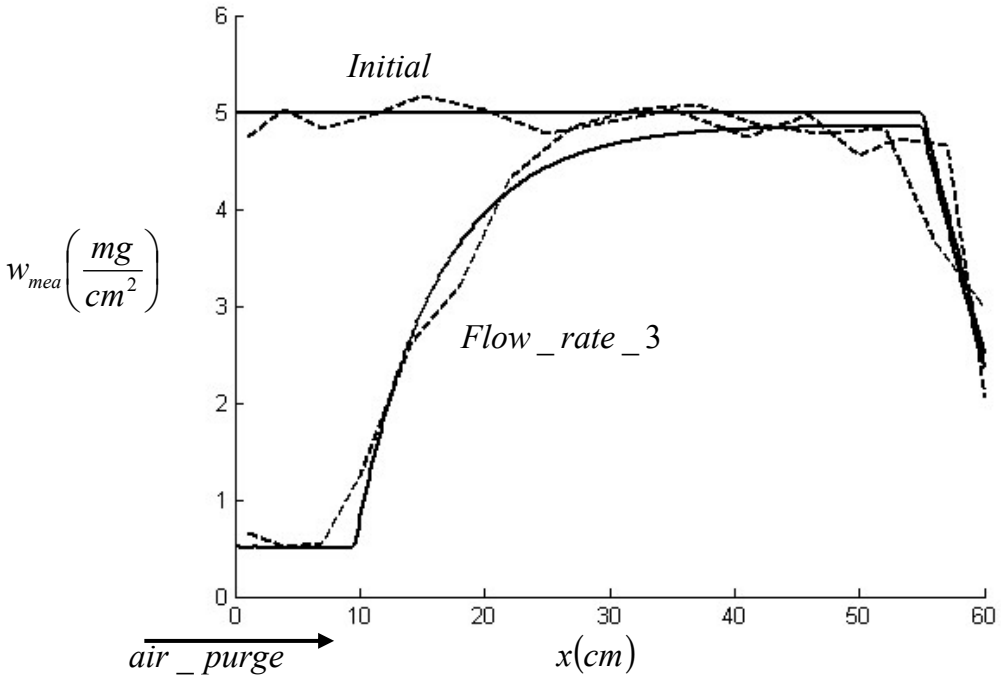

Figure 6. The MEA water content as a function of the distance along the channel obtained from the model (continuous line) and experiment (dashed line) after a dry air purge for 90 seconds of a fuel cell at a temperature of $60^0 C$.

MEA Water Content During Natural Cooling After Shutdown

Water movement in fuel cell stacks during natural cooling after shutdown can affect several aspects of fuel cell operation during a subsequent start up. Recently, water movement through MEA was observed at Ballard when a temperature gradient was enforced across a fuel cell. The water movement in the cell is directed towards the cold plate. The experiments performed to measure the water transfer rate through the MEA in a single cell were successfully correlated as a function of temperature and temperature gradient across the cell.

In this paper we develop a stack model to predict the MEA water content distribution along the stack during a natural cooling process after shutdown. For this purpose we use a stack insulated on all sides except on one stack end, so that the stack cooling and the water transfer from the MEA to the plate channels due to temperature gradients is one dimensional along the stack, see Figure 7. We use a one-dimensional, transient heat conduction model that contains a heat transfer coefficient at the non-insulated end of the stack to predict the stack cooling due to natural convection. The heat transfer coefficient is obtained by measuring temperatures in the stack end hardware during operation. The temperature profile along the stack is obtained from the heat transfer model as time increases during natural cooling.

The fuel cell stack in Figure 7 is operated such that the MEA water content at shutdown is uniform along the cell and along the stack. During the stack natural cooling after shutdown, the water transfer rate from the MEA to the plate channels in each cell of the stack can be calculated as a function of time from the average cell temperature and the cell temperature gradient (obtained in the heat transfer model) using the single cell correlation obtained at Ballard. The remaining MEA water content in each cell of the stack can be calculated by subtracting the total MEA water transferred to plate channels from the initial known value of MEA water content at shutdown.

The model and experimental results for the temperature distribution along the stack at different times during natural cooling is presented in Figure 8 and the MEA water content in different cells along the stack obtained from the model and the experiment at the end of the stack natural cooling is plotted in Figure 9. The model and experimental results are found to be in good agreement for both heat and water transfer processes. Although the temperature gradient across a cell is quite small during stack cooling, see Figure 8, there is significant movement of MEA water into plate channels at the end of the stack cooling, see Figure 9. The cell with the smallest MEA water content after natural cooling is situated near the non-insulated end of the stack (largest temperature gradient during cooling), and its value of the MEA water content is half the initial value at shutdown. Similar models have been recently used at Ballard in the design of new generation fuel cell stacks.

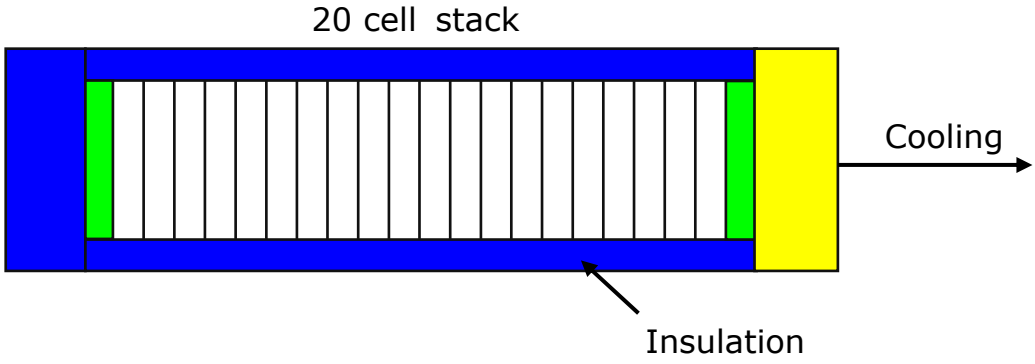

Figure 7. A schematic of a fuel cell stack insulated on all sides except one stack end.

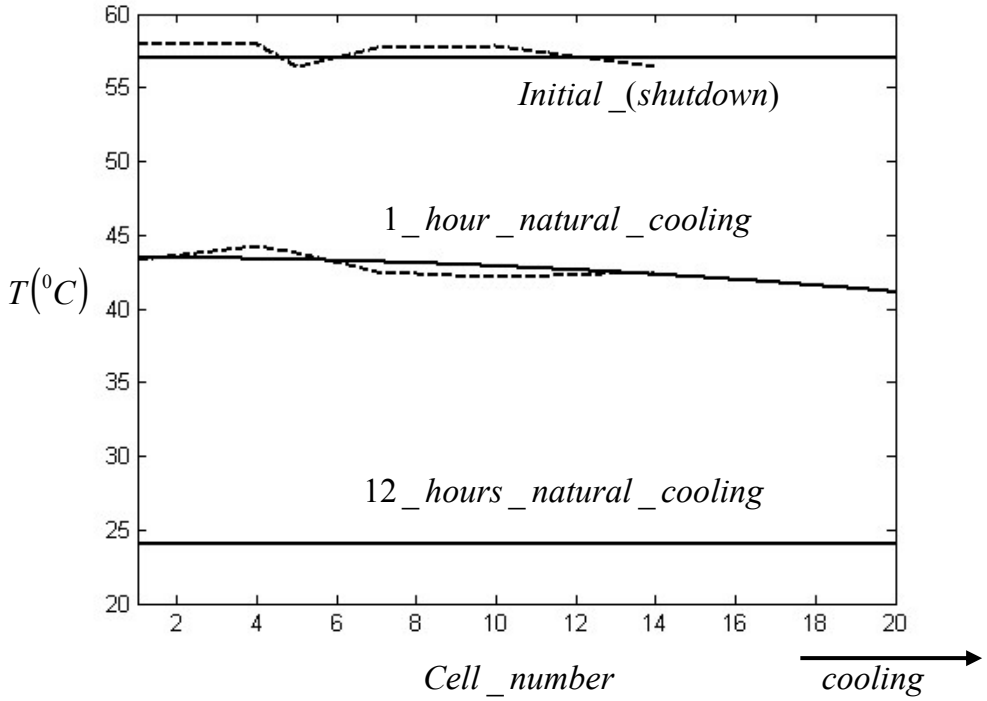

Figure 8. The temperature distribution along the length of the stack obtained from the model (continuous line) and the experiment (dashed line) at different times during the stack natural cooling process

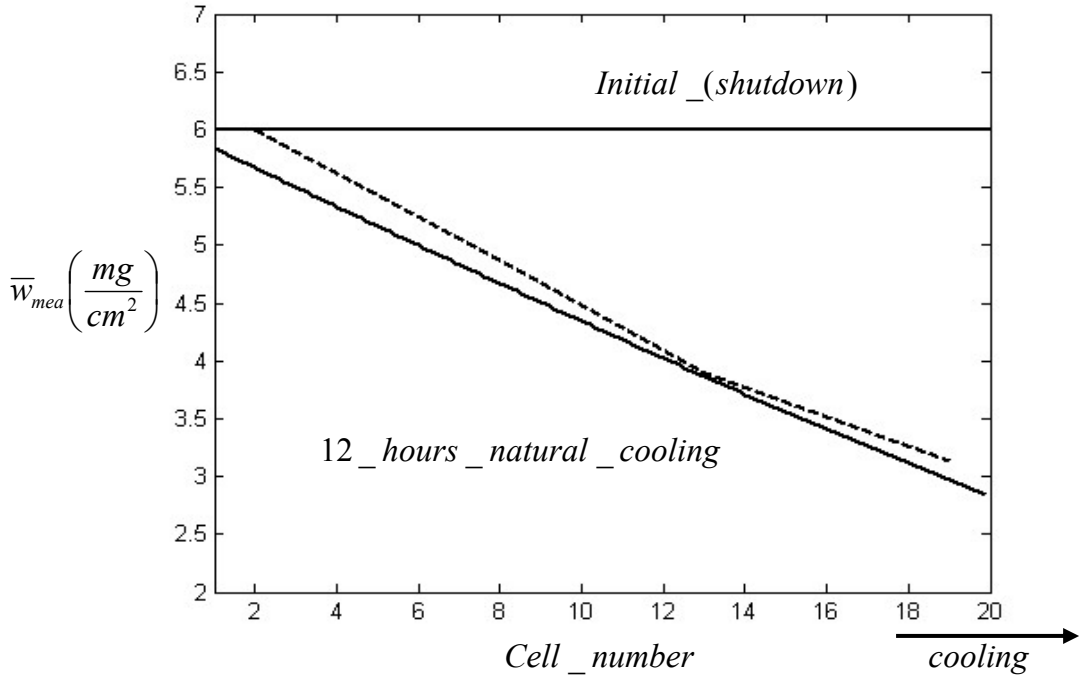

Figure 9. The MEA water content (cell average) along the length of the stack obtained from the model (continuous line) and the experiment (dashed line) at the end of the stack natural cooling process

Conclusion

Models for predicting the MEA water content during steady state operation, purging after shutdown and natural cooling after shutdown were presented and validated using experimental data obtained at Ballard Power Systems. Simplifying assumptions were used to model the water transport process through different fuel cell components, but the models are computationally fast and sufficiently robust. These models provide a very useful tool for the design of operating conditions as they can be used to control the MEA water content through different stages of an operating cycle.

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