# Dynamic Modeling and Analysis of PEM Fuel Cells for Startup from Subfreezing Temperatures

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## *Abstract*

Rapid start-up of a fuel cell from frozen conditions is a key challenge in the development of commercially viable automotive PEM (Polymer Electrolyte Membrane) fuel cells. Parasitic power, space and cost constraints make *bootstrap start* an attractive option, wherein the fuel cell is started up on its own without external heating. Bootstrap startup from subfreezing temperatures involves dynamic coupling of (mass, energy and momentum) transport and electrochemical reactions. As such, it is extremely difficult to empirically isolate factors limiting startup performance and intuitively predict the sensitivity of bootstrap start to cell design and operating parameters.

Presented in this work is a study of bootstrap start using physics-based dynamic models of various fidelity. They include detailed fuel cell model, semi-detailed stack model and system level stack model. The detailed model captures the strongly coupled reaction and transport through the various sub-layers in a PEM fuel cell, namely the gas diffusion layers, catalyst layers and the polymer membrane. Comparisons of model predictions and experimental data for voltage response during bootstrap start show reasonable agreement, validating the modeling approach. The model was then deployed to analyze the startup behavior from sub-freezing conditions. The model prediction of start-up temperature dynamics and the voltage response were in good agreement with the test data. These models are used for conceptual and detailed design of fuel cell stack and power plant system.

## *Introduction*

The need for energy efficient vehicles is growing worldwide and the EPA is setting stringent environmental regulations on emissions for the near future. Both these factors are driving investments into the area of fuel cells for power generation in transportation applications. Based on the analysis done by the Department of Energy (DOE), fuel cell vehicles are expected to comprise nearly 8% of the total light vehicle market by 2030[1]. To enable this, the primary challenge for the fuel cell cars is to exceed the performance of an IC engine for fuel savings benefits but with comparable cost, reliability and safety level. Though fuel cells have been known for a century now, and several advancements have been made to identify materials to improve the efficiency, research to enhance durability of the fuel cells and lower costs of existing technology is still in early stages. A subset of the targets set by DOE of relevance to a fuel cell that needs to operate at extreme conditions are given in table 1. The specific power and cost are also critical for the commercialization of fuel cell cars, however are not included here to keep the discussion simple. Several scientific breakthroughs in the areas of catalysts for improved performance, low cost materials with similar performance, balance of plant components for tight energy integration and compactness, robust control of the fuel cell systems etc. are required. Many of these are being worked on, however the timeline, by 2010, for demonstration of fuel cell systems at comparable price as IC engine and life of 5000 hours under realistic driving conditions, is rather challenging. One of the many challenges is operation of a fuel cell at temperatures below freezing point of water. Most of Northern USA, Northern Europe and Japan experience temperatures below –10 deg C during colder parts of the year. Almost 80% of the automotive market would require freeze capability. This is main focus of this discussion.

Table 1: Subset of technical targets for 50 KWe net integrated fuel cell power systems operating on direct hydrogen set by DOE[2]

| Characteristics | Units | Calender year | |
|---|---|---|---|
| | | 2005 | 2010 |
| Cold start-up time to Max. power | | | |
| -20 Deg C ambient temperature | sec | 60 | 30 |
| +20 Deg C ambient temperature | sec | 30 | 15 |
| Durability[a] | hours | 2000[b] | 5000[c] |
| Survivability[d] | deg C | -30 | -40 |

[a] Perfromance targets must be achieved at the end of the durability time period
[b] Includes thermal cycling
[c] Includes thermal and realistic drive cycles
[d] Achieve performance targets at 8-hour cold-soak at temperature

Operation of a fuel cell system at extreme conditions is challenging for the reasons described next. At extremely hot and humid conditions, the heat rejection from the fuel cell system becomes an issue along with water balance. At low temperatures, the water in the fuel cell and balance of the plant freezes, potentially affecting the operability and durability of the fuel cell. Water in a fuel cell is both critical for long life of the fuel cell and a concern for operation from sub-zero temperatures. Water is necessary in the fuel cell to keep the membrane humidified and maintain high proton conductivity and minimize durability issues due to dry out. The membrane is believed to contain water that is free (freezes close to 0 deg C) loosely bound (freezes between -10 and -20 deg C) and non-freezing (-120 deg C). It is conceivable that operation of the fuel cell becomes harder as the ambient temperatures decrease below 0 deg C[3]. The presence of water in the fuel cell, while the ambient at sub-zero temperature, can result in freezing of water potentially causing membrane MEA rupture, mechanical damage, delamination etc. These adverse effects may be aggravated by operation of the fuel cell from the frozen state. The key impact is decay in performance and shortened life of the fuel cell. While operation of the fuel cell stack is challenging at low temperatures, the balance of the plant poses another set of issues to deal with.

There are several strategies, to meet the freeze requirements listed in table 1, being pursued by research engineers and scientists. Two key approaches are a) to prevent freezing within the cell and b) allow freeze to occur and recover cell performance to nominal value. In the former case, the cell is kept warm with heaters and possible additional insulation. In this case, the addition of insulation and heaters lowers the specific power and specific energy of the power generation system. Another option is to allow the fuel cell to freeze and subsequently start-up the cell from frozen conditions when required. In this case, the cell tends to incur decay with multiple start-ups without adding to system complexity. There are several reasons for this decay, possibly overheating of the stack before coolant is available at the right temperature in some designs or possibly start-up issues due to blocked channels in solid bipolar plate design. To avoid the complications of frozen water, antifreeze (glycol based fluids) can be used as a coolant. However, the lower heat transfer coefficient of such fluids increases either the parasitic power requirements or size of the radiator (heat dissipation unit). The coolant also increases the burden during start-up, due to additional thermal mass that must be heated. Furthermore, the possibility of leakage of antifreeze to the MEA through sealants or other means could degrade the performance of the fuel cell due to electrode poisoning or change in properties of the different layers in fuel cell.

The trades described earlier can be evaluated through a combination of experiments and modeling. Designing experiments to answer questions regarding the fundamentals of fuel cell is very challenging, as there is often a strongly coupled dynamics between heat transfer, mass transfer and electrochemistry. For example, to design an experiment to understand the water movement within the fuel cell during the start-up from frozen conditions, several issues need to be answered. Freeze-thaw cycling of dry membrane electrode assemblies (MEA) showed that the toughness of the membranes and MEAs decreases while also incurring chemical changes[4]. The extent of water in the different layers and the location prior to start-up of the fuel cell often determines if a successful start-up can be achieved. During operation at these low temperatures, the water produced is distributed within in the cell and heat generated is used to warm up the cell. The rate of water production and heat dissipation is critical for a start-up. Often times the start-ups are either not reproducible or show loss in performance as multiple start-stop cycles are accrued. The underlying reasons for the observed phenomenon is not clear.

In this paper we present a modeling approach in conjunction with experiments to establish a framework to conceptualize, design, test and analyze fuel cell systems over a wide range of operational conditions.

### *Modeling and Analysis*

In order to delineate the strong coupling between electrochemical performance, mass transport and energy transfer to the different layers (more so during a frozen condition) models at various levels of fidelity are developed. These include a) detailed fuel cell models capturing three phases of water and startup from frozen conditions to predict stack performance, b) semi-detailed fuel cell stack model to capture stack dynamics, c) reduced order models of fuel cell stack to capture system dynamics.

*Detailed Models:* The aim of these models is to understand the transport of mass and heat within the layers of the fuel cell of and their role on the performance of a fuel cell. This understanding enables design of better fuel cells by engineering the right materials with right properties. These models include the mass and energy balance in all layers with details of transport in porous medium, vapor liquid equilibration kinetics within open pores and channels, saturation permeability dependence for water movement, electronic resistance, protonic conductivity, osmotic drag in the membrane etc. The model includes the physics of phase transition of water as well. Both dynamic and steady state performance data is obtained with these models. Shown in Fig. 1 is the voltage-current (VI) performance curve of

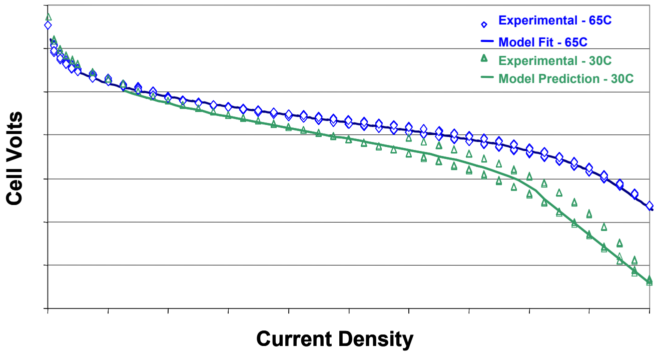

Fig. 1 Voltage -current characteristic of the fuel cell as predicted by the model (solid lines) and experiments (open symbols). Good agreement between the model predictions and experiments is observed

a representative fuel cell. The symbols represent the experimental data at two different temperatures and the solid line represents the numerical prediction of the performance from the model. The good agreement between the two indicates that the underlying physics is well captured, including the temperature effects. Furthermore, the same model is used to predict the response of the fuel cell to a dynamic change in operational current density, shown in Fig. 2. With an increase in current density the cell potential decreases to a value lower than the steady state and increases subsequently to the steady-state potential, showing a higher order dynamic response. This behavior is attributed to the dynamics of reactant concentration at the electrode due to change in the reactant flow and the time to establish steady state water equilibration and concentration profiles in the gas flow layers.

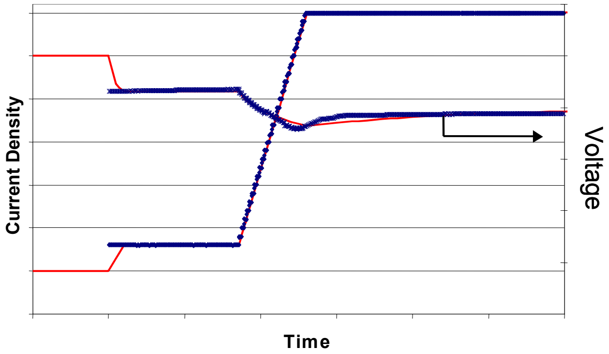

Fig. 2 The response of a fuel cell during an up transient in current is shown. The solid line is the model prediction while the symbols are experimental data.

Semi-detailed fuel cell stack model: The aim of these models is to understand physics at a stack level and apply it for stack design. In order to capture the system level effects a fuel cell stack model having essential first order physics is developed. The thermal effects like heat generation, heat loss, heat conduction in different layers, water production and water loss are captured. The temperature gradients within a stack and the overall power generated by the stack are obtained from these models with minimal computational time. Several stack design concepts are often evaluated with these models prior to building and testing. Fig. 3 shows the temperature of different cells in a stack when started from a temperature below zero deg C. The cells close to the endplates incur large heat loss to the endplates and take very long time come up in temperature. The center cells exchange minimal heat with their neighbors and respond to the start-up fairly well.

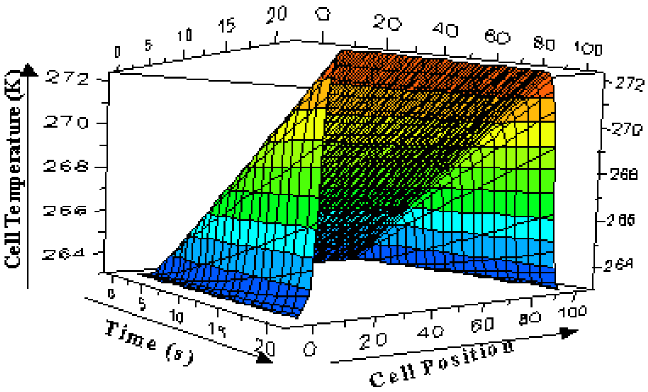

Fig. 3 shows the response of a fuel cell stack during a start-up from subzero temperatures. The center cells that do not lose heat to the neighboring cells come up in temperature much faster than the cells close to the pressure plates that lose heat.

System level models: The aim of these models is to understand physics at a system level. The semi-detailed stack model along with the essential balance of the plant components is used to represent the system. The performance requirements set by the DOE to provide full power in 30 sec would translate to having a fully functional system at full load in 30 sec. In systems with glycol or water as a coolant, they need to be warmed up to the required temperature prior to flowing it through the stack in the required time (less than 30 sec). In order to enable this the stack needs to generate sufficient power to provide to the wheels, operate the required balance of plant components and warm the coolant. While doing this, there is a potential for the stack to overheat before the coolant is available, resulting in damage to the stack. Physics of this nature will be captured during the design phase to reduce the risk of components integration and any catastrophic failures. Shown in figure 4 is the simulated temperature of the middle cell in a stack, started up from subzero temperatures at three different current densities. It is seen that the cell temperature increases rapidly due to the heat released in the stack, with the maximum rate exhibited by the higher current density start-ups. The higher power generated in the stack is at high current densities allows the coolant to be warmed up by the excess power and enables full automotive operation in relatively short times. However, in the case when the current density is low the stack tends to overheat prior to warming up the coolant to sufficient temperatures.

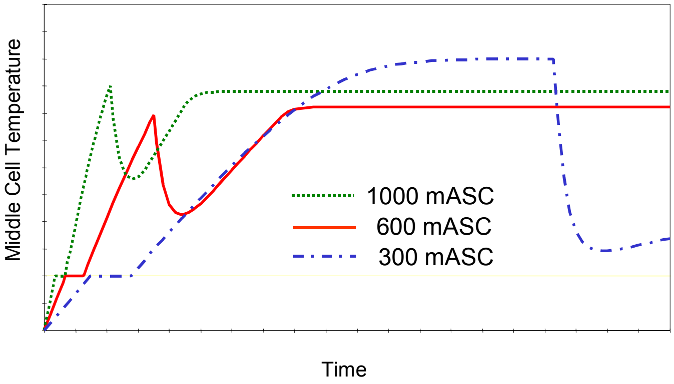

Fig. 4 The temperature profile of the middle cell in a stack operating at different current densities.

Conclusions:

Automotives powered by fuel cells are required to operate under extreme weather conditions similar to those powered by internal combustion engine. Operation of a fuel cell at sub-zero temperatures is an area being researched. We presented a modeling and analysis framework developed to predict the performance of a fuel cell, operation of a fuel cell, fuel cell stack and fuel cell system from subzero temperatures. These models are being used to effectively design freeze capable fuel cell systems.

## References

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