

Numerical Models for PEMFC Cold Tart: A Review

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ABSTRACT

Startup from subzero temperature is one of the major challenges for polymer electrolyte membrane fuel cell (PEMFC) to realize commercialization. Below the freezing point (0°C), water will freeze easily, which blocks the reactant gases into the reaction sites, thus leading to the start failure and material degradation. Therefore, for PEMFC in vehicle application, finding suitable ways to reach successful startup from subfreezing environment is a prerequisite. As it's difficult and complex for experimental studies to measure the internal quantities, mathematical models are the effective ways to study the detailed transport process and physical phenomenon, which make it possible to achieve detailed prediction of the inner life of the cell. However, review papers only on cold start numerical models are not available. In this study, an extensive review on cold start models is summarized featuring the states and phase changes of water, heat and mass transfer. To begin with, the states of water in PEMFC are discussed. Then, the distinct stages for cold start process are introduced. Last but not least, various numerical models are reviewed by dividing into four categories: zero, one, two, and three dimensional models. In particular, the sets of governing equations of three dimensional models are presented in detail. Finally, the cold start strategies from the aspects of material/structure and cold start process are recommended, and the four strategies: material/structure optimization, gas purging, thermal insulation, and heating, are reviewed in detail. For conclusion, it is suggested that a proper numerical model of PEMFC which features internal physical phenomenon inside cell comprehensively is a strong tool to investigate cold start process and provide much information for successful startup. Besides, reasonable cold start strategies should be established to demonstrate successful startup from subzero temperature.

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INTRODUCTION

Polymer electrolyte membrane fuel cell (PEMFC) is considered as one of the most promising sources of power, which will substitute conventional power in vehicle application due to its low operation temperature, zero emission, and high efficiency. However, there are several challenges to be overcome before commercialization, such as durability, stability, and cost. In winter condition, it is inevitable for vehicles to drive at subfreezing temperature, and under the circumstances, water freezing could cause adverse effects for PEMFC vehicles. As it is, ice formation will block the reactant into the reaction sites and result in serious damage to the structure of the membrane electrode assembly (MEA) due to the expansion of the volume in phase change. Hence, startup from subzero temperature is a major challenge for PEMFC. Table 1 lists present fuel cell vehicles produced by the world famous automotive manufacturers. It is found that the driving range is advantageous compared with electronic vehicles, but nonetheless, the cold start capabilities need further improvement. As is shown, though some of the vehicles can work below -30°C, most fuel cell vehicles employ various assisted cold start methods. Therefore, the suitable approach to successful and rapid startup for PEMFC at subfreezing temperature is required to be studied to promote commercialization.

Table 1. Cold start capability of several typical commercial fuel cell vehicles on market.

Countries	Companies	Vehicles	Driving range/km	Cold-start temperature/°C
Japan	Toyota	Mirai	700 (under JC08)	-30
Japan	Honda	FCV-Clarity	≥700 (under JC08)	-30
Korea	Hyundai	ix35	600	-30
China	SAIC	Roewe 950	400	-20
Germany	Benz	B-Class	400	-25
Korea	KIV	Borrego	685	-20
America	GM	Equinox	240 (by EPA)	-15

Actually, the PEMFC operation is a complex process including transport of mass, momentum, energy and charges which would take place simultaneously. During the cold start process, water inside the

fuel cell, both remained in previous cell operation and produced in the present reaction sites, would freeze at subfreezing temperature and for the phenomena, the operating condition of PEMFC vehicle application becomes more complex. As is mentioned, ice formation in cells could lead to significant deterioration in cell performance and durability. Conventional methods usually achieve successful cold start by using various assisted external heating such as resistance heating using DC from batteries, coolant heating and catalytic hydrogen/oxygen reaction inside the PEMFC, which can easily heat the stack from subzero to normal operation temperature, but these methods might often increase the volume and weight of the system, as well as the installation costs and operation complexity. In order to put forward reasonable methods to enable the fuel cell with no or little performance degradation at the subfreezing temperature, the comprehensive study of cold start physics is demanded.

During the last decades, tremendous numerical and experimental studies have been conducted to study the cold start phenomena. Experimental studies can be generally divided into *in situ* and *ex situ* studies [1]. Most of the previous cold start experiments of the PEMFC in literature are related to the two categories:

1. The *ex situ* cold start experiments [2]-[6]. These experiments are conducted when the components are removed from the cell in a non-assembled and non-functional form, to focus on the material degradation after freeze/thaw cycles and measure the physical properties of the individual components at subfreezing temperature.
2. The *in situ* cold start experiments [7]-[10]. These experiments are conducted when the PEMFC are operated, thus measuring property characterization and focusing on the performance degradation after freeze/thaw cycles.

The different experimental types and methods are illustrated in Table 2. McDonald et al. [2] conducted an *ex situ* freeze/thaw thermal cycling between 80°C and -40°C, in the study, it was observed that no degradation for dry MEA and no water phase change in the membrane. Thompson et al. [3] measured the conductance of the Nafion membrane at subzero temperature through *ex situ* experiments, as a result, it was observed that the changes of the membrane conductance/conductivity were similar to Cappadonia et al. [5][6]. Cho et al. [4] studied the freeze/thaw cycles at -10 °C and the results showed the PEMFC performance may decrease with unpurged initial condition. Kagami et al. [7] conducted the *in situ* experiments, in their work, the PEMFC cold start processes from subfreezing temperature under constant current densities were directly studied, meanwhile, the effects of MEA characteristics and initial water content were investigated. Furthermore, they found that without external heating a successful unassisted cold start can only be achieved above -5°C. This conclusion was consistent with Yan et al. [8], who focused on the cold start process to investigate the effects of startup temperature on cold start performance. Ge and Wang [9] conducted *in situ* visualization experiments through designing a transparent cell with a silver mesh used as the cathode GDL. Through the experiments, it was concluded that the freezing-point depression of water in the cathode catalyst layer should be less than 2°C. Ishikawa et al. [10] also used visualization method through *in situ* experiments, and they observed super cooled liquid water at a subfreezing temperature of -10°C.

The experimental observation and results have laid a solid foundation for numerical modeling. Since the experimental studies sometimes have the drawbacks such as difficulty to perform the different experimental measurements simultaneously, difficulty to reach the harsh operation condition, and high cost for materials and testing instruments, mathematical models are gradually becoming strong

Table 2. The types and methods with the results of experimental studies for PEMFC cold start.

Author	Types	Experimental methods	Experimental results
McDonald et al. [2]	Ex situ	Freeze/thaw cycling	No degradation for dry MEA and no water phase change was in membrane
Thompson et al. [3]	Ex situ	Membrane conductance measuring	Sharp conductance decrements at temperatures with water phase transitions
Cho et al. [4]	Ex situ	freeze/thaw cycling	The PEM performance may decrease with unpurged initial condition.
Cappadonia et al. [5][6]	Ex situ	Membrane conductance measuring	Sharp conductance decrements at certain temperature with different water contents
Kagami et al. [7]	In situ	Cold start processes	Without external heating a successful unassisted cold start can only be achieved above -5°C.
Yan et al. [8]	In situ	Cold start processes	Starting operation at -5°C without irreversible performance loss when the cell was initially dry.
Ge and Wang [9]	In situ	Visualization	The freezing-point depression of water in the cathode catalyst layer should be less than 2°C.
Ishikawa et al. [10]	In situ	Visualization	Super-cooled liquid water at a subfreezing temperature of -10°C were observed

tools for cold start research in the recent years. However, there are still few papers in literature reviewing the previous numerical studies for PEMFC cold start phenomena comprehensively. In this paper, a comprehensive review of numerical models is presented. To well understand the cold start phenomena, the states and phase change of water in PEMFC are firstly discussed. Then, the specific stages through cold start process are analyzed. Furthermore, various numerical models are classified into four categories: zero, one, two, three dimensional models. In particular, the set of governing conservation equations for transient multiphase model in three dimensions is presented in detail. In addition, the cold start strategies are presented from four aspects. Finally, different dimensional mathematical models and cold start strategies in recent years are summarized, which are of great reference value on the PEMFC cold start studies. In hope of proposing guideline for establishing reasonable cold start strategies, numerical simulations are effective means to deep understand the physics inside PEMFC.

STATES OF WATER

Due to the differences in material and local operating conditions among the components of PEMFC, the states and phase change process of water can be different. Many researches have been launched on the state of water in PEMFC at the subfreezing temperature. Using differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) can directly observe the state of water, and depending on these technologies, Thompson et al. [3], Cappadonia et al. [5][6], Yoshida et al. [11], and Pineriet al. [12] studied the water freezing inside the cells. Moreover, the amounts of the different types of water were also determined with DSC by Nakamura, K [13]. Typically, the states and phase change of water among the membrane, CL, GDL, and flow channel are a little different no matter whether at subfreezing temperature or at the normal temperature. For cold start, it is considered that the formation of liquid water can almost be neglected since it freezes to ice (note that liquid water and ice can coexist when the local cell temperature is at freezing point in PEMFC). Therefore, water generally exists in forms of vapor, and ice in the pore region of GDL and CL for cold start. On account of the fact that the water in membrane and CL plays an important role in ion transfer (water molecules bond to the sulphuric acid (H^+SO_3^-)), the states of water in membrane and CL sometimes are classified systematically for well understanding the water transport in PEMFC. Figure 1 illustrates the schematic of a single PEMFC with the structure of each cell component for cold start condition and the Figure 2 shows the schematics of water phase change in different components of PEMFC for cold start [1]. As is shown, the state of water in PEMFC can be divided into four types: non-frozen water, frozen water, liquid water, vapor and ice.

In membrane, the ionomer of membrane consists of hydrophobic backbones, flexible perfluorocarbons (gas permeable) and hydrophilic cluster with H^+SO_3^- which can absorb large quantities of water to form hydrated hydrophilic regions. Jiao et al. [1] classified the state of water in membrane into non-frozen water and frozen water on the basis of the observations of the freezing behavior of water by DSC and NMR. Non-frozen water was further classified into the non-

freezable, freezable and free water based on bonding strength between the water molecules and the sulphuric acid in reference [14]. According to the research of Eikerling et al. [15] and Roudgar et al. [16], water can also be divided into surface water and bulk water. Surface water is bound to H^+SO_3^- tightly and bulk water is considered as liquid which is bound to H^+SO_3^- loosely. The gas diffusion layer (GDL) is usually made up of porous carbon paper or carbon cloth, where the porosity is around or higher than 0.5. Normally, water can exist in the pore regions in forms of vapor, liquid and ice in GDL. As mentioned earlier, since the liquid water formation can be neglected for cold start, the water usually exists in forms of vapor and ice in the pores regions. Due to the difference between local temperature and the freezing temperature, as well as vapor pressure and water saturation pressure, the phase change of water will occur. When the local temperature is above the freezing point of water, if the vapor pressure is higher than the saturation pressure, vapor will condense to liquid, otherwise liquid will evaporate to vapor; when the local temperature is below the freezing point of water, if the vapor pressure is higher than the saturation pressure, vapor will desublimates to ice. However, according to the research of Jiao et al. [1], ice will never sublime into vapor under the operation condition, the sublimation process is not considered even if the vapor pressure is lower than the saturation pressure. In catalyst layer (CL), the carbon and platinum particles are presented as the catalyst and for electron transport, and the ionomer is presented for proton transport. The state of water in the pore regions of CL is the same as in the pore regions of GDL and the water in the ionomer of CL is also same as in the membrane. As the CL is where the reaction takes place and is connected with the membrane and GDL, phase change in CL might be complex. To simplify the phase change process, one assumption proposed in reference [48] was that when the water in the ionomer of CL freezes, it leaves the ionomer and only forms ice in the pore regions of CL. The assumption was based on the experimental observation that the frozen water dose not contribute to the proton transport in ionomer [3]. In the flow channel, the state of water is similar to as in the GDL. It should be mentioned that for cold start, since water freezes in the CL and GDL first, then sticking on the solid materials and non-humidified gases are often supplied for PEMFC to reduce the amount of ice formation, the formation of ice in the flow channel are often neglected. In general, the states of water in different components of PEMFC are summarized in Table 3.

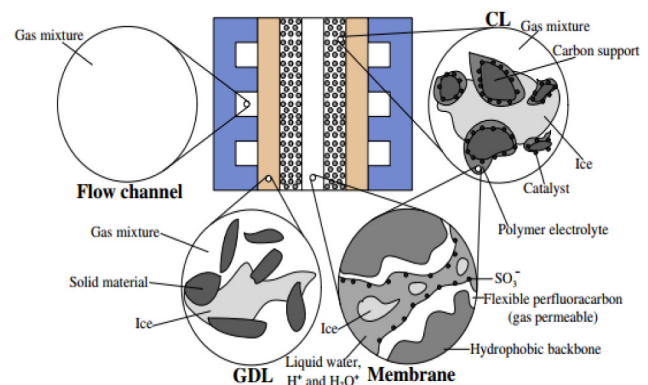


Figure 1. Schematic of a single PEMFC with the structure of each cell component for cold start [1].

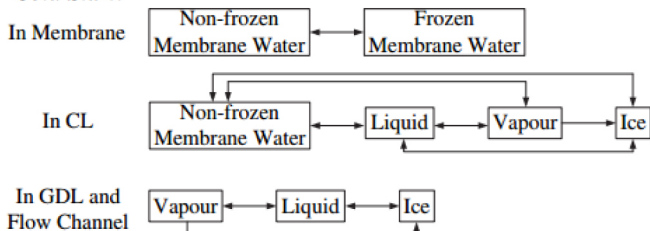
Cold Start:

Figure 2. Schematics of water phase change in different components of PEMFC for cold start [1].

Table 3. State of water in different components of PEMFC at subfreezing temperature.

Component	Location	State of water
Membrane	Ionomer	Ice, liquid, non-frozen water, frozen water and vapor
GDL	Pore region	Ice, liquid, and vapor
CL	Pore region	Ice, liquid, and vapor
	Ionomer	Ice, liquid, non-frozen water, frozen water and vapor
Flow channel	Everywhere	Vapor, liquid, and ice (the ice formation might be ignored)

ANALYSIS OF THE COLD START PROCESS

In order to develop the models which describe the physics of water transport and heat balance, the cold start process needs a good study. For cold start, the water contents in cell will increase steadily with time since the oxygen reduction reaction (ORR) is still active at the subfreezing temperature and would produce water. Water may freeze in the pores of the catalyst layer, which can block the reactant gas into the reaction sites, thus leading to the start failure. Meanwhile, the water turning into ice phase will bring about the volume increase, which would lead to irreversible structure damage. As a result, the cold start fails and the durability is reduced.

Mao et al. [17] introduced that the cold start can be fully described by three interacting process: ice formation based on water balance; temperature rise based on energy balance; and cell voltage drop-down as a function of ice formation. They regard that a typical cold start process was divided into four stages: (a) at first stages the fuel cell starts up and water is produced at the cathode to raise the water vapor concentration until the saturation vapor pressure limit is reached and no ice formation occurs in CL; (b) the water produced at the cathode will precipitate as ice in the CL once vapor saturation is reached in CL. At this stage, the waste produced heat will warm up the fuel cell,

and if the cell temperature is still below freezing before the CL is filled up with ice, the fuel cell will be shut down, otherwise, the fuel cell temperature will be raised to the freezing point. (c) if the cell temperature successfully rises to the freezing point before the CL is fully covered by ice, the ice in CL will start to melt absorbing the produced waste heat and the cell temperature will stay the same at the freezing point until all ice vanishes. (d) when all ice melts in the CL, the cell temperature will continue to rise to a normal operating temperature, and the cell cooling system must be initiated to maintain steady operation. According to the four stages, it was summarized that a single criterion of the successful startup is the cell temperature rises above freezing before the cathode CL is completely filled with ice, and it was suggested that to provide a higher likelihood of self-startup, increasing startup temperature, lowering the initial water content of membrane, and reducing thermal mass of bipolar plates and applying proper thermal insulation are practical methods. Similarly, Wang et al. [18] considered that water in cathode may exist in the ionomer, gaseous, and ice phases at subfreezing condition (assuming no super cooled liquid exists). They suggested that the cold start process of PEMFC can be described by the three stages, see Figure 3.

Stage 1: water accumulation in the ionomer and gas phases till the saturation vapor pressure limit is reached.

Stage 2: the ionomer and gaseous phases are saturated, and water is added to the solid phase, therefore this stage is characterized by ice volume growth within the catalyst layer.

Stage 3: the fuel cell reaches 0 °C, leading to melting of the residual ice in the catalyst layer due to fuel cell heat generation.

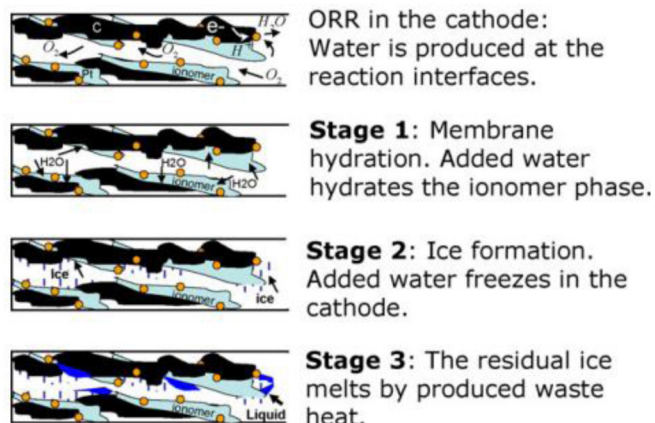


Figure 3. The three stages of fuel cell cold start [18].

As seen above, although the defined amounts of stages may be different, the cold start process are fundamentally the same. Apparently, cold start is essentially a transient process and dynamic behavior. Since the process is clear, the mathematical model to simulate the process is a strong tool to research the dynamic characteristics.

MODELING STUDIES ON COLD START OF PMFC

According to the previous content, the analysis on the state of water and cold start process in PEMFC provided the premise for numerical modeling. In fact, numerous cold start models have been developed to consider either single cells or stack in an effort to better understand the detailed transport processes and physic phenomena. On the basis of the spatial dimensions of different computational domain, these models generally can be categorized into one, two, and three dimensional models. It should be noted that the zero dimensional are related to some analytic models and lumped or layered models. The spatial dimension of different computational domain was schematically illustrated in Figure 4 [19].

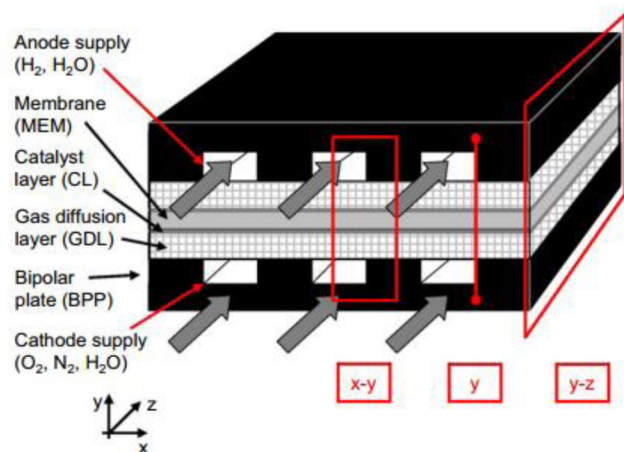


Figure 4. The spatial dimension of different computational domain [19].

In early works of fuel cell modeling, researchers used one dimensional models in the y direction (sandwich) considering the through-plane transport plays the leading role. Water transport, heat transfer, temperatures distribution, and electrical potentials variation were analyzed for given boundary conditions and the coupled heat and mass transfer were often simplified. These models require insignificant computation power and can provide enormous information. The major limitation is that the detailed transport phenomenon in other two direction cannot be taken into account, for example, the effects of the structure of flow channel and current distribution cannot be analyzed. Two dimensional models may be an improvement to one dimensional models. They offer a more realistic view of certain phenomena as spatial variations are considered. These models may use an along-the-channel domain in the y - z direction or a sandwich domain in the x - y direction. Along-the-channel model domains can be used to analyze quantities along the gas channel and to study the effects of flow structure. Sandwich models are mainly used for the analysis of fluxes, heat and mass transfer and concentrations including the effect of the bipolar plate and gas channel. One and two dimensional models may include the same conservation equations as three-dimensional models, so they provide

much information with sufficient accuracy if the boundary and initial conditions are carefully selected. Three dimensional models (x - y - z direction) are best suited if the overall PEMFC behavior is of interest. They can be seen as a combination of both two dimensional computational domains discussed above and have the ability to study the blocking effect of the bipolar plates, detailed current density distribution, or the effectiveness of a flow-field design.

Zero Dimensional Models

Given that some of the mathematic models either considered the components in cells are not continuous or only focused on parametric studies, these are divided into zero dimensional models. At the beginning of fuel cell cold start modeling, researchers used lumped or layered stack models which consider the stack or component temperature are uniform, and most of the early lumped stack models focus on the thermal transfer in the normal temperature. Amphlett [20] developed the transient, lumped stack models based on the energy and mass balance, and the general form of their model was

$$MC \frac{dT}{dt} = \dot{q}_{theor} - \dot{q}_{elec} - \dot{q}_{sens} - \dot{q}_{loss}$$

However, they just evaluated the normal temperature condition, and the sub-freezing temperature was not considered. Weisbrod et al. [21] discussed cold start dynamics by developing a lumped stack model of heat requirements and water transients during startup from subfreezing temperatures. It's found that the external heat source can obviously reduce the stack startup time. However, due to regarding the stack as a lumped system, the temperature distribution was not possible to be simulated. For improvement, Sundaresan and Moore [22] conducted a layered cold start stack model by preforming energy balance and heat transfer, which considered the water phase change and the thermal effects. This model can predict the temperature distribution in a stack and also reveal the effects of the endplate thermal mass and the internal heating method for PEMFC cold start. Although ice formation and latent heat released during phase change of water were considered in the model, the ice fraction was pre-calculated simply from the water production rate without considering water transport mechanisms in the fuel cell and the effects of ice formation in the CL. Therefore, the lumped and layered models still had some drawbacks. Besides, some parametric analytic models were also considered as the zero dimensional models. Mao et al. [23] developed a physical model for PEMFC cold start based on the principles of water and heat balance, ice formation in the CL, and its impact on voltage losses. In the model, the effects of operating conditions, such as the startup temperature and initial water content in the membrane, on the performance of PEMFC cold start were taken into account. Wang et al. [24] conducted the analytical studies drawing out a series of significant parameters. The model revealed that high startup temperature, dry membrane initially, low thermal mass of bipolar plates and proper thermal insulation can result in a higher likelihood of self-startup. These analytical models can only