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Numerical studies of cold-start phenomenon in PEM fuel cells

Hua Meng*

Center for Engineering and Scientific Computation, School of Aeronautics and Astronautics, P.O. Box 1455, Zhejiang University, Hangzhou, Zhejiang 310027, PR China

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1. Introduction

Successful startup of a PEM fuel cell from subfreezing temperatures is a crucial research issue for automotive applications. During the cold-start process, water inside the fuel cell, both retained after the previous cell operation and produced during the present operation, would freeze under a subzero temperature. The ice could subsequently melt if the cell temperature would rise above 0 °C. This freeze/thaw cycle could compromise the fuel cell performance, material and component integrity. In order to fully understand this important phenomenon, much research effort has recently been expended in this area.

The existing experimental researches on the PEM fuel cell cold-start phenomenon have been conducted from different perspectives. McDonald et al. [1] focused on the physical and chemical changes in the membrane and the membrane-electrode assembly (MEA) after repetitive freeze/thaw thermal cycling between 80 and -40 °C, and no catastrophic failures were observed in the membranes and MEA, which were assembled in the fuel cell stack under ambient humidity conditions. Cho et al. [2] studied the cell per-formance degradation after repetitive thermal cycling from 80 to -10 °C, and found that the cell performance could decrease at a rate of 2.3% due to water freezing and melting. To prevent cell performance loss, they [3] proposed the gas-purging and solution-purging methods, which effectively eliminated cell performance

ABSTRACT

In this paper, a PEM fuel cell model for cold-start simulations has been employed for numerical investigations of the cell startup characteristics from subfreezing temperatures. The effects of many key parameters on fuel cell isothermal cold-start behaviors have been carefully examined. Numerical results indicate that a high gas flow rate in the cathode gas channel, a low initial membrane water content, a low current density under the constant current condition, and a high cell voltage under the constant cell voltage operation are beneficial for the PEM fuel cell isothermal cold-start processes. Increasing the startup cell temperature would significantly delay ice formation and consequently lead to longer cold-start time. Therefore, incorporating internal and external heating sources in the cell design scheme is very important for achieving fast and successful cold start of a PEM fuel cell from subfreezing temperatures.

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Electrochimica Acta

degradation. The research work of Hou et al. [4] investigated the effectiveness of the purging method with low-humidity gases fed into a PEM fuel cell.

Instead of focusing on the thermal cycling effects, Kagami et al. [5] directly studied PEM fuel cell cold-start processes from subfreezing temperatures under constant current densities. They found that a successful self-starting without external heating could only be achieved with the startup temperature above -5 °C. This conclusion is consistent with that of Yan et al. [6], who investigated cold-start processes using a PEM fuel cell with a 25 cm² active area.

In order to elucidate the fundamental cold-start characteristics, Oszcipok et al. [7] conducted isothermal potentiostatic single-cell experiments, during which the fuel cell was purged using dry gases and placed inside a constant-temperature environment at -10 °C. They performed statistic analysis of the experimental results and showed that dry membrane and high air flow rates were beneficial for PEM fuel cell cold start. They also concluded that during the cell operation, the product water first increased the membrane humidity; after the membrane was fully hydrated, the product water started to freeze. They [8] further established a simple physical model to aid better understanding of the cold-start processes and the related fundamental mechanisms.

Tajiri et al. [9] introduced an experimental procedure of equilibrium purging using partially humidified gases with well-controlled relative humidity to effectively dictate the initial water distribution inside a PEM fuel cell. Based on this method, they studied isothermal cold-start processes under a constant current density from a subzero temperature of -30 °C. They concluded that the membrane played a key role in enhancing the intrinsic capability of PEM fuel



^{*} Tel.: +86 571 87952990; fax: +86 571 87953167. *E-mail address:* menghua@zju.edu.cn.

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cell cold start. Tajiri et al. [10] also experimentally investigated the parametric effects on PEM fuel cell cold start, including the purging methods, startup temperatures, current densities, and membrane thicknesses.

Aiming to visualize the ice formation mechanisms in a PEM fuel cell during startup from subfreezing temperatures, Ge and Wang [11] developed a transparent cell with a silver mesh used as the cathode gas diffusion layer (GDL) for direct observation of ice formation on the catalyst layer surface. They found that with a startup temperature at -5 °C, water existed in the cathode catalyst layer in gaseous and solid phases, and concluded that the freezing-point depression of water is no larger than 2 °C and thus played a negligible role in cell cold-start applications. Ge and Wang [12] further studied the fundamental characteristics during PEM fuel cell coldstart processes. In addition to narrow down the freezing-point depression of water in the cathode catalyst layer to 1.0 ± 0.5 °C. they suggested that the gas-purging time should be between 90 and 120 s. Ishikawa et al. [13] also observed water generation and freezing phenomena with both visible and infrared images during PEM fuel cell cold start at -10 °C. In contrast to Ge and Wang [11,12], they reported that water generated below the freezing point was in a super-cooled state. Ishikawa et al. [14] made further studies in this area and recently found that the super-cooled liquid water would not exist if the fuel cell was not thoroughly purged, leaving a small amount of liquid water inside the cell before cold start. The remaining liquid water would freeze and serve as seed ice to initiate the ice formation process of the product water during the cell cold start. Therefore, the super-cooled liquid water could only exist with thorough purging of the cell before its cold-start, removing all the liquid water and consequently the potential seed ice. Even with the existence of the super-cooled liquid water, the cell performance degradation was still dictated by the ice formation at the GDL/MEA interface during the cell cold start. More research work is still needed in this area to further clarify this issue.

Thompson et al. [15] investigated low-temperature proton transport inside the Nafion membrane. They observed a crossover in the activation energy for proton transport with temperature coinciding with water phase transition, and concluded that water phase transition inside the membrane would affect proton transport mechanisms. Their results contradicted those of Tajiri et al. [9], who concluded that no water phase transition occurred inside the membrane. Therefore, more research work is apparently required in this area, as well. Thompson et al. [16] also developed an experimental procedure to study the electrochemical kinetics of the oxygen reduction reaction (ORR) in a PEM fuel cell operating at subfreezing temperatures, and they found no fundamental change in reaction mechanism.

In parallel to experimental studies, numerical modeling and simulation of the PEM fuel cell cold-start phenomenon has also been conducted. Mao and Wang [17] and Wang [18] both developed analytic models to gain fundamental understandings of the coldstart behaviors of PEM fuel cells, and they investigated the effects of a number of key parameters, including the initial membrane water content and the startup temperature, on the cell cold-start processes.

Ahluwalia and Wang [19] developed a two-dimensional model, considering the through-membrane and along-channel directions, to determine the electric field, current distribution, species concentration, and ice formation and melting in a PEM fuel cell starting up from subfreezing temperatures. They made parametric studies to determine optimized conditions for achieving rapid self-start. Mao and Wang [20] developed a three-dimensional PEM fuel cell model based on a single-domain framework, considering ice formation in the cathode catalyst layer and GDL. They applied the numerical model for predicting cell performance and revealing

three-dimensional distributions of current density, temperature, membrane water content, and ice fraction in a PEM fuel cell undergoing isothermal cold start.

Meng [21] recently developed a multi-dimensional PEM fuel cell model with accommodation of ice formation in the cathode catalyst layer based on a previously established mixed-domain approach [22-25], which has been used for solving two-phase transient phenomena. The numerical model has been applied for elucidating fuel cell isothermal cold-start processes at a subfreezing temperature of -20 °C under both constant current and constant cell voltage conditions. Numerical results indicated that the cold-start process of a PEM fuel cell with an initial low water content inside the membrane would experience a two-stage evolution, including an initial cell performance increase attributable to membrane hydration by the product water and an subsequent performance drop due to ice formation in the cathode catalyst layer, which would block oxygen transport and cover up the active catalyst surface. The trend is consistent with the experimental results of Oszcipok et al. [7,8] and Tajiri et al. [9,10].

In this paper, the PEM fuel cell model for cold-start simulations developed by Meng [21] are applied in a two-dimensional cross section for parametric studies of the isothermal cold-start phenomenon, focusing on the effects of many key parameters, including the initial membrane water content, the air flow rate in the cathode gas channel, the startup temperature, the current density, and the cell voltage, on the startup processes and the related intrinsic mechanisms.

2. Theoretical formulation

The transient multi-phase multi-dimensional PEM fuel cell model for cold-start simulations have been presented in an earlier publication [21], and thus are only briefly described in this paper.

The transient conservation equations in the gaseous phase are

Mass conservation:

$$\frac{\partial [\varepsilon(1 - s_{ice})\rho]}{\partial t} + \nabla \cdot (\rho \vec{u}) = S_{\rm m} \tag{1}$$

Momentum conservation:

$$\frac{1}{\varepsilon(1-s_{\rm ice})}\frac{\partial(\rho\bar{u})}{\partial t} + \frac{1}{\varepsilon^2(1-s_{\rm ice})^2}\nabla (\rho\bar{u}\bar{u}) = -\nabla p + \nabla \cdot \tau + S_{\rm u}$$
(2)

Species conservation:

$$\frac{\partial [\varepsilon^{\text{eff}}(1 - s_{ice})c_i]}{\partial t} + \nabla \cdot (\vec{u}c_i) = \nabla \cdot (D_i^{\text{eff}} \nabla c_i) + S_i$$
(3)

In Eq. (1), the source term, S_m , arises from the coupling of the flow-field and the species transport processes, including the phase-change effect, and the details have been discussed in a previous publication [23]. It should be noted that in the present two-dimensional calculations, since the convective effect can be neglected, this mass source term would not exert any influence on the numerical results. The above equations are established in a mixed-domain framework [22–25]. The effect of ice formation on the effective gaseous species diffusion is considered by the following expression:

$$D_{i}^{\text{eff}} = D_{i}\varepsilon^{1.5}(1 - s_{ice})^{1.5}$$
(4)

In addition, ice coverage of the active catalyst surface is modeled as

$$a^{\rm eff} = (1 - s_{\rm ice})a \tag{5}$$

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