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Numerical evaluation of a dual-function microporous layer under subzero and normal operating temperatures for use in automotive fuel cells

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ABSTRACT

In a previous study, we proposed a dual-function microporous layer (MPL) to improve the cold-start capability of polymer electrolyte fuel cells (PEFCs). The conceptual MPL design is to use an ionomer-based binder with low Pt loading, thereby allowing the MPL to provide additional volume for ice storage during cold-start PEFC operations. Although the benefit of using a dual-function MPL was numerically elucidated in our previous study, the question regarding the use of this new MPL under normal PEFC operation remains to be addressed. In this paper, we extend our discussion to the effects of a dual-function MPL under subzero to normal operating temperatures. The three-dimensional (3D) cold-start PEFC model developed in our previous study is modified for transient PEFC simulations to consider a wide range of operating temperatures from −20 °C to 80 °C. Simulation results show a negligible performance drop at the normal PEFC temperature of 80 °C, because of the presence of the dual-function MPL in a PEFC membrane electrode assembly. In addition, water back flow from the cathode to anode is reduced on using the dual-function MPL, owing to the additional water uptake driven by its ionomer content. This study clearly demonstrates that this dual-function MPL technology may be applied to automotive PEFC stack development without sacrificing fabrication cost and cell performance during normal PEFC operations.

1. Introduction

The successful startup of polymer electrolyte fuel cells (PEFCs) under subzero temperature has been recognized as one of the remaining challenges to be overcome for commercializing fuel cell vehicles. During cold start, water produced by the oxygen reduction reaction (ORR) in the cathode catalyst layer (CL) turns into ice/frost. Subsequently, the spread of ice/frost in the cathode CL reduces active reaction sites and blocks oxygen transport, finally leading to a cascading cell shutdown. Furthermore, repetitive ice filling/melting in CLs leads to irreversible damages in membrane electrode assemblies (MEAs), including the destruction of CL porous structure, Pt particle loss, and interfacial delamination between the cathode CL and membrane [1]. These degradation processes definitely damage the durability of MEAs and significantly shorten the lifetime of PEFC stacks.

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Theoretical studies to clarify the cold-start physics and the associated problems have been actively conducted, as reported in literature. Simple analytical cold-start PEFC models were presented by several modeling groups [2–6]. Sundaresan and Moore [2] developed a one-dimensional (1-D) layered model and investigated the effects of endplates on the cold-start behavior of PEFC stacks. On the basis of the simulation results, they suggested optimum startup strategies, namely internal stack heating, coolant circulation during warm-up, thermal mass minimization, endplate heating, and using a metal-based bipolar plate (BP). Khandelwal et al. [3] conducted 1-D transient thermal PEFC stack simulations and analyzed stack temperature distributions, startup time, and external heating requirements during startup from sub-freezing temperatures. They summarized critical stack design and operating parameters such as coolant temperature, initial ice (residual water), operating current density, and BP thermal mass to improve the cold-start capability of PEFC stacks. Mao and Wang [4] developed a mathematical cold-start model, wherein water and heat balance equations were coupled to predict the ice fraction and cell temperature evolution during cold start. They studied the theoretical impacts of the initial water content in the membrane and the thermal mass of a BP on the cold-start behavior of PEFCs. Wang [5] developed an analytical cold-start model and conducted a parametric study using values such as the Damköhler number and cathode CL tortuosity. Wang et al. [6] further suggested three stages of cold start and analyzed the effects of BP thermal mass, cathode CL thickness, and initial membrane water content on these stages.

Multidimensional and multiphase cold-start models have been developed in several other studies [7–23] in order to explore the effects of cold-start phenomena more precisely. Some studies have attempted to optimize cold-start operating conditions such as startup temperatures, initial water contents, and startup current densities [7–18], while others have investigated the effects of design parameters of a PEFC on cold-start behavior [19–23]. Detailed discussions on early PEFC cold-start studies are also found in literature [17,20–23].

Although the aforementioned numerical studies provide a better insight into cold-start behavior, they focus only on temperatures below zero and have a limited applicability. In general, a PEFC in a vehicle must operate over the entire range of external environmental temperature (−40 °C to +40 °C) [24]; thus, designs to overcome challenges or improve PEFC cold-start behavior must be tested under normal operating conditions.

In a previous study [23], we proposed a novel microporous layer (MPL) design to increase the overall ice storage capacity of an MEA. The MPL was fabricated using an ionomer-based binder (such as a Nafion® solution) with a significantly lower Pt loading compared to a typical CL to reduce superfluous costs. This design enables a dual-functional role of the MPL, i.e., one that works as a typical MPL under normal operating conditions and two as a part of the cathode CL under cold-start conditions. We demonstrated numerically that a dual-function MPL greatly improves the cold-start behavior of a PEFC by providing additional ice storage volume. However, the issue regarding the effect of a specialized MPL for cold-start operations on the PEFC performance under normal operating conditions remains to be addressed. In order to maintain the overall MEA fabrication costs commensurate with that of a typical MEA, the Pt loading of the cathode CL must be reduced in the case where a dual-function MPL is included in the MEA. The lower Pt loading may, however, potentially decrease the overall PEFC performance at normal operating temperatures.

The present study is an extension of our previous work [23] and aims to numerically evaluate the performance of dual-function MPL from subzero to normal operating temperatures. In subsequent sections, we briefly describe the three-dimensional (3D) transient PEFC model, emphasizing on new modifications carried out for transient PEFC simulations at normal operating temperatures (e.g., 80 °C), as well as subzero temperatures (e.g. −20 °C). We then define the simulation cases with different MEA configurations and discuss simulation results in detail. Finally, we summarize the major findings of this study.

2. Numerical model

A 3D non-isothermal electrochemical transport-coupled cold-start PEFC model developed in our previous study [17] is modified further to consider subzero to normal operating temperatures. Since the development of a cold-start PEFC model is described in detail in our previous papers [17,20–23], we present only a brief description of it in this paper. The current model invokes the following assumptions:

(1) Incompressible and laminar flow owing to small pressure gradients and flow velocities.
(2) Ideal gas mixtures.
(3) Negligible gravitational effect.
(4) Isotropic and homogeneous porous layers.
(5) Instantaneous desublimation of water vapor at saturation below zero temperature.
(6) Instantaneous sublimation of ice above zero temperature.
(7) Negligible electrochemical double-layer charging and discharging characteristics.

2.1. Three-dimensional transient PEFC model

On the basis of the above assumptions, this transient PEFC model is governed by the following five conservation equations:

Mass conservation:

$$\frac{\partial(\varepsilon_s\rho_s)}{\partial t}+\frac{\partial(\varepsilon\rho)}{\partial t}+\nabla\cdot(\rho\vec{u})=S_m \tag{1}$$

Momentum conservation:

$$\frac{1}{\varepsilon}\left[\frac{\partial(\rho\vec{u})}{\partial t}+\frac{1}{\varepsilon}\nabla\cdot(\rho\vec{u}\vec{u})\right]=-\nabla p+\nabla\cdot\tau+\rho\vec{g}+S_u \tag{2}$$

Species conservation:

$$\frac{\partial\left(\varepsilon^{eff}C_i\right)}{\partial t}+\nabla\cdot(\vec{u}C_i)=\nabla\cdot\left(D_i^{eff}\nabla C_i\right)+S_i \tag{3}$$

Energy conservation:

$$\frac{\partial\left((1-\varepsilon)\rho C_pT\right)_{cell}}{\partial t}+\frac{\partial\left(\varepsilon\rho C_pT\right)_g}{\partial t}+\nabla\cdot\left(\rho C_p\vec{u}T\right)=\nabla\cdot\left(k^{eff}\nabla T\right)+S_T \tag{4}$$

Charge conservation: