INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 682–691

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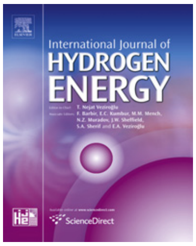

Effects of cathode catalyst layer design parameters on cold start behavior of polymer electrolyte fuel cells (PEFCs)

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ARTICLE INFO

Article history:
Received 28 February 2012
Received in revised form
12 May 2012
Accepted 29 May 2012
Available online 3 July 2012

Keywords:
Polymer electrolyte fuel cell
Cold start
Ice formation
Cathode catalyst layer
Numerical modeling

ABSTRACT

We present a theoretical study on the effects of key catalyst layer (CL) design parameters on the cold start behavior of a polymer electrolyte fuel cell (PEFC) using a three-dimensional transient cold start model developed in a previous study [1,2]. Among several CL design parameters, we adopt the ionomer fraction (ε_I) and weight ratio of Pt to carbon support ($wt\%_{Pt-C}$) in the cathode CL as CL design variables for this study. Therefore, other design parameters such as CL thickness and the oxygen reduction reaction (ORR) kinetic parameter are accordingly adjusted due to changes in ε_I and $wt\%_{Pt-C}$ for cold start simulations. The calculated results confirm that these two design parameters provide control of the ice storage capacity and water absorption potential of the cathode CL, and consequently have a substantial influence on the cold start behavior of a PEFC. We provide a guideline to design and optimize a cathode CL and membrane electrode assembly (MEA) for improved PEFC cold start capability.

1. Introduction

During startup of a polymer electrolyte fuel cell (PEFC) from subzero temperatures, water produced by the oxygen reduction reaction (ORR) inside the cathode catalyst layer (CL) can freeze into ice or frost that subsequently blocks oxygen transport and reduces the active electrochemical area. This leads to deterioration in cell performance and finally cold start failure if enough ice plugs the pores of the cathode CL during cold start. More importantly, it has been reported that continuous water freezing and melting inside the cathode CL during cold start cycles irreversibly damages CL pore structure and cell durability [3–9]. Therefore, the cathode CL plays a key role in determining the cold start behavior of PEFCs. The design of the cathode CL should be optimized not only to stabilize startup of a PEFC in subfreezing conditions, but also to maintain optimum cell performance during normal PEFC operations.

Computational modeling of cold start phenomena in PEFCs has been carried out by many fuel cell modeling groups [10–21]. Mao and Wang [10] developed an analytical cold start model and studied the effects of initial water content in the membrane and the thermal mass of a bipolar plate (BP) on the cold start behavior of PEFCs. Wang [11] developed an analytical cold start model based on the lumped thermal method and conducted a parametric study in terms of dimensionless parameters such as the Damköhler number and cathode CL tortuosity. Wang et al. [12] further suggested three stages of cold start, and analyzed the effects of BP thermal mass, cathode CL thickness, and initial membrane water content.

Multi-dimensional multi-phase cold start models have been developed to investigate the multidimensional effects of cold start phenomena. Mao et al. [13] developed a three-dimensional (3-D) cold start model and validated it against experimental data measured by Tajiri et al. [14]. Mao et al. [13] provided multi-dimensional contours of ice evolution in the cathode CL, and numerically studied the influence of startup current density and membrane thickness on cold start behavior. Jiang et al. [15] studied non-isothermal cold start phenomena using the cold

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http://dx.doi.org/10.1016/j.ijhydene.2012.05.154

start model of Mao et al. [13]. They compared isothermal and non-isothermal cold start simulation results and found that rising cell temperatures during non-isothermal cold start mitigates the ice formation rate in the cathode CL, and leads to successful cold startup. Jiang and Wang [16] numerically compared potentiostatic and galvanostatic startups at −20 °C and found that the potentiostatic startup resulted in better PEFC cold start behavior. In addition, they found that lowering the cell thermal mass improved cold start performance of PEFCs. Recently, Jiang et al. [17] proposed a current-ramping method to achieve rapid startup of PEFCs from a subfreezing temperature. They investigated various current-ramping rates and presented the optimum current-ramping rate for successful startup. Recently, Jiao and Li [18] developed a multi-dimensional cold start model in which a non-equilibrium state between the water in the electrolyte phase and the water in the open pore region of the CL was additionally taken into account. Jiao and Li [19] also performed a parametric study in terms of startup cell voltage, initial water content in the membrane and CLs, initial ice fraction, startup temperatures, the surrounding heat transfer coefficient, and anode inlet humidity. They investigated the effects of membrane thickness and the ionomer fraction in CLs under various initial and operating conditions [20]. Most recently, Nandy et al. [21] studied the effect of cathode CL thickness on PEFC cold start using a one-dimensional (1-D) cold start model based on Mao et al. [13] and Jiang et al. [15]. Their numerical calculations indicate that using a thicker CL is advantageous for successful startup from subzero temperatures. However, more detailed CL design parameters such as Platinum (Pt) loading, the ionomer fraction, and the weight ratio of Pt to carbon support were not taken into account in their cold start study.

Although many cold start models and simulation results have been presented in the literature, a detailed parametric study in terms of key CL design parameters such as ionomer fraction, Pt loading, CL thickness, and carbon–Pt weight ratio has not yet been attempted. In this study, we precisely analyzed the effects of cathode CL design parameters on the cold start behavior of PEFCs using a previously developed 3-D cold start PEFC model, i.e. validated against the experimental data measured under various cold start conditions [1]. Our goal is to numerically elucidate cold start phenomena under various designs of the cathode CL, and provide a guideline to design and optimize the CL and MEA in automotive PEFCs.

2. Numerical model

A previously developed 3-D multi-phase electrochemical-transport coupled cold start model was used in this study. The following assumptions were made with the present model:

(1) Incompressible and laminar flow due to a small pressure gradient and small flow velocities.
(2) The gas mixtures obey the ideal gas law.
(3) The effect of gravity is negligible.
(4) Gas diffusion layers (GDLs) are treated as an isotropic and homogeneous porous layer, and are characterized by effective porosity and permeability.
(5) Instantaneous desublimation of water vapor at saturation.
(6) Negligible electrochemical double layer charging and discharging at catalyst layers.

The transient PEFC cold start governing equations based on these assumptions are as follows.

Mass Conservation:

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

where the mass source terms are as follows [22]:

For the anode CL:

$$S_{m,a}=-MW_{H_2}\frac{j_a}{2F}+MW_{H_2O}\left[\nabla\cdot\left(D_{H_2O}^{mem}\nabla C_{H_2O}\right)-\nabla\cdot\left(n_d\frac{i_e}{F}\right)\right] \tag{2}$$

For the cathode CL:

$$S_{m,c}=MW_{O_2}\frac{j_c}{4F}-MW_{H_2O}\frac{j_c}{2F}+MW_{H_2O}\left[\nabla\cdot\left(D_{H_2O}^{mem}\nabla C_{H_2O}\right)-\nabla\cdot\left(n_d\frac{i_e}{F}\right)\right] \tag{3}$$

Equation (2) represents hydrogen consumption and water transport through the membrane. Equation (3) accounts for oxygen consumption and water production by the ORR and the water transport through the membrane in the cathode CL.

Momentum Conservation:

$$\frac{1}{\varepsilon}\left[\frac{\partial(\rho\vec{u})}{\partial t}+\frac{1}{\varepsilon}\nabla\cdot(\rho\vec{u}\vec{u})\right]=-\nabla p+\nabla\cdot\tau+S_u \tag{4}$$

The momentum source term for the porous medium (GDL and CL) is devised to recover Darcy's law. For the membrane, velocity $\vec{u}$ is assumed to be zero due to the impermeable characteristics of the polymer membrane. Thus, the momentum source terms S_u can be expressed as follows.

$$\text{In the GDL/CLs}: \quad S_u=-\frac{\mu}{K}\vec{u} \tag{5}$$

$$\text{In the membrane}: \quad \vec{u}=0 \tag{6}$$

Species Conservation:

$$\frac{\partial\left(\varepsilon^{eff}C_i\right)}{\partial t}+\nabla\cdot(\vec{u}C_i)=\nabla\cdot\left(D_i^{eff}\nabla C_i\right)+S_i \tag{7}$$

S_i in Eq. (7) represents species source/sink terms as follows:

$$\text{For water in the CLs}: \quad S_i=-\nabla\cdot\left(\frac{n_d}{F}i_e\right)-\frac{s_i j}{nF}+S_{sg} \tag{8}$$

$$\text{For water in the GDLs}: \quad S_i=S_{sg} \tag{9}$$

$$\text{For other species in the CLs}: \quad S_i=-\frac{s_i j}{nF} \tag{10}$$

The first and second terms on the right-hand side of Eq. (8) represent electro-osmotic drag and species consumption/production by the electrochemical reactions, respectively. S_{sg} in Eqs. (8) and (9) is the ice formation rate, and is calculated from the water concentration equation. Once the water vapor in the CLs and GDLs exceeds the saturation concentration, the extra water vapor beyond the saturation level is immediately turned into ice under the assumption of instantaneous desublimation.