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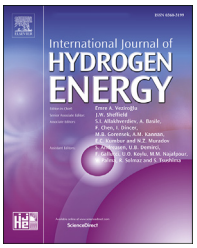

Numerical investigation of cold-start behavior of polymer electrolyte fuel cells in the presence of super-cooled water

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ABSTRACT

In this study, a mathematical model has been developed to simulate the transient cold-start processes of polymer electrolyte fuel cells. The super-cooled water is assumed to exist within the cell. The non-equilibrium water transfer between the membrane and the catalyst layer is considered. The models of water freezing and ice melting in the catalyst layer and gas diffusion layer have been established. For the first time, the randomicity of the freezing process is captured by introducing a freezing probability function. Based on this model, the cold-start processes of a single polymer electrolyte fuel cell starting at various operating and initial conditions have been simulated numerically. The results indicate that the cold-start performance of the cell is determined by the water storage potential of the electrolyte in cathode catalyst layer. For each startup temperature and operating current load, there is a most appropriate initial membrane water content, which corresponds to the longest cell shutdown time. When the cold-start process is failed, the ice is mainly accumulated in the cathode catalyst layer. The ice distribution becomes more non-uniform as the cold-start temperature is lower.

Introduction

Polymer-electrolyte fuel cells (PEFCs) are electrochemical devices, which directly convert the chemical energy into electrical energy. Useful features such as high-power density, simple design, safe construction, low noise and zero emissions make PEFCs particularly suitable for home appliance, vehicles and transportation tools [1]. However, the startup capability under freezing conditions (or cold-start), which is required for PEFCs systems operated in a subzero environment, is still a significant technical barrier for commercialization [2]. The water produced by the oxygen reduction reaction in the cathode side would freeze into ice. When the catalyst layers (CLs) are fully covered by ice, the reaction sites are blocked from the fuel or oxidant. The electrochemical reaction within the cell would be ceased.

During the previous decade, both experimental and numerical studies have been carried out to understand the cold-start fundamentals of PEFCs. In experimental studies [3–8], the overall low-temperature cell performances were predominately concerned. Base on the experimental evidence, one-dimensional analytical models have been developed to simulate the variation of PEFCs performance during the cold-

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start processes [9–12]. The PEFCs were separated into different layers in order to obtain the one-dimensional temperature distribution within the cell. More recently, multi-dimensional multiphase models have been established to study the key physical and transport phenomena during the cold-start processes [13–24]. The performance of PEFCs coupling with heat transfer and ice formation was predicted. The fraction of ice occupying open pores depends on the rate of product water diffusing into the ionomeric membrane as well as the rate of product water transporting into the gas diffusion layer (GDL) in the form of vapor phase. It was claimed that liquid-water transport out of the CLs was found irrelevant unless the cell temperature closely approaches the freezing point. Until now, no models include freezing process of liquid water, and the super-cooled water is not accounted consequently.

More recently, due to the progress of in-situ visualization and detection methods, such as neutron imaging [25–27], the cold-start processes, especially ice formation processes within porous media of PEFCs have been received in-depth study. In all cases, generation of product water was observed in the super-cooled state instead of ice, particularly between −2 °C and −20 °C. It was pointed out that without an initiating nucleation, liquid water could exist in a PEFC under sub-zero temperature in the form of super-cooled water [28,29]. The freezing of super-cooled water could be triggered either by activation of the phase change or due to the presence of a nucleation site. If no nucleation site was encountered, no freezing occurred and the pathways of super-cooled water through the porous layers would be created. As a result, the operation period of the cell could be extended significantly [30]. Generally, the freezing mechanism closely depends on the startup temperature. At temperature down to −20 °C, all product water was observed to freeze immediately in the cathode catalyst layer (CCL) [31,32]. However, at higher temperatures the super-cooled water could exist and spread to the GDL and even the gas channels (GCs) before freezing [32]. Thus, freezing of super-cooled water can be initiated in the CLs, GDLs or even in the GCs. When the super-cooled water freezes, the ice may exist as small isolated islands over the ionomer surface initially. This may allow adequate oxygen access to the catalyst through the lateral direction. As the ice accumulates, the isolated islands merge, which can effectively disable oxygen transport toward the catalyst, shutting down local catalyst activity [33]. Recently, Yang [34] considered the flow of super-cooled water in micro-porous layer (MPL) as well as cathode gas channel. The super-cooled water was assumed to freeze if the local temperature was below the freezing point, meanwhile part of the super-cooled water could move out of CLs due to liquid pressure. Furthermore, a comprehensive review has been made by Luo [2], where the transport phenomena including super-cooling, phase change and transport of water within the membrane (MEM), CLs, MPLs, and GDLs is emphasized.

The purpose of this work is to develop a three-dimensional, multiphase, and transient model to predict the cold-start behaviors of PEFCs. It includes not only the interrelated transport phenomena of mass, momentum, species, charge, and heat, but also ice formation/melting as well as coupling the electrochemical reactions. The main emphasis is on exploring the behavior of super-cooled water and the resultant dynamic responses of a PEFC under various operating and initial conditions. The present paper is organized as follows. The three-dimensional, multiphase model, including the model of super-cooled water is given in the next section. The results and discussion section presents the validation of the model and the parametric studies for the effects of startup and operation conditions on the cold-start performance of PEFCs. The final conclusions are given at the end.

Numerical model

A PEFC with single GC is considered. All the major components of a PEFC including the bipolar plates (BPs), GCs, GDLs, CLs and MEM are considered. Fig. 1 shows the computational domain and mesh for the cold-start simulations. The cell parameters and material properties are given in Table 1.

Water transport and basic assumption

The schematic of water phase change and transfer inside the cell is shown in Fig. 2. During the operation period of PEFC, the product water is assumed to be in the "dissolved" phase, which is treated as membrane/ionomer water [35–37]. The MEM hydration/dehydration is taken into account by considering the mass transfer between vapor and membrane water. Corresponding process is marked with label "①" in Fig. 2. As the electrochemical reaction continues, the content of membrane water increases. When the content of membrane water becomes saturated, it will desorb from the electrolyte and change to liquid water, as the process marked with label "②". For the cold-start process with sub-zero temperature, this liquid water is thermodynamically unstable, i.e. super-cooled water. The evaporation/condensation between the liquid and vapor water is considered, as the process marked with label "③". If the cell temperature is below the freezing point T_f, the freezing process, marked with label "④", would occur. The modeling of the freezing process will be discussed in detail in the following section. When the freezing process occurs, the over saturated membrane water attributed to the electrochemical reaction will freeze into ice through process "⑤". In previous literatures [17,18], the ice crystals were assumed to be formed within the membrane. However, for a water-saturated perfluorinated membrane, it has been suggested ice crystals never formed inside the membrane [38,39]. When the freezing process occurs, water will desorb out of the membrane. In this study, unlike the model in Refs. [17,18], we assume that the water never crystallizes inside the membrane/electrolyte. The over saturated water vapor will desublimate to ice through process "⑥". Here, the sublimation of ice is ignored. It is worthy to note that the melting process is also included as marked with label "④", when the cell temperature rises above the freezing point.

Some other assumptions used in the model are as follows:

(1) Ideal gas mixture;
(2) Incompressible laminar flow in gas channel and porous components of a PEFC as a result of small pressure gradient and flow velocity.