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Numerical analysis of effects of gas crossover through membrane pinholes in high-temperature proton exchange membrane fuel cells

Purushothama Chippar [a], *Kyeongmin Oh* [a], *Whan-Gi Kim* [b], *Hyunchul Ju* [a,*]

[a] *School of Mechanical Engineering, Inha University, 253 Yonghyun-Dong, Nam-Gu, Incheon 402-751, Republic of Korea*

[b] *Department of Applied Chemistry, Konkuk University, 322 Danwol, Chungju 380-701, Republic of Korea*

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ABSTRACT

Durability is a major issue in the widespread commercialization of proton exchange membrane fuel cells (PEMFCs). Various failure modes have been identified over their long runtime. These mainly originate from membrane and catalyst layer failures. One of the most common failure modes in PEMFCs is due to pinhole formation in the membrane and resultant reactant gas crossover through the membrane. Gas crossover induces several critical problems in PEMFCs, including severe reactant depletion in the downstream regions, mixed potential at the electrodes, and formation of local hot spots by hydrogen/oxygen catalytic reaction, which indicates that the cell performance decreases with increasing gas crossover. In this study, we numerically investigate the effects of gas crossover on the performance of a high-temperature PEMFC based on a phosphoric-acid-doped polybenzimidazole (PBI) membrane. In contrast to previous gas-crossover studies [1,2] in which uniform gas crossover throughout the entire membrane has been simply assumed, our focus is on examining the impacts of localized gas crossover due to membrane pinholes. Numerical simulations are carried out via arbitrarily assuming pinholes in the membrane. The simulation results clearly show that the presence of pinholes in the membrane significantly disrupts the species, current density, and temperature distributions. Our findings may improve the fundamental and detailed understanding of localized gas-crossover phenomena through the membrane pinholes and the influence of these phenomena on high-temperature PEMFC operation.

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1. Introduction

High-temperature proton exchange membrane fuel cells (PEMFCs) based on polybenzimidazole (PBI) membranes doped with phosphoric acid (PA) have received much attention recently for their application as distributed energy or combined heat and power resources owing to their high operating temperature (100 °C–200 °C). When compared with a perfluorosulfonic acid (PFSA)-membrane-based low-temperature PEMFC, a high-temperature PEMFC offers several advantages including fast electrode kinetics, enhanced mass transport, simple water and thermal management, and higher tolerance to carbon monoxide (CO). The PBI membranes doped with PA reported in the literature have shown good proton conductivity

* *Corresponding author*. Tel.: +82 32 860 7312; fax: +82 32 868 1716.
E-mail addresses: hcju@inha.ac.kr, hxj122@gmail.com (H. Ju).

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[3], thermal stability [4], and negligible electro-osmotic drag [5] at elevated temperatures up to 200 °C without humidification of reactant gases. Several experiments have focused on the physiochemical properties of PBI membranes [6–10] and their application to hydrogen fuel cells [8,11–14]. Ma et al. [7] and Li et al. [8] exhaustively studied the influences of temperature, doping level, and relative humidity (RH) on proton conductivity of the PA-doped PBI membranes.

In addition to membrane performance, durability of the PBI membrane is another critical issue that must be solved before the PBI membrane can be considered as a viable product. Zhai et al. [15] performed a life-cycle assessment of high-temperature PEMFC based on a PA-doped PBI membrane at an operating temperature of 150 °C. Their measurements showed that catalyst agglomeration and PA evaporation are the major causes of cell performance degradation. They also observed the formation of cracks in the membrane after several hundred hours of runtime. These cracks lead to severe hydrogen crossover from the anode to the cathode that further degrades the cell performance. Liao et al. [16] investigated oxidative degradation of PA-doped PBI membranes via a Fenton test. Their data revealed considerable membrane weight loss during the test, and the attack of hydroxyl (–OH) radicals at the carbon atom linking imidazole and benzenoid rings initiated membrane degradation, leading to the breakdown of the imidazole rings. Chang et al. [17] also carried out a Fenton test in which the PBI membrane was treated with hydroxyl (–OH) and hydroperoxy (–OOH) radicals for approximately 24 h. Their degradation data showed that several pinholes formed in the PBI membrane were due to the attack of –OH and –OOH radicals and resulting chemical oxidative degradation.

While gas crossover through the membrane is indicative of membrane degradation, the gas permeability of the PBI membrane can be controlled by PA-doping level and temperature. Wainright et al. [3] measured the methanol vapor permeability of a PA-doped PBI membrane at operating temperatures ranging from 120 °C to 192 °C and found that methanol crossover through the PBI membrane is much lower than that through a Nafion membrane. He et al. [9] studied the characteristics of hydrogen and oxygen crossover through a PBI membrane as a function of temperature and PA-doping level. Their measurements showed that the gas permeability of the PBI membrane increases with temperature and PA-doping level. The trend in the experimental data implies that separation of polymer backbones is considerable under higher PA-doping conditions.

Besides these experimental efforts, several theoretical high-temperature PEMFC models have been developed to improve the fundamental understanding of high-temperature PEMFC operating characteristics and to optimize cell components and operating conditions [18–25]. However, the effects of membrane pinholes and resulting hydrogen and oxygen crossover on high-temperature PEMFC performance have not been extensively studied. For PFSA-membrane-based low-temperature PEMFCs, Weber [26] developed a gas-crossover model and incorporated it into the one-dimensional (1D) PEFC model presented in previous work by Weber [27]. He examined the effects of membrane pinhole size, number, and location on the cell performance. Nam et al. [2] performed a numerical gas-crossover study with a 3D low-temperature PEMFC model. However, they assumed a uniform gas-crossover rate throughout the membrane even though the membrane degradation caused by pinhole formation is a fairly local phenomenon.

In our study, we incorporated a gas-crossover model into a 3D high-temperature PEMFC model developed in previous work [25]. The gas-crossover model rigorously considers hydrogen/oxygen dissolution into PA and subsequent diffusion through PBI membranes. We also take into account in the gas-crossover model both the effect of a mixed potential in the cathode catalyst layer (CL) due to the hydrogen crossover and the effect of hydrogen/oxygen catalytic combustion in the anode CL due to the oxygen crossover. The main aim of this study is to investigate the influences of pinhole distribution in the membrane on multidimensional profiles of species, temperature, and current density as well as the overall cell performance.

2. Numerical model

Our 3D, two-phase, nonisothermal, electrochemical-transport coupled high-temperature PEMFC model is based on previous publications [1,25], which provide more detailed descriptions of the model. The governing equations of the high-temperature PEMFC model, relevant source terms, and electrochemical properties at the anode and cathode CLs are summarized in Tables 1–3, respectively. Readers are referred to our previous publications [1,25] for a more detailed description of the model.

2.1. Model assumptions

The assumptions made with respect to the model include the following:

(1) The flow is incompressible and laminar because of a small pressure gradient and low flow velocities.
(2) The gas mixtures obey the ideal gas law because of low pressure and high-temperature operation.
(3) Water exists in the gas phase because of high operating temperatures (above the boiling point of water).
(4) The dependence of PBI membrane proton conductivity on RH is assumed to be negligible because of the high operating temperature range of the high-temperature PEMFC and resultant very low RH.
(5) The local proton conductivity in the membrane pinholes is assumed to be 10 times lower than that in the no-pinhole region.

2.2. Transport properties

The diffusivity and solubility of oxygen in concentrated PA can be expressed in terms of the weight percentage of PA, m^{PA}, and temperature as in [19]:

$$D_{O_2}^{PA} = 10^{-9} \exp\left[\left(-192.55(m^{PA})^2 + 323.55(m^{PA}) - 125.61\right) + \frac{\left(62010(m^{PA})^2 - 105503(m^{PA}) + 40929\right)}{T}\right], \quad (22)$$

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