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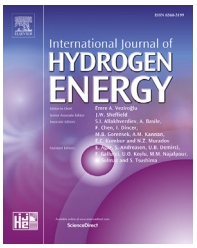

Studies of the methanol crossover and cell performance behaviors of high temperature-direct methanol fuel cells (HT-DMFCs)

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ABSTRACT

The high temperature-direct methanol fuel cell (HT-DMFC) based on phosphoric acid (PA)-doped polybenzimidazole (PBI) membranes shows promise as a passive-type DMFC system because it can operate using highly concentrated methanol fuel. In this paper, the methanol crossover and cell performance behaviors of the HT-DMFCs were investigated using a one-dimensional (1-D) HT-DMFC system model that fully accounts for the electrochemical reactions, key species transport and heat generation inside a cell, and the evaporation processes of liquid methanol/water fuel in the evaporator. The model was first validated against experimental HT-DMFC data measured over a wide range of methanol feed concentrations and operating current densities, and operating characteristics of HT-DMFCs were then explored in detail. Particular emphasis was placed on conducting a comparative study of HT-DMFCs with traditional liquid feed low temperature-DMFCs based on perfluorosulfonic acid membranes. The simulation results showed that a HT-DMFC can operate well under highly concentrated methanol fuel above 12 M due to the minimal degree of methanol crossover through the PA-doped PBI membrane.

Introduction

Direct methanol fuel cells (DMFCs) using perfluorosulfonic acid (PFSA) membranes, such as DuPont Nafion® have been studied widely over the past decade. Several technical issues hindering the commercialization of DMFCs need to be solved. Two of the most notable issues are severe methanol crossover through the membrane and complicated water management in DMFC systems. Owing to the inherent water uptake characteristics of PFSA membranes, methanol crossover is inevitably present under the supply of an aqueous methanol solution. Furthermore, an innovative water management scheme should be developed to mitigate the considerable water imbalance between the anode and cathode sides wherein a sufficient amount of water is required for the anode due to the methanol oxidation reaction (MOR) and electro-osmotic drag through the membrane, whereas the excess water generated by the oxygen reduction reaction (ORR) floods the cathode, limiting oxygen transport to the reaction sites, and the overall cell performance.

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PA-doped PBI membranes enable operations at elevated temperatures between 100 and 200 °C without requiring a sufficient water content for effective proton conduction [1–3]. In particular, the high temperature PBI membrane is well suited to residential fuel cell systems for combined heat and power (CHP) generation, leading to simple water management and enhanced tolerance for CO in reformatted fuel. The high temperature operating capability of PBI membranes can be also very beneficial to DMFCs, wherein by increasing the operating temperatures above 100 °C, flooding is eliminated while the electrochemical kinetics and reactant transport are improved. More importantly, it was reported that the methanol crossover rate through the PBI membranes is much slower than that of the PFSA membranes [4,5]. Therefore, attempts have been made to apply high temperature PBI membrane to DMFCs [6–12]. Wainright et al. [6] applied PBI membranes to DMFCs to take advantage of the low methanol permeation characteristics of a PBI membrane at elevated temperatures. Wang et al. [7] demonstrated prototype high temperature (HT) DMFCs with a PBI membrane and reported a power density of 0.1 W cm^{-2} at 200 °C. Lobato et al. [8] tested HT-DMFCs under different operating temperatures, methanol/water molar ratios, and oxygen partial pressures. Their experimental data showed that keeping the optimal methanol to water ratio was critical to avoiding the mass transport limitation of either water or methanol for the MOR. They also reported that the rate of methanol crossover through Nafion was approximately two orders of magnitude higher than the PBI membrane. Mamlouk et al. [9] compared experimentally the HT-DMFCs using the PBI membrane with Nafion-based low temperature (LT) DMFCs. Although the HT-DMFC exhibited a higher open circuit potential and superior CO tolerance at the cathode, they reported that the sluggish methanol oxidation kinetics in a PA environment in the anode and the decrease in proton conductivity of the PBI membrane due to PA loss were major drawbacks in HT-DMFCs. Zhao et al. [10] examined the effects of the operating temperature and methanol feed concentration in the passive type HT-DMFC system. They achieved a peak power density of 22.1 mW cm^{-2} at 180 °C when neat methanol was fed directly to the system. Ahmad et al. [11] reported a novel hybrid Nafion-PBI-zirconium phosphate (ZP) membrane by casting mixtures. The hybrid Nafion-PBI-ZP membrane had better stability at HT and the selectivity factor, which is the ratio of the proton conductivity to the methanol permeability of the hybrid Nafion-PBI-ZP membrane, was approximately 2 times higher than Nafion 117 despite being measured at room temperature. Diaz et al. [12] measured the methanol permeability in various membranes, such as Nafion 117, PA-doped PBI, and ABPBI under different operating temperatures, ranging from 20 to 90 °C. They showed that the ABPBI membrane is much better than the other membranes in terms of the proton conductivity and methanol permeability above 90 °C. Compared to the experimental studies, there have been relatively few modeling and simulation works of HT-DMFC reported in the literature. Scott et al. [13] developed a 1-D HT-DMFC model that accounts for the potential and concentrations distribution in the electrodes. The HT-DMFC model was validated against the experimental data over the temperature range of 125–175 °C under a dilute methanol feed concentration of 1 M. On the other hand, methanol feed/recirculation module including the evaporator and condenser of the methanol solution was not modeled in their work, which does not allow a detailed thermal analysis of the HT-DMFC system operations.

The previous studies clearly revealed several favorable features of operating DMFCs at elevated temperatures above 100 °C. In particular, the relatively lower methanol permeation through the PBI membranes potentially allows passive typed DMFC operations under high methanol feed concentrations, which greatly improves the energy density of a DMFC system. In this study, we developed a HT-DMFC system model, rigorously accounting for the major key system components, i.e., fuel supply/recirculation modules as well as a HT-DMFC stack. This model was first validated against the experimental data measured over a wide range of methanol feed concentrations and operating current densities and the advantages of the PBI membrane-based HT-DMFC were explored in detail. Particular emphasis was placed on a comparative study of two different DMFCs with PFSA and PBI membranes, wherein methanol crossover and the resulting mixed potential at the cathode electrode were estimated and compared.

Numerical model

Model description and assumptions

A 1-D HT-DMFC model was developed based on the LT-DMFC models developed in our previous studies [14–18]. The HT-DMFC model was applied to a 1-D computational domain comprised of diffusion media (DM), a catalyst layer (CL) on both the anode and cathode sides, and a membrane, as shown schematically in Fig. 1 with the detailed species transfer processes. Tables 1 and 2 list the detailed cell dimensions, operating conditions, and physiochemical and kinetic parameters for the HT-DMFC simulations, respectively. The specific assumptions used in the model are as follows:

(1) The gas phase obeys the ideal gas law, which is valid because all the gases in the DMFC are maintained at a low pressure relative to their respective critical pressures.
(2) The temperature gradient along the cell thickness is neglected in the 1-D model due to the use of the thin MEAs in the DMFCs.
(3) An isotropic and homogeneous porous diffusion layer is assumed, and it is characterized by the effective porosity and permeability.
(4) The effects of the polytetrafluoroethylene (PTFE) loading on the thermal conductivity of DM can be neglected. This assumption is based on several experimental data sets, in which the thermal conductivity of DM was reduced slightly by the low PTFE contents (<20 wt%) [29,30].
(5) The effects of CO_2 blockage on the cell performance are negligible.
(6) Complete consumption of methanol at the cathode CL after crossing over the membrane from the anode to the

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