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Experimental and numerical study on the water transport behavior through Nafion® 117 for polymer electrolyte membrane fuel cell

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ABSTRACT

A novel model explaining the water transport mechanism through Nafion® 117 is developed to understand the effects of parameters such as phase difference, pressure, mass flow rate, and temperature for applying polymer electrolyte membrane (PEM) fuel cell application. The model considers water uptake characteristics based on the polymer membrane structure and adopts four different processes to explain water permeability considering interfacial transport across the boundary. To understand the effect of phase difference, we change the relative humidity at each inlet of the experimental apparatus from 10% to 100%. The results suggest that capillary pressure is the most dominant factor in water transport across the membrane. When we change the pressure at each side of the apparatus from 1 to 3 bar, the water transport amount is maximized at 1 bar for each inlet. The mass flow rate varies from 1 to 5 Lpm. Owing to changes in molar concentration, the amount of water transport is increased when the mass flow rate at dry side inlet is minimized. Moreover, the temperature effects on the water transport amount is analyzed. As the temperature increases, the amount of water transport at the dry and wet side outlet is increases and decreases, respectively, because of the interaction between diffusivity and surface tension. The above results are verified using measured data and compared with calculated results obtained by a conventional method. In the end, this study developed the empirical equation which can be used in the fuel cell model.

1. Introduction

Over the past few decades, polymer electrolyte membrane (PEM) fuel cells have gained considerable attention in the automobile industry as a substitute for internal combustion engines. However, there are several problems on PEM fuel cells, such as system size and durability. The problem regarding system size can be solved by reducing the stack size with increasing power density, whereas the problem regarding durability can be solved by extending fuel cell life by maintaining stable operating conditions [1]. Among the components of a fuel cell system, the stack and membrane humidifier are the main devices associated with the above problems, and the membrane is the most important material used in these two devices. In the stack and membrane humidifier, the membrane is used as the water exchange and proton transfer medium. Although various types of membranes are used in PEM fuel cells, Nafion is the most commonly used, and commercially produced membrane [2].

Generally, water transport through the membrane can be categorized as three types: hydraulic permeation (liquid–liquid permeation), pervaporation (liquid–vapor permeation), and vapor permeation (vapor–vapor permeation). And, these processes can be limited by interfacial mass transport [3–6]. These mechanisms of mass transport are explained experimentally and numerically. In experimental researches, some studies showed the characteristics of water sorption of ionomer [7–9]. Others presented the results of mass transport through the membrane in different operating conditions [10–15]. Others explained structure of the ionomer that can be affect mass transport [16–19]. Theses studies are helpful to understand the phenomena in the membrane, however, these experiments were conducted in limited conditions and these conditions cannot reflect all operating conditions of fuel cell. So, their studies were little unsatisfactory to describe all results occurring at fuel cell. On the other hand, previous numerical studies tried to be able to explain the phenomenon in the Nafion. Some studies attempted to explain the transport across the membrane considering liquid and gas phases [20–22]. Others

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focused on trends of mass transport in various operating conditions [23–28]. Only few researchers considered the microstructure of a membrane to calculate water transport [29,30]. Although former numerical studies have been explained the mechanism for the water transport in the membrane, they just applied linear relationship multiplied by constant diffusion coefficient that is intrinsic material properties. This linear form is inadequate to consider enormous results from previous studies, and the diffusion coefficient cannot be constant under diverse operating conditions [31]. Of course there are other equations with higher-order terms to express mass transport across the membrane, but they could not reflect all the necessary parameters that are important for fuel cell operation. A reliable theoretical framework for the mass transport through Nafion is necessary that should consider water sorption characteristics, membrane microstructure, interfacial mass transport, and specific behavior of water molecules in different phases.

In this study, we analyze water sorption and mass transport across the Nafion® 117 as a function of relative humidity, pressure, mass flow rate, and temperature using water uptake and permeation. We first discuss the results of water transport through Nafion® 117 under variable relative humidity conditions to determine the effect of different phases such as gas or liquid. Then, we show how pressure difference affects water transport across Nafion® 117 under constant relative humidity. Furthermore, the mass flow rate and temperature are varied while the other parameters are maintained constant. The experimental results are analyzed using our novel model, considering the characteristics of water sorption, morphology of Nafion® 117, and two-phase flow in the membrane, to improve the fundamental understanding of the parameters affecting water transport. Lastly, we suggest novel equation that can apply to fuel cell model.

2. Methodology

In this section, we describe the theoretical framework for the water transport mechanism and the experimental setup used for analyzing water transport.

2.1. Modeling

A perfluorosulfonic acid polymer such as Nafion® 117 consists of a hydrophobic perfluoronated backbone and hydrophilic sulfonic acid functional groups. Two kinds of domains result from these structural characteristic. A hydrophobic perfluoronated backbone acts as the polymer matrix. It supports structure. Meanwhile, the other builds the water channel network in the hydrated condition. Based on the characteristics of the membrane, we suggest that Nafion® 117 has a parallel-pore structure, as shown in Fig. 1(a). The ionic phase forms a 4-nm-diameter cylindrical cluster, and each cylinder is 1 nm away from each other [19]. This cylindrical cluster is hydrophilic and plays the role of a channel for liquid water, *i.e.*, hydraulic permeation. The remainder of the membrane is hydrophobic and acts as a channel for water vapor, *i.e.*, vapor permeation. Based on the characteristics of pervaporation which is derived from permeation and evaporation, we will treat this process as combination of above two processes. Because they have the same driving force and carriers [32–34].

Since the mechanism of water transport through Nafion® 117 is closely related to water uptake in the membrane, we examine the characteristics of water sorption in the membrane. In this study, the water uptake processes in the membrane are divided into two steps based on the interpretation of the isopiestic sorption curve: relative humidity 0–75%, and over 75% [20]. Each former step stands for the case of vapor permeation and pervaporation, and

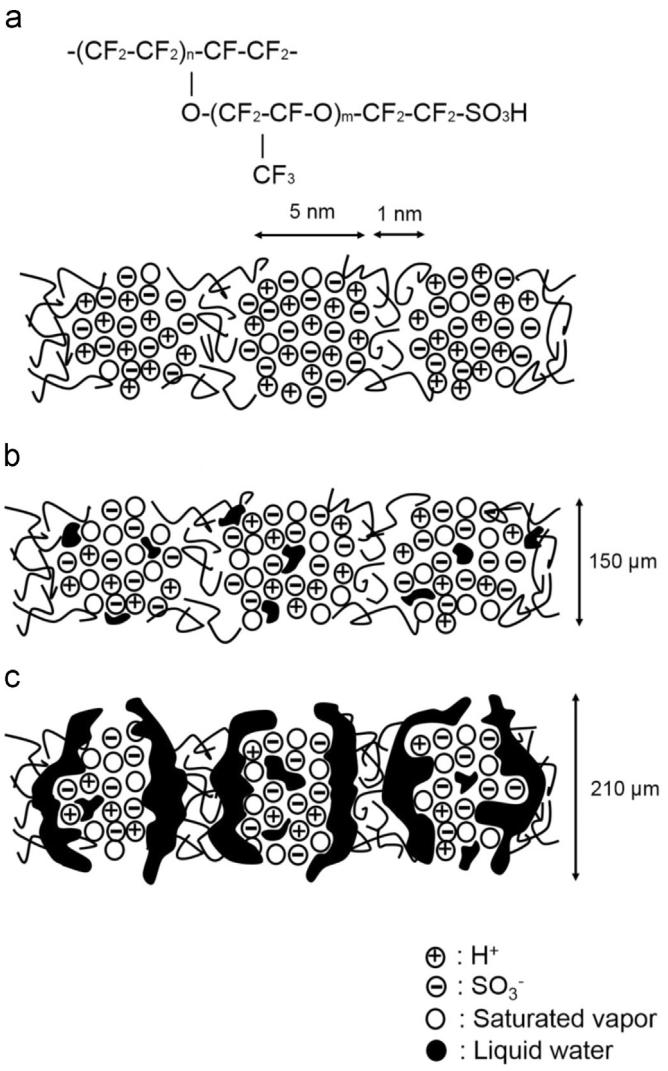

Fig.1. Schematic diagram of microstructures of Nafion® 117 and diffusion process of water molecules for different activities: (a) $0 < a \leq 0.15$, (b) $0.15 < a \leq 0.75$, and (c) $0.75 < a \leq 1$.

latter step stands for hydraulic permeation, respectively. Initially some gases such as vapor or air might be transferred through the hydrophobic domain of Nafion® 117. And the membrane begins to absorb liquid water by increasing the amount of moisture. In this region, the dissociation of the protons from the acidic sites occurs and they develop hydronium ions with the absorbed water. The absorbed water is chemically bonded to ionic clusters. Therefore, we assume that liquid water exists as hydronium ions in the membrane (the concept of the existence of these ions is the same as the concept of water content employed in other studies) and that water molecules move across the membrane in the form of hydronium ions. These solvated hydronium ions hardly contribute to membrane swelling, and they only form a cylindrical ionic cluster with a charged site, as shown in Fig. 1(b). This is why a relatively flat region is observed in the isopiestic sorption curve in this range [7,10,29]. And the thickness of the membrane in the region is not swell; approximately 150 μm [8]. After hydronium ions piled up at one side, flux of proton begins to move. We included this phenomenon as back diffusion. Considering above processes, equilibrium of mass transfer through the membrane is achieved.

When the relative humidity is higher than 75%, the charged site reaches saturation, so liquid water begins to condense near the