Differences in the oxygen permeation behavior of perfluorinated and hydrocarbon-type polymer electrolyte membranes at elevated temperatures

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ABSTRACT

Differences in the oxygen permeation behavior of perfluorinated and hydrocarbon (HC)-type polymer electrolyte membranes (PEMs) were systematically investigated at 80 and 90 °C under controlled relative humidity. We evaluated oxygen permeability under different humidity conditions, using dry–wet and wet–wet configurations, which correspond to the dry H_2–wet (humidified) O_2, and wet H_2–wet O_2 conditions, respectively. For perfluorinated PEMs, permeation behavior was significantly dependent on the growth of ionic-water channel networks, and an unusual depression of permeability at 90 °C and 70% RH (wet–wet) compared to that at 80 °C under the same humidity conditions was also observed due to slight stiffening of the membrane. For HC-type PEMs, on the other hand, the permeation behavior was likely to depend on the free volume inside the membrane, which undergoes a large dimensional change with swelling. The gas permeation behavior and gas diffusion pathways of perfluorinated and HC-type PEMs are essentially different because of differences in the structural changes between the membranes.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have recently received considerable attention as a next-generation power source, since from the practical viewpoints of energy efficiency and environmental friendliness, they compare favorably with present energy sources. Polymer electrolyte membranes (PEMs), such as perfluorinated and hydrocarbon-type (HC-type) PEMs, have been developed as a key component of PEFCs [1]. However, improved performance at high temperatures of over 100 °C and low humidity is required for their further development. This has led to the development of different types of PEMs, particularly perfluorinated PEMs such as Nafion®, Aquivion®, Aciplex®, and Flemion®, which are excellent materials due to their high mechanical, thermal, and chemical stabilities, in addition to their high proton conductivity [2–5]. Although these PEMs have been further improved in terms of their chemical and mechanical stabilities for high-temperature fuel cell operation, even above 100 °C, serious problems still remain with their cost and recycling properties. HC-type PEMs have also been extensively studied from the viewpoints of cost, environmental friendliness, and high-temperature stability [6–9]. Aromatic HC-type PEMs composed of random or block copolymer systems based on engineering plastics such as polyether

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ether ketone [10,11], polyether sulfone [12–14], polyimide [15–17], and polyphenylene [18,19] are considered to be among the most promising PEM candidates because of their heat resistance and mechanical stability, in addition to their high proton conductivity and low gas permeability.

An understanding of the correlation between the structural and mass transport properties, including proton conductivity and gas permeability, of PEMs under conditions similar to those used for PEFC operation is necessary for the development of PEFCs. Aside from high proton conductivity, a low gas permeability is essential for PEMs because the crossover of H_2 and O_2 across the membrane has a negative impact on not only the overall efficiency of PEFCs, but also the membrane durability [1]. In contrast to this necessity for low gas permeability in the PEM, a higher gas permeability is required for the ionomer in the catalyst layer (CL), with which the carbon support is often thinly coated [20,21]. Since the oxygen transport resistance in the CL directly relates to the PEFC performance, the investigation of the oxygen diffusivity and solubility in the ionomer phase of the CL has also generated much recent interest [22–24]. Therefore, the study of the gas permeation behavior of the PEM and the ionomer in the CL is crucial for design of high-performance PEFCs. The membrane structure can be altered during hydration [25], and this can be expected to change the gas permeability. We have previously reported that the increase in gas permeation in hydrated Nafion® membranes at above 60% relative humidity (RH) is controlled by the gradual increase in overall flexibility caused by hydration at low temperatures (below 40 °C) [26]. However, this theory remains controversial, despite the many studies on the gas permeability of perfluorinated PEMs that have so far been reported [26–37]. Furthermore, compared to perfluorinated PEMs, there have been relatively few reports concerning gas permeation behavior of HC-type PEMs [15,31,35] at elevated temperatures that correspond to the fuel cell operating conditions, despite the many HC-type PEMs that have been developed. It should be emphasized here that the gas permeation behaviors of perfluorinated and HC-type PEMs should be compared at the same conditions, and the correlations between membrane behavior and structure should be investigated.

Here we report a systematic study of gas permeation behavior among perfluorinated and HC-type PEMs, namely Nafion®, Aquivion®, and sulfonated polyether ether ketone (SPEEK), to demonstrate the difference in the gas transport properties for both membrane types. Moreover, as a first attempt to understand the structure–property relationship, we investigate the correlation between the gas permeability and dynamic viscoelasticity of perfluorinated and HC-type ionomer membranes at elevated temperatures under dry and humid conditions.

2. Experimental

The chemical structures of the polymers studied here are shown in Fig. 1. The perfluorinated PEMs, Nafion®, and Aquivion® [38], were purchased from DuPont, USA, and Solvay Specialty Polymers Japan K.K., respectively.
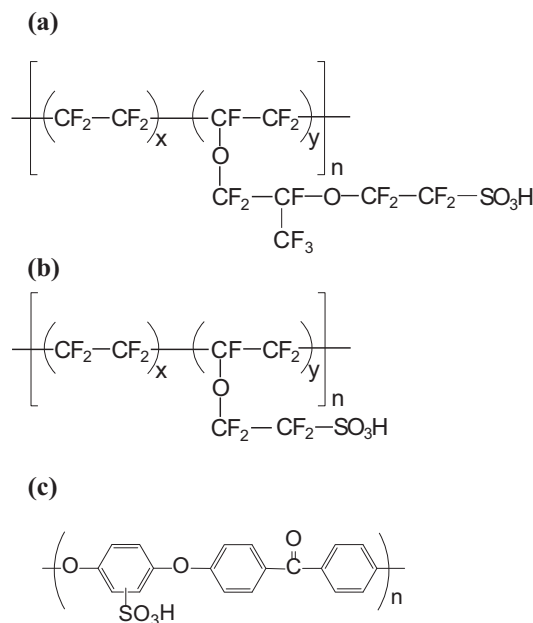

Fig. 1. Chemical structures of Nafion®, Aquivion®, and SPEEK.

The Nafion® N112, N115, N117, and N1110 samples, had an ionic exchange capacity (IEC) of ca. 0.92 meq/g, and thicknesses of 50 μm, 126 μm, 176 μm and 250 μm, respectively. The Aquivion® E87-30, 50 and 100 samples had a shorter side chain than that of the Nafion® [38], with an IEC of ca. 1.15, and thicknesses of 30 μm, 50 μm and 100 μm, respectively. The HC-type PEM, SPEEK, was produced in our own laboratories. SPEEK was synthesized by sulfonation of commercial PEEK obtained from Polyscience Inc. The ion exchange capacity (IEC) was determined by back titration to be 1.87 meq/g. Films of 50 μm thickness were prepared by casting N-methyl-2-pyrrolidone (NMP) solutions onto flat glass plates and drying at 80 °C under vacuum. The membranes were detached from the glass plates, immersed in 0.5 M sulfuric acid overnight for complete protonation, rinsed with deionized water, and then dried under ambient conditions.

Gas permeability analysis was performed on membranes that were dehydrated and stored in dry N_2 for at least 3 h before measurement. The analysis was performed by the equal pressure method, with a GTR-Tech 30XFST apparatus equipped with a Yanaco G2700T gas chromatograph, by monitoring the amount of H_2 that permeated across the membrane from one side to the other (upside). O_2 was also supplied simultaneously from the other side (downside). Ar and He were used as carrier gases of permeated H_2 and O_2, respectively, in the gas chromatograph, as shown in Fig. 2a. The RH dependence of the H_2 and O_2 permeability coefficients, PH_2 and PO_2, was investigated from 0% to 90% RH at high temperatures. The dry (0% RH)–H_2 and wet (humidified)–O_2, and wet–H_2 and wet–O_2 conditions were tested, as shown in Fig. 2b. The membrane was set in a cell with a gas inlet and a gas outlet, where temperature was controlled. H_2 and O_2 were supplied at a flow rate of 30 mL/min. The