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Novel technique for measuring oxygen crossover through the membrane in polymer electrolyte membrane fuel cells

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ABSTRACT

In this study, the exact amount of oxygen crossover that reacts with hydrogen has been investigated using a mass spectrometer system. By measuring the amount of oxygen crossover that reacts with hydrogen, the exact amount of oxygen crossover that affects membrane degradation and/or water generation can be calculated under the fuel cell operating conditions. The amount of oxygen crossover that reacts with hydrogen is expressed as an effective oxygen crossover ratio, which is in a range between 0.927 and 0.933 under the fuel cell operating temperature conditions. This means that approximately 93% of the entire oxygen crossover through the membrane can affect membrane degradation and/or water generation at the anode catalyst layer. Thus, the effective oxygen crossover ratio should be considered as a novel index of oxygen crossover because it represents the exact amount of oxygen crossover that reacts with hydrogen.

1. Introduction

In recent times, thin membranes with thickness ranging from 18 to 50 μm have been widely adopted in polymer electrolyte membrane fuel cells (PEMFCs) to improve fuel cell efficiency and allow high current density operations. However, the use of thin membranes aggravates gas crossover and may decreases fuel cell durability. It is well known in the literature [1,2] that hydrogen crossover from the anode side to the cathode side may deteriorate the durability of PEMFC. On the other hand, as shown in Fig. 1, oxygen can also permeate from the cathode side to the anode side. Oxygen crossover also causes several problems related to limiting the durability of PEMFCs. Willsau et al. [3] reported that oxygen crossover influenced the electrochemical carbon corrosion in a cathode gas diffusion layer (GDL). It is well known that the air/fuel boundary is created at the anode side if oxygen is transported from the cathode side to the anode side. This increases the potential of the cathode to a value greater than the open circuit voltage and quickly corrodes the cathode carbon layer [4,5]. Another problem caused by oxygen crossover is membrane degradation [6–8]. Oxygen crossover does provide a means for the formation of hydrogen peroxide and thus oxygen-containing radicals, which can deteriorate the membrane durability.

As oxygen crossover causes the degradation of the membrane, several techniques including the time-lag method [9–11], the volumetric method [12], the electrochemical monitoring method [13–19] and the direct gas detection method using gas chromatography (GC) [20,21] or mass

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Nomenclature

D	diffusion coefficient, $cm^2\ s^{-1}$
E	activation energy, kJ mol^{-1}
J	gas permeation rate, mol $s^{-1}\ cm^{-2}$
k	permeability coefficient, mol $cm^{-1}\ s^{-1}\ atm^{-1}$
k^0	maximum permeability coefficient, mol $cm^{-1}\ s^{-1}\ atm^{-1}$
l	membrane thickness, m
P	partial pressure, Pa
R	gas constant, J $mol^{-1}\ K^{-1}$
S	solubility coefficient, mol cm^{-3}
T	temperature, K

Greek letter

β	effective oxygen crossover ratio

Superscript

A	anode side
C	cathode side

Subscript

O_2	oxygen gas

spectrometry (MS) [22–27] have been used to measure the oxygen crossover rate. Both the time-lag and volumetric methods apply higher pressure at one side of the membrane, then the gas molecules start sorbing into the high-pressure side of the membrane (upstream), and subsequently diffuse to the opposite low-pressure side of the membrane (downstream). The time-lag method involves monitoring the transient accumulation of species due to permeation on a fixed volume in a downstream reservoir [11], whereas the volumetric method obtains the flow rate in the downstream [12]. These two methods offer a simple and effective technique for determining the oxygen permeation rate, but they are not suitable for the fuel cell operating conditions (*i.e.*, wide ranges of humidity and temperature). Therefore, the use of results from these methods may be limited in both numerical and experimental studies of PEMFCs. For *in-situ* measurements of oxygen crossover under the fuel cell operating conditions, electrochemical monitoring and direct gas detection methods are employed. In the electrochemical monitoring technique, one of the sides is exposed to an acid solution with a counter electrode while a reactive gas is supplied to the other side of the membrane. Current is then generated due to gas crossover and the crossover rate through the membrane can be estimated by measuring the current over time [17]. However, the electrochemical monitoring technique is still limited under actual operating conditions of PEMFCs because one side of the membrane should be exposed to the acid solution which is not a reactant gas for the fuel cell operation. Another way to measure the oxygen crossover rate of PEMFCs is to use direct gas detection methods. Recently, direct gas detection methods using GC or MS were newly suggested to measure the gas crossover rate under the actual fuel cell operating conditions. Broka et al. [20] and Mohamed et al. [21] reported oxygen permeability through a Nafion® 117 membrane by using the GC system at different values of temperature and relative humidity (RH). Shim et al. [23] performed oxygen crossover measurements using the MS system. An illustration in Baik and Kim [22] shows that the direct gas detection system is connected at the exit of the conventional fuel cell system, implying that the oxygen crossover rate under the actual fuel cell conditions can be measured. The measurements of the oxygen crossover rates under conditions that are as close as possible to actual conditions of PEMFCs appear to be important; therefore, the direct gas detection method using GC or MS is more suitable for oxygen crossover measurements.

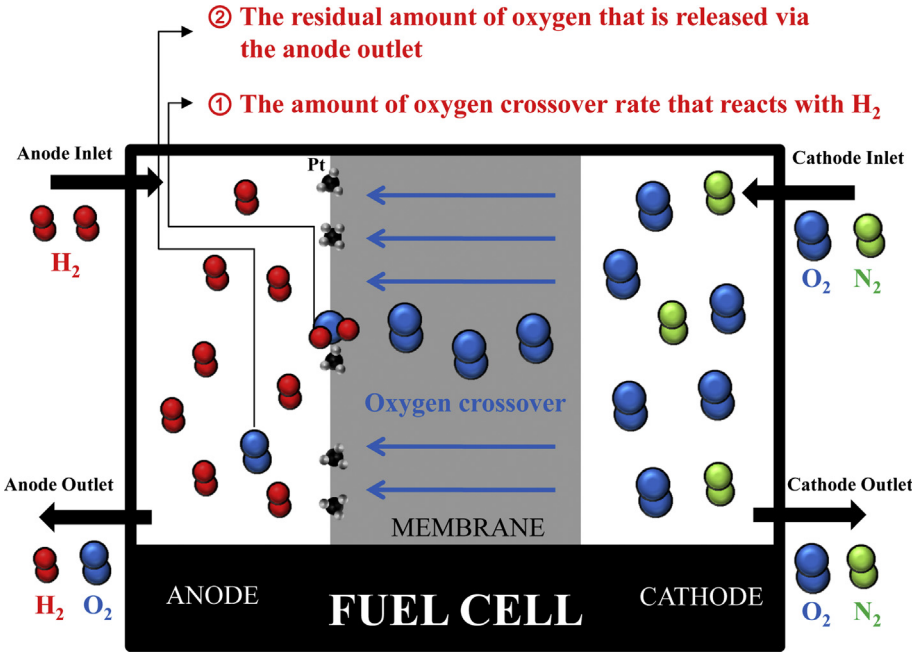

Fig. 1 – Schematic diagram of oxygen crossover through the membrane in a PEMFC.