



Water uptake, ionic conductivity and swelling properties of anion-exchange membrane



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HIGHLIGHTS

- The swelling properties of the A201 membrane are investigated at different temperatures.
- Water sorption of the A201 membrane occurs with negative excess volume of mixing.
- Percolative nature of the ion transport has been identified in the A201 membrane.

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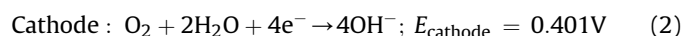
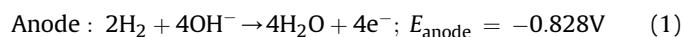
ABSTRACT

Water uptake, ionic conductivity and dimensional change of the anion-exchange membrane made by Tokuyama Corporation (A201 membrane) are investigated at different temperatures and water activities. Specifically, the amount of water taken up by membranes exposed to water vapor and membranes soaked in liquid water is determined. The water uptake of the A201 membrane increases with water content as well as temperature. In addition, water sorption data shows Schroeder's paradox for the AEMs investigated. The swelling properties of the A201 membrane exhibit improved dimensional stability compared with Nafion membrane. Water sorption of the A201 membrane occurs with a substantial negative excess volume of mixing. The threshold value of hydrophilic fraction in the A201 membrane for ionic conductivity is around 0.34, above which, the conductivity begins to rise quickly. This indicates that a change in the connectivity of the hydrophilic domains occurs when hydrophilic fraction approaches 0.34.

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1. Introduction

With the advantages of using non-precious electrocatalysts and reduced corrosion problems, anion-exchange membrane fuel cells (AEMFCs) have become a very promising energy conversion technology, and are expected to be an alternative to proton exchange membrane fuel cells (PEMFCs). The chemical reactions in hydrogen fueled traditional AEMFCs are presented below:



Oxygen is reduced at the cathode to produce OH^- , which transports through the anion-exchange membrane (AEM) to the anode side and combines with the hydrogen to generate water [1].

At the heart of the AEMFC, the AEM is one of the most significant components contributing to cell performance. In the last few years, significant effort has been devoted to development and synthesis of AEMs [2–5]. However, a commercial AEM with performance similar to PEMFC with Nafion membrane is still unavailable. Since the emergence of a commercial AEM tailored for AEMFC by Tokuyama Corporation, the performance and durability of the AEMFC achieved a substantial improvement. Nevertheless, it is still far below current PEMFC performance.

Similar to Nafion membrane, AEM can conduct ions only in the presence of water. In addition, water is one of the reactants in the oxygen reduction reaction. Therefore, humidified gases are fed into

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the fuel cell under most operating conditions. Water content of the AEM and ionomer varies with current, which also affects the transport properties of the AEM. Decrease in water content leads to a reduction of conductivity of the AEM, which might cause ohmic loss.

Currently, the A201 membrane from Tokuyama is the most popular and commercially available AEM used in AEMFCs. It is 28 μm in thickness at dry state, consists of hydrocarbon backbone and quaternary ammonium functional groups terminated side chains. In the last few years, many in-situ experiments have been completed by researchers to investigate performance, durability, CO_2 tolerance and electro-osmotic drag coefficient of the A201 membrane [6–11]. Ex-situ testing for sorption and diffusion of water in the A201 membrane were also performed. Li et al. [12] measured water uptake of A201 membrane under different relative humidities at 30, 40 and 60 $^\circ\text{C}$, and found that Schroeder's paradox existed in the AEM. They reported that the water diffusion coefficient in the membrane is in the order of $10^{-10} \text{ m}^2 \text{ s}^{-1}$, which is close to Nafion membrane. They also reported that the water transfer coefficient is in the range of 10^{-6} – 10^{-5} m^{-1} . However, the swelling properties of the A201 membrane have not being studied in recent publications. As water is absorbed in the membrane, the hydrophilic domains swell with increasing hydration. How does the swelling of the membrane affect the ion transport through the A201 membrane? Since the ion transport is basically related to the network structure of functional groups associated with water, the answer to this question requires more detailed research about the conductivity and microstructure of the AEM as a function of water content.

To better understand the transport mechanisms and swelling properties of the AEM, we did ex-situ membrane tests with well established techniques and equipment for studying various properties [13]. The objective of this work is to investigate the membrane conductivity and the dimensional change as functions of temperature and water content of the membrane.

2. Experimental

2.1. Materials

AEM, A201 membrane with ion exchange capacity (IEC) of 1.7 mmol g^{-1} was provided by Tokuyama Corporation, Japan. The membrane characterized in this paper was not pretreated. Deionized water was used in all the experiments.

2.2. Water uptake & conductivity

Water uptake and ionic conductivity were measured in an isometric system at different temperatures and water vapor pressures [14].

A membrane sample was placed in a chamber with fixed volume, which was evacuated at a test temperature below 1 Pa to remove any residual water in the membrane as well as in the chamber. A small amount of water (5–40 μL) injected into the chamber was observed to evaporate very quickly. Ideal gas law associated with the vaporization of the injected water was used to determine the expected pressure (theoretically), p_{exp} .

$$p_{\text{exp}} = \frac{m_w RT}{M_w V} \quad (4)$$

where V is the volume of chamber, m_w the mass of water injected, R universal gas constant, T temperature, and M_w the molecular weight of water. After the membrane is equilibrated with water vapor, the actual pressure, p_{act} can be determined by the pressure

transducer in the chamber. The difference between p_{exp} and p_{act} is attributed to the water absorbed by the AEM. The mole of water absorbed by the membrane (n_w) is calculated by the following equation:

$$n_w = \frac{V(p_{\text{exp}} - p_{\text{act}})}{RT} \quad (5)$$

Membrane water content is determined by the activity of water vapor in the chamber since equilibrium is assumed. The activity in the vapor phase (a_w) is

$$a_w = \frac{p_{\text{act}}}{p_{\text{sat}}} \quad (6)$$

where p_{sat} is the saturation pressure of water. The water content of the membrane (λ) is calculated by dividing n_w with IEC and the mass of the membrane (m_m):

$$\lambda = \frac{n_w}{\text{IEC} \cdot m_m} \quad (7)$$

Water uptake of the AEM in equilibrium with liquid water was measured by weighing the membranes before and after soaking in the liquid water for 24 h.

Within the chamber, the ionic conductivity of the membrane was measured by an AC impedance technique in the surface direction (in-plane). The membrane was cut into 2 cm wide \times 4 cm long pieces. Fig. 1 shows the schematic of test equipment for membrane resistance measurement. Each sample was clamped between a set of graphite electrodes spaced 0.17 cm apart. Conductivity of the membrane was calculated using the following equation.

$$\sigma = \frac{L}{R_m A} \quad (8)$$

where σ is conductivity (S cm^{-1}), L the distance between two electrodes (cm), A cross area of the membrane (cm^2), and R_m the measured resistance of the membrane (Ω).

2.3. Dimensional change

The dimensional change of the AEM was also measured as functions of temperature and water activity using a custom built creep instrument within an environmental chamber [15]. Samples were cut into 3 cm long, 1 cm wide pieces and clamped in the jaw of the creep instrument and dried in N_2 at 80 $^\circ\text{C}$ for 2 h before testing. A small stress (0.05–0.1 MPa) was applied on the sample to pull it straight such that no creep would occur in this situation. After drying the sample, the temperature in the chamber was adjusted to the desired test temperature. Water vapor was introduced by feeding the chamber with humidified N_2 . The length of the sample was monitored in real time as the water activity in the chamber was held stable. The equilibrium dimensional change was recorded when the rate of length change was smaller than 0.1% h^{-1} . The

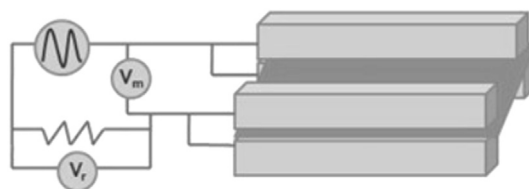


Fig. 1. Schematic of the test equipment for membrane resistance measurement.

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