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Water Transport during Ion Conduction in Anion-Exchange and Cation-Exchange Membranes

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Water transport during ion conduction through an anion-exchange membrane (AEM) immersed in an aqueous solution of HNO₃ and KOH was investigated. We have developed an apparatus to accurately measure small changes in volumes of the aqueous solution at each side of the membrane by capillary tubes during the passage of an electronic current through the membrane. In contrast to the previously reported apparatus, the present apparatus can be applied to an AEM in various aqueous solutions of electrolytes, and measurements under conditions close to those in actual solid alkaline fuel cells are therefore possible by using alkaline solutions. The water-transport number for AEM in HNO₃ was larger than that in KOH, indicating the importance of selecting the appropriate aqueous solution of electrolytes. It is possible to determine whether anions or cations are conductors in electrolyte membranes with unknown properties.

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Fuel cells are expected to become important in the future for solving energy/environmental problems. By using fuel cells, it is possible to extract electric energies with high efficiency through the production of H₂O from H₂ and O₂, with clean exhaust gases. These devices consist of two electrodes with catalysts (usually Pt) and an electrolyte membrane between them. Polymer electrolyte fuel cells (PEFCs) and solid alkaline fuel cells (SAFCs) use a proton-conducting membrane and an anion-exchange membrane (AEM) with OH⁻ conduction, respectively.¹ Either fuel gases or O₂ are converted into cations or anions at one of the electrodes, and the resultant ions penetrate through the membrane to reach the other electrode, where H₂O production occurs. In many cases, the membrane should be humidified to achieve good ion conductivity, and water transport is accompanied by ion conduction.²⁻¹¹ It is important to control water transport and the extent of humidification. For example, lack of water leads to drying of the membrane, resulting in low ion conductivity, while supplying too much water leads to overflow of water. Ideally, it is desirable to develop electrolyte membranes that show high ion conductivity without humidification. Characterization of the degree of water transport is thus important to develop high performance fuel cells.

Nafion is the most frequently used proton-conducting membrane in PEFC, and water transport in Nafion has been investigated.²⁻¹¹ Fuller et al. measured water transport by setting a concentration cell in which both sides of the membrane were exposed to water vapors with different partial pressures.² A more direct observation of water transport during proton conduction was reported by Zawodzinski et al.^{3,4} In that work, the two faces of Nafion were immersed in distilled water and the membrane was pressed between two Pd electrodes. An electric current was passed between the two Pd electrodes through the membrane and the changes in volumes of water on both sides were measured by capillary tubes. Meier et al. measured the changes in the volumes of the aqueous solution on both sides of Nafion by an improved method.⁵ They used 1 mol/L aqueous solution of HCl and Ag/AgCl electrodes. Two reactions, AgCl + e⁻ → Ag + Cl⁻ and Ag + Cl⁻ → AgCl + e⁻, occurred at the cathode and at the anode, respectively, and the creation of bubbles of H₂ and O₂ gases at the electrodes could be avoided to accurately measure the volume of the aqueous solution. However, this method is limited to measurements in HCl solution, and it is not clear whether this method is applicable for OH⁻ conduction in an AEM that occurs in an actual SAFC.

SAFCs have the potential to become less-expensive Pt-free devices because their overpotential for cathode reaction is low.¹²⁻¹⁵ However, the extent of water transport in an AEM used in SAFCs

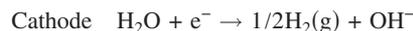
has not been elucidated. The use of HCl solution may not be appropriate for measurements of water transport in an AEM because there are few OH⁻ ions in HCl solution and Cl ions easily react with the AEM, resulting in the contamination of the membrane. It is desirable to develop a method that is applicable for various membranes in various alkaline and acid solutions to simulate water transport in SAFCs and PEFCs.

In the present work, water transport during ion conduction in an AEM immersed in alkaline and acid aqueous solutions was studied by measurements of changes in the volumes of aqueous solutions on both sides of the AEM, and the results were compared with the results for Nafion. We have developed an apparatus for accurate measurements of small degrees of water transport. Ambiguity in measurements due to evaporation and expansion/shrinkage of the aqueous solution was minimized with this apparatus. This apparatus uses Pt electrodes on which H₂ and O₂ production occurs, but the bubbles can be eliminated from the aqueous solution to accurately measure the volumes of the solution. This apparatus is therefore applicable for various membranes in various electrolyte solutions. For both Nafion and the AEM, the number of water molecules that penetrate through membranes per conduction of one ion (water transport number, *n*) was found to be different in HNO₃ and KOH solutions, indicating the importance of the appropriate choice of the aqueous solution. It is also possible to identify whether anions or cations are conductors in ion conduction from the direction of water transport.

Experimental

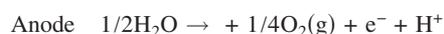
An apparatus was made to measure the transport of water through membranes during the electrolysis of an aqueous solution of an electrolyte (HNO₃ with pH 2.1 and 5.1, and KOH with pH 8.9 and 11.9) across membranes. A Nafion NRE-212 membrane or an AEM (provided by Tokuyama Co. Ltd.) was immersed in the aqueous solution, as shown in Fig. 1. An electric current was passed between two Pt electrodes through the membrane, and changes in the volumes of the aqueous solution at the anode and cathode were measured by capillary tubes.

During OH⁻ conduction, the following reactions occurred



When a potential was applied across the membrane, the liquid moved with the anions from the cathode to the anode. Each OH⁻ ion was accompanied by *n* molecules of H₂O. The ratio of the decrease in H₂O at the cathode to the increase in H₂O at the anode was (1 + *n*)/(1/2 + *n*) (≈ 1 when *n* ≫ 1).

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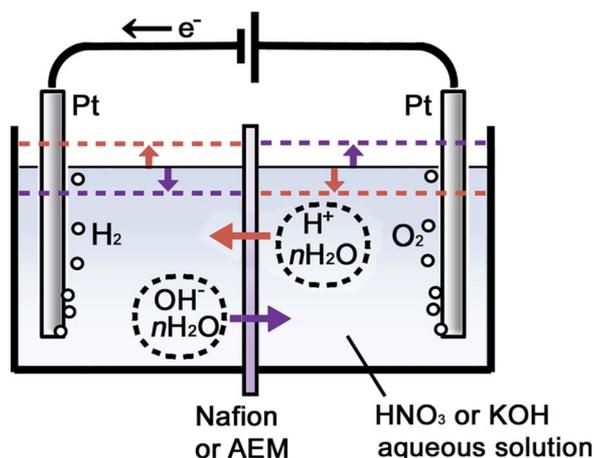
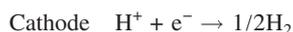


Figure 1. (Color online) Principle of measurements of water-transport numbers.



When a potential was applied across the membrane, the liquid moved with the cations from the anode to the cathode. Each H^+ ion was accompanied by n molecules of H_2O . The ratio of the decrease in H_2O at the anode to the increase in H_2O at the cathode was $(1/2 + n)/n$ (≈ 1 when $n \gg 1$). Thus, we could determine the number n of water molecules per conduction of one ion in membranes by observing the changes in the volumes of the aqueous solutions on both sides of the cell. It is possible to distinguish proton conduction and OH^- conduction from the volumes of the aqueous solutions even when n is zero if careful measurements are conducted.

A more realistic illustration and a picture of the apparatus are shown in Fig. 2a and b. The apparatus was made of glass and a membrane was sandwiched between two glass flanges with silicone O-rings. The AEM was initially a Cl-terminated type and it was kept in 1 mol/L aqueous solution of NaOH for 24 h to convert it to an OH-terminated type. The Nafion membrane and the AEM were cut in 20 mm diameter circles. The effective area of membranes on each side determined by the size of an O-ring 15 mm in diameter was 176 mm^2 ($7.5 \times 7.5 \times 3.14 \text{ mm}$). The Nafion membrane or AEM was supported by two porous glass disks for the maintenance of its shape. Two Pt wires (0.1 mm in diameter) were inserted through capillary tube 1, and the Pt anode and cathode were connected at the ends of the wires. An electric current of $70 \mu\text{A}$ – 2 mA was passed between the two electrodes with a constant-current mode by a power supply with a maximum potential of 70 V.

There are two difficulties in accurately detecting small changes in the volumes of aqueous solutions. First, during electrolysis, O_2 and H_2 produced at the anode and cathode, respectively, flow out through tube 1. To avoid spouting of the aqueous solution and to eliminate any gases from the aqueous solution, the volume of aqueous solution was measured by two capillary tubes, tubes 1 and 2 (each 1 mm in diameter), as shown in Fig. 2c and d. During measurements of volume, there should be an aqueous solution in tubes 1 and 2, and therefore the apparatus was tilted (Fig. 2c). During electrolysis, the apparatus was raised (Fig. 2d) so that the levels of the aqueous solution in capillary tube 1 moved down to lower positions where the diameter was 4–6 mm, and spouting of the aqueous solution was avoided.

The second difficulty in accurately detecting small changes in the volumes of aqueous solutions is that the evaporation of water and the thermal expansion/shrinkage of the aqueous solution lead to ambiguity in measurements of volume of the aqueous solution. To minimize the effect of expansion/shrinkage, the volume of the aqueous solution was minimized to 2.5 mL on each side of the mem-

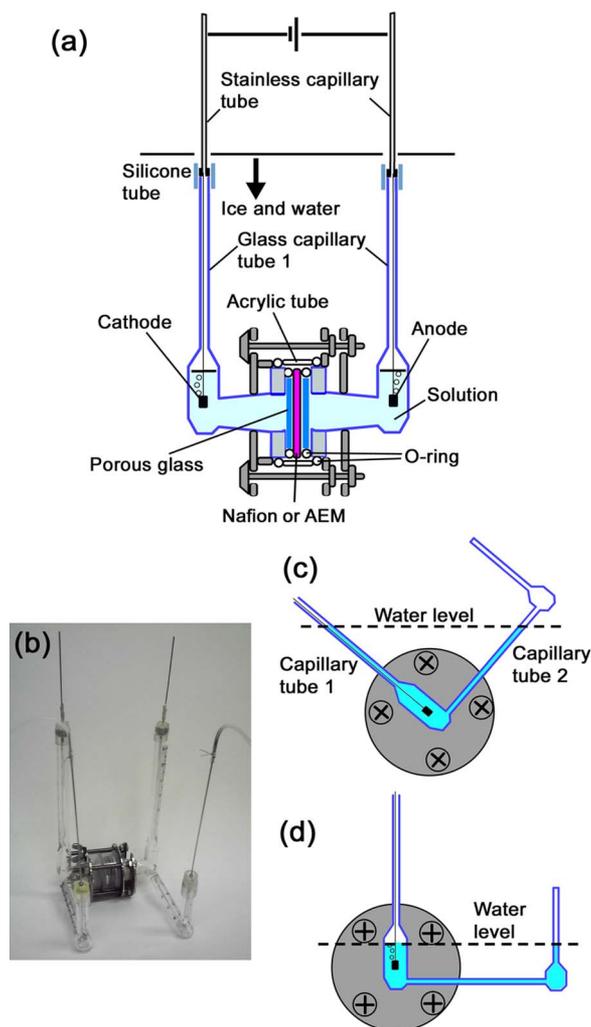


Figure 2. (Color online) An apparatus for measurements of water-transport numbers. (a) A schematic illustration of the apparatus. (b) A picture of the apparatus. (c) Tilted apparatus and the level of aqueous solution during measurements of the volume of aqueous solution. (d) Level of aqueous solution during electrolysis.

brane. The apparatus was sunk in ice and water to keep the electrolyte solution at a low temperature, which also minimized the evaporation of water. For this purpose, the membrane was waterproofed by an acrylic tube with two silicone O-rings. Capillary tubes 1 and 2 were extended with stainless capillary tubes 0.07 mm in diameter. These tubes reduced the evaporation of water and also acted as electric wires. The connections between the glass and the stainless capillary tubes were waterproofed by silicone tubes. The error in measurements of volume of an aqueous solution due to ambiguity in reading the scale on the capillary tubes by the naked eye (0.5 mm) was about 0.025 mmol.

Results and Discussion

Figure 3a shows the changes in the volumes of the solution as functions of electric charge passed through Nafion immersed in HNO_3 solution at pH 2.1. The electric current was set at 1.2 mA. The volume at the cathode side increased, while that at the anode side decreased. These results indicate that the conductor of ion conduction is a cation, consistent with the well-known proton conductivity of Nafion. The water-transport number, n , derived from the slope of these results was 6. This value is close to the previously reported values of 1.5–6.5 for Nafion immersed in a HCl aqueous solution.⁵

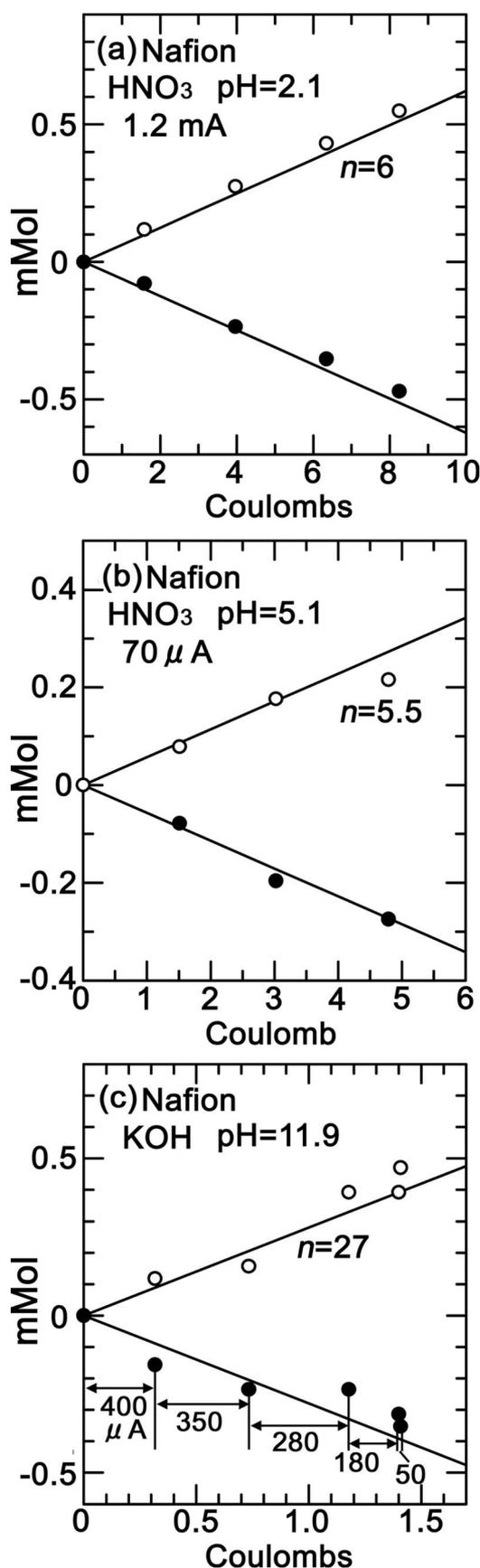


Figure 3. Changes in volumes of aqueous solutions at the anode and cathode sides during electrolysis through Nafion. (a) Results with HNO₃ at pH 2.1. (b) Results with HNO₃ at pH 5.1. (c) Results with KOH at pH 11.9. Open and closed circles are results at the cathode and the anode, respectively.

Water transport was studied for Nafion using dilute HNO₃ solution at pH 5.1. The electric current had to be set at 70 μ A because of extremely high resistance, and the measurements took about 2 days. The volume of the aqueous solution at the cathode side increased and that at the anode side decreased, as shown in Fig. 3b, indicating that the conductor in this ion conduction is H⁺. The value of n was estimated to be 5.5, which is close to that for HNO₃ at pH 2.1 (Fig. 3a). This indicates that the ratio of H₂O to H⁺ in the aqueous solution does not greatly affect the value of n .

When KOH solution at pH 11.9 was used, the resistance between the two electrodes was higher than that in the case of HNO₃. This indicates that the density of protons that act as conductors is small in KOH solution and that the conductivity of K⁺ in Nafion is small. Nevertheless, water transport could be measured by setting the electric current at a lower value of 0.4 mA, as shown in Fig. 3c. Because the resistance continued to increase during measurements, this current had to be further reduced during measurements, and the current was 50 μ A when the measurements were stopped. The water-transport number, n , was estimated to be 27. This value is higher than the value of 6 obtained for HNO₃. After the measurements, we replaced the aqueous solution of KOH at the cathode side with a new aqueous solution of KOH, but conductivity did not recover. After the solution at the anode side had been replaced with a new aqueous solution of KOH, the conductivity was almost completely recovered. The Nafion after measurements in KOH solution showed a resistance (about 80 k Ω) in the aqueous solution of HNO₃ similar to that of a new Nafion membrane in an aqueous solution of HNO₃. These results suggest that the Nafion is not damaged during measurements in an aqueous solution of KOH and that the decrease in conductivity during measurements in an aqueous solution of KOH is due to the decrease in the number of K⁺ ions at the anode side.

Figure 4a shows the results for an AEM immersed in HNO₃ solution at pH 2.1. The resistance was high compared with the results for Nafion shown in Fig. 3a, indicating that the ion conductivity of proton and NO₃⁻ in the AEM was small. While the initial electric current was set at 1 mA, the resistance rapidly increased as the electric current passed through the AEM. The measurements had to be conducted with low electric currents at high voltages close to the maximum of the power supply (70 V). Nevertheless, water transport in the AEM was recognized, as the volume of aqueous solution increased at the anode side, while that at the cathode side decreased. This tendency is opposite to that for Nafion, indicating that the conductor was either NO₃⁻ or OH⁻. The n value was estimated to be 5 from the initial results below 2 C. Then the resistance rapidly increased and the n value also significantly increased to about 17. The transformation around 2 C is thought to occur due to conversion of the AEM from OH⁻-terminated type to NO₃⁻-terminated type. Because the AEM was immersed in 1 mol/L aqueous solution of NaOH before measurements, the interior of the AEM should be terminated by OH⁻ before measurements. It is known that the affinity of adsorption of anions in an AEM is higher for NO₃⁻ than for OH⁻.¹⁶ As the electric current passes through the OH⁻-terminated AEM, NO₃⁻ ions penetrate into the AEM and OH⁻ ions in the AEM are substituted by NO₃⁻. OH⁻ conduction may initially occur and this substitution is thought to be completed at 2 C. After this stage, there is little possibility of OH⁻ conduction, and NO₃⁻ conduction starts resulting in high resistance and large n value. There is a model of electro-osmosis that predicts that conduction of large ions show large n values,¹⁷ and this model is consistent with the results shown in Fig. 4a and also the fact that the n value for Nafion in KOH solution is higher than that for Nafion in HNO₃ solution, as shown in Fig. 3a-c. After the measurements, we replaced the aqueous solution at the anode side with a new HNO₃ solution, but conductivity did not recover. After the solution at the cathode side had been replaced with a new HNO₃ solution, the conductivity recovered. After measurements with an aqueous solution of HNO₃, the resistance of the AEM was measured in a KOH aqueous solution, and the resultant resistance (about 36 k Ω) was similar to that of a new

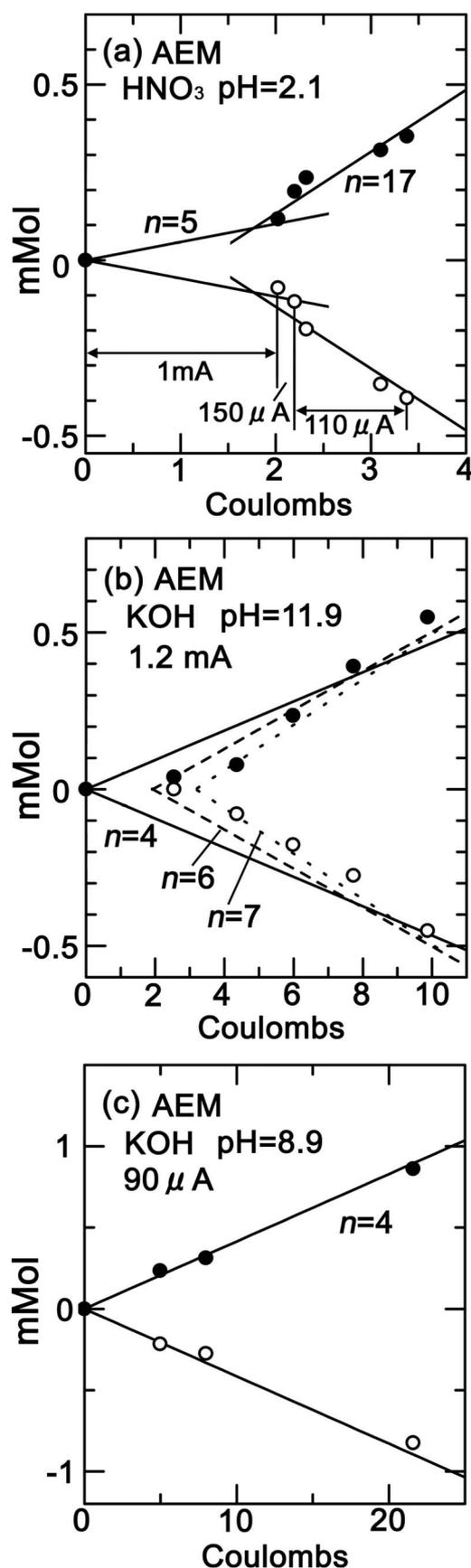


Figure 4. Changes in volumes of aqueous solution at the anode and cathode sides during electrolysis through the AEM. (a) Results with HNO₃ at pH 2.1. (b) Results with KOH at pH 11.9. (c) Results with KOH at pH 8.9. Open and closed circles are results at the cathode and the anode, respectively.

AEM membrane in an aqueous solution of KOH. Thus, the AEM was not damaged during measurements in an aqueous solution of HNO₃, and the decrease in conductivity during measurements in an aqueous solution of HNO₃ was due to the decrease in the number of NO₃⁻ ions at the cathode side.

When KOH solution was used, the resistance was lower and more stable than that in the case of HNO₃, indicating that the conductivity of OH⁻ in an AEM is much better than that of NO₃⁻. Figure 4b shows the results for an AEM immersed in KOH solution obtained by setting the electric current at 1.2 mA throughout. The volume of aqueous solution increased at the anode side and that at the cathode side decreased, indicating that the conductor was OH⁻. Changes in volumes of the aqueous solution were slow below 2 C and became fast above 2 C. Initially, a large amount of OH⁻ existed in the AEM because the AEM was immersed in a 1 M aqueous solution of NaOH before measurements. During OH⁻ conduction in the AEM immersed in a dilute aqueous solution of KOH, the density of OH⁻ in the AEM may decrease and the AEM may absorb water. These may result in a structural change of the AEM, resulting in increases in the value of n above 2 C. The n values were estimated to be 4–7. These values are close to the value of 5 estimated from the results for HNO₃ below 2 C shown in Fig. 4a.

For comparison, water transport was studied for an AEM using a dilute KOH solution at pH 8.9. Because the resistance was extremely high, the electric current was set at 90 μ A and the measurements took about 2 days. The results, presented in Fig. 4c, show an increase and a decrease in the volumes of aqueous solution at the anode and cathode sides, respectively, with the value of n being 4, which is close to that for KOH at pH 11.9 (Fig. 4b). The conductor in this ion conduction is thought to be OH⁻.

The above results indicate that water transport in the cation-exchange membrane and AEM can be studied easily by choosing appropriate aqueous solutions of acids and alkalines with the present apparatus. The resistance and n values were high for Nafion with KOH solution and for the AEM with HNO₃ solution. n values for the AEM with KOH solutions at different pH values were similar. These results indicate that water transport should be measured with the appropriate choice of aqueous solutions, acid solution, and alkaline solution for Nafion and the AEM, respectively, to simulate water transport during the operation of actual PEFCs and SAFCs. In the case of an AEM immersed in HNO₃, OH⁻ conduction occurred only below 2 C, as shown in Fig. 4a. Nevertheless, the water-transport number n during OH⁻ conduction in the AEM could be determined from results below 2 C, indicating a high level of accuracy of the present method. This is mainly because the volume of aqueous solution on each side was minimized to be only 2.5 mL, which is significantly smaller than that for previously reported apparatus. Therefore, errors of measurements due to thermal expansion/shrinkage of the aqueous solution were small in the present method, indicating a wide applicability of the present apparatus for the study of water transport through various membranes immersed in various aqueous solutions of electrolytes.

Various properties of an AEM, including diffusion^{18–25} (diffusion of water, NaCl, ethanol, methanol, and ethylene glycol), uptake of a solvent,^{18–20,22,23} sorption,²⁶ ion conductivity (through a plane and across membranes),^{19,20,22,24–26} ion-exchange capacitance,^{19,20,22,23} and crossover of fuel,^{21,27} have been investigated. The diffusion coefficient of the solvent and that of the fuel, as well as the n value, are important parameters for developing electrolytes for fuel cells with less overflow/drying at electrodes and less crossover of fuels. It has been reported that in many cases the permeability of methanol, ethanol, ethylene glycol, and vanadium ions into an AEM is smaller than that into Nafion.^{19,22–25} In the present study, the n value ranged from 5.5 to 27 for Nafion and from 4 to 17 for the AEM, and it is difficult to compare the n values between Nafion and the AEM. However, the present results indicate that the n value is strongly dependent on the kind of conductor.

In the present study, water transport occurred from the anode to the cathode sides in Nafion, and from the cathode to the anode sides in the AEM regardless of the kind of aqueous solution of electrolytes. These facts guarantee that the direction of water transport is a good indicator to distinguish between a cation-exchange membrane and an AEM.

Conclusions

Water transport in anion conduction through an AEM immersed in aqueous solutions of HNO₃ and KOH was studied, and the results were compared with the results for Nafion immersed in these solutions. The numbers of water molecules that penetrated through the AEM per conduction of one anion were determined to be 17 and 4 in HNO₃ and KOH solutions, respectively. We conclude that measurements should be conducted with an acid solution for Nafion and with an alkaline solution for AEM to simulate water transport in an actual PEFC with proton conduction and in an SAFC with OH⁻ conduction. We have developed a small apparatus to accurately study water transport during ion conduction through various membranes immersed in various aqueous solutions of electrolytes. By using this apparatus, it was possible to study water transport in OH⁻ conduction through an AEM under conditions close to those in an actual SAFC, which is difficult using previously reported methods. It is also possible to determine whether anions or cations are conductors in membranes with unknown properties from the directions of water transport.

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