

Investigation of water transport through membrane in a PEM fuel cell by water balance experiments

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Abstract

Water balance in a polymer electrolyte membrane fuel cell (PEMFC) was investigated by measurements of the net drag coefficient under various conditions. The effects of water balance in the PEMFC on the cell performance were also investigated at different operating conditions. Experimental results reveal that the net drag coefficient of water through the membrane depended on current density and humidification of feed gases. It was found that the net drag coefficient (net number of water molecules transported per proton) ranged from -0.02 to 0.93 , and was dependent on the operating conditions, the current load and the level of humidification. It was also found that the humidity of both anode and cathode inlet gases had a significant effect on the fuel cell performance. The resistance of the working fuel cell showed that the membrane resistance increased as the feed gas relative humidity (RH) decreased. The diffusion of water across Nafion membranes was also investigated by experimental water flux measurements. The electro-osmotic drag coefficient was evaluated from the experimental results of water balance and diffusion water flux measurements. The value of electro-osmotic drag coefficient, ranging from 1.5 to 2.6 under various operating conditions, was in agreement with literature values. The electro-osmotic drag coefficient, the net flux of water through the membrane and the effective drag as a function of operating conditions will also provide validation data for the fuel cell modeling and simulation efforts.

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1. Introduction

Proton exchange membrane fuel cells have attracted great attention in recent years as a promising replacement for traditional engines, primarily due to their high power density and ultra-low emission features [1–3]. Though PEM fuel cell technology has undergone significant development over the past decade, high performance with increased stability and reliability as well as low cost are yet to be achieved before fuel cells can replace internal combustion engines. One of the critical problems and design issues of PEMFCs is water management because the membrane's hydration in PEMFCs determines the performance and durability of a PEMFC. If the membrane is not properly hydrated, it exhibits higher ionic resistance and can

even be irreversibly damaged in extreme cases. Therefore, polymer membrane materials used in PEMFCs must be hydrated in order to maintain high proton conductivity, and at the same time, excess water must be removed to prevent flooding. Membrane hydration is affected by the water transport phenomena in the membrane itself, which in turn is affected by the condition of the inlet gases and the operating parameters of the fuel cell. Therefore, it is very important to maintain an optimal water balance during the operation of PEMFCs. The water balance must be maintained to ensure that optimal performance is achieved.

Water is mainly transported inside the membrane by electro-osmotic drag (water molecules are dragged by the current-carrier protons from the anode to the cathode), back diffusion (caused by the process in which water is transferred into the membrane due to the water concentration gradient from the cathode to the anode), and convection (due to pressure gradients in the fuel cell). However, the convection effect is generally negligible

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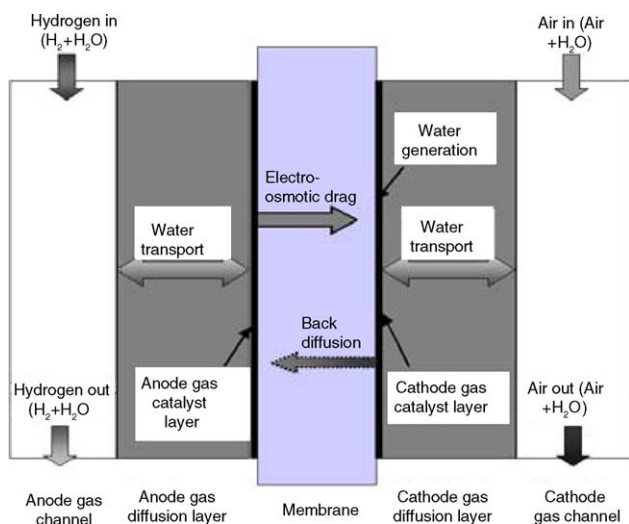


Fig. 1. Schematic of the water transport process in typical hydrogen PEM fuel cell.

compared to the effects of electro-osmotic drag and the back diffusion, due to a very low membrane hydraulic permeability. Fig. 1 is a schematic of the water transport process in a typical hydrogen PEM fuel cell. The two main water transport processes in the membrane are electro-osmotic drag and back diffusion; these affect the water balance in a PEMFC and determine the membrane hydration. Because the water level in a fuel cell strongly affects not only the membrane properties, but also reactant transport and electrode reaction kinetics, maintaining an optimal water balance between the anode and cathode is important in achieving good cell performance. The electro-osmotic coefficient is the transport number of water in the membrane and is a measure of the number of water molecules that are carried with each proton moved from the anode to the cathode. The electro-osmotic coefficient mainly depends on the temperature and water content. The electro-osmotic coefficient has been measured by various techniques such as open-circuit potentials [4], streaming potentials [5] and direct methanol FC analysis [6–8]. LaConti et al. [9] used a pair of Ag/AgCl electrodes to drive protonic current across the membrane in contact on both sides with a 0.1 M HCl aqueous solution. The equivalent water drag coefficient measured at room temperature was 3.5–4.0 $\text{H}_2\text{O}/\text{H}^+$ for a membrane pretreated by boiling at 100 °C. Zawodzinski et al. [10,11] studied the H_2O uptake and transport properties of Nafion 117 membranes equilibrated with liquid water at 30 °C. The electro-osmotic drag coefficient was determined by the membrane H_2O content. Fuller et al. [12] measured the transport number of water in Nafion 117 membrane over a wide range of water content using a concentrated cell. The results showed that the transport number of water was about 1.4 for a membrane equilibrated with saturated water vapor at 25 °C, and it decreased slowly as the membrane was dehydrated, falling sharply towards zero as the concentration of water approached zero. Ren et al. [6] reported a method for determining the water drag coefficient of an Nafion 117 membrane in an operating DMFC. The net water transport in a PEMFC, characterized by the effective drag coefficient, is relatively easy to measure. The net water transport

is commonly characterized using the net water transport coefficient, which is defined as the average number of water molecules dragged by one proton from the anode to the cathode side. The net water transport coefficient can be affected by factors like current density, temperature, feed gas humidity, gas pressure, gas stoichiometry, membrane materials, water content of the membrane and flow field pattern of the fuel cell. The characteristics of the gas diffusion layer also affect the water transport in the fuel cell by diffusion and convection.

The production of water at the cathode results in a gradient in the water activity across the Nafion membrane. This gradient will result in the diffusion of water from the cathode to the anode. The water diffusion coefficient has been measured by various techniques including NMR, streaming potential, water-flux measurements, and others [13–21]. Morris and Sun [21] measured the density and dimensional changes of Nafion 117 as a function of the water content. They found that the diffusion coefficient of water in Nafion and the electrical conductivity of Nafion were strongly dependent on the water content. Zawodzinski et al. [11] measured the diffusion coefficient of ^1H as a function of the membrane's water content by nuclear magnetic resonance (NMR) techniques. Fuller [13] measured the Fickian diffusion coefficient of water by measuring the flux across Nafion membranes equilibrated with water on one side and flowing nitrogen gas on the other. Nguyen and White [22] derived an expression for the Fickian diffusion coefficient of water in Nafion, based on fuel cell performance data in the literature and the electro-osmotic drag measurements of Springer et al. [23]. As a function of water content, the diffusion coefficient is expected to decrease as the water content decreases because the water is more tightly associated with the sulfonic acid sites. Motupally et al. [24] measured the water diffusion coefficient by the water flux method. They found that the diffusion of water across Nafion membranes was a function of the water activity gradient using experimental data. The gradient in the activity of water across the membrane was varied by changing the flow rate and pressure of nitrogen gas on one side of the membrane.

Water transport through working PEMFCs and its effect on the performance of PEMFCs has been examined by theoretical [25–32] and experimental methods [33–37]. Bernardi and Verbrugge [25–27] developed a model to determine fuel cell operating conditions that would result in optimal balance between water that is formed in the fuel cell reaction and that must be removed to prevent flooding. The modeling results revealed that humidification of reactant gases could be adjusted as the current density was varied to accommodate the changing demand for water in the fuel cell. The analytical results also identified conditions under which reactant transport limitations govern the behavior of the fuel cell. Nguyen and White [22] developed a water and heat management model for fuel cell and used the model to investigate the effectiveness of various humidification designs. Their model accounts for water transport across the membrane by electro-osmosis and diffusion, heat transfer from the solid phase to the gas phase, and latent heat associated with water evaporation and condensation in the flow channels. Their modeling results showed that, at high current density ($>1 \text{ A cm}^{-2}$), ohmic loss in the membrane accounted

for a large fraction of the voltage loss in the cell, and back diffusion of water from the cathode side of the membrane was insufficient to keep the membrane hydrated (i.e., conductive). Consequently, to minimize the ohmic loss, the anode stream must be humidified, and when air is used instead of pure O₂, the cathode stream must also be humidified. Yi and Nguyen [28] developed an along-the-channel model for evaluating the effects of various design and operating parameters on the performance of a proton exchange membrane (PEM) fuel cell. Results from the model showed that the performance of a PEM fuel cell could be improved by anode humidification and positive differential pressure between the cathode and anode to increase the back transport rate of water across the membrane. Okada et al. [5,14] used a linear transport equation based on the diffusion of water and the electro-osmotic drag to analyze water concentration profiles in the membrane. Eikerling et al. [29] proposed a model accounting for the electro-osmotically induced drag of water from anode to cathode and the counter flow with a hydraulic pressure gradient. Dutta et al. [30] reported a three-dimensional numerical simulation of straight channel PEM fuel cells. The model results revealed that the inclusion of a diffusion layer created a lower and more uniform current density compared to cases without diffusion layers. The results also showed that the membrane thickness and cell voltage have a significant effect on the axial distribution of the current density and net rate of water transport. The predictions of the water transport between cathode and anode across the width of the flow channel showed the delicate balance of diffusion and electro-osmosis and their effect on the current distribution along the channel. Wang et al. [31] developed a model with two-phase flow and transport in the air cathode of proton exchange membrane fuel cells. The model was able to handle the situation where a single-phase region co-exists with a two-phase zone in the air cathode. Janssen [32] presented a steady-state two-dimensional fuel cell model. The water transport in a proton exchange membrane fuel cell was described and discussed. The inclusion of the liquid water transport into the model turned out to be essential for explaining their experimental results on the effective drag coefficient and its dependence on operating conditions as well as on variations of the components that constitute the membrane electrode assembly. Siegel et al. [33] were able to draw a conclusion about the effect of gas moisture content on the performance of their fuel cells. Commer et al. [34] used continuum theory and molecular dynamics (MD) computer simulations to investigate the effect of water content on proton transport in polymer electrolyte membranes.

Experimental studies on water transport in working fuel cells have been mainly investigated by bulk measurements [35–39]. Jansen and Overvelde [35] examined the water transport in the proton-exchange-membrane fuel cell by measurements of the effective drag coefficient. Zawodzinski et al. [10,11] studied the H₂O uptake and transport properties of Nafion 117 membranes at 30 °C. Sena et al. [36] examined the effect of water transport in a PEFC at low temperatures operating with dry hydrogen. In their work, an experimental study of the polarization response of a H₂/O₂ PEMFC was carried out at low temperatures as a function of the membrane thickness. Andreaus and Scherer [37]

studied the water balance in a solid polymer electrolyte and its effects on the performance of a polymer electrolyte fuel cell by electrochemical impedance spectroscopy (EIS) and the current pulse method (CPM). Choi et al. [38] determined the net electro-osmotic drag coefficient of Nafion 115 and Hanwha membrane by measurement of the fluxes of water discharged from anode and cathode at different current densities. Some researchers also reported water transport in working fuel cells by detailed distribution measurements [39–41]. An in situ neutron imaging technique has been used for evaluation of water management systems in operating PEM fuel cells [39,40]. Bellows et al. [40] used neutron radiography technique to study water distribution in membranes. Their results gave indication of the existence of water gradients. Mench et al. [41] measured water distribution in a segmented polymer electrolyte fuel cell using an on-line gas chromatograph. Mennola et al. [42,43] studied mass transport phenomena in free-breathing fuel cells using experimental and modeling methods.

The aim of the present work was to study the water transport in the membrane of a PEM fuel cell under a wide range of operating conditions. The experiments was designed to explain the observed behavior regarding the net water transport. The diffusion of water across Nafion membranes was also investigated by experimental water flux measurements. The water transport parameter and electro-osmotic drag coefficient will be evaluated from the experimental results of water balance and diffusion water flux measurements. A relatively small number of researchers have examined the effect of humidification through experiments. However, these results are not complete. In this paper, the effects of inlet gas humidification, current density and feed gas pressure on water transport in fuel cell will be investigated and discussed. The effect of inlet gas humidification, pressure on fuel cell performance will also be presented and discussed.

2. Experimental

2.1. Fuel cell test system and fuel cell operation conditions

The experiments were conducted on a fuel cell test-bed system, built in-house. A 25 cm² fuel cell (hardware from Fuel Cell Technologies Inc., and a 25 cm² MEAs from E-Tek with Nafion 117 and 1 mg cm⁻² platinum catalyst loading) were used in all experiments.

The fuel cell performance was evaluated at an operating temperature of 80 °C, pressure of 1 atm, and at differing humidity levels for both the inlet gases. Pure hydrogen and air were used as reactant gases, and were humidified by passing each gas stream through an external humidifier. The stoichiometries of the feed gases were both kept at 2 except as stated. The relative humidity of air was varied from 10% to 100%, while the humidity of hydrogen was changed from 0% to 100%. Temperatures of gas lines between humidifiers and the cell, and between the cell and dew point meters were maintained at 95 °C. The ac impedance was measured using a frequency generator/analyzer (Solartron, FRA 1260). Impedance spectra were obtained at frequencies between 10 kHz and 0.1 Hz with 10 steps per decade.

2.2. Measurement of water flux in a PEM fuel cell with current for net-drag coefficient

The net electro-osmotic drag coefficient is defined as the number of net water molecules transported from anode to cathode per proton and it was calculated from water mass balance in the PEM fuel cell. To eliminate any water transport by hydraulic pressure difference across the membrane, the back pressures on the anode and cathode compartments were kept equal at 1 atm. Water discharging from both the anode and the cathode effluent streams was condensed and trapped in a U-shaped drying tube with Dryerite® (anhydrous CaSO₄, W.A. Hammond Drierite Co.) at the end of each tube.

2.3. Measurement of water flux through in a PEM fuel cell without current

The water flux measurements without current were carried out in the fuel cell described previously. Water preheated to 80 °C was circulated through one side of the fuel cell and nitrogen passed through the other side. The measured water flux data were independent of the temperature of the inlet nitrogen stream. For experimental simplicity, unheated nitrogen was passed through the gas side. Water was delivered at the other side with a fixed rate of 50 mL min⁻¹. The flow rate of hydrogen was controlled at a range of 0–300 mL min⁻¹ at standard temperature and pressure. The pressure of each side of the cell was controlled with a back-pressure regulator and recorded with pressure gauges on the outlet and inlet of either side of the membrane. All experiments were conducted under conditions of pressure on both the sides of the membrane maintained approximately the same. The hydrogen gas with differing relative humidity was fed to the fuel cell anode. To measure the amount of water diffusion across the membrane, water carried out by hydrogen was condensed and trapped in a U-shaped dry tube, as described in Section 2.2.

3. Results and discussion

3.1. Net water transport through membrane in a PEM fuel cell under various conditions

3.1.1. Current density on water transport through membrane

Water transport in the membrane by electro-osmotic drag and back diffusion is usually affected by fuel cell temperature, current density, humidity of feed gases and membrane water content. The effect of current density on net electro-osmotic drag coefficient are investigated in the present paper. The flux of water discharged from anode and cathode at different current densities were measured and the net electro-osmotic drag coefficient of Nafion 117 membrane was calculated (see Fig. 2). The net electro-osmotic drag coefficient decreased sharply with current density, but it reached a nearly constant value when the current density was over 400 mA cm⁻². As the current density increased, the flow of protons and water from the anode to cathode increased linearly with current density and protons compete for water molecules. At the same time, water was generated

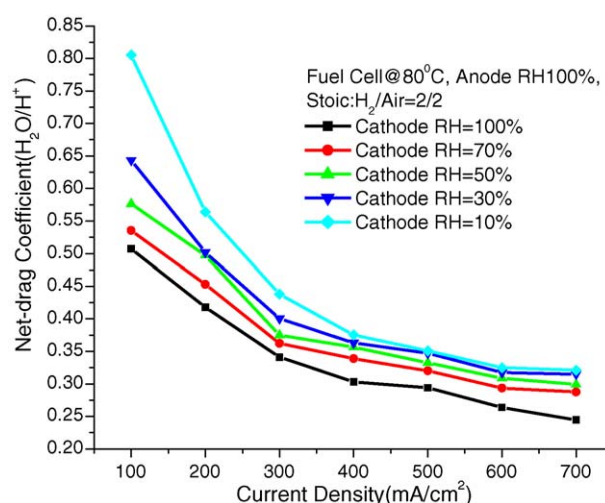


Fig. 2. Net electro-osmotic drag coefficient at various current densities and air humidity.

at the cathode catalyst layer by the oxygen reduction reaction (ORR). The produced water in cathode catalyst layer may diffuse through the membrane from the cathode to the anode (see Fig. 1). The quantity of produced water by ORR in cathode catalyst layer also increased linearly with current density. The water concentration gradient in the membrane close to the cathode side increased with current density, and therefore, the back-diffused water from cathode to anode increased. This is why the net electro-osmotic drag coefficient decreases with current density. The balance between electro-osmotic drag and back diffusion determines hydration and proton conductivity of membrane. In their two-dimensional PEMFC model, Nguyen and White [22] stated that, at high current density, the transport from the anode by electro-osmotic drag exceeds transport to the anode by back diffusion from the cathode and the membrane will dry out. As the membrane becomes dehydrated, the membrane pores shrink, which further limits the back diffusion of water. For this reason, Nguyen and White [22] concluded that water transport due to back-diffusion is not sufficient to prevent membrane dehydration.

3.1.2. Humidity of feed gas on water transport through membrane

The effects of relative humidity of feed gases on net-drag coefficient are shown in Figs. 2 and 3. Fig. 2 is the result of net electro-osmotic drag coefficient at various current densities and air humidity when the hydrogen feed was fully saturated. When almost dry (10%RH) air was supplied to the cathode, while fully saturated H₂ was feeding at the anode side, the cathode was humidified mainly by product water that diffuses from the cathode/membrane interface to the channel and also by water delivered by the electro-osmotic process from the anode. When the relative humidity of the airflow increased from 10% to 100% at 80 °C, the water content in the air increased and the water gradient through the membrane increased. Therefore, the water net drag coefficient of the membrane decreased due to the increasing of the water back flux from the cathode to the anode. The net electro-osmotic drag coefficient was larger when air feed

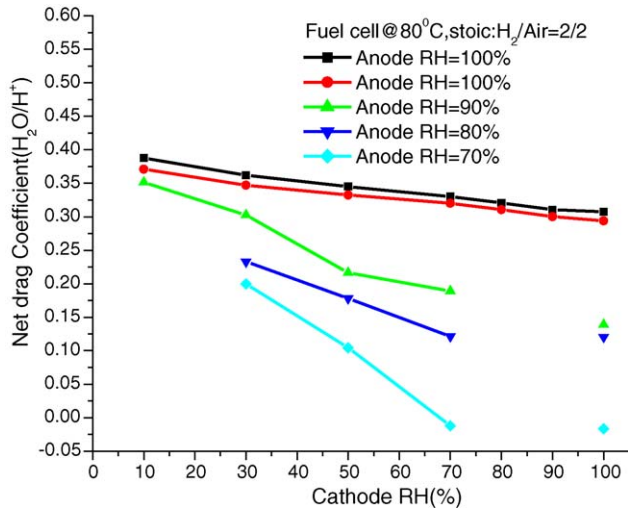


Fig. 3. Net electro-osmotic drag coefficients at hydrogen and air humidity at 500 mA cm^{-2} .

was maintained at low humidity at low current density. This is because the water transported by back-diffusion is low when less water is supplied at the cathode side. When the cathode was humidified, the water supply for the membrane at low current densities was achieved via the cathode, but the contribution of the anode became more important as current density was gradually increased. Jansen and Overvelde [35] were able to draw more general conclusions about the humidification of the inlet gases at higher temperatures in their measurement of the net drag transport in a PEMFC. They considered drag to be the sum of the water transport phenomena, and measured drag by comparing the water content at the inlets and outlets of both gas streams. Jansen and Overvelde [35] used 50 cm^2 membrane electrode assemblies (MEAs) operating between 60°C and 80°C with cathode pressures of 1.5–3 bar and anode pressures of 1.5–4 bar. The gases used were either fully saturated or dry. At 60°C , the fuel cell was able to operate with both inlet gases in the dry state. The net rate of water flow was very high toward the anode and water was drawn away from the cathode. In this work, at 80°C , the membrane became dehydrated when dry oxygen was used, regardless of the saturation level of the hydrogen. The use of dry hydrogen resulted in a very large negative drag that could potentially dry out the cathode, even when saturated oxygen was used. Similar to Jansen and Overvelde, Morner and Klein [44] used only two points for evaluating the effect of inlet gas humidity and found that use of humidified air improved stack performance, particularly at higher stack temperatures.

Fig. 3 shows the calculated values for the net drag coefficient at various hydrogen and air humidity at the current density of 500 mA cm^{-2} . The results show a dramatic decrease of the effective drag coefficient when drier hydrogen was fed to the anode, while saturated air was fed to the cathode. The water transported from the cathode to the anode results in preventing the dehydration of the membrane since there is sufficient water in the cathode due to product and drag water. The amount of water needed to saturate the anode is what determines the drag coefficient in these cases. Due to the fast back diffusion to the

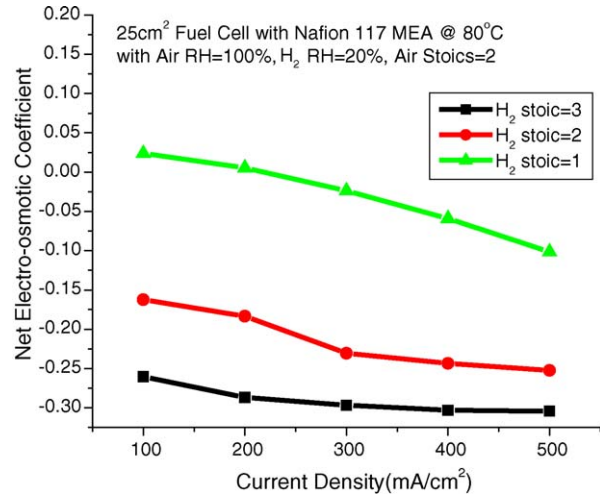


Fig. 4. Effect of hydrogen stoichiometry on net drag coefficient.

anode, the water concentration at the anode/membrane interface becomes increased, and in turn, reduces the water content at the membrane/cathode catalyst interface. Low humidity of hydrogen at the anode side means that there is less water feed into the anode of the fuel cell, and less water transport to the membrane will lead to partial dehydration of membrane. A low electro-osmotic drag coefficient means less water was transported by electro-osmotic drag but more generated water was drawn to the anode side. When feed hydrogen humidity is so low and not sufficient for saturated anode, a negative net drag value may be obtained. In the case of dry air being fed to the cell, the back flux is much smaller and the humidity at the anode will be higher, and

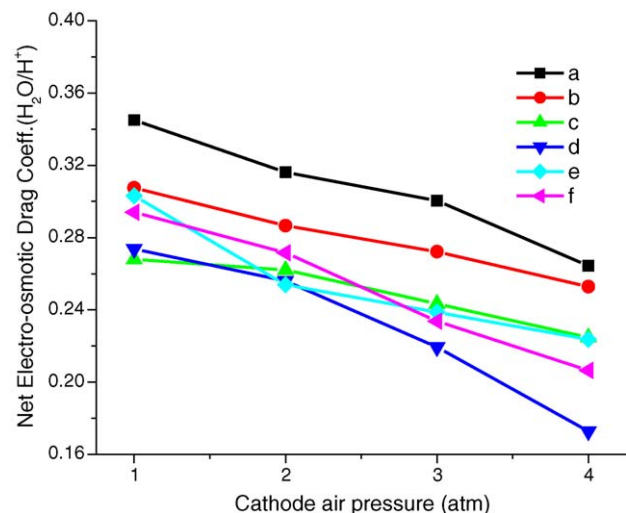


Fig. 5. Effect of pressure on water net electro-osmotic drag coefficient in a PEM fuel cell. Fuel cell@ 80°C , stoic.: $\text{H}_2/\text{air}=2/2$. ((a) current density = 500 mA cm^{-2} , anode humid.: 90%, cathode humid.: 100%, anode pressure: 1 atm; (b) current density = 500 mA cm^{-2} , anode humid.: 100%, cathode humid.: 100%, anode pressure: 1 atm; (c) current density = 500 mA cm^{-2} , anode humid.: 100%, cathode humid.: 100%, anode pressure: 2 atm; (d) current density = 500 mA cm^{-2} , anode humid.: 100%, cathode humid.: 100%, anode pressure: 3 atm; (e) current density = 400 mA cm^{-2} , anode humid.: 90%, cathode humid.: 100%, anode pressure: 1 atm; (f) current density = 400 mA cm^{-2} , anode humid.: 100%, cathode humid.: 100%, anode pressure: 1 atm).

therefore the effect of a water-content-dependent permeability will be smaller.

Fig. 4 shows the effect of hydrogen stoichiometry on the net drag coefficient. Experimental cases included dry inlet hydrogen (20% RH) used at the anode and fully saturated air at the cathode. In the case of dry hydrogen/saturated air, a higher hydrogen stoichiometry resulted in a low net drag coefficient. More water was supplied to dry hydrogen when operating with dry hydrogen; this means that more product water at membrane/cathode catalyst interface was transferred from cathode to anode. Therefore, more net water was transferred from the cathode to the anode side with increasing flux of dry hydrogen. When the H_2 stoichiometry was decreased, the drag coefficient was less negative. The results obtained for a dry H_2 gas suggest that a severe drying out of the membrane and catalyst layers can occur near the anode inlet.

3.1.3. Pressure of feed gas on water transport through membrane

Water can be transported by convection due to pressure gradients in the fuel cell. Though water transport through convection is very small compared to that of electro-osmotic drag and back diffusion, the effect of pressure on the water net electro-osmotic

drag coefficient was examined in a PEM fuel cell (Fig. 5). A small reduction in the net drag coefficient was found when a pressure difference was applied. It was found that a higher pressure at the cathode side would result in greater saturation of the gas stream; in this case, a slight drop of net drag coefficient is expected. An increase in hydrogen pressure at the anode side means that there is less water fed into the anode of the fuel cell, and less water transport to the membrane, leading to dehydration of the membrane. This result is similar to that of feeding a gas with low humidity.

3.2. Diffusion water flux through the membrane and evaluation of electro-osmotic drag coefficient

The water flux across the Nafion membrane in a PEMFC fed with humidified H_2 at the anode and liquid water at the cathode is shown in Fig. 6. At various hydrogen flow rates, the water flux was measured at a temperature of 80°C and a pressure of 1.0 atm. The measured water flux across the membrane exhibited a linear dependence on the hydrogen flow rate. The flux of water diffusing across the membrane increased with an increase in the hydrogen flow rate. For example, the flux of water increased from $0.05\text{ g min}^{-1}\text{ cm}^{-2}$ to $0.25\text{ g min}^{-1}\text{ cm}^{-2}$ as the flow rate

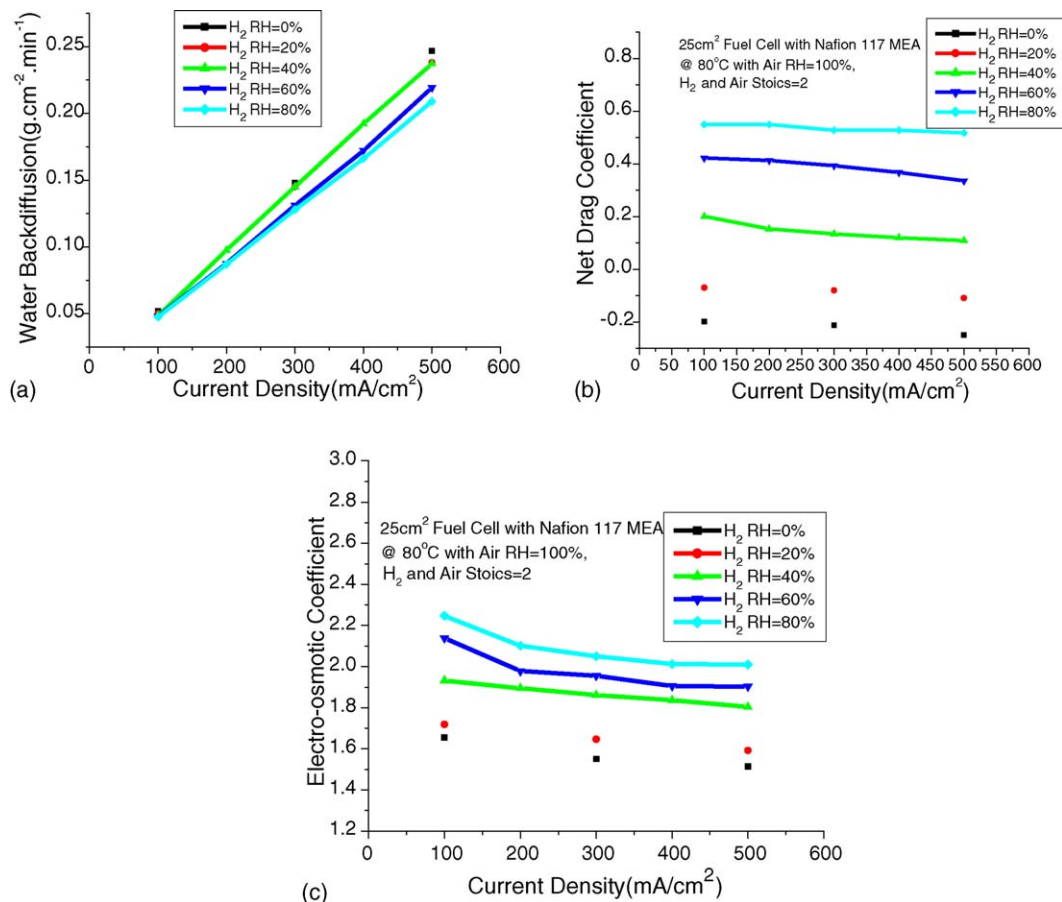


Fig. 6. Water transport properties of membrane in a PEMFC at 80°C . (a) Water flux across a N117 membrane in a H_2 /air fuel cell. The cell was fed with various humidified H_2 (1 atm, RH varied from 0% to 80%) at the anode and liquid water (80°C) at the cathode. (b) Net electro-osmotic drag coefficient at various current densities. The fuel cell was fed with various humidified H_2 (1 atm, RH varied from 0% to 80%) at the anode and fully saturated air at the cathode at 80°C . (c) Electro-osmotic drag coefficient evaluated from the results (a) and (b).

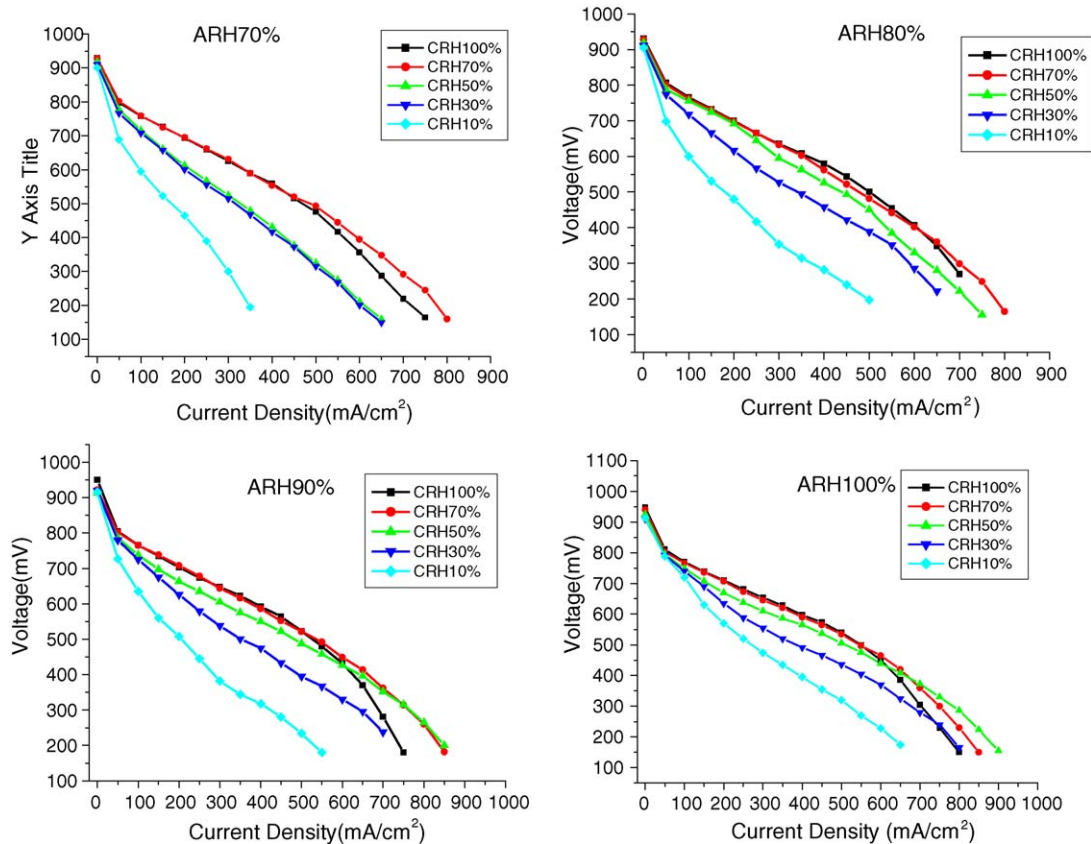


Fig. 7. Polarization curves for the cell at different air humidities.

of hydrogen increased from $34.82 \text{ mL} \cdot \text{min}^{-1}$ (100 mA cm^{-2}) to $174.1 \text{ mL} \cdot \text{min}^{-1}$ (500 mA cm^{-2}). Water diffused across the Nafion membrane from the liquid side to the gas side due to a gradient in the activity of water. At a constant temperature, an increase in the hydrogen flow rate resulted in an increase in the total flux of water across the membrane due to the decrease in the water activity in equilibrium with the membrane on the gas side. The beneficial effect of this backward water diffusion is to keep the membrane at the anode side from experiencing severe dehydration during fuel-cell operation.

Fig. 6 also includes the results for the net electro-osmotic drag coefficient (Fig. 6b) at various current densities while the fuel cell was fed with various humidified H_2 (1 atm, RH varied from 0% to 80%) at the anode and fully saturated air at the cathode at 80°C . The electro-osmotic drag coefficient (Fig. 6c) was evaluated from the experimental results of water balance (Fig. 6b) and diffusion water flux measurements (Fig. 6a). The measurement of water electro-osmotic drag coefficients in a Nafion[®] 117 (N117) membrane has been reported in several journal articles. LaConti et al. [9] reported a water drag coefficient of $3.5\text{--}4.0 \text{ H}_2\text{O}/\text{H}^+$ for a membrane at room temperature using a pair of Ag/AgCl electrodes to drive protonic current across the membrane, which was in contact on both sides with a 0.1 M HCl aqueous solution. Zawodzinski et al. [10] reported a water drag coefficient of $2.5 \text{ H}_2\text{O}/\text{H}^+$ for a pre-swollen N117 membrane at room temperature by measuring the water flux across a Pd(H)/N117/Pd(H) cell under constant-current condi-

tions. Okada et al. [5] reported a similar value for the H^+ -form N117 membranes immersed in HCl solutions using streaming potential measurements. Ren et al. [5,6] reported the water electro-osmotic drag coefficients of an N117 membrane in an operating DMFC from 2.0 at 15°C to 5.1 at 130°C . The electro-osmotic drag coefficient determined in this work ranged from 1.5 and 2.6 under operating conditions and was in agreement with the literature results.

3.3. Effects of humidity on fuel cell performance and cell resistance by ac impedance

The tested air humidity levels ranged from 10% to 100% and for hydrogen were 70%, 80%, 90% and 100%. Polarization curves were obtained for different relative humidity levels of the air and hydrogen, respectively. Fig. 7 shows the polarization curves obtained at low, medium, and high hydrogen relative humidity levels with a low air relative humidity. The best performance observed for the cases with low air humidity was the one with high hydrogen humidity level. This observation is consistent with the results of Nguyen and White [22] who found that, at high current density, the transport from the anode by electro-osmotic drag exceeded transport to the anode by back diffusion from the cathode, thus leading to membrane dehydration and performance degradation. Low humidity air can exacerbate this effect by reducing the rate of back diffusion from the cathode. Humidification of the anode gases helps counteract this effect

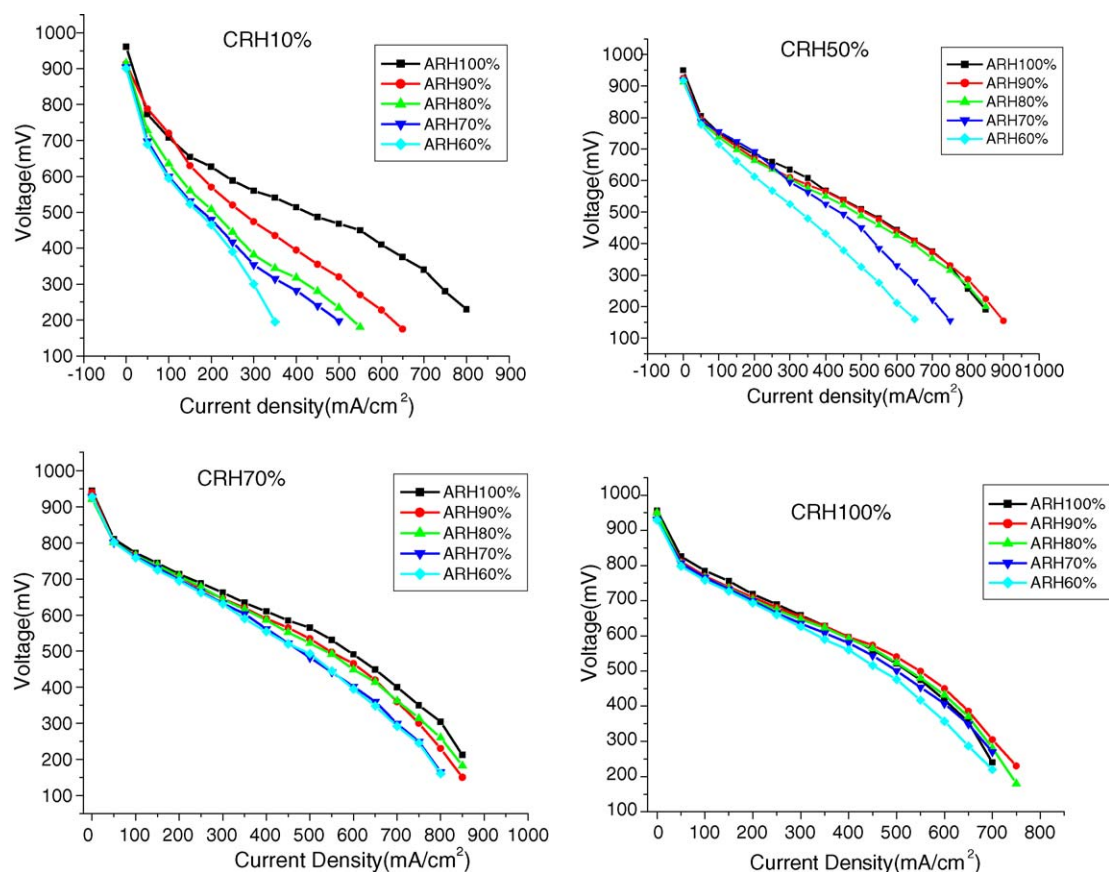


Fig. 8. Polarization curves for the cell at different hydrogen humidities.

leading to higher performance at high levels of anode humidification.

Fig. 8 shows the polarization curves for the cell at different hydrogen humidities. The trend toward improved performance with higher humidity levels of hydrogen was not observed. Similarly, for high air relative humidity levels, the performance was only marginally improved with increased hydrogen humidification. These results suggest that with the medium and high levels of air humidification, there was sufficient back diffusion to keep the membrane hydrated and that further humidification of the anode did not significantly improve the performance. Overall, the best performance occurred at low air relative humidity and high hydrogen humidity.

Potential losses in the operation of a PEMFC include activation, ohmic, and mass transport over-potentials at both the anode and the cathode. For the calculation of these overpotentials, an accurate description of the net flux of water across the membrane is essential to evaluate the hydration of the membrane in a working PEMFC. The conductivity of the membrane and the ohmic overpotential of the PEMFC are governed by the hydration level of the membrane, while the hydration of the membrane depends on the net amount of water transported across the membrane. In this work, the membrane resistance was measured to compare with water transport experimental results. Many groups have previously studied the conductivity of Nafion membranes by ac impedance spectroscopy or DC techniques using either two or four electrodes, as well as by some other techniques [45–55].

A few groups have looked at the performance of the membrane in situ in the PEMFC using ac and current pulse technique. The membrane resistance reported here was obtained by using the ac impedance method. The contact resistance of the tested cell was negligible. The impedance of the fuel cell was measured under conditions of varying feed gas humidity at current density levels of 100 to 500 mA cm⁻². The measurements were performed at a cell temperature of 80 °C. The humidity of the air was varied from 30% to 100% while hydrogen humidity was 80% and 100%. Fig. 9 shows the results of the fuel cell internal resistance as a function of feed gas humidity at 80 °C. The resistance of the working fuel cell in Fig. 9 shows that the membrane resistance was a strong function of feed gas relative humidity and increased as the relative humidity decreased. The cell internal resistance increased when the air inlet RH decreased from 100% to 70%, 50% and to 30%, with the hydrogen inlet relative humidity maintained at 100%, and the resistance changed from 0.189 Ω cm² to 0.191, 0.264 and 0.376 Ω cm² at 400 mA cm⁻². The membrane ionic resistance increased slightly as the hydrogen inlet relative humidity was reduced from 100% to 80% with the air inlet RH maintained between 100% and 70%. However, when decreasing the hydrogen inlet RH from 100% to 80%, while reducing the air inlet relative humidity to 50% and 30%, the ionic resistance increased significantly from 0.263 and 0.376 Ω cm² to 0.383 and 0.517 Ω cm² at 400 mA cm⁻², respectively.

Fig. 10 shows the effect of air pressure on the polarization performance. An increase in the pressure from 1 atm to 4 atm

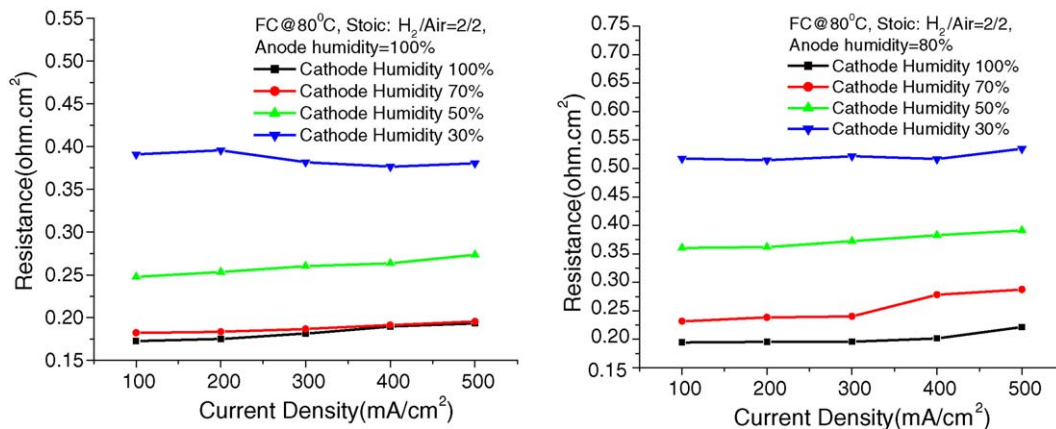


Fig. 9. Fuel cell internal resistance at different feed gas humidities.

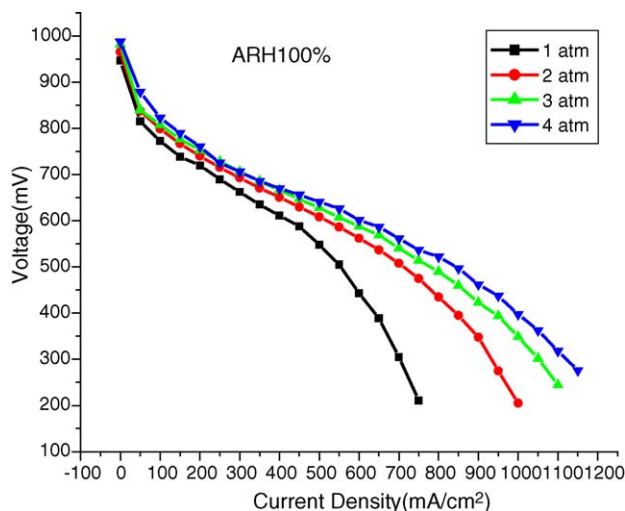


Fig. 10. Effect of air pressure on fuel cell performance.

resulted in a significant improvement in performance, mainly due to the increase in oxygen partial pressure. The vapor partial pressure at the cathode was decreased when feed air pressure increased.

4. Conclusions

Water balance in a polymer electrolyte membrane fuel cell (PEMFC) was investigated by measurements of the net drag coefficient as a function of operating conditions. Experimental results revealed that the net drag coefficient of water through the membrane depended on the current density and humidification of feed gases. Net drag coefficients (net number of water molecules transported per proton) ranging from 0.93 to -0.20 were found, under operating conditions and was found to change with changes in the current and type of humidification. The electro-osmotic drag coefficient was evaluated from the experimental results of water balance and diffusion water flux measurements. The value of electro-osmotic drag coefficient was found to range between 1.50 and 2.60 under operating conditions. Obtained values were in agreement with values reported previously in the literature. It was also found that the humidity

of both anode and cathode inlet gases had a significant effect on fuel cell performance. The experimental results showed that a decrease in the cathode relative humidity has a more detrimental effect on cell performance compared to a decrease in the anode humidity. The resistance of the working fuel cell showed that membrane resistance was a strong function of feed gas relative humidity; it increased when decreasing relative humidity. Increasing the pressure from 1 atm to 4 atm resulted in a significant improvement in performance. The experimental results can be used to define conditions of correct hydration of the membrane.

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