

Short communication

Preparation of Pt/zeolite–Nafion composite membranes for self-humidifying polymer electrolyte fuel cells

Dong-Hoon Son, Raj Kishore Sharma, Yong-Gun Shul, Hansung Kim*

Department of Chemical Engineering, Yonsei University, 134 Shinchon-Dong, Seodaemun-gu, 120-749 Seoul, Republic of Korea

Received 29 August 2006; accepted 19 November 2006

Available online 8 January 2007

Abstract

A novel Pt/zeolite–Nafion (PZN) polymer electrolyte composite membrane is fabricated for self-humidifying polymer electrolyte membrane fuel cells (PEMFCs). A uniform dispersion of Pt nanoparticles with an average size of 3 nm is achieved by ion-exchange of the zeolite HY. The Pt nanoparticles embedded in the membrane provide the catalytic sites for water generation, whereas the zeolite HY-supported Pt particles absorb water and make it available for humidification during cell operation at elevated temperature. Compared with the performance of ordinary membranes, the performance of cells with PZN membranes is improved significantly under dry conditions. With dry H₂ and O₂ at 50 °C, the PZN membrane with 0.65 wt.% of Pt/zeolite (0.03 mg Pt cm⁻²) gives 75% of the performance obtained at 0.6 V with the humidified reactants at 75 °C. Impedance analysis reveals that an increase in charge-transfer resistance is mainly responsible for the cell performance loss operated with dry gases.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Polymer electrolyte fuel cells; Platinum/zeolite; Self-humidification; Nafion; Composite membrane

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted strong attention as next-generation power sources for mobile, portable and residential applications [1–3]. Currently, PEMFC systems employ perfluorosulfonic acid membranes, such as Nafion produced by Du Pont, as an electrolyte membrane. In order to maintain high proton conductivity in the membrane, it should be in hydrated state at the operating temperature because of the hydrophilic nature of the sulfonic acid groups attached to the polymer backbone [4,5]. This is generally achieved by humidifying reactant gases prior to their entry into the cell and by using the water produced in the cell reaction. Since an external humidification method makes the system complicated and decreases the energy efficiency, operation of a PEMFC without a humidification sub-system is considered as one of the most promising application technologies. Therefore, current research efforts are focused on endowing the membrane with a self-humidification ability [6,7].

To maintain the level of water content in the membrane during cell operation with dry reactants, the preparation of a composite membrane containing Pt particles has been proposed. In this case, the self-humidifying action essentially involves three steps, namely: (i) permeation of H₂ and O₂ through the membrane; (ii) internal absorption of reactant gases on embedded Pt particles; (iii) recombination of internally absorbed H₂ and O₂ on Pt catalytic sites [8]. Several methods have been proposed to incorporate Pt particles into a Nafion membrane. One approach is to disperse Pt nanocrystals in the membrane by the equilibrium impregnation reduction method [9,10]. This procedure involves intrinsic problems such as the presence of a considerable amount of residual impurities and the difficulty in controlling the Pt loading. Platinum particles have also been prepared by the sputtering method [11]. Liu et al. [12] produced a self-humidifying composite membrane by casting a mixture of Nafion solution and Pt/C or Pt black catalyst on to a porous PTFE film. Unfortunately, however, the presence of Pt or Pt/C through the membrane contributes to the formation of an electron conducting path and increases the risk of short-circuit formation and fire within the fuel cell [13].

The self-humidification performance of membranes has been improved further by introducing hygroscopic materials such as

* Corresponding author. Tel.: +82 2 2123 5753; fax: +82 2 312 6401.
E-mail address: elchem@yonsei.ac.kr (H. Kim).

ZrP, SiO₂ and TiO₂ [9,14–16]. These materials are expected to retain the water produced at the Pt particles that results in enhanced cell performance under non-external humidification. Despite the positive effect of hygroscopic materials, their concentration and distribution in the membrane remained critical in order to obtain optimum cell performance.

In an attempt to overcome the problem of humidification under dry gas conditions, we have proposed a novel Pt/zeolite–Nafion (PZN) self-humidifying membrane. Zeolite is a microporous crystalline solid with a well-defined structure which consists of silicon, aluminum and oxygen. It has been widely used as a non-conducting catalyst support because the ion-exchange capability of zeolite makes it possible to synthesize nanoscale metal particles [17,18]. In addition, the zeolite material contains acidic protonic entities on its surface, which makes it more hydrophilic than carbon [19]. Therefore, it is expected to behave also as a water reservoir. Nafion–zeolite composite membranes have been studied earlier for their molecular-sieving properties and selective transport of hydrogen ions over methanol molecules [20]. On the other hand, they have rarely been applied for the self-humidification of PEMFCs. In the present work, a novel Pt/zeolite–Nafion composite membrane is fabricated and demonstrated for as a means for self-humidifying PEMFCs. The effect of Pt/zeolite loading and performance of the membrane with respect to the operating conditions are discussed in detail.

2. Experimental

2.1. Membrane preparation

For Pt-exchanged zeolites, 3 g of zeolite HY was washed with 800 cm³ of de-ionized water and dried at 383 K for 2 days. The zeolite powder was then dispersed in 1000 cm³ of water and a calculated amount of aqueous solution of PtCl₄ was added drop-wise with stirring to obtain a catalyst with the desired metal loading (10 wt.%). Stirring was continued for 10 h and reduction of the incorporated Pt complex within the zeolite was carried out using 0.1 M NaBH₄. After 10 h of stirring, the platinized zeolite sample was filtered and dried under a flow of nitrogen at 383 K. The resulting power sample was then added to calculated volumes of 15 wt.% Nafion solution. The solution was then mixed ultrasonically to form a homogeneous ink. The suspension was used to cast the membrane and subsequently dried in a vacuum oven at 80 °C to obtain complete evaporation of the solution. The thickness of the composite membranes was controlled to about 50 μm. For simplification, the formed Pt/zeolite–Nafion composite membrane is denoted as PZN.

2.2. Membrane-electrode assembly fabrication

A commercial E-TEK electrode (30 wt.% Pt/C, 0.5 mg cm⁻²) was used as both the anode and the cathode for all tests in order to eliminate experimental errors that may originate from electrode preparation steps. Prior to preparation of the membrane-electrode assembly, a total of 0.8 mg cm⁻² of Nafion solution was applied to each E-TEK electrode by means of spray

technique. The Nafion-impregnated electrodes and the prepared PZN composite membrane were hot-pressed at 120 °C for 3 min at a pressure of 3 t to form a membrane-electrode assembly (MEA).

2.3. Cell operation and performance

The performance of the cell was evaluated by measuring the current density versus cell voltage using a commercial test system (Wonatech). Hydrogen and oxygen reactant gases were supplied to the cell from storage tanks via mass-flow controller and without humidification. The operation temperature was varied from 30 to 75 °C.

2.4. Analysis of composite membrane characteristics

The electrochemical responses of the MEAs prepared with PZN membranes with respect to the different humidification conditions were characterized with an impedance analyzer (IM6 (Zahner Co.)). The frequency was varied from 10 mHz to 100 kHz and the ac signal amplitude was 10 mV. The reference and counter electrodes were connected to the anode at which hydrogen oxidation takes place and the anode was linked to the cathode.

Water uptake was measured by weighing the membrane after immersion in de-ionized water for 10 h. The samples were weighed after drying in a vacuum oven at 90 °C for 10 h. The water content was estimated by the difference in weight.

The particle size of the Pt/zeolite was determined by means of high-resolution transmission electron microscopy (HR-TEM, JEM-30100 model). Energy dispersive analysis by X-rays (EDAX) was used to determine the ratio of Pt in the zeolite.

Infrared absorbance measurements were carried out, using an FT-IR spectrometer (BOMEM DA8), on the self-humidified PZN composite membrane and the fully-dried PZN membrane in order to verify the presence of water produced by the recombination of hydrogen and oxygen permeated from the anode and the cathode.

3. Results and discussion

The particle size and distribution of Pt in the zeolite HY was studied using HR-TEM. Images observed at different magnifications are presented in Fig. 1, together with images of pure zeolite for comparison. As shown in Fig. 1(a and b), pure zeolite HY is found to have a structure that is composed of a uniform porous network. From a low-magnification image with 10 wt.% Pt loading (Fig. 1(c)), uniformly dispersed Pt particles of almost the same size are clearly observed in the zeolite HY. Further analysis at high magnification (Fig. 1(d)) reveals a clear difference in the microstructure of the Pt/zeolite composite. The average particle size of Pt in the Pt/zeolite composite is found to be around 3–4 nm. This dimension is much smaller than that of Pt black. Most importantly, no agglomeration of Pt particles is found. The Pt content in the Pt/zeolite was studied by EDAX and found to be approximately 10 wt.% (see Table 1), which is in agreement with the targeted value.

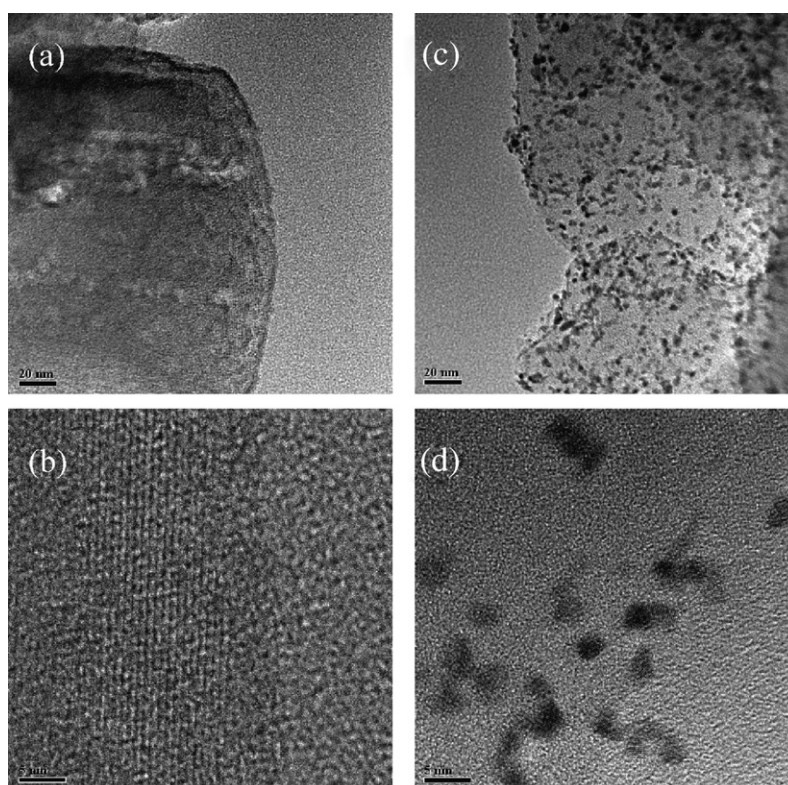


Fig. 1. HR-TEM images of zeolite HY (a and b) and Pt/zeolite powder with 10 wt.% Pt loading (c and d) at different magnifications of 100 and 500 K, respectively.

The water generation capability of the PZN composite membrane was tested under completely dry conditions. The PZN composite membrane was dried in a vacuum oven at 90 °C for 3 days and then placed between two gas-diffusion layers in the fuel cell. Dried hydrogen and oxygen gases were supplied to the fuel cell test station at ambient pressure and room temperature for 10 days. After that, infrared absorption measurements were carried out for this PZN composite membrane and the fully-dried PZN membrane for comparison. As shown in Fig. 2, a characteristic peak for H–O–H bending at 1600 cm^{-1} and broad water sorption bands over the hydroxyl-stretching region at 3500 and 3600 cm^{-1} , which are typically observed when zeolite HY is exposed to water molecules, are found only for the PZN composite membrane operated with dry H_2 and O_2 [11,21]. As evidenced by the IR absorption spectra, the presence of water molecules due to the catalytic recombination of hydrogen and oxygen gases confirms the self-humidifying capability of the PZN composite membrane.

The polarization curves of cells with PZN membranes and Nafion 112 membrane operated under fully-humidified conditions at 75 °C are given in Fig. 3. While the PZN membrane exhibits a slightly lower performance than Nafion 112, the performance of the cells using 0.65 wt.% Pt/zeolite exceeds that

of the cell using a Nafion 112 membrane. This is attributed to the fact that the Pt/zeolite particles in the self-humidifying composite membranes can effectively consume reactant gases permeated through membrane by a recombination reaction and thereby alleviate the mixed potential problem associated with the crossover of the reactants. Therefore, the cathode overpotential is lowered and the cell performance is improved. This effect is confirmed by examining the open-circuit voltage (OCV) because a cell with less fuel and oxidant crossover leads to a higher OCV value. It is obvious that the cell with a 0.65 wt.%

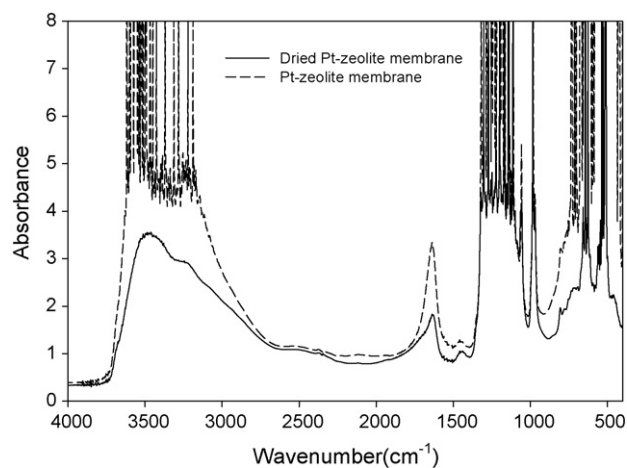


Fig. 2. Infrared absorbance spectra of dried Pt/zeolite membrane (straight line) and Pt/zeolite membrane operated with dried H_2 and O_2 without electrodes for 10 days at room temperature (dashed line).

Table 1
EDX analysis for Pt/zeolite powder

Element (wt.%)	Pt	Al	Si	O
	9.84	9.62	37.17	43.37

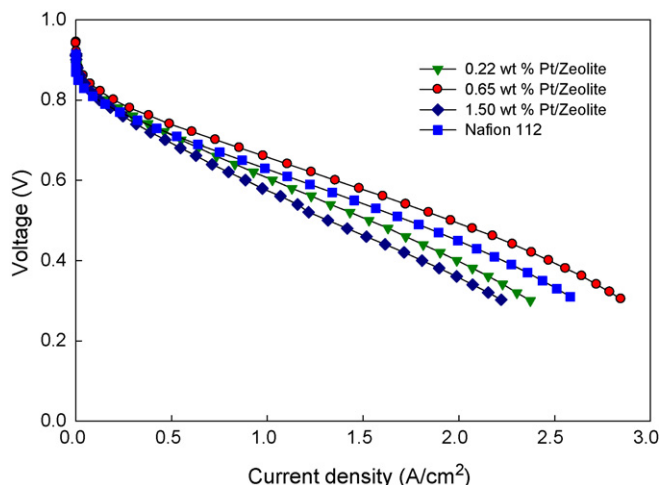


Fig. 3. Polarization characteristics of MEAs fabricated with Nafion 112 and PZN composite membrane with 0.65 wt.% Pt/zeolite operated with external humidification at 75 °C and 1 atm pressure.

Pt/zeolite membrane has a higher OCV than a cell with a Nafion 112 membrane.

In order to study the effect of Pt/zeolite loading on the ability to effect self-humidification, polarization curves of the PZN composite membrane with varying Pt loadings were measured under no external humidification at 50 °C. The results are presented in Fig. 4 for an increase in the weight percentage of Pt/zeolite from 0.22 to 1.5 wt.% in the PZN composite membrane. In the low current density region, the cell performances are almost identical. By contrast, discrepancy is noticeable in the high current density with increasing Pt/zeolite loading. It is concluded that a PZN membrane with 0.22 wt.% of Pt/zeolite ($0.01 \text{ mg Pt cm}^{-2}$) cannot provide sufficient catalytic sites for the recombination reaction to produce water. When the amount of Pt/zeolite embedded in the membrane is more than 1.5 wt.% ($0.07 \text{ mg Pt cm}^{-2}$), the cell performance is reduced due to the negative effect of an increase in membrane resistance. In general, as the amount of Pt particles in the membrane increases,

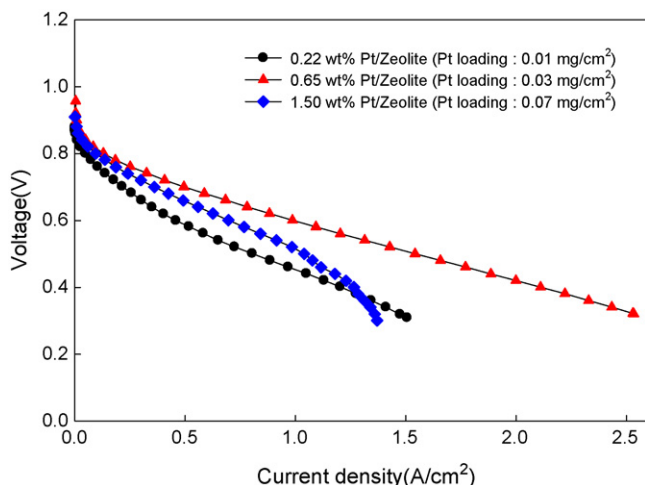


Fig. 4. Polarization curves of single cell using PZN membranes with various Pt/zeolite loadings measured at 50 °C and 1 atm with dry H₂ and O₂.

the resistance of the composite membrane increases due to hindrance of proton conduction within the membrane [22]. The PZN membrane with 0.65 wt.% Pt/zeolite ($0.03 \text{ mg Pt cm}^{-2}$) displays higher performance and lower cell resistance than the others. With dry H₂ and O₂, it provides about 75% of the performance obtained with humidified reactants. In this work, the amount of required Pt is quite small to provide satisfactory proton conductivity without external humidification in comparison with the other approaches.

For a self-humidifying membrane to exhibit good performance in a fuel cell, the catalyst loading, size and the distribution of the catalyst are important factors. If the preparation method of Pt particles is not properly selected, the particles will coalesce and grow larger. This results in a decrease in the active area of the catalyst and thereby causes a reduction in the catalytic efficiency of the recombination of hydrogen and oxygen. When fine Pt particles were coated by a sputtering method, the optimum amount of Pt particles embedded in the membrane for the self-humidification was reported to be about 0.15 mg cm^{-2} [22]. With the equilibrium impregnation reduction method, 0.09 mg cm^{-2} of Pt was used for the self-humidification membrane [9]. The loading was reduced further to 0.06 mg cm^{-2} by employing Pt/C in which Pt particles were supported by carbon of high surface-area [12]. There still exists, however, a strong possibility of the formation of an electron-conducting path via a network of dispersed Pt particles. This would result in non-uniform water generation, that would cause localized drying of the membrane with a high resistance for proton transfer and therefore hot spots at elevated temperature. With a Pt/zeolite-embedded membrane, there is no possibility to create an electrical path through the membrane since the zeolite used as a catalyst support is a non-conducting material. Platinum particles of less than 3 nm prepared by the ion-exchange process of zeolite allow a high active surface-area of catalyst to be obtained that results in a reduction in the amount of Pt used.

A comparison of the water uptake of PZN membranes is given in Table 2. Higher water uptake is observed with increasing content of Pt/zeolite in the membrane, despite the lower content of Nafion resin. This is due to the water absorbency of zeolite in the composite membranes. Whereas the PZN composite membrane cell shows reasonable performance and proton conduction under self-humidifying conditions, it supports the idea of water generation by the catalytic recombination reaction on Pt and retention of water by zeolite in PZN composite membranes.

Electrochemical impedance spectroscopy (EIS) was used to study the change in resistance of the self-humidifying PZN composite membrane as a function of Pt/zeolite loading with and

Table 2
Water uptake as function of Pt loading in Pt/zeolite Nafion composite self-humidifying membrane

Membrane	Water uptake (%)
Nafion 112	6.3
0.22 wt.% PZN membrane	10.4
0.65 wt.% PZN membrane	15.2
1.50 wt.% PZN membrane	38.6

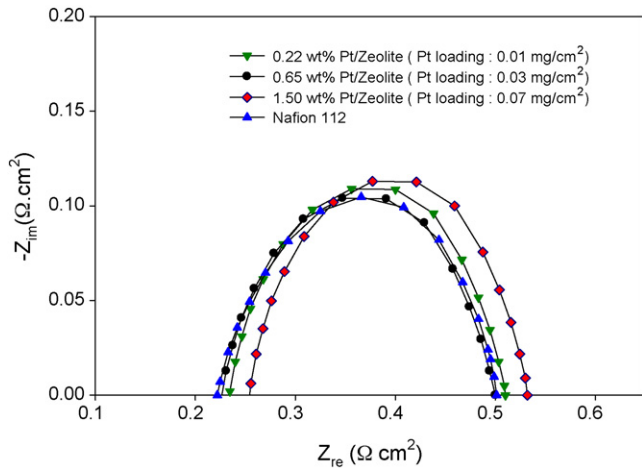


Fig. 5. Nyquist plot of PZN membranes for various Pt/zeolite loadings at 75 °C and 1 atm pressure with external humidification.

without external humidification. A Nyquist plot for the resistance of the humidified PZN composite membrane is shown in Fig. 5. The intercept of the semi-circle at high frequency might be attributed to the internal distributed ohmic resistance and the charge-transfer resistance is indicated by the diameter of the arc. No significant change in the ohmic resistance of the membrane is observed. The external humidification already supplies water for the required rate of proton conduction through the membrane and hence under external humidifying conditions, the resistance of all the composite membranes is nearly 0.22–0.25 $\Omega \text{ cm}^2$.

When cells previously operated using humidified gases are operated using dry gases, the ohmic resistance of membrane increases slightly due to the lack of water, as shown in Fig. 6. The ohmic resistance with a loading of 0.65 wt.% Pt/zeolite is the lowest, i.e., approximately 0.33 $\Omega \text{ cm}^2$ whereas for other loadings, resistance is more than 0.62 $\Omega \text{ cm}^2$. This result is in accordance with that of the polarization curves in Fig. 4. It is observed that both the lower and higher limits of Pt loading cause increase in the resistance of the membrane, which indicates that the 0.65 wt.% Pt/zeolite is the optimum loading of Pt for gen-

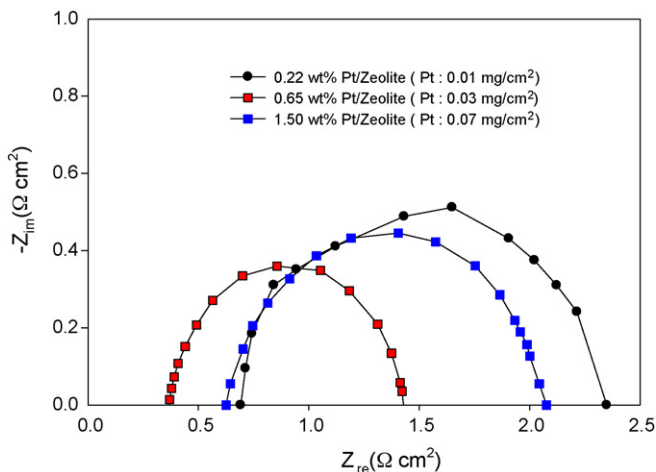


Fig. 6. Nyquist plot of PZN membranes with respect to Pt loading operated at 50 °C and 1 atm pressure under dry conditions.

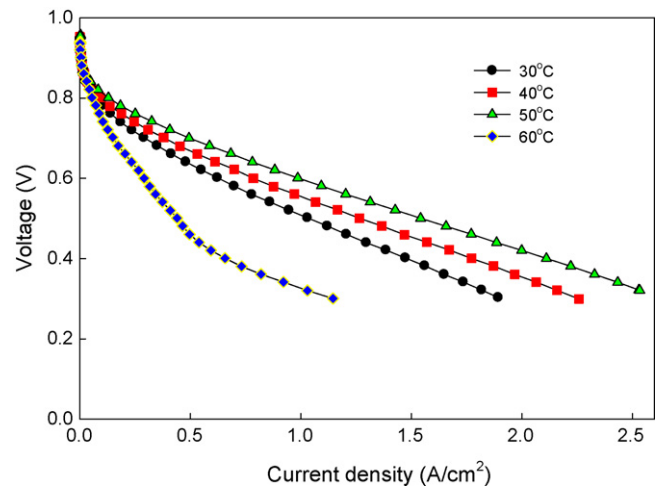


Fig. 7. Polarization curves of MEA using PZN composite membrane (0.65 wt.% Pt/zeolite) measured at different operating temperatures without external humidification.

erating the water required for hydrogen and oxygen catalytic recombination to form water in a self-humidifying PZN membrane during fuel cell operation. Other than increasing the ohmic resistance, the increase in the diameter of the low-frequency arc that represents the charge-transfer resistance is responsible for the major contribution to the increase in cell resistance. For a PZN membrane with 0.65 wt.% Pt/zeolite, the charge-transfer resistance increases by 0.78 $\Omega \text{ cm}^2$ while the ohmic resistance increases by only 0.11 $\Omega \text{ cm}^2$. These results can be explained by taking into account the fact that the contact area between the polymer electrolyte and the catalyst in the catalyst layer is decreased due mainly to constriction of the polymer electrolyte as the membrane dehydrates. This leads to a decrease in the area of electrolyte that covers the platinum catalyst. Consequently, the reaction area decreases [12]. The transport of protons tends to occur with difficulty and gives rise to an increase in the interfacial charge-transfer resistance of the cell. Based on this observation, it is reasonable to conclude that increase in charge-transfer impedance is the dominating factor that causes poor fuel cell performances under dry conditions.

The cell performance of a PZN composite membrane at different operating temperatures without any external humidification is presented in Fig. 7. With increasing cell temperature, the cell performance is enhanced due to the improved kinetics of the cell reaction and better proton transport. When the temperature is raised to 60 °C, a dramatic decrease in cell performance is observed. It is considered that water loss due to vaporization overwhelms the benefit of kinetic improvement at higher temperatures and leads to dehydration of the MEA and a decrease in cell performance.

4. Conclusions

In this work, a novel Pt/zeolite-embedded Nafion polymer electrolyte (PZN) is proposed as a self-humidifying membrane for PEMFCs. The particle size of the Pt is found to be around 3 nm by HR-TEM studies. The particles are prepared by ion-

exchange of zeolite HY. Zeolite is employed not only as a non-conducting support for holding Pt particles to prevent an electrical short-circuit in the membrane, but also as a water retention material. Based on the results of FT-IR and water uptake experiments, the excellent cell performance of the PZN membrane under dry conditions is attributed to a recombination reaction of hydrogen and oxygen on the surfaces of the Pt particles, together with maintenance of the water level by the zeolite due to its hygroscopic property. Impedance analysis reveals that an increase in charge-transfer resistance is mainly responsible for the loss in cell performance when dry gases are used. With dry H₂ and O₂ at 50 °C, a PZN membrane with 0.65 wt.% of Pt/zeolite (0.03 mg Pt cm⁻²) shows 75% of the performance obtained at 0.6 V with humidified reactants at 75 °C.

Acknowledgment

The authors gratefully acknowledge the Korea Research Foundation for sponsoring this work (KRF-2005-005-J01402).

References

- [1] D.M. Bernardi, J. Electrochem. Soc. 137 (1990) 3344.
- [2] K. Kordesch, G. Simader, Fuel Cells and their Application, Wiley-VCH, Weinheim, 1996.
- [3] R. Srinivasan, R. Mosdel, P. Stevens, C. Yang, Annu. Energy Environ. 24 (1999) 281.
- [4] T.A. Zawodzinski, C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 1041.
- [5] Y. Sone, P. Ekdunge, D. Simonsson, J. Electrochem. Soc. 143 (1996) 1254.
- [6] W.H.J. Hogarth, J.B. Benziger, J. Power Sources (2006) (available online).
- [7] D. Staschewski, Int. J. Hydrogen Energy 21 (1996) 381.
- [8] M. Watanabe, H. Uchida, M. Emori, J. Electrochem. Soc. 145 (1998) 1137.
- [9] H. Hagihara, H. Uchida, M. Watanabe, Electrochim. Acta 51 (2006) 3979.
- [10] C. Wang, Z.X. Liu, Z.Q. Mao, J.M. Xu, K.Y. Ge, Chem. Eng. J. 112 (2005) 87.
- [11] T.H. Yang, Y.G. Yoon, C.S. Kim, S.H. Kwak, K.H. Yoon, J. Power Sources 106 (2002) 328.
- [12] F. Liu, B. Yi, D. Xing, J. Yu, Z. Hou, Y. Fu, J. Power Sources 124 (2003) 81.
- [13] B. Yang, Y.Z. Fu, A. Manthiram, J. Power Sources 139 (2005) 170.
- [14] H.K. Lee, J.I. Kim, J.H. Park, T.H. Lee, Electrochim. Acta 50 (2004) 761.
- [15] H. Uchida, Y. Ueno, H. Hagihara, M. Watanabe, J. Electrochem. Soc. 150 (2003) A57.
- [16] L. Wang, D.M. Zing, Y.H. Liu, Y.H. Cai, Z.G. Shao, Y.F. Zhai, H.X. Zhong, B.L. Yi, H.M. Zhang, J. Power Sources (2006) (available online).
- [17] M. Watanabe, H. Uchida, K. Ohkubo, H. Igarashi, Appl. Catal. B 46 (2003) 595.
- [18] E. Yasumoto, K. Hatoh, T. Gamou, U.S. Patent No. 5,702,838 (December 30, 1997).
- [19] P.V. Samant, J.B. Fernandes, J. Power Sources 125 (2004) 172.
- [20] V. Tricoli, F. Nanetti, Electrochim. Acta 48 (2003) 2625.
- [21] L.M. Parker, D.M. Bibby, G.R. Burns, Zeolites 11 (1991) 293.
- [22] S.H. Kwak, T.H. Yang, C.S. Kim, K.H. Yoon, J. Power Sources 118 (2003) 200.