



# Poly(1-vinylimidazole)/Pd-impregnated Nafion for direct methanol fuel cell applications

Ai Hua Tian<sup>a,b</sup>, Ji-Young Kim<sup>a</sup>, Jin Yi Shi<sup>a,b</sup>, Keon Kim<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Korea University, Seoul 136-701, South Korea

<sup>b</sup> Jilin Institute of Chemical Technology, Jilin 132022, China

## ARTICLE INFO

### Article history:

Received 4 February 2008

Received in revised form 7 March 2008

Accepted 17 April 2008

Available online 9 May 2008

### Keywords:

Palladium

Poly(1-vinylimidazole)

Modified Nafion

Direct methanol fuel cell

Methanol crossover

## ABSTRACT

Nafion is modified by incorporating poly(1-vinylimidazole)/Pd composites into the ion cluster channels of the membrane. The poly(1-vinylimidazole)/Pd-impregnated (PVI/Pd-impregnated) membranes is characterized by means of X-ray photoelectron spectroscopy (XPS), proton conductivity and methanol permeability measurements and compared with those of the untreated Nafion. The dependence of the membrane proton conductivity and methanol permeability on the poly(1-vinylimidazole) (PVI) and palladium contents in the PVI/Pd-impregnated Nafion is studied. The performance of the cells employing the PVI/Pd-impregnated Nafion is evaluated using a direct methanol fuel cell (DMFC) unit cell. It is found that the best cell performance is obtained when Nafion is impregnated with the PVI/Pd composite solution for 20 h. This result suggests that there exists an optimum content of palladium and PVI in the modified membrane to obtain a high-proton conductivity and low-methanol permeability that result in a high-cell performance.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Direct methanol fuel cells (DMFCs), as energy efficient and environmentally friendly power sources, are attractive for transportation, distributed power and portable power applications [1,2]. Unfortunately, the polymer electrolyte membrane currently used in DMFCs exhibits high-methanol permeability, which causes a significant reduction of both the cathode potential and the fuel utilization. This results in significant degradation of the fuel cell performance.

Nafion is the best-known perfluorosulfonated polymer membrane, which has been used as a commercial polymer electrolyte membrane [3]. It is widely accepted that Nafion has a microphase-separated structure, which is characterized by a hydrophobic polytetrafluoroethylene backbone chain and regularly spaced, shorter, perfluorovinyl ether side-chains, each terminated by a strongly hydrophilic sulfonate ionic group. The hydrated protons move through the channels produced by phase separation and Nafion can obtain high-proton conductivity in the hydrated state. Simultaneously, this provides channels for the methanol molecules to pass through.

In addition to the efforts made to develop new proton electrolyte membranes [4–7], many attempts have been made to modify Nafion for DMFC applications. Two main methods have been used to accomplish this. One is the surface modification of Nafion [8–16], while maintaining the structure as well as the inherent proton conductivity of Nafion. The other involves structure modification of Nafion [17–21] to reduce the size of the ion clusters in the membranes, because the transport properties are strongly dependent on the membrane structure [22,23].

Because palladium (Pd) is a hydrogen permeable and methanol impermeable metal [11,12], palladium modified Nafion has been investigated by many researchers in an attempt to reduce the methanol permeation of Nafion while retaining its proton conductivity. Due to the high degree of incompatibility between palladium and Nafion polymer, however, severe cracking problems occur on the Pd layers and give rise to unstable performance of the modified cells [11–16].

A material that can bind well with both Nafion and palladium is needed. Considering that polymeric ligands which contain functional groups are usually used to bind transition metal ions [24], we take advantage of the complexing properties of poly(1-vinylimidazole), due to the electron donor nitrogen in the imidazole ring, to chelate the palladium ion. Furthermore, a high degree of compatibility between Nafion and PVI is expected due to the possibility of acid–base interactions between the imidazole nitrogens and sulfonic acid protons [17].

\* Corresponding author. Tel.: +82 2 953 1172; fax: +82 2 953 1172.

E-mail address: [kkim@korea.ac.kr](mailto:kkim@korea.ac.kr) (K. Kim).

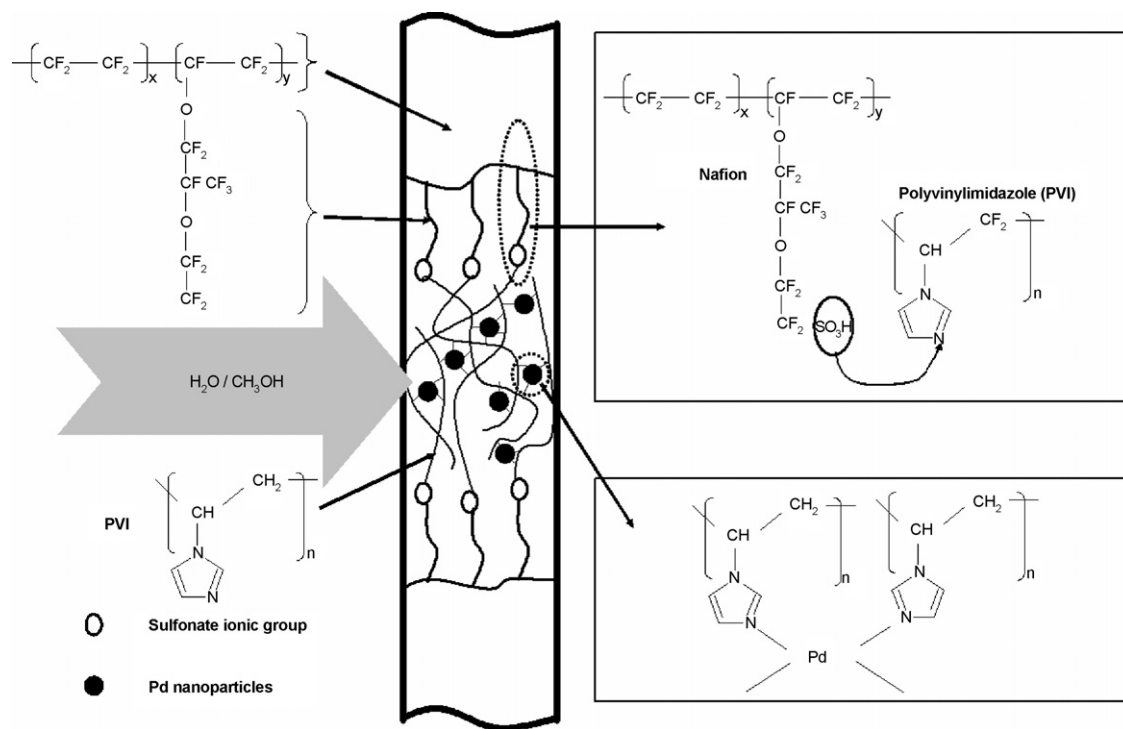


Fig. 1. Complex formation mechanism among sulfonic acid group of Nafion, the imidazole nitrogen of PVI and palladium ions.

In the present investigation, we have developed an approach in which the concepts of the composite membranes and the barrier method described above are combined. A commercial Nafion 115 membrane is modified by impregnating it with PVI/Pd composites solution (PVI/Pd-solution) followed by hydrogen reduction.

Phase separation in the Nafion membrane is assumed to be in the polymer which is characterized by a hydrophobic backbone fluorocarbon phase and hydrophilic SO<sub>3</sub><sup>-</sup> end groups that form adjacent aqueous domains for the proton conductivity. According to Haubold et al. [25], a sandwich structure is created, consisting of a shell region with the side-chains and an embedded core region, that is either empty or flooded with water-methanol. The PVI molecules in the membrane exhibit an acid-base interaction with the sulfonic acid groups in the Nafion membrane. The incorporation of PVI affects the hydrophilic sites and decreases the size of the hydrophilic cluster. Therefore, the amount of water-methanol solution in the channels used to hydrate the sulfonic acid groups decreases with increasing PVI content, which means that the methanol crossover as well as the proton conductivity of the modified membrane is reduced in proportion to the PVI content in the membrane. To compensate for the proton conductivity loss, palladium is added as a proton conductor.

The modification of the membrane based on the complexation mechanism described above is shown schematically in Fig. 1. Thus, we expect to improve the membrane's conductivity and decrease its methanol permeability by making use of the PVI/Pd-modified structure of Nafion.

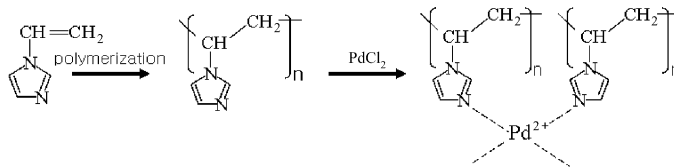
## 2. Experimental

The modified membrane preparation procedure involved the following steps: pre-treating the commercial Nafion, synthesis of the poly(1-vinylimidazole)/Pd composites, impregnating the PVI/Pd composites into Nafion, fabrication of the membrane electrode assemblies (MEAs), and the in situ reduction of the palladium

ions in the modified membrane by feeding it with hydrogen on the cell test station.

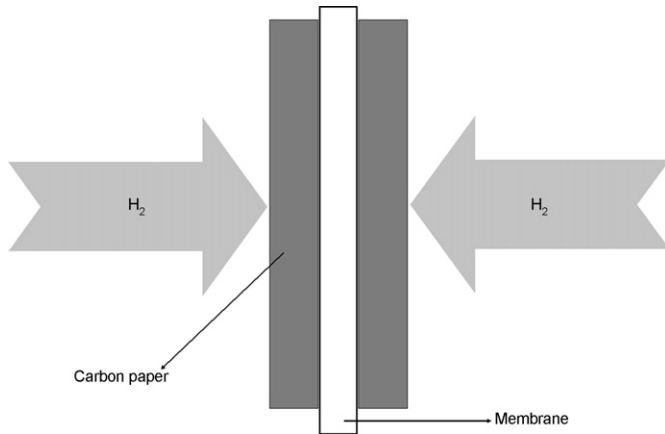
### 2.1. Synthesis of poly(1-vinylimidazole)/Pd composites

1-Vinylimidazole (VI) was polymerized using the thermal initiator, AIBN, at 100 °C for 6 h. Then, 0.1 g of poly(1-vinylimidazole) was added in 2 mL 10% HCl solution. After the PVI had been completely dissolved by stirring, PdCl<sub>2</sub> solution (0.25 mL, 5% in 10% HCl) was added dropwise to the polymer solution under vigorous stirring to prevent precipitation of the polymer. Finally, the PVI/Pd solution was diluted to 200 mL. The synthesis scheme of the poly(1-vinylimidazole)/Pd composites is given below.



### 2.2. Preparation of PVI/Pd-impregnated membrane

All of the membranes in this study were made of Nafion 115 (Du Pont, USA). Before the experiment, the commercial Nafion 115 membranes were pretreated in the usual way [26]. A well-sealed vessel was used to contain the PVI/Pd solution prepared previously for the impregnation process. The pretreated Nafion 115 membrane was cut into strips (4 cm × 4 cm) and soaked in the PVI/Pd solution in the vessel. The impregnation processes were started by putting the vessel in an oven, and raising the temperature to 90 °C. After soaking the sample in the PVI/Pd solution for 5, 10, 15, 20, 25 or 30 h, it was taken out of the vessel and rinsed several times with hot deionized water at 90 °C to remove the excess PVI/Pd solution. The PVI/Pd-impregnated membranes soaked for the various times are referred to as PVI/Pd-5h, PVI/Pd-10h, PVI/Pd-15h, PVI/Pd-20h,



**Fig. 2.** Schematic diagrams showing sample preparation in DMFC configuration for physico-chemical characterization.

PVI/Pd-25h and PVI/Pd-30h, respectively. All of the membranes were stored by sandwiching them between filter papers to obtain a dry and even form for further use.

After the PVI/Pd-impregnated membrane was fabricated into membrane electrode assemblies and placed on the fuel cell test station, the palladium ions in the modified membrane were reduced by purging with hydrogen before feeding the cell with methanol and oxygen.

### 2.3. Physico-chemical characterization

Because the palladium ions in the modified membrane were reduced in situ by hydrogen after the membrane was hot pressed and fixed in the cell hardware, samples without hot pressing had to be prepared by another method in order to characterize the PVI/Pd-impregnated membrane. The sample preparation procedure is shown in Fig. 2. Modified Nafion 115, which had been soaked in PVI/Pd solution for certain times, was placed between two gas-diffusion layers. After being coupled with sealing gaskets and set in the fuel cell fixture, 40 mL min<sup>-1</sup> of hydrogen was supplied for 2 h to reduce the palladium ions. All of the steps were the same as those in the unit cell test except that the sample was not hot pressed, in order to be able to remove the reduced membrane from the gas diffusion layers for the physico-chemical characterization study.

To confirm the chemical state and the loading of PVI and palladium impregnated in Nafion, the membranes were analyzed by X-ray photoelectron spectroscopy (XPS, PHI5800) that was performed with monochromatic Al K $\alpha$  187.850 and 58.700 eV radiation operated at 250 W in a vacuum of  $1.33 \times 10^{-7}$  Pa.

The proton conductivity of the membrane was determined from the membrane resistance measured by AC impedance spectroscopy that was conducted by applying a small alternating voltage (5 mV) and varying the frequency of the voltage from 100 mHz to 100 MHz by means of an impedance analyzer (IM6-Zahner Co.). The impedance at the intersection of the high-frequency curve with the real axis was taken as the membrane resistance,  $R_b$ . The proton conductivity,  $\sigma$ , was calculated as follows:

$$\sigma = \frac{L}{A \times R_b} \quad (1)$$

where  $L$  is the membrane thickness and  $A$  is the active surface-area of the membrane.

The methanol permeability of the membranes was measured using a classical diffusion cell at room temperature. The cell consists of two compartments, A and B, one of which (A) was filled

with a mixed solution of 8 vol% methanol and 0.9 vol% 1-butanol, and the other (B) with only 0.9 vol% 1-butanol solution. The 0.9 vol% 1-butanol solution in both compartments was used as an internal standard. The membrane was clamped vertically between the two compartments, with each compartment containing a magnetic stirring bar for solution agitation during the permeation experiments. The change in methanol concentration with time in compartment B was measured using a capillary gas chromatographic instrument (HP5890). The methanol permeability ( $P$ ) was determined by:

$$P = -\frac{\ln[1 - (c_B(t)/c_A)]}{t - t_0} \frac{V_B L}{A} = -\text{slope} \delta \frac{V_B L}{A} \quad (2)$$

where  $V_B$  is the volume of compartment B,  $L$  the thickness of the membrane,  $A$  the cross-section area, slope  $\delta$  the slope of the  $\ln[1 - (c_B(t)/c_A)]$  vs.  $t$  plot, and  $c_A$  and  $c_B$  are the methanol concentrations in compartments A and B, respectively [27].

### 2.4. Membrane electrode assemblies and cell tests

The electrodes used in this study were fabricated by spraying catalyst inks on carbon paper according to the procedure described in earlier work [28]. The catalysts used in the electrodes were carbon-supported Pt–Ru (3 mg cm<sup>-2</sup>, HISPEC10000, Johnson Matthey) for the anode and carbon-supported Pt (3 mg cm<sup>-2</sup>, HISPEC9100, Johnson Matthey) for the cathode. The gas-diffusion layers were 30BC (SGL, Germany). The MEA was fabricated by placing a membrane between a Pt–Ru anode and a Pt cathode followed by hot pressing at 160 °C and  $3.92 \times 10^2$  Pa for 5 min. Then, the MEA was coupled with sealing gaskets and installed on a single-cell test station. The two half-cells were held together by four bolts that were fastened with a torque wrench set at a predefined torque (30 N cm).

Before the cell test, hydrogen was supplied to each side of the cell at a flow rate of 40 mL min<sup>-1</sup> for 2 h to reduce the palladium ions in the PVI/Pd-impregnated membrane. The cell was then activated by feeding it with H<sub>2</sub>O for 30 min, followed by feeding with 0.5 M methanol and oxygen for 12 h at 80 °C. Cell measurements were performed by pumping a 2 M or 5 M methanol solution into the DMFC anode at a flow rate of 0.6 mL min<sup>-1</sup> and non-humidified oxygen into the cathode at a flow rate of 100 mL min<sup>-1</sup>. The current–voltage and power density curves were investigated via the use of an electronic load. The measurements were repeated until reproducible polarization curves were obtained (cell conditioning), a process that took several days.

## 3. Results and discussion

### 3.1. Physico-chemical characterization

Fig. 3 shows a typical XPS survey spectrum obtained to confirm the constituents and state of the PVI/Pd-impregnated Nafion. Besides the content of Nafion, such as its carbon, fluorine, oxygen and sulfur constituents, signals due to PVI (distinguished by N 1p) and palladium (Pd 3d) are also observed. High-resolution XPS spectra are obtained to compare the chemical state of palladium in the modified membrane before and after hydrogen reduction (Fig. 4). The calibration of the binding energy scale is performed by taking the C 1s photoelectron peak (binding energy = 284.6 eV) as the internal reference. The XPS spectrum shows that  $E_b$ Pd3d5/2 decreases to match Pd(0) after reduction, which indicates that the palladium ions were well reduced.

The atomic concentrations listed in Table 1 show that as the time of impregnation increases, the contents of PVI (N 1p) and Pd (Pd 3d) also increase.

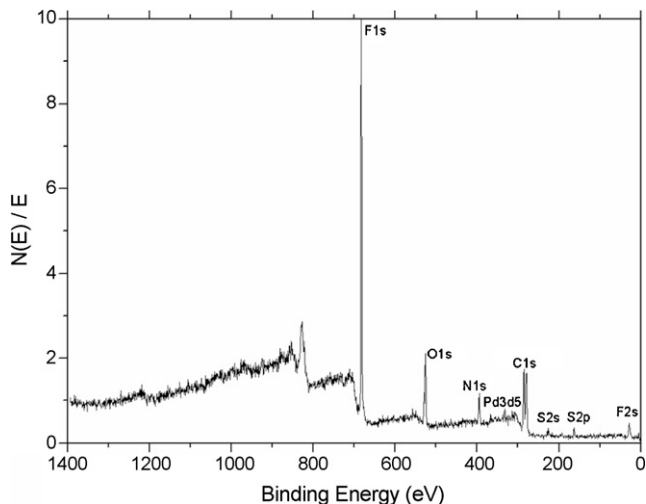


Fig. 3. Survey XPS spectrum of PVI/Pd-modified membrane.

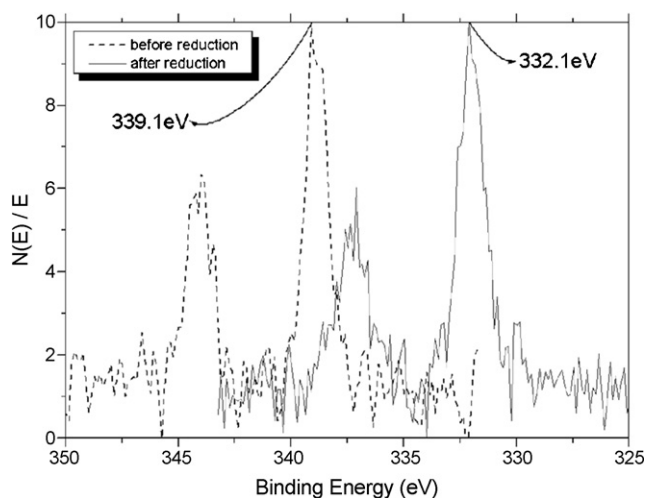


Fig. 4. Detailed Pd 3d XPS spectra of PVI/Pd-modified membrane before and after hydrogen reduction.

### 3.2. Methanol crossover

The methanol permeability of three types of modified membrane, PVI/Pd-10h, PVI/Pd-20h and PVI/Pd-30h, were measured and compared with that of an untreated Nafion. The concentration of methanol that permeated through the clamped membrane is represented in Fig. 5 as a function of time. A linear correlation between  $\ln[1 - (c_B(t)/c_A)]$  and the permeation time is observed in Fig. 6; the methanol permeability can be obtained from the slope of the straight line. The results presented in Table 1 show that methanol

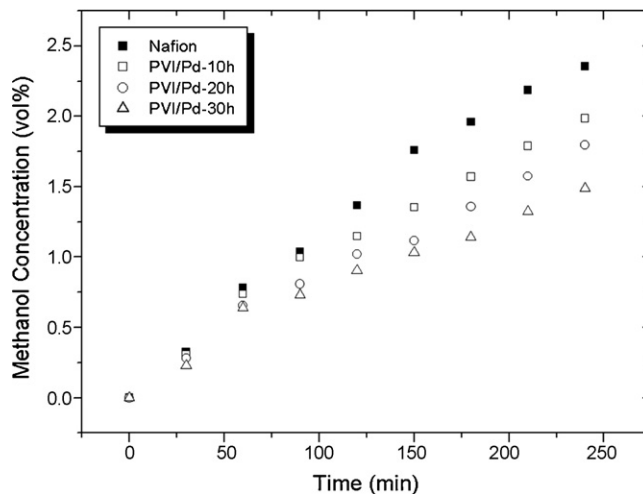


Fig. 5. Methanol concentration in compartment B in relation to time during methanol permeation.

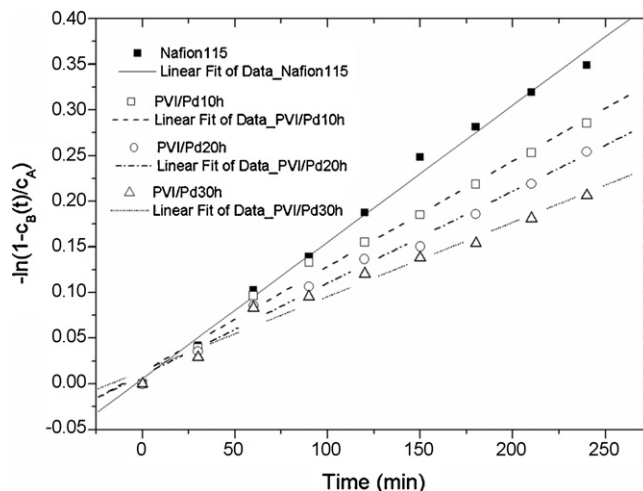


Fig. 6.  $-\ln[1 - (c_B(t)/c_A)]$  vs. time of methanol permeation.

permeability is effectively decreased in the modified membrane at 25 °C.

For the Nafion membrane, while the hydrophobic polymer matrix is comparatively impermeable, methanol diffuses primarily through the hydrophilic domains, i.e., methanol transport mainly occurs through the ion-cluster pores and the connecting ion channels. After impregnation, the PVI stabilized palladium may mainly exist around the hydrophilic ion-clusters and the ion channels and change the microstructure of Nafion, thereby increasing the tortuosity of the methanol transport channels. It is noted that the presence of PVI and palladium in the water-rich domains of the

Table 1  
PVI and palladium content, methanol permeability and proton conductivity of Nafion and PVI/Pd-modified membrane

Membrane	Atomic concentration (%)		Methanol Permeability ( $\text{cm}^2 \text{min}^{-1}$ ) (25 °C)	Conductivity ( $\text{S cm}^{-1}$ )		
	N(1p)	Pd(3d)		30 °C	60 °C	80 °C
Nafion115	0.40	0	$1.074 \times 10^{-4}$	$6.06 \times 10^{-2}$	$7.41 \times 10^{-2}$	$7.81 \times 10^{-2}$
PVI/Pd-5h	1.78	0.10		$4.19 \times 10^{-2}$	$5.15 \times 10^{-2}$	$5.58 \times 10^{-2}$
PVI/Pd-10h	4.87	0.27	$8.308 \times 10^{-5}$	$4.20 \times 10^{-2}$	$5.35 \times 10^{-2}$	$5.91 \times 10^{-2}$
PVI/Pd-15h	5.54	0.30		$4.70 \times 10^{-2}$	$5.95 \times 10^{-2}$	$6.37 \times 10^{-2}$
PVI/Pd-20h	5.60	0.32	$7.234 \times 10^{-5}$	$6.93 \times 10^{-2}$	$8.28 \times 10^{-2}$	$8.75 \times 10^{-2}$
PVI/Pd-25h	7.46	0.42		$3.30 \times 10^{-2}$	$3.46 \times 10^{-2}$	$3.61 \times 10^{-2}$
PVI/Pd-30h	9.01	0.52	$5.824 \times 10^{-5}$	$3.05 \times 10^{-2}$	$3.38 \times 10^{-2}$	$3.53 \times 10^{-2}$



membrane causes a remarkable reduction in methanol permeability. It is expected that all of the PVI/Pd-modified membranes exhibit lower methanol crossover than that of Nafion 115. The higher the content of PVI and palladium, the lower the methanol crossover.

### 3.3. Proton conductivity

It is believed that the transport mechanism is mainly linked to the hydrophilic domains that are comprised of clusters and pores with different sizes and amounts of absorbed water [20]. The conductivity of Nafion membranes is known to increase with increasing water content, because of the increasing contribution of the Grotthuss mechanism [21]. Similarly, the hydrogen ion mobility is likely to decrease as the size of the water-rich clusters decreases. Due to the basic character of the imidazole nitrogen, the transfer of the proton from the sulfonic group occurs with the formation of a hydrogen or ionic bond. Thus, the involvement of the sulfonic groups in PVI crosslinking leads to a decrease in the effective ion-exchange capacity and proton conductivity of the modified membrane.

In the case of the PVI/Pd-impregnated membrane, PVI/Pd-impregnation causes a reduction in both the methanol and water contents in the hydrophilic domain of Nafion. The proton conductivity will decrease with increasing PVI content, because of the dependence of the conductivity on the water content. Also, the conductivity will increase with increasing palladium content, due to the 'pseudo-proton conducting' property [20] of palladium, and palladium allows the selective transport of protons and water molecules, while restricting the passage of methanol molecules. So, the competing effects of reduced proton conductivity, due to the incorporated PVI, and increased proton conductivity, due to the incorporated palladium, must be considered.

The proton conductivities of the PVI/Pd-impregnated membranes, which were impregnated with different contents of PVI and palladium, were evaluated at 30, 60 and 80 °C, and compared with that of Nafion (Table 1). At low PVI and palladium contents, the proton conductivities of the PVI/Pd-impregnated membranes are lower than that of the untreated Nafion at all temperatures. The proton conductivities increase as the time of impregnation is increased initially, and decreases after 20 h of impregnation. This shows that there is an optimum ratio of PVI content to Pd content and this will be studied in further work.

Usually, a reduction in methanol permeability is accompanied by a significant loss in proton conductivity. Nevertheless, the PVI/Pd-20h membrane presented higher proton conductivity than that of the untreated Nafion. Considering its lower methanol permeability than the untreated one, the PVI/Pd-20h membrane is expected to have a high-cell performance.

### 3.4. DMFC tests

The DMFC polarization curves for all of the PVI/Pd-impregnated membranes with different PVI/Pd contents (defined as different soaking times) are shown in Figs. 7 and 8 along with the reference curve of the Nafion115-based MEA.

It should be noted that both the proton conductivity and methanol crossover have a significant impact on the DMFC performance curves. Fig. 7 shows the polarization curves for the cells fed with 2 M methanol and non-humidified oxygen at different operation temperatures, namely 30, 60 and 80 °C. The MEA fabricated from a PVI/Pd-20h membrane provides the highest power density, as expected.

Although the proton conductivities of the PVI/Pd-10h and PVI/Pd-15h modified membranes are lower than that of the untreated Nafion, the  $V-I$  curves are above that of Nafion at 30 and 60 °C because of the significant reduction in methanol crossover.

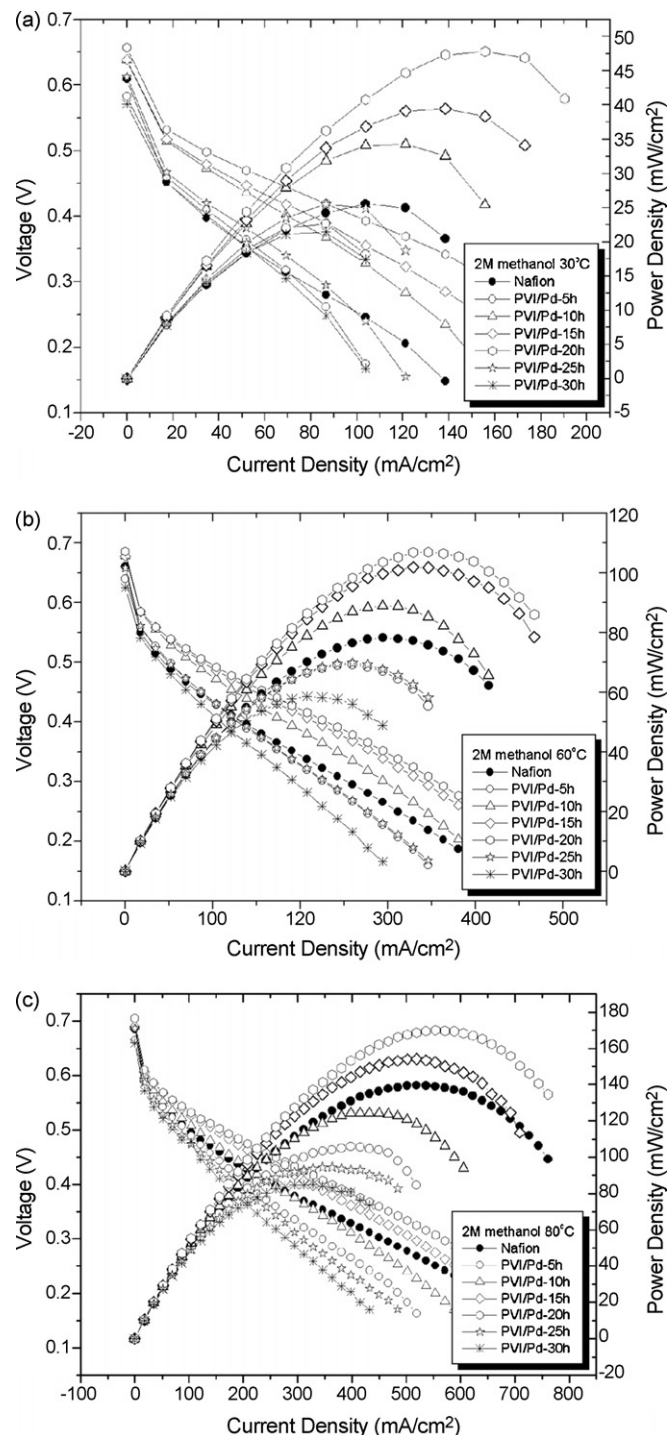
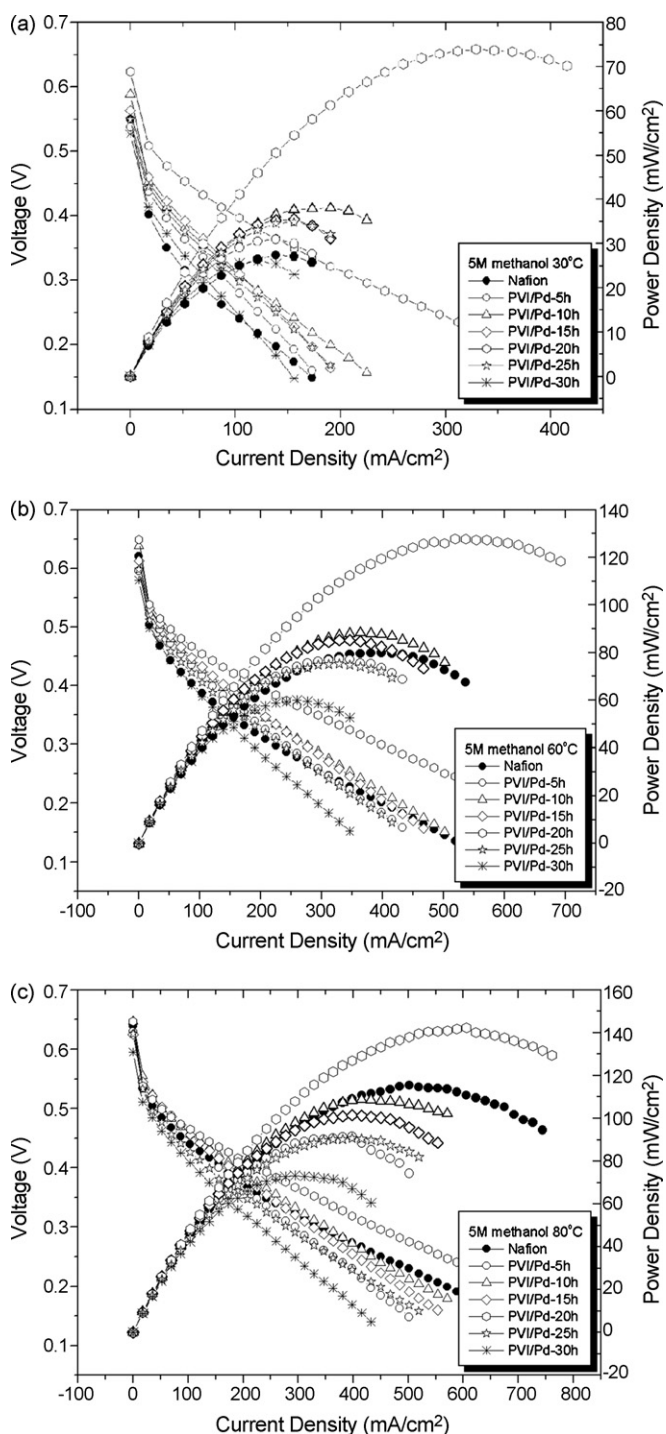


Fig. 7. Comparison of performance of PVI/Pd-impregnated Nafion and bare Nafion115 at different temperatures, (a) 30 °C, (b) 60 °C and (c) 80 °C (0.6 mL min<sup>-1</sup> of 2 M methanol, 100 mL min<sup>-1</sup> of non-humidified oxygen).

The PVI/Pd-10h membrane presents a lower performance than that of Nafion at 80 °C because of the higher methanol crossover at higher temperatures, while the  $V-I$  curves of PVI/Pd-15h are still above that of Nafion because it provides a more effective barrier than the PVI/Pd-10h membrane. Similarly, the  $V-I$  curves for the PVI/Pd-25h and PVI/Pd-30h modified membranes are below that of the untreated Nafion, because the better methanol barrier property of the PVI/Pd modified membranes is offset by their inferior proton conductivity.



**Fig. 8.** Comparison of performances of PVI/Pd-impregnated Nafion and bare Nafion115 at different temperatures, i.e., (a) 30, (b) 60 and (c) 80 °C (0.6 mL min<sup>-1</sup> 5 M methanol; 100 mL min<sup>-1</sup> non-humidified oxygen).

The polarization curves for the cells fed with 5 M methanol and oxygen at 30, 60 and 80 °C are presented in Fig. 8. A higher methanol concentration implies a higher methanol permeability. All of the PVI/Pd-impregnated membranes, except for the PVI/Pd-30h membrane, exhibit better performance than untreated Nafion at an operation temperature of 30 °C, due to their lower methanol crossover as compared with that of Nafion. As the temperature is increased, the cell performance of the PVI/Pd-impregnated membranes, which show better performance at 30 °C, becomes worse

than that of Nafion. This shows that the methanol barrier of the PVI/Pd-impregnated Nafion membranes is not as effective when operated at high temperature as when they are operated at low temperature, due to the high methanol crossover at high temperatures. This means that, for PVI/Pd-impregnated Nafion operated at a relatively high-methanol permeability (that is, high temperatures and high concentration of methanol), the power gain due to the reduced methanol crossover does not sufficiently compensate for the power loss due to the reduced proton conductivity. Since the PVI/Pd-20h membrane has better proton conductivity and lower methanol permeability than Nafion, it presents the best performance during cell tests under all test conditions.

Apparently, the reduced methanol permeation in the modified membranes is offset by the lower proton conductivity. Thus, the optimum combination of proton conductivity and methanol crossover needs to be found.

#### 4. Conclusions

Nafion 115 has been modified by incorporating poly(1-vinylimidazole)-stabilized palladium into the ion cluster channels of the membrane. In this way, advantage can be taken of both the complexing properties of PVI and the methanol-impermeable and proton conducting properties of palladium. The PVI/Pd composite forms a complex with the sulfonic acid groups in the channels, and this can change the size of the hydrophilic clusters, the degree of water absorption, methanol permeability, and proton conductivity. It is found that methanol permeability decreases with increasing PVI content, but this is accompanied by a decrease in proton conductivity. On the other hand, increasing the Pd content enhances the proton conductivity. Considering the competing effects of the power loss due to the reduced proton conductivity and the power gain due to the reduced crossover, the PVI/Pd-impregnated membranes show competitive performance when compared with untreated Nafion. Among the PVI/Pd-impregnated membranes, the PVI/Pd-20h membrane gives the best performance. The results of cell tests on PVI/Pd-impregnated membranes with different contents of PVI and palladium show that there exists an optimum combination of PVI and palladium contents.

#### Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korea Government (MOEHRD) (KRF-2005-211-C00069), as well as by the Korea Science and Engineering Foundation through the Seoul R&BD program.

#### References

- [1] A.S. Arico, S. Srinivasan, V. Antonucci, *Fuel Cells* 1 (2001) 133.
- [2] B.D. McNicol, D.A.J. Rand, K.R. Williams, *J. Power Sources* 83 (1999) 15.
- [3] A. Kenneth, Mauritz, R.B. Moore, *Chem. Rev.* 104 (2004) 4535.
- [4] S.N. Nunes, B. Ruffmann, E. Rikowski, S. Vetter, K. Richau, *J. Membr. Sci.* 203 (2002) 215.
- [5] B. Ruffmann, H. Silva, B. Schulte, S.P. Nunes, *Solid State Ionics* 162 (2003) 269.
- [6] D.H. Jung, Y.B. Myoung, S.Y. Cho, D.R. Shin, D.H. Peck, *Int. J. Hydrogen Energy* 26 (2001) 1263.
- [7] Y. Woo, S.Y. Oh, Y.S. Kang, B. Jung, *J. Membr. Sci.* 220 (2003) 31.
- [8] M. Walker, K.-M. Baumgartner, J. Feichtinger, M. Kaiser, E. Rauchle, J. Kerres, *Surf. Coat. Technol.* 116 (1999) 996.
- [9] S. Han, J.W. Lee, C. Kwak, G.S. Chai, I.H. Son, M.Y. Jang, *J. Power Sources* 167 (2007) 74.
- [10] L.J. Hobson, H. Ozu, M. Yamaguchi, S. Hayase, *J. Electrochem. Soc.* 149 (2002) A1185.
- [11] S.R. Yoon, G.H. Huang, W.I. Cho, I.-H. Oh, S.-A. Hong, H.Y. Ha, *J. Power Sources* 106 (2002) 215.
- [12] W.C. Choi, J.D. Kim, S.I. Woo, *J. Power Sources* 96 (2001) 411.
- [13] Z.Q. Ma, P. Cheng, T.S. Zhao, *J. Membr. Sci.* 215 (2003) 327.

- [14] J. Prabhuram, T.S. Zhao, Z.X. Liang, H. Yang, C.W. Wong, J. Electrochem. Soc. 152 (7) (2005) A1390.
- [15] H. Sun, G. Sun, S. Wang, J. Liu, X. Zhao, G. Wang, H. Xu, S. Hou, Q. Xin, J. Membr. Sci. 259 (2005) 27.
- [16] T. Hejze, B.R. Gollas, R.K. Sauerbrey, M. Schmied, F. Hofer, J.O. Besenhard, J. Power Sources 140 (2005) 21.
- [17] B. Bae, H.Y. Ha, D. Kim, J. Electrochem. Soc. 152 (2005) A1366.
- [18] Y.J. Kim, W.C. Choi, S.I. Woo, W.H. Hong, Electrochim. Acta 49 (2004) 3227.
- [19] Y.-M. Kim, K.W. Park, J.-H. Choi, I.-S. Park, Y.-E. Sung, Electrochem. Commun. 5 (2003) 571.
- [20] P. Dimitrova, K.A. Friedrich, B. Vogt, U. Stimming, J. Electroanal. Chem. 532 (2002) 75.
- [21] D. Kim, J. Sauk, J. Byun, K.S. Lee, H. Kim, Solid State Ionics 178 (2007) 865.
- [22] T.A. Zawodzinski, J. Davey, J. Valerio, S. Gottesfeld, Electrochim. Acta 40 (1995) 297.
- [23] T.A. Zawodzinski, T.E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, S. Gottesfeld, J. Electrochem. Soc. 140 (1993) 1981.
- [24] N. Pekel, O. Güven, Colloid Polym. Sci. 277 (1999) 570.
- [25] H.-G. Haubold, Th. Vad, H. Jungbluth, P. Hiller, Electrochim. Acta 46 (2001) 1559.
- [26] C.K. Dyer, J. Power Sources 106 (2002) 31.
- [27] V. Tricoli, J. Electrochem. Soc. 145 (1998) 3798.
- [28] A.H. Tian, J.-Y. Kim, J.Y. Shi, K. Kim, K. Lee, J. Power Sources 167 (2007) 302.