Evaluation of a palladinized Nafion™ for direct methanol fuel cell application

Yo Jin Kim, Won Choon Choi, Seong Ihl Woo, Won Hi Hong*

Department of Chemical and Biomolecular Engineering, KAIST, 373-1, Kusong-dong, Yuson-g-gu, Taejon 305-701, South Korea

Abstract

Palladinized Nafion™ was prepared via ion-exchange and chemical reduction method. Palladium precursors and solvent systems determined the efficiency of the incorporation and distribution of nanoparticles. The tortuous thin Pd film was formed on the surface of membrane when Na^+–Nafion™ and water were used. Pd nanoparticles enhanced the water uptake of Nafion™ and reduced its methanol uptake. And dispersed Pd nanoparticles in Nafion™ disturbed the proton conduction and methanol permeation simultaneously in Nafion™ cluster. In order to reduce methanol permeation of Nafion™ and keep its high conductivity, it was more efficient for Pd nanoparticles to distribute near the surface of membrane. Palladinized Nafion™ improved the performance of DMFC single cell operation by reducing the methanol permeation.
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Keywords: DMFC; Methanol crossover; Nafion™; Hybrid membrane; Palladium

1. Introduction

In direct methanol fuel cell, methanol can be used directly as fuel instead of hydrogen without reforming. In PEMFC or DMFC, polymer electrolyte membranes were used, which have proton-conducting path produced by fixed functional group or gel of proton conductor. Especially, polymer electrolytes for DMFC have low fuel (methanol and air) permeability in addition to good ion conductivity. Permeation of fuels causes the mixed potential phenomena and decreases the efficiency of using fuel.

Typically perfluorosulfonated polymer, Nafion™ has been used as commercial polymer electrolyte membrane. It has the SO^{3-} side chains fixed at CF backbones. Due to its structure, the phase separation occurs between hydrophilic regions and hydrophobic ones in hydrated (well swelled with water) Nafion™. The hydrated protons move through the channels produced by this phase separation and Nafion™ can obtain high proton conductivity in the hydrated state. However, phase separation simultaneously gives channels for methanol and water molecules to pass through. Typ-

ically, in proton-conducting polymer electrolyte, proton conductivity depends on the mobility of water molecules according to the vehicle mechanism ($H^+ \cdots (H_2O)_n$). In order to block transport of methanol molecule with high affinity to water, the hydrophilicity of electrolyte directly related to proton conductivity should be decreased.

Alternatives to commercial polymeric proton-conducting membranes include inorganic hybrid membranes. Among them, a variety of simple blends of polymer and inorganic conductor have been investigated. In other works, Nafion™ was used as a template and the reactions for the incorporations of inorganic phases such as silicon oxide [1–4], ORMOSIL [5–9], metal oxide [10], metal phosphonate [11] and heteropolyacids [12] were initiated and catalyzed by SO_3^- groups of Nafion™. Especially, it was incorporated with metal nanoparticles by ion exchanges of metal precursor ions with counter ions of SO_3^- group. Through this method, it has been used as support of metal catalysts [13,14]. Recently, Watanabe and his co-workers investigated Nafion™–Pt nanoparticle composite membranes in order to self-humidify polymer electrolyte in PEMFC and reduce the methanol permeability. In these researches, Pt nanoparticles acted as the nanoreactor in which water was produced via oxygen reduction or methanol was removed via methanol oxidation [15,16].

* Corresponding author. Tel.: +82-42-869-3919;
fax: +82-42-869-3910.
E-mail address: whhong@mail.kaist.ac.kr (W.H. Hong).

In our study, Nafion[TM] was palladinized by ion-exchange and chemical reduction. Nafion[TM]–palladium thin film hybrid membrane was investigated in order to reduce the methanol permeation and remain the conductivity of Nafion[TM] by other researchers since palladium is hydrogen permeable metal [17–20]. Smotkin explained the proton conducting of palladium as following [20]. Protons can be discharged at the interface between the anode catalytic surface and electrolyte. The discharged protons can chemisorb as hydrogen onto the surface of the hydrogen permeating metal and the metal is transformed into the metal hydride. In order for the hydride system to maintain neutrality, a proton is ejected. Hydrogen atom diffuses across these metal hydrides. The protons are generated when molecular hydrogen is stripped of two electrons yielding two protons. Pd metal has an fcc structure with a lattice parameter of 0.3887 nm. Upon the absorption of hydrogen the lattice expands isotropically retaining its fcc structure, At a low equilibrium pressure of hydrogen, hydrogen dissolves in the dilute α phase. When the H/Pd ratio is 0.015 at 298 K, the Pd becomes a phase hydride where the lattice parameter causes the hydrogen diffusivity to increase. Hydrogen diffuses relatively rapidly in Pd. We will use the term "pseudo-proton conducting" in order to represent this phenomenon.

Considering this pseudo-proton conducting of palladium, we incorporated palladium nanoparticles into Nafion[TM] matrix by exchange-reduction methanol and investigated the effect of these nanoparticles on the methanol permeability and proton conductivity.

2. Experimental

All membranes in this study were Nafion[TM] 117 (Du Pont, USA). They were pretreated as follows. First, they were boiled in 10 wt.% H_2O_2 for 2 h and then immersed in 10 wt.% H_2SO_4 for 1 h. And they were cleaned in deionized water between each step. Na^+ form Nafion[TM] was prepared by immersing in NaOH 0.1 N solution for 24 h.

Palladium(II) acetylacetonate and tetraamminepalladium(II) chloride hydride were used as palladium precursors. Water, 60% (w/w) methanol solution and 60% (w/w) isopropyl alcohol solution were used as solvent. Solvent solution dissolved palladium precursor and swelled Nafion[TM] membrane. Nafion[TM] (5 cm × 5 cm) samples were immersed in palladium precursor solutions for 4 h. And then, they were immersed in sodium borohydride solution for chemical reduction of palladium precursors until the bubbles in solution disappeared completely. Table 1 shows the preparation conditions of each sample. The palladinized membranes are protonized with 10 wt.% H_2SO_4 before any tests.

The amount of the impregnated palladium into Nafion[TM] was determined by the changes of Nafion[TM] sample mass and concentration of precursor solution between, after and before the impregnation. The latter was measured with UV-Vis (HP 8452).

In order to investigate the sorption behavior of samples, they were equilibrated with pure water and pure methanol at room temperature, after being vacuum-dried at 80 °C for 24 h and weighed.

The conductivities of the fully hydrated membranes were measured by complex impedance analysis using a Solatron 1255 frequency response analyzer over a frequency range of 0.1 Hz–10 MHz with AC perturbation of 10 mV. Stainless steel electrodes with 12 mm diameter were used as blocking electrodes. The methanol permeability of membranes were measured by methods of Choi et al. [19].

Morphologies and Pd distributions of palladinized Nafion[TM] were investigated by scanning electron microscopy and energy dispersive spectroscopy (LEO 1455VP with SE (secondary electron), QBSD (quadrant backscattering detector), CL VPSE (variable pressure secondary electron)). Pd nanoparticles in the bulk phase of membrane were confirmed by TEM (EM-912 Omega, Carl Zeiss).

Small angle data were gathered on Bruker small angle X-ray scattering (SAXS) with general area detector diffraction (GADDS) equipped with Cu Kα radiation generator (3 kW), 2-dimension area detector (Hi-star), and goniometer. The distance between samples and detector was 300 mm. After subtraction of instrumental background, all scans were normalized according to the procedure described elsewhere [21].

Table 1
Palladinization of Nafion[TM] for various conditions

Condition: no.–solvent–precursor–ionic forms of Nafion[TM][a]	Mass (g) of Pd/volume of Nafion[TM] (cm^3)	Extent of palladinization (mol Pd/mol SO_3^- in Nafion[TM] (%))	Degree of slow reduction of metal precursor in solvent system (colors of membrane and solution before adding $NaBH_4$)
1–MeOH–Acac–Na	0.0027	1.32	High (black particles)
2–MeOH–Acac–H	0.0132	6.56	Low (transparent, yellow)
3–MeOH–Amm–Na	0.0146	7.26	No (transparent)
4–MeOH–Amm–H	0.0290	14.44	Low (transparent, yellow)
5–IPA–Amm–Na	0.0217	10.82	Low (transparent, yellow)
6–IPA–Amm–H	0.0059	2.93	High (black particles)
7–Water–Amm–Na	0.0268	13.36	No (transparent)
8–Water–Amm–H	0.0241	12.02	Low (transparent, yellow)

Acac—Pd(II)[$CH_3COCH=C(O)CH_3$]$_2$; Amm—$(NH_3)_4Cl_2Pd(II).H_2O$; Na—$CF–SO_3^-H^+$ (in Nafion[TM]); H—$CF–SO_3^-H^+$ (in Nafion[TM]).
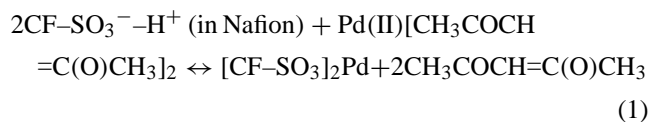[a] MeOH: methanol, IPA: *iso*-propanol.

Between Pd-plugged membrane and Nafion[TM], performance of DMFC single cell was compared. Each MEA was prepared as follows. Carbon papers (TORAY) were wet-proofed and coated with gas diffusion layers and subsequent electrocatalyst layers. Gas diffusion layer consisted of carbon black and PTFE binder. Anode and cathode catalyst were PtRu black and Pt black (Johnson Matthey, Inc.), respectively. The average catalyst loading of each electrode was 2 mg/cm^2 and its active area was 2 cm × 2 cm. The electrodes were assembled with the membranes by hot pressing at 120 °C and 100 kg$_f$/cm^2 for 2 min. This MEA was installed in a fuel cell test station and tested with 2 M methanol and oxygen. Flow rate of methanol and oxygen were 2 and 500 cm^3/min.
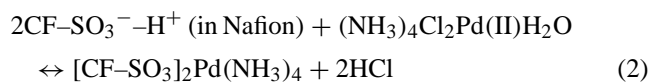
3. Results and discussion

The ion exchange reaction as followed occurred inside Nafion[TM] during the processing. When dissociating in solvent, palladium acetylacetonate forms the Pd(II)$^{2+}$ whereas tetraamminepalladium(II) chloride hydride forms the Pd(NH3)4^{2+} complex ions.
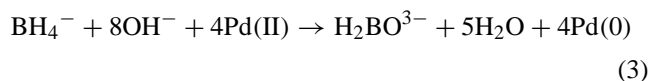
For palladium(II) acetylacetonate:

$$2CF\text{–}SO_3{}^-\text{–}H^+ \text{ (in Nafion)} + Pd(II)[CH_3COCH$$
$$=C(O)CH_3]_2 \leftrightarrow [CF\text{–}SO_3]_2Pd + 2CH_3COCH=C(O)CH_3 \tag{1}$$

For tetraamminepalladium(II) chloride hydride:

$$2CF\text{–}SO_3{}^-\text{–}H^+ \text{ (in Nafion)} + (NH_3)_4Cl_2Pd(II)H_2O$$
$$\leftrightarrow [CF\text{–}SO_3]_2Pd(NH_3)_4 + 2HCl \tag{2}$$
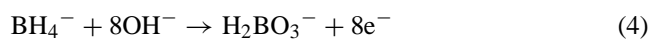
Exchanged Pd(II) or Pd(II) complex was reduced into Pd(0) by chemical reduction method. Reduction of Pd(II) occurred in two ways [22].

Chemical reduction:

$$BH_4{}^- + 8OH^- + 4Pd(II) \rightarrow H_2BO^{3-} + 5H_2O + 4Pd(0) \tag{3}$$

Electroless reduction:

$$BH_4{}^- + 8OH^- \rightarrow H_2BO_3{}^- + 8e^- \tag{4}$$

$$8e^- + 4Pd(II) \rightarrow 4Pd(0) \tag{5}$$

Upon be contacting with reductant, Pd(II) impregnated in Nafion[TM] was reduced into palladium nucleation site. As the size of particle increases, the growth mechanism of particle clusters changes into electroless reduction.

Table 1 shows the efficiency of each reaction system for palladinization of Nafion[TM]. During the impregnation of metal precursor, exchanged Pd(II) ions were reduced slowly. The degree of this phenomenon was different for each solvent system.
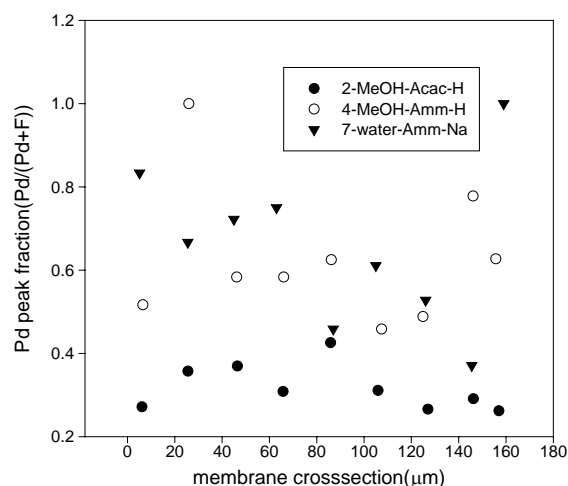

Fig. 1. EDX profiles of palladinized Nafion[TM]'s cross-sections.

In the case of tetraamminepalladium(II) chloride hydride, Pd(II) ions existed in the form of complexes Pd(NH$_3$)$_4{}^{2+}$ which were reduced slower than Pd(II)$^{2+}$ ions dissociated from palladium(II) acetylacetonate. And Pd(II)$^{2+}$ in palladium(II) acetylacetonate was ion-exchanged with Na$^+$ faster than H$^+$ whereas Pd (NH$_3$)$_4{}^{2+}$ in tetraamminepalladium(II) chloride hydride was ion-exchanged more easily with H$^+$ which was able to form HCl with Cl$^-$. For the case of sample 1 and 6, a part of Pd(II) ions were reduced into Pd(0) fast because of alcoholic solvent and counter ions of Nafion[TM]. Since the Pd(0) cannot exchange with H$^+$, the amount of palladium incorporated into Nafion[TM] matrix decreased significantly.

Difference in the degree of Nafion[TM]'s swelling in each solvent affected the distribution of Pd nanoparticles in Nafion[TM] matrix. The EDX profiles of palladinized Nafion[TM]'s cross-sections are as shown in Fig. 1. Although the contents of palladium of sample 4 and 7 were similar, the latter had the highest palladium peak nearer from the
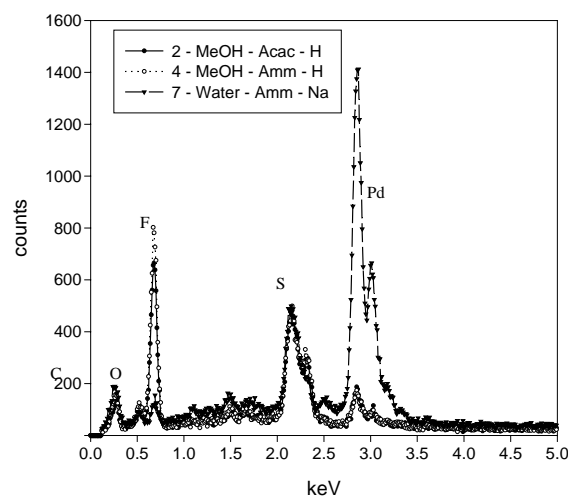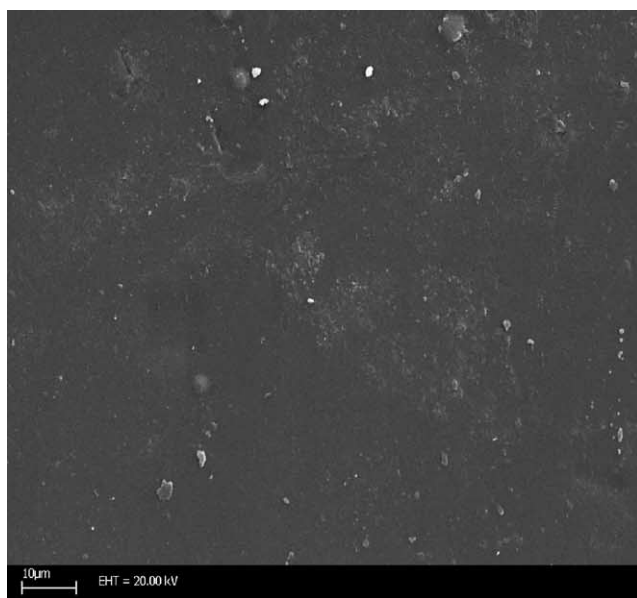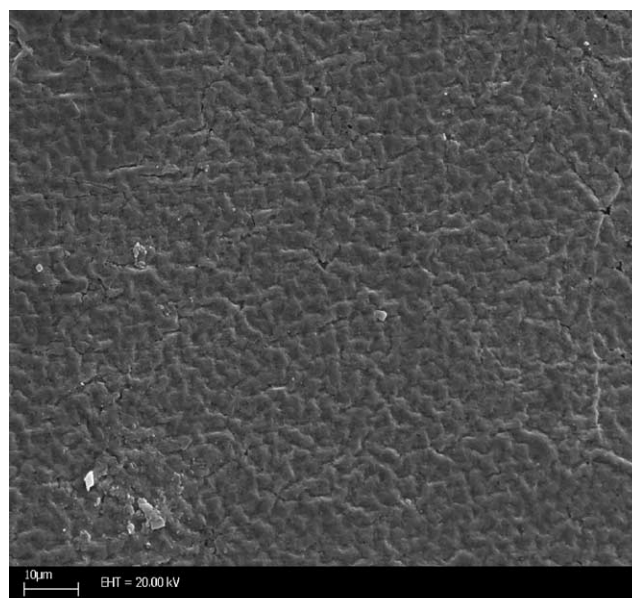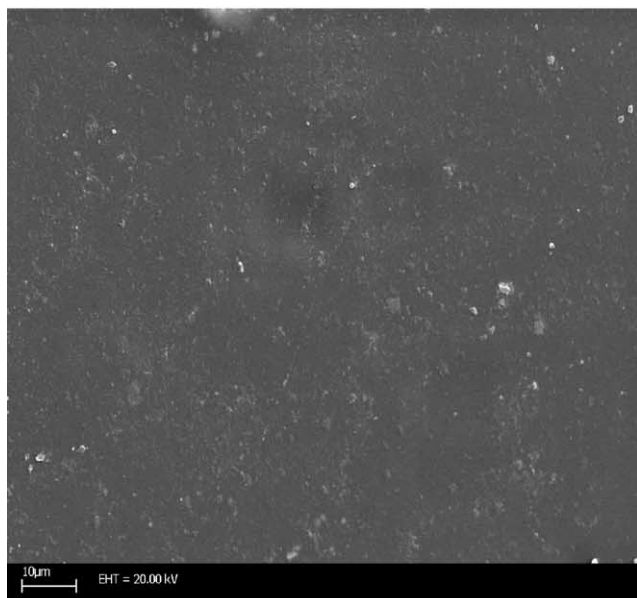

Fig. 2. EDX profiles of palladinized Nafion[TM]'s surface.

<center>(a)</center>

<center>(c)</center>

<center>Fig. 3. (*Continued*).</center>

<center>(b)</center>

Fig. 3. SEM images of palladinized Nafion[TM]'s surfaces: (a) 2–MeOH–Acac–H; (b) 4–MeOH–Amm–H; (c) 7–water–Amm–Na.

surface of membrane. This is obviously due to the lower degree of Nafion[TM]'s swelling in water. EDX analysis on the surface of samples (Fig. 2) shows the difference of these two samples more obviously. For samples 2, 4 and 7, the peak ratios of Pd/S are 155/477, 97/499 and 665/499, respectively. The high Pd peak for samples 7 represents the thin tortuous Pd film at its surface as shown in Fig. 3. In the case of sample 2 and 4, the EDX profiles were almost similar with those of Nafion[TM] and metal nanoparticles were covered completely by Nafion[TM] matrix.

Fig. 4 confirms that Pd nanoparticles were formed in the bulk phase of membrane and there were a clear difference

between the palladium precursors. The use of tetraamminepalladium(II) chloride hydride formed 40–50 nm of palladium particles while palladium(II) acetylacetonate formed 5–10 nm of particles. According to the previous studies [21,23–28], the size of ionic cluster was measured between 3 and 10 nm depending on the states of hydration by SAXS, SANS and electron microscopy. On the other hand, by AFM, the clusters have a range of sizes from 5 to 30 nm at humidities of $(9–34) \pm 2\%$ and it is probably due to the formation of cluster agglomeration [24]. The cluster agglomeration was studied and confirmed theoretically by integral equation theory [28]. We expected that the size of cluster in water/methanol solution may be a little larger than that in water. It is because the sorption of methanol decreases the hydrophobicity of Nafion[TM]'s backbones. According to the previous study [29], the restricted hydrophobicity of polymer's backbone increased the size of particles size when other protective polymers were used for the formation of metal nanoparticle. We can expect that the size of palladium particles formed from palladium(II) acetylacetonate was in a range of single ionic cluster and that in the case of tetraamminepalladium(II) chloride the size of particles was the order of cluster agglomerates.

According to the previous SAXS studies of Nafion[TM] [21], the scattering maximum at $q \sim 2.0 \, \text{nm}^{-1}$ for a dry Nafion[TM] was seen as in Fig. 5 and this peak was attributed to scattering by a quasi array of clusters. As the content of Pd nanoparticles incorporated into Nafion[TM] matrix increased, the peak intensity was decreased. This is due to the disturbance of the difference of X-ray scattering between hydrophobic backbones and hydrophilic clusters by incorporated Pd nanoparticles into nanoclusters of Nafion[TM]. However, the q_{max} did not shift with the increase of the Pd con-
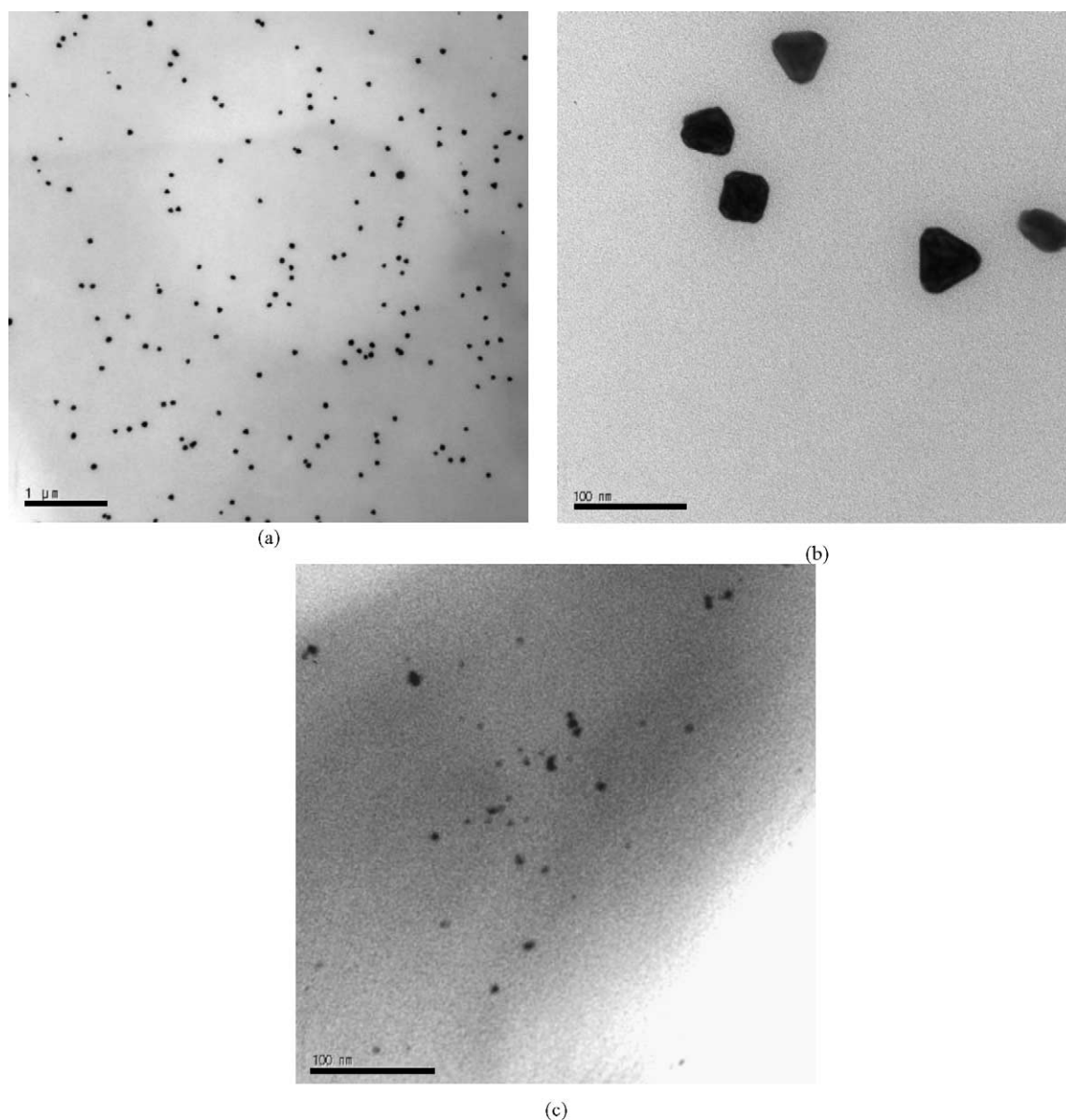
Fig. 4. TEM images of Pd nanoparticles in the bulk phase of palladinized membrane: (a) and (b) 4–MeOH–Amm–H; (c) 2–MeOH–Acac–H.

tent. It means that Pd nanoparticles did not disturb the inter-cluster spacing of Nafion^{TM} in spite of the in situ formation of Pd nanoparticles in the ionic cluster or its agglomerates.

In order to investigate the affect of changes in hydrophilicity and void volume of modified Nafion^{TM} on the mass transfer and ion conduction in them, the solvent sorption, methanol permeability and proton conductivity were measured for each sample.

In Fig. 6, the solvent sorptions of palladinized samples were compared with unfilled Nafion^{TM}. For all palladinized samples, water uptake was higher than for unfilled Nafion^{TM} whereas above a certain amount of incorporated Pd, methanol uptake was lower than for unfilled Nafion^{TM}. According to these results, Pd nanoparticles that were dispersed in nanoclusters of membrane increased the affinity

of hybrid membrane to more polar H$_2$O. In addition, they incorporated into Nafion^{TM} filled and blocked nanoclusters formed by the phase separation reduced the uptake of less polar methanol. However, using IPA as a solvent and tetraamminepalladium(II) chloride hydride as a palladium precursor, Nafion^{TM} swelled and relaxed to the almost four times volume of dry one. This swelled and relaxed structure did not recover completely after palladinization and drying. Therefore, samples using IPA showed much higher solvent uptake than Nafion^{TM}.

Table 2 compares the conductivity and permeability of each sample. As Pd nanoparticles dispersed more in bulk phase of Nafion^{TM} matrix (e.g. sample 4) conductivity and methanol permeability reduced simultaneously, compared with unfilled Nafion^{TM}. Pd nanoparticles in bulk phase may
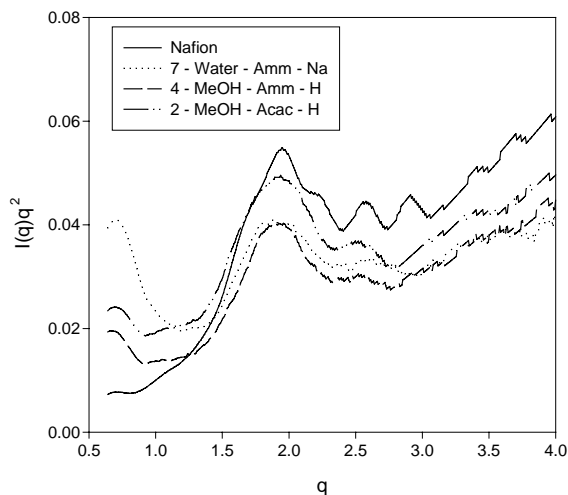
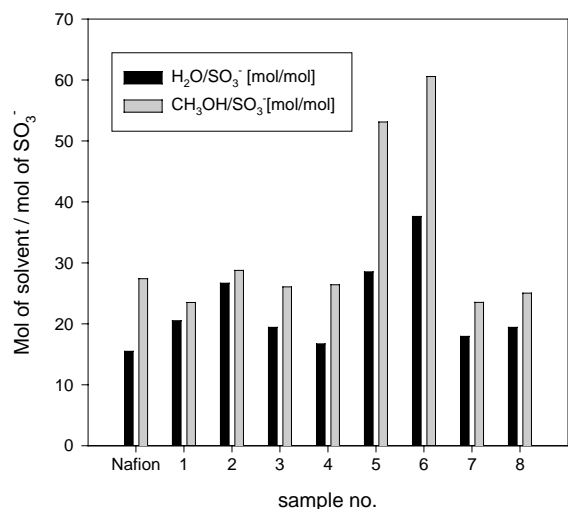Fig. 5. SAXS profiles for pure Nafion^{TM} and various palladinized Nafions.

Fig. 6. Solvent sorption of palladinized Nafion^{TM}.

inhibited the interaction of H^+ with SO_3^- in Nafion ^{TM} matrix since Pd nanoparticles in bulk phase were formed by the ion-exchanges with the counter ions of SO_3^-. However, the reductions of proton conductivity for palladinized sam-

Table 2
Conductivity and methanol permeability of Nafion^{TM}

Condition: no.–solvent–precursor–ionic forms of Nafion$^{TM a}$	Relative conductivity to Nafion^{TM}'s	Relative permeability to Nafion^{TM}'s
Nafion^{TM}	–	–
1–MeOH–Acac–Na	0.64	0.79
2–MeOH–Acac–H	0.70	1.00
3–MeOH–Amm–Na	0.57	0.84
4–MeOH–Amm–H	0.68	0.76
5–IPA–Amm–Na	0.52	0.98
6–IPA–Amm–H	0.82	1.15
7–Water–Amm–Na	0.94	0.61
8–Water–Amm–H	0.72	0.69

[a] MeOH: methanol, IPA: *iso*-propanol.

ples were not significantly large due to the pseudo-proton conducting of Pd particles. Especially, sample 7 that had the tortuous thin film of palladium covering the surface of membrane showed the similar conductivity with Nafion^{TM}. If the amount of palladium particles distributed near the surface of membrane is large or Pd tortuous film is formed on the surface of membrane, the continuity between catalyst layer, Pd film and electrolyte can be increased. It is because Pd film has electron-conductivity and simultaneously acts as proton conductor. Discharged H_2 can be chemisorbed on the Pd upon emitting from the anode and for the neutrality of palladium hydride a proton is emitted from Pd tortuous layer. Therefore, the loss of discharged protons at the interface and the resistance of H_2 diffusion in the bulk phase of membrane to meet Pd phase is reduced. At the cathode/electrolyte interface, Pd tortuous film can also help the stripping of electron from H_2 and its conducting to cathode catalyst phase due to its electron conductivity. Additionally Pd film did not decrease the hydrophilicity of membrane surface due to its tortuosity. Pd film had a excellent bonding with membrane, without cracking or exfoliation and no critical interface which result in a significant resistance.

Since Pd nanoparticles and Pd tortuous film can block the pathway of methanol diffusion which is mainly consisted of ionic cluster agglomerates, the diffusion coefficient of methanol can be decreased. Comparing the palladinized samples with a similar amount of palladium (e.g. sample 4 and 7), we could concluded that Pd tortuous film is more efficient than Pd nanoparticles for reducing the methanol diffusion. It can be because Pd tortuous film acts as a blocking "layer" with large surface area and long pathway. The samples using IPA as solvent, due to the relaxed morphology of Nafion^{TM}, could not reduce the methanol permeation.

Fig. 7 shows the effect of Pd content on the properties of the membrane when using the same solvent system of sample 7. Initially, conductivity increased and methanol permeability decreased as the amount of incorporated Pd increased, and above a certain amount the rapid increase of conductivity and permeability appeared. It can be seen that this is due to the expansion of cluster and increase of hydrophilicity by excess amount of Pd nanoparticles.

In Fig. 8, the results of single cell operation at 40 °C were compared between the unfilled and palladinized Nafion^{TM} (sample 7). At this temperature, the efficiency of operation for palladinized Nafion^{TM} was improved clearly. When the back-pressure was applied to cathode side, the difference of efficiency decreased. This feature showed indirectly the improved methanol blocking of palladinized Nafion^{TM} since the back –pressure applied to cathode side reduced the methanol permeation. And it can be seen that surface tortuous palladium layer did not increase the interfacial resistance, compared with the smooth Pd film such as sputtered film and Pd membrane and that Pd that has similar characteristics with Pt, helped the electrocatalysis of electrode.
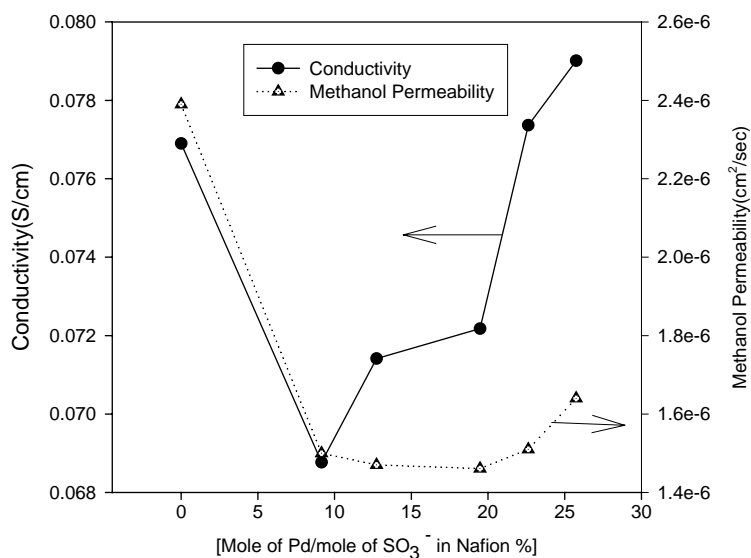
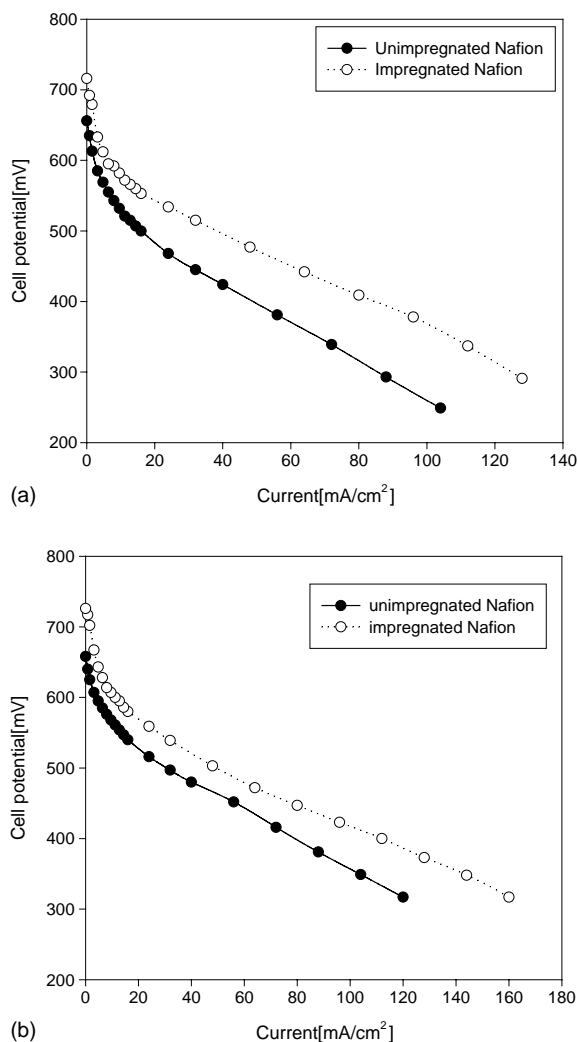Fig. 7. Permeability and conductivity with content of Pd into Nafion^{TM}.

4. Conclusion

Palladinized Nafion^{TM} was prepared via ion-exchange and chemical reduction method. Tetraamminepalladium(II) chloride hydride was more efficient for the preparation of palladinized membrane since Pd(II) existed the complex ions, Pd(NH$_3$)$_4^{2+}$ and these were reduced slower in alcohol solution than Pd(II)$^{2+}$ dissociated from palladium(II) acetylacetonate. And the nanoparticles from tetraamminepalladium(II) chloride hydride were larger in size than those from palladium(II) acetylacetonate.

In addition, solvent system determined the diffusion of ions from metal precursor due to the difference of swellability. Thereby, the tortuous thin Pd film was formed on the surface of membrane when Na$^+$–Nafion^{TM} and water were used. This thin film reduced the methanol permeability significantly. Pd nanoparticles increased the water uptake of Nafion^{TM} and reduced its methanol uptake. And dispersed Pd nanoparticles in Nafion^{TM} disturbed the proton conduction and the methanol permeation simultaneously in Nafion^{TM} cluster. In order to reduce the methanol permeation of Nafion^{TM} and keep its conductivity high, it was more efficient for Pd nanoparticles to distribute near the surface of membrane. Palladinized Nafion^{TM} improved the performance of DMFC single cell operation by reducing the methanol permeation (sorption and diffusion).

Acknowledgements

(a)

(b)

Fig. 8. Comparison of results of cell operation between unpalladinized and palladinized Nafion^{TM} at 40 °C: (a) 0 oxygen pressure; (b) 14.7 psia oxygen pressure.

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