

Surface-modified Nafion membrane by oleylamine-stabilized Pd nanoparticles for DMFC applications

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Abstract

The surface of Nafion was modified by applying palladium nanoparticles as methanol barrier materials to decrease methanol crossover and improve the performance of fuel cells. The properties of the Pd-modified membrane, in terms of conductivity, methanol permeability, percentage of liquid uptake as well as the performance of its membrane electrode assembly (MEA) in the direct methanol fuel cell, were analyzed and compared with those using bare Nafion. The modified membrane showed considerable improvement on reducing methanol loss without decreasing proton conductivity. The DMFC performance of modified membrane was superior to that of bare Nafion both at a typical fuel state of 2 M and at high concentration of 5 M, implying that the palladium-modified Nafion can be a good alternative approach for DMFC applications.

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1. Introduction

The direct methanol fuel cell (DMFC) has received increasing attention for application in portable electronic devices and transportation [1,2]. This is largely due to the fact that methanol as a liquid at room temperature and ambient pressure lends methanol systems a great advantage over systems based on other fuels, such as hydrogen gas or compressed natural gas [3,4]. In DMFCs, methanol can be fed directly for the purpose of converting chemical energy to electrical energy. However, to use DMFCs commercially, there still remain problems to be overcome in terms of efficiency and power density, in which low electrocatalytic activity and methanol crossover are currently the biggest technological barriers [5–7]. In order to improve the performance of DMFCs, it is necessary to eliminate or to reduce the loss of fuel across the cell. Two different strategies can be used to solve this problem. The first one is to develop new membrane [8–12], because the present perfluorosulfonic polymer membranes which are now commonly used are known to be quite permeable to methanol. The second one is to modify

the existing perfluorosulfonic polymer membrane to improve the performance [13–15]. This study will focus on the second approach utilizing Pd nanoparticles.

Pd and Pd alloys are quite widely used as electrodes for hydrogen diffusion [16,17]. As a methanol impermeable and proton conducting material [18,19], palladium is very promising for use in DMFCs. A number of reports have been published on modification of Nafion by introduction of palladium [18–26]. They all showed reduced methanol crossover in the cell, but the membranes that showed lower methanol permeability usually exhibited lower proton conductivity as well, compared to Nafion alone. For example, Pd-sandwiched membranes which were formed by sandwiching a dense Pd foil between two Nafion 115 membranes were investigated by Pu and Huang [17]. Though the membrane was active for proton transport and the methanol permeability was decreased, the cell performance with the Pd-sandwiched membrane was still very poor. Pd-impregnated nanocomposite Nafion membrane [20,21] showed that both methanol permeability and ion conductivity decreased, because the dispersed Pd nanoparticles in the Nafion membrane influenced the proton conduction and methanol permeation simultaneously. For Nafion modified by self-assembling multi-layer Pd nanoparticles [22], though the methanol crossover had a considerable decrease of 99.14%, with the conductiv-

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ity remaining 83.9%, it only covered a very limited range of experiments.

Deposition of Pd or Pd alloys on the surface of Nafion membrane has been usually accomplished by sputtering, requiring high vacuum conditions and was an effective method to modify the Nafion [18,19,23,24]. Most of this kind of modified membrane had decreased methanol crossover, and improved performance for the fuel cells. But there were many cracks in the film, and the Pd films were unstable due to the presence of the cracks and were easily delaminated from the membrane surface and methanol crossover became severe. This technique has a number of disadvantages, particularly the required vacuum conditions. Swelling due to hydration of the membrane during operation in the DMFC, results in the formation of cracks in the vacuum-deposited Pd layer.

Pd electroless plated Nafion membrane had been studied by Sun et al. and Hejze et al. Similarly, some cracks were found on the surface of the electroless plated Pd membrane [25] and the membrane should be kept in deionized water to be maintained fully hydrated in order to avoid crack formation [26].

In the present investigation, we modified the anode side of Nafion by brushing a thin film of oleylamine-stabilized palladium, which can be easily dispersed in organic solvents. Only modifying the surface of Nafion can keep the bulk of the membrane intact, thus, providing the best chance of maintaining the inherent conductivity of Nafion. This kind of crack-free surface-modified membrane reduced methanol crossover while maintaining proton conductivity and thus, provided a good performance.

2. Experimental

2.1. Membrane preparation and modification

All membranes in this study were Nafion 115 (DuPont, USA). They were pretreated as follows [2]; first, they were boiled at 80 °C in 3% H₂O₂ solution, deionized water (DI), 0.5 M H₂SO₄ solution and again in DI water, each for 1 h. Then the membranes were dried naturally in the air for no less than 4 h.

The Pd nanoparticles were synthesized by heating 0.1 mmol dichloro(1,5-cyclooctadiene)-palladium (99%, Aldrich) with 2 g oleylamine (70%, Aldrich) from room temperature to 150 °C. After heating at 150 °C for 3 h, the resulting reaction mixture was left to cool to room temperature and methanol was added to precipitate the Pd nanoparticles. After removal of the supernatant, the particles were redispersed in 5 mL toluene to obtain the methanol barrier materials. Then they were brushed onto the anode side of Nafion 115 by a camel hair brush. After several brushings and weighings, the loading of the barrier materials on Nafion was about 0.01 mg cm⁻².

2.2. Characterization of membrane

Transmission electron microscopy (TEM, JEOL JEM-2010) was used to examine the morphology of synthesized barrier materials. X-ray photoelectron spectroscopy (XPS, PHI5800 with monochromatic Al K α 187.850 and 58.700 eV radiations

operated at 250 W in a vacuum of 10⁻⁹ torr) analysis was performed to confirm the state of palladium on the surface of Nafion and field emission scanning electron spectroscopies (FE-SEM, Hitachi S-4300) were taken to obtain information on the quality of the palladium applied.

Liquid uptake of the membrane was calculated by measuring the changes in weight before and after hydration on modified membrane as well as Nafion 115 [27]. The percentage sorption and the degree of swelling was calculated using the following equations:

$$\text{Uptake (\%)} = W(\%) = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 and W_1 are weight of the membranes before and after liquid soaking.

Proton conductivity of the membranes were determined from impedance data taken after an appropriate equilibrium period, over a frequency range of 100 mHz to 100 kHz with AC perturbation of 5 mV using an impedance analyzer (IM6-Zahner Co.). The conductivity (σ) was determined from the bulk resistance (R_b) obtained from the complex impedance plot, Nyquist plot [28].

2.3. Methanol permeability

A two-reservoir cell was used for the measurement of methanol permeability [29]. One reservoir A ($V_A = 23.70 \text{ cm}^3$) was filled with solution of methanol (8 vol.%) and 1-butanol (0.9 vol.%) in deionized water and the other reservoir B ($V_B = 23.70 \text{ cm}^3$) was filled with 1-butanol (0.9 vol.%) in deionized water. The two reservoirs had a transport channel with a membrane separating them. Both reservoirs were vigorously stirred during the permeation experiments. The methanol flux was established across the membrane driven by the concentration difference between the reservoirs. The change of methanol concentration with time in reservoir B was measured using a capillary gas chromatographic instrument (HP5890). The methanol permeability was calculated from the relation of methanol concentration and permeation time.

2.4. Membrane electrode assembly (MEA) fabrication

In order to test the membranes in a fuel cell station, MEAs were prepared with home-made electrodes according to the following procedure.

A mixture of catalyst, distilled water, Nafion solution and isopropanol was sprayed onto a commercially available carbon gas diffusion layer by air brush (GP-2, Fuso Seiki Co., Ltd. Japan) to fabricate electrodes. Catalyst inks were prepared in the following way: supported catalysts (anode: 40% Pt and 20% Ru on Vulcan XC-72R Carbon, ca. atomic ratio 1:1, 3 mg cm⁻²; cathode: 60% Pt on Vulcan XC-72R Carbon, 3 mg cm⁻² from Johnson Matthey) were wet with a small amount of water to prevent catalyst burning, then 30% Nafion solution was added and the mixtures were sonicated for 2 min. Further, appropriate amount of isopropanol was added and sonicated again for 8 min. After sonication, the catalyst ink was sprayed onto the

carbon papers (GDL30BC, SGL). The electrodes were dried at 80 °C for 30 min in oven after being painted with catalyst ink. After several times of weighing–spraying–drying–weighing, the electrodes were made with desired catalysts loading.

The modified membrane was sandwiched between two electrodes, and the resulting membrane electrode assembly (MEA) was then hot-pressed for 5 min at 160 °C under 40 kgf cm⁻². Similarly, MEA using Nafion 115 was fabricated for comparative test. All MEAs had a size of 1.7 cm × 1.7 cm.

2.5. DMFC cell test

The MEAs were coupled with gas-sealing gaskets and placed in a single cell test station. The anode was supplied with 2 M methanol at a flow rate of 0.6 mL min⁻¹. The cathode was supplied with non-humidified oxygen at a flow rate of 100 mL min⁻¹ or supplied with non-humidified air at a flow rate of 150 mL min⁻¹ under ambient pressure. The aqueous methanol solution was used in a single flow through the cell without recirculation into a reservoir in order to maintain a constant methanol concentration.

The cells were operated at the temperatures of 30, 60 and 80 °C. The unit cell performances were characterized by polarization curves which were obtained using an electronic loader by varying the current. All the experimental results were obtained under steady-state conditions.

Additionally, 5 M methanol was used to evaluate the possibility of using high methanol concentrations in conjunction with DMFC.

3. Results and discussions

3.1. Characterization of membranes

Fig. 1 showed the TEM images of palladium nanoparticles stabilized by oleylamine. The palladium particles showed a multi-armed structure with a diameter of 2–3 nm. These Pd nanoparticles well dispersed in organic solvents were used to modify Nafion membrane to restrict the methanol crossover.

XPS measurement was performed to confirm the stable state of Pd after being applied onto the surface of Nafion. A typical XPS survey spectrum is shown in Fig. 2. Besides the presence of carbon, fluorine and oxygen, i.e. the constituents of Nafion, signals due to palladium are also observed. The chemical state of palladium was investigated by considering its high-resolution XPS spectrum (Fig. 3). Calibration of the binding energy scale was performed by taking the C1s photoelectron peak (binding energy = 284.6 eV) as the internal reference. XPS spectrum showed that the data for E_pPd 3d_{5/2} was 335.975 eV that matches to Pd(0).

The morphologies of the surface and cross-sections of modified Nafion membrane were investigated by SEM. From Fig. 4, we can clearly see that the oleylamine-stabilized Pd film appeared uniform and smooth, without cracking or exfoliation and no critical interface, which result in a significant resistance. Methanol barrier materials were well attached to the Nafion membrane even after hydrating and drying.

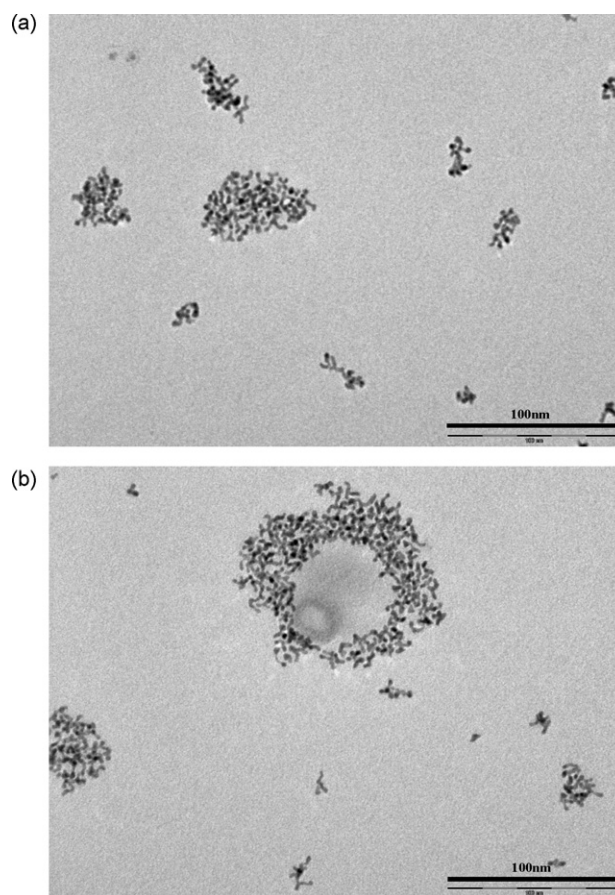


Fig. 1. TEM images of oleylamine-stabilized palladium.

3.2. Liquid uptake and conductivity

Table 1 lists the water uptake and methanol uptake obtained by soaking the membranes in the respective solutions at room temperature. The Pd-modified membrane exhibited more water uptake and less methanol uptake than bare Nafion. Previously, it was shown that Pd nanoparticles enhanced the water uptake of

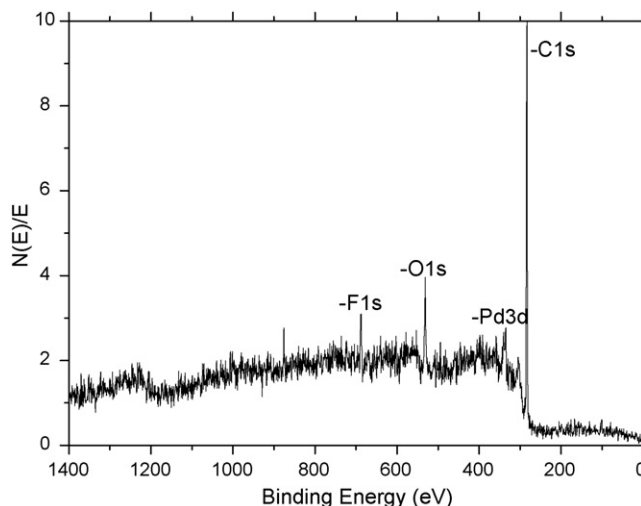


Fig. 2. Survey XPS spectrum of a Pd-modified membrane.

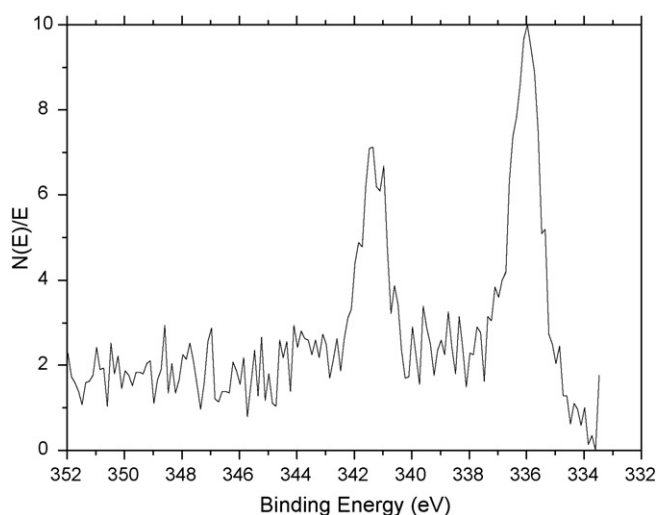


Fig. 3. Detailed Pd3d XPS spectrum of Pd-modified membrane.

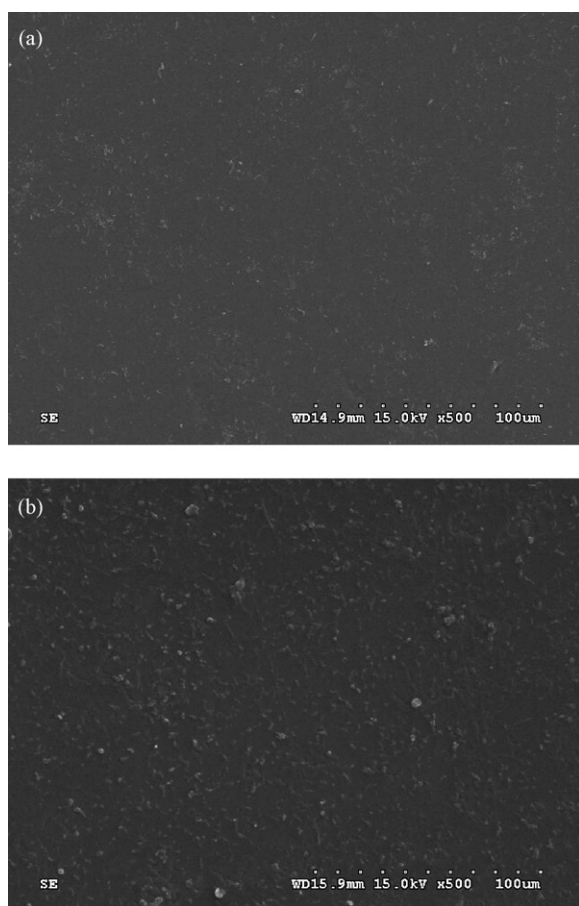


Fig. 4. SEM images of (a) Nafion and (b) Pd-modified membrane.

Nafion and reduced its methanol uptake [21]. According to these results, Pd nanoparticles increased the affinity of the membrane for the more polar H₂O. In addition, they reduced the uptake of the less polar methanol, that is, the modified membrane showed a slightly higher selective tendency towards water than towards methanol. The differences between the liquid uptakes of the two membranes, Pd-modified membrane and bare Nafion, were not too large, because only one Nafion surface was modified; the liquid uptake was only changed on the modified side and the liquid absorption of the unmodified side was unchanged. Both membranes had little swelling when soaked in water, while both membranes swelled and relaxed from 3.5 cm × 3.5 cm to 4.5 cm × 5 cm when soaked in methanol. This swelled and relaxed structure of Nafion did not recover completely after drying, but the modified membrane recovered very well after drying. Fig. 5 shows us the dried Nafion and Pd-modified membrane after soaking in 99.5% methanol for 24 h. The modified membranes can be easily distinguished from the Nafion membrane by their light gray appearance.

Typically, in proton-conducting polymer electrolyte, proton conductivity depends on the mobility of water molecules according to the vehicle mechanism (H⁺ . . . (H₂O)*n*). Increasing the water uptake of Nafion will enhance conductivity. Applying barrier materials to modify proton exchange membrane always decreases methanol crossover and proton conductivity simultaneously [18,20–22]. But our modified membrane showed comparable conductivity to Nafion (Table 1). This indicated that the modified membrane allows selective permeability to the water molecules or hydrogen ions.

3.3. Methanol permeability

The relationship of the methanol concentration in the reservoir B with time, as described by Tricoli [30], is given by:

$$V_B \frac{dc_B(t)}{dt} = A \frac{DK}{L} (c_A - c_B(t))$$

where c_A and c_B are the methanol concentration in A reservoir and B reservoir, A and L , the area and thickness of the membrane, D and K , the methanol diffusivity and partition coefficient between the membrane and the adjacent solution and V_B is the volume of B reservoir. Here, we assumed that D and K are independent of the methanol concentration at the beginning of the experiment. The equation above can be solved to give:

$$V_B \ln \left[1 - \frac{c_B(t)}{c_A} \right] = -\frac{PA}{L} (t - t_0)$$

Table 1
Liquid uptake, conductivity and methanol permeability of Nafion and Pd-Nafion

Membrane	Water uptake (W%)	Methanol uptake (W%)	Conductivity (S cm ⁻¹)			Methanol permeability (cm ² min ⁻¹) (20 °C)
			30 °C	60 °C	80 °C	
Nafion115	18.40	67.24	0.0606	0.0741	0.0801	8.02 × 10 ⁻⁵
Pd-Nafion	25.17	56.25	0.0615	0.0778	0.0832	6.41 × 10 ⁻⁵

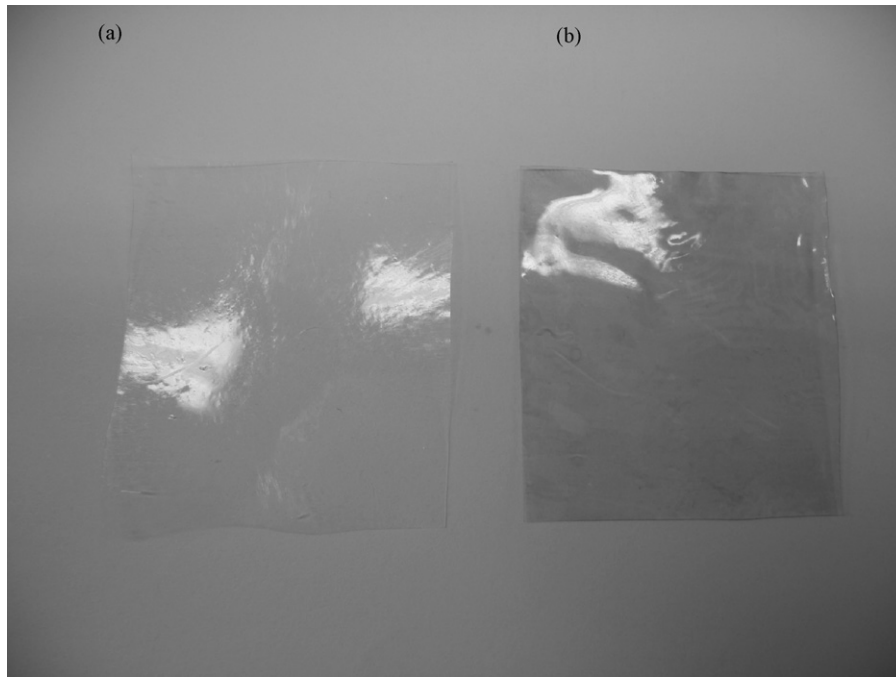


Fig. 5. Dried (a) Nafion 115 and (b) Pd-modified Nafion 115 after soaking in methanol for 24 h.

P , defined as the product DK , is the membrane permeability and t_0 is the time lag.

The concentration of methanol which permeated through the clamped membrane is represented in Fig. 6 as a function of time. The linear behavior is observed in Fig. 7 and the methanol permeability can be obtained from the slope of the straight lines. The permeability values at room temperature are listed in Table 1. We can observe from these values that modified membrane has a permeability about 20% lower than Nafion 115. The modified membrane could have a relatively lower methanol permeability by applying more and dense palladium barrier materials.

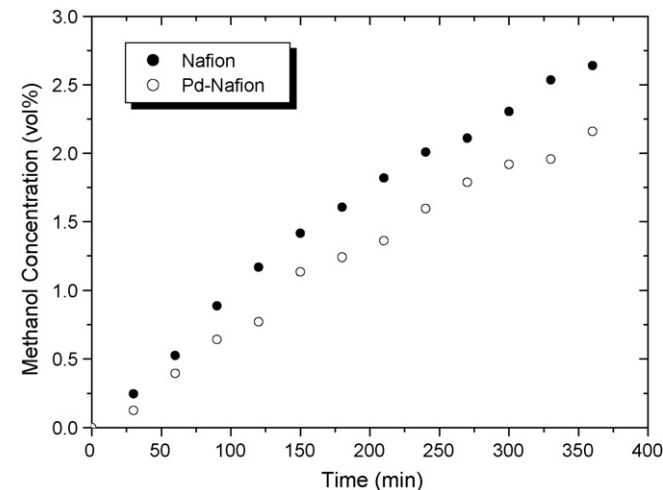


Fig. 6. Methanol concentration in reservoir B in relation to time during methanol permeation.

3.4. Cell performance

After installing the MEA in the fuel cell fixture, the cell was activated by fed H_2O at $80^\circ C$ for at least 30 min followed by being fed with 0.5 M methanol and oxygen at $80^\circ C$ for 12 h to achieve steady-state performance. Afterwards, the cell was operated under different conditions. Current density (I) versus voltage (V) and power density (W) curves of an MEA were obtained by increasing the current stepwise using an electronic loader. All cell tests were operated without humidification.

Fig. 8 shows the polarization curves for an MEA employing a modified membrane fed with 2 M methanol and oxygen at different operation temperatures, 30, 60 and $80^\circ C$. These results were compared with the performance of an MEA based on com-

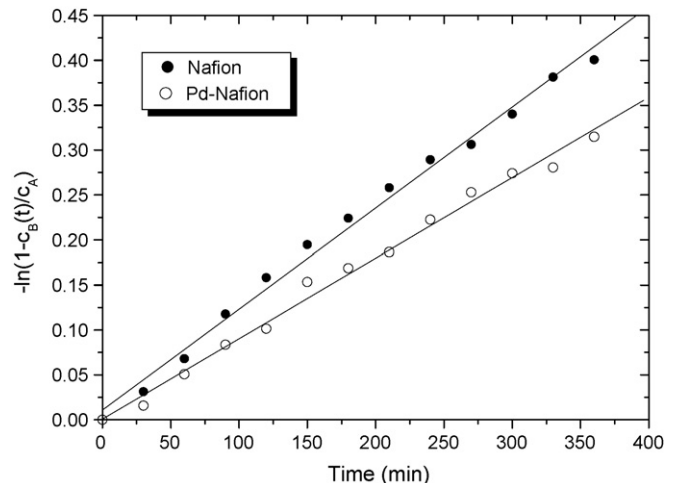


Fig. 7. $-\ln(1-(c_B(t)/c_A))$ vs. time of methanol permeated.

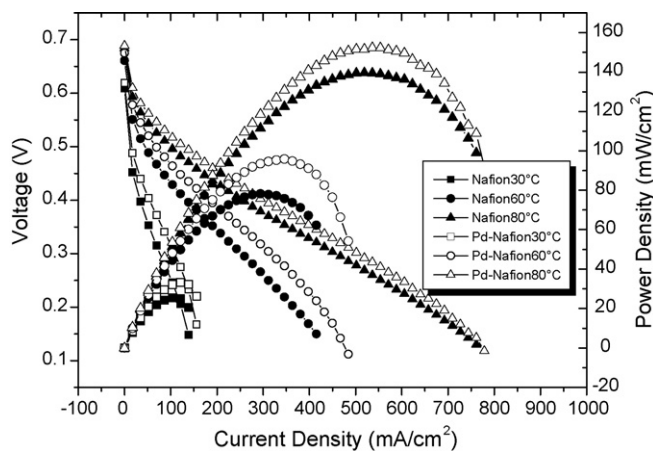


Fig. 8. Comparison of performances of Pd-Nafion membrane and bare Nafion 115 (0.6 mL min^{-1} of 2 M methanol, 100 mL min^{-1} of non-humidified oxygen).

mercial Nafion 115, when operated under the same condition. Fig. 9 shows polarization curves when the cells were fed with air. The modified membrane provided better performance than the unmodified Nafion membrane over the entire ranges of current density and temperature, however, we can see the difference in maximum power density between the two membranes which were varied with temperature. At 80°C , the performance of the modified membrane was not much higher than Nafion, as it was at 60°C . This can be explained by the higher methanol crossover at higher temperatures [2]. The modified membrane can reduce, but cannot eliminate the methanol crossover through the cell. When operated under high temperature, the porous barrier was not as effective as at lower temperatures.

Fig. 10 shows the polarization curves for Pd-modified membrane versus bare Nafion, when 5 M methanol was fed in a unit cell. The modified membrane showed higher performance than bare Nafion. It was also found that maximum power density of Pd-modified membrane at 30 and 60°C increased with increasing concentration of methanol, while the maximum power density of bare Nafion was maintained as 2 M methanol. For

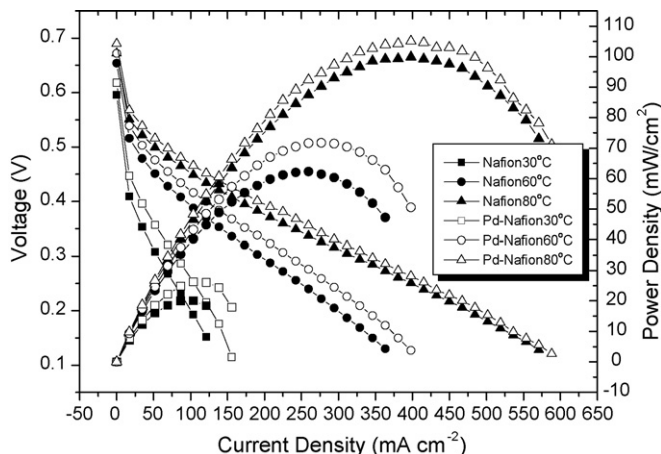


Fig. 9. Comparison of performances of Pd-Nafion membranes and bare Nafion 115 (0.6 mL min^{-1} of 2 M methanol, 150 mL min^{-1} of non-humidified air).

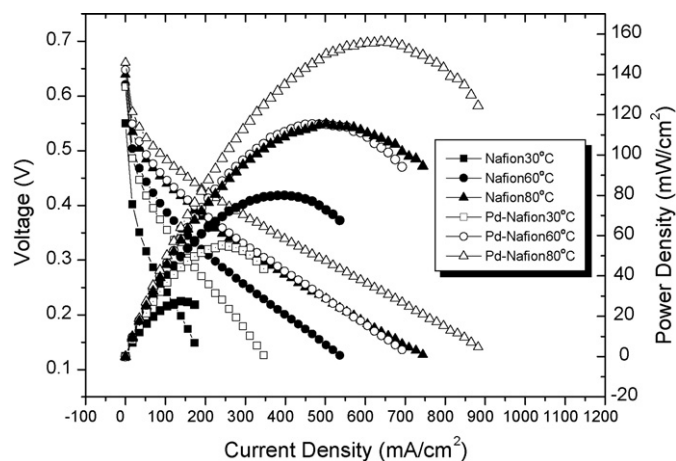


Fig. 10. Comparison of performances of Pd-Nafion membranes and bare Nafion 115 (0.6 mL min^{-1} of 5 M methanol, 100 mL min^{-1} of non-humidified oxygen).

operation at 80°C , the maximum power density of Pd-modified membrane was increased only slightly, while the maximum power density of the bare Nafion was decreased. Thus, Pd-modified membrane showed promising for high concentration methanol cell to reduce the volume of the system and the usage of fuel.

As far as the open circuit voltage (OCV) was concerned, when 5 M methanol was used, the OCVs were lower than that of 2 M for both membranes. The OCV of the Pd-modified membrane was higher than that of bare Nafion and a higher OCV implies a lower methanol crossover from anode to cathode [31]. Therefore, we conclude that the Pd-modified membrane can reduce methanol crossover through the membrane while maintaining proton conductivity. In particular, the Pd-modified membrane could be operated in a DMFC using high-concentration methanol, which can satisfy the requirement to reduce reactant volumes for portable applications as well as to achieve high energy density performance.

4. Conclusions

Oleyamine-stabilized palladium nanoparticles with multi-armed structures, has been synthesized and used to modify the surface of Nafion 115. Oleyamine-stabilized palladium was applied to the surface of Nafion instead of being incorporated into the Nafion matrix, which will not disturb the intercluster spacing of Nafion, and thus, provide a better chance of maintaining the inherent conductivity of Nafion. The DMFC performance with the Pd-modified membrane was better than that of bare Nafion when operated with 2 M methanol. Even for a high concentration of 5 M, the modified membrane showed much better performance than that of unmodified Nafion. In contrast with the bare Nafion, the Pd-modified membrane showed reducing methanol loss without decreasing the proton conductivity. However, the well-adhering and crack-free modified surface should be optimized to form a denser film to effectively reduce more methanol crossover.

In conclusion, reduced methanol permeability, good conductivity and high cell performance for both 2 M and 5 M methanol

operations makes the palladium-modified Nafion an interesting candidate for DMFC applications.

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