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Modification of polymer electrolyte membranes for DMFCs using Pd films formed by sputtering

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Abstract

Composite polymer electrolyte membranes were fabricated by depositing Pd films on the surface of Nafion™ membranes by sputtering, and the modified membranes were investigated for their morphologies, methanol permeabilities, protonic conductivities and performances for direct methanol fuel cells (DMFCs). The Pd film acted as a barrier to methanol crossover, but at the same time it also reduced proton conductivity. Though both the methanol permeability and the protonic conductivity through the modified membranes decreased with increasing Pd thickness, the cell performances were almost independent of the Pd thickness. The effects of methanol concentration on the protonic conductivity and the cell performance were also investigated. And, the role of Pd films in DMFCs is discussed in some detail.

Keywords: Direct methanol fuel cell; Polymer electrolyte membrane; Palladium layer; Sputtering; Methanol crossover

1. Introduction

Direct methanol fuel cells (DMFCs) are attracting intense research interest due to their possible use as power sources for various portable and transportation applications. Much effort has been made in the development of highly active catalysts, electrolyte membranes, electrodes, membrane and electrode assemblies (MEAs), and stacks. But the technological achievements obtained till now are estimated to be far from commercialization. There are many hurdles to be overcome for the DMFC technologies to be commercially viable. These include low catalyst activity, high methanol crossover through the electrolyte membranes, low electrode performance, etc.

Methanol transport across the membrane is the most important problem to be overcome because it causes depolarization losses at the cathode and conversion losses in terms of lost fuel and thus leads to poor performance [1]. A number of different approaches have been taken to tackle this problem, either by eliminating or, by at least, reducing the methanol crossover. One approach is to develop new electrolyte membranes that are resistant to methanol permeation. Wainright et al. [2] suggested polybenzimidazole (PBI) for use as a polymer electrolyte when doped with an amphoteric acid such as phosphoric acid or sulfuric acid. They reported that the acid-doped PBI membrane exhibited excellent oxidative and thermal stability, and good mechanical flexibility at elevated temperature (200 °C). It also had good protonic conductivity at elevated temperature, an almost zero electro-osmotic drag number and low methanol gas permeability. Kerres et al. [3] synthesized sulfonated blend membranes via a crosslinking process that consisted of the disproportionation between SO_2H groups that occured during membrane formation. The blends were obtained from mixing PSU-SO_3H and PSU-SO_2H in different sulfinic acid/sulfonic acid ratios. Guo et al. [4] fabricated PEMs from poly[bis(3-methylphenoxy)phosphazene] by first sulfonating the base polymer with SO_3 and then solution-casting thin films. The sulfonated and crosslinked polyphosphazene membrane showed a lower swelling in both water and methanol and a 30% lower conductivity compared to those for Nafion 117. Recently, there have been some studies on the formation of polystyrene sulfonic acid (PSSA)-g-polyvinylidene fluoride (PVDF) which was synthesized by grafting polystyrene onto PVDF followed by sulfonation.

Another approach is to modify commercially available Nafion membranes by using fillers. Jia et al. [5] impregnated Nafion membranes with poly(1-methylpyrrole) by in situ polymerization. This could lead to a decrease of more than 90% in the permeability of the membranes to methanol, although the ionic resistance of such heavily loaded membranes became too high for high power fuel cells. At lower

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poly(1-methylpyrrole) loadings, a decrease in methanol permeability by as much as 50% was observed without a significant increase in ionic resistance. Yang et al. [6] fabricated a composite Nafion–zirconium phosphate electrolyte membrane. A DMFC with a composite membrane exhibited a good performance at operating temperatures of up to 150 °C. Maximum power densities of 380 and 260 mW/cm^2 were achieved under oxygen and air feed, respectively, under the conditions of 2 M CH_3OH and 4 atm (abs) on both sides of the electrodes. Miyake et al. [7,8] fabricated sol–gel derived Nafion/silica hybrid membranes for DMFC applications. The hybrid membrane with silica content of 20 wt.% showed significantly lower methanol uptake and permeation rate than those of Nafion membranes.

Another approach is to utilize the unique properties of palladium which is permeable to protons, but completely resistant to methanol transport. Pu et al. [9] investigated the performance of composite membranes that were formed by sandwiching a dense Pd foil (25 μm thick) between two Nafion 115 membranes. Though the Pd-sandwiched membrane was active for proton transport and methanol crossover is eliminated, the performance of a PEMFC with the membrane appeared to be very poor. Recently, Choi et al. [10] reported a study on the performances of DMFCs which had been obtained employing Pd-layered Nafion membranes. The thin palladium films were deposited on the surface of Nafion 117 membranes using a sputtering technique. The membrane with a Pd layer of 20 nm-thick showed a much improved performance in a DMFC compared to the unmodified Nafion. But this study covered a very limited range of experiments and thus, no further information was available.

In this paper, we present experimental results on the performance of DMFCs employing Nafion membranes modified by sputter-deposited thin Pd films. Methanol crossover and ionic conductivity were also measured to characterize the composite membranes.

2. Experimental

2.1. Preparation of Pd-layered membranes

Thin layers of Pd were deposited on the surface of Nafion^{TM} membranes by a sputtering technique under an argon pressure of 6×10^{-3} Torr from a Pd target. The substrate holder which held Nafion membranes was kept rotating during deposition to ensure uniformity of Pd films throughout the membranes. The Pd-layered membranes were then subject to further characterization.

2.2. Measurement of methanol permeability and ionic conductivity

Methanol permeation rates were measured using an in-house permeation cell at 25 °C as shown in Fig. 1 where a small piece of membrane was placed in a specially designed fixture. A 5% methanol solution was fed on one side of the membrane and pure water was circulated through the other side (permeate side) of the membrane. The concentration of methanol in the permeate stream increased with time and it was measured by a refractive index detector which was interfaced to a computer with software to calculate methanol permeability. Ionic conductivity, i.e. protonic conductivity, of the membrane was measured at 25 °C by an impedance spectroscopic method using a computer-aided frequency analyzer (Zhaner, IM6). In our experiment, the conductivity cell was designed so that the sample membrane was in contact with water to ensure complete saturation of the membrane by water during measurement. And in some experiments, the water was replaced by methanol solution to examine the effect of methanol.

2.3. Measurement of single cell performance for DMFC

Single cell performance for DMFC was measured using MEAs consisting of a Nafion membrane, platinum black

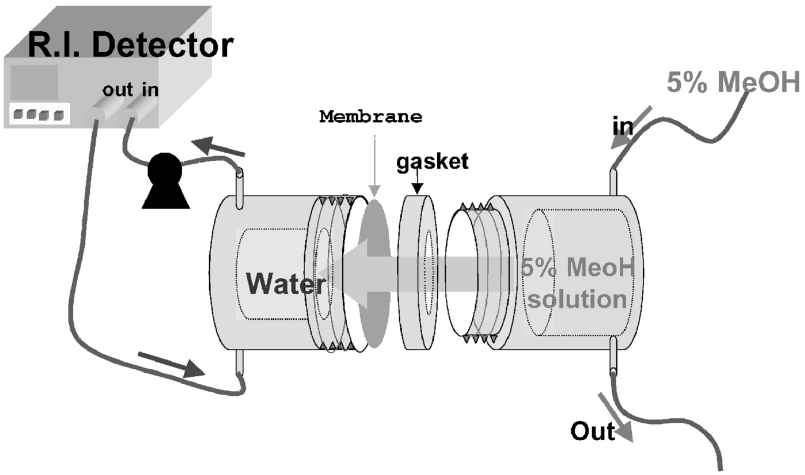


Fig. 1. Schematic diagram of a methanol diffusion cell.

cathode catalyst (catalyst loading = 3 mg/cm^2) and platinum–ruthenium anode catalyst (catalyst loading = 3 mg/cm^2). The catalysts were purchased from Johnson Matthey, Inc. Teflonized carbon paper (Toray) was used for the diffusion layers.

All experiments were carried out using a small-scale DMFC with an external electrode area of 28 cm^2. The cell consisted of an MEA sandwiched between two rectangular graphite plates which had flow channels. The anode feed was a 2 M methanol aqueous solution and the cathode feed was a pure oxygen gas under ambient pressure. The cell was electrically heated to enable isothermal operation at 90 °C.

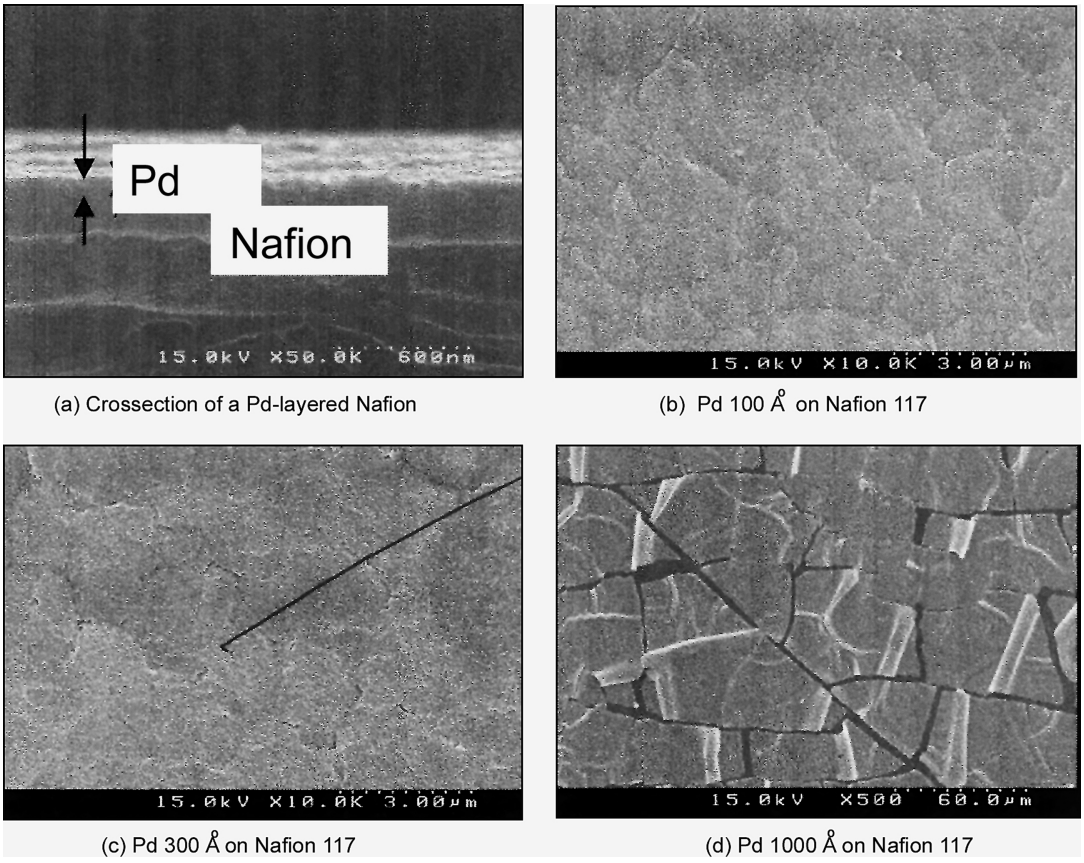
3. Results and discussion

3.1. Characterization of Pd films

Thin palladium films were deposited on the Nafion membranes and they were characterized for their morphology using scanning electron microscopy (SEM). Fig. 2 shows the SEM images of Pd-deposited Nafion membranes. We can see the palladium film deposited on the Nafion membrane from Fig. 2(a). The Pd films thinner than 300 Å were dense and appeared to be well attached to the membrane, but there were many cracks in the 1000 Å films in Fig. 2(d). The Pd films thicker than 1000 Å were very unstable and were easily delaminated from the membrane surface. Thus, we could not get thicker films than 1000 Å. This is mainly due to the difference in expansion coefficients between Nafion membranes and Pd films. When the composite membrane is immersed in water, the Nafion membrane swells very much, but the Pd film can not expand as much as the membrane, so there eventually develop cracks in the Pd films. We analyzed the Pd film formed on the membrane by X-ray diffraction and, as shown in Fig. 3, we could confirm that the film was pure Pd metal.

3.2. Protonic conductivity and methanol permeability

Fig. 4 shows the change of protonic conductivity as a function of the thickness of Pd film formed on the Nafion 117 membrane. As explained in Section 2, protonic conductivity was measured at room temperature and the value of the bare (unmodified) Nafion 117 membrane itself was 0.0206 S/cm which was somewhat lower than that reported in the literature (0.08 S/cm). The difference may be caused by differences in the method of measurement. In the literature platinum electrodes were placed on the same surface of a membrane and thus surface conductivity was measured. In our experiment, we placed the electrodes on opposite



(a) Crossection of a Pd-layered Nafion

(b) Pd 100 Å on Nafion 117

(c) Pd 300 Å on Nafion 117

(d) Pd 1000 Å on Nafion 117

Fig. 2. SEM images of Pd films formed on Nafion 117 membranes.

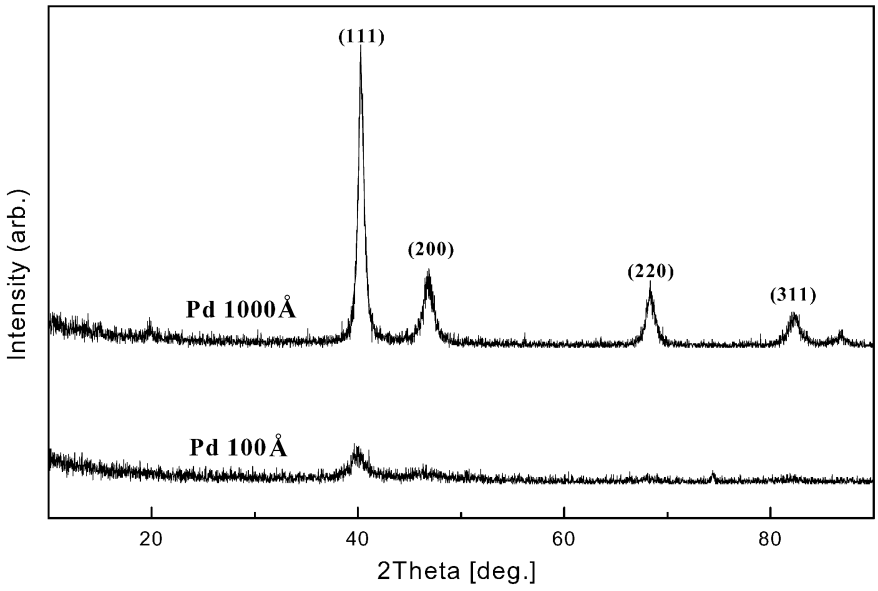


Fig. 3. XRD patterns of Pd thin films formed on Nafion 117 membranes.

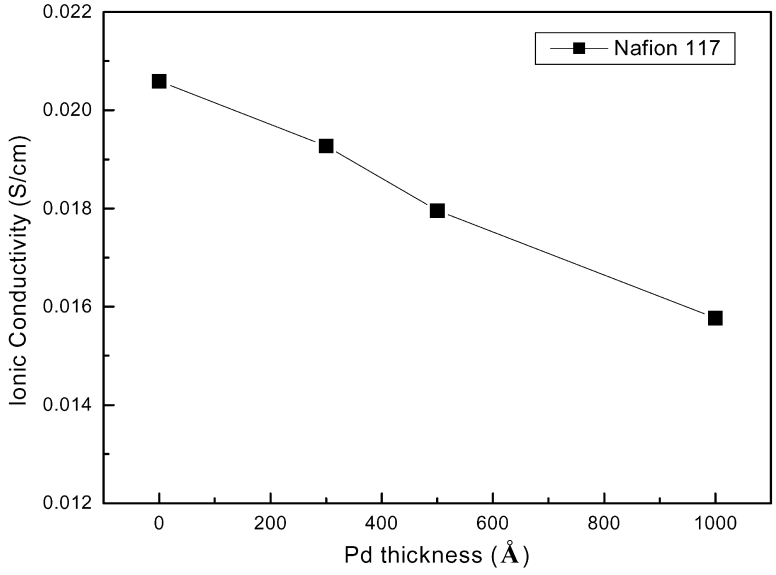


Fig. 4. Effect of Pd thickness on ionic conductivity of Pd-layered Nafion 117 membranes.

sides of the membrane and thus we measured the protonic conductivity across the thickness of the membrane. As shown in Fig. 4, protonic conductivity decreased with increasing Pd thickness. For the Pd-1000 Å film, 30% reduction in conductivity was observed.

Nafion membranes swell in a methanol solution much more than in pure water. In this regard, we investigated the effect of methanol concentration by changing the concentration of methanol in the solution which was in contact with the membrane in the conductivity cell as explained in Section 2. Two composite membranes with different Pd thicknesses were examined. As shown in Fig. 5, the protonic conductivities were found to be almost independent of methanol concentration under the given conditions, regardless of Pd thickness.

In Fig. 6, the liquid methanol permeability at 25 °C is shown as a function of Pd thickness formed on both Nafion 115 and Nafion 117 membranes. The permeabilities of the composite membranes decreased with increasing Pd thickness and they varied from 2.90×10^{-6} to 2.23×10^{-6} cm^2/s by deposition of Pd film of 1000 Å on the Nafion 117 membrane, which amounted to 23% reduction. For the Pd-1000 Å–Nafion 115 membrane, permeability decreased as much as 44% from 2.97×10^{-6} to 1.67×10^{-6} cm^2/s. The degree of reduction in methanol permeability is much less than that is expected. The palladium films formed on the

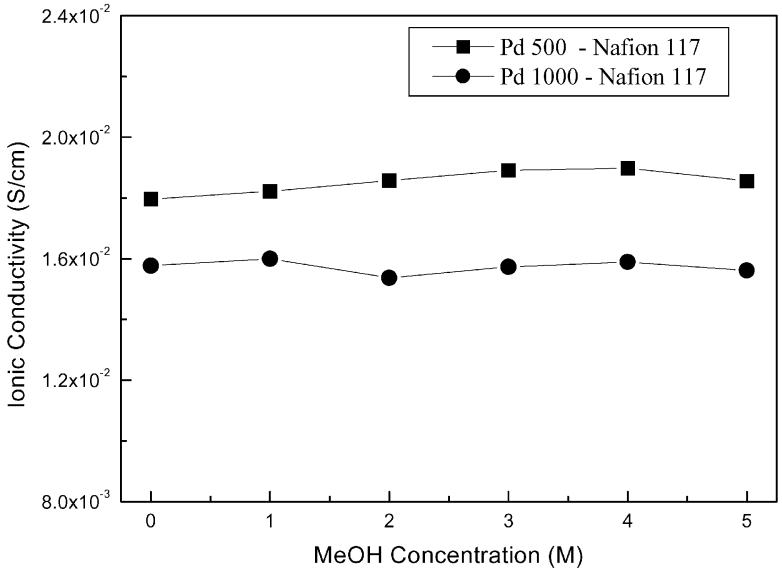


Fig. 5. Effect of methanol concentration on ionic conductivity of Pd-layered Nafion 117.

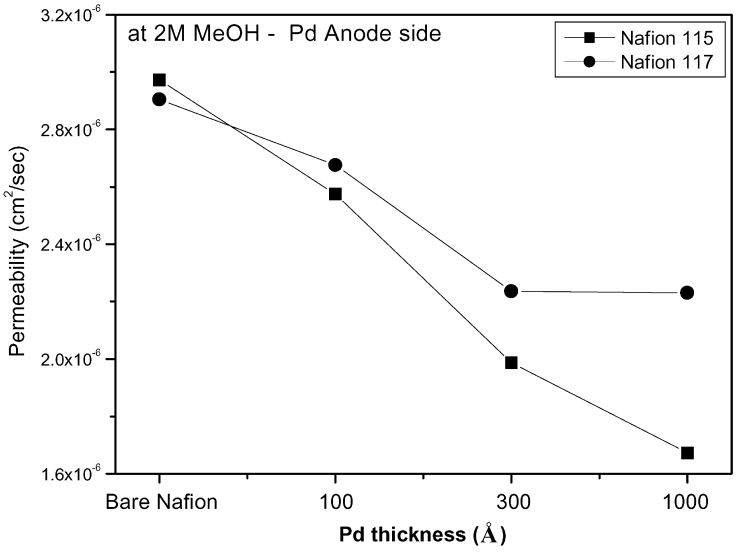


Fig. 6. Effect of Pd thickness on methanol permeability through Pd-layered Nafion membranes.

membrane have a silver-like color and are easily distinguished from the Nafion membrane. The Pd films thinner than 300 Å look very dense as shown in Fig. 2. But in view of the methanol permeability data, they are sure to be very porous. And, the insufficient resistance of the Pd-1000 Å membrane against methanol crossover may be ascribed to the cracks formed in the film.

3.3. Cell performance

The membrane–electrode assemblies were investigated in a single cell test station. After installing the MEA in the fuel cell fixture, internal humidification and steady-state performance were achieved by operating the fuel cell with methanol (1 M) and oxygen (ambient pressure) at 90 °C for 12 h. Afterwards, current–voltage (*I–V*) and power density curves were obtained by increasing current stepwise using an electronic loader. At first, experiments were carried out to measure the performances of the MEAs using bare (unmodified) Nafion membranes. Fig. 7 shows the performance data for the MEAs with bare Nafion 115 and Nafion 117 membranes, respectively. The thinner membrane, Nafion115 (125 ml) had a better performance than the thicker one, Nafion 117 (175 ml): the maximum power densities were 224 and 204 mW/cm^2 at 680 mA/cm^2, respectively. This result, as reported by others [11,12], shows that the higher protonic conductance of Nafion 115 compensates for its larger methanol crossover when compared with Nafion 117 membrane.

The effects of methanol feed concentration were also investigated. As shown in Figs. 8 and 9, the highest perfor-

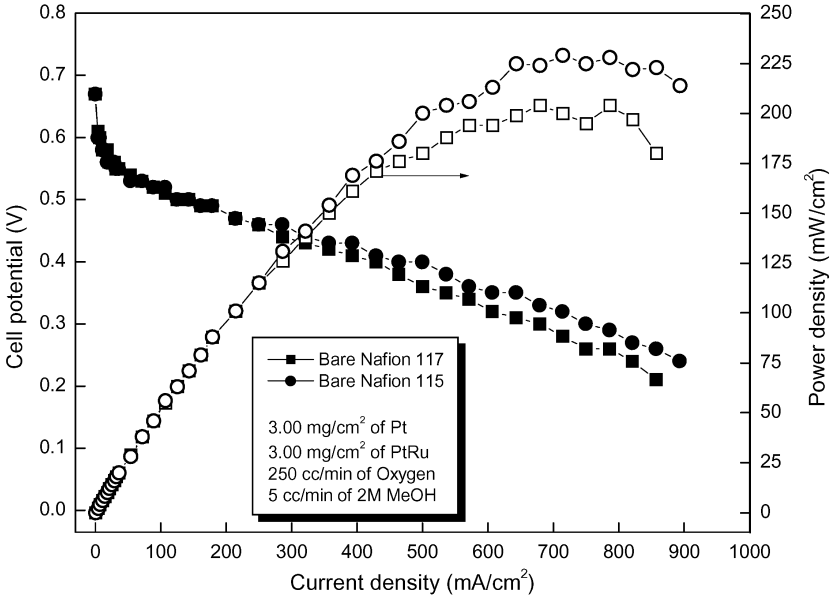


Fig. 7. Comparison of performances of bare Nafion 115 and Nafion 117.

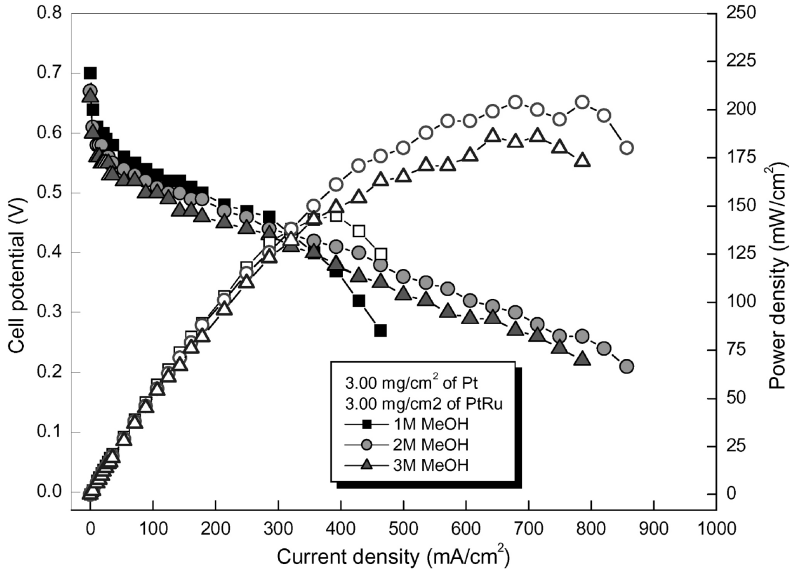


Fig. 8. Effect of methanol concentration on the performance of the cells using Nafion 117 as a PEM.

mances were obtained with a 2 M methanol feed for both membranes. But, the Nafion 115 had a better performance than the Nafion 117 throughout the concentration range tested. The current–voltage curves obtained with the Pd-layered membranes exhibited a slight decrease (Fig. 10), but the shapes of the *I–V* curves were almost the same as that of the unmodified membrane. The effect of Pd thickness was not so apparent, and the cell voltages measured at a current density of 500 mA/cm^2 were almost the same for all the Pd-layered membranes (Fig. 11). From these results, we can assume a trade-off between the protonic conductivity and the methanol crossover. In the presence of Pd film, methanol crossover is diminished but at the same time protonic conductivity also decreases. As a result, it appears that the cell performance is insensitive to the thickness of Pd film, which is more obvious in the case of Nafion 117 membrane.

In view of Fig. 10, we can find an interesting fact that at the current densities lower than 300 mA/cm^2, all the *I–V* curves fall into one line regardless of the presence and thickness of Pd films. But at the current densities higher than 300 mA/cm^2, there appear gaps among the curves which diverge with increasing current density. As reported by others [12,13], methanol crossover through an MEA is inversely proportional to current density and thus, its effect on the performance is more prominent at low current densities. That is, at low current densities cell performance can be increased by the presence of a Pd film which acts as a barrier to methanol crossover, but at high current densities

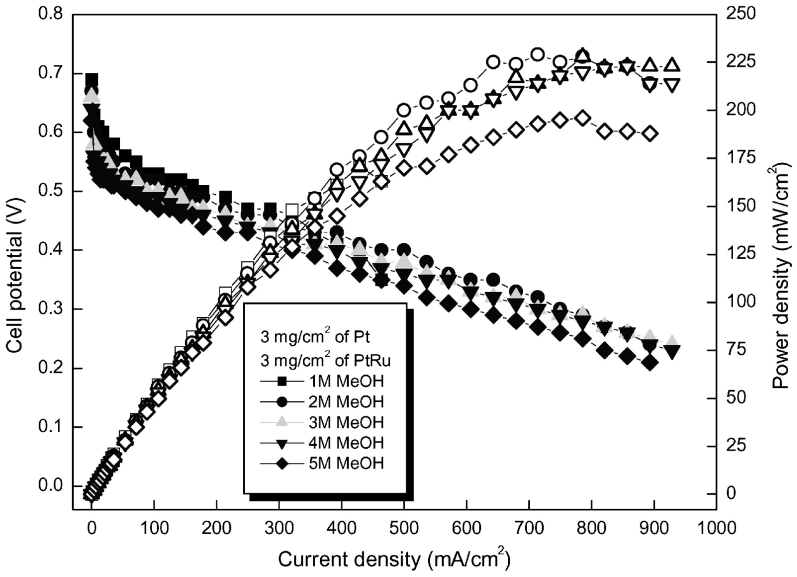


Fig. 9. Effect of methanol concentration on the performance on the cells using Nafion 117 as a PEM.

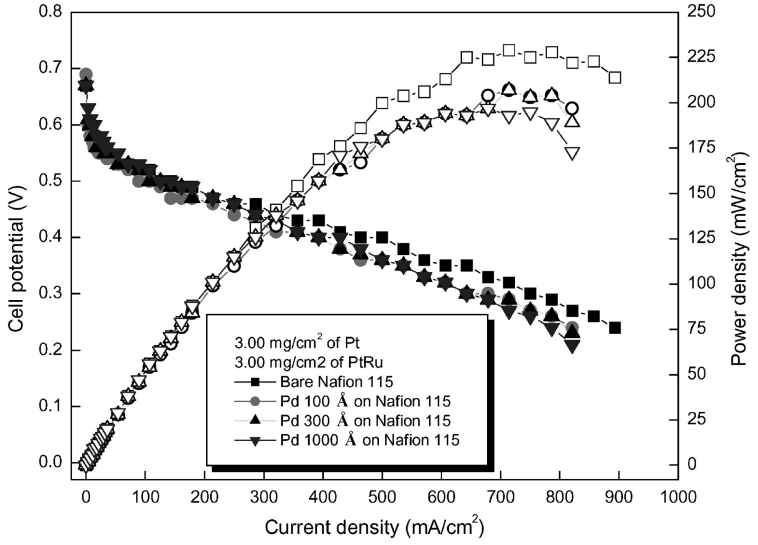


Fig. 10. Performance of Pd-layered Nafion 115 membranes.

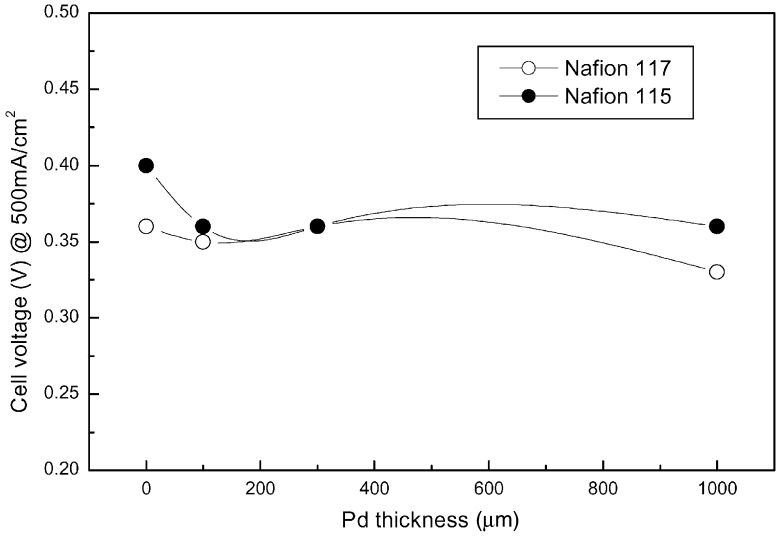


Fig. 11. Effect of Pd thickness on the performance.

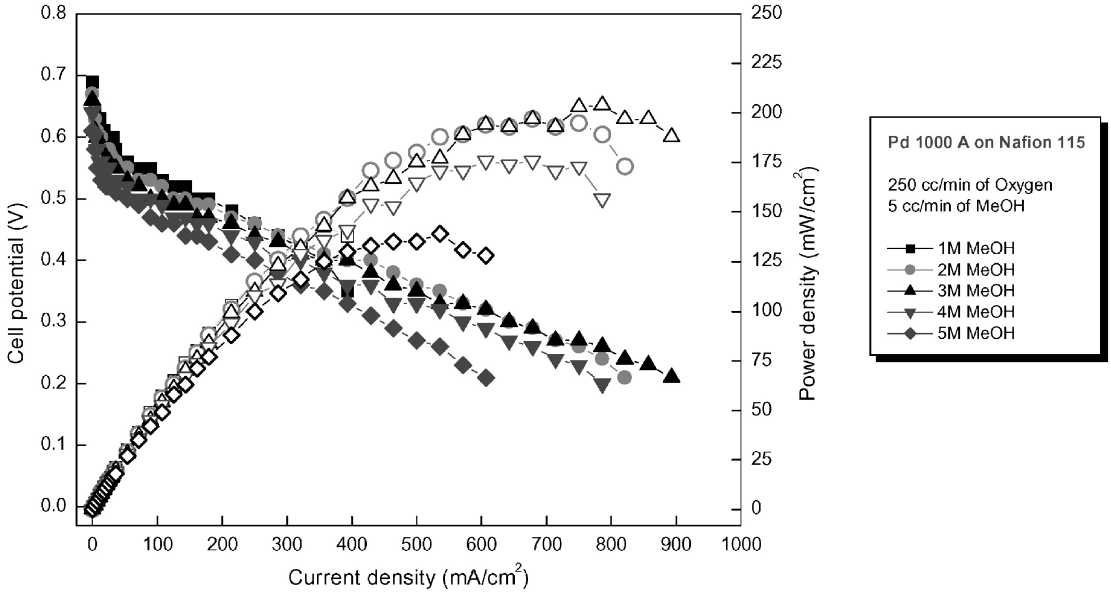


Fig. 12. Effect of methanol concentration on the performance.

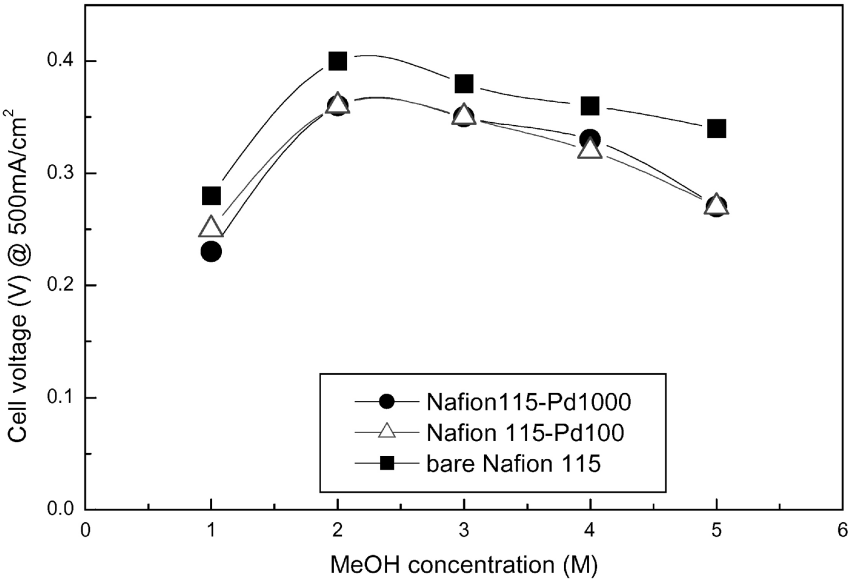


Fig. 13. Effect of methanol concentration on the performance.

cell performance is affected more by protonic conductivity of the membrane and thus, the Pd film can have an adverse effect on performance. Our result, however, is different from that of Choi et al. [10] who observed significant increase in DMFC performance by depositing a Pd film of 20 nm thick on a Nafion 117 membrane by sputtering. At present we are not able to figure out the reason behind the discrepancies between the two results.

Figs. 12 and 13 show the change in performance of the Pd-1000 Å membrane with methanol feed concentration. Similar to the bare membrane, the performance of the Pd membrane has a maximum point at a methanol concentration of 2 M and it decreases gradually with increase in methanol concentration beyond that.

4. Conclusions

This research has shown that thin palladium films can be deposited on polymer electrolyte membranes by a sputtering technique and the films thus formed have some effects on the performance of DMFCs by altering methanol permeability and protonic conductivity of the membranes. Pd films thinner than about 300 Å adhered well to the polymer membranes without cracks. But cracks develops as the Pd film thickened, and it was impossible to fabricate stable Pd films thicker than 5000 Å because the films easily peeled off from the membranes when they were in contact with water or methanol solution. The Pd films act as barriers to both methanol crossover and proton transport through the mem-

branes. The cell performance appeared to be independent of the thickness of the Pd films. This is because of the trade-off between protonic conductivity and methanol crossover in the presence of the Pd film. Though we could not achieve significant enhancement in the cell performances even with the Pd-layered membranes, it is anticipated that the Pd-layered membrane may have an effect of increasing durability on a DMFC in the long run because it reduces the methanol crossover.

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