Short communication

Operation of thin Nafion-based self-humidifying membranes in proton exchange membrane fuel cells with dry H₂ and O₂

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Abstract

With an aim to study the possibility of operating the proton exchange membrane fuel cells (PEMFC) with dry H₂ and O₂ reactants, a thin double-layer composite membrane consisting of one layer of Pt/C catalyst dispersed recast Nafion and another layer of plain recast Nafion has been investigated in PEMFC. The Pt/C particles dispersed Nafion layer and the plain Nafion layer were, respectively, on the anode and cathode sides of the membrane-electrode assembly (MEA). The Pt/C catalyst particles present in the membrane provide the sites for the catalytic recombination of H₂ and O₂ permeating through the membrane from the anode and cathode to produce water. The water generated directly humidifies the membrane and allows the operation of PEMFC with dry reactants. The electrochemical performances of the composite membranes with dry and humidified reactants are compared with those of the native Nafion membrane to identify the optimum operating conditions with self-humidifying membranes.
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1. Introduction

Proton exchange membrane fuel cells (PEMFC) have drawn much attention as an alternative power source for transportation and stationary applications [1,2]. The state-of-the-art PEMFCs operate at around 80 °C with H₂ and O₂/air as the reactants. Perfluorosulfonic acid membranes such as the Nafion membranes are currently used as the electrolyte due to their favorable chemical and mechanical stabilities along with their high proton conductivity in the hydrated state [3]. However, these membranes need to be wet to provide satisfactory proton conductivity because of the hydrophilic nature of the sulfonic acid groups attached to the polymer backbone and the necessity to hydrate the ionic clusters [4,5]. Therefore, for the fuel cell to function properly, the reactants are usually humidified through an external humidification subsystem prior to entry into the cell. However, operation of the PEMFC without external humidification can reduce the overall weight while offering significant cost saving. Also, the operation of PEMFC without the humidification subsystem can simplify the water and thermal management in the cell.

To suppress the dehydration of the membrane during operation with dry reactants, Watanabe et al. [6–9] proposed self-humidifying membranes with highly dispersed nanometer size Pt and/or metal oxides. The Pt particles in the membrane were conceived to act as water generation sites by catalytic recombination of hydrogen and oxygen reactant gases permeating through the membrane from the anode and the cathode. The generated water can directly humidify the membrane. However, the presence of Pt particles through the whole membrane increases the risk of short circuit and/or fire due to hot spots within the fuel cell. In addition, it is difficult to control the amount of Pt in the membrane using Watanabe's method. Recently, Liu et al. [10] reported a self-humidifying composite membrane prepared by casting a mixture of Nafion solution and Pt/C catalyst onto a porous PTFE film. Although

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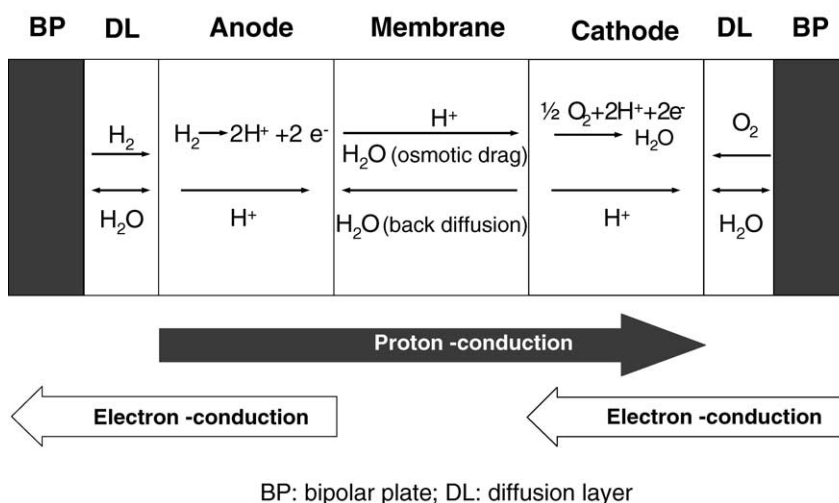 *E-mail address:* rmanth@mail.utexas.edu (A. Manthiram).

Fig. 1. Various water transport processes that could occur in a typical proton exchange membrane fuel cell.

gravity may lead to a gradient distribution of Pt/C through the membrane, the possibility of short circuit due to the electronically conducting Pt/C particles is still a concern.

On the operation aspect, the water balance in a PEMFC involves the following mechanisms (Fig. 1): (1) water supply from the reactants if an external humidification subsystem is applied, (2) water electro-osmotic drag from the anode to the cathode with proton conduction, (3) water produced at the cathode due to the cell reaction, and (4) water back-diffusion from the cathode to the anode due to the water concentration gradient. Numerical simulation of water management models indicates that water production associated with a current density of $1000\,\mathrm{mA\,cm^{-2}}$ is sufficient to completely hydrate a dry $50\,\mu\mathrm{m}$ thick Nafion 112 membrane in roughly $10\,\mathrm{s}$ [11]. Thus, theoretically, it is possible to operate the PEMFC without external humidification by carefully controlling the operating conditions.

Buchi and Srinivasan [12] operated PEMFC without external humidification using Nafion 115 as the electrolyte and found that the back-diffusion of product water from the cathode to the anode is the dominant process for water management in the cell over a wide range of operating conditions. However, the cell performance obtained without humidification was much lower than that obtained with external humidification. This is probably due to the limited water back-diffusion through the thick Nafion 115 membranes ($125\,\mu\mathrm{m}$ in dry state), which are now commonly replaced by Nafion 112 ($50\,\mu\mathrm{m}$ in dry state) in PEMFCs.

We present here a thin double-layer composite membrane consisting of one layer of plain Nafion and another layer of Pt/C catalyst dispersed recast Nafion. While the layer containing Pt/C was used on the anode side, the plain Nafion layer was used on the cathode side. This structure not only satisfies the requirement of self-humidifying the membrane close to the anode side, but also inhibits a short circuit through the membrane. The performances of the composite membrane and plain Nafion membrane in PEMFC are compared with

an aim to identify the optimum dry operating conditions for the composite membrane.

2. Experimental

The Nafion/Pt–C composite membranes were prepared by a recasting method. A 1:2 mixture of commercial 5 wt.% Nafion solution (DuPont Fluoroproducts) and isopropyl alcohol was ultrasonically mixed for half an hour with an appropriate amount of commercial 20 wt.% Pt on Vulcan XC-72R (E-TEK) catalyst, poured into a flat-bottom glass dish, and dried at $90\,^{\circ}\mathrm{C}$ for about $12\,\mathrm{h}$. The loading of Pt metal in the $\sim\!30\,\mu\mathrm{m}$ thick membrane thus prepared was $0.02\,\mathrm{mg\,cm^{-2}}$. Another layer of recast plain Nafion membrane of around $30\,\mu\mathrm{m}$ was also prepared by a similar process, but without Pt/C. These two membranes were then hot-pressed into an integral film at $150\,^{\circ}\mathrm{C}$ for $5\,\mathrm{min}$ with a force of $3\,\mathrm{ton}$. For a comparison, a control Nafion membrane with two layers of plain recast Nafion membranes was also prepared in a similar way with the same thickness. The double-layer composite and plain Nafion membranes thus prepared are designated hereafter, respectively, as N–NPtC and N–N. Both the sets of membranes were treated by boiling for over $1\,\mathrm{h}$ each with 5% H_2O_2, $1\,\mathrm{M}\ H_2SO_4$, and deionized water. The thus-prepared membranes in acid form were stored in deionized water before use.

Commercial 20% Pt/Vulcan (E-TEK) was used as both the anode and cathode catalysts. The electrodes for single cell testing consisted of gas-diffusion and catalyst layers [13]. The gas diffusion layer was prepared by spraying a mixture of the Vulcan XC-72R carbon black, solvent (mixture of water and isopropyl alcohol in a volume ratio of 1:2), and 40 wt.% PTFE onto a teflonized carbon cloth and sintering at $300\,^{\circ}\mathrm{C}$ for $2\,\mathrm{h}$. The catalyst layer was prepared by spraying a mixture of the required amount of the carbon-supported catalyst, solvent (mixture of water and isopropyl alcohol in a volume

ratio of 1:2), and commercial 5 wt.% Nafion solution (with 33 wt.% dry Nafion in the catalyst layer) onto the gas diffusion layer and drying in a vacuum oven at 90 °C for 1 h. All the electrodes had a constant Pt metal loading of 0.4 mg cm^{-2}.

The membrane-electrode assembly (MEA) was then fabricated by uniaxially hot-pressing the anode and cathode onto the membrane at 130 °C for 2 min. For preparing the MEA with the double-layer composite membrane, the anode was pressed onto the side containing Pt/C powders and the cathode was pressed onto the plain Nafion side. The MEAs were evaluated with a commercial fuel cell test system (Compucell GT, Electrochem) and a single cell test rig with 5 cm^2 active geometrical area. The pressures of the anode and cathode gases were both kept at 1 atm throughout this study. Room temperature dry H$_2$ and O$_2$ were fed at 1.5 and 3 times of their stoichiometric requirements for a current density of 1000 mA cm^{-2}, respectively, into the anode and cathode. When humidification was applied, the humidifier temperature was kept the same as the cell temperature.

3. Results and discussion

To operate the single cell with dry H$_2$ and O$_2$, the cell was usually kept at open circuit at the operating temperature for about half an hour; then the current density was increased slowly from a low value to a high value. The cell was operated at each current density for about 20 min, and 10 cell resistance values were recorded in the last 5 min. A comparison of the variations of the cell resistance with the current density of the MEAs fabricated with N–NPtC and N–N membranes and operated with dry H$_2$ and O$_2$ is shown in Fig. 2. It can be seen that the cell resistances are very high at low current densities due to the lack of the product water back-diffusion from the cathode to the anode. On slowly increasing the current density, more water is produced at the cathode and the increased water concentration gradient between the cathode and the anode enhances the water back-diffusion, hydrating the anode side and decreasing the cell resistance dramatically. From Fig. 2, it can also be observed that the cell with N–NPtC membrane has lower cell resistance at each current density
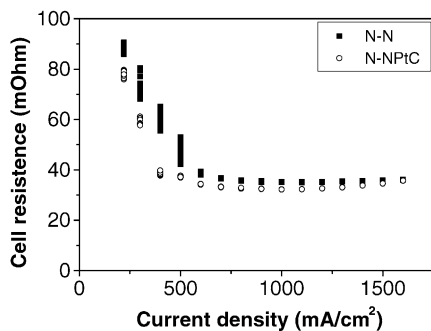

Fig. 2. Variations of the cell resistance with the current density of the MEAs fabricated with the plain N–N and composite N–NPtC membranes and operated with dry H$_2$ and O$_2$ at 60 °C.
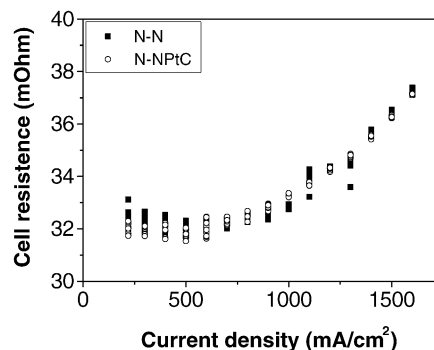

Fig. 3. Variations of the cell resistance with the current density of the MEAs fabricated with the plain N–N and composite N–NPtC membranes and operated with humidified H$_2$ and O$_2$ at 60 °C.

compared to that with the N–N membrane. Especially at low current densities, where the water back-diffusion effect is limited, the difference in cell resistance is large between the two cells, indicating the self-humidifying effect in the N–NPtC membrane. The large resistance fluctuations shown in Fig. 2 at low current densities in both the cases indicate a poor water management in the cells when the water back-transport is limited.

Fig. 3 compares the variation of the cell resistance with the current density of the cells fabricated with N–NPtC and N–N membranes and operated with humidified H$_2$ and O$_2$ at 60 °C. The results are different from those obtained with dry reactants. At low current densities, both electro-osmotic drag and back-diffusion effects are limited and the cell resistance is relatively low due to the external humidification. With an increase in the current density, more water is produced at the cathode side and the water back-diffusion effect prevails over the electro-osmotic effect, leading to a slight decrease in the cell resistance. However, when the current density is increased further, the insufficient compensation of the electro-osmotic drag by the back-diffusion of water to the anode leads to a drying out of the membrane at the anode side and an increase in the cell resistance. From Figs. 2 and 3, we also can observe that the cell resistances obtained with the dry reactants at high current densities such as 1500 mA cm^{-2} are very close to those obtained with humidified reactants, indicating that water produced at the cathode is sufficient to hydrate the thin film under proper operating conditions.

Fig. 4 compares the variations of the cell voltages with time for both the cells operated with dry H$_2$ and O$_2$ at a constant current density of 1000 mA cm^{-2}. It can be seen that the cell with the N–NPtC membrane has a higher cell voltage output than that with the N–N membrane, indicating a smaller cell resistance (Fig. 2). It may also suggest a suppressed H$_2$ and O$_2$ crossover in the former since the N–NPtC membrane could provide the sites for the catalytic recombination of H$_2$ and O$_2$ permeating through the membrane from the anode and cathode, respectively, thus alleviating the mixed potential problem associated with the crossover of the reactants. In this regard, open circuit voltage (OCV) values are good
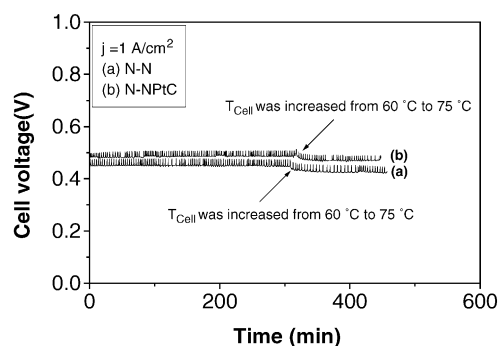
Fig. 4. Variations of the cell voltage output with time of the MEAs fabricated with the plain N–N and composite N–NPtC membranes and operated with dry H_2 and O_2 at a constant current density of 1 A cm^{-2}.
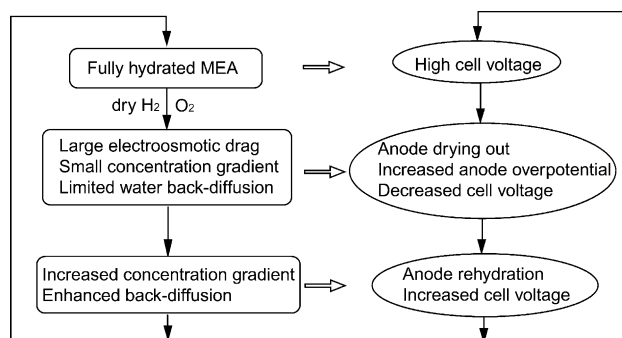

Fig. 5. Scheme of water transport in the cell and the corresponding performance of a PEMFC operated at a constant high current density of 1 A cm^{-2} with dry H_2 and O_2.

measurements of the fuel (H_2) and oxidant (O_2) crossover through the membranes. The electrodes used in both the cells were prepared identically and their activities can be assumed to be the same. Therefore, the cell with less fuel and oxidant crossover would lead to a higher OCV value. We had difficulty in obtaining stable OCV values when dry H_2 and O_2 were used due to the safety concerns arising from the serious crossover of reactants through the membrane in the dry state. However, we did record the OCV values of the two cells with humidified H_2 and O_2, and the results are given in Table 1. It is obvious that the cell with the N–NPtC membrane has higher OCV values at various temperatures from 50 to 75 °C, indicating that the incorporation of Pt/C catalyst powders into the Nafion membrane suppresses the crossover of H_2 and O_2 gases, most probably due to the effect of the catalytic recombination of the permeating H_2 and O_2 at the Pt particle sites inside the membrane.

From Fig. 4, it can also be seen that when dry H_2 and O_2 are used, the cell voltage output shows periodic fluctuations. The fluctuations are believed to be related to the water management issue in the MEA during the cell operation. Although the incorporation of Pt/C powders could enhance the hydration of the membrane, water-back diffusion becomes dominant at high current densities, thus having a larger impact on the cell performance. A possible water transport cycle in the MEA and the corresponding cell performance are given in Fig. 5. The cycle starts with a cell operating at a constant high current (5 A) and a high cell voltage with a fairly hydrated initial state through the MEA. With dry H_2 and O_2, no external water is available due to the absence

Table 1
Comparison of the open circuit voltages of cells fabricated with the plain N–N and the composite N–NPtC membranes at different temperatures with humidified H_2 and O_2

Membrane	Open-circuit voltage (V)[a]		
	50 °C	60 °C	75 °C
N–N	0.878	0.879	0.883
N–NPtC	0.953	0.945	0.942

[a] The temperature values refer to the cell temperature.

of humidification. The high current being delivered by the cell is accompanied by a large electro-osmotic drag transporting of water from the anode to the cathode. The initial small water concentration gradient through the MEA leads to a limited water back-diffusion from the cathode to the anode. The combination of the two effects leads to an increased water concentration gradient through the MEA, resulting in a dramatic dehydration of the anode side. This dehydration is manifested as an increase in the overpotential at the anode, which leads to a decreased cell performance and lower cell voltage output. With the diminishing of the cell voltage output level, the water concentration gradient from the cathode to the anode side is increased further because the hydration state at the cathode is kept due to the constant current delivered by the cell; this facilitates the water back-diffusion from the cathode to the anode. Consequently, the rehydration of the anode side leads to a decrease in the resistance and anode overpotential, and the cell performance improves, which is reflected by the increase in the cell voltage output at the same current. Thus, the whole water transport cycle begins again, leading to a periodic fluctuation of the cell voltage output as observed in Fig. 4.

To verify the proposed water transport cycle indicated in Fig. 5, the change in the cell voltage output was investigated by varying the operating condition, and the results are shown in Fig. 6. At the initial state, the cell was operated with dry H_2 and O_2, and the cell voltage output fluctuation is obvious as shown in the beginning part of region (i) of Fig. 6. Then the anode H_2 was humidified while the cathode O_2 was kept dry. It can be seen that after some time of operation, the cell voltage fluctuation disappears and pretty stable output is obtained, indicating that the anode side is well hydrated due to the external humidification and confirming the water balance cycle given in Fig. 5. When the H_2 is changed to be dry again, the fluctuations of the cell voltage start to be observed again as shown in region (ii) of Fig. 6. When O_2 instead of H_2 is humidified, the cell voltage fluctuation can still be observed as shown in region (iii) of Fig. 6, and the voltage value is slightly lower than those obtained in regions (i) and (ii). This is possibly due to the flooding problem at the cathode side. Product water from the cell reaction and
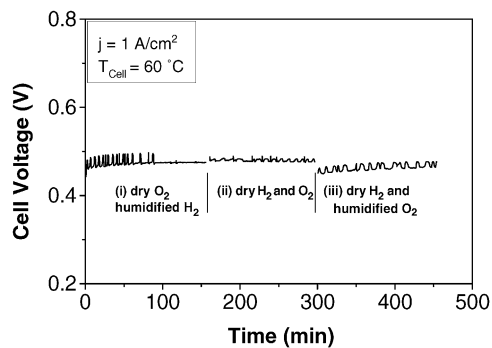
Fig. 6. Variations of the cell voltage output of the MEAs fabricated with the composite N–NPtC membrane on changing the humidification state of the reactants. The cell was operated at 60 °C and 1 A cm^{-2}.

the extra water due to the external humidification may fill the pores of the cathode, making the transport of the oxidant O_2 to the catalyst sites difficult.

Figs. 7 and 8 compare the polarization characteristics of the double-layer composite (N–NPtC) and plain Nafion (N–N) membranes in PEMFC with and without external humidification at various temperatures. These *V–I* curves were recorded after the cells had been operated at 1000 mA cm^{-2} for at least half an hour and equilibrated states similar to that shown in Fig. 4 were obtained. It can be seen that the composite membrane shows better performance in both the cases of with and without external humidification. From Fig. 7, it can also be observed that when the fuel cell is operated with humidified H_2 and O_2, the performance improves with
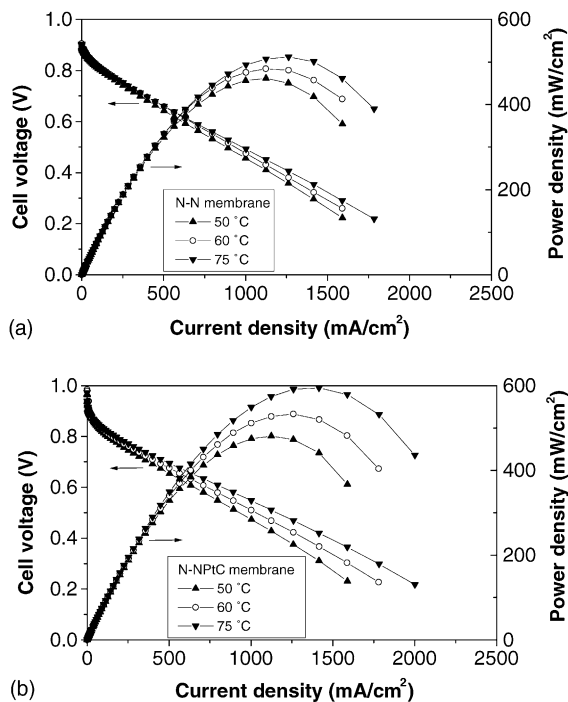

Fig. 7. Polarization characteristics of the MEAs fabricated with the (a) plain N–N membrane and (b) composite N–NPtC membrane and operated with humidified H_2 and O_2 at different temperatures.
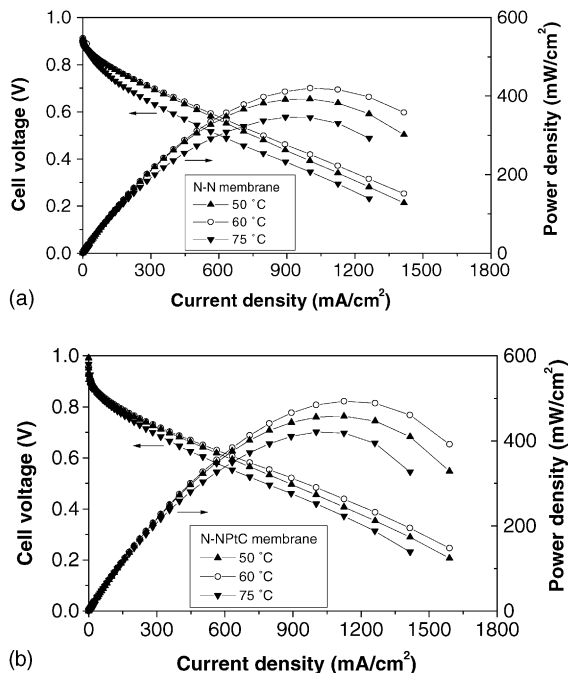

Fig. 8. Polarization characteristics of the MEAs fabricated with the (a) plain N–N membrane and (b) composite N–NPtC membrane and operated with dry H_2 and O_2 at different temperatures.

the cell operating temperature due to the improved kinetics of the cell reaction and proton transport. However, when the dry reactants are used, the best performance is obtained at 60 °C for both the native membrane and the composite membrane (Fig. 8). This is because water loss due to vaporization becomes more serious at higher temperatures (75 °C), leading to a dehydration of the MEA and a decrease in cell performance.

The relative currents generated at different cell voltages with dry H_2 and O_2 as compared to those obtained with humidified reactants are compared in Table 2 for the MEAs fabricated with the plain N–N and composite N–NPtC membranes. For both the membranes, the fractions of current density decrease with increasing temperature due to the more serious water vaporization problem at higher temperatures

Table 2
Comparison of the fraction of current density delivered by a PEMFC fabricated with the plain N–N and the composite N–NPtC membranes on operating with dry H_2/O_2

Membrane designation	Cell temperature (°C)	Fraction of current density at the voltage of[a] (%)				
		0.8 V	0.7 V	0.6 V	0.5 V	0.4 V
N–N	50	90	85	85	85	85
N–N	60	79	81	83	85	87
N–N	75	48	49	56	62	67
N–NPtC	50	97	93	94	95	96
N–NPtC	60	85	85	89	92	93
N–NPtC	75	59	58	62	67	71

[a] The fraction of current density was calculated in comparison to that obtained on operating with humidified H_2 and O_2.

although the maximum power density is obtained at 60 °C in both the cases when dry reactants are used (Fig. 8). At each temperature, the fractions of current density delivered by the PEMFC with the N–NPtC membrane are higher than those delivered by the PEMFC with the N–N membrane. For example, the cell with the N–N membrane on operating at 60 °C with dry reactants generate 79–87% of the current generated with humidified reactants at the cell voltages of 0.8–0.4 V. On the other hand, the cell with the N–NPtC membrane generates 85–93% of the current under similar conditions. These results indicate the pronounced effect of the incorporated Pt/C powder in self-humidifying the membrane and improving the cell performance with dry reactants.

4. Conclusions

The performances of thin double-layer composite membranes consisting of one layer of Pt/C catalyst dispersed Nafion and another layer of recast Nafion have been compared with those of plain Nafion membrane in PEMFC with dry and humidified H_2 and O_2 reactants. Although both the membranes could be operated with dry H_2 and O_2 due to the back-diffusion of the water produced at the cathode, the composite membranes show better performance than the plain Nafion membrane under both dry and humidified conditions. With dry H_2 and O_2, the composite membrane shows about 90% of the performance obtained with the humidified reactants while the plain Nafion membrane shows about 80% under similar conditions. The better performance with higher OCV values of the MEAs with the composite membrane is attributed to the catalytic recombination of H_2 and O_2 permeating through the membrane from the anode and cathode to produce water. The self-humidification fuel cell system presented here is more suitable for stationary applications where frequent starting and switch off of the system are not necessary.

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