

Short communication

# Operation of a proton exchange membrane fuel cell under non-humidified conditions using a membrane–electrode assemblies with composite membrane and electrode

Singaram Vengatesan, Hyoung-Juhn Kim<sup>\*</sup>, Sang-Yeop Lee, EunAe Cho, Heung Yong Ha, In-Hwan Oh, Tae-Hoon Lim

*Fuel Cell Research Center, Korea Institute of Science and Technology, 39-1 Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Republic of Korea*

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## Abstract

Composite membranes with hydrophilic substances can retain water and allow the operation of proton exchange membrane fuel cells (PEMFCs) under non-humidified conditions. In this work, thin Nafion composite membranes with silica are prepared to operate a PEMFC with dry fuel and oxidant. In addition, the role of silica in the catalyst layer as a water retainer is studied. In particular, the anode and the cathode are modified separately to elucidate the effect of silica. The incorporation of silica in the membrane and the catalyst layer enhances single-cell performance under non-humidified operation. The cell performance of membrane–electrode assemblies using the composite membrane and electrode is higher than that of a MEA using commercial Nafion 111 membrane under non-humidified conditions.

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**Keywords:** Composite membrane and electrode; Membrane–electrode assembly; Non-humidified operation; Polymer electrolyte membrane fuel cell; Silica; Water retention

## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered to be promising energy generators for future vehicles and portable devices [1]. Nafion-type perfluorosulfonic acid polymers are used widely as the electrolyte due to their favourable chemical, mechanical and thermal stability [2]. The membranes have to be hydrated in order to achieve good proton conductivity. Therefore, they are usually humidified by means of an external system. For simplicity and compactness, therefore, operation of fuel cells without external humidification is essential [3].

There are numerous reports for the operation of PEMFCs under dry conditions [3–10]. Among them, the use of self-humidifying membranes that are made by incorporating inorganic materials into proton conducting polymers is currently of interest [7,9,10]. It is believed that inorganic particles such as SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>, when added to the membrane act as

water absorbers and can provide sufficient proton conductivity by keeping the membrane in a well-hydrated state under low humidity or dry conditions. Some authors [3,11–14] have introduced Pt along with inorganic particles to generate water in the membrane. Also, if a fuel cell is operated under dry conditions, the water generated by the electrochemical reaction is the only source of humidification. So, the effective management of product water in the cell is very important. With proper design and operation of a PEMFC, excellent water management can be achieved [15].

In this work, non-humidified operation of a fuel cell is achieved by using a thin composite membrane and a composite electrode that are modified with silica. Generally, the catalyst layer and membrane on the anode side are dehydrated during dry operation, whereas the cathode side is hydrated by product water. This water can diffuse back to the anode side, especially in the case of thin membranes. Previous work [16] on non-humidified operation using thin membranes showed an improved cell performance due to enhancement of water back-diffusion. On the other hand, the application of a thin membrane causes high gas cross-over and subsequent degradation in cell

<sup>\*</sup> Corresponding author. Tel.: +82 2 958 5299; fax: +82 2 958 5199.  
E-mail address: [hjkim25@kist.re.kr](mailto:hjkim25@kist.re.kr) (H.-J. Kim).

performance. Recently, Ahn et al. [17] operated single cells under a dry condition using membrane–electrode assemblies (MEAs) with different equivalent weight ionomers incorporated in the electrodes. It was found that the low equivalent weight ionomer exhibited better performance by retaining more water molecules in electrodes. Consequently, in the approach adopted here, it is planned to add water-retaining silica particles in both the catalyst layer and the membrane to keep them in a well hydrated state. The electrochemical behaviour of single cells using this technique is studied under non-humidified conditions.

## 2. Experimental

### 2.1. Preparation of silica–Nafion composite membrane

The silica–Nafion composite membrane was prepared with tetraethylorthosilicate (TEOS) and 20 wt.% Nafion (Dupont Fluoroproducts). The TEOS was hydrolyzed with 0.1 M HCl solution. The solution was mixed with 20 wt.% Nafion solution and stirred for 2 h to obtain a silica–Nafion composite mixture. The solution was cast on a glass plate, dried at 60 °C for 3 h, and then heated at 130 °C for 3 h to obtain the composite membrane. With this procedure, composite membranes with different TEOS contents were prepared. The membranes were treated by successive boiling for 1 h in 5% H<sub>2</sub>O<sub>2</sub>, 0.5 M H<sub>2</sub>SO<sub>4</sub> and water to obtain the acid form of the membranes. Also, a recast Nafion membrane that was not modified with silica was prepared using the same procedure, to serve as a reference material. The thickness of all membranes was about 32 ± 2 μm in the dry state.

### 2.2. Preparation of membrane–electrode assemblies (MEAs)

The catalyst inks for the electrodes were prepared by mixing 40 wt.% Pt/C (E-Tek Inc.), 5 wt.% Nafion solution (Dupont) and isopropyl alcohol (Baker HPLC grade reagent). The catalyst inks were sprayed on to the pretreated composite membrane, which had a platinum loading of 0.3 and 0.4 mg cm<sup>-2</sup> in the anode and the cathode, respectively. The catalyst-coated membrane

(CCM) was dried overnight at 50 °C. The same procedure was used to make the MEAs employ recast Nafion or Nafion 111 membranes.

The catalyst layer with silica was prepared by mixing silica sol, which was prepared from hydrolysis of TEOS, and then was sprayed on the membrane. The silica content in the catalyst layer was varied from 0 to 10 wt.% (relative to the Nafion content in the catalyst layer).

### 2.3. Analysis of MEA and single-cell tests

Single cells were assembled with CCM, gas-diffusion media (Sigracet GDL 30 BC), Teflon gaskets, and graphite blocks. Hydrogen and oxygen were fed to the anode and the cathode, respectively, at the same flow rate of 400 cm<sup>3</sup> min<sup>-1</sup> under ambient pressure. When using air as the oxidant, the flow rate of air was fixed at 1500 cm<sup>3</sup> min<sup>-1</sup>.

Before operating the cell using dry reactants, the cell was activated at 80 °C under 100% humidified conditions at the anode and the cathode. The cell was operated in a galvanostatic mode at 1 A cm<sup>-2</sup> for 5 h under the above conditions. Then, the cell temperature was decreased to ambient temperature and operated with dry reactants at 1 A cm<sup>-2</sup> for 24 h before recording the current–voltage (*i*–*V*) characteristics of the MEAs.

The impedance of the single cells was measured by means of a.c. impedance spectroscopy. The instrument (Zahner electric IM6) was used in a potentiostatic mode at 0.8 V with an amplitude of 5 mV from 10 mHz to 10 kHz.

The surface and cross-section of each composite membrane was examined with a scanning electron microscope (SEM).

## 3. Results and discussion

### 3.1. Effect of silica in composite membrane

A SEM micrograph of the silica–Nafion composite membrane that was prepared with 10 wt.% TEOS in the Nafion membrane is presented in Fig. 1. The silica particles are distributed uniformly on the surface and have an average size of around 220 nm.

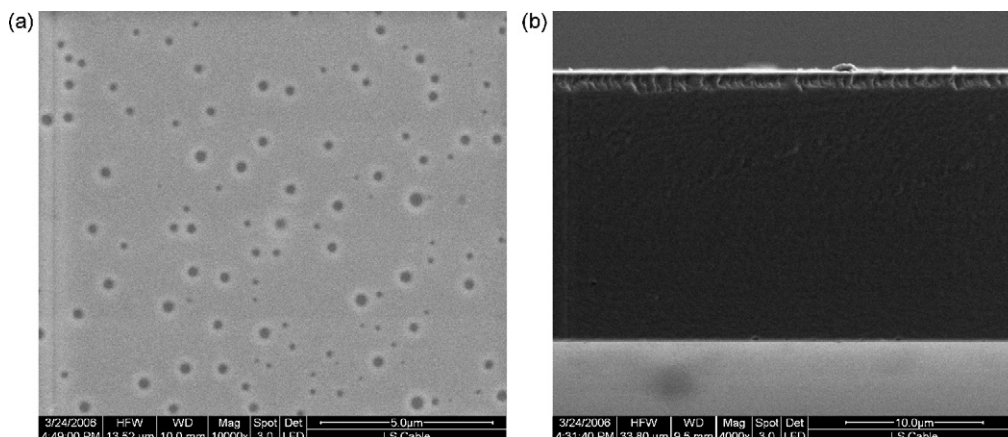


Fig. 1. Scanning electron micrographs of (a) surface and (b) cross-section of silica–Nafion composite membrane with 10 wt.% TEOS.

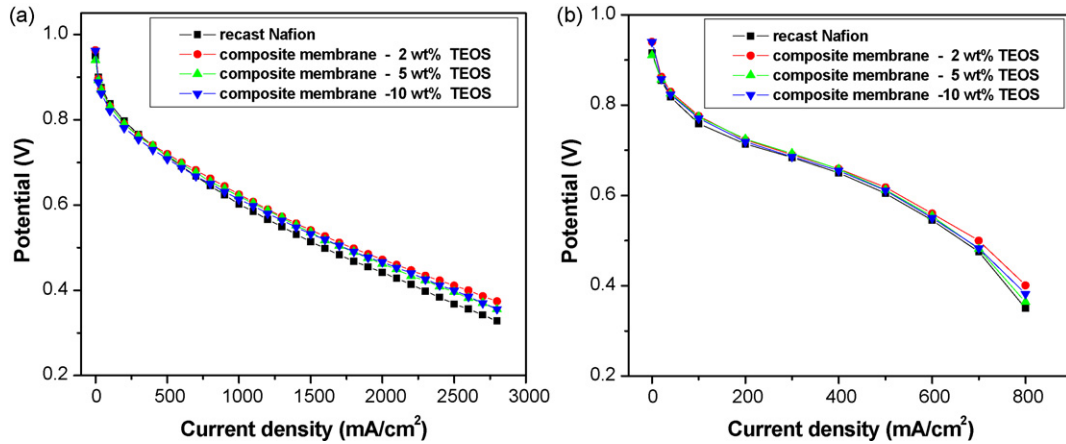


Fig. 2.  $i$ - $V$  characteristics of single cells operated at 34 °C using MEAs with various amounts of silica in the composite membrane under dry (a)  $H_2/O_2$  and (b)  $H_2/air$ .

To observe the effect of silica on cell performance under non-humidified conditions, the silica content was varied in the composite membrane. The single-cell performance of MEAs under non-humidified conditions using composite membranes with various amount of silica (2, 5 and 10 wt.%) is shown in Fig. 2. From the  $i$ - $V$  curve, it is observed that the composite membrane displays a higher cell performance than that obtained with the pristine recast Nafion membrane. As the silica content is increased, however, the cell performance decreases. This is due to the fact that a high silica content in the membrane increases its resistance and eventually reduces its proton conductivity, which was further confirmed by impedance analysis. The impedance spectra of single cells operated using composite membranes with various silica contents are illustrated in Fig. 3. The data show that the ohmic resistance of composite membranes is slightly higher than that of the pristine recast Nafion membrane, which is due to the resistance caused by the inorganic particles in the composite membrane. Also, the charge-transfer resistance increases considerably as the silica loading is increased in the composite membranes because of the same reason.

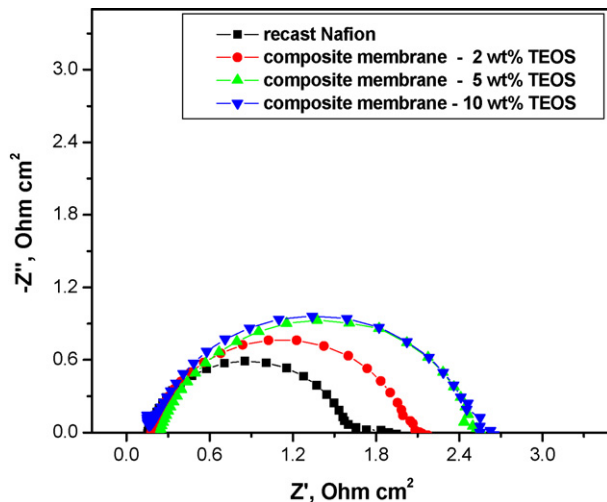


Fig. 3. a.c. impedance spectra of single cells using MEAs with various silica contents in the composite membrane under dry conditions.

### 3.2. Effect of silica in anode catalyst layer

During dry operation of a single cell, the anode catalyst layer becomes more dehydrated than the cathode and it is therefore essential to keep water in the anode side [4]. To determine the efficacy of silica as a water retainer, it was added to the anode catalyst layer. The silica-Nafion composite membrane with 2 wt.% TEOS, which showed the best cell performance under non-humidified conditions (Fig. 2), was used for the MEA fabrication. The single-cell performance of MEAs with various amounts of silica in the anode catalyst layer (1, 5, and 10 wt.% relative to the Nafion content in the catalyst layer) is presented in Fig. 4. With  $H_2/O_2$  operation, the cell performance of the MEA with 1 wt.% TEOS in the anode layer was similar to that of the MEA without silica in the anode layer. Also, the cell performance decreases as the silica content is increased (Fig. 4(a)). When  $H_2/air$  is used for the operation (Fig. 4(b)), however, the performance of the MEAs with 1 wt.% TEOS in the anode layer is lower in the low current density region and higher in the high current density region than that of MEA without silica incorporation. Because thin membranes were used for both MEAs, it was expected that water back-diffusion would be very active in both cases. In fact, however, the back-diffused water is retained by silica particles in anode layer and thus maintains a well-hydrated state, which results in an improvement in performance in the high current density region. On the other hand, when the silica content is increased in the anode side, the performance decreases at all current densities. This is mainly due to the charge-transfer (CT) resistance associated with the mass transport (MT) problem caused by a high amount of silica in the catalyst layer. The impedance spectra of single cells with various amounts of silica in the anode layer are presented in Fig. 5. The MEA with a high silica content (10 wt.% TEOS) exhibits a large CT resistance, which confirms the  $i$ - $V$  characteristics in Fig. 4.

### 3.3. Effect of silica in cathode catalyst layer

To observe the effect of silica in the cathode catalyst layer, single cells were operated using MEAs with various contents of silica in the cathode. A silica-Nafion composite membrane with

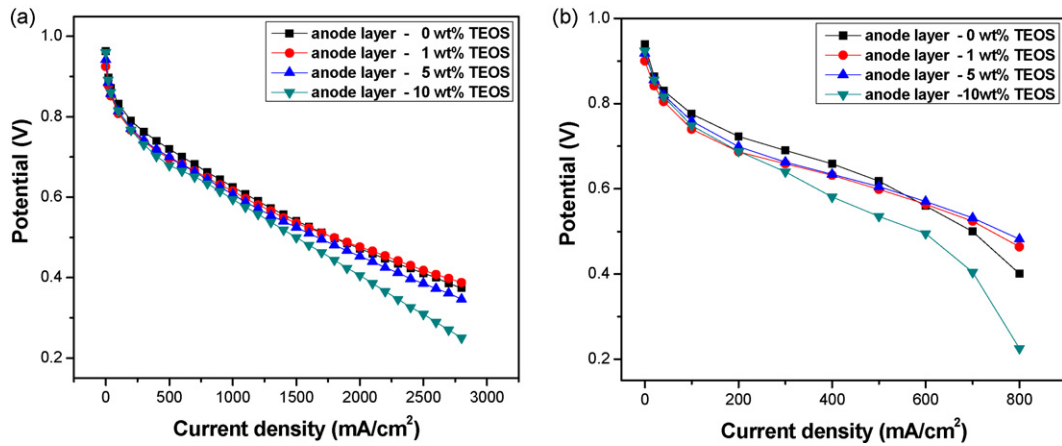


Fig. 4. Polarization curves of cells operated at 34 °C using MEAs with various amounts of silica in anode catalyst layer under dry (a) H<sub>2</sub>/O<sub>2</sub> and (b) H<sub>2</sub>/air.

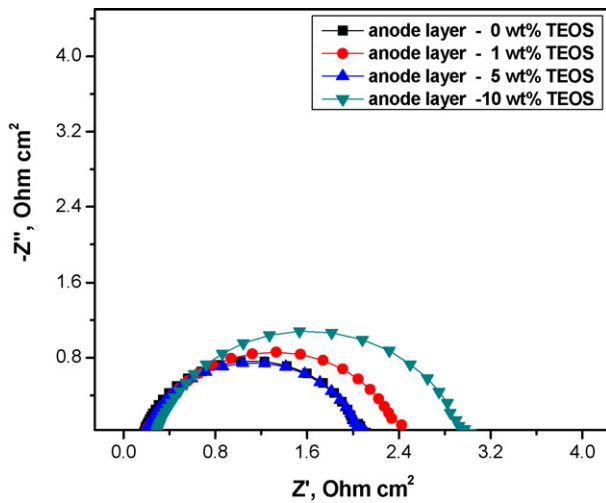


Fig. 5. Effect of silica in anode catalyst layer on impedance characteristics of single cells operated under non-humidified conditions.

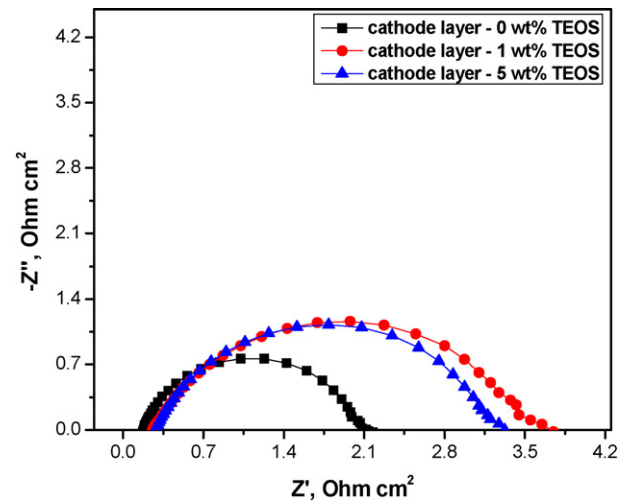


Fig. 7. Effect of silica in cathode catalyst layer on impedance characteristics of single cells operated under non-humidified conditions.

2 wt.% TEOS was used as the membrane for MEA fabrication. Compared with the influence of silica in the anode layer, the silica in the cathode layer results in a decline in performance, even with small amount of silica. This implies that silica plays a

negative role in the cathode layer, as the water produced there is sufficient to humidify the catalyst layer (Fig. 6). The impedance spectra of single cells are depicted in Fig. 7 and demonstrate a very high ohmic resistance as well as a mass-transport resistance.

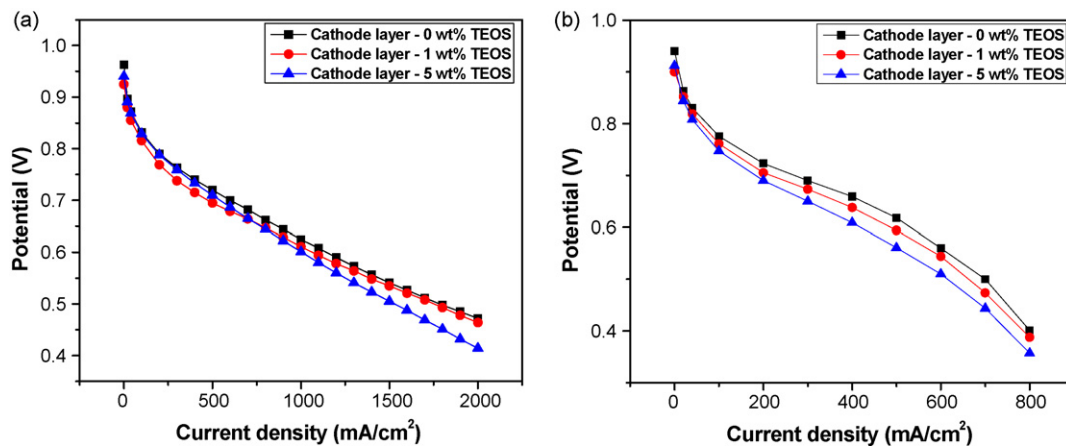


Fig. 6. *i*-*V* curves of single cells operated at 34 °C using MEAs with various amounts of silica in cathode catalyst layer under dry (a) H<sub>2</sub>/O<sub>2</sub> and (b) H<sub>2</sub>/air.



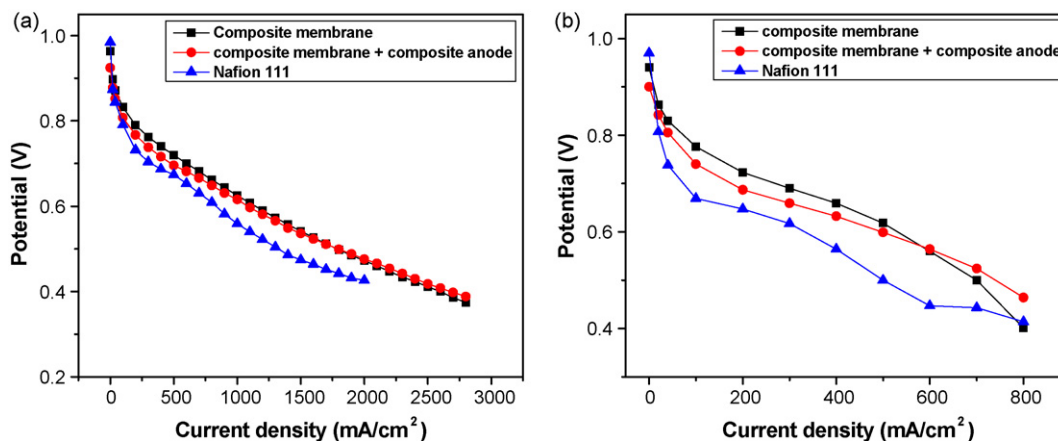


Fig. 8. Comparison of single-cell performances of different MEAs at 34 °C under dry (a) H<sub>2</sub>/O<sub>2</sub> and (b) H<sub>2</sub>/air.

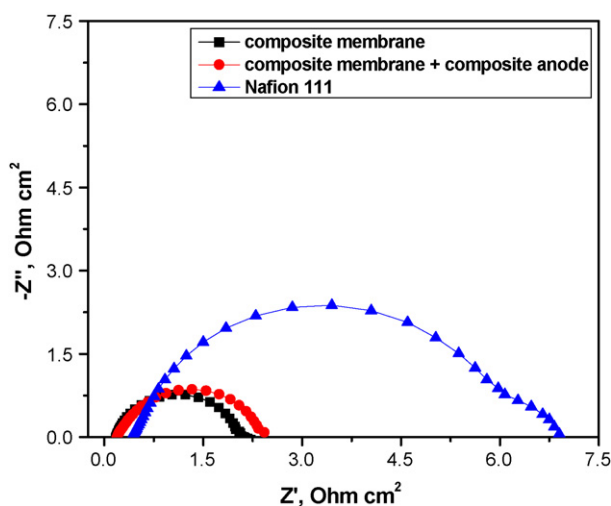


Fig. 9. a.c. impedance spectra of single cells with different MEAs under dry conditions.

Finally, the cell performance of composite membranes was compared with a commercial Nafion 111 membrane, as shown in Fig. 8. The cell performance of the commercial Nafion 111 membrane is lower than that of the composite membrane and the composite electrode. The commercial Nafion 111 membrane does not retain water under non-humidified conditions and the phenomenon is more prominent when air is employed as the oxidant. This strongly demonstrates the water-retaining capabilities of the composite membrane and the electrode for dry operation. The impedance spectra of single cells are given in Fig. 9. MEAs with a composite membrane and a composite anode layer show lower resistances than that of a MEA with a Nafion 111 membrane. In case of the Nafion 111 membrane, the charge-transfer resistance is very high because of reduced proton conduction through membrane due to insufficient water in the membrane under dry conditions.

#### 4. Conclusions

Silica–Nafion composite membranes have been prepared using a solution-casting process. The single cells are operated

under non-humidified conditions with a composite membrane and an electrode which are modified with silica. The role of silica as a water retainer in the membrane, as well as in the catalyst layer is studied by varying the amount of silica. Silica in the anode catalyst layer has a more prominent effect on cell performance than that in the cathode catalyst layer under dry conditions. This implies that the silica prevents anode dehydration by retaining more water during dry operation, and the MEA with a composite membrane and electrode displays higher performance than a pristine MEA with a Nafion 111 membrane under dry conditions, which reflects the water-retaining capacity of silica.

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