

Using SiO₂ Nanopowders in Anode Catalyst Layer to Improve the Performance of a Proton Exchange Membrane Fuel Cell at Low Humidity

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Abstract

In this study, the transfer method is employed to add hydrophilic SiO₂ nanopowders to a Pt/C catalyst ink to form an anode catalyst layer on a proton exchange membrane (PEM). The SiO₂-layered membrane electrode assembly improves the performance of the PEM under low- or zero-humidification conditions. When the PEM fuel cell (PEMFC) undergoes electrochemical reaction, the moisture content of the PEM exhibits a substantial influence on the transmission of protons. To ensure the moisture content remains high, an external humidifier is typically employed to humidify the majority of PEMFCs. However, self-humidifying PEMFCs could utilize the water produced by the fuel cell reaction, thereby eliminating the need for an external humidifier. In this study, various SiO₂ loadings were added to an anode catalyst layer, and the cell temperature and gas humidification conditions were adjusted to determine the influence of the SiO₂ loadings on the fuel cell performance. The results show that adding SiO₂ is preferable to not adding SiO₂ when the fuel cell temperature is 50°C.

Keywords

Proton Exchange Membrane Fuel Cell, Self-Humidifying, SiO₂

1. Introduction

Fuel cells are a type of energy conversion device. They follow electrochemical principles when converting the chemical energy from fuels (*i.e.*, hydrogen) and oxidants (*i.e.*, oxygen) into electrical energy. Fuel cells provide a high energy-conversion rate and possess various environmentally friendly characteristics. Proton exchange membrane fuel cells (PEMFCs) are a type of fuel cell that is highly suitable for low-temperature operations, and has high specific power. Numerous previous studies have asserted that fuel cells to be the optimal future clean power option for fields related to distributed power generation, mobile power for communication, and electric

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vehicles [1] [2].

A membrane electrode assembly (MEA) is the core element of fuel cells. The MEA is where fuel and oxidants undergo electrochemical reactions to produce electrical energy. The MEA comprises an anode, a cathode, and a proton exchange membrane (PEM) located between the two. Currently, PEMFCs typically adopt solid polymer electrolyte membranes, where protons within the membrane become hydrated protons, and are conducted from the anode to the cathode. The water in the membrane can be considered the proton-conducting carrier. Thus, a higher level of water content within the polymer membrane accelerates the proton conduction rate. Therefore, maintaining adequate water content within the PEM is crucial to PEMFCs [3] [4].

Previous studies have focused primarily on supplying water or maintaining adequate moisture to the PEM of PEMFCs by employing external humidifying auxiliary systems that increase the humidity of the reaction gas entering the fuel cell stack. However, this also increases the complexity of the fuel cell system. Without external humidifying systems or conditions for the fuel cell, the water produced from the cathode-side reaction becomes the only water source for maintaining the moisture of the PEM within the fuel cell. The water molecules inside the PEM are transported by the following 2 mechanisms: 1) they are transported with protons by electromigration from the anode to the cathode during the electro-osmosis process, forming electromigration water; and 2) the back-diffusion water is returned to the anode from the cathode with the concentration gradient effect. When the back-diffusion water fails to replenish the electromigration water within a certain time, the anode-side in the membrane becomes dry, causing a significant decline in proton electric conductivity. Therefore, developing and examining a self-humidifying PEMFC that does not require a humidifying auxiliary system is crucial for promoting the commercialization of PEMFCs in the future.

Research on self-humidifying fuel cells can be divided into the following 3 categories: 1) self-humidifying flow fields; 2) self-humidifying PEMs; and 3) self-humidifying MEAs. In the self-humidifying flow field method, the flow field is designed to enable the water produced in certain parts of the cathode-side during the electrochemical reactions to provide a relatively humidified or moisturized environment for the MEA [5] [6]. Several studies have shown that self-humidifying PEMs are currently the most commonly employed technology applied in research on self-humidifying PEMFCs [7]-[11].

The MEA method optimizes or modifies the diffusion layer, catalyst layer, PEM, and the formed MEA to improve the back-diffusion effect of water produced by the cathode-side's electrochemical reaction moving to the anode-side, as well as increasing the MEA's ability to retain water, thereby preventing the anode and PEM from drying out. Efforts have been made to minimize the humidification of the ionic polymer by introducing SiO₂ either in the catalyst layer or on the gas diffusion layer [12]-[14]. Based on the self-humidifying MEA concept, we strengthened the hydrophilicity of hydrogen electrodes and developed a simpler method for producing a self-humidifying MEA. Hydrophilic oxide particles were added to the ink that was used to form the hydrogen electrode catalyst layer, and we employed a transfer process to construct the self-humidifying MEA. In this study, the effect of various amounts of SiO₂ was examined and experiments were conducted under low-humidity conditions.

2. Experimental Methods

The hydrophilic oxide selected for this experiment was SiO₂. Based on the manufacturing process, SiO₂ can be categorized as produced by either 1) the precipitation method, or 2) the vapor method. SiO₂ produced using the vapor method possesses uniform particle size distribution and a comparatively larger specific surface area, and the vapor method is currently the mainstream manufacturing method. SiO₂ can also be divided into hydrophilic and hydrophobic SiO₂, depending on whether surface alkyl processing is applied. Hydrophilic SiO₂ produced using the vapor method covers a larger specific surface area. Additionally, its surface possesses an OH group and is highly absorbent to moisture. Therefore, for this study, we selected Degussa AEROSIL 200, which is a hydrophilic SiO₂ produced using the vapor method with a specific surface area (200 m²/g).

Among the various MEA manufacturing methods, the transfer method generally provides superior results and performance compared to traditional methods; thus, the transfer method was used in this study [15] [16]. In addition to providing a superior expected result and performance compared to traditional methods, the thin film catalyst layer produced using the transfer method is less likely to cause flooding phenomena, even under conditions of high hydrophilicity. The production process for the self-humidifying MEAs used in this experiment involved adding various quantities of SiO₂ to compare how varying the level of SiO₂ affects the performance un-

der various cell temperatures and humidification conditions.

2.1. MEA Production

For this study, the hydrophilicity of the anode-side's catalyst layer was reinforced to ensure that the anode was able to absorb more water than the cathode, which improved the back-diffusion effect of water produced by the cell cathode. To produce the anode (hydrogen electrode), the following procedure was performed. First, the Pt/C catalyst, SiO₂, Nafion solution, deionized water, and isopropyl alcohol were mixed and prepared in the appropriate proportions to produce the catalyst ink (Pt/C catalyst and Nafion solution weight ratio, 3:1). The catalyst ink was then stirred (120 rpm) at 80°C until a certain degree of viscosity was achieved. The transfer paper was coated with the catalyst ink (0.3 mg/cm² Pt content) to form the hydrogen electrode. To produce the cathode (oxygen electrode), similar steps were performed, except no SiO₂ was added to the catalyst ink, which was coated directly onto the GDL.

To produce the MEA using the transfer method, a coating fixture with a size identical to that of the electrode was first produced. Next, the coating fixture was placed onto the transfer paper, which was coated with the catalyst ink. Subsequently, the transfer paper was placed into a circulation oven and dried for 1 h at 80°C. After drying, the paper was measured to determine whether the required loading level had been achieved. The entire manufacturing process followed the traditional method combined with the hot-pressing technique of the transfer method, where the anode was constructed using transfer paper that was coated with various mixture ratios of the Pt/C- SiO₂ ink, and the cathode was constructed using a gas diffusion electrode that was coated with the Pt/C catalyst ink. A Nafion 112 membrane was inserted between the transfer paper and the gas diffusion electrode. Next, the upper and lower presses were preheated for 60 s at 140°C, and the pressure was increased to 40 kgf/cm² for 90 s before removal. Finally, self-humidifying MEA was produced.

2.2. Fuel Cell Performance Test

For the electric current and voltage (I-V) performance curve test in this experiment, hydrogen and air were used as the reaction gases, and humidifying bottles were used to control the humidity of the reaction gases. Prior to the test, the MEA was left to activate for 10 h. To reduce the influence of various operation variables, a fixed H₂ flow rate of 200 sccm, an air flow rate of 500 sccm, and a zero gas back-pressure were applied. The I-V test was repeated 15 times, and the data obtained during the 15th iteration was selected to plot the I-V curve to compare how adding the SiO₂ affected the fuel cell performance under the various fuel cell temperatures and humidifying conditions.

3. Results and Discussion

In this study, energy dispersive spectroscopy (EDS) mapping appended to scanning electron microscopy (SEM) was employed to analyse the electrode surface. The water contact angle was measured to investigate the hydrophilic effect of adding (or not adding) SiO₂. The cell I-V curve test was employed to assess whether adding the SiO₂ improved the cell performance.

3.1. Electrode Surface Composition Analysis

After coating the SiO₂-loaded catalyst ink directly onto the GDL, EDS mapping was performed to analyze the composition and observe the distribution or dispersion of the SiO₂. **Figure 1** shows the composition analysis results from the EDS mapping of the SiO₂-coated GDL. **Figure 1(a)** shows the emergence of several particles on the specimen surface. Combining **Figures 1(a)-(c)** indicates an increasing presence of Si and O elements proximal to these particles. Therefore, we concluded that these were SiO₂ particles. Because the SiO₂ employed in this study was nanopowder, we assumed that these particles were also created by the aggregation of the SiO₂ nanopowder. The EDS mapping analysis showed a slightly worse SiO₂ dispersion and an uneven distribution, which could cause uneven water absorption, thereby influencing the self-humidification effect. Thus, the ink technique for the dispersion of hydrophilic nanopowders requires further improvement.

3.2. Measuring the Water Contact Angle

The water contact angle test is used to measure the hydrophilicity of a surface; the lower the angle, the greater

the hydrophilicity. During the experiment, the water contact angle was calculated by dripping water onto the GDL and calculating the average value after 3 measurements. The measurement results in **Figure 2** show that the water contact angle value of the non-coated GDL was 118°, which decreased to 45° after SiO₂ coating. This

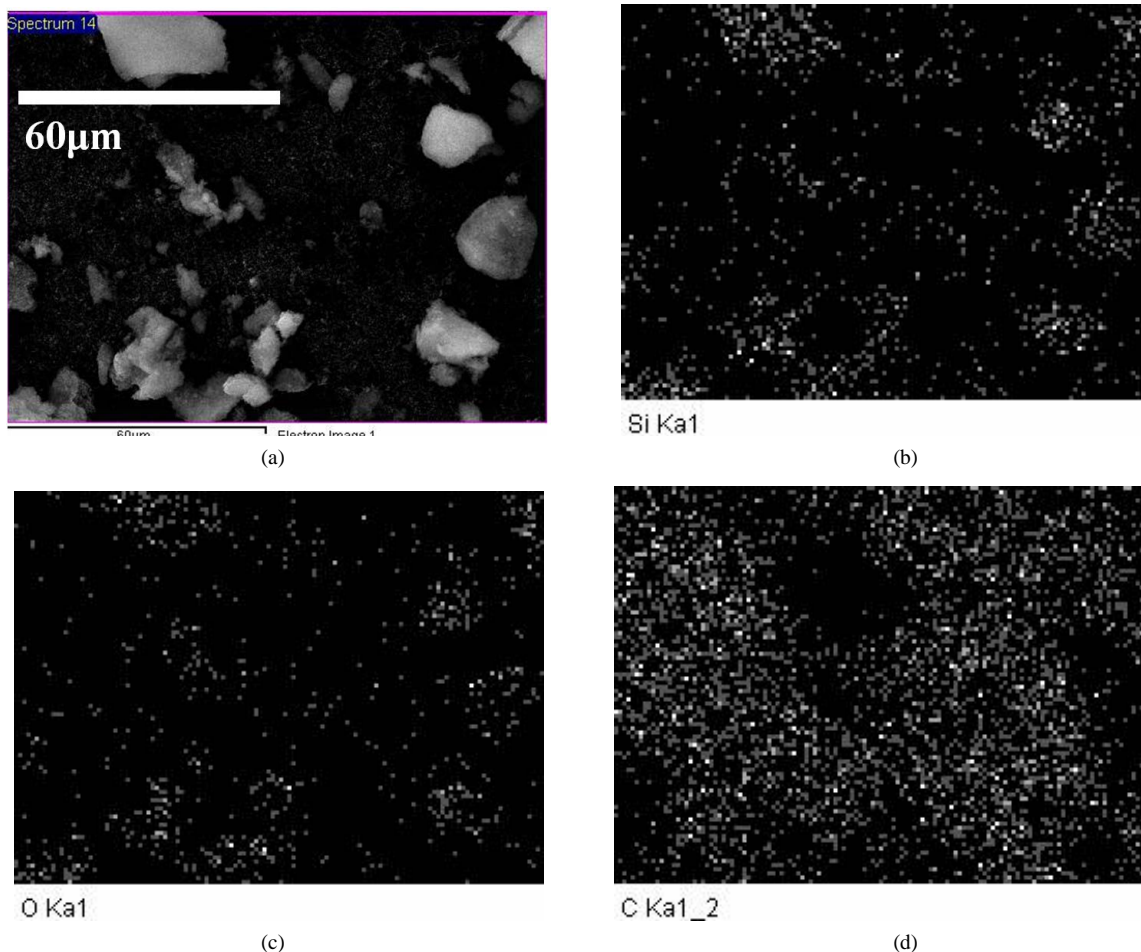


Figure 1. EDS mapping of the gas diffusion layer coated with SiO₂. (a) Surface morphology; (b) Si element; (c) O element; (d) C element.

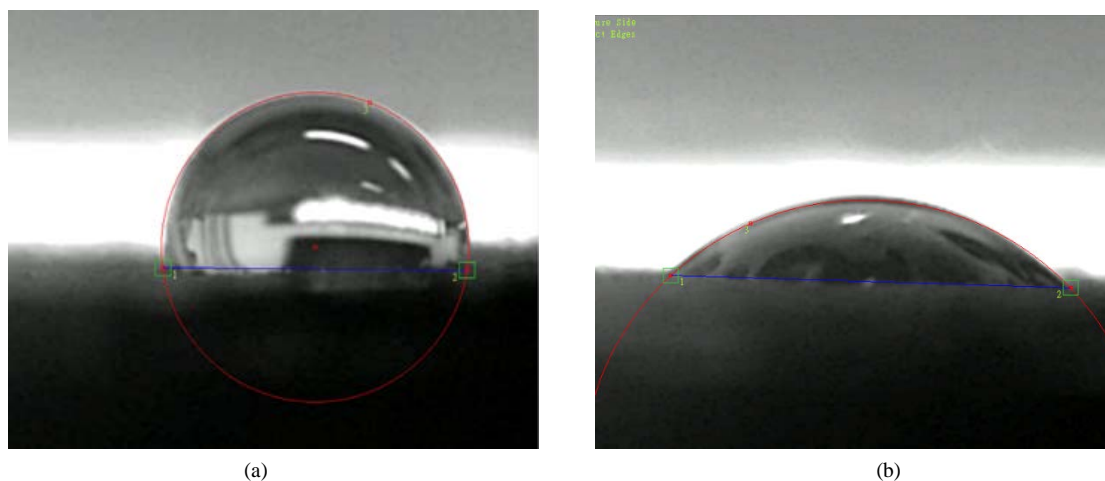


Figure 2. Water contact angle for the GDL (a) non-coated; and (b) SiO₂-coated. (a) Non-coated; (b) SiO₂-coated.

indicates that adding the SiO₂ nanopowders enhanced the hydrophilicity. In other words, after adding the SiO₂, the specimen was better able to absorb water, which supports our initial assumption.

3.3. I-V Performance Curve Test

For the electric current and voltage (I-V) performance curve test in this experiment, hydrogen and air were used as the reaction gases, and common humidifying bottles were employed as the humidifier. We investigated how adding various amounts of SiO₂ to the hydrogen electrode's catalyst layer affects the cell performance under the following 3 independent conditions: 1) the temperature of the humidified bottles was 70°C; 2) the temperature of the humidified bottles was 50°C; and 3) the reaction gas was not humidified.

Figure 3 shows the I-V performance test results for adding varying amounts of SiO₂ when the gas was humidified at 70°C and the fuel cell temperature was maintained at 70°C (**Figure 3(a)**) and 50°C (**Figure 3(b)**). A fuel cell temperature of 70°C is common for the majority of PEMFC operations. Based on the properties of the fuel cell test station used in this experiment, the 70°C gas humidification temperature delivered the appropriate amount of water vapor into the fuel cell. Consequently, the tests conducted under these conditions facilitate the assessment of the general performance of PEMFCs. When the fuel cell temperature was maintained at 70°C (**Figure 3(a)**), the test results showed that the SiO₂-loaded catalyst layer outperformed the non-loaded layer; however, the difference was minor. When operated at 0.5 V, the measured current density was approximately 535 mA/cm² for both fuel cells (*i.e.*, with and without the SiO₂).

Figure 3(b) shows that adding SiO₂ to the catalyst layer had minimal influence on the fuel cell performance. However, the fuel cell with the SiO₂-loaded catalyst layer outperformed the fuel cell with the non-loaded layer. When operated at 0.5 V, the non-loaded fuel cell produced a current density of 494.1 mA/cm². The optimum performance was achieved after adding 0.06 mg/cm² SiO₂, which produced a current density of 527.1 mA/cm². Because the gas humidifying temperature was 20°C higher than the fuel cell temperature under these test conditions, supersaturated water vapor conditions were observed and the water vapor in the fuel cell was likely to undergo condensation. The slightly superior performance of the fuel cell with the SiO₂-loaded catalyst layer indicates that despite the excessive gas humidity, the addition of hydrophilic SiO₂ did not cause any observable flooding problems and negative effects on the fuel cell performance. Therefore, we hypothesize that when employing the transfer method to construct the anode catalyst layer, it is difficult to disrupt the hydrophobicity of the original GDL. This may be considered an advantage for constructing self-humidifying PEMFC using the transfer method.

Figure 4 shows the I-V performance tests for adding various amounts of SiO₂ when the gas was humidified at 50°C, and the fuel cell temperature was maintained at 70°C (**Figure 4(a)**) and 50°C (**Figure 4(b)**). The results in **Figure 4(a)** show that the gas humidifying temperature was 20°C lower than that of the fuel cell. Consequently, this difference in temperature caused a shortage of water vapor when the gas entered the fuel cell from the humidifying bottles; accordingly, this was considered a low-humidification test condition. The test results showed that the fuel cells with the SiO₂-loaded catalyst layer outperformed the fuel cells with the non-loaded layer;

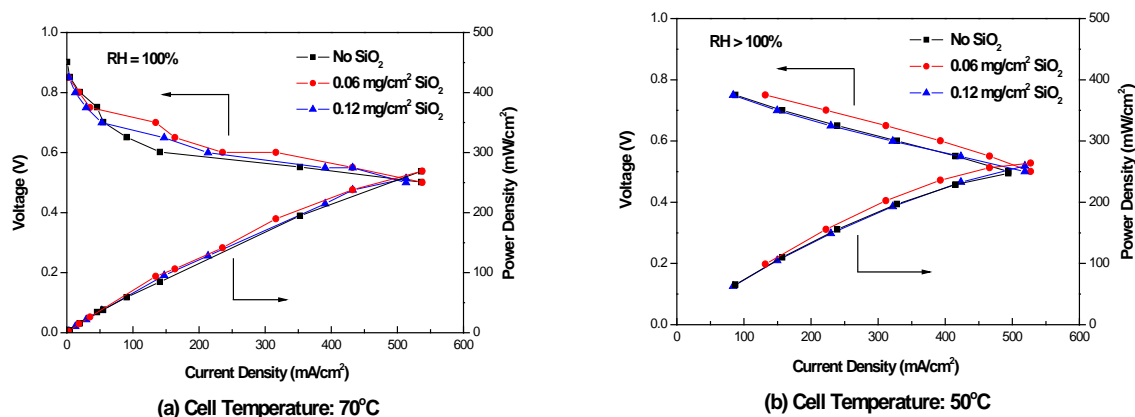


Figure 3. I-V test results for various amounts of SiO₂; gas humidified at 70°C; fuel cell temperature set to (a) 70°C, and (b) 50°C.

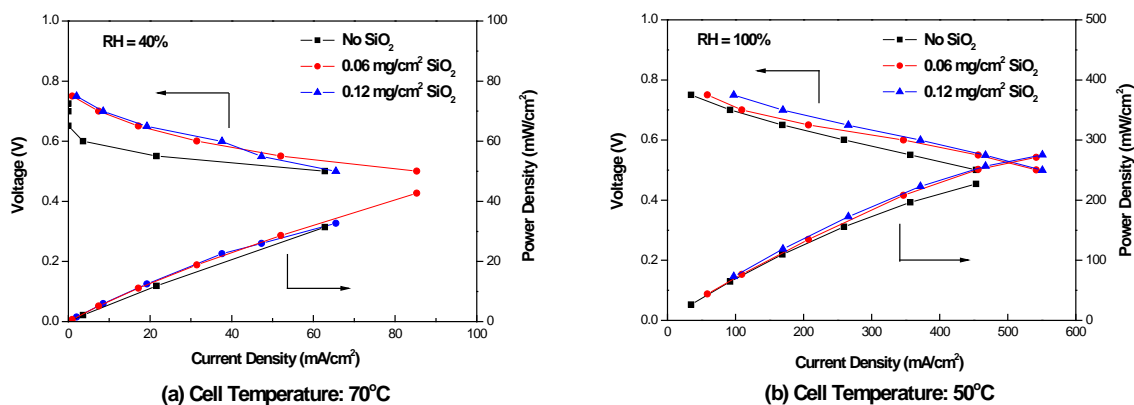


Figure 4. I-V test results for various amounts of SiO₂; gas humidified at 50°C; fuel cell temperature set to (a) 70°C and (b) 50°C.

however, the practical value of the performance was minor and the difference was minimal. When operated at 0.5 V, the fuel cells with 0.06 mg/cm² SiO₂ attained the optimum performance, and the current density was measured at 85.3 mA/cm².

Figure 4(b) shows that identical gas humidifying temperature and fuel cell temperatures should produce sufficient water vapor to hydrate the fuel cell. Furthermore, the fuel cells with the SiO₂-loaded catalyst layer outperformed the fuel cells with the non-loaded catalyst layer under these testing conditions. When operated at 0.5 V, the current density was measured at 453.4 mA/cm² for the non-layered fuel cells. The optimum performance was attained by adding 0.12 mg/cm² SiO₂, the current density of which was measured at 550.1 mA/cm². The fuel cells with a cell temperature set at 50°C performed significantly better those with a cell temperature set at 70°C. This result explains the difference in performance under high and low humidification.

The I-V performance tests when the gas was not humidified could directly verify whether the fuel cells were capable of self-humidification. **Figure 5** shows the I-V performance test results when the gas was not humidified and the fuel cell temperature was maintained at 70°C (**Figure 5(a)**) and 50°C (**Figure 5(b)**).

Figure 5(a) shows that the performance of the fuel cell was extremely poor; thus, few data were recorded for the tests without humidification. **Figure 5(b)** shows the results for the I-V performance test where the fuel cell temperature was maintained at 50°C. The rationale for conducting the 50°C fuel cell test was that we believed the loss of the water produced by the fuel cells was caused by high temperatures within the cells. This also indicates that satisfying the PEMFC self-humidifying requirement would be difficult, regardless of whether a self-humidifying functional design was added to the fuel cell. Therefore, an ideal temperature for self-humidifying PEMFC operations must be established and identified. The results in **Figure 5(b)** clearly show that the SiO₂-loaded catalyst layer outperformed the non-loaded layer. When operated at 0.5 V, the current density for the non-loaded layer was only 2.43 mA/cm², which offers little to no electricity generation value. After 0.06 mg/cm² SiO₂ was added, the current density increased to 9.36 mA/cm²; however, this current density also has no practical value. After adding 0.12 mg/cm² of SiO₂, the current density increased to 93.9 mA/cm², which approaches actual practical values. Compared to the fuel cells with the non-loaded catalyst layer, the current density of this fuel cell is higher and shows a clear improvement.

At a fuel cell temperature of 50°C, the addition of a specific amount of SiO₂ could enhance the performance of fuel cells. However, for fuel cells at 70°C, the effect was non-existent. We contend that this phenomenon was caused by the increased fuel cell temperature, which contributed to evaporation rather than retention of the water produced within the fuel cell. The addition of SiO₂ water adsorption effects offers an insufficient explanation for the water loss caused at high temperatures. This also shows the limitations that self-humidifying fuel cells have regarding fuel cell temperatures. During the electrochemical reaction, the PEMFC also released heat; therefore, standard fuel cell stacks are typically equipped with air- or water-cooling mechanisms to ensure the fuel cell temperature is maintained within a specified range. Thus, understanding the appropriate reaction temperature for PEMFCs is also extremely crucial. Although fuel cells are only operable at 50°C, if a sufficient and consistent performance can be verified, feasible applications for self-humidifying PEMFCs can be identified.

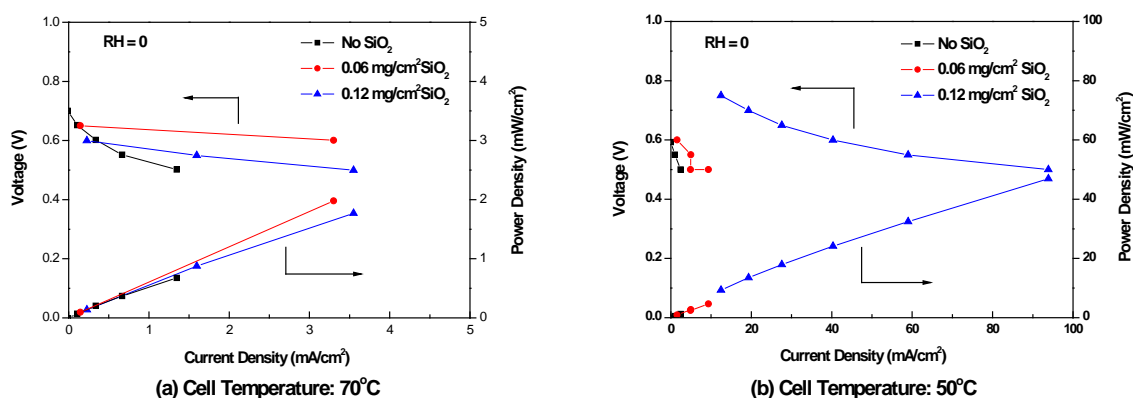


Figure 5. I-V test with for various amounts of SiO₂; zero gas humidification; fuel cell temperature set to (a) 70°C and (b) 50°C.

4. Conclusions

This research primarily examined the effect of adding SiO₂ to the catalyst layers when using the transfer method to produce an MEA. Among the various methods for manufacturing MEAs, the transfer method generally provides superior performance compared to traditional methods; therefore, it was employed in this study. The transfer method not only provided the anticipated superior performance over traditional methods, but also the thin film catalyst layer produced using this method was substantially more hydrophilic and less prone to flooding. By examining the water contact angle test data, we found that the hydrophilicity of the specimen surface improved following the addition of SiO₂. Thus, we contend that adding SiO₂ nanopowders to catalyst layers can contribute to self-humidification effects.

When the fuel cell temperature was set to 50°C, the SiO₂-loaded specimen outperformed the non-loaded specimen, and the improvement was substantial. However, when the fuel cell temperature was set to 70°C, the difference between the loaded and non-loaded specimens was minor under identical test environments. We contend that this phenomenon may be attributable to rapid drying of the membrane in the 70°C fuel cell; consequently, the self-humidifying effects of the SiO₂ specimen were hindered. However, at the optimum fuel cell temperature, adding hydrophilic SiO₂ nanopowders into the catalyst layer could enhance the performance of fuel cells.

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