



Short communication

Enhancement of polymer electrolyte membrane fuel cell performance by boiling a membrane electrode assembly in sulfuric acid solution

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ABSTRACT

A catalyst-coated membrane (CCM) as used in the membrane electrode assembly (MEA) of a polymer electrolyte membrane fuel cell is treated by dilute sulfuric acid solution (0.5 M) at boiling temperature for 1 h. This treatment improves the single-cell performance of the CCM without further addition of Pt catalyst. The changed microstructure and electrochemical properties of the catalyst layer are investigated by field emission scanning electron microscopy with energy dispersive X-ray, mercury intrusion porosimetry, waterdrop contact angle measurement, Fourier transform-infrared spectrometry in attenuated total reflection mode, electrochemical impedance spectroscopy, and cyclic voltammetry. The results indicate that this pretreatment enhances MEA performance by changing the microstructure of the catalyst layer and thus changing the degree of hydration, and by modifying the Pt surface, thus enhancing the oxygen reduction reaction.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are currently of interest because of their capability for high energy conversion efficiency, with a rapid response time, very low emissions, a potentially renewable fuel source [1–3]. Recently, PEMFCs have been used in commercial applications, in residential and portable power sources. However, the cost and low catalytic efficiency of rare metals such as platinum are still important barriers to the commercialization of PEMFCs [4]. Several methods have been studied in an attempt to improve the efficiency of the platinum catalyst in the PEMFCs, including the development of an alloyed electrocatalyst for use in the electrochemical reaction [5–8], inventing a new membrane electrode assembly (MEA) fabrication method to extend the three-phase reaction zone, and introducing a new method to prepare the electrode in an optimized catalyst layer structure [9–11]. Qi and Kaufman [12] found that the treatment of MEA by steaming or boiling increased its performance. They have shown that the enhanced performance is anticipated to be due to

an increased catalyst utilization that results from an increase in the number of three-phase network by boiling and steaming a MEA. However, they have provided no evidence and have not characterized any structural or chemical change in MEAs by their treatment methods.

Various treatment methods toward enhancement of fuel cell performance have also been investigated by other groups [13,14]. It is clear that improving the gas and liquid mass transport as well as extending the three-phase network are important in achieving a high efficiency of platinum in the catalyst layer. However, researchers have not been able to clarify causes of increased performance by structural or chemical change in MEAs by their treatment methods.

We here report a simple method for the development of an effective catalyst layer. In this study, we prepared a MEA containing a conventional catalyst-coated membrane (CCM), and then soaked it in a boiling dilute sulfuric acid solution (0.5 M). This treatment improved the single-cell performance of the CCM without further addition of a catalyst. In addition, the changes in morphology and chemical properties of the catalyst layer were evaluated using field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray (EDX), mercury intrusion porosimetry, waterdrop contact angle measurement, and Fourier transform-infrared spectrometry (FT-IR) in attenuated total reflection (ATR) mode. The purpose of this paper is to investigate the character of the treated MEA in acid solution that enhanced its performance, that is, the

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change of structure in MEA and the modifying the catalyst surface in cathode electrode.

2. Experimental

The catalyst ink was obtained by mixing carbon-supported platinum (40 wt.% Pt/C, Johnson Matthey) ultrasonically in isopropyl alcohol (IPA) and a 5 wt.% Nafion solution (Dupont). The CCM was then fabricated by spraying the catalyst ink directly onto both sides of the polymer electrolyte membrane, Nafion 112, and the catalyst loading was 0.15 mg cm^{-2} [15]. The active area of the MEA was 5 cm^2 . For the treatment cell, the prepared MEA was soaked in boiling dilute sulfuric acid solution (0.5 M) at 100°C for 1 h and then rinsed with deionized water for more than three days. The anode and cathode gas diffusion layers containing the microporous layer were then placed on both sides of the CCM. Graphite plates with a serpentine channel were used for the single-cell test, and the single cells were operated using humidified or non-humidified hydrogen and air gas on the anode and cathode, respectively, with a stoichiometric ratio of 1.5:2. The test was conducted at atmospheric pressure using gases that were supplied while maintaining the temperature of the single cell at 70°C and 30°C . It is difficult to confirm the increase of ionic conductivity in high temperature (70°C) and using fully humidified gases. In order to eliminate the influence of water produced by oxygen reduction reaction (ORR), single-cell test was also conducted in operating condition of non-humidification in low temperature (30°C).

Cyclic voltammetry (CV) was carried out to determine the electrochemical surface area (ESA) using a potentiostat–galvanostat (IM-6, Zahner). The voltage range of the CV was between 0.1 V and 1.2 V, and the scan rate was 100 mV s^{-1} . For the CV experiments, humidified nitrogen gas was fed to the cathode as the working electrode, and humidified hydrogen gas was fed to the anode as the counter electrode and the reference electrode. The electrochemical properties of the prepared MEA were then examined by electrochemical impedance spectroscopy (IM-6, Zahner) at frequencies ranging from 100 kHz to 1 Hz, with 10 points per logarithmic decade being recorded. The single cell was operated without humidification at 30°C and was maintained at the steady state of 1.0 A and 2.0 A of cell current during each impedance measurement. The changes in morphology and chemical properties of the catalyst layer were evaluated using FE-SEM (JSM 6700F, JEOL Ltd.) with EDX (7421, OXFORD), mercury intrusion porosimetry (Auto Pore IV 9500, Micromeritics Instrument), waterdrop contact angle measurement (KRÜSS Measuring Instruments DSA-10), and FT-IR (Nicolet, Thermo) in ATR mode.

3. Results and discussion

FE-SEM analysis was conducted to evaluate the morphological difference between the untreated and treated MEA. As shown in Fig. 1, the structures of the catalyst layer surfaces of both untreated (a) and treated (b) MEA have many pores with diameters larger than 100 nm and a few pores in the micrometer range, which indicates that treatment with sulfuric acid solution does not affect the apparent morphology of the MEA. The insets of Fig. 1(a) and (b) show results of the waterdrop contact angle measurement of catalyst layer surfaces of each MEA for determining hydrophilicity. Contact angle measurements were carried out using the static sessile drop method with a $1.0\text{-}\mu\text{L}$ water droplet volume. In the insets of Fig. 1(a) and (b), the baseline of a water droplet is assigned as the boundary layer between the water droplet and catalyst layer surface. The contact angle of untreated MEA is 159.6° , while that of treated MEA is 97.6° . This result implies that, as a result of the sulfuric acid treatment, the catalyst layer of treated MEA is more

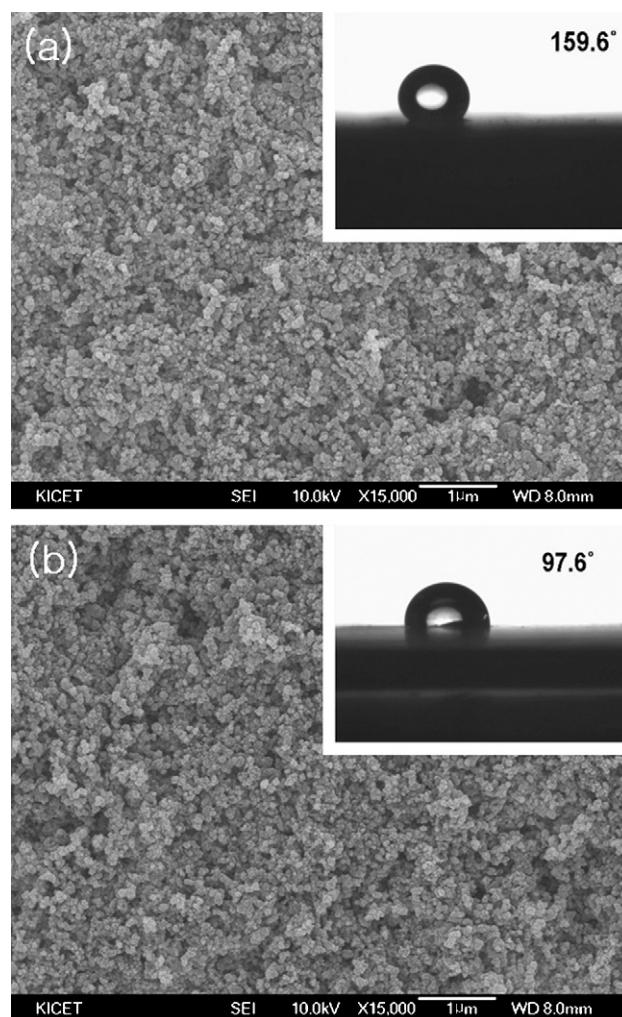


Fig. 1. FE-SEM images and waterdrop contact angles (the insets) of the catalyst layers surface of (a) untreated and (b) treated MEAs.

hydrophilic than that of untreated MEA. In order to confirm the causes of hydrophilicity in the catalyst layer, an EDX analysis for determining the O/C atomic ratio was performed during FE-SEM measurements. Table 1 showed an oxygen atomic ratio in treated MEA increased by 1.63% compared with that of untreated MEA. Prior research has well established that attached functional groups, including those with oxygen, such as $-\text{COOH}$, $-\text{OH}$, and $>\text{C}=\text{O}$ on the carbon surface makes the catalyst layer surface hydrophilic [16,17]. To confirm the character of the changed pore distribution of the catalyst layer by sulfuric acid treatment, specific pore distribution for pore sizes ranging from 3 nm to $300 \mu\text{m}$ were measured using mercury intrusion porosimetry. As shown in Fig. 2, the distribution of specific pore volumes was very similar between untreated and treated MEA, within $0.05\text{--}0.1 \mu\text{m}$ pore size; in particular, specific pore volumes of treated MEA decreased from 0.30 mL g^{-1} to 0.23 mL g^{-1} at $0.07 \mu\text{m}$ of pore size. However, according to prior research, the hydrophilicity of the catalyst layer increases with increasing porosity of the catalyst layer within a $0.01\text{--}0.1 \mu\text{m}$ range [18]. Because our result is contradicts these previous result, fur-

Table 1
The O/C atomic ratios from EDX analysis.

Sample	C (%)	O (%)
Untreated MEA	95.88	4.12
Treated MEA	94.25	5.75

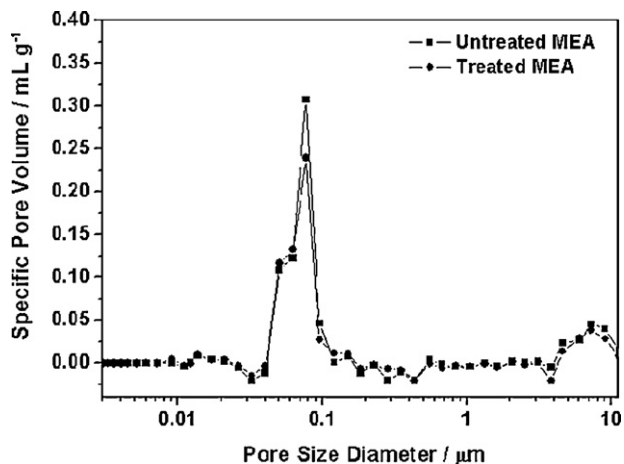


Fig. 2. The specific pore distribution of the catalyst layers of untreated and treated MEA with pore diameters by mercury intrusion porosimetry.

ther studies are needed to elucidate the relations between porosity and/or pore distribution in the catalyst layer and its hydrophilicity. Analysis by FT-IR in ATR mode was conducted in order to verify the cause of the increased hydrophilicity of the MEA catalyst layer treated by sulfuric acidic solution. Fig. 3 shows FT-IR ATR spectra of the untreated and treated MEA. A spectrum, collected as 32 scans of the number with a resolution of 4 cm^{-1} , was recorded from 4000 cm^{-1} to 400 cm^{-1} . The peak around 1210 appears due to the asymmetric CF_2 present on the untreated MEA and the peak around 1151.9 was due to the symmetric CF_2 bond of the untreated MEA [19]. It is noteworthy that the symmetric CF_2 peak remained at 1151.9 , whereas the asymmetric CF_2 peak at 1210.0 shifted to 1214.3 in response to sulfuric acid treatment, which indicates that there is a chemical environment change of the ionomer in the catalyst layer induced by the sulfuric acid treatment. Nafion is made from polytetrafluoroethylene (PTFE), which is strongly hydrophobic. But when an HSO_3 group, which is highly hydrophilic, is bonded ionically to the end of the side chain of PTFE by the “sulphonating” process, a hydrophilic region is added to a generally hydrophobic substance. Therefore, the blue shift of the asymmetric CF_2 peak indicates an increased hydrophilic nature in the catalyst layer of treated MEA, in turn caused by the changes in the Nafion structure. According to the aforementioned FT-IR and EDX analyses, the causes in increase of hydrophilicity of the catalyst layer by sulfuric acid treatment can be classified into two categories: one, the

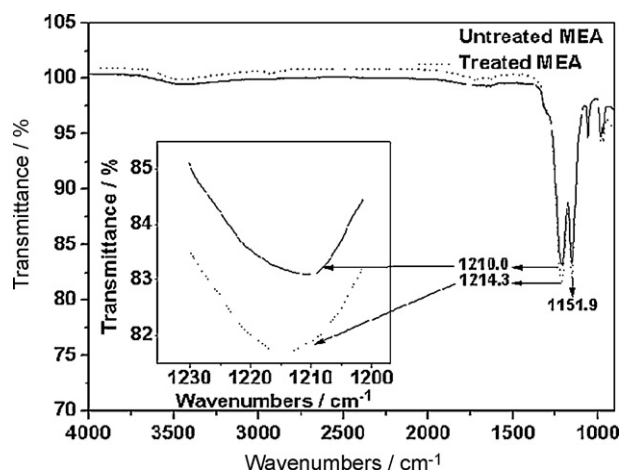


Fig. 3. FT-IR spectra of the catalyst layers surface of untreated and treated MEAs.

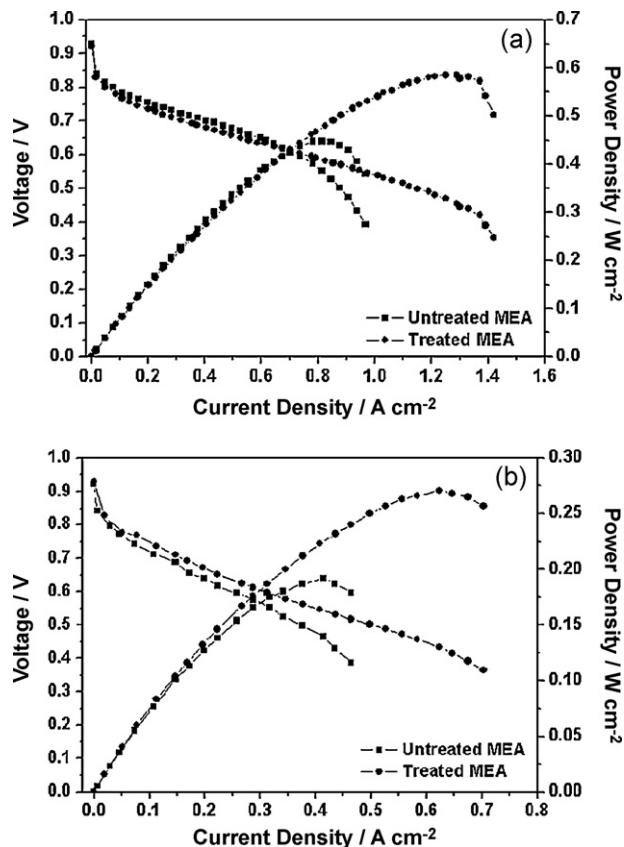


Fig. 4. Polarization curves of untreated and treated MEAs with flowing (a) humidified H_2/air gases at 70°C and (b) non-humidified H_2/air gases at 30°C .

increase of the number of oxygen functional groups on carbon supports, and the other is a change in the chemical environment of the ionomer in the catalyst layer.

The single-cell performance measurement, which is shown in Fig. 4, was obtained by operating the cell temperature at 70°C (humidified) and 30°C (non-humidified). As shown in Fig. 4(a), when the single cell was operated using fully humidified gases with a cell temperature of 70°C , the performance of the cell containing treated MEA was slightly lower than that containing untreated MEA in a high voltage range (above 0.65 V), whereas the single-cell performance of treated MEA was significantly higher than that of untreated MEA in the low voltage region (below 0.60 V); in particular, the performance of its single cell was increased by approximately 46% compared with that of untreated MEA at 0.40 V .

From these results, we suggest that the MEA treatment using sulfuric acid solution might provide a better catalyst layer structure, which results in the improvement of the mass transfer resistance on PEMFC. On the other hand, as seen in Fig. 4(b), when a single cell was operated using non-humidified gases with a cell temperature of 30°C , the current density increased by 25%, from 250 mA cm^{-2} to 313 mA cm^{-2} at 0.60 V as a result of treatment. In addition, this increase in performance was more significant at 0.40 V , as was indicated by an increase in current density from 455 mA cm^{-2} to 665 mA cm^{-2} , a 47% increase. Moreover, the maximum power density of the single cell increased by 41%, from 192 mW cm^{-2} to 271 mW cm^{-2} , in response to sulfuric acid treatment, which indicates that the treatment enhances the MEA performance throughout the entire voltage region. For the PEMFC to be used as a power source for a portable electronic device, auxiliary equipment such as a humidifier and heater may need to be

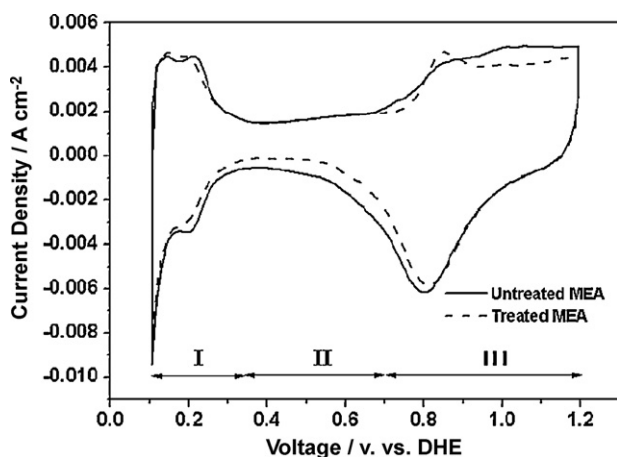


Fig. 5. Cyclic voltammetry (CV) curves for untreated and treated MEAs.

removed from the fuel cell system. It is therefore an important development that performance was enhanced by a simple treatment during operation with a low cell temperature (30 °C) and without humidification of supplied gases.

In Fig. 5, CVs for the treated and untreated MEA are presented. The electrochemical surface area of the catalyst layer was evaluated from the voltammogram by dividing the charge corresponding to the area under the hydrogen desorption region by $210 \mu\text{C}$ [20–22]. The ESAs of untreated and treated MEA were $14.03 \text{ m}^2 \text{ g}^{-1}$ and $13.52 \text{ m}^2 \text{ g}^{-1}$, respectively. The CV result of the untreated MEA was not changed after the treatment, which implies that the treatment does not affect the ESA of the MEA. However, an obvious difference in the onset potential of OH adsorption on the Pt surface between untreated and treated MEA was observed. The three characteristic potential regions for MEA electrodes are well defined in Fig. 5 for all voltammograms: the so-called H_{upd} (underpotential deposition of hydrogen) region between 0.10 V and 0.35 V (region I) is followed by the double-layer potential region up to about 0.70 V (region II), where, in turn, the adsorption of oxygenated species begins (region III, OH_{ads} -region). Notice that the onset of hydroxide adsorption on Pt is not only determined by the Pt–OH energetics itself, but also by those of Pt– O_2 . The positive shift of the OH_{ads} -region on the treated MEA electrode can therefore also be associated with a reduced anion adsorption due to the changes in Pt surface structure. It is possible that the Pt surface might be modified to an oxygen reduction reaction friendly Pt plane of around (1 1 0) or (1 0 0) by the sulfuric acid treatment. As a consequence, the increase in the rate of ORR on treated MEA electrode can be attributed to a lower adsorption of oxygen atoms, since OH can effectively block the active sites required for the adsorption of O_2 or the splitting of the O–O bond, in agreement with Adzic's work [23].

The resistances of the MEA were measured using EIS, as shown in Fig. 6, and the resulting Nyquist plots were obtained at 1.0 A (Fig. 6(a)) and 2.0 A (Fig. 6(b)) of cell currents, respectively. The ohmic resistance (R_{Ω}) of the MEA can be derived from the high frequency region of semicircles and the diameter of the semicircle is generally regarded as corresponding to the charge transfer resistance (R_C). As seen in Fig. 6(a), the R_{Ω} of treated MEA was 0.042Ω , nearly twice the magnitude of the impedance of untreated MEA. The higher impedance magnitude R_{Ω} of the treated MEA than the R_{Ω} of untreated MEA at low cell current (1.0 A) might be caused by the decreased electric conductivity of the catalyst layer by attached functional groups containing oxygen on carbon surfaces. In addition, the diameter of the semicircle in the treated MEA was also slightly larger than that of untreated MEA, which means the sulfuric acid treatment increased the MEA's R_C .

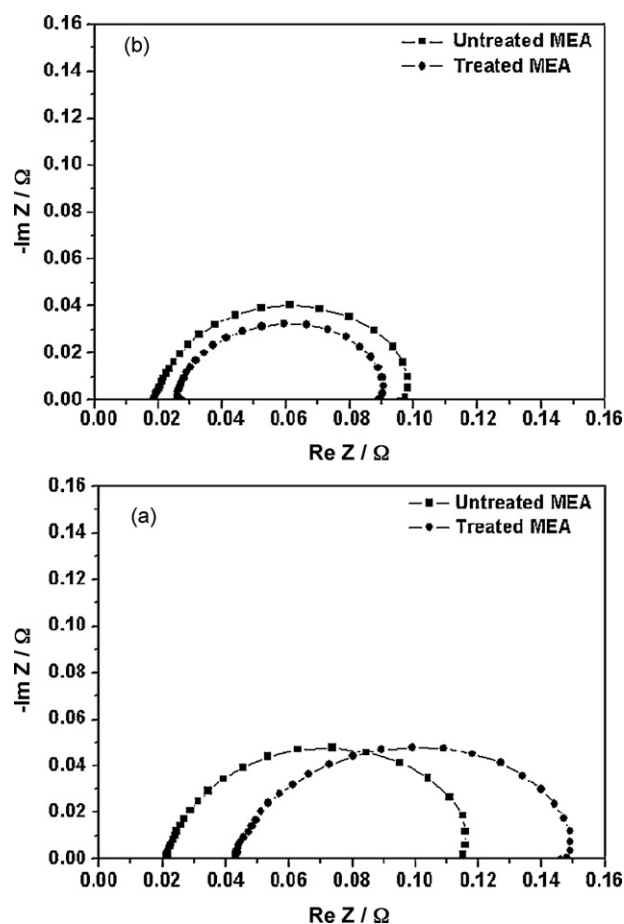


Fig. 6. Electrochemical impedance Nyquist plots with untreated and treated MEAs at (a) 1.0 A and (b) 2.0 A of cell currents.

As seen in Fig. 6(b), the impedance magnitude of the treated MEA obviously changed in both the high and low frequency region, at higher cell current (2.0 A) conditions, indicating that water content increases with a more active ORR at cathode catalyst layer. The R_{Ω} of the untreated MEA remained constant with increasing current, as indicated by the 0.020Ω value of the high frequency region, whereas the R_{Ω} of the treated MEA declined from 0.042Ω to 0.026Ω with increasing current in the single cell. The R_{Ω} of the MEA depends on the ionic conductivity of the polymer used in the electrolyte membrane and the ionomer used in the catalyst layer. In addition, the water content of the MEA significantly influences its ionic resistance, and the treated MEA is more sensitive to water generated inside the electrode than is the untreated MEA. Therefore, this change in ionic conductivity indicates that treatment affects the chemical properties of the ionomer in the catalyst layer of the MEA [24]. Moreover, the diameter of the semicircle of the treated MEA was smaller than that of the untreated MEA at a cell current of 2.0 A. Springer and Raistrick has suggested the thin-film/flooded-agglomerate model, which assumes a chemical electrode that contains agglomerates of the carbon-supported catalyst and ionomer [25]. In this model, the rate determining step for the electrochemical reaction is the thin-film diffusion process in Nafion as ionomer that covers the agglomerate or catalyst surface [10,25]. Prior research suggests that the sulfuric acid solution treatment improves the R_C of the catalyst layer by changing the pore structure and the chemical properties of the ionomer in the catalyst layer, resulting in enhanced diffusion of oxygen and protons.

4. Conclusion

In summary, the single-cell performance of MEA treated by sulfuric acidic solution was remarkably improved. We propose the explanation that the treatment increases the ORR activity in the cathode catalyst layer by increasing its hydrophilicity, and changing the pore structure and chemical properties of the ionomer in catalyst layer.

Boiling a MEA in sulfuric acid solution can remarkably improve single-cell performance in a PEM fuel cell. In particular, when operation conditions are at a low temperature (30 °C) while supplying non-humidified hydrogen gas and air, the performance of the single cell was increased by approximately 47% compared with that of untreated MEA. In addition, the changed microstructure and electrochemical properties of catalyst layer were characterized for verifying causes of increased MEA performance by FE-SEM with EDX, mercury intrusion porosimetry, waterdrop contact angle measurement, FT-IR at ATR mode, EIS, and CV measurement.

The results of this investigation offer a simple process that dramatically improves the performance of state-of-the-art MEA in PEM fuel cells without adding any expensive materials such as Pt and Pt-alloy into the MEA.

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