Short communication

Modification and improvement of proton-exchange membrane fuel cells via treatment using peracetic acid

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Abstract

Electrodes and catalyst-coated membranes (CCMs) were treated using peracetic acid. After such a treatment, the properties and performance of these electrodes and CCMs were changed in several aspects. First, their catalytic activity was increased compared to the untreated counterparts. Second, their ability to hold water within the catalyst layers was increased so that the cathode did not need to be humidified. Third, if the cathode was humidified together with the anode, some of the electrodes were more readily to be flooded than the untreated counterparts.
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1. Introduction

The performance of electrodes for a proton-exchange membrane (PEM) fuel cell is affected by many factors. Some of the factors are intrinsic to the electrodes. These factors (excluding the gas diffusion medium) include the catalyst type and loading, Nafion content, PTFE content, and the structure (e.g. porosity, tortuosity) of the catalyst layer. Some of the factors are external, and are related to the operating conditions such as the cell temperature, and the stoichiometry, humidification and pressurization of the reactants. An optimization is normally needed in order to match the external conditions with the electrode's internal properties.

We have taken efforts to modify the internal properties of electrodes in order to enhance their performance under mild operation conditions. We found that if an electrode or catalyst-coated membrane (CCM) was steamed or boiled, its performance would increase [1]. We also found that if a CCM or a membrane–electrode assembly (MEA) was exposed to elevated temperature and pressure, it was activated, resulting in a much higher performance [2,3].

We also found that an electrode could be activated by producing hydrogen via proton reduction within the catalyst layer [4]. We do not fully understand how hydrogen evolution works. We think that it is related to the structure change of the electrode, and propose that one such change could be related to the porosity and tortuosity of the catalyst layer.

Hydrogen evolution may not be able to be conveniently performed within a complete fuel cell system under all situations. Therefore, we started looking for methods to activate the electrodes before a stack is assembled. One method would be chemically producing bubbles within an electrode.

Peracetic acid (i.e. peroxyacetic acid), CH_3COOOH, produces gaseous oxygen when it decomposes under heating conditions. So, peracetic acid can be used as a bubble-producing agent.

In the past, we used nitric acid to increase the wettability and proton conductivity of the surface of carbon particles for PEM fuel cells, and enhanced performance was achieved [5]. Since peracetic acid is also a strong oxidant, we expect that it could lead to the oxidation of carbon support particles as well.

This paper reports the results when electrodes and CCMs were treated using peracetic acid.

2. Experimental

2.1. Preparation of electrodes

Catalyst mixtures were prepared by directly mixing carbon-supported catalysts with a Nafion solution (5%, DuPont). The mixture was stirred thoroughly before it was applied onto a gas diffusion medium such as ELAT

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or carbon paper. The electrodes were dried in an oven at 135 °C for 30 min.

2.2. Treatment of electrodes and CCMs using peracetic acid

Peracetic acid (32 wt.% solution in dilute acetic acid) was sprayed onto electrodes and CCMs with a peracetic acid loading target of 50 mg/cm^2. A large quantity of bubbles were seen to be released from the electrodes and CCMs. Peracetic acid decomposes thermally especially at temperatures higher than 55 °C. Heavy metals, transition metals and their salts can cause a catalytic decomposition [6]. Upon decomposition, peracetic acid produces acetic acid and oxygen. Therefore, when the electrode and CCM were sprayed with peracetic acid, a large number of oxygen bubbles were released. The decomposition process could also be catalyzed by Pt particles existing within the electrode and CCM. An IR lamp was used to accelerate the decomposition and to evaporate the resulting acetic acid.

The above electrodes were hot-bonded onto a Nafion 112 membrane at 130 °C for 3 min to form a membrane–electrode assembly (MEA).

When the CCM was tested, a carbon paper-type gas diffusion medium was attached to both the anode and cathode catalyst layers without any bonding.

2.3. Test of MEAs

Single cell tests were performed using a homemade 10 cm^2 active area test fixture. The test fixture was composed of a pair of metal plates with serpentine flow-fields. The plates were coated with metal nitride for corrosion protection. Rod-like heaters were inserted into the plates to control the cell temperature. Air and pure hydrogen were used as the reactants. If humidification was carried out, the reactants were passed through stainless steel water bottles prior to allowing them to enter the cell.

MEAs were first activated at elevated temperature (T) and pressure (P). This elevated T/P activation was carried out at a cell temperature of 75 °C, hydrogen humidification temperature of 95 °C, air humidification temperature of 90 °C, hydrogen pressure of 20 psig, and air pressure of 30 psig. Such an activation condition is denoted hereinafter as 75 (cell)/95 (H$_2$)/90 (air) °C, 20 (H$_2$)/30 (air) psig [2,3]. During the activation, the fuel cell performance was recorded every 30 min. When no further increase in performance was observed, the activation procedure was considered to be complete. The load was varied using a rheostat when voltage (V)–current density (I) curves were collected.

The temperatures were then returned to 35 (cell)/45 (H$_2$)/45 (air) °C, and the pressurization was released. The stoichiometries of air and hydrogen were controlled to about 10× at a current density of 2.0 A/cm^2 using flow meters. Unless otherwise stated, the following data were collected under such experimental conditions.

3. Results and discussion

In this study, since pure hydrogen was used as the fuel, the entire fuel cell performance was determined by the cathode. Therefore, the treatment was focused on the cathode.

Fig. 1 shows the performance of MEAs whose cathode Pt loading was 0.24 mg/cm^2 made from a supported catalyst with 46% Pt on high surface carbon particles (800 m^2/g). The catalyst layer contained 35% Nafion. It is clear that the electrode treated using peracetic acid performed marginally better than the untreated one in the entire current density region. This implied that the treatment increased the catalyst utilization.

A slightly larger improvement was observed when commercial CCMs were treated, as shown in Fig. 2. This CCM had a cathode Pt loading of 0.3 mg/cm^2, but its other information (e.g. catalyst type, Nafion content, PTFE content, etc.) was not known to us.

In the experiments shown in Figs. 1 and 2, the cell temperature was at 35 °C, and both H$_2$ and air were humidified at 45 °C.

It was observed that the treatment using peracetic acid changed the ability of the MEA to handle water. Fig. 3 illustrates the performance of two MEAs under both humidified and unhumidified air conditions. When air was not humidified, it entered the cell at ambient temperature. The cathodes were made using E-TEK 20% Pt/Vulcan XC-72, and the catalyst layers contained 30% Nafion with a Pt loading of 0.49 mg/cm^2. For the untreated MEA, its performance using either humidified or unhumidified air was almost the same; so, only the $V–I$ curve when wet air was used is shown. For the treated MEA, its performance was higher than that of the untreated one at current densities less than 1.0 A/cm^2, indicating its higher catalyst utilization. When unhumidified air was used, its performance was better than that of the untreated one in the entire current density region. But when humidified air was used, its performance became lower than that of the untreated one at current densities higher than 1.0 A/cm^2.

These experimental results implied that the treatment enhanced the electrode's ability to retain water within the catalyst layer. Hence, the fuel cell could perform very well without humidifying air. Eliminating the need to humidify air is an advantage in the sense that humidification components could be avoided, leading to a smaller and lighter system.

However, a drawback is that the cathode would be more readily flooded to result in a lower performance at higher current densities. Hence, a more delicate humidification control would be needed if electrodes were treated using peracetic acid.

Fig. 4 shows the performance of the above MEAs during the activation process. The temperatures were 75 (cell)/95 (H$_2$ humidification)/90 (air humidification) °C, and pressurization of 20 (H$_2$)/30 (air) psig. Apparently, in the lower
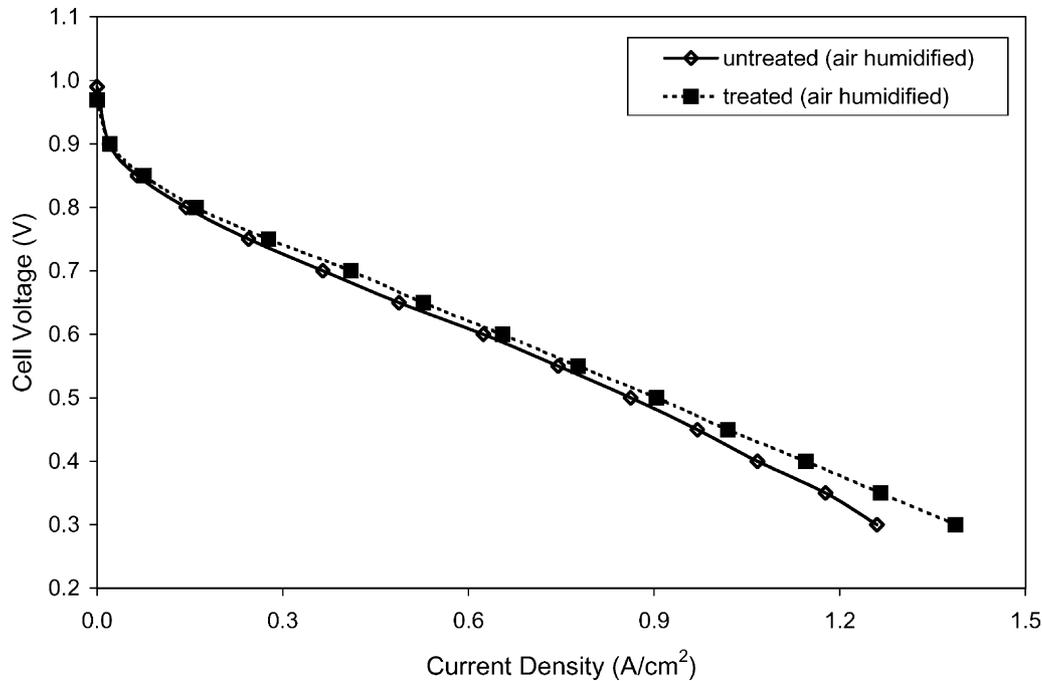
Fig. 1. Effect of peracetic acid on the performance of an MEA whose cathode had a Pt loading of 0.24 mg/cm^2 made using 46% Pt/C. Temperatures 35/45/45 °C; 35% Nafion within catalyst layer; Nafion 112 membrane; ELAT gas diffusion medium.

current density, activation region, the treated MEA performed much better than the untreated counterpart. When air was not humidified, the treated one performed better than the untreated one in the entire current density region. When air was humidified, the cell voltage dropped quickly at current densities higher than 0.8 A/cm^2 for the treated

MEA, and its performance became lower than that of the untreated one.

Since peracetic acid is a strong oxidizer, it could modify the surface properties of carbon particles by forming functional groups such as phenol (–OH), carbonyl (=CO) and carboxyl (–COOH) [7]. The formation of these groups
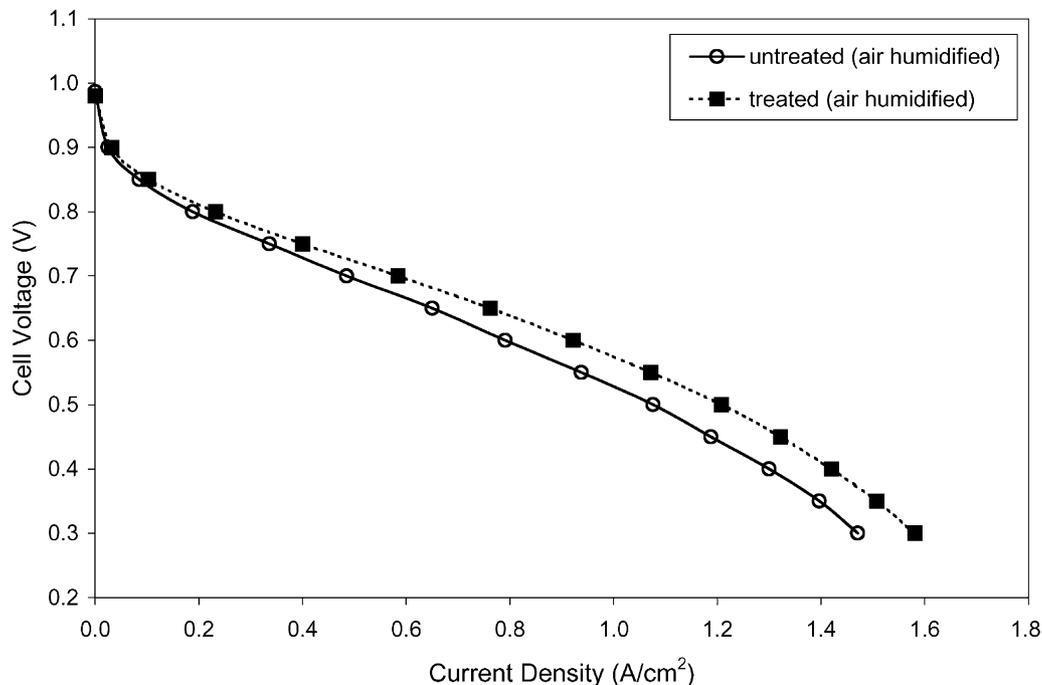
Fig. 2. Effect of peracetic acid on the performance of a commercial CCM whose cathode had a Pt loading of 0.30 mg/cm^2. Temperatures 35/45/45 °C; carbon paper gas diffusion medium.
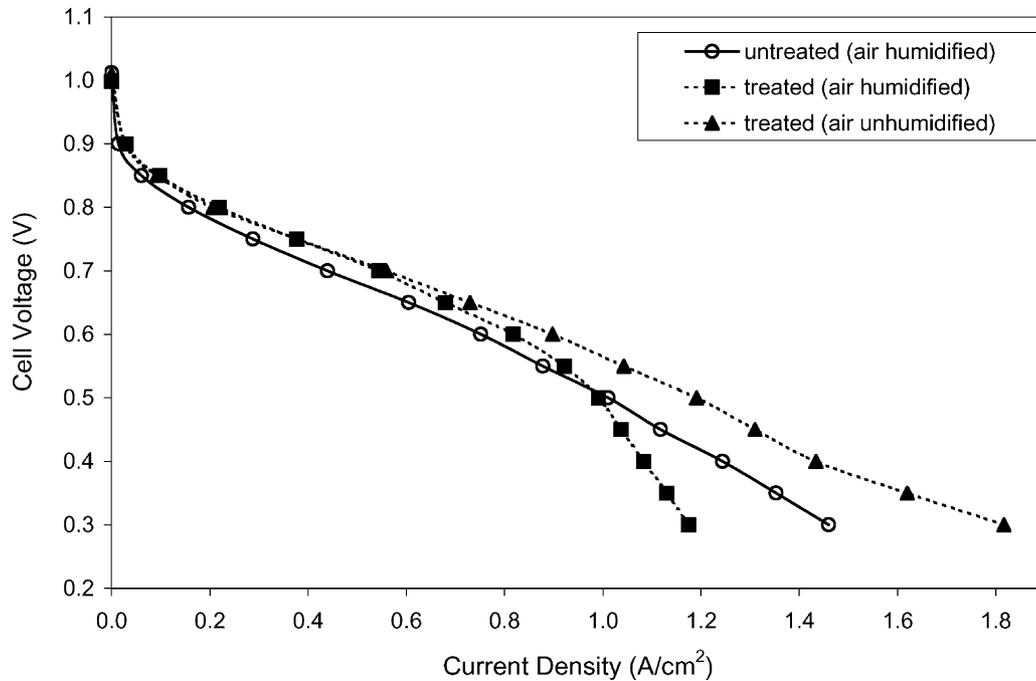
Fig. 3. Effect of peracetic acid on the performance of an MEA whose cathode had a Pt loading of 0.49 mg/cm^2 made using E-TEK 20% Pt/Vulcan XC-72. Temperatures 35/45/45 °C; 30% Nafion within catalyst layer; Nafion 112 membrane; carbon paper gas diffusion medium.

will increase the hydrophilicity of carbon so that its ability to hold water is increased. This will favor a fuel cell operation using unhumidified air. At the same time, carboxyl groups are pretty acidic, which could increase proton conductivity at the catalyst surface, leading to higher catalyst utilization.

As mentioned earlier, when peracetic acid decomposes, gaseous oxygen is formed. When oxygen bubbles out from the catalyst layer, it could change the catalyst layer structure by enhancing the porosity and tortuosity, which also lead to a higher fuel cell performance.
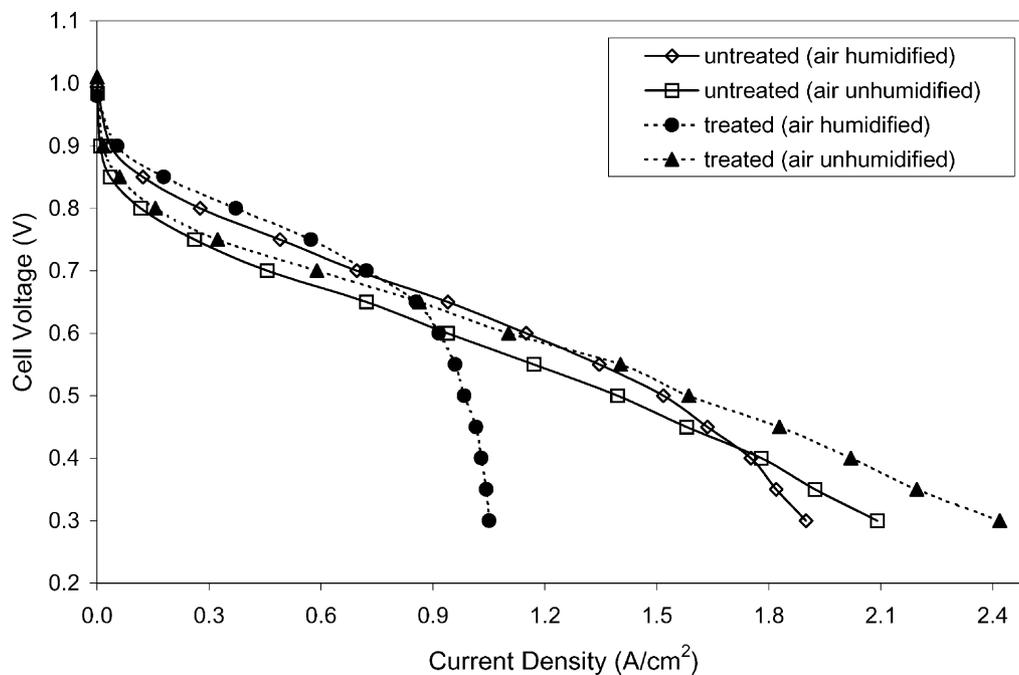
Fig. 4. Effect of peracetic acid on the performance of an MEA whose cathode had a Pt loading of 0.49 mg/cm^2 made using E-TEK 20% Pt/Vulcan XC-72. Temperatures 75/95/90 °C; pressures 20/30 psig; 30% Nafion within catalyst layer; Nafion 112 membrane; carbon paper gas diffusion medium.

4. Conclusions

Catalyst utilization and thus fuel cell performance was increased by treating electrodes and CCMs using peracetic acid. The treatment increased the electrode's ability to retain water within the catalyst layer; hence, air humidification was not needed. It was proposed that the treatment increases the wettability and proton conductivity at the surface of carbon particles, and enhances the porosity and tortuosity of the catalyst layer.

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