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Polydimethylsiloxane treated cathode catalyst layer to prolong hydrogen fuel cell lifetime

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ABSTRACT

In operation of hydrogen fuel cells for vehicle, carbon corrosion induced by frequent on/off operation significantly causes degradation of performance and durability of fuel cells, aggregating and losing Pt particles. It is critical to develop durable cathode and understand the mechanism of degradation in hydrogen fuel cells for commercialization. In this study, we prepared polydimethylsiloxane treated cathode, which is hydrophobic, for improving durability in hydrogen fuel cells. In addition, effect of hydrophobic cathode on durability was investigated by various analyses. We observed that the polydimethylsiloxane (PDMS) treated cathode contributed to limit both mass transfer limitation and carbon corrosion by efficient water withdrawal. Based on our results, we provide the possibility of PDMS treatment to decline the performance degradation in fuel cells.

1. Introduction

With development of an internal combustion engine, fossil fuels, such as gasoline and diesel, have been broadly utilized as fuel for vehicle. However, an exhaustion of fossil fuels and an environment problem have become more serious due to indiscreet usage of them. As a result, developing alternative energy, such as battery and fuel cells, have been brought up in these days. Furthermore, most of major automobile companies have been encouraged to develop a zero emission vehicle (ZEV), which is expected to replace the internal combustion vehicle in the future.

A hydrogen fuel cell vehicle has been attracted as the ZEV due to its various advantages, such as high energy density, low emissions, high efficiency, and silence. However, there have been critical problems such as water flooding and carbon corrosion, which are directly related to its performance and durability, to commercialize the hydrogen fuel cells [1–7]. Water flooding is a phenomenon which is attributed to mass transfer limitation blocking pathway of oxygen by water produced from oxygen reduction reaction and supplied with oxygen. In order to prevent water flooding, hydrophobic agents such as dimethyl silicone oil and polytetrafluoroethylene have been generally added to the gas diffusion layer (GDL) to improve hydrophobicity of GDL for effective removal of water [8–13]. Carbon corrosion is a reaction which takes place on carbon support and a GDL due to high potential induced by frequent on/off operation of fuel cells [2]. Many approaches, such as coating of metal oxide on carbon, replacing carbon with metal oxide, and alloying Pt with water electrolysis catalysts, have been studied to develop the durable catalyst [14–17]. However, many researches have seldom connected water flooding with the carbon corrosion, even though carbon corrosion occurs due to reaction between carbon and water at a cathode (see Eq. (1)) [18].

$$C + H_2O \rightarrow CO_2 + 2H^+ + 2e^- E^\circ = 0.207\,V \quad (1)$$

In this paper, we prepared a hydrophobic cathode catalyst layer by polydimethylsiloxane (PDMS) treatment for reducing both water flooding and carbon corrosion. Furthermore, effect of hydrophobic cathode on performance degradation was investigated by various analyses such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron probe micro-analysis (EPMA), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry. In addition, we evaluated performance and durability of normal and PDMS-treated catalyst layer in fuel cells

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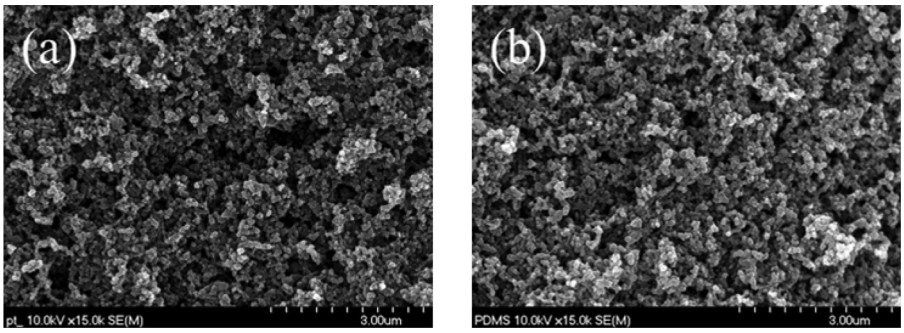

Fig. 1. SEM images of electrode surface (a) before and (b) after coating of PDMS on Pt/C coated micro-porous layer of GDL.

systems by polarization curves and accelerated stress test (AST), respectively.

2. Experimental

For fabricating a PDMS treated electrode, a Pt/C-loaded GDL (10BC, SGL) substrate and 3 g of solidified precursor were placed in a chamber made of stainless steel. The PDMS (Sylgard 184, Dow Corning) was used as precursor with a curing agent (Sylgard 184, Dow Corning) for solidification [19]. The ratio of PDMS to curing agent is 10:1. The chamber was heat-treated in a box furnace at 200 °C for 1 h. Contact angles were measured to evaluated a surface energy change before and after PDMS treatment by a contact angle analyzer (Pheonix 300, Surface Electro Optics Co.). Morphology and composition changes of a Pt/C-loaded GDL before and after PDMS treatment were investigated by SEM (S-4700, HITACHI), TEM (JEM-2100, JEOL), EPMA (EPMA-1610, SHIMADZU), and XPS (Multilab 2000, THERMO VG SCIENTIFIC).

For a normal cathode, catalyst ink containing 46.8% Pt/C (Tanaka, 0.3 mg cm^{-2}) mixed with Nafion ionomer (Sigma–Aldrich, 30 wt.% of Pt/C loading amount) was sprayed onto a GDL (SGL, 10BC) of 9 cm^2, as described in our previous work [20]. To fabricate a PDMS treated cathode, first catalyst ink that consists of 46.8% Pt/C mixed with Nafion ionomer solution (8 wt.% of amount of Pt/C) was sprayed onto a GDL. And then additional Nafion ionomer solution (22 wt.% of Pt/C loading amount) as outer ionomer was sprayed on the Pt/C-loaded GDL after PDMS treatment for better proton conductivity between electrode and membrane. Anodes were constructed in the same way with that of the general cathode. After the electrodes were prepared, they were placed on either side of a Nafion 212 membrane (Dupont) and the membrane electrode assembly (MEA) were pressed at 140 °C temperature for 5 min.

A fuel cell test station (Nara cell-tech corp.) and a single cell with parallel serpentine flow channel were used to evaluate the performance of the fuel cell. Each MEA was activated under a constant voltage of 0.55 V over 12 h. The cell temperature and relative humidity (RH) of the anode and the cathode was fixed at 60 °C and 100%, respectively. The base flow rates of hydrogen and oxygen were fixed at 100 sccm and flow rates for them were controlled in accordance with the stoichiometry value of 2.0. For AST process [21], cathode voltage was cycled from 1.0 to 1.5 V (*vs* Dynamic hydrogen electrode (DHE)) at a scan rate of 500 mV s^{-1} by using a potentiostat/galvanostat instrument (PGSTAT1287N, Autolab), supplying hydrogen of 100 sccm to the anode and nitrogen of 100 sccm to the cathode. Cyclic voltammetry for obtaining electrochemical surface area (ESA) and current–voltage polarization curves were evaluated at every 1000 cycle of AST. The cyclic voltammetry was recorded at a scan rate of 50 mV s^{-1} and for the current-voltage polarization curves, current was stepped up by 500 mA and current was maintained for 15 s at each step to obtain stable performance.

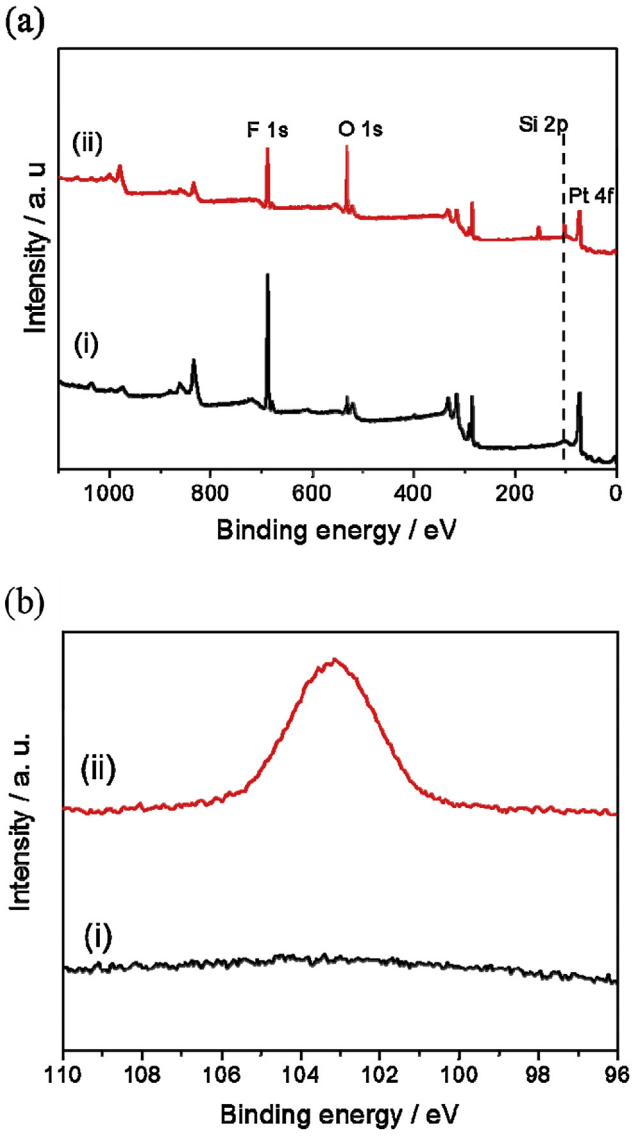

Fig. 2. (a) XPS survey spectra and (b) Si 2p spectra of electrode surface: (i) normal and (ii) PDMS treated electrode.

3. Results and discussion

SEM analysis of electrode surface was conducted to evaluate a morphological change of Pt/C-loaded GDL surface before and

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