



Preparation and characterization of durable catalyst via diazonium reaction in PEMFC



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ABSTRACT

The electrochemical catalytic durability can be enhanced by the post treatment of diazonium reaction. The diazonium salts which have fluorine, acid, and nitrile functional groups were grafted on the surface of Pt based catalyst with 1–3 wt%. Pt/GKB6-Dia4F, which was a catalyst with fluorine functional group, showed the excellent properties in durability as well as in mass activity. After the durability test, electrochemical surface area (ECSA) and mass activity of the Pt/GKB6-Dia4F were maintained by 81.9% and 75.3%, respectively. These were higher than those of pristine catalyst, which were 60.8% and 58.9%, respectively. The causes of these enhancements were investigated in the aspect of electrostructure of platinum or wettability of the catalyst. In XPS, the valid Pt4f peak shifts of the treated-catalysts were not detected, but the indisputable changes of the surface properties via diazonium reaction were detected. This indicates that the main factor affecting the catalytic durability is the wettability of the catalyst. Therefore, we conclude that diazonium reaction is an effective method to change the surface property of the catalyst, which can enhance the catalytic durability.

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1. Introduction

Nowadays, polymer electrode membrane fuel cells (PEMFC) have received considerable attention as an alternative power source for automobile systems due to high power and energy density, high efficiency and zero emission for air pollutants [1]. However, for commercialization of fuel cell vehicles (FCVs), there are some technical problems to be solved; cost and durability. In case of durability, FCVs require stable operation over 5000 h [2,3]. It means that all the FCVs components must achieve the lifespan above 5000 h. The PEMFCs are operated in the unfavorable conditions, that is, acid electrolyte, wide-range of temperature and humidity, and long operating time. In addition, the harsh operation conditions of vehicle, that is, start-up/shut-down, low temperature start-up, rapid acceleration, sudden stop, and low or no humidification driving at elevated temperature, make the degradation of membrane and electrode assembly (MEA) components degradation accelerate more and more [2,3].

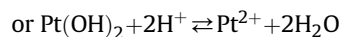
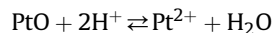
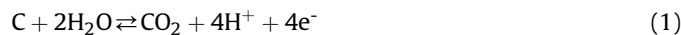
Among these aspects, degradation of the catalyst, which consist of the active material based on platinum of 2–5 nm in size and the supporting material with large surface area and high conductivity, is a major obstacle to the commercialization of FCV [4,5]. To achieve this, many researchers have been studying about the catalytic durability. Firstly, the durability of the active metals has been enhanced with the increased particle size, which is obtained through the heat-treatment at high temperature in order to prevent the dissolution and agglomeration of platinum particles by voltage cycling [6–9]. In addition, alloy and de-alloy catalysts, core-shell catalyst with a Pt shell and recently Nano-frame catalyst have been diversely studied [10–14]. Another theme of the catalytic durability is to prevent carbon corrosion which occurs during the start-up/shut-down or fuel starvation situations in FCV operation. The main approach is to use the highly graphitized carbon, which is obtained through the heat-treatment at high temperature, instead of using the carbon with high surface area [15]. Other approaches using metal oxides or CNT/CNF as the supporting materials have been demonstrated as well [16–20].

This study is to modify the wettability of a catalyst using the diazonium reaction and study its effect on catalytic durability. In degradation mechanism, the distribution of water surrounding the

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catalyst is important. The electrochemical mechanisms of the carbon corrosion and Pt dissolution have been suggested as shown in the following reactions [21–28].



Eqs. (1) and (2) shows that water is the main oxygen source for carbon corrosion and Pt dissolution, respectively. If water is hindered from moving to catalyst, the carbon corrosion and Pt dissolution will be suppressed. Therefore, the method which controls the distribution of water or ionomer by changing the wettability of a catalyst is an effective means to increase the catalytic durability. In this study, the chemical reactions of diazonium salts which contain various functional groups were applied to change the wettability of the catalyst. Since this reaction is occurred easily in room temperature, it is very effective for mass production of the catalyst. Although this approach has been carried out at several research groups, most studies are applying the diazonium reaction to the carbon support and then loading the platinum on the treated-carbon [29–34]. Compared to the previous methods, our approach is to load the platinum on the high graphitic carbon, and then to apply the diazonium salts with changing various functional groups on the surface of catalyst. The reason for using high graphitic carbon as the **supporting material** is owing to its durability in carbon corrosion as well as its nature of having clean surface compared to that of high surface area carbon. By applying different functional groups, the activity and durability of each catalyst were characterized and evaluated.

2. Experimental

2.1. Materials and preparation methods of Pt-based catalyst

To enhance the electrochemical stability, surface properties of the carbon supported-catalysts were modified with diazonium salts which have several kinds of functional groups. First, the pristine Pt based-catalyst which was loaded on the highly graphitized carbon was prepared in-house and the commercial Pt based-catalyst (47.2 wt% Pt, TEC10F50E, Tanaka Kikinzoku Co. Inc., denoted as Pt/F) was selected as a reference catalyst. Heat-treated Ketjen Black in Ar atmosphere at 2,000 °C (Ketjen Black EC-600JD, Mitsubish Chemical Co., denoted as GKB6), which showed high degree of graphitization, was used as a **supporting material**, and H_2PtCl_6 (10% water base solution, T&I Chem. Co.) was used as the active material source. The in-house Pt based-catalyst was prepared with a sub-substrate method [35,36]. In this method, fumed silica (surface area of $380 \text{ m}^2 \text{ g}^{-1}$, Aldrich Co.) was used as the sub-substrate material to supplement the insufficient surface area of GKB6. The sub-substrate method was performed as follows; the mixture of GKB6 and fumed silica was used as the substrate. The weight ratio of metal, GKB6 and fumed silica was adjusted to 1, 1 and 3, respectively. The final loaded-amount of platinum was calculated to be 50 wt%. An appropriate amount of precursor solution was dropped on the mixed substrate under ultrasonic vibration. The slurry was dried in an ultrasonic bath in order to distribute the metal precursor evenly. After drying, it was heat-treated at 200 °C in hydrogen atmosphere for 2 h. The fumed silica contained in the

prepared catalysts was removed in 10 wt% NaOH aq. solution (Aldrich Co.) by stirring for 12 h, and then it was filtered and washed thoroughly with distilled water. Finally, the pristine Pt/GKB6 catalyst was acquired after drying for 12 h in a freeze dryer.

2.2. Modification of surface properties by using diazonium reaction

Diazonium reaction is a very favorable method to control the surface property. According to the functional groups of the diazonium salts, the property of the catalyst was changed to hydrophilic or hydrophobic. Three kinds of diazonium salts, such as fluorine, acid and nitrile groups, were used for diazonium reaction. 5-Amino-2 (Trifluoromethyl)-benzimidazole (96%, Sigma-Aldrich, denoted as Dia1F), 5-Amino-2-fluoro benzotrifluoride (98%, TCI Co., LTD., denoted as Dia2F), 4-Amino-3-nitrobenzotrifluoride (99%, TCI Co., LTD., denoted as Dia3F) and 4-Amino benzo trifluoride (98%, TCI Co., LTD., denoted as Dia4F) were used as the functional group of fluorine. 3, 4-Diaminobenzoic acid (97%, Sigma-Aldrich, denoted as Dia5A) and 5-Amino-1-naphthalenesulfonic acid (98%, TCI Co., LTD., denoted as Dia6A) were used as the functional groups of acid. 4-Amino phthalonitrile (98%, Sigma-Aldrich, denoted as Dia7N) and 4-Amino benzonitrile (98%, Sigma-Aldrich, denoted as Dia8N) were used as the functional groups of nitrile. The last letter of F, A, and N means the characteristic functional groups.

To cover up the full surface coverage of the catalyst, these reactions were carried out as follows; 1 g of the pristine Pt/GKB6 was dispersed in 500 mL of deionized water and stirred vigorously for 2 h with a magnetic stirrer. 4 mmol of the diazonium salt was added and stirred for 20 min, and then 8 mmol of NaNO_2 (ACS reagent, Sigma-Aldrich) was added directly to the aqueous suspension. After stirring for 20 min, 1 mL of 0.5 M HCl (Fisher) was added. The reaction mixture was stirred overnight at ambient temperature and vacuum filtered. The treated-catalyst was washed by successive deionized water and methanol several times. Finally the modified catalyst was dried in freeze dryer for 12 h.

2.3. Characterization and evaluation of the prepared catalysts

Physicochemical properties of the prepared catalysts were characterized by several analysis tools. Particle size and distribution of the reference and pristine catalysts were measured by X-ray diffraction (XRD, X'pert PRO MPD, PANalytical) and Field emission-Transmission electron microscope (FE-TEM, TECNAI microscope F30, FEI-company). The amount of metal loading and diazonium salt were calculated by a thermogravimetric analysis (TGA, Rubotherm). An X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific) was very useful technique for analyzing the output of diazonium reactions.

All the electrochemical characterization, activity and durability studies were performed using a half-cell method. The half-cell experiment was performed in 0.1 M HClO_4 aq. solution using a VSP potentiostat (Bio Logic Science Instruments), a Pt-mesh counter electrode, and an Ag/AgCl reference electrode [0.197 V vs. reversible hydrogen electrode (RHE)]. A rotating disk electrode (RDE) with a glassy carbon disk (0.196 cm^2) was used as the working electrode. The loading amount of metals on the glassy carbon was controlled with slurry solution concentration. The working electrodes were fabricated as follows; 15 mg of the prepared catalysts were sonically distributed for 20 min in 2.5 mL of 0.05 wt% Nafion[®] solution (1100 EW, DuPont) diluted with isopropyl alcohol (IPA). 6 μL of the slurry was dropped on the glassy carbon electrode and dried for 10 min, and then 7 μL of 0.05% Nafion[®] solution was dropped to the electrode as a cover layer. Measurements were performed in cyclic voltammetry (CV) and linear sweep voltammetry (LSV) modes in N_2 atmosphere at 25 °C.

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