

Preparation of low Pt loading electrodes on Nafion (Na⁺)-bonded carbon layer with galvanostatic pulses for PEMFC application

Jaeseung Lee, Jungsook Seo, Kookil Han, Hasuck Kim*

Department of Chemistry, Seoul National University, San 56-1, Sillim 9-dong, Kwanak-gu, Seoul 151-747, Republic of Korea

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Abstract

Low Pt loading electrodes were prepared by galvanostatic pulse electrodeposition on a Nafion-bonded carbon layer. Since the electrodeposition of Pt in aqueous solution occurred only on carbon surface with some ion conductivity (Nafion-Na⁺), it was possible to significantly reduce the thickness of the catalyst layer as well as the amount of Pt loading. Thus, it provided enhanced utilization efficiency of catalyst. This method consisted of a three-step procedure in the following order: deposition of Pt particles on a Nafion-bonded carbon layer, heat treatment, and a protonation process. The electrochemical surface areas of the Pt deposits were determined by cyclic voltammetry. Other physical properties of the deposit were characterized by transmission electron microscopy, X-ray diffraction measurements, and X-ray photoelectron spectroscopy. The amount of Pt deposit was determined by inductively coupled plasma-atomic emission spectroscopy. The performance of the prepared electrode was compared with conventional electrodes, which were prepared with 20 wt.% Pt/C from E-TEK. The performance of the membrane electrode assemblies employing electrodeposited electrodes (0.025 mg Pt cm⁻² on the anode and 0.3 mg Pt cm⁻² on the cathode) has shown competitively higher values than those of the conventional electrodes (0.3 mg Pt cm⁻² on both electrodes). These results indicate a noticeable increase in the catalyst utilization due to the deposition of Pt particles taking place only in the three-phase reaction zone.

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1. Introduction

Fuel cells have been receiving considerable interest as power sources because they exhibit high-energy efficiency and are environment-friendly. Among all fuel cell systems, polymer electrolyte membrane fuel cells (PEMFCs) are considered to be one of the most promising energy conversion devices, particularly for stationary power generation and as vehicular power sources [1–3]. In recent years, the research and development in fuel cells have been accelerated, however, at present, the cost of fuel cell systems is still too high to become commercially viable products. Low Pt loading and improved mass activity are required since Pt, which is used as the catalyst, is rare and expensive. For these reasons, many studies have been directed towards the development of electrodes with high performance with low Pt loadings [4–8].

Conventionally, Pt catalysts have been prepared by the chemical reduction of Pt salts. Subsequently, these Pt particles are adsorbed on carbon with a high surface area to prepare Pt/C powder. The most common method to produce the catalyst layer is to mix the Pt/C agglomerates with a solubilized polymer electrolyte such as Nafion ionomer and apply the paste on a porous support by decal or blade process or spray method. Inactive catalyst sites are always present in the catalyst layer prepared by the conventional method. These inactive sites are not available for fuel cell reaction because the electrochemical reaction is limited only at the interface between the polymer electrolyte (e.g., Nafion) and the Pt catalyst that is exposed to the reactant, known as the three-phase reaction zone [9].

For this reason, the electrodeposition of Pt has been suggested by a number of workers and the main intention is to deposit small Pt particles at the polymer electrolyte/electrode interface [10–14]. Pt has been electroreduced from an aqueous solution on various materials such as glassy carbon [15–17], carbon/Nafion interfaces [18–20], and PEMFC electrodes [10–12,21–23]. Taylor et al. used the Pt(NH₃)₄²⁺ complex to deposit Pt particles of

* Corresponding author. Tel.: +82 2 880 6638; fax: +82 2 889 1568.
E-mail address: hasuckkim@snu.ac.kr (H. Kim).

2–3 nm on Nafion-bonded carbon electrode with electrochemical catalyzation technique [20]. They floated the gas diffusion electrode (GDE) on the surface of a solid polymer electrolyte (SPE; Nafion) solution to impregnate the Nafion and to form a thin layer of Nafion on the surface of the uncatalyzed carbon electrode. Pt ions diffused through the thin Nafion layer and were electrodeposited only at the regions with proper ionic and electronic conductivities. On the other hand, Antoine and Durand impregnated carbon with H_2PtCl_6 and applied electrochemical pulses in order to deposit Pt on a Nafion active layer [10]. These two methods aimed to prepare catalysts with high Pt utilization from an aqueous electrolyte. However, in a fuel cell system, some polymer electrolyte covered the Pt particles thus to prevent reactant gases to contacting with the catalyst. Recently, Kim et al. reported pulse electrodeposition technique for PEMFC electrodes [11,23]. In this technique, Pt was deposited on the surface of the carbon electrode, followed by heat treatment and Nafion impregnation. In this case, the impregnated polymer electrolyte also covered the Pt particles, and thus, some Pt particles were not exposed to the reactant. In addition, some Pt particles were not always in good contact with the electrolyte phase because Nafion could not penetrate into the catalyst layer easily. In terms of the three-phase reaction zone, these electrodes may face problems of poor electrolyte contact or poor reactant diffusion.

In order to overcome these problems, the electrodeposition technique was applied on a Nafion-bonded uncatalyzed carbon electrode. The use of Nafion as a proton conducting binder in the catalyst layer has been demonstrated to increase the Pt utilization significantly. In the first-generation PEMFCs, catalyst layers containing PTFE (polytetrafluoroethylene)-bonded Pt electrocatalysts with a high loading of 4 mg Pt cm^{-2} were used as the PEMFC electrodes [5]. Srinivasan et al. reported high performance electrodes with a low catalyst loading of $0.35 \text{ mg Pt cm}^{-2}$ [24,25]. This achievement was possible mainly by using Nafion instead of PTFE as the catalyst binder. For using a Nafion-bonded carbon electrode, it is necessary to modify the heat treatment process because Nafion is thermally unstable above 150°C [26]. Another approach for the heat treatment is improving the mechanical properties of Nafion ionomer. It is reported that when the protons in Nafion ionomer were exchanged by other cations, the thermal stability of Nafion ionomer was improved [27–31]. The molecular structure of Nafion consists of a poly(tetrafluoroethylene) (PTFE) backbone with perfluorinated pendant chains terminated by sulfonate groups in the acid form.

Mauritz and Moore performed DMA (dynamic mechanical analysis) studies of various Nafion membranes including the acid form and other cationic forms [26]. After the conversion of Nafion- H^+ to sodium-sulfonated form (Nafion- Na^+), the ionomer exhibited a significant shift in the α relaxation to a temperature near 250°C . This form of ionomer is no longer melt-processible due to strong Coulombic interactions that yield a dynamic electrostatic network. Due to this thermal stability, the Nafion-bonded electrodes are possible to treat to 250°C .

In this study, we report on the electrode preparation method for low Pt loadings on Nafion-bonded carbon electrodes using

a current pulse electrodeposition technique and a modified heat treatment. The main feature of this method is the location of Pt deposition that is limited only to the three-phase reaction zone areas and thereby we can get improved performance with low Pt loadings. It was possible to prepare PEMFC electrodes with high catalyst utilization.

2. Experimental

2.1. Deposition of Pt on glassy carbon electrodes; Potential sweep method

The deposition behavior of Pt on glassy carbon electrodes was studied in aqueous solution with an electrochemical analyzer (BAS, 100B/W, Bioanalytical Systems). In order to use the sodium-sulfonated form of Nafion (Nafion- Na^+), it was necessary to make the Pt precursors and electrolytes free of protons. Therefore, $10 \text{ mM K}_2\text{PtCl}_4$ and 0.5 M NaCl were used as the Pt precursor and electrolyte, respectively. A standard three-electrode cell was employed. The glassy carbon electrode with a diameter of 0.3 cm was used as a working electrode. A Pt foil served as a counter electrode and an Ag/AgCl electrode was used as a reference electrode.

Pt nanoparticles were electrodeposited on the glassy carbon by scanning the potential from 800 to -200 mV (versus NHE) at a scan rate of 10 mV s^{-1} . After the Pt deposition, the electrode was cleaned with purified water and the deposits were then electrochemically characterized by cyclic voltammetry employing the same electrochemical analyzer. A common electrochemical cell containing $1 \text{ M H}_2\text{SO}_4$ solution was used for the measurements. CVs were generally recorded at a scan rate of 10 mV s^{-1} . All the potentials were referred to the NHE.

2.2. Preparation of Nafion-bonded carbon electrodes

Nafion-bonded carbon electrodes were prepared by using a gas diffusion layer (GDL; LT 1200-W) from the Electrochem Inc. In order to localize Pt at the membrane/carbon interface, it is critical to prepare carbon blank electrode with an optimum amount of Nafion, hydrophilicity, and thickness.

Vulcan XC-72 carbon powder and Nafion solution (Aldrich, 5 wt.% in water/aliphatic alcohols, 1100 EW) were mixed with isopropyl alcohol, and the mixed solution was placed in an ultrasonic bath. Glycerol and the equivalent amount of aqueous solution of sodium hydroxide were then added to the mixture to form a hydrophilic layer and to convert H-form of Nafion to sodium-sulfonated Nafion (Nafion- Na^+), respectively. The resulting mixture was ultrasonically homogenized and was applied on the hydrophobic GDL by spraying. The hydrophilic carbon layer was loaded with 0.3 mg cm^{-2} of carbon.

2.3. Electrodeposition

The galvanostatic pulse deposition of Pt was carried out in a two-electrode cell by using an electrochemical instrument (VoltaLab80, Radiometer). The electrodeposition was made on the Nafion-bonded carbon blank electrode in a Pt plating bath

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