

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

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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<sup>+</sup>), 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<sup>-2</sup> on the anode and 0.3 mg Pt cm<sup>-2</sup> on the cathode) has shown competitively higher values than those of the conventional electrodes (0.3 mg Pt cm<sup>-2</sup> 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(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> complex to deposit Pt particles of

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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  $\text{H}_2\text{PtCl}_6$  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  $4 \text{ mg Pt cm}^{-2}$  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  $150^\circ\text{C}$  [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- $\text{H}^+$  to sodium-sulfonated form (Nafion- $\text{Na}^+$ ), the ionomer exhibited a significant shift in the  $\alpha$  relaxation to a temperature near  $250^\circ\text{C}$ . 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  $250^\circ\text{C}$ .

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- $\text{Na}^+$ ), it was necessary to make the Pt precursors and electrolytes free of protons. Therefore,  $10 \text{ mM K}_2\text{PtCl}_4$  and  $0.5 \text{ M NaCl}$  were used as the Pt precursor and electrolyte, respectively. A standard three-electrode cell was employed. The glassy carbon electrode with a diameter of  $0.3 \text{ cm}$  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  $-200 \text{ mV}$  (versus NHE) at a scan rate of  $10 \text{ mV s}^{-1}$ . 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  $10 \text{ mV s}^{-1}$ . 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- $\text{Na}^+$ ), respectively. The resulting mixture was ultrasonically homogenized and was applied on the hydrophobic GDL by spraying. The hydrophilic carbon layer was loaded with  $0.3 \text{ mg cm}^{-2}$  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

containing  $\text{K}_2\text{PtCl}_4$  and  $\text{NaCl}$  at room temperature. The concentration of electrolyte was kept constant (0.5 M) and the concentration of Pt was ranged from 5 to 80 mM. Before Pt deposition, the Nafion-bonded carbon electrode was mounted on the electrode holder coupled with a Pt foil as a current collector. They were assembled with a Pt mesh ( $2\text{ cm}^2$ ) as an anode at a distance of 5 mm. The assembled holder was immersed into a Pt bath for 2 min so that the assembly is soaked sufficiently. Immediately after the deposition, the electrochemically catalyzed electrode was rinsed thoroughly with ultrapure water to remove any residue of the Pt precursor. The amount of deposited Pt on the electrode was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) after treatment of the electrode with aqua regia. The morphology and size of the deposited Pt particles were examined by transmission electron microscopy (TEM; JEOL Co., JEM-200CX). X-ray diffraction (XRD) measurements were performed to confirm the particle size and its lattice parameters with a MAC Science Power Diffraction system (Model M18XHF-SRA) using a  $\text{Cu K}\alpha$ -source operated at 50 keV and 200 mA, and with a scan rate of  $1^\circ\text{ min}^{-1}$ . After the electrodeposition process, the electrodes were heated at  $250^\circ\text{C}$  in  $\text{H}_2$  (10%)/ $\text{N}_2$  (90%) gas for 30 min. Before and after the heat treatment of the electrode, the oxidation states of Pt were measured by X-ray photoelectron spectroscopy (XPS; Pohang Accelerator Laboratory, 4B1). The protonation process was carried out by immersing the electrodeposited layers into 0.1 M  $\text{H}_2\text{SO}_4$  solution for 30 min with mild heating ( $80^\circ\text{C}$ ). The electrodes were then thoroughly rinsed with a copious amount of water.

Model electrodes consisting of Nafion-bonded carbon layers on glassy carbon substrates were used in order to investigate the electrochemical properties of the deposits. For the preparation of the carbon layers on glassy carbon, the same carbon suspension with Nafion- $\text{Na}^+$ , which was used for the preparation of PEMFC electrodes were used. The suspension was similarly sprayed onto a glassy carbon disc with a diameter of 0.3 cm. Pt deposition was also carried out by the same procedure. Then, the electrode was rinsed with purified water in order to remove all the remaining Pt precursors and solvents, and dried for 30 min in the air. The deposits were electrochemically characterized by CV with an electrochemical analyzer (BAS, 100B/W, Bioanalytical Systems). The electrochemical surface area (ESA) of Pt was calculated using the fact that the monolayer adsorption of hydrogen corresponds to  $210\ \mu\text{C cm}^{-2}_{\text{Pt}}$  [32]. The specific surface area was calculated from the ratio of ESA to Pt loading. The amount of Pt on glassy carbon electrodes was also determined by ICP-AES.

#### 2.4. MEA fabrication and unit cell operation

The cathode catalyst slurry was prepared by thoroughly mixing the supported catalyst (Pt/C, 20 wt.% E-TEK), Nafion solution (5 wt.%), and an appropriate amount of isopropyl alcohol. The ratio of the supported catalyst to Nafion was typically 2:1 by weight. The well-mixed slurry was applied on a GDL (E-TEK, LT 1200-W) with  $0.3\text{ mg Pt cm}^{-2}$ . The electrodeposited electrode and the sprayed electrode were placed on either side

of the Nafion 112 membrane (DuPont) as the anode and cathode, respectively. The assembly was hot-pressed at  $100\text{ kgf cm}^{-2}$  for 3 min at  $135^\circ\text{C}$ . For comparison, conventional MEAs were also prepared by spraying both electrodes using the same GDL on both sides with a Pt loading of  $0.3\text{ mg cm}^{-2}$ .

Electrochemical polarization behavior were obtained by using a home-made test fixture with an active area of  $1.4\text{ cm}^2$ . The gas flow rates were kept constant at four and eight times of stoichiometric values calculated at current density of  $1\text{ A cm}^{-2}$  for  $\text{H}_2$  and air, respectively. All measurements were made at  $70^\circ\text{C}$  and pressures of 2 bar (absolute) on both sides. The gas humidification temperatures were 10 and  $5^\circ\text{C}$  higher than the cell temperature for  $\text{H}_2$  and air, respectively.

### 3. Results and discussion

#### 3.1. Deposition of $\text{PtCl}_4^{2-}$ on glassy carbon

Pt complexes used as precursor exhibit various deposition patterns depending on their oxidation states, type of ligand, electrolytes, substrates, and deposition conditions. Since the Nafion ( $\text{Na}^+$ )-bonded carbon electrodes were used as the substrate for the electrodeposition,  $\text{K}_2\text{PtCl}_4$  and  $\text{NaCl}$  were used as the Pt precursor and electrolyte, respectively. Fig. 1 shows the CV behavior of the deposition of  $\text{PtCl}_4^{2-}$  on a glassy carbon electrode (Fig. 1(a)) and the electrochemical property of the deposits in 1 M  $\text{H}_2\text{SO}_4$  solution (Fig. 1(b)). In the negative scan, no significant current is observed up to 0 mV and there exists a well-defined reduction peak at  $E_p = -124\text{ mV}$  versus NHE. In the reverse scan, Pt deposition continues up to 300 mV. This result shows that a substantial overpotential is necessary to drive the formation of Pt nuclei on carbon surface. After Pt deposition, the electrode was taken out from the precursor solution, rinsed thoroughly with water, and then transferred to an electrochemical cell containing 1 M  $\text{H}_2\text{SO}_4$ . A cyclic voltammogram was recorded from 0 to 1000 mV versus NHE with a scan rate of  $10\text{ mV s}^{-1}$ . A typical cyclic voltammogram of Pt was obtained, as shown in Fig. 1(b).

#### 3.2. Current pulse electrodeposition from $\text{PtCl}_4^{2-}$ on Nafion-bonded carbon electrode

The performance of the Pt catalyst prepared by electrodeposition is greatly influenced by the deposition conditions such as the concentration of Pt precursor, composition and concentration of electrolyte, total charge density, peak current density, duty cycle, and temperature. Many researchers have reported on the optimum parameters of galvanometric deposition [11,14,23,33]. However, the best parameters always differed due to different substrates, Pt precursors, and electrolytes. Under our experimental conditions, the optimum conditions for the deposition from  $\text{PtCl}_4^{2-}$  on a Nafion-bonded carbon layer in  $\text{NaCl}$  solution was determined as a duty cycle of 10/100 ms and a peak current density of  $300\text{ mA cm}^{-2}$ . During the deposition, the amount of loaded Pt was controlled by varying the total charge used for the electrodeposition and the concentration of the Pt precursor. In order to control the amount of loaded Pt, the total charge

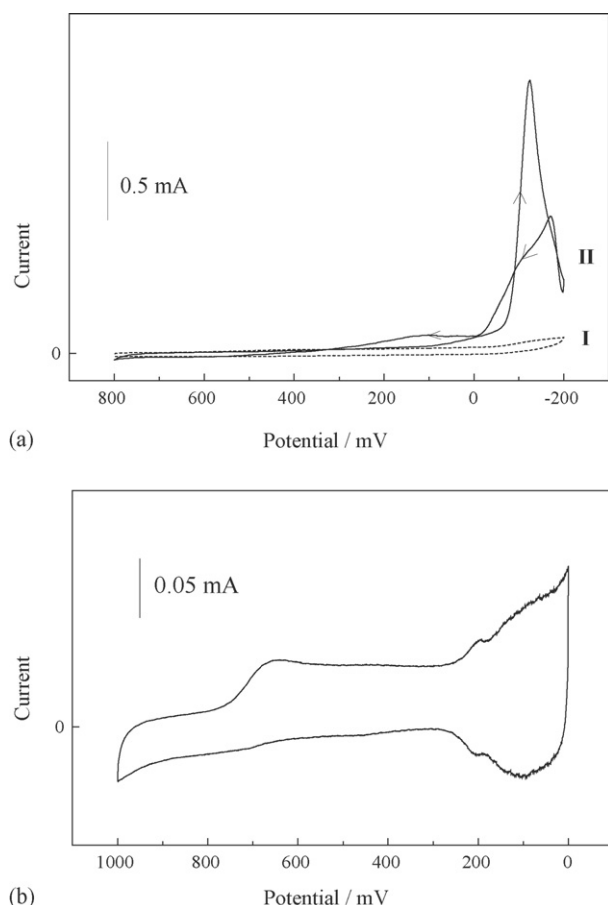


Fig. 1. Deposition of PtCl<sub>4</sub><sup>2-</sup> on glassy carbon. (a) Electrochemical reduction by potential sweep on a glassy carbon electrode. Curve I shows the baseline of the glassy carbon electrode in 0.5 M NaCl solution. Curve II shows the electrochemical reduction of Pt on glassy carbon in 10 mM PtCl<sub>4</sub><sup>2-</sup> + 0.5 M NaCl solution with a scan rate of 10 mV s<sup>-1</sup>. (b) Cyclic voltammogram of deposits in 1 M H<sub>2</sub>SO<sub>4</sub> solution with a scan rate of 10 mV s<sup>-1</sup>.

density and concentration of the Pt precursor were varied from 0.5 to 8 C cm<sup>-2</sup> and from 10 to 80 mM, respectively. Table 1 shows the amount of loaded Pt determined by ICP-AES. In general, the amount of Pt increases with the total charge and concentration of PtCl<sub>4</sub><sup>2-</sup>. The amount of platinum was directly proportional to the concentration of PtCl<sub>4</sub><sup>2-</sup>, while it increased slightly with a change in the charge density due to limited mass transfer.

Table 1  
Amount of Pt loading (mg cm<sup>-2</sup>) with different total charge densities and concentrations of PtCl<sub>4</sub><sup>2-</sup>

Total charge density (C cm <sup>-2</sup> )	Concentration of PtCl <sub>4</sub> <sup>2-</sup>			
	10 mM	20 mM	40 mM	80 mM
0.5	0.011	0.025	0.053	0.139
1	0.015	0.032	0.069	0.193
2	0.025	0.043	0.086	0.246
4	0.030	0.057	0.114	–
6	0.037	0.067	0.148	–
8	0.044	0.088	0.158	–

The morphology of Pt particles was observed by TEM, and the images are presented in Fig. 2. These images were obtained from a series of deposits with a total charge density of 1 C cm<sup>-2</sup> and PtCl<sub>4</sub><sup>2-</sup> concentrations of 10, 20, 40, and 80 mM. Fig. 2(a) shows that a uniform size of Pt particles of about 3–4 nm are obtained on the Vulcan XC-72 surface from 10 mM PtCl<sub>4</sub><sup>2-</sup> solution.

By comparing Fig. 2(a)–(d), it is concluded that the increase in the concentration of PtCl<sub>4</sub><sup>2-</sup> does not lead to a significant increase in the particle size. Thus, even with 80 mM PtCl<sub>4</sub><sup>2-</sup> solution, we were able to obtain Pt particles with a diameter of about 5 nm. The average size of the Pt particles was also calculated using the Debye-Scherrer equation from XRD data. The particle size of all deposits was ranged between 3 and 5 nm. While the particle size increased slightly, the total amount of deposited Pt increased linearly with the concentration of PtCl<sub>4</sub><sup>2-</sup>. By using this method, we can obtain a Pt loading up to 0.25 mg cm<sup>-2</sup> without a significant increase in the particle size. Generally, in PEMFC, a Pt loading of less than 0.3 mg cm<sup>-2</sup> has been used for cathode and less than 0.15 mg cm<sup>-2</sup> for anode [1]. Based on the experimental data in Table 1, it was possible to utilize these deposition conditions to prepare both electrodes for PEMFC. In addition, it seems possible to prepare electrodes with higher Pt loadings by using higher concentrations and high charge densities.

After electrodeposition, the electrodes were heat-treated at 250 °C in a reducing atmosphere with 10% hydrogen and 90% nitrogen for 30 min. An XPS study was carried out to investigate the surface property of deposits before and after the heat treatment. Fig. 3(a) shows the Pt 4f X-ray photoelectron spectrum of the deposit before the heat treatment. The spectrum was deconvoluted into three components labeled as Pt(0), Pt(II), and Pt(IV) with binding energies of 71.1, 73.3, and 74.5 eV, respectively. The relative intensities (%) of the three components were 73, 21, and 6, respectively (Table 2). The Pt 4f<sub>7/2</sub> signal at 71.1 eV can be assigned to Pt with zero valency [34]. Fig. 3(b) represents the Pt 4f X-ray photoelectron spectrum of the heat-treated deposit. The spectrum was also deconvoluted into three components as before. The relative intensities of Pt, Pt(II), and Pt(IV) were obtained as 85, 12, and 3, respectively. It is noteworthy that the relative intensity of metallic Pt in the heat-treated deposits is considerably higher than those of the non-treated deposits, which indicates the reduction of oxidized Pt during the heat treatment occurs.

Table 2  
Binding energies and relative intensities of deposits as observed from the Pt 4f X-ray photoelectron spectra in Fig. 3

Sample	Species	Binding energies of 4f <sub>7/2</sub> (eV)	Relative intensities (%)
Before heat treatment	Pt	71.1	73
	Pt(II)	73.3	21
	Pt(IV)	74.5	6
After heat treatment	Pt	71.1	85
	Pt(II)	73.2	12
	Pt(IV)	74.7	3



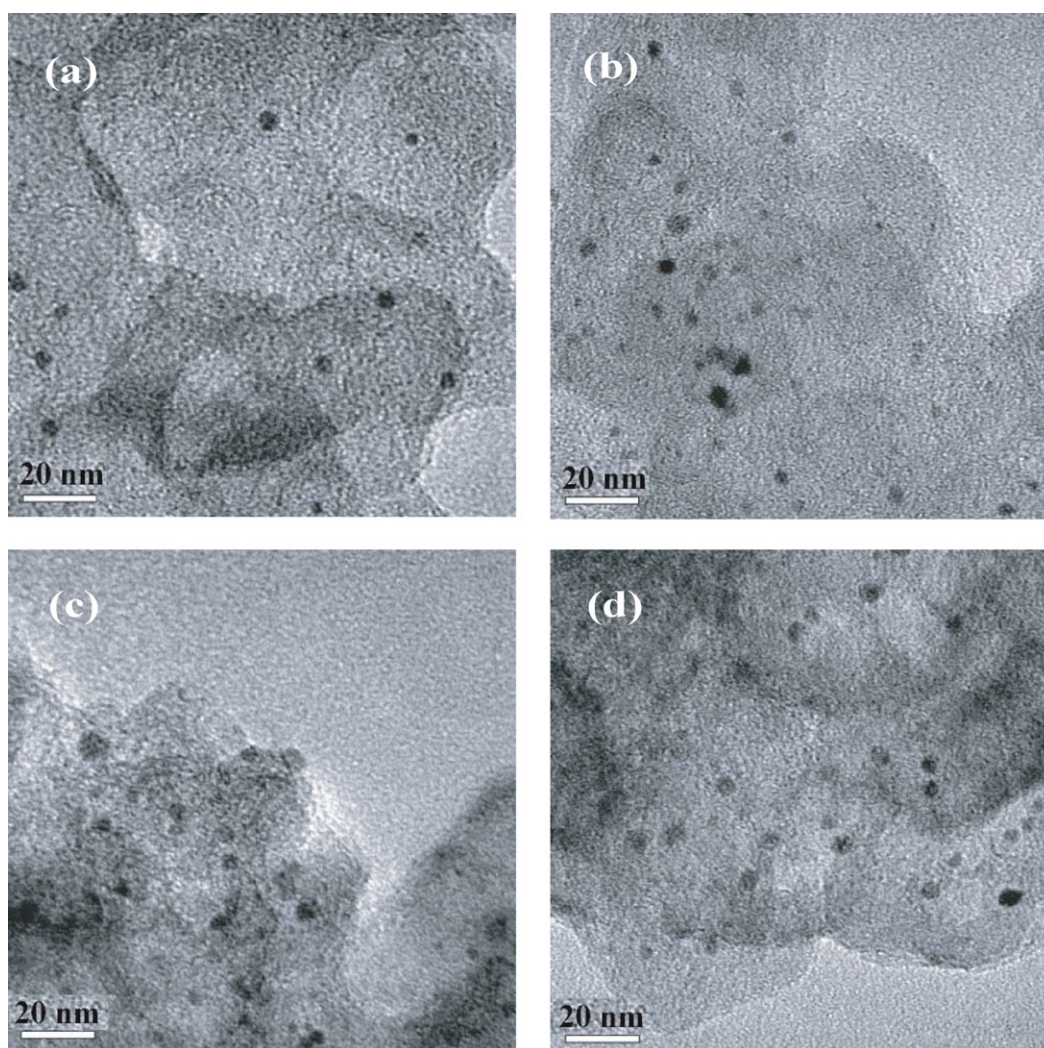


Fig. 2. TEM images of electrodeposited Pt particles on Vulcan XC-72 prepared with different concentrations of  $\text{PtCl}_4^{2-}$ . (a) 10 mM, (b) 20 mM, (c) 40 mM, and (d) 80 mM.

### 3.3. Unit cell performance

Fig. 4 shows the polarization curves from the PEM fuel cell prepared by using two different types of anodes. One was prepared by using the electrodeposited Pt on Nafion-bonded carbon electrode and the other was prepared by conventional method using the E-TEK catalyst. The pulse electrodeposited electrode was prepared under conditions of  $300 \text{ mA cm}^{-2}$  of peak current density and 10/100 ms of on/off time. The electrode was deposited from 20 mM  $\text{PtCl}_4^{2-}$  solution with a total charge density of  $0.5 \text{ C cm}^{-2}$ . The amount of Pt in the electrode was determined as  $0.025 \text{ mg cm}^{-2}$  (Table 1). The conventional MEAs were fabricated by spraying the catalyst slurry with  $0.3 \text{ mg Pt cm}^{-2}$  on GDL on the anode sides. In comparison with the conventional electrode made with catalysts from the E-TEK, the electrode prepared by electrodeposition contains only 8.3% of Pt of the E-TEK shows a similar performance in low current region and a better performance in high current region. It is certain that a less amount of Pt is required with the electrodeposition method to exhibit the same performance as the electrodes prepared by the conventional method. It is concluded that the

MEAs prepared by electrodeposition on a Nafion-bonded carbon electrode exhibit a higher utilization of catalyst as compared with the conventional MEAs.

Fig. 5 shows the polarization curves of the PEM fuel cell prepared by current pulse electrodeposition. In order to observe the effect of the amount of Pt, the loading amount was controlled by varying the concentration of  $\text{PtCl}_4^{2-}$  (10 and 20 mM) and charge density ( $0.5\text{--}8 \text{ C cm}^{-2}$ ). In Fig. 5(a), the polarization curves were obtained with the electrode deposited in 10 mM  $\text{PtCl}_4^{2-}$  solution. The performance of MEA expectedly increases with the total charge density from  $0.5$  to  $2 \text{ C cm}^{-2}$ . In Table 1, as the charge density increases from  $0.5$  to  $2 \text{ C cm}^{-2}$ , the amount of Pt increases from  $0.011$  to  $0.025 \text{ mg cm}^{-2}$ . For charge densities higher than  $2 \text{ C cm}^{-2}$ , MEAs show similar performances although the amount of Pt increases. This indicates that electrodes with more than  $0.025 \text{ mg cm}^{-2}$  of Pt exhibit less catalyst utilization efficiencies. It can be concluded that, under our experimental conditions, the optimum amount of Pt on the anode without losing in performance is about  $0.025 \text{ mg cm}^{-2}$ . These results agree well with the polarization curves in Fig. 5(b), which were obtained with the electrodes deposited in 20 mM  $\text{PtCl}_4^{2-}$

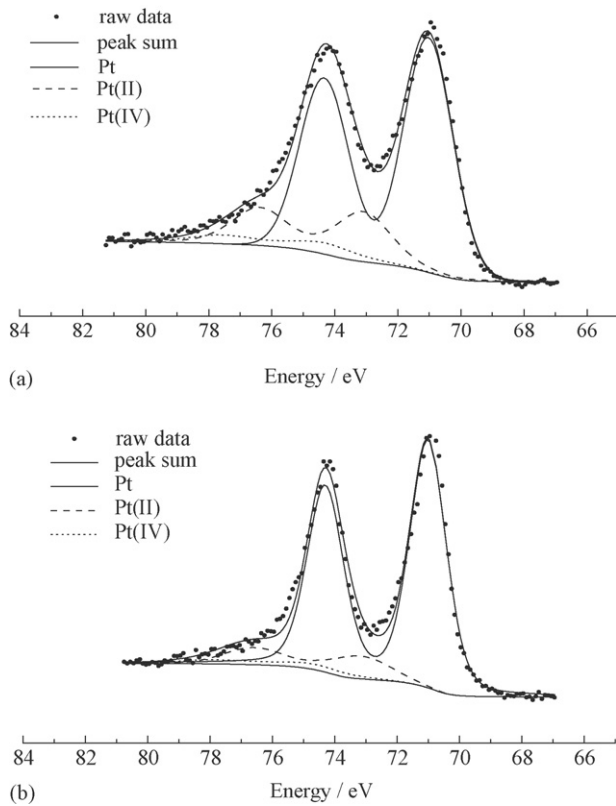


Fig. 3. Pt 4f X-ray photoelectron spectra of the deposit. (a) Before heat treatment and (b) after heat treatment.

solution. All electrodes have more than  $0.025 \text{ mg cm}^{-2}$  as seen in Table 1, no further increase, however, in their performance is observed.

The effect of Nafion loading on the performance has been reported by Passalacqua and co-workers, who varied the Nafion content from 14 to 66 wt.% [35]. It is well accepted on the optimum Nafion loading of approximately 33 wt.% [36–39], which refers to the weight fraction with respect to the amount of catalyst including Pt. Since Nafion loading in our experiment refers to the weight fraction with respect to the amount of carbon, the

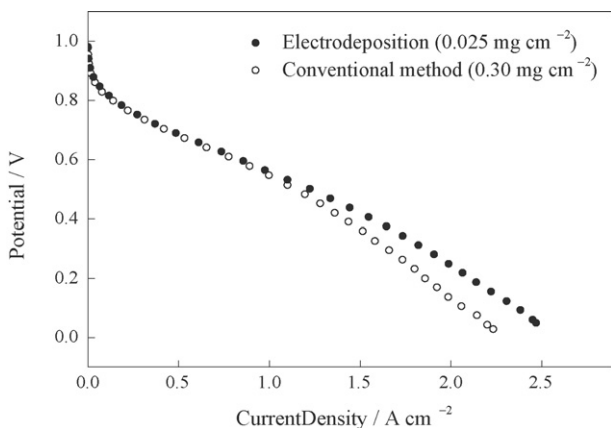


Fig. 4. Unit cell performance of low Pt loading electrodes prepared by electrodeposition and conventional method.

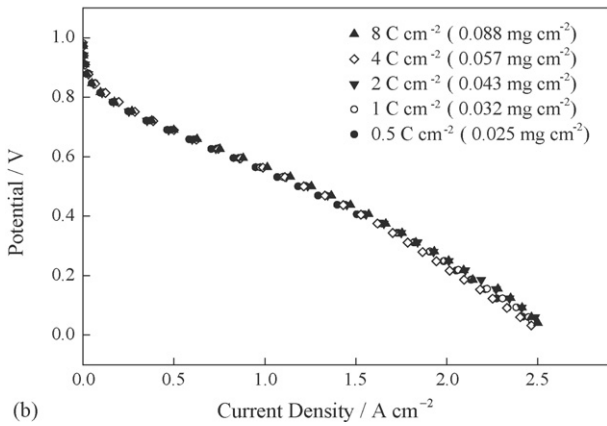
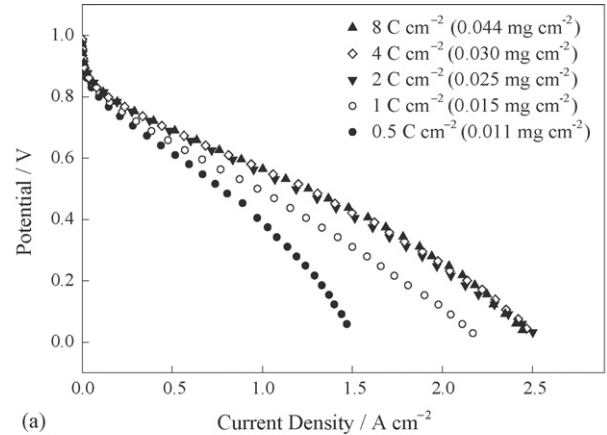


Fig. 5. Polarization curves of the electrodes prepared with different charge densities ( $0.5\text{--}8 \text{ C cm}^{-2}$ ). (a)  $10 \text{ mM PtCl}_4^{2-}$  and (b)  $20 \text{ mM PtCl}_4^{2-}$ . The electrodeposited electrodes were used as the anodes. These MEA performances show the effect of Pt loading controlled by charge density and concentration of  $\text{PtCl}_4^{2-}$ .

reported optimum Nafion loading corresponds to about 40 wt.% in our definition. Therefore, we varied the Nafion content from 25 to 55 wt.%. Fig. 6 shows the polarization curves obtained using the electrode deposited from  $20 \text{ mM PtCl}_4^{2-}$  solution with a total charge density of  $2 \text{ C cm}^{-2}$ . The unit cell performance

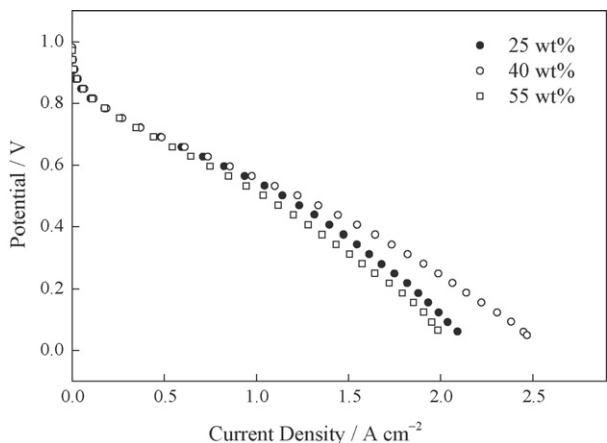


Fig. 6. Effect of Nafion content in the electrode ( $0.043 \text{ mg Pt cm}^{-2}$ ) prepared from  $20 \text{ mM PtCl}_4^{2-}$  with a total charge density of  $2 \text{ C cm}^{-2}$ .

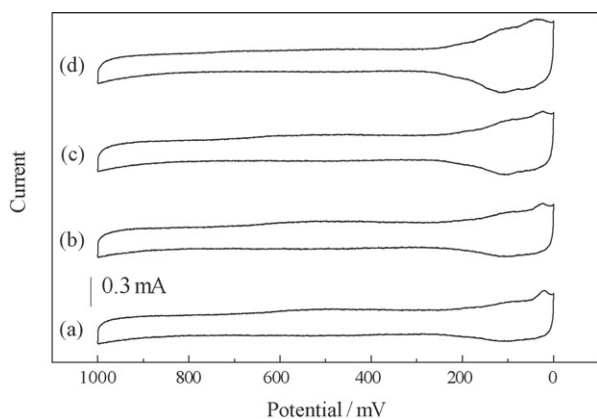


Fig. 7. Cyclic voltammograms of the deposit on glassy carbon with Nafion-bonded carbon layer prepared from different concentrations of  $\text{PtCl}_4^{2-}$ . (a) 10 mM, (b) 20 mM, (c) 40 mM, and (d) 80 mM.

increases with the Nafion content from 25 to 40 wt.%. When the Nafion content increases further to 55 wt.%, the performance, however, decreases. This indicates that the additional Nafion appears to block catalyst particles contacting with the carbon substrate for electrical contact.

#### 3.4. Electrochemical properties of the deposits

In order to investigate the electrochemical properties of the deposit, we carried out cyclic voltammetry using a glassy carbon electrode covered with Nafion-bonded carbon layer. For the preparation of the deposit, the same process as PEM electrode fabrication was followed, and the same amount of Pt deposit on the glassy carbon also was made. The amount of Pt in both cases was confirmed by ICP-AES measurements. Fig. 7 shows the cyclic voltammograms of electrodeposited electrodes prepared by using different concentrations of  $\text{PtCl}_4^{2-}$ , and the calculated electrochemical surface areas are listed in Table 3. The electrochemical surface area increased with the concentration of  $\text{PtCl}_4^{2-}$ , indicating that a larger amount of Pt was deposited from a high concentration bath. However, as the concentration of  $\text{PtCl}_4^{2-}$  increased, the specific surface area decreased because of the overlapping of Pt particles. From the TEM and XRD results, the particle size of Pt increases slightly with the increase in the concentration of  $\text{PtCl}_4^{2-}$ . These results support the idea that the overlapping of Pt particles causes decrease of the specific surface area as well as slight increase in particle size.

Table 3

Pt surface area calculated from the hydrogen absorption peak in cyclic voltammograms (Fig. 7)

$\text{PtCl}_4^{2-}$ (mM)	Electrochemical surface area ( $\text{cm}^2$ Pt)	Specific surface area ( $\text{m}^2$ Pt $\text{g}^{-1}$ Pt) <sup>a</sup>
5	4.03	158.5
10	4.85	114.3
20	6.83	75.49
40	9.69	49.69

<sup>a</sup> Calculated using the amount of Pt loading from Table 1.

## 4. Conclusions

In this paper, the fabrication method of fuel cell electrodes with low Pt loadings was presented. Pt was electrodeposited on an uncatalyzed carbon electrode in  $\text{PtCl}_4^{2-}$  solution. The uncatalyzed carbon electrode consisted of a hydrophobic gas diffusion layer and a hydrophilic layer. The hydrophilic layer was made by spraying a mixture of sodium-sulfonated form of Nafion (Nafion- $\text{Na}^+$ ), glycerol, carbon black (Vulcan XC-72), and isopropyl alcohol on a hydrophobic carbon layer. This method was able to produce electrodes with a Pt loading of  $0.025 \text{ mg cm}^{-2}$ , which is a significantly low loading. Small and uniform Pt particles were obtained by controlling the concentration of Pt precursor and current density using sodium form of Nafion, which can be heated to  $250^\circ\text{C}$ . This electrodeposited electrode exhibited a similar performance compared to a conventional thin film electrode with a Pt loading of  $0.3 \text{ mg cm}^{-2}$ . This result indicates a definite increase of utilization efficiency, which is believed due to the deposition of Pt particles take place only in the three-phase reaction zone. In order to redefine the optimum conditions and parameters for the deposition of small-sized and uniform Pt particles on the carbon surface, additional variables and materials are under evaluation. Applying this method to prepare cathode electrodes is also under investigation.

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