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Preparation of Pt/Electro-conductive polymer loaded carbon composite for improvement of electrode durability for fuel cells

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The platinum nanoparticles/Electroconductive polymer; e. g., polypyrrole(PPy) and polyaniline(PANi) composite loaded on carbon was synthesized successfully by following process; oxidation of carbon, ion-exchange of H^+ and platinum ion, and the polymerization of pyrrole using the platinum ion dispersed on carbon as oxidant in the previous study. The thin layer of polypyrrole suppresses the ionization to platinum ion and distribute into electrolyte under operational condition of fuel cells. The catalytic activity and the size of the platinum particles of synthesized composite had less change than the conventional electrocatalyst, platinum nanoparticles/carbon composite (Pt/C), during the durability test, multiple scanning of the cyclic voltammetry. The catalytic activity for the Pt/PPy/C was held during the durability examination up to 12500 cycles between -0.2-1.0 V vs Ag/AgCl without a coagulation and crystal growth of the platinum particles.

Introduction

Polymer electrolyte fuel cells (PEFCs) have attracted enormous interest as a primary power source for electric vehicles (EVs) and a portable power source for many electric devices as well as an onsite type with the cogeneration systems which have many advantages in terms of the environment and the energy problems (1, 2).

In the viewpoint of the electrode durability, some studies suggested that the platinum catalyst diffuses into the ion-exchange membrane by the oxidation of platinum during the oxygen reduction at the open circuit voltage (3). The conventional electrocatalyst, Pt/C, has some problems in fuel cell operation; e. g. the degradation of carbon as catalytic support, the poisoning of catalyst by CO and methanol and high cost performance of platinum. It is necessary to notice that the deterioration of catalytic activity derives from the ionization of platinum, is followed by dissolution and re-deposition to platinum metal into electrolyte such as Nafion®.

Polypyrrole (PPy) is a representative conductive polymer and many reports have been released to apply this polymer to capacitor and cell materials. In addition, some of them researched the role of PPy with platinum as a catalyst (4-6). The composite of PPy and gold metals were synthesized by Selvan et al.(7-9) in which PPy/Au was prepared by soft process with $HAuCl_4$. In the previous study, we reported one-step synthesis of platinum nanoparticles/polypyrrole composite (Pt/PPy) using H_2PtCl_6 as oxidant and platinum ion source. Simultaneously, pyrrole monomer played a role as reductant for Pt(IV) to Pt metal (10, 11). The size of Pt nanoparticles in Pt/PPy observed by transmission electron microscope was ca. 2.0 nm with uniformly dispersed condition in PPy.

Previously we have attempted the optimization of the reaction condition of the Pt/PPy composite and measured the catalytic activity for oxygen reduction in order to make a high dimensional structure of the gas diffusion electrode (12). The oxidation of pyrrole (Py) into polypyrrole and the reduction of Pt(IV) to Pt metal particles is proceeded using H_2PtCl_4 by the following reaction at room temperature. We have presented the preparation method of Pt/polypyrrole composite loaded on surface oxidized carbon (13).

In this study, the Pt/polypyrrole and Pt/polyaniline composites were loaded on the surface-oxidized carbon support using the similar reaction of the onestep synthesis of Pt/PPy and Pt/PANi composites. The durability and diffusion of Pt catalyst are discussed. We will discuss and characterize the property of Pt/PPy/C for the application of catalyst of PEFC in detail.

Experimental

Oxidation process of carbon surface The Pt/Electroconductive polymer/C composite for electrodes of PEFC was made with several procedures consisting of the carbon oxidizing (13), the ion-exchanging (13, 14) and oxidative polymerization (12) of monomer, pyrrole and aniline solution. Vulcan XC-72R carbon particles were immersed and oxidized with 2.0 mol/l KMnO_4 and 63wt% HNO_3 aqueous solutions for 4 hours at 343 K. After filtration with the filter holder, ADVANTEC KST-47, and washing with hot double distilled water to remove extra ionic species of KMnO_4 , oxidized carbon particles were dispersed in 4 mol/l HCl for 17 hours. Finally, the prepared carbon was filtrated, washed and dried out under vacuum at room temperature overnight. The existence of some acidic groups on the carbon surface was characterized and determined by titration method in the previous study (12).

Loading platinum with the ion-exchange process The obtained carbon with the oxidizing process was immersed in aqueous tetraammine platinum complex hydroxide; $[\text{Pt}(\text{NH}_3)_4](\text{OH})_2$ solution (Tanaka Precious Metal) and stirring for 1 h to ion-exchange with platinum ion. After stirring, the resulting sample was filtrated, washed with distilled water. The amount of Pt ion supported on carbon was determined quantity by inductively-coupled plasma atomic emission spectrometer (ICP-AES) ULTIMA2000 (Horiba Jobin Yvon) after elucidation of loaded platinum ion by ion-exchanging by hydrochloric acid solution.

Oxidative polymerization of polypyrrole and polyaniline

The carbon/polypyrrole composite was prepared by the same procedure described in Ref. 12. Pyrrole monomer (Merck) solution was applied to the solution dispersing carbon with platinum ion and stirring for 24 h. The reduction of platinum ion to platinum metal and the oxidation of Py monomer to PPy proceeded simultaneously during the stirring. After stirring, obtained Pt/PPy/C was filtrated and dried under vacuum overnight. Pt on carbon (Pt/C) and PPy on carbon (PPy/C) were synthesized as a reference sample for the comparison of the electrocatalytic activity with Pt/PPy/C. The Pt/C was prepared hydrogen reduction for 4 h at 120°C under hydrogen atmosphere after the ion-exchange process (13, 14). In the case of PPy/C, aqueous iron(III) chloride (FeCl_3) solution was used as the oxidant of Py. The reaction during pyrrole and FeCl_3 was described in Ref. (7-9). Pyrrole monomer and FeCl_3 solution were stirred for 24 hours at room temperature (15). After stirring, PPy/C was separated by filtration and dried at 110°C in vacuo.

Carbon/polyaniline composite was prepared by the similar method as the Pt/PPy/C composite. However, the oxidant activity of aniline was weaker than polypyrrole and polyaniline did not deposited on carbon using aniline monomer only. Then the mixed solution containing aniline and FeCl_3 was used to reduction of platinum ion. Additionally, HCl solution was added in aniline/ FeCl_3 mixed solution in order that polyaniline had a positive charge under the acidic circumstance. An additional effect for controlling a loading amount of the platinum was confirmed by quantitative analysis by ICP-AES measurement of the platinum and iron ionic species. The amount of reduced platinum particle loaded on carbon surface was measured by ICP-AES after elucidation with aqua regalis in acid media.

Characterization of platinum particles loaded on carbon support The morphology of Pt/Electroconductive polymer/C was observed by the field emission electron scanning microscope (FE-SEM) by JEOL JSM-6335F and the high-resolution transmission electron microscopy (HR-TEM) by JEOL JEM2010. The samples for HR-TEM observation were prepared by delivering the solution dispersed Pt/PPy/C drop into Cu mesh. The bipolaron band of the PPy polymer was characterized using diffuse reflectance infrared (DR-IR) spectroscopy with FT-IR 615R coupled with a diffuse reflectance attachment DR-600B (JASCO). X-ray photoelectron spectroscopy (XPS) by JPS-9010MC (JEOL) was measured in order to estimate the valency of platinum ionic and metal species loaded onto carbon particles.

Confirmation of the catalytic activity In order to confirm of the catalytic activity, the CO stripping method was applied. Gaseous carbon monoxide (CO) was purged into 0.5 M H_2SO_4 solution for 40 minute at 100 mV vs. Ag/AgCl to achieve the adsorption on the electrocatalyst completely. Afterwards, nitrogen gas was purged into the cell to remove excess CO in the electrolyte for 40 minute. After that, CV was performed from -0.2 to +1.0 V vs. Ag/AgCl with scan rate; 10 mV/s. An active surface area of catalyst was obtained by the integration the amount of charge calculated from the CO oxidation peak, assuming a monolayer of linearly adsorbed CO and the Coulombic charge required for oxidation as $420 \mu\text{C}/\text{cm}^2$.

Cyclic voltammetry In order to evaluate the catalytic activity of Pt/PPy/C for cationic conditions, cyclic voltammogram was measured with Voltalab PGZ402. The mixture of Pt/PPy/C and 5% Nafion solution was coated on the grassy carbon electrode as cathode. Platinum plate (1 cm^2) and 0.5 M H_2SO_4 aq. were used as anode and electrolyte respectively. The scan range was from -0.2 V to 1.0 V vs. Ag/AgCl reference electrode. The durability was confirmed by the multiple sweeps up to 12500 cycles. The quantity of platinum species solved out to electrolysis solution during durability test was measured by the ICP measurement.

Results and Discussion

Pt/PPy/C composite Obtained carbon oxidized with aqueous KMnO_4 and HNO_3 mixed solution indicated the carboxylic and phenol group on the XPS spectra. This result agreed with the previous studies (12, 13, 16-18). The amount of Pt ion in royal water was evaluated by ICP measurement was about 8.8 wt%.

In SEM micrographs and mapping data shown in Fig. 1, the morphology of Pt/PPy/C was observed and each element composed of sample, C, N and Pt, were in the same position.

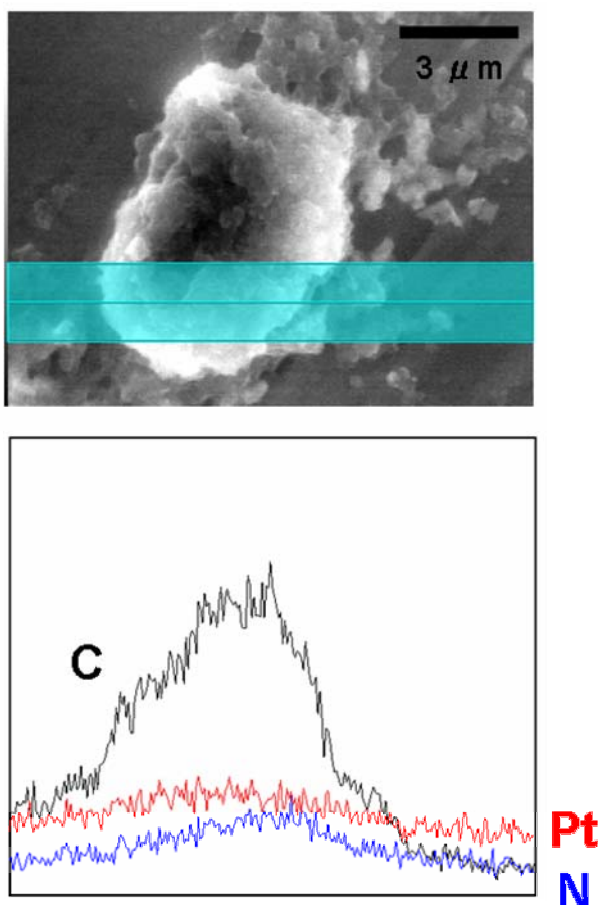


Fig.1 SEM image and distributions of element, C, Pt, and N in Pt/PPy/C composite.

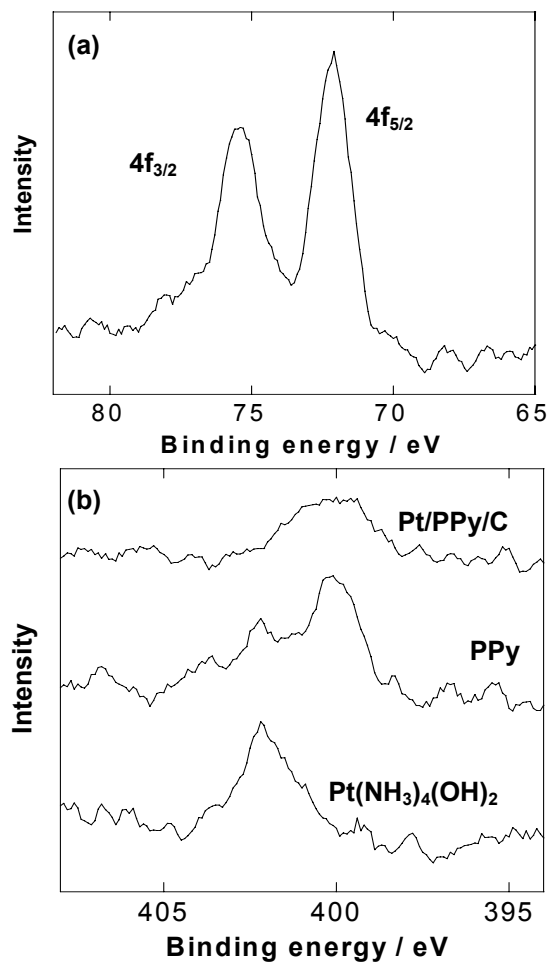


Fig.2. XPS spectra of (a) Pt and (b) N element of Pt/PPy/C comparing with PPy and [Pt(NH₃)₄(OH)₂].

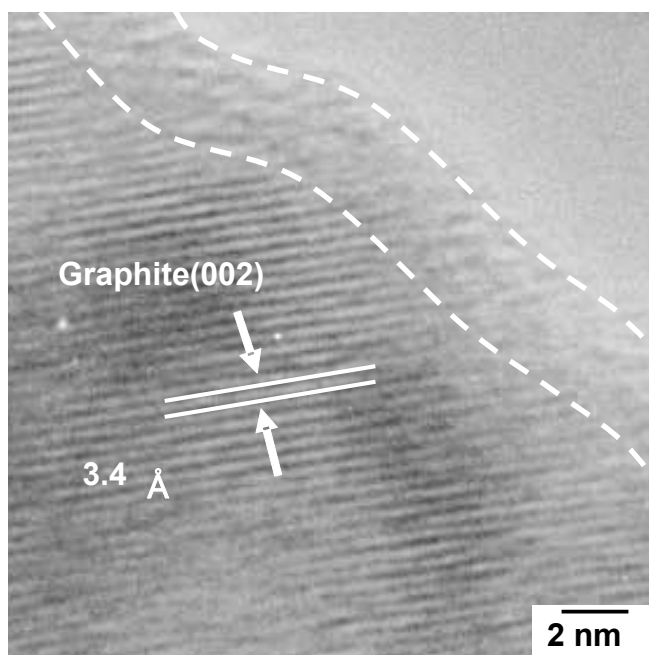


Fig. 3. HR-TEM image of Pt/PPy composite loaded carbon. The parts of surrounded by white lines which indicate a polypyrrole layer.

binding energy of Pt $4f_{5/2}$ appeared at 72.1 eV and at 75.5 eV, are about 2 eV higher than that of platinum metal, because of the size effect in accordance to previous study in which binding energies of nanosized particles got higher compared with bulk materials (19). On the other hand, the binding energy of N 1s of Pt/PPy/C appeared about 400 eV. In order to confirm that the peak was derived from whether polypyrrole or platinum precursor, $\text{Pt}[(\text{NH}_3)_4(\text{OH})_2]$, Fig. 2(b) shows the comparison of these peak. In this case, N1s peak of the Pt/PPy/C composite sample has bipolaron bands of polypyrrole polymerized on carbon. As described on Ref. 12, platinum particle was well dispersed on carbon. HR-TEM images of deposited PPy layer on carbon surface are shown in Fig. 3. It is shown that the polypyrrole layer was observed at the surface of the carbon of which thickness is ca 2-3 nm.

Pt/PANi/C composite TEM images of the sample of Pt/PANi/C composite is shown in Fig. 4. The deposited PANi layer prepared by the oxidative polymerization was observed on the carbon surface codeposited with the platinum particles. The distribution of the diameter of platinum particles was more broadened than the particles deposited in polypyrrole, however, it is less than ca. 10nm. The loaded platinum has a good crystallinity with Pt (111) plane.

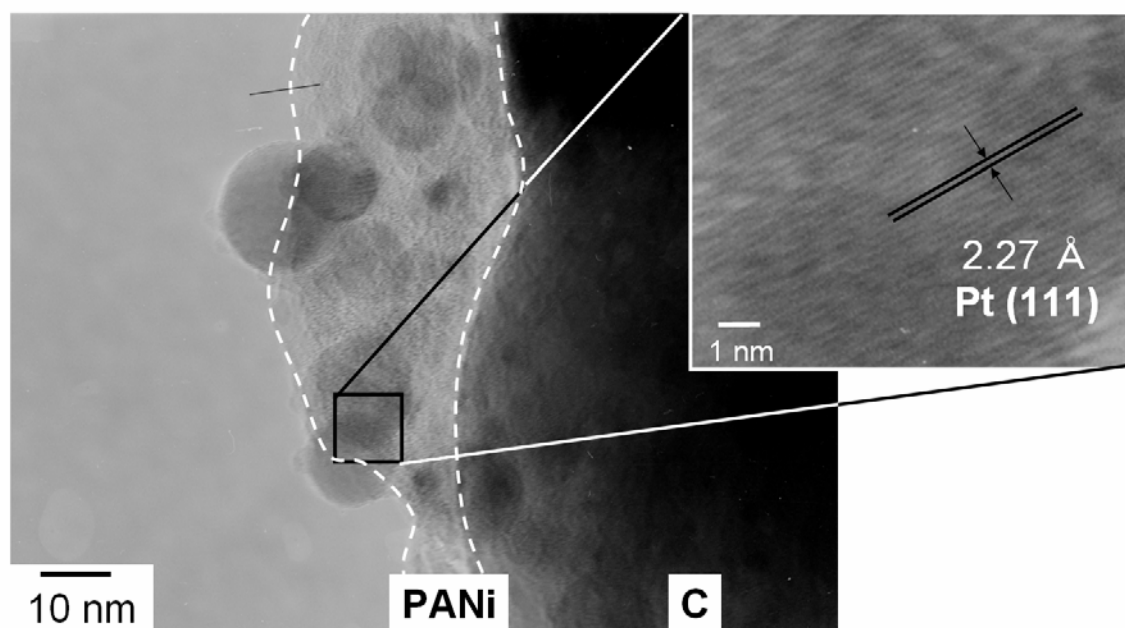


Fig. 4. HR-TEM images of the interface structure on Pt/PANi/C composite and fine structure of platinum particles on the carbon support.

In Figure 5a and 5b, N 1s XPS spectra of the Pt/PANi/C composite sample before and after oxidative polymerization. In Fig. 5a, the single N1s bands was observed which assigned to the NH_3 species contained in $[\text{Pt}(\text{II})(\text{NH}_3)_4]^{2+}$ complex. This peak was removed by the reducing of Pt complex and several peaks appeared as shown in Fig.5b. Obtained N1s spectra were deconvoluted by the Gaussian formulae. There are three bands assigned to nitrogen atoms in imine group at 398.2 eV, amine group at 399.6 eV, and cationic species ($-\text{NH}^+$) at 400.7 eV, respectively. It is indicated that the polyaniline

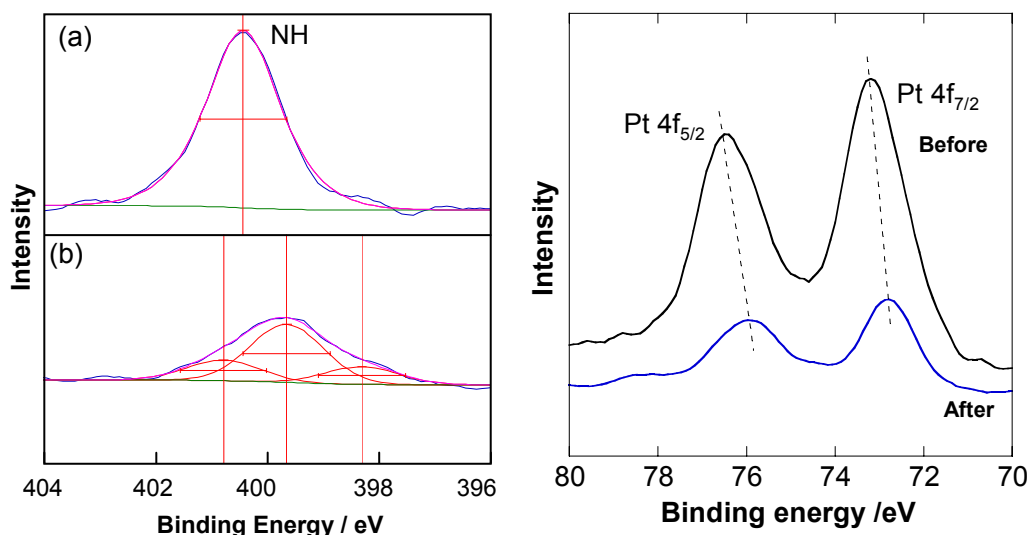


Fig. 5. XPS spectra of (a) N1s of loaded platinum species assigned to $[\text{Pt}(\text{NH}_3)_4]^{2+}$ adsorbed on carbon surface by ion-exchanging procedure, (b) N1s Pt/ polyaniline composite loaded on carbon support after oxidative polymerization and (c) their Pt 4f_{5/2} and Pt 4f_{7/2} bands.

was deposited on carbon surface of which thickness was around 10 nm with Au nanoparticles. In XPS spectra of Pt, the both bands of Pt 4f_{5/2} and Pt 4f_{7/2} shifted toward lower binding energy during the oxidation polymerization of polyaniline simultaneously.

CV measurement Cyclic voltammograms of (c) the platinum oxidation and reduction process on cathode reaction for Pt/PPy/C composite and PPy on carbon support in initial condition were shown in Fig. 6. Usually, oxide layer is formed from 0.8 V to 1.0 V vs. Ag/AgCl and oxide reduction occurred around 0.6 V vs. Ag/AgCl under oxygen atmosphere as is the case for bulk platinum working electrode (20, 21). In addition, hydrogen adsorption and desorption peak appear around 0 V to 0.2 V vs. Ag/AgCl. In this case, oxygen reduction reaction (ORR) occurred from 0.4 V to 0.2 V vs. Ag/AgCl and there was no peak attributed to hydrogen adsorption and desorption as shown in Fig. 6a. To reduce the probability that the ORR activity of sample attribute to polypyrrole not platinum, we discussed about PPy/C in the same condition. As a result shown in Fig. 6(b), PPy/C had no distinct peak from 0 V to 1.0 V vs. Ag/AgCl.

For fuel cell application, Pt/PPy/C needs to have constant property during cell operation.

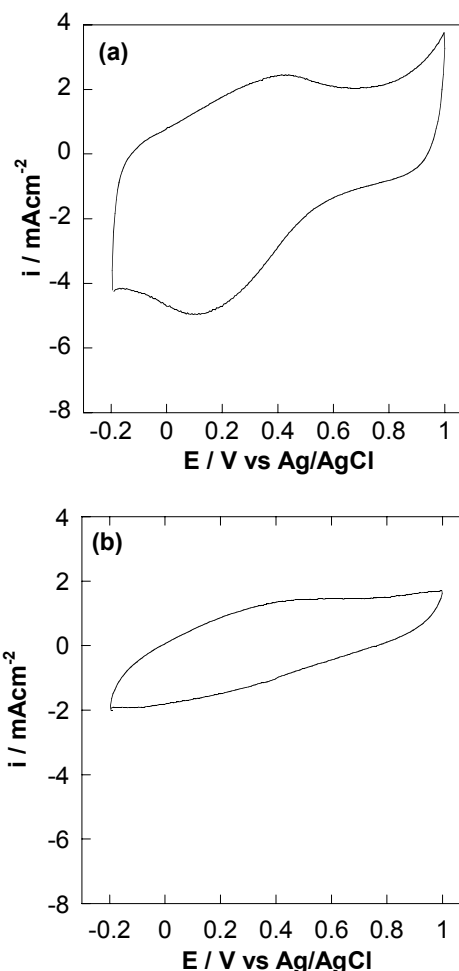


Fig. 6. Cyclic voltammograms of (a) Pt/PPy/C and (b) PPy/C, scanning rate 200 mV/s in 0.5 M H₂SO₄.

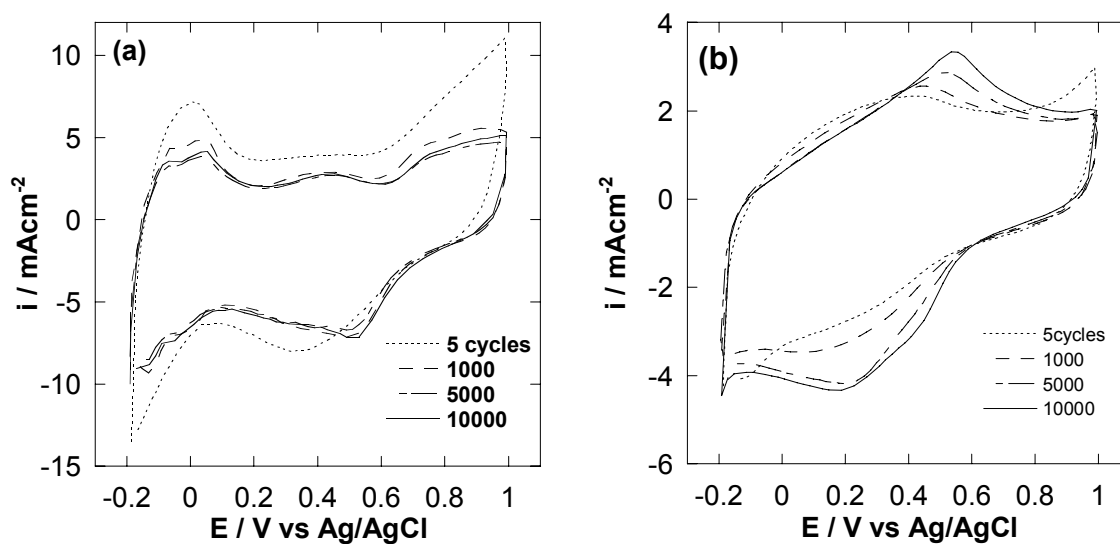


Fig. 7. Cyclic voltammograms of (a) Pt/PPy/C and (b)Pt/C composite during 10000 cycles scanning rate 200 mV/s in 0.5 M H₂SO₄.

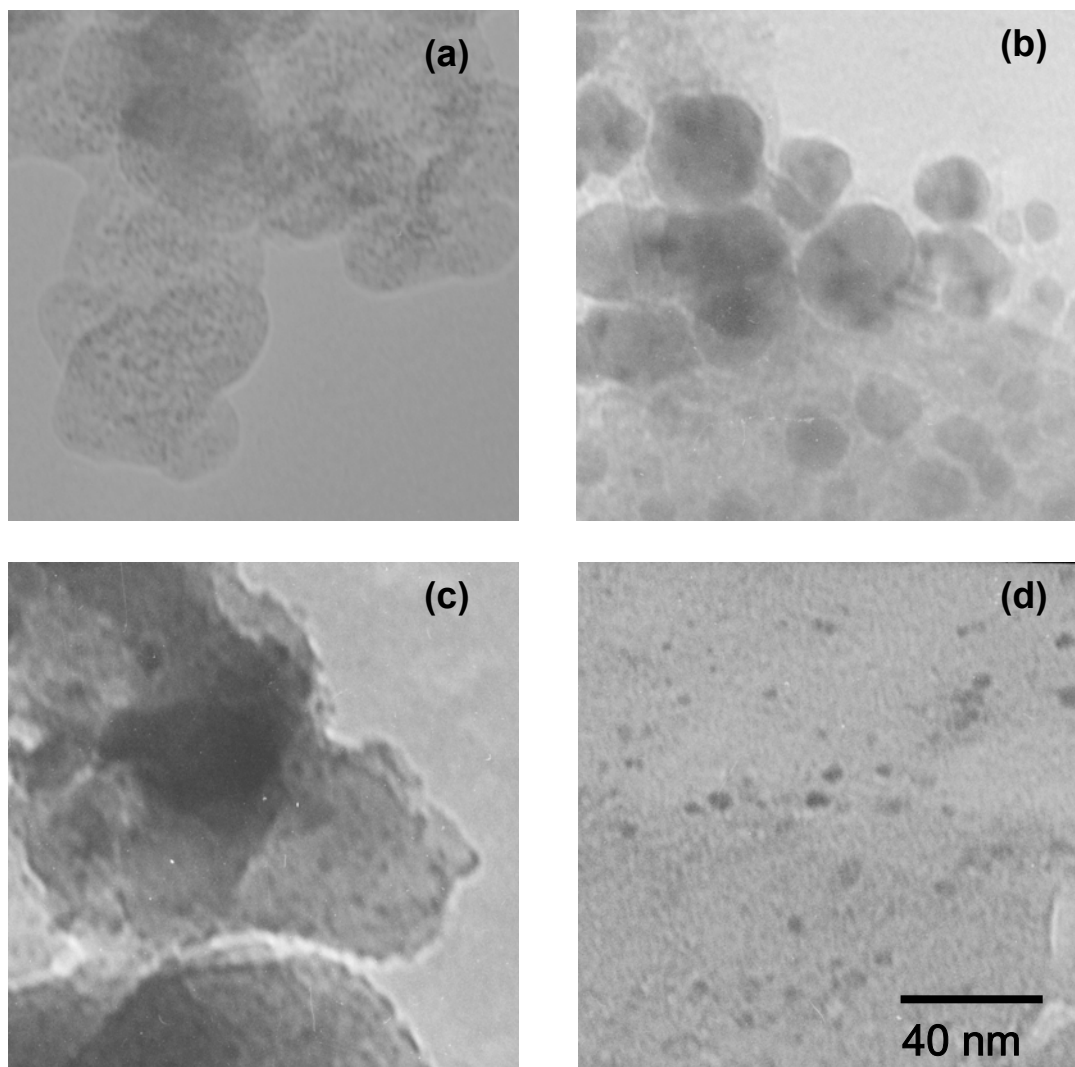


Fig.8 TEM images of (a) before, and (b) after 10000 cycles scanning of Pt/C. (c) and (d) are the images before and after 10000 cycles scanning of Pt/PPy/C respectively.

Therefore, sample was applied 1.0 V vs. Ag/AgCl for 50 h at which it is known as the open circuit potential of PEFC. And Yasuda et al. confirmed that platinum nanoparticles oxidized to Pt(II) or Pt(IV) ion were diffuse to electrolyte around 1.2 V vs NHE (22). The variation of cyclic voltammograms during durability test with scanning applied voltage showed in Fig. 7a. During the five times of the initial scanning, the platinum activity certainly changed and the oxidation peak of hydrogen obviously appeared and slightly changed after initial scanning. It is suggested that the state of platinum nanoparticles did not change so much and ORR activity was kept during cyclic operations. According to the results of CO stripping test, initial performances of platinum catalytic activities were not so different between the Pt/C ($106\text{ m}^2/\text{g-Pt}$) and Pt/PPy/C ($95.4\text{ m}^2/\text{g-Pt}$) composites.

For the cell performance, the operations of start-up and shutdown are also important in terms of degradation of electrode and they correspond to sweep voltage. Then, potential cycling was performed up to 10000 cycles for Pt/C and Pt/PPy/C as shown in Fig. 8. After 10000 cycles, the current density of the Pt/C composite got lower and the size of platinum particles changed drastically from about 2-3 nm to 30-40 nm. On the other hand, the output power and the mean particle size of Pt/PPy/C did not change so much during the sweep. In Fig. 8, the difference of the Pt particle sizes before and after scanning could be observed. It is suggested that the polypyrrole layer suppressed the dissolving of platinum particles loaded on carbon and Pt/PPy/C had higher durability than Pt/C. However, in the case of PPy/C shown as Fig. 9, it seems that polypyrrole on carbon came to have another structure or morphology during scanning up to 1000 cycles. As a result of multiple sweeping test, platinum and polypyrrole of Pt/PPy/C were considered to be stabilized with each other. The polypyrrole layer was regarded as the one to suppress the dissolution of the platinum to the electrolyte. However the amount of platinum in H_2SO_4 was much more than that of Pt/C. It is suggested that platinum ions loaded on carbon surface by ion-exchange process were not completely reduced through the polymerization of polypyrrole. And some of platinum ions were still in the ionic state on the carbon. In the future prospect, we are going to reduce platinum ion completely by some method after the preparation of Pt/PPy/C and improve the structure of Pt/PPy/C to more contribution of all platinum particles to ORR.

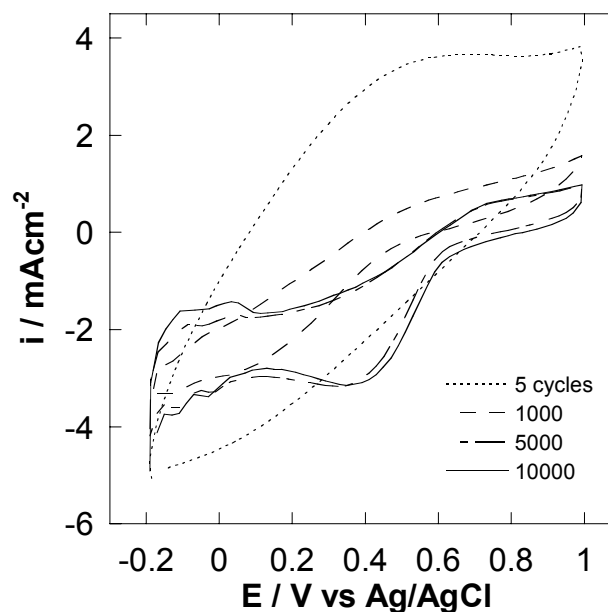


Fig. 9. Cyclic voltammogram of PPy/C. Sweeping cycles is up to 10000 cycles.

Conclusions

Pt/PPy/C was synthesized successfully by oxidizing carbon, followed by ion-exchange procedure and one-step polymerization of pyrrole and reduction of platinum ion. The electrocatalytic activity of sample was equal to conventional catalyst, Pt/C. And it is

suggested the high durability of Pt/PPy/C comparing with Pt/C and PPy/C by scanning test. However, platinum element dissolved out to H₂SO₄ electrolysis was detected and the amount could not be negligible. There is still room for improvement of the fabrication of Pt/PPy/C for practical application.

Acknowledgments

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