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Preparation of Pt/polypyrrole Loaded Carbon Composite in Order to Improve Electrode Durability for Fuel Cells

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Platinum nanoparticles/polypyrrole composite was loaded on carbon utilized for catalyst layer in order to improve the electrode durability. The carbon surface was oxidized by potassium permanganate and nitrate acid. Formed acidic functional group on the carbon surface was ion-exchanged by tetraammine platinum hydroxide complex. Loaded platinum complex contributed to the one-step polymerization of pyrrole, and the thin layer of polypyrrole was formed with the thickness of ca.3 nm. The nanolayer of polypyrrole interacted with carbon surface electrostatically and hindered diffusion of the platinum particle oxidized by cathode reaction on the cyclic voltammetry. The catalytic activity was held during durability examination up to 12500 cycles between -0.2-1.0 V vs Ag/AgCl.

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 electric devices as well as an onsite type with the cogeneration system. During a long term from 1950's, improvements of cell performance for output power, I-V character, and catalyst materials against CO poisoning, etc., have been quite important subjects of the R&D on fuel cells. These results contributed the practical use of the carious kinds of fuel cell systems. However, in the viewpoint of the electrode durability, some studies intended that the platinum catalyst diffuse into the ion-exchange membrane by oxidation during the oxygen reduction at the open circuit voltage. Yasuda et al. confirmed that platinum nanoparticles oxidized to platinum (II) or platinum (IV) ions diffuse to ionomer far from the catalytic layer of the gas diffusion electrode at the cathode reaction in high potential circumstance about 1.0-1.2 V vs NHE (1). The diffusing ions are reduced by the permeating hydrogen molecular in the ionomer phase. Such reduced platinum particles cannot contribute the electrode catalytic activity and cause the degradation of the catalyst. Similar degradation process was observed at a lot of studies of PEFCs or direct methanol fuel cells (DMFCs) (2, 3).

It is necessary to prevent the coagulation and diffusion of the platinum catalyst and its shortage of the durability. For the purpose of prevention of the platinum diffusion, Shintaku and Tamano et al. presented that the embedding platinum particles into carbon supports is available as the catalyst without agglomeration of platinum during cell operation using heat treatment of Pt-C composite (4-6). In this process, the heat treatment at ca.300-400ºC was necessary for embedding the Pt dispersion. In future prospects, such a anti-diffusive platinum nanoparticles are required to improve the durability performance of the fuel cell.

Previously we have prepared the Pt/PPy composite by one-step polymerization method (7, 8). We have attempted optimization of the reaction condition of Pt/PPy composite and measured the catalytic activity for oxygen reduction in order to make a high dimensional structure of the gas diffusion electrode. The oxidation of pyrrole(Py) into polypyrrole and the reduction of Pt(IV) to Pt(0) is proceeded using H_2PtCl_4 by the following reaction at room temperature. Applying this method, the Pt catalyst can be supported simultaneously during the polymerization of PPy. Prepared platinum particles were stabilized and dispersed uniformly by the polymerized polypyrrole having a diameter of ca.1.6 - 2.0 nm and the conduction of the polypyrrole was observed. It was concluded that the Pt/PPy composite is expected to the electrode materials.

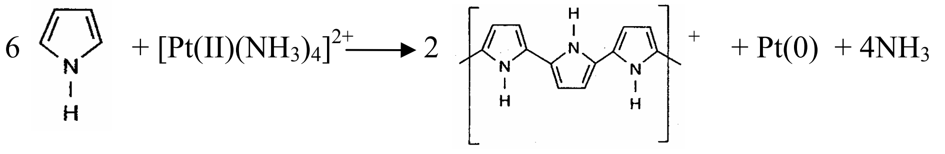
In this study, we developed platinum (Pt) particle/ polypyrrole(PPy) loaded carbon composite by one-step polymerization reaction pyrrole using platinum complex. Since platinum source is ion-exchanged platinum species on the carbon surface, a limited amount of polypyrrole was loaded on carbon with reduced platinum. A cyclic voltammetry was performed between 0-1.0 V vs NHE in order to confirm the oxygen reduction reaction (ORR) and the durability.

Experimental

Samples

Electrode Materials Electrode for the Pt/PPy/C composite were prepared from Vulcan XC-72R carbon powder with 250 m^2/g of the speficic surface area, platinum complex $[Pt(NH_3)_4](OH)_2$ and aqueous pyrrole solution. Carbon particles were dispersed and oxidized by 2.0 mol/l $KMnO_4$ and 63 wt% HNO_3 aqueous solutions for 4 hours as the same method in the previous study (9, 10). The dispersion solution was filtrated and the carbon was washed thoroughly with hot doubly distilled water until the ionic species of $KMnO_4$ and nitrate was removed. Surface oxidized active group on carbon was ion-exchanged by the aqueous 4 mol/l HCl solution for 20hrs. Finally, the obtained carbon was washed by water and filtered at 2 atm by the pressurized filter system equipped with ADVANTEC KST-47 filter holder. The amount of the acidic group on the carbon surface was quantitatively measured by pH titration method is described in Ref. 9.

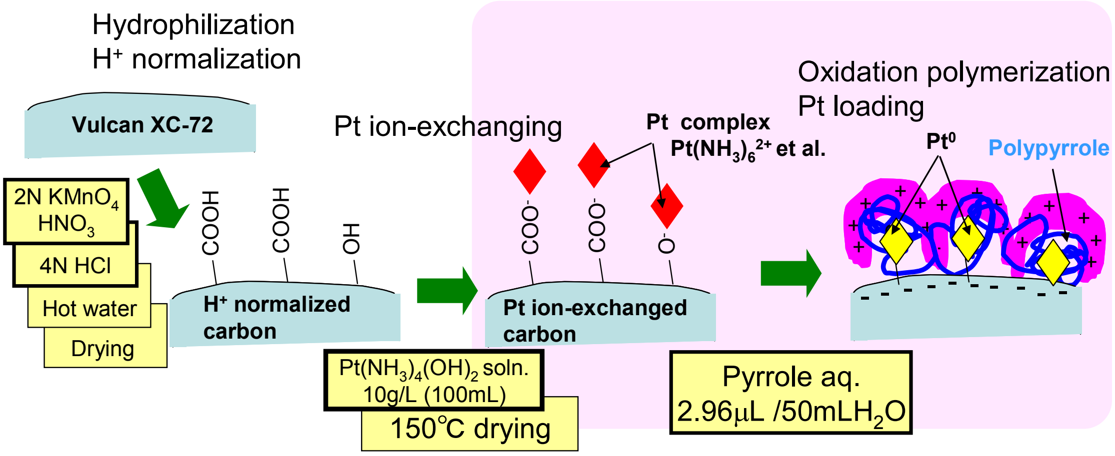
Loading Platinum and Polypyrrole The surface acidic group was ion-exchanged by neutralization with aqueous tetraammine platinum hydroxide; $[Pt(NH_3)_4](OH)_2$ solution (10). The loading amount of the platinum complex was measured by inductively-coupled plasma atomic emission spectrometer(ICP-AES) ULTIMA2000 (Horiba Jobin Yvon). After drying, the Pt ionized carbon was put into the pyrrole aqueous solution. Immediately, the oxidation of platinum and polymerization of pyrrole proceeded simultaneously as follows;



[1]

Obtained Pt/PPy/C composite was centrifuged and removed from the reaction solution. Composite powder was dried at vacuum dryer at ca. 110ºC. A series of these methods was illustrated in Scheme 1.

Scheme 1. Oxidation and Pt/PPy loading process on carbon materials for preparing the Pt/PPy/C composite.



Characterization of Pt/PPy/C composite

Obtained composite was observed by high resolution transmission electron microscope JEM2010 (JEOL). The distribution of the platinum particles was measured by Energy Dispersive X-ray (EDX) analysis module EX-64125JMU equipped field emission scanning electron microscope (FE-SEM) JSM-6335F (JEOL). The valency and bonding circumstance of platinum and carbon surface were measured by X-ray Photoelectron Spectroscopy (XPS) JPS-9010MC (JEOL). The existence of bipolaron in polypyrrole was confirmed with infrared spectroscopy FT-IR 615 R (JASCO Instruments).

Activity and Durability Examination

In order to evaluate of catalytic activity of the composite, a cyclic voltammogram was measured with Hokuto Denko HZ-3000 for the Pt/PPy composite samples. Nafion® solution (5 wt%, Aldrich) was added to Pt/PPy-carbon composite as a binder. The composite was supported by the glassy carbon electrode. The electrode is set into 0.5 mol/l H_2SO_4 aqueous solution with N_2 or O_2 bubbling. Mainly the oxygen reduction reaction (ORR) was measured at -0.2 to 1.0 V vs Ag/AgCl (0.199V) which is corresponded to from 0 to 1.2 V vs NHE (10). We carried out three kinds of examination for the evaluation of Pt/PPy/C composite electrode as the cathode. At first, the cathode potential was held at 1.0 V vs Ag/AgCl for 50 hours statically in order to confirm the stability of the polypyrrole, because the redox potential of PPy is lower than oxidation potential of platinum. Secondly, cyclic voltammetry was performed for the composite in order to repetition of the oxidation and reduction of the platinum species at initial condition of the loading process. A scan rate was 50 mV s^{-1} for potential cycling. After 500 times sweeping between -0.2 and 1.0 V vs Ag/AgCl, the cyclic voltammetry was performed and compared with the initial one. Finally, long term potential cycling was carried out for the durability examination. In this case, the scan rate was 200 mV/s between -0.2 to 1.0 V vs Ag/AgCl. Repetition period was up to 12500 times which take ca. 41 hours. For each measurement, the catalytic layer was renewed on the glassy carbon electrode.

Results and Discussion

Sample Preparation

After oxidizing the surface of carbon particles, the amount of oxidized functional group was ca. 0.8 meq. / g-carbon of the ion-exchange capacity for the sample oxidized by 2.0 mol/l $KMnO_4$ and 63 wt% HNO_3 aqueous solution. According to XPS measurement, the carbon surface was modified by mainly carboxylic group with high acidity as shown in Figure 1.

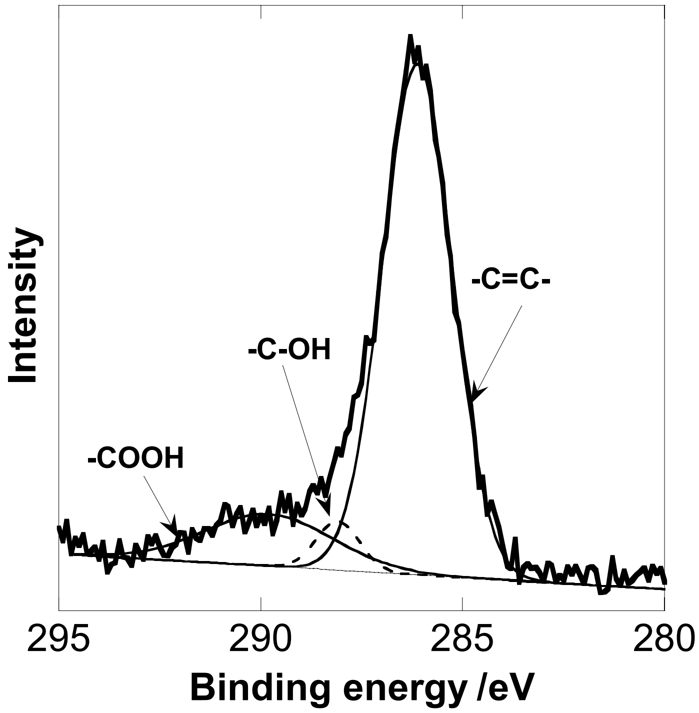


Figure 1. XPS profile and assignments of the bonding of carbon species for oxidized carbon.

The amount of ion-exchanged platinum complex is 1.14 meq.-Pt/g-carbon, which corresponds to 0.222 g-Pt/g-C, i.e., 18.2 wt% of loading amount. Since $[Pt(NH_3)_4](OH)_2$ has a Pt(II) ion, acidic group was ion-exchanged by mixed condition of monodentate, i.e., Carbon-COO-$[Pt(NH_3)_4]$-OH or (Carbon-COO-)$_2$-$[Pt(NH_3)_4]$. In any case, the platinum ions are adsorbed chemically on carbon surface.

After ion-exchanging procedure, pyrrole monomer was added stoichiometrically in accordance with Eq.[1], so that the unit of the platinum complex can oxidize and combine six pyrrole molecules for two monomeric units of polypyrrole. According to previous study (7, 8), monomeric pyrrole polymerized as soon as the platinum complex adsorbed carbon particle was added and color of the pyrrole solution was changed to black. In this case, the change of the solution color was hidden by the color of carbon particles, however the reaction proceeded without waste use of platinum. Since the polymer chain has positive charge and polypyrrole bonded with carbon functional group which has negative groups electrostatically, platinum particles was enclosed between carbon and polypyrrole chain. As a result of the reaction, platinum loading on the carbon surface combined by the polypyrrole began after 1 hour of the beginning of the polymerization as shown in Figure 2a. After 2 hours, by the TEM image observation as shown in Figure 2b, platinum particles are uniformly dispersed on carbon support with polypyrrole. The size distribution of loaded platinum particle ranged at 3-8 nm of which range is a little larger than the results of Pt/C composite around 2 nm by Yasuda et al. (10). It is suggested that the platinum species are concentrated into agglomerated parts under the interaction between polymerized polypyrrole and carbon surface. The thickness of polypyrrole layer is about 2-3 nm including platinum particles as shown in Figure 3.

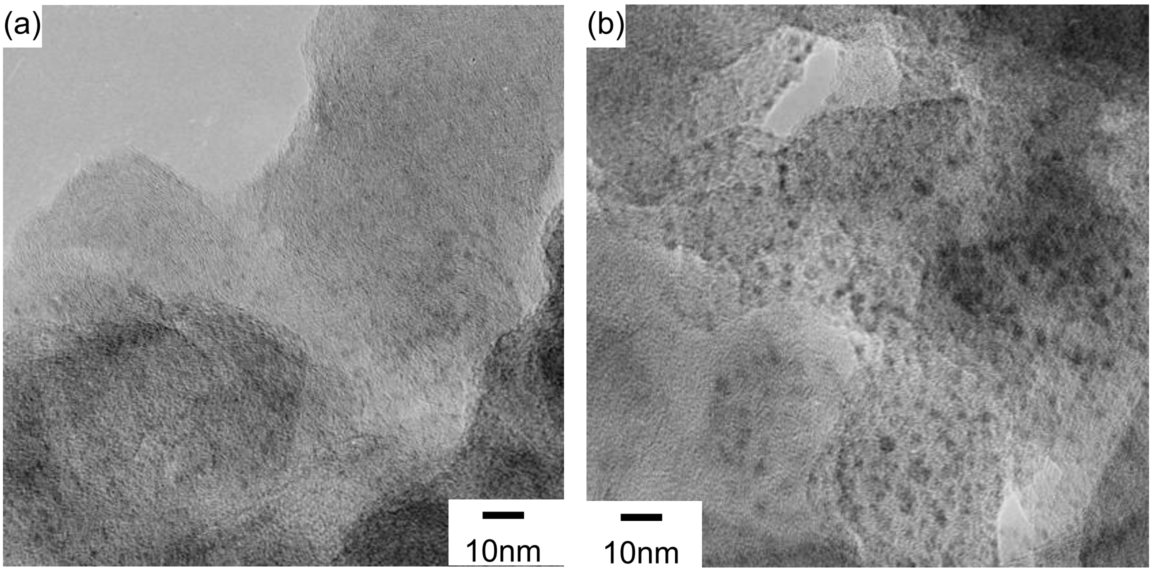


Figure 2. HR-TEM image of Pt/PPy composite loaded carbon. Polymerization reaction period: (a) 1hour and (b) 2 hours.

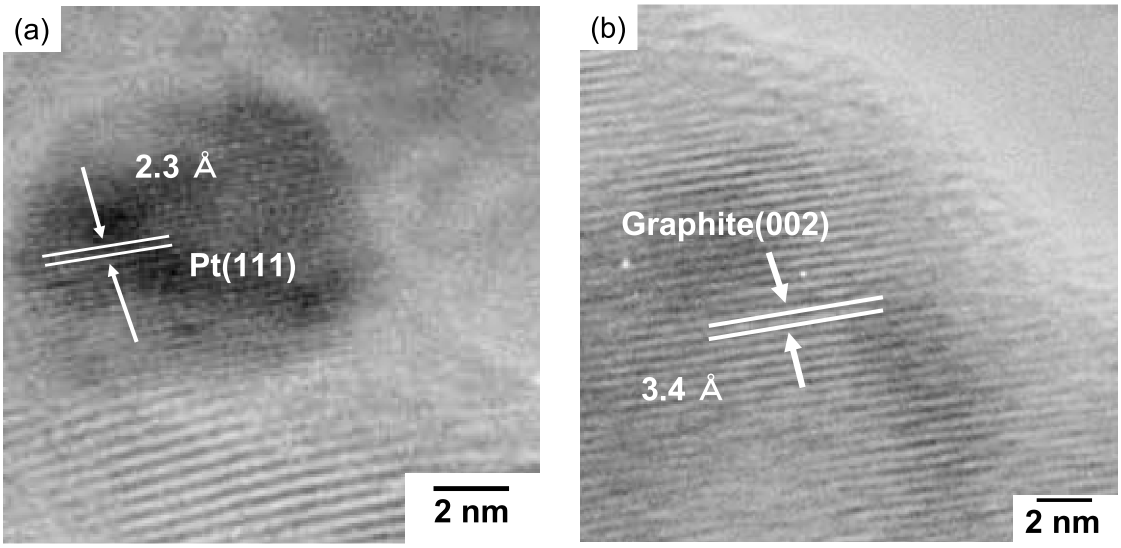


Figure 3. HR-TEM image of Pt/PPy composite loaded carbon. The parts of surrounded by white lines which indicate a polypyrrole layer.

Although such layer seems to be interfering layer for gas diffusion and mass transfer, however, the catalytic activity is held during operation. The performance of the catalyst is described later. In any case, the polypyrrole layer covered most part of carbon surface. As shown in Figure 4, the EDX profiles show that the element distribution of platinum and nitrogen are consistent with carbon distribution. Additionally, XPS profiles of obtained platinum species and nitrogen species is shown in Figure 5. For Pt profiles in Figure 5a, Pt peaks of $5f_{5/2}$ and $5f_{7/2}$ were observed at ca. 72 and 76 eV corresponding to the bulk platinum metal; Pt(0). In the other hand, N peaks for Pt/PPy/C sample is observed at the same energy as the pure polypyrrole power as a reference sample at ca.400 eV. Since platinum ammine complex has a higher energy at 405 eV, platinum species was completely reduced. The nitrogen peak can be assigned to the nitrogen in polypyrrole chain. It is suggested that the platinum reduction and polymerization of polypyrrole proceeded simultaneously in almost every part of the carbon surface only two hours at ambient temperature.

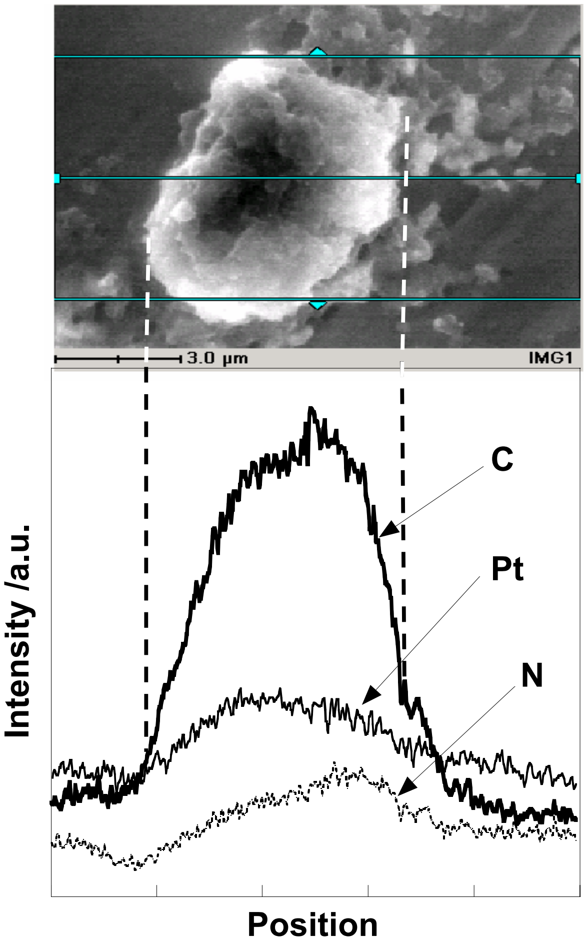


Figure 4. SEM image and its EDX profiles of related elements of Pt/PPy carbon composites.

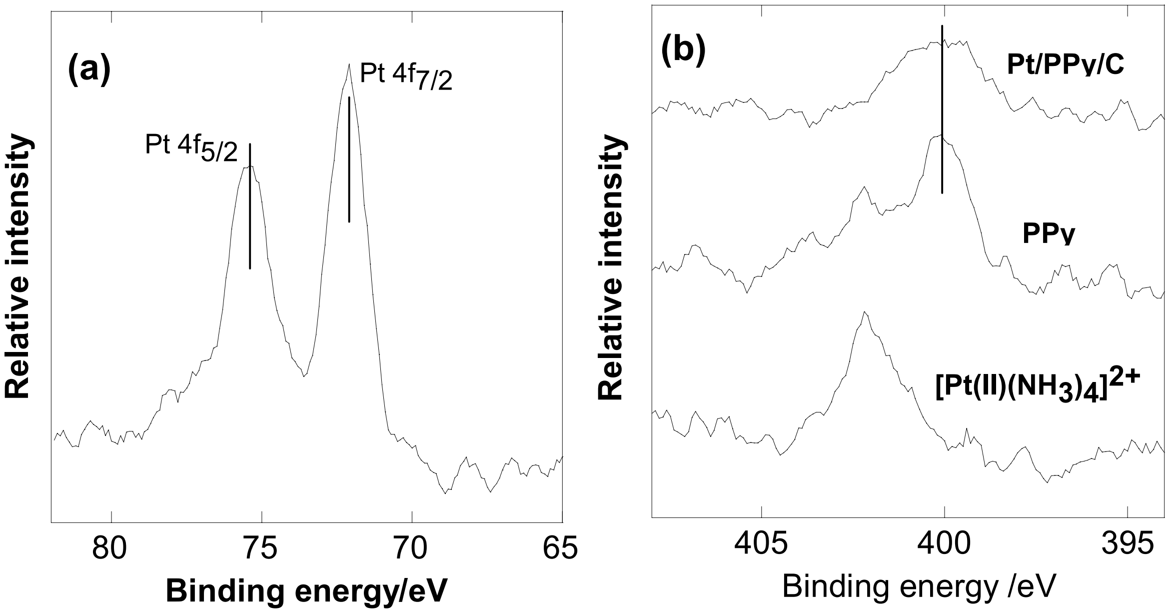


Figure. 5. XPS profiles of (a) Pt and (b) N elements for Pt/PPy/C composite. In (b), PPy: pure polypyrrole powder, $[Pt(II)(NH_3)_4]^{2+}$: tetraammine platinum hydroxide.

Cyclic Voltammetry for Pt/PPy/C Composite

We measured electrocatalytic activity of Pt particles before and after the oxygen reduction reaction. Figure 6 shows that cyclic voltammogram for Pt/PPy-carbon composite. For the system using the Pt/PPy carbon composite, the reduction peak assigned oxygen reduction reaction (ORR) was observed during O_2 bubbling at 1.0 V vs

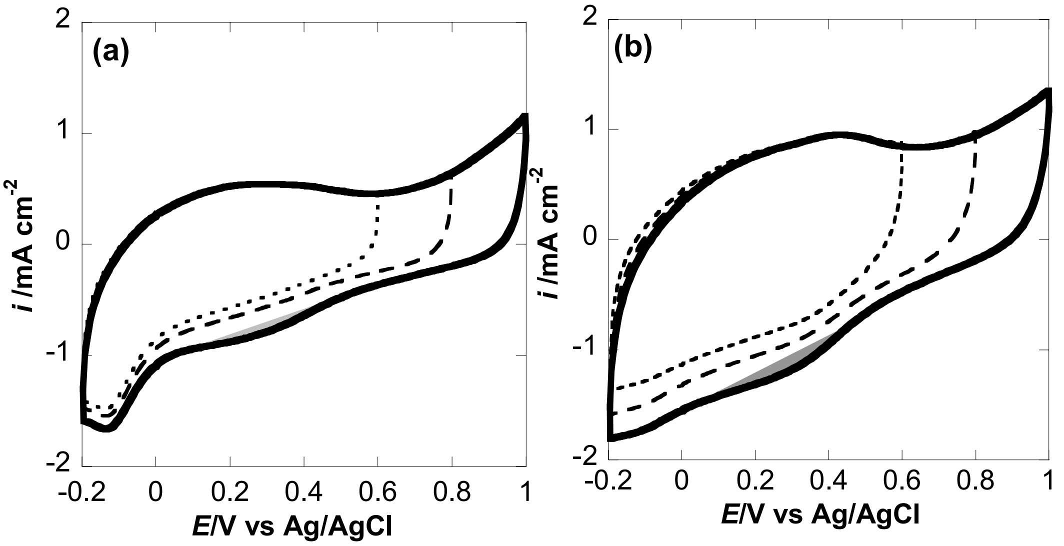


Figure 6. Cyclic voltammograms of Pt/PPy composite (a)before and (b) after oxygen reducing reaction in O_2 gas flow at 1.0 V vs Ag/AgCl. for 50 hrs. Pt loading amount: 0.4 mg/cm^2. Temperature: 30°C.

Ag/AgCl which corresponded to the open circuit voltage of PEFCs for 50 hours. It is suggested that the platinum catalytic activity was kept during high potential reaction circumstance. Generally, the platinum degradation was promoted the repetition of the oxidation and reduction of the platinum species (12). The ORR peak was most obvious signal of the platinum degradation for cathodic reaction of the oxygen. In Figure 6, the ORR peak was observed at 0.1 V vs Ag/AgCl which corresponding to the reduction of $PtO_x{\cdot}yH_2O$ (13). Increasing sweeping range of cycling up to 1.0 V vs A/AgCl, the oxidation peak appeared clearly and corresponded ORR peak stood out at 0.2-0.3 V vs Ag/AgCl. Thus the platinum oxidation and reduction peaks are observed in this potential cycling. In the case of the 500 times cycling operations, we compared the cyclic voltammogram using Pt/C and Pt/PPy/C composites as shown in Figure 7. Using Pt/C composite without polypyrrole, the ORR peaks are gradually reduced and after 500 times potential cycling, degradation of the catalytic activity proceeded to less than half of original current intensity. On the other hands, using Pt/PPy/C composite, the ORR peak was observed continuously during potential cycling examination as shown in Figure 8a. It is suggested that polypyrrole layer can protect the degradation of platinum catalyst against the diffusion of the oxidized platinum species into ionomer. Here, there was anxiety about the elimination of platinum reaction sites by covering of polypyrrole on platinum surface in Pt/PPy/C composite. However, ORR peaks are equal to the original intensity using Pt/C composite and little decreasing of the peak intensity was observed and thus the hindrance of ORR by polypyrrole was not found. Here, it is confirmed that polypyrrole layer which loaded by oxidation polymerization with platinum complex cations embedded on carbon surface is available for the prevention of the degradation.

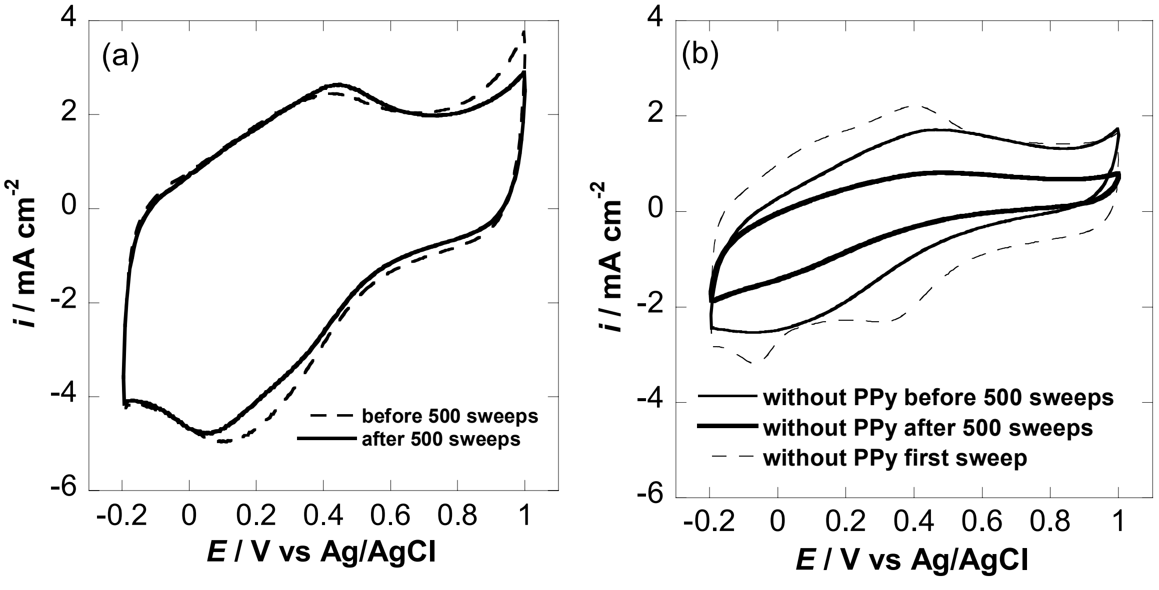


Figure 7. Cyclic voltammograms of (a) Pt/PPy/C composite and (b) Pt loaded carbon electrode before and after oxygen reducing reaction in O_2 gas flow under potential cycling at -0.2 to 1.0 V vs Ag/AgCl. for 500 times. Pt loading amount: 0.4 mg/cm^2. Temperature: 30°C.

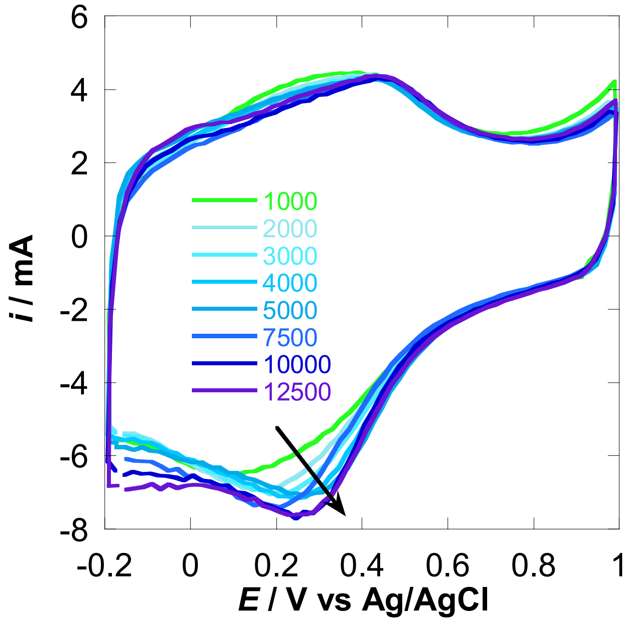


Figure 8. Cyclic voltammograms of Pt/PPy/C composite during oxygen reducing reaction in O_2 gas flow under potential cycling at -0.2 to 1.0 V vs Ag/AgCl. for 12500 times. Pt loading amount: 0.4 mg/cm^2. Temperature: 30°C.

The potential cycling was performed up to 12500 times as shown in Figure 8 in order to confirm the durability of Pt/PPy/C composite for the electrode catalyst. The ORR peak was still observed during the potential cycling test from the beginning to 12500 times and the intensity does not change considerably. It is expected that the embedding procedure of platinum particle is the novel techniques for extending the activity and durability for the fuel cell catalysts. In this study, the evaluation of the electrode catalytic activity on the oxygen reduction reaction was measured only. It should be confirm the platinum diffusion by the electron microscope. An optimization of the loading amount will be also carried out in the future progress.

Acknowledgments

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