

Preparation of Carbon Supported Pt and Pt alloy Catalysts by Alcohol Reduction for Polymer Electrolyte Fuel Cells

Taeyoon Kim and Koichi Kobayashi

Advanced Research Center for Energy and Environment, Musashi Institute of Technology, 1-28-1, Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

Fax: 81-03-5707-2163, e-mail: kkobaya@eng.musashi-tech.ac.jp

A new method for preparation of carbon supported Pt and PtRu alloy catalysts by alcohol reduction using polyvinylpyrrolidone as stabilizer was investigated. The prepared catalysts were characterized by UV-visible spectroscopy, X-ray diffraction, electron microscopy, and X-ray photoelectron spectroscopy. This method has advantages over its simplicity and the straight reduction of chloride salt without any modification. Also highly uniform nanoparticles were obtained and the structure and morphology of catalysts could be easily controlled. The aggregation of particle was suppressed by polyvinylpyrrolidone in both processes of colloidal formation and thermal treatment of carbon supported catalysts. Comparison of the catalyst prepared by this method with commercial catalysts shows that it has a promising activity in oxygen reduction and methanol oxidation.

Key words: carbon supported Pt, alcohol reduction, stabilizer, polymer electrolyte fuel cell

1. Introduction

Carbon supported platinum (Pt/C) and platinum-ruthenium alloy (PtRu/C) are the most popular electrocatalysts for the cathodic reduction of oxygen and/or the anodic oxidation of hydrogen in proton exchange membrane fuel cell (PEMFCs) and anodic oxidation of methanol in direct methanol fuel cell (DMFC), respectively. However, the high cost of noble metal such as platinum prevented these fuel cells from commercialization. Therefore, much effort has been focused on the development of carbon supported platinum and alloy catalysts which show high platinum efficiency and electrocatalytic activity [1-4]. The common preparation method of fuel cell catalysts is sulfite-complex method [5] that is based on the oxidation and subsequent reduction of metal sulfite salts. Although sulfite-complex method has an advantage over the use of chloride salts directly, this is very complex and requires much time. In recent days, new preparation methods of Pt/C and/or PtRu/C catalysts using colloid technique were researched. Bonnemant et al. [6] and Delcourt et al. [7] reported the preparation method of PtRu/C electrocatalyst.

Much attention has been paid to the alcohol reduction method by using stabilizer as simple preparation method of metal nanoparticle [8-10]. This method can control not only the size but also the morphology of metal nanoparticle. Terahashi et al. [9] reported the method to control the size of polymer-protected Pt nanoparticles by alcohol reduction. They could control the Pt particle size by changing the alcohol concentration in water and the amount of polymer stabilizer. Toshima et al. [8] investigated the formation mechanism of the metal nanoparticle by alcohol reduction and their catalytic activity as homogeneous catalyst. Also Hsing et al. [10] firstly applied this method to the preparation of heterogeneous catalysts by using dodecyltrimethyl(3-sulfo-propyl) ammonium hydroxide as stabilizer.

In present work, the preparation method of Pt/C and PtRu/C by alcohol reduction by using polyvinylpyrrolidone as stabilizer was investigated. This method

has advantages over its simplicity and the straight reduction of chloride salt without any modification. Also highly uniform nanoparticle can be obtained and the structure and morphology of catalysts can be easily controlled. For the preparation of Pt/C and PtRu/C that show high platinum efficiency and electrocatalytic activity, the effects of stabilizer concentration, Pt loading amount and heat treatment condition on the size and morphology of metal nanoparticle on carbon support were studied by physicochemical characterization. Also the electrocatalytic activity of prepared catalysts was compared with commercial catalysts for cathodic oxygen reduction reaction and anodic methanol oxidation by single fuel cell test.

2. Experimental

A hydrogen hexachloroplatinate(IV) hexahydrate and ruthenium(III) chloride dissolved 1-propanol aqueous solution (1-propanol:H₂O=4:1 volumetric ratio, 20ml) was added to the 1-propanol aqueous solution (30ml) of poly(N-vinyl-2-pyrrolidone) (PVP, average molecular weight of 10000). After mixed sufficiently at room temperature, the mixed solution was refluxed with vigorous stirring for 1-3 hours under air to make metal nanoparticle. The amount of PVP was adjusted from PVP/metal (molar ratio) = 1 to 10 in order to control the size distribution of metal nanoparticles. The appropriate amount of carbon powder (Ketjenblack, specific surface area of 1000m²g⁻¹) was added into the metal colloid solution. After the mixture was mixed completely in sonic-bath for 30min, the resulting suspension was dried at 60°C for 24hours. The dried mixture was ground up using a pestle and a mortar and then the resulting powder was calcined at 300-400°C for 2-4 hours in a tube furnace under 10vol% hydrogen in nitrogen mixture to remove the polymer stabilizer. The platinum contents of Pt/C were from 20 to 70wt%, and the platinum and ruthenium contents of PtRu/C were 18wt% and 9wt% (1:1 atomic ratio), respectively. The reduction of precursor metal ion into Pt nanoparticles in alcohol solution was checked by UV-Visible spectrophotometer.

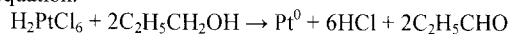
The size and its distribution of metal nanoparticles were measured by transmission electron microscopy. The crystal structure of catalysts was measured by X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda=0.1542\text{nm}$). From the broadening of (220) diffraction peak in XRD spectra, the average crystal size was calculated by Debye-Scherrer equation. In order to examine the thermal decomposition of PVP, thermogravimetric analysis was performed under nitrogen atmosphere. The surface composition of catalysts was checked by X-ray photoelectron spectroscopy.

In order to the electrocatalytic properties of synthesized carbon supported platinum catalysts, the polarization test and impedance measurement of single fuel cell were performed. The catalyst ink mixtures were prepared by addition of 5wt% Nafion solution and highly pure water into the dried catalyst powder. To prepare the membrane /electrode assembly(MEA), anode and cathode inks were uniformly printed onto a piece of carbon paper (Toray TGP-90) treated by PTFE solution to give a 0.46mgcm^{-2} Pt loading on the anode and 0.18mgcm^{-2} Pt on the cathode for H_2/O_2 PEMFC test and 0.14mgcm^{-2} Pt, 0.07mgcm^{-2} Ru loading on the anode and 0.46mgcm^{-2} Pt on the cathode for DMFC test. After drying at 60°C for 30 min, the catalyst layers were attached to a Nafion membrane by hot pressing at 130°C and 2MPa for 2min. The performance of single fuel cell was examined in a Globe Tech test station. The active area of single cell was 4cm^2 . For PEMFC test, oxygen and pre-humidified hydrogen were supplied to the cathode and the anode with 200sccm, respectively. The hydrogen gas was pre-humidified at 15°C higher than the temperature of single cell. For DMFC, 1.5M methanol and oxygen were supplied to the anode and the cathode with 0.8ml/min and 100sccm, respectively. In addition, the ac impedance measurements were performed by scanning frequency from 15kHz to 10mHz under galvanostatic or potentiostatic control of the cell using an impedance analyzer(ZAHENR, Model IM6e).

3.Results and Discussion

Formation of Pt nanoparticle

The reduction of metal ion to form metallic particle was measured by the UV-vis absorption spectra of PVP-stabilized metal colloids with reaction time(Fig.1). Before the reduction of the Pt precursor, the absorbance peak at 267.5nm corresponding to the ligand-metal charge transfer transition of the $[\text{PtCl}_6]^{2-}$ was measured. As the reaction time was increased, this peak decreased, indicating that the reduction of $[\text{PtCl}_6]^{2-}$ is more progressed to form Pt metal according to following equation.



After 15min, the peak at 267.5nm was disappeared and the broad tailing absorption peak was appeared. These results are agreed well with other studies. Teranishi et al.[9] and Duff et al.[11] suggested that as Pt nanoparticle is formed, the broad tailing peak is increased due to the band structure of the Pt particles.

As the reduction of the Ru precursor was progressed, the absorbance peak at 248.5nm corresponding to the ligand-metal charge transfer transition of the Ru ion was decreased and the absorption peak at about 323nm was

increased. This peak is a surface plasma absorption of Ru metal. Ru precursor was reduced to form Ru particle by the alcohol reduction as following equation.

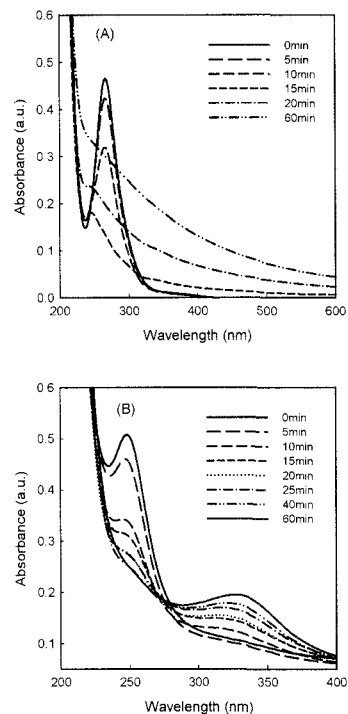
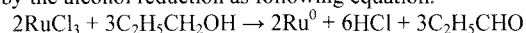


Fig.1. UV-vis spectra of (A) Pt(PVP/Pt=1) and (B) Ru (PVP/Ru=1) colloid solution in alcohol reduction .

It is well known that polyvinylpyrrolide as protective agent stabilizes nanoparticles by suppression their aggregation. In order to investigate the effects of PVP on the growth of Pt nanoparticle, the alcohol reduction was performed with different amounts of PVP. The amount of PVP was changed from PVP/Pt(molar ratio in respect with repeat unit M.W. of PVP)=1 - 20. As the amount of PVP was increased, the size of Pt nanoparticle decreased. Also the size of Pt particle was very mono-dispersed as the standard deviation of the particle size was lay in 0.25 - 0.34 nm in all samples. In the absent of PVP, $[\text{PtCl}_6]^{2-}$ was rapidly reduced to Pt and Pt nanoparticles were very unstable and sedimented. Terahasi et al.[9] and Toshima et al.[8,12] suggested that PVP prevents metal nanoparticles from aggregation by the coordination of carbonyl groups to the surface metal atoms of metal nanoparticles protected by PVP. The interaction of PVP and Pt(or Pt ion) was confirmed by our XPS measurements, which is agreed well with their reports. Therefore, we could conclude that the amount of PVP is very important factor to control the size of Pt nanoparticle in alcohol reduction method.

Preparation and characterization of carbon supported platinum and alloy catalysts

Carbon supported catalysts were prepared by adsorbing surfactant-stabilized preformed metal colloids on carbon support for high-area fuel cell catalysts with well defined and small particle with narrow particle size

distribution. The stabilizer, PVP could be removed by thermal treatment 10vol% hydrogen in nitrogen mixture. In order to examine the thermal decomposition of PVP, thermo-gravimetric analysis was performed under N_2 for carbon-supported catalysts and PVP-free Pt/C and PtRu/C were checked by XPS. Most PVP(above 98%) of all samples were removed after thermal treatment above 300°C.

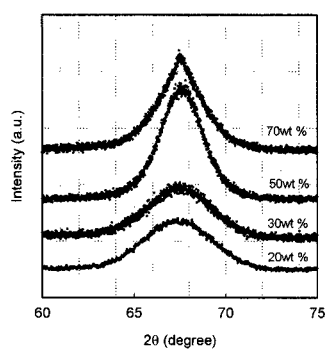


Fig.2. XRD patterns of Pt/C with various Pt loadings treated at 300°C for 4hours.

Figure 2 shows XRD patterns of carbon supported platinum catalysts with various Pt loadings treated at 300°C. All peaks can be indexed as the platinum face-centered cubic(fcc) phase based on the data of the JCPDS, indicating the formation of Pt nanoparticles by alcohol reduction. From the broadening of (220) diffraction peak, the average particle size of Pt was calculated by Debye-Scherrer equation. One of most important factors in designing fuel cell catalyst is platinum loading on carbon support because the electrocatalyst layer should be reasonably thin. This minimizes the cell potential losses due to the rate of proton diffusion and reactant gas permeability in the depth of the catalyst layer and maximizes platinum utilization during operation. In general, particle size increases with increasing metal loading. Although particle size increased with platinum loading and thermal treatment temperature as expected, coalescence of particles during thermal treatment was suppressed efficiently by PVP. Below 30wt%, the coalescence of particles was prevented completely at 300°C and even at 70wt% Pt/C, the Pt crystallite size was still less than 4nm. This is significantly better than Pt crystalline size of 5.5-6nm for an unsupported Pt black in Ballard Power Systems and 4.5nm for carbon supported Pt catalyst in Johnson Matthey.

The X-ray diffraction peaks of the PtRu/C catalysts(Pt 18wt% and Ru 9wt%, 1:1 atomic ratio) were slightly shifted to higher 2θ values with respect to the same reflections in Pt/C which indicate that the incorporation of Ru into the fcc structure of Pt. On the other hand, the diffraction peaks of catalyst treated thermally at 300°C were the same to those of Pt/C. Peaks associated to typical faces of the hexagonal closed packed(hcp) structure of pure metallic Ru did not appear in clear form, but the presence of metallic Ru could not be discarded because the peak intensity of Ru is very low as well as overlapped with the peak of Pt. In fact, the diffraction peaks of Ru were checked in Ru colloid and

Ru/C prepared by this method. The average particle size of PtRu/C from the broadening of (220) diffraction peak was 2-3.2nm, which shows negligible increase compared with Pt/C.

The change in surface composition of the PtRu bimetallic particles after the different thermal treatment was measured by XPS. As shown in table 1, the surface atomic ratio of Ru to Pt was changed from 1 to 0.3 with increasing temperature. This is demonstrated that the Ru decorated Pt bimetallic nanoparticle could be obtained at lower temperature region and the decorated Ru on the surface of Pt was incorporated into the Pt bulk with increasing temperature to make the PtRu alloy(solid solution formation) nanoparticle. The formation of PtRu alloy was confirmed by the decrease of lattice constant. The face-centered cubic(fcc) lattice parameter, a_{fcc} , was calculated by precise measurements of the (220) diffraction peak. The a_{fcc} values of PtRu/C are shown in Fig.3 as a function of the treated temperature and Ru content. As the treated temperature and Ru content increase, the a_{fcc} values of PtRu/C are decreased which indicates that the incorporation of Ru into the fcc structure of Pt.

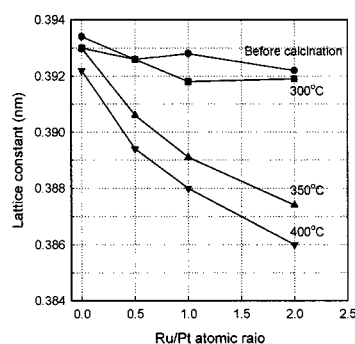


Fig.3. Variation in the a_{fcc} values of PtRu/C(Ru/Pt=0-2) with different calcination temperatures.

These results demonstrate that the Ru content and calcination temperature have a significant influence not only on the dispersion state, but also on the amount of Ru incorporation into the fcc structure of PtRu/C.

Table 1. The particle size and surface composition of Pt/C and PtRu/C catalysts with various thermal conditions.

Samples	Temp. (°C)	Particle size (nm)	Lattice constant(Å)
Pt-PVP colloid		2.0	3.93
20wt%Pt/C	300	2.1	3.93
30wt%Pt/C	300	2.3	3.93
50wt%Pt/C	300	3.5	3.93
70wt%Pt/C	300	3.8	3.93
20wt%Pt/C	350	2.9	3.93
20wt%Pt/C	400	3.0	3.92
^a 27wt%PtRu/C	300	2.2	3.92
^b 27wt%PtRu/C	350	2.9	3.89
^c 27wt%PtRu/C	400	3.2	3.88
27wt%PtRu/C	500	4.7	3.86

The molar ratio of Pt and Ru of PtRu/C is 1

The surface compositions of PtRu/C are 0.98^a, 0.56^b, and 0.32^c (Ru:Pt atomic ratio).

Electrochemical characterization of carbon supported platinum and alloy catalysts

Highly dispersed carbon supported platinum could be prepared by alcohol reduction method even for high loadings (up to 70wt%). In order to characterize the prepared Pt/C electrocatalyst, the electrocatalytic activity for O₂ reduction as a cathode was evaluated and compared with commercial catalyst by single fuel cell test. Figure 4 shows the polarization curves for the prepared Pt/C and commercial catalyst in PEFC operation. The electrocatalytic activities of the prepared 30wt% Pt/C and commercial 30wt% Pt/C were almost the same due to similar particle sizes of both catalysts. From this result, the prepared Pt/C by alcohol reduction exhibits comparable catalytic activity with respect to the commercial catalyst. For the prepared catalyst including polymer stabilizer without thermal treatment, the cell performance was very poor. It seems to be reason why the formation of three phase boundary (reactant/platinum/Nafion) and mass transfer of reactant are suppressed by polymer stabilizer. Therefore, the removal of stabilizer is necessary for highly active catalyst. To examine the catalytic activity of the prepared catalyst, ac impedance measurements were carried out at 700mV. Similar values of electrode/electrolyte interface resistance for oxygen reduction reaction obtained in both MEAs with the prepared catalyst and commercial catalyst proved the polarization result.

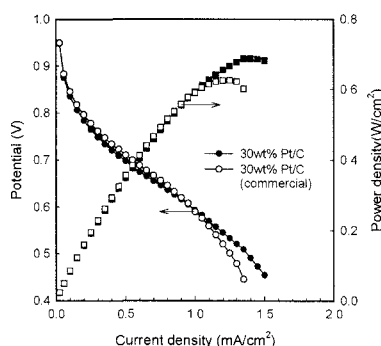


Fig.4. Cell polarization curves of MEA with prepared Pt/C and commercial Pt/C catalyst.

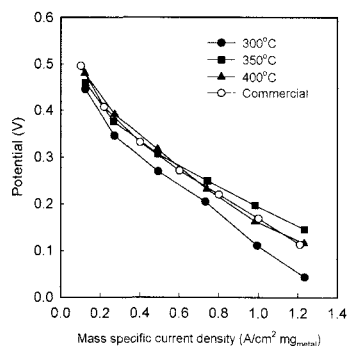


Fig.5. Cell polarization curve of MEA with prepared PtRu(1:1)/C at various calcination temperatures in methanol oxidation (commercial catalyst, PtRu/C: 18wt% Pt 14wt%Ru).

The alloying state and surface composition of PtRu/C could be controlled by calcination temperature. In order to characterize the prepared PtRu/C catalysts with calcination temperature, the electrocatalytic activity for methanol oxidation as an anode was evaluated, and compared with commercial catalyst (PtRu/C: 18wt% Pt 14wt%Ru) by single fuel cell test. As shown in Fig.5, the cell performance of MEA with PtRu/C catalyst calcined at 350°C ($a_{fcc}=0.389\text{nm}$, Ru:Pt=0.558) exhibited higher than that of PtRu/C catalyst calcined at 300°C ($a_{fcc}=0.392\text{nm}$, Ru:Pt=0.975), and was similar to that of PtRu/C catalyst calcined at 400°C ($a_{fcc}=0.388\text{nm}$, Ru:Pt=0.316). These observations suggest that the formation of Pt alloy (solid-solution) is the most important factor for highly active catalyst in methanol oxidation. Also the difference of catalytic activity of PtRu/C with similar particle size may be a result of different surface composition. A quantitative explanation for these results is difficult at present. Recent reports [13] suggest that the incorporation of Ru into the Pt catalyst is effective for improvement of tolerance and catalytic activity by the electronic modification (so-called ligand mechanism). Also Ru as an ad-atom on the catalyst surface promotes the formation of active oxygen which facilitates the transfer of oxygen to CO for CO oxidation to CO₂ (so-called bifunctional mechanism) [14]. Further studies concerning the effects of surface and bulk composition are in progress.

The electrocatalytic activity of the prepared PtRu/C catalysts calcined at 350°C was slightly higher than that of commercial catalyst. The results of impedance measurement at 300mV were agreed well with the polarization results. Since the structure and composition of PtRu/C can be controlled by this method, this study may give one a clue about optimization of high activity catalysts of some specific fuel cell application.

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