Synthesis of Pt–Co Alloy by Ultra–low Catalyst Loading Technology for PEFC

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Abstract

Platinum–cobalt (Pt–Co) alloy catalyst has been synthesized by the ultra–low catalyst loading technology based on ion–exchange reaction between metal cations of catalyst precursor and proton of ionomer existing on carbon surface followed by reduction reaction of their ion–exchanged cation using hydrogen gas. The alloying degree of the catalyst at 7 atom% of alloyed Co content is 0.6 despite the low reduction temperature of 200 ℃. Its catalytic activity is 1.5 times higher than that of pure Pt catalyst synthesized by same catalyst loading technology.

Key words : Ultra–low catalyst loading technology ; Pt–Co alloy catalyst ; Alloying degree

1　Introduction

Polymer electrolyte fuel cell (PEFC) is expected as a clean power source for electric vehicles or residential co-generation system because of its high energy efficiency. The most important technical objective for commercialization of PEFC is the cost reduction by decreasing Pt amount of catalyst. For the purpose, we have developed the ultra–low catalyst loading technology.[1-4] Pt catalyst in this technology is loaded mainly on the active site which is located on the interface between the carbon surface and the ionomer cluster. The loading technology is based on ion–exchange reaction of Pt complex cation and the proton of ionomer existing on the carbon surface followed by chemical reduction of its cation under hydrogen gas atmosphere. The utilization of Pt in catalyst is so high that the Pt amount of catalyst is able to decrease to one third of commercially available Pt/C catalyst.[4] However, the decrease rate is not yet enough for the final objective. Recently there have

been reports on the high activity of Pt alloyed metals with various transition metals for oxygen reduction reaction (ORR).[5, 6] In this study, we attempted to synthesize Pt–Co alloy catalyst using this loading technology for the further improvement of catalytic activity.

2　Experimental

2.1　Preparation

Carbon–supported Pt catalyst was prepared by following procedures : (1) preparation of ionomer–coated carbon powders by spray–drying of mixed slurry with ionomer solution and carbon powders ; (2) ion–exchange of proton in the ionomer for $[Pt(NH_3)_4]^{2+}$ ion by immersing the powders into $[Pt(NH_3)_4]Cl_2$ solution at 80 ℃ for 6 h ; and (3) reduction of the ion–exchanged ion under hydrogen atmosphere at 150 ℃ for 8 h.

Carbon–supported Pt–Co alloy catalyst was synthesized using above–mentioned Pt catalyst by following two procedures : ion–exchange of proton in the ionomer for Co^{2+} ion by immersing Pt catalyst

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into $CoCl_2$ solution at 80 ℃ for 6 h and reduction of Co^{2+} ion under hydrogen atmosphere at 200 ℃ for 8, 24, and 48 h. The synthesized alloy catalyst was then rinsed by 0.5 M H_2SO_4 to remove residual Co^{2+} ion.

2.2　Characterization

The alloying degree, that is, the content ratio of alloyed Co (Co_{al}) to total Co (Co_{tot}) is given by

$$\frac{Co_{al}}{Co_{tot}} = \frac{X_{Co}\,(100-Co_{tot})}{(1-X_{Co})\,Co_{tot}} \qquad (1)$$

where Co_{tot} is Co atomic content in the Pt–Co alloy catalyst obtained from inductively coupled plasma (ICP) analysis. Furthermore, Co atomic fraction (X_{Co}) is evaluated by Vegard's law :

$$X_{Co} = \left[\frac{a_{UL}-a_0}{a_S-a_0}\right]X_S \qquad (2)$$

where a_{UL} is lattice parameter of synthesized alloy catalyst obtained from Pt peak of X–ray diffraction pattern, a_0 and a_s are lattice parameters of bulk Pt (0.3925 nm) and Pt_3Co (0.3831 nm) respectively, and Xs is Co atomic fraction (0.25) in Pt_3Co catalyst.[7] Co_{tot} contains not only alloyed Co but also non–alloyed Co. Morphologies and compositions of the alloy catalyst were evaluated by the transmission electron microscope (TEM) equipped with energy dispersive spectroscopy (EDS) analysis.

2.3　Electrochemical property

The electrochemical active surface area and the ORR activity of alloy catalyst were measured by the rotating disk electrode (RDE). The measurements were performed in 0.1 M $HClO_4$ solution at room temperature by using Ag/AgCl reference electrode. The potential was corrected to that of RHE. The electrode catalyst ink for carbon–supported Pt–Co alloy catalyst was prepared by ultrasonically mixing it with ethanol aqueous solution. The ink was then placed on the glassy carbon surface of the RDE. After drying, a drip of ionomer solution was applied onto the surface of catalyst to ensure better adhesion of the catalyst on the glassy carbon surface. Prior to the ORR measurement, the working electrode surface was cleaned and electrochemically stabilized

by potential cycling between 0.05 and 1.0 V vs RHE at 0.1 V s^{-1} in 0.1 M $HClO_4$ solution saturated with N_2 gas. The electrochemical active surface area of Pt in catalyst was calculated from the hydrogen desorption charge obtained by cyclic voltammetory. Hydrodynamic voltammetory with rotation rate ω of 1000–2750 rpm for ORR were measured under the potential sweep rate of 10 mV s^{-1} between 1.0 and 0.4 V vs RHE in 0.1 M $HClO_4$ solution saturated with O_2. Kinetically controlled current (I_k) was obtained with Koutecky–Levich Plots (i.e., Plots of the inverse of observed current I^{-1} vs. $\omega^{-1/2}$) by extrapolating the regression lines on the plots to the y intercept. Kinetically controlled current density (J_k) was calculated by dividing I_k with the active surface area.

3　Results and discussion

XRD patterns of carbon-supported Pt–Co alloy catalyst and pure Pt catalyst are shown in Fig. 1. The diffraction peaks for Pt (111), (220), and (311) of Pt–Co alloy catalyst are found out to shift to higher angles compared with that of pure Pt catalyst. This result indicates that Pt and Co are alloyed under low reduction temperature of 200 ℃. This phenomenon is recognized to derive from location of nanosized Pt and Co particles in limited site of ionomer cluster.

The effects of reduction time of Co^{2+} ion on Co con-
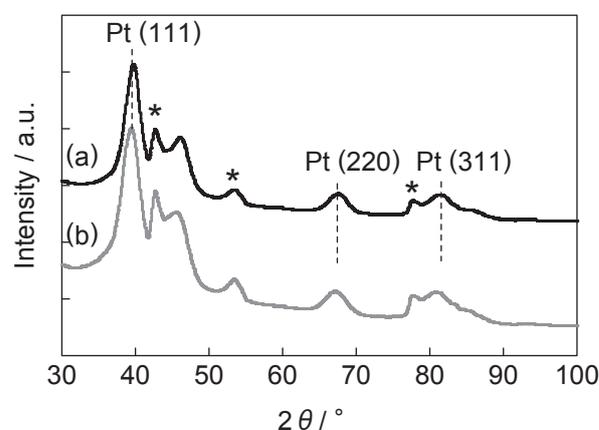
Fig. 1　XRD patterns of carbon-supported Pt–Co alloy catalyst reduced at 200 ℃ for 24 h prepared by one time Co loading (a) and pure Pt catalyst (b).
＊Refers to reflection from carbon.

tents and alloying degree in Pt-Co alloy catalyst are shown in Fig. 2. The contents of total Co and alloyed Co increase with reduction time and reach constant values of 3.2 and 2.5 atom% at 24 h, respectively. The alloying degree defined as ratio of alloyed Co content to total one slightly decreases with the time.

The effects of number of Co loadings on Co contents and alloying degree were investigated. Changes in Co contents and alloying degree as a function of number of Co loadings are shown in Fig. 3. The total
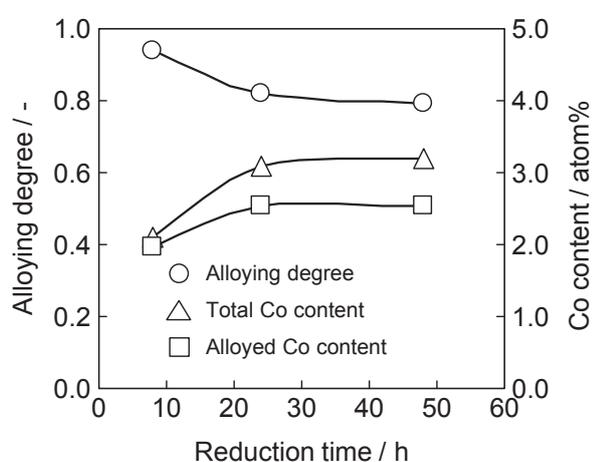
and alloyed Co contents increase with the number and reach saturated values of 10.8 and 6.7 atom% beyond four, respectively. The increase of total Co content seems to be caused by newly supplying Co^{2+} ion at the location near Pt particle. This phenomenon is recognized that Pt particle contributes to reduction reaction of Co^{2+} ion. The alloying degree further decreases down to the value of 0.6. This means the increase of non-alloyed Co content. To investigate the cause of this increase, the morphology observation and composition distribution measurement of Pt-Co alloy catalyst were conducted by TEM-EDS. Fig. 4 (a) and (b) show the TEM images for carbon-supported Pt-Co alloy catalyst prepared by one and six times Co loadings, respectively. It is found out that particles are uniformly dispersed with average size of 4 nm for one time Co loading. On the other hand, the aggregations of large size of more than 10 nm are observed besides small particles after six times Co loadings. Results of EDS analysis for particles and aggregations are shown in Table 1. It is found that the Co contents of the particles observed by EDS almost correspond with the Co contents by Vegard's law. In contrast, Co content of the aggregation is remarkably high compared with that of the particles. These results seem to indicate that most of non-alloyed Co locate in the aggregation particles even after H_2SO_4 rinsing process.

The ORR activity of Pt-Co alloy catalyst was evaluated by rotating disk electrode. Effect of alloyed

Fig. 2　Changes in Co contents and alloying degree of Pt-Co alloy catalyst as a function of Co^{2+} ion reduction time. Reduction temperature: 200 ℃. Number of Co loadings: 1.

Fig. 3　Changes in Co contents and alloying degree of Pt-Co alloy catalyst as a function of number of Co loadings. Reduction condition for Co^{2+} ion: 200 ℃ for 24 h.
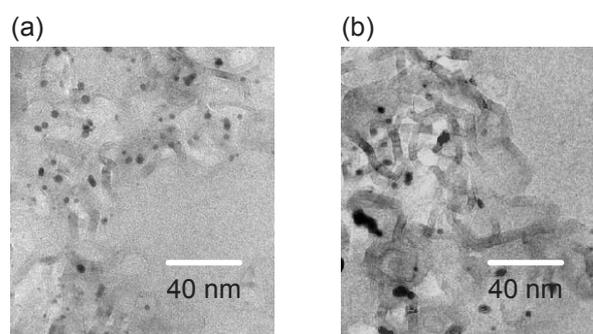
Fig. 4　TEM images of carbon-supported Pt-Co alloy catalyst reduced at 200 ℃ for 24 h under hydrogen atmosphere prepared by one (a) and six (b) times Co loadings.

Table 1　Co contents of Pt-Co alloy catalyst in average-sized and aggregation particles prepared by different number of Co loadings by EDS analysis.

Number of Co loadings	Co content / atom%	
	Average particles	Aggregation particles
1	2.1	–
6	6.5	11.6

Co content on J_k ratio of Pt-Co alloy catalyst to pure Pt catalyst as a criterion for ORR activity at 0.6 V is shown in Fig. 5. The J_k ratio turns out to increase with the alloyed Co content above 3 atom% and reach the value of 1.5 at 7 atom%.

4　Conclusions

Carbon-supported platinum-cobalt (Pt-Co) alloy catalyst has been synthesized by the ultra-low catalyst loading technology based on ion-exchange reaction followed by hydrogen reduction process to improve the catalytic activity. Characterization by TEM-EDS and electrochemical properties by RDE measurements were investigated to elucidate the effect of alloy formation on catalytic activity. The obtained results are summarized as follows.

(1) Pt-Co alloy catalyst is obtained under low reduction temperature of 200 ℃.

(2) The alloying degree of Pt-Co alloy catalyst is able to reach the value of 0.6.

(3) The activity of the Pt-Co alloy catalyst is 1.5 times higher than that of pure Pt catalyst at the 7 atom% of alloyed Co content.
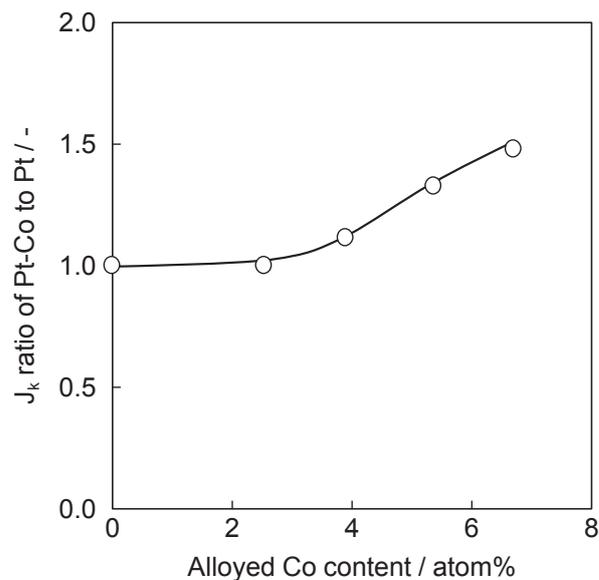
Fig. 5　Effect of alloyed Co content on J_k ratio of Pt-Co to Pt in 0.1 M $HClO_4$ saturated with O_2 at 25 ℃.

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