



Platinum oxidation responsible for degradation of platinum–cobalt alloy cathode catalysts for polymer electrolyte fuel cells

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H I G H L I G H T S

- ▶ Large particles and hot annealing improves Pt–Co alloy catalyst durability.
- ▶ The Pt 4f XPS spectra suggests that high Pt(OH)₂ contents increase Pt dissolution.
- ▶ Applying the potential step of 1.2 V, Pt oxides, PtO and PtO₂, were produced.
- ▶ Pt–Co alloy catalyst durability can be improved by preventing Pt oxidization.

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Platinum oxidation of Pt–Co alloy catalysts for polymer electrolyte fuel cells was investigated for a series of Pt–Co alloy catalysts with different specification. The chemical state of platinum evaluated by soft X-ray photoemission spectroscopy was compared with the electrochemical properties to elucidate the origin of catalyst degradation. Increase in the particle size of Pt–Co alloy catalysts caused the decrease in the concentration of platinum hydroxide and improved the catalyst durability. Applying potential cycling below 1.0 V, only platinum hydroxide was observed, while platinum oxides, PtO and PtO₂, appeared after potential cycling up to 1.2 V. The peak shift of Pt 4f spectra after the potential cycling implies that these platinum hydroxide and oxide are dissolved and deposited on another platinum catalyst in a reduced metallic state, which causes the catalyst degradation.

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1. Introduction

Polymer electrolyte fuel cell (PEFC) is developed as a clean and high efficiency energy source for stationary, auto mobile, mobile applications. Platinum nano-particles loaded on carbon support are used as conventional PEFC cathode catalysts for oxygen reduction reaction. For commercialization of the PEFC system, it is necessary to decrease the amount of platinum loading because platinum is an expensive and rare material [1]. Platinum alloyed with a first row transition metal is one of the most promising candidate materials due to its higher catalytic activity than the pure platinum catalyst

[2–4]. In particular, Pt–Ni and Pt–Co alloys have been reported to show the highest activity among the Pt alloy catalysts [2,3]. High durability of Pt alloy catalysts is another important requisite for commercialization of the PEFC system. In conventional platinum nano-particle catalysts, the growth of the particle size decreases the active area and cell performance [5]. Dissolved platinum ions from nano-particles may deposit on other platinum particles, leading to the increase in the particle size, named Ostwald's ripening [6,7]. Mitsushima et al. [8] have suggested that the platinum dissolution is accelerated by potential cycling, and that platinum oxidation and reduction should be responsible for the platinum dissolution. There have been some reports on the durability of Pt alloy catalysts [9,10]. The Pt–Co alloy catalyst shows higher durability than the platinum nano-particle catalyst both in accelerating testing and under PEFC operation. Matsutani et al. [11] have studied the particle size effect on the stability of cell

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Table 1
Loading conditions, annealing temperature, and particle size before and after potential cycling between 0.6 V and 1.0 V of Pt–Co alloy catalysts.

| Sample name | Pt loading (wt%) | Co loading (wt%) | Annealing temperature | Initial particle size (nm) | Particle size after potential cycling (nm) |
|-------------|------------------|------------------|--------------------------|----------------------------|--|
| A: 47L | 46.9 | 5.2 | 900 °C [11] | 6.1 | 5.9 |
| B: 28L | 28.3 | 2.4 | 900 °C [11] | 4.1 | 5.2 |
| C: 47H | 47.0 | 4.3 | Higher than 1000 °C [11] | 7.5 | 7.0 |
| D: 28H | 28.1 | 3.9 | Higher than 1000 °C [11] | 5.8 | 5.4 |

performance for platinum and Pt–Co alloy catalysts and have found that irrespective of catalyst type, large particle catalysts are stable. We compared Pt 4f states of Pt–Co alloy catalysts with Pt nano-particle catalysts [12] and concluded that platinum oxidation induces large degradation of Pt nano-particle catalysts. However, the mechanism for the high durability of the Pt–Co alloy catalyst is not clear yet.

In this study, we have investigated the origin of degradation of the Pt–Co alloy catalysts. To investigate the Pt–Co alloy catalyst degradation precisely, we have investigated platinum oxidation of Pt–Co alloy catalyst by monitoring Pt 4f core levels of Pt–Co alloy catalysts with different particle size in membrane electrode assembly (MEA) before and after potential cycling at different upper potential during potential cycling.

2. Experimental

We have investigated four types of Pt–Co alloy catalyst powders with different catalyst loading and annealing temperature made by Tanaka Kikinokogyo as listed in Table 1. The Pt–Co alloy particles were loaded on high surface area carbon, annealed and then rinsed by nitric acid [11]. We denote here the catalysts by platinum loading percentage and annealing temperature. For example, the catalyst A 47L means 47% of platinum loading and low annealing temperature. The catalyst powder was mixed with a perfluoro-sulfonate ionomer solution, Aciplex SS (made by Asahi Kasei) to produce a catalyst ink. The ink was then spread and dried on a support film to make a decal sheet. A pair of the decal sheets was hot-pressed on an electrolyte membrane to make an MEA. A pair of non-woven carbon sheets covered with a micro porous layer was attached on both sides of the MEA as gas diffusion layers (GDL). Potential cycling was applied to MEA on the following conditions. Cell temperature was maintained at 80 °C by external heaters. Fully humidified hydrogen was introduced to the anode and fully humidified nitrogen to the cathode. Square-shaped potential waves were applied to the cell by 10,000 cycles. The potential was kept at lower potential for 3 s and upper potential for another 3 s in one cycle. The lower potential was 0.6 V and the upper potential was 1.0 V. The potential condition was selected to minimize the carbon corrosion which might be significant over 1.0 V [13,14]. In order to evaluate the upper potential effect, we also conducted the potential cycle between 0.6 V and 1.2 V. Electrochemical surface area (ECA) of the samples was evaluated as indicator of catalyst degradation. ECA was calculated by integrating hydrogen adsorption charge in cyclic voltammogram (CV) measurements and dividing it by 0.21 mC cm^{-2} [15]. The CV measurements were conducted at cell temperature of 30 °C, where fully humidified hydrogen and nitrogen were introduced to the anode and the cathode, respectively. The potential was applied from 0.05 V to 1.0 V with a sweep rate of 10 mV s^{-1} , regulated using an electrochemical measurement system (HZ5000, Hokuto Denko). To evaluate the catalyst particle size and the structural change of the catalyst layer, transmission electron microscopy (TEM) images were obtained using transmission electron microscope (H-7100FA, Hitachi) operated at an acceleration voltage of 100 kV. Soft X-ray photoemission spectroscopy (SXPES) measurements were conducted on initial MEA

and cycle-tested MEA at BL27SU of SPring-8. For MEA samples, GDLs were removed and X-rays were irradiated on the GDL side of the cathode catalyst layer. Incident photon energy was set at 1 keV with the energy resolution of 200 meV. The measurements were conducted in an ultra-high vacuum below $4 \times 10^{-8} \text{ Pa}$ at room temperature. Binding energies were calibrated by the peak energy of the Au 4f line. The probing depth of the SXPES photoelectrons was approximately 3.4 nm at the Pt 4f line.

3. Results and discussion

3.1. Change of chemical states of platinum of Pt–Co alloy catalysts

Four types of Pt–Co alloy catalysts from A to D listed in Table 1 were evaluated in terms of their durability against potential cycling between 0.6 V and 1.0 V for 10,000 cycles. The mean particle sizes of initial catalysts are 6.1, 4.1, 7.5 and 5.8 nm, respectively as listed in Table 1. The ECAs during the potential cycling are compared in Fig. 1. The ECA of the catalysts A 47L, B 28L and D 28H decreased, suggesting that the catalysts were degraded by the potential cycling. Platinum dissolution might cause the ECA decay in those catalysts analogous to Pt nano-particle catalysts. TEM images of all MEA samples at the interface between the membrane (upper side of the pictures) and the cathode are shown in Fig. 2. The large grain of Pt can be observed at the interface between the catalyst layer and the membrane of the cycle-tested MEAs. Part of the dissolved platinum from the catalysts deposited to make the large grain. This platinum deposition is apart from the carbon support and isn't included in the ECA. Therefore after the potential cycling the ECA of catalysts A 47L, B 28L and D 28H decreased with decreasing the amount of the active Pt. The particle sizes distributions, measured from the TEM images, are shown in Fig. S1 of the supporting material. The mean values of the particle size after the potential cycling are compared in Table 1. Pt dissolution may also decrease the particle size of the

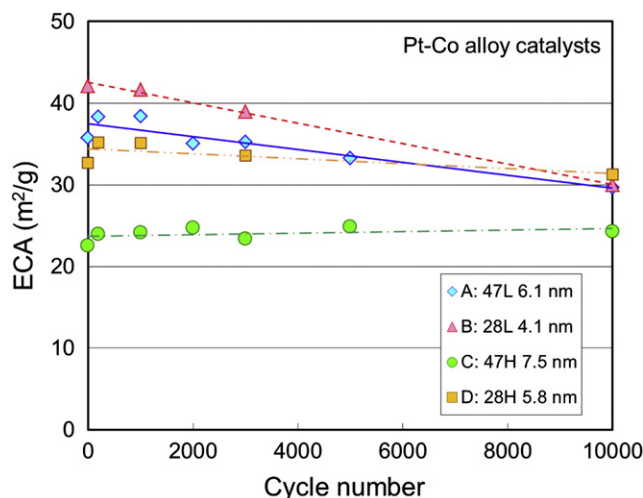


Fig. 1. The comparison of ECA decay on Pt–Co catalysts during potential cycling.

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