

## Properties of Pt-Co-Si/C alloy catalysts prepared by chemical vapor deposition as fuelcell cathodes in PEMFCs

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### Introduction

Catalysts for proton exchange membrane fuel cells (PEMFCs) are generally evaluated by their activity as a reduction electrode (cathode) because oxygen reduction reaction (ORR) on the electrode has a significant effect on the overall fuel-cell performance [1-2]. There have been many studies on Pt-alloy catalysts, which show improved activity and stability in the ORR compared with Pt-only catalysts.

Another concern in the development of Pt alloy catalysts for fuel cells is the dissolution of added promoter components in the acidic matrix of the cells, which eventually lowers the activity of the alloy catalysts [3-5]. In this study, it has been attempted to enhance the performance and stability of the catalysts as a cathode in PEMFCs by preparing them using a chemical vapor deposition (CVD) method, which allows the selective deposition of Co and Si on the Pt surface.

### Experimental

Co was deposited on the surface of a 10wt% Pt/C catalyst (Johnson Matthey Co., 120m<sup>2</sup>/g Pt) using a CVD (CoCp(CO)<sub>2</sub>) or impregnation (CoCl<sub>2</sub>·6H<sub>2</sub>O) method. After Co deposition, the catalyst was treated in a flowing hydrogen-nitrogen stream (H<sub>2</sub>/N<sub>2</sub>= 1/5) at temperatures up to 650 °C for 2 h in order to allow added Co to form a PtCo alloy. The catalysts prepared by the above procedure are designated as PtCo(C) and PtCo(I), respectively. Si was deposited on PtCo(C) by CVD using a SiH<sub>4</sub>/Ar mixture, which was injected as pulses into the stream of H<sub>2</sub> flowing into a reactor containing the catalyst at 250 °C.

The performance of the prepared electrode was examined by a half-cell test, which was carried out using pure oxygen dissolved in 1 M H<sub>2</sub>SO<sub>4</sub> at 60 °C and the cell potential controlled with a potentiostat (EG&G, M263). The stability of the PtCo catalysts was examined by measuring the amounts of catalyst components dissolved in sulfuric acid after an extended period. The dissolved metal ions were analyzed by ICP-AES.

### Results and Discussion

Table 1 shows the relative amounts Co dissolved from the sample catalysts before and after the test reaction. The relative amounts of dissolved Co were 0.63 for PtCo(I)650 and only 0.3 for PtCo(C)600, which indicated that Co was dissolved from PtCo(C) to a smaller extent than from PtCo(I). The mass activity of PtCo(I) was degraded by 65%, whereas PtCo(C) showed only 36% degradation, after the corrosion test which was carried out for 6000 sec (Fig. 1(a)). Accordingly, the catalyst degradation is correlated with the amounts of Co dissolved in the acidic solution. The higher corrosion resistance of PtCo(C) was attributed to more intimate interactions of Co with the Pt surface than in the case of PtCo(I).

The effect of added Si on the corrosion of PtCo(C) was also investigated (Table 1). The maximum mass activity of PtCo600(C)-Si(C) was obtained at Si/Pt = 0.1, which is approximately 1.4 times higher than that of PtCo600(C) obtained for the same Co/Pt ratio (Fig. 1(b)). Co dissolution in the acidic solution was lowered to 15% by the addition of Si to PtCo(C) (Table 1) because the formation of CoSi<sub>2</sub>, which has good thermal and chemical stabilities, enhanced the acid resistance of the catalyst.

Table 1. The ratio of Co/Pt (before: 200sec, after: 6000sec)

catalyst	before test(A)	after test(B)	(A-B)/A*100
PtCo(I)650	1	0.37	63
PtCo(C)600	0.2	0.14	30
PtCo(C)600-0.1Si(C)	0.2	0.17	15

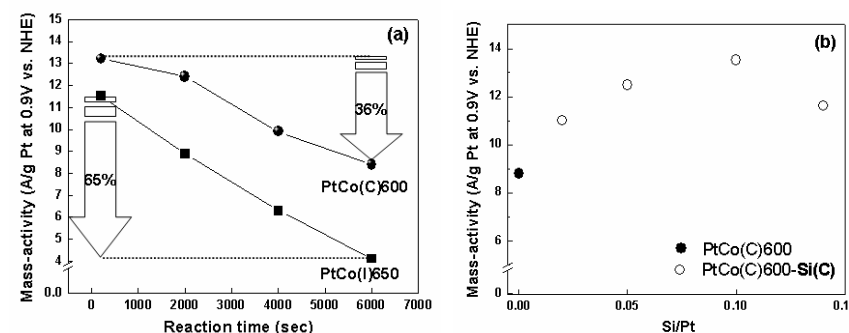


Figure 1. Mass-activity for PtCo catalysts (a) with reaction time, (b) with the amounts of added Si at 6000sec. ((a) : Co/Pt=0.2, 1 for PtCo(C), PtCo(I))

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