

Improvement of Durability in Au core/Pt Shell Structured Catalyst with PtRu Shell Formation

Takehito Nishikawa^a, Naoya Aoki^b, Hideo Inoue^b,
Hideo Daimon^a and Minoru Inaba^a

^a Faculty of Science and Engineering, Doshisha University,
Miyakodani, Tatara, Kyotanabe, Kyoto 610-0321, Japan

^b Ishifuku Metal Industry, Aoyagi, Soka, Saitama 340-0002, Japan

Introduction

Since very expensive Pt catalysts are used in the PEFCs, a reduction in Pt usage is a key issue for cost reduction of the PEFCs. Core/shell structured catalysts are a strong candidate for both reduction of Pt usage and enhancement ORR activity. From the viewpoint of chemical stability, we selected Au as a core material because Au is the most stable metal [1-3]. However, durability of the Au core/Pt shell structured catalyst (Pt/Au/C) is concerned because it is known that Pt forms solid solution with Au. In order to suppress the dissolution of the Pt shell atoms into the Au core, we synthesized small size Au and AuPt cores [4]. In this study, PtRu shell/Au core structured catalyst (PtRu/Au/C) was synthesized to inhibit Pt dissolution into the core. The durability of the PtRu/Au/C catalyst is presented.

Experimental

Au core NPs were synthesized with two-phase protocol [5]. Briefly, $[\text{AuCl}_4]^-$ was transferred into toluene phase using tetraoctyl ammonium bromide, and dodecanethiol (DDT) was added as a stabilizing agent, followed by reduction using NaBH_4 . The Au NPs were loaded on a carbon support (Ketjen black EC 300J) and they were heat-treated under air at 603 K for 1 h to remove the DDT. The Pt shell was formed on the Au core surface with the modified Cu-UPD method [6]. 100 mg of Au core NPs supported on carbon (Au/C) were dispersed in 50 mM H_2SO_4 containing 10 mM CuSO_4 and stirred at 303 K for 24 h with co-existence of Cu mesh. After the stirring, the Cu mesh was removed and K_2PtCl_4 was added into the solution to prepare Pt/Au/C catalyst. PtRu/Au/C catalyst was synthesized with the addition of K_2PtCl_4 and RuCl_3 after the modified Cu-UPD process mentioned above.

Durability of the catalysts was evaluated with a rectangular potential cycling test (0.6 V for 3 s/1.0 V for 3 s) in Ar saturated 0.1 M HClO_4 at 333 K. ORR activity of the catalysts was evaluated by the RRDE technique in O_2 saturated 0.1 M HClO_4 at 298 K. The catalysts were characterized with XRD, TG-DTA, XRF and TEM.

Results and Discussion

The TEM observation showed that the mean diameters of the Au/C core (after the heat treatment) and Pt/Au/C catalyst are 2.7 nm and 3.5 nm, respectively. The XRF analysis revealed that the composition of the Pt/Au/C catalyst is $\text{Pt}_{40}\text{Au}_{60}$ (at.%), which is close to the value assuming the formation of Pt monolayer on the Au core.

Durability test result of the Pt/Au/C catalyst are shown in Fig. 1 together with that of a commercially available carbon supported Pt catalyst (Pt/C, TEC10E50E, 2.8 nm, 46.1 wt.%, TKK). Even though the small Au core was used (2.7 nm), the Pt/Au/C catalyst showed inferior durability to that of the Pt/C catalyst. TEM and XRF analyses revealed that there are little changes in the particle size and composition of the catalysts before and after the durability test. Therefore, it is concluded that the Pt shell formed a solid solution with the Au core.

The Pt/Au/C catalyst was heat-treated to form the solid

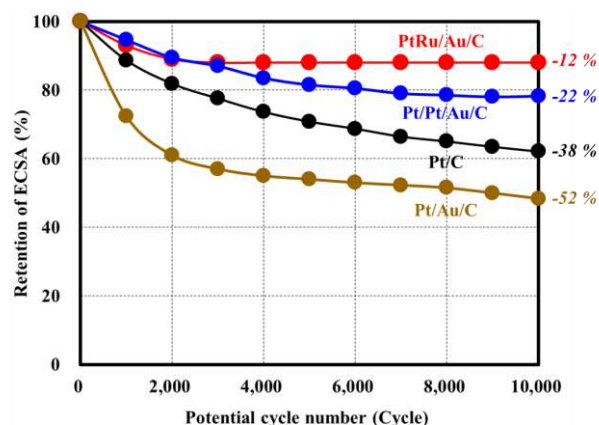


Fig. 1. Durability Pt/Au/C, Pt/Pt/Au/C and PtRu/Au/C catalysts.

solution in advance, and the Pt ML shell was formed again on the catalyst. The Pt/Pt/Au/C catalyst showed improved durability compared with the Pt/Au/C catalyst (Fig. 1). However, the ORR mass activity of the catalyst was poor because the heat treatment increased the Pt atoms in the core which do not contribute to the ORR. When the Au NPs are used as the core material, the inhibition of the Pt shell dissolution seems difficult because even the Pt/Pt/Au/C catalyst showed 22 % decrease in ECSA after the durability test.

Heats of mixing between two noble metals (composition: $\text{A}_{50}\text{B}_{50}$) are listed in Table 1 [7], indicating that Ru are easily mixed with Pt than Au and is hardly mixed with Au than Pt. The decrease of the ECSA in the PtRu/Au/C catalyst was 12 % after the durability test (Fig. 1). Therefore, it is presumed that the addition of the Ru inhibits the Pt dissolution into the Au core.

Table 1 Heat of mixing in $\text{A}_{50}\text{B}_{50}$ (kJ/mol)

		B		
		Pt	Au	Ru
A	Pt	0	+7	-1
	Au	+7	0	+22

Although the PtRu/Au/C catalyst showed improved durability, its initial ORR activity was lower than that of the Pt/C one. However, it was found that the ORR activity of the PtRu/Au/C catalyst was improved with the potential cycling in O_2 saturated HClO_4 at 298 K (0.05-1.0 V vs. RHE). It has been reported that the ORR activity of the PtRu monolayer formed on Pd(111) is higher than that of Pt monolayer [8]. Hence, it is considered that the addition of the Ru to the Pt shell has a possibility for simultaneous improvement in durability and ORR activity.

Acknowledgement

This work was supported by New Energy and Industrial Technology Development Organization (NEDO), Japan.

References

- [1] M. Inaba et al., ECS Trans, **33** (1), 231 (2010).
- [2] H. Tsuji et al., The 218th ECS Meeting, Abstract #858, Las Vegas (2010).
- [3] M. Inaba and H. Daimon, ECS Trans., **50** (2), 65 (2012).
- [4] H. Daimon et al., The 222nd ECS Meeting, Abstract #1653, Honolulu (2012).
- [5] M. J. Hostetler et al., Langmuir, **14**, 17 (1998).
- [6] X. Wang et al., The 220th ECS Meeting, Abstract #933, Boston, (2009).
- [7] F.R. de Boer, Cohesion in Metals-Transition Metal Alloys, North-Holland, Amsterdam (1999).
- [8] J. Zhang et al., J. Am. Chem. Soc., **127**, 12480 (2005).