

## Change in ORR activity of Pd core/Pt shell structured catalyst with potential cycling durability test

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### Introduction

Core/shell structured catalyst is a strong candidate for reducing usage amount of expensive Pt and improving ORR activity in the PEFCs. It has been reported that the ORR activity of the Pt monolayer ( $Pt_{ML}$ ) is enhanced when it is formed on Pd(111) single crystal and on Pd NPs core [1, 2]. However, lower redox potential of the Pd with respect to that of the Pt causes dissolution of the Pd core during potential cycling durability test [3].

In this study, carbon supported Pd core/Pt shell structured catalyst (Pt/Pd/C) was successfully synthesized with combination of modified Cu under potential deposition and Pt replacement reaction processes [4]. Changes in morphology, composition and ORR activity of the Pt/Pd/C catalyst during the potential cycling durability test are investigated.

### Experimental

Carbon supported Pd core (Pd/C, 4.2 nm, 46 wt.%, Ishifuku Metal Industry) was dispersed in DI water containing 50 mM  $H_2SO_4$  and 10 mM  $CuSO_4$  by ultrasonication and stirred at 303 K for 20 h with coexistence of Cu mesh under Ar atmosphere [4]. Cu monolayer ( $Cu_{ML}$ ) was formed on the Pd core surface by contact of the Pd/C core with the Cu mesh. After the stirring, the Cu mesh was removed and 2 mM  $K_2PtCl_4$  was added at 278 K and stirred for 30 min. With this process, the  $Cu_{ML}$  was replaced by the Pt shell and the Pt/Pd/C catalyst was obtained. The core and catalyst were characterized with TG-DTA, XRD, XRF and TEM. CV of the Pt/Pd/C catalyst was measured in Ar saturated 0.1 M  $HClO_4$  at 298 K and ORR activity of the catalyst was evaluated with RRDE technique in  $O_2$  saturated 0.1 M  $HClO_4$  at 298 K. Durability of the catalyst was evaluated with 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 353 K.

### Results and Discussion

XRD patterns of the Pd/C core and Pt/Pd/C catalyst are shown in Fig. 1. Any diffraction from Pt is not observed and symmetry of Pd (220) diffraction is retained after the Pt shell formation, implying that the Pt shell covered the Pd core surface without formation of Pt particles. It was calculated that the Pt shell formed on the Pd core surface corresponds to 1.5 times of the  $Pt_{ML}$ .

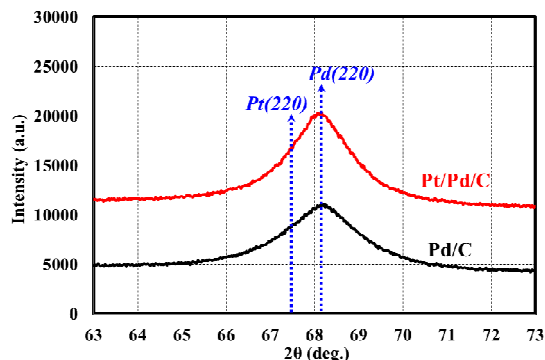


Fig. 1. XRD patterns of Pd/C core and Pt/Pd/C catalyst.

ORR activity of the Pt/Pd/C catalysts is summarized in Table 1. The initial ORR specific and mass activities are superior to those of a commercially available carbon supported Pt catalyst (Pt/C, 2.8 nm, 46 wt.%, TKK). The ORR activity of the Pt/Pd/C catalyst was highly enhanced after the potential cycling durability test at 353 K.

Table 1 ORR activities of Pt/Pd/C and Pt/C catalysts

Catalyst	Specific activity ( $\mu A/cm^2$ )	Mass activity (mA/mg-Pt)
Pt/Pd/C (Initial)	525	567
Pt/Pd/C (After durability test@353 K)	2300	760
Commercial Pt/C	350	255

TEM images of the Pt/Pd/C catalysts are shown in Fig. 2. The morphology of the catalyst changed into rounded shape and the mean diameter decreased from 5.6 nm to 4.1 nm after the durability test at 353 K. Electrochemical surface area of the catalyst decreased by 61 % and 43 % of the Pd core was dissolved out after the durability test.

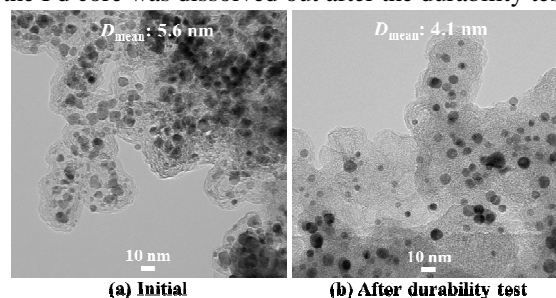


Fig. 2. TEM images of Pt/Pd/C catalysts before and after potential cycling durability test at 353 K.

Changes in the ORR activity and Pd composition during the durability test at 353 K are demonstrated in Fig. 3. There are little changes in the Pd composition after 1,000 potential cycling. It should be noted that the ORR specific activity is largely enhanced between 5,000 and 10,000 potential cycling, which increased the ORR mass activity of the Pt/Pd/C catalyst by more than 3 times of the initial mass activity of the Pt/C catalyst. The highly enhanced ORR activity in the Pt/Pd/C catalyst with the durability test is considered to be due to (1) compressive strain in the  $Pt_{ML}$  caused from the dissolution of the Pd core (-43 %) (2) re-construction of the surface Pt atoms (rounded shape).

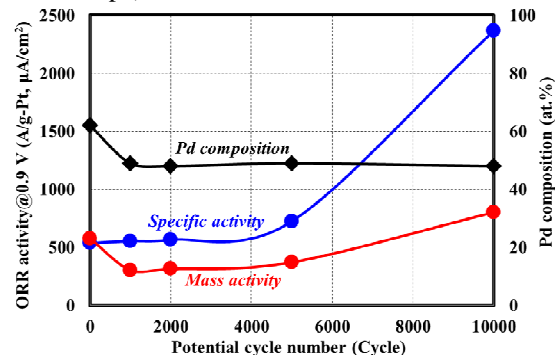


Fig. 3. Changes in Pd composition and ORR activity of Pt/Pd/C catalyst during potential cycling durability test at 353 K.

### Acknowledgement

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

### References

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