Durability Enhancement of Pd Core-Pt Shell Structured Catalyst with SiO₂ and Carbon Coatings

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Decrease in Pt usage is crucial for cost reduction of the PEFCs and Pt core-shell structured catalyst is a promising candidate for the decrease [1]. Recently, we have successfully synthesized a carbon supported Pd core-Pt shell structured catalyst (Pt/Pd/C) *via* a modified Cu-UPD/Pt displacement method and found that oxygen reduction reaction (ORR) mass activity of the catalyst was moderately enhanced with an accelerated durability test (ADT) although electrochemical surface area (ECSA) was severely decreased [2]. In this study, SiO₂ and carbon coatings were investigated in order to mitigate the ECSA decay and further enhance the ORR mass activity of the Pt/Pd/C catalyst.

1 g of carbon supported Pd core (Pd/C, 4.5 nm, 30 wt.%, Ishifuku Metal Industry) was dispersed in 600 ml of 50 mM H_2SO_4 containing 10 mM $CuSO_4$ and stirred for 5 h at 278 K with coexistence of a metallic Cu sheet under Ar atmosphere in which Cu monolayer (Cu_{ML}) was under potentially deposited on the Pd core surface. Then, the Cu sheet was removed and K_2PtCl_4 was added to displace the Cu_{ML} with the Pt_{ML}, forming the Pt/Pd/C catalyst [2]. SiO₂ was coated on the catalyst through a sol-gel route by using 3-aminopropyltriethoxysilane as a seed for the main precursor of tetraethoxysilane. The catalyst was finally heat-treated at 623 K to promote dehydration reaction [3]. Carbon coating was conducted by using dopamine as a precursor. The Pt/Pd/C catalyst was dispersed and stirred in *tris*-HCl (pH 8.5) buffer solution containing the dopamine at 303 K for 5 h under O₂ atmosphere [4]. The Pt/Pd/C catalyst was characterized *via* TG, XRD, XRF, TEM, TEM-EDX and CV measurements. The ORR activity of the catalyst was measured by rotating disk electrode technique at 1,600 rpm in O₂ saturated 0.1 M HClO₄ at 298 K. The ADT was performed by using rectangular potential cycling of 0.6 V (3 s)-1.0 V (3 s) *vs*. RHE in Ar saturated 0.1 M HClO₄ for 10,000 cycles at 353 K.

Figure 1 demonstrates ECSA decay of the catalysts over the ADT cycle. The decay was suppressed with the heat treatment at 623 K owing to particle size increase (green circle). The decay was further mitigated with the SiO₂ and the carbon coatings (blue and red circles). TEM observation revealed that agglomeration of the Pd@Pt NPs was well suppressed with the coatings.
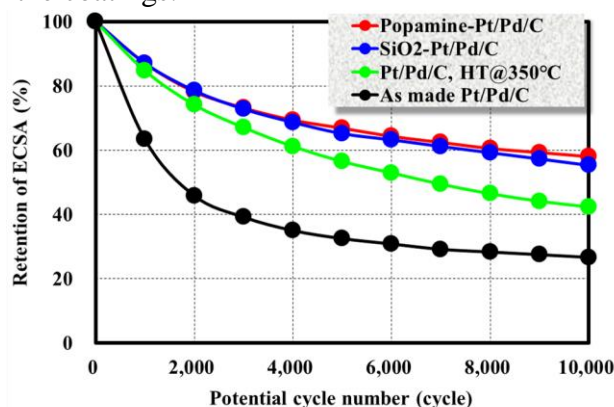

Fig. 1. Change in ECSA of Pt/Pd/C catalyst with ADT cycle.

ORR mass activities after the ADT are summarized in Table 1 in comparison with a reference Pt/C catalyst (TEC10E50E, 47 wt.%, TKK). The activities of the Pt/Pd/C catalysts coated with the SiO₂ and the dopamine are 960 A g⁻¹$_{Pt}$ which are 5.3-fold of the Pt/C catalyst. The high ORR mass activity even after the ADT is attributed to the mitigation of the ECSA decay with the coatings.

Table 1. ORR mass activities of Pt/Pd/C and Pt/C catalysts after ADT

Catalyst	ORR mass activity@0.9 V after ADT
As made Pt/Pd/C	384
Pt/Pd/C HT@350°C	525
SiO₂-Pt/Pd/C	960
Dopamine-Pt/Pd/C	960
Pt/C	180

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