

Scale-up Synthesis of Au Core/Pt Shell Structured Catalysts and Their Electrochemical Properties

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Introduction

A reduction in usage amount of the expensive Pt is a key issue for cost reduction of the PEFCs. In addition, higher oxygen reduction reaction (ORR) activity and durability are demanded in the cathode catalysts of the PEFCs. Core/shell structured catalyst is a strong candidate for decreasing the Pt usage and enhancing the ORR activity. From the viewpoint of chemical stability, we selected Au as the core metal particle because the Au is the most stable metal [1-3]. The Pt monolayer (Pt_{ML}) shell has been formed on the core surface using Cu under potential deposition (Cu-UPD) technique. However, this technique requires precise potential control and weight of the treated core is of the order of μg. We developed new methods for the Pt_{ML} shell formation which do not need the potential control and are suitable for scale-up synthesis [3,4]. In this study, the electrochemical properties of the Au core/Pt shell structured catalysts (Pt/Au/C) prepared with the methods are described.

Experimental

100 mg of Au cores (3.0 nm) supported on Ketjenblack (Au/C, 21.5 wt.%, Ishifuku Kinzoku Metal Industry) were dispersed in 50 mM H₂SO₄ with ultrasonication and K₂PtCl₄ was added. The solution was stirred at 303 K for 24 h under Ar atmosphere. Hereafter, this method is called the “immersion method”. We developed another method for the Pt shell formation. 100 mg of Au/C was dispersed in 50 mM H₂SO₄ with ultrasonication and 10 mM CuSO₄ was added. The solution was stirred at 303 K under Ar atmosphere with co-existence of Cu mesh. After the stirring for 20 h, the Cu mesh was removed and K₂PtCl₄ was added in the solution. This method is called the “modified Cu-UPD method”. The resulting Pt/Au/C catalysts were washed with pure water and dried in air at 333 K.

Electrochemical surface area (ECSA) and Pt coverage were determined by cyclic voltammetry in Ar saturated 50 mM H₂SO₄ at 298 K. The ECSA of the catalysts was calculated from hydrogen desorption wave and the Pt coverage was calculated from a decrease in reduction wave of the Au oxide after the Pt shell formation. The ORR activity of the catalysts was evaluated using the RRDE technique in oxygen saturated 0.1 M HClO₄ at 298 K. The durability of the Pt/Au/C catalysts was evaluated by rectangular potential cycling (0.6 V for 3 s/1.0 V for 3 s) in Ar saturated 0.1 M HClO₄ at 333 K. The Pt/Au/C catalysts were characterized with XRD, TG-DTA, XRF and TEM.

Results and Discussion

The XRF analysis showed that the composition of the Pt/Au/C catalyst prepared by the immersion method was Pt₃₀Au₇₀ (at.%), indicating that the Pt shell formed on the Au core corresponds to 60 % of Pt ML. On the other hand, the composition of the catalyst prepared by the modified Cu-UPD method was Pt₅₄Au₄₆, which is close to Pt ML formation. The Pt coverage in the immersion and the modified Cu-UPD methods were 65 % and 73 %, respectively (Table 1). In the modified Cu-UPD method, although the amount of Pt corresponded to Pt ML, its Pt coverage was lower than 100 %, suggesting that part of the Pt shell forms multi-layers.

Table 1 Electrochemical properties of Pt/Au/C and Pt/C catalysts

Catalyst	Pt shell formation	Pt coverage (%)	Specific activity (μA/cm ²)	Mass Activity (A/g-Pt)
Pt/Au/C	Immersion method	65	271	119
Pt/Au/C	Modified Cu-UPD	70	494	315
Pt/Au/C	Conventional Cu-UPD	73	479	279
Pt/C	-	-	350	255

The LSVs of the Pt/Au/C catalysts are shown in Fig. 1, and the ORR activity is summarized in Table 1 together with those of a commercially available Pt/C catalyst (TEC10E50E, 2.8 nm, 46.1 wt.%, TKK). The ORR specific and mass activities of the Pt/Au/C catalyst prepared by the modified Cu-UPD method are comparable to those of the catalyst synthesized with the conventional Cu-UPD method, implying that the Pt shell formation with the modified Cu-UPD method successfully performed. In contrast, the Pt/Au/C catalyst prepared by the immersion method showed inferior ORR activities, which is considered to be due to the lower Pt coverage.

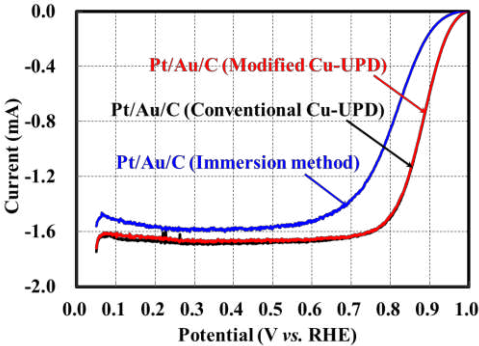


Fig. 1. LSVs of Pt/Au/C and Pt/C catalysts.

Durability of the Pt/Au/C catalysts is demonstrated in Fig. 2. The Pt/Au/C catalyst prepared by the modified Cu-UPD method showed higher durability than that of the catalyst prepared by the conventional Cu-UPD method.

From these results, it is concluded that the modified Cu-UPD method for the Pt shell formation is promising for scale-up synthesis of the core/shell structured catalysts.

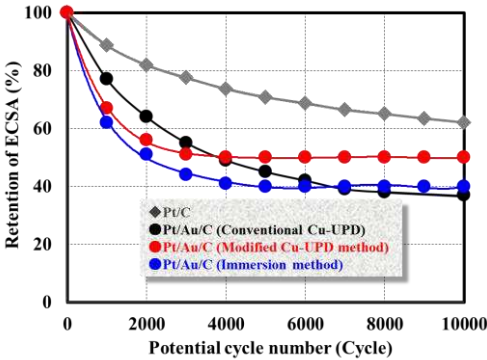


Fig. 2. Durability of Pt/Au/C and Pt/C catalysts.

Acknowledgement

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