

ORR activity of Pd core/Pt shell structured catalyst synthesized with scale-up process

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Introduction

The PEFC are clean and useful power sources for the house and vehicle because of their small size and high power density. However, usage amount of expensive Pt catalysts should be decreased for the cost reduction of the PEFC. Core/shell structured catalyst is a strong candidate for the decrease of the Pt usage. In addition, it has been reported that ORR activity of Pt monolayer (Pt_{ML}) formed on Pd(111) single crystal is higher than that of Pt(111) single crystal [1]. In general, the Pt_{ML} is formed on the core materials using Cu under potential deposition (Cu-UPD) technique [2]. The conventional Cu-UPD technique, however, requires precise potential control and amount of the treated core is micro-gram order, which is obstacle to the mass-production of the core/shell structured catalysts.

Wang et al. have reported modified Cu-UPD technique without the precise potential control [3]. In this report, Pd core/Pt shell structured catalyst (Pt/Pd/C) was synthesized with the modified Cu-UPD technique in order to develop a basis for the scale-up synthesis of the catalyst.

Experimental

2 g of Ketjen black EC 300J supported Pd core (Pd/C, 4.2 nm, 30 wt.%) was dispersed in DI water containing 50 mM H₂SO₄ and 10 mM CuSO₄ by ultrasonication and stirred at 303 K for 12 h with coexistence of Cu mesh under Ar atmosphere. After the stirring, the Cu mesh was removed and 2 mM K₂PtCl₄ was added at 278 K. With this process, the Cu shell formed on the Pd core surface was replaced by the Pt shell and the Pt/Pd/C catalyst was obtained. The Pt/Pd/C catalyst was characterized with ICP. CV of the catalyst was measured in N₂ saturated 0.1M HClO₄ at 298 K. ORR activity of the catalyst was evaluated with RRDE technique in O₂ saturated 0.1M HClO₄ at 298 K.

Results and Discussion

We changed timing of the K₂PtCl₄ addition after the removal of the Cu mesh. In example (1), the K₂PtCl₄ was added 1 min. later after the Cu mesh removal and 120 min. later in example (2). CVs of the Pd/C core, Pt/Pd/C catalysts and a commercially available carbon supported Pt catalyst (Pt/C, 2.8 nm, 40 wt.%) are shown in Fig. 1. We focused on the peak potential in the reduction wave of surface metal oxide species observed in 0.7-0.8 V vs. RHE. We estimated Pt coverage condition with peak potential in the reduction wave because Pt and Pd have different reduction peak potential. The Pt/Pd/C catalyst in example (2) showed lower reduction peak potential than that of the catalyst in example (1) and the peak potential was close to the Pd/C core. On the other hand, the Pt/Pd/C catalyst in example (1) showed almost same reduction peak potential as the Pt/C catalyst. Therefore, it is considered that the Pt coverage in example (1) is much higher than that in example (2).

The metal loading and the ORR activity of the Pt/Pd/C

catalysts are summarized in Table 1. The Pt/Pd/C catalyst in example (2) has lower Pt loading than that in example (1), which is coincident with the CVs data in Fig. 1 by reason that CV indicate the main metal which covers surface of particle. The Pt/Pd/C catalyst in example (1) showed inferior ORR activity to that of the Pt/C catalyst.

In this study, we demonstrated the synthesis of the Pt/Pd/C catalyst using the modified Cu-UPD technique. Although the technique showed potential for the mass-production, optimization of the Pt shell formation process is required for the improvement of the ORR activity. In the presentation, the ORR activity of the Pt/Pd/C catalyst synthesized with the optimized process will be presented.

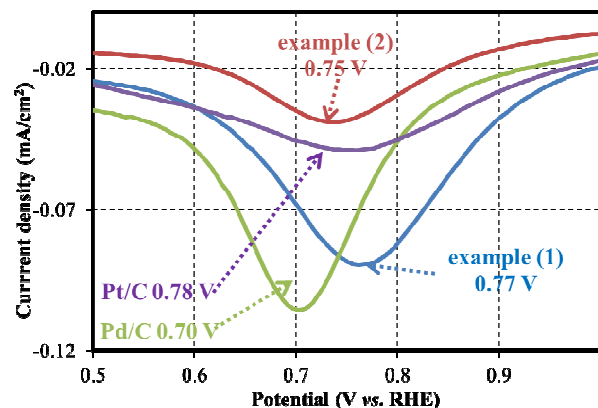


Fig. 1. CV comparison of Pt/Pd/C, Pd/C, Pt/C.

Table 1. The metal loadings and ORR activity

	loading (wt.%)		ORR activity	
	Pt	Pd	MA (mA/g-Pt)	SA (μA/cm ²)
example (1)	23.9	19.9	141	216
example (2)	6.8	28	-	-
Pt/C	40	-	268	785
Pd/C	-	30	-	-

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