

Porous PtRuCo Thin Film Catalyst Prepared
by Electrodeposition and Dealloying Methods
for Anode of Direct Methanol Fuel Cell

Yuta Watanabe¹, Yoshitatsu Misu¹, Tokihiko Yokoshima²,
Toshiyuki Momma^{1,2}, and Tetsuya Osaka^{*1,2}

¹Graduate School of Advanced Science and Engineering,
Waseda University, 3-4-1, Okubo, Shinjuku-ku, Tokyo
169-8555, Japan

²Research Institute for Science and Engineering, Waseda
University, 3-4-1, Okubo, Shinjuku-ku, Tokyo 169-8555,
Japan

Introduction

PtRu alloy catalysts are considered as the most promising anode catalyst in DMFCs due to their high activity and CO tolerance in methanol oxidation reaction (MOR). We have proposed PtRu catalyst prepared by electrodeposition and dealloying methods. Electrodeposition can selectively deposit the electrocatalysts onto conductive materials and we have achieved preparing the electrocatalysts on the on-chip fuel cell^[1] and on carbon paper, e.g., mesoporous Pd-Co^[2]. Moreover, dealloying method was combined in order to prepare electrocatalysts with large surface area^[2].

In our previous work, we reported porous PtRuCu thin film catalyst^[3]. It showed higher maximum current density in MOR than PtRu catalyst prepared by electrodeposition itself, but its onset potential was lower than the PtRu catalyst. Moreover, the dissolution of Ru was occurred during the dealloying process of Cu from PtRuCu alloy.

We explored the new dealloying metal by replacing Cu to improve the catalytic activity. Since Co shows the superior electrochemical properties, it is selected to prepare porous PtRuCo thin film catalyst in this study.

Experimental

The standard plating bath containing 0.5 M Na₂SO₄, 26.7 mM K₂PtCl₄, 13.3 mM RuCl₃, and 150 mM CoSO₄ was prepared. The conventional three-electrode cell with an Au substrate, a Pt wire and Ag/AgCl/KCl (saturated) electrode was used as a working electrode, counter and reference electrode, respectively. PtRuCo was electrodeposited applying consecutive potentiostatic deposition, in briefly; (1) Pt-rich under layer was electrodeposited by at 0 V for 10 s. (2) Afterward, PtRuCo layer was electrodeposited at -0.75 V for 150 s. The as-deposited PtRuCo was dealloyed by immersing in an air-saturated 0.5 M H₂SO₄ overnight. The morphology was observed using HR-SEM. The electrochemical surface area (ECSA) was calculated by using the profile of CO stripping voltammetry. The activity for MOR was evaluated by cyclic voltammetry (CV).

Results and discussion

First, various candidates, i.e., Sn, Ni, Fe, and Co, were investigated to find new dealloying metal. All the candidate single metals show high CO tolerance when it alloys with Pt and more negative redox potential than Cu due to prevention of dissolving Ru during the dealloying process. CVs were performed in the bath containing single metal ion of the candidate to evaluate the suitability for electrodeposition method. Among them, Ni and Co showed higher reduction current than that of blank. Moreover, oxidation current was observed in anodic scan of the CV curve of only Co. This result indicates Co can be electrochemically dealloyed. Afterward, porous Pt-M

binary alloys (M=Ni, Co, Cu: Cu was used as a reference) were prepared to evaluate increasing the surface area of PtRu alloy with porous structure formed by dealloying. The ECSAs were calculated by measuring the charge collected in the hydrogen desorption region obtained in CV curves of 0.5 M H₂SO₄ solution. It is obtained that PtCo showed the largest ECSA among the porous Pt-M. Thus, Co was considered as the most suitable dealloying metal to prepare porous PtRu-based alloy.

Next, characteristics of porous PtRuCo thin films prepared by electrodeposition and dealloying methods were investigated. The SEM images of prepared porous PtRuCo thin film catalyst are shown in Fig. 1. Cracks formed on the surface are shown in Fig. 1a and the cross-sectional image (Fig. 1b) indicates that the structure consists of the clustering columns causing pores on the surface. This pore structure indicates that higher surface area has been prepared. In comparison of ECSA of PtRuCo with that of PtRu, PtRuCo showed ca. 2.8 times higher ECSA than PtRu. Fig. 2 shows CVs for MOR on PtRuCo, PtRuCu and PtRu thin film catalysts. In Fig. 2a, the maximum current density of PtRuCo is higher than PtRuCu. It is considered that this result derives from the high surface area of PtRuCo. Moreover, its onset potential was comparable to that of PtRu. From these results, the improved catalytic performance in MOR was achieved with PtRuCo compared to PtRuCu and PtRu

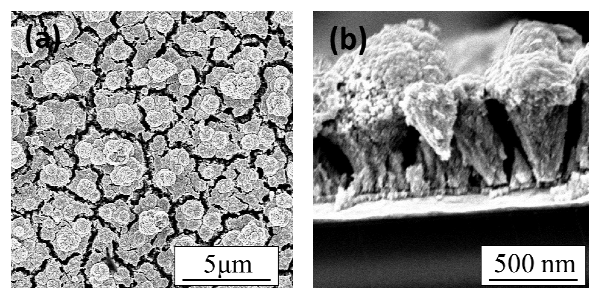


Figure 1. (a) Plane SEM image and (b) cross SEM image of porous PtRuCo thin film catalyst.

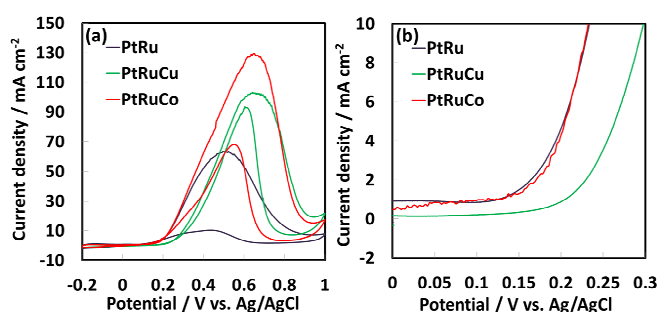


Figure 2. (a) CV curves for MOR on porous PtRuCo, porous PtRuCu and PtRu thin film catalyst (b) magnification of the region of 0-0.3 V in (a).

Acknowledgements

This work was partly supported by the Grant-in-Aid for specially promoted research "Establishment of electrochemical device engineering". Authors thanks to Sugimoto lab., Shinshu University about examination of CO stripping voltammetry.

Reference

- [1] S. Tominaka, S. Ohta, H. Obata, T. Momma, T. Osaka, *J. AM. CHEM. SOC.*, (2008), 130, **10456-10457**.
- [2] T. Hayashi, T. Yokoshima, T. Momma, T. Osaka, *79th Meeting Abst. of Electrochem. Soc. Jpn.*, (2012), **446**.
- [3] Y. Misu, T. Yokoshima, T. Momma, T. Osaka, *Autumn Meeting Abst. of Electrochem. Soc. Jpn.*, (2011), **57**.