Dissolution Behavior of Pt-Co Binary Alloy Thin Films in Sulfuric Acid

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Introduction

Pt-Co binary alloy has attractive attention because it has higher oxygen reduction reaction ability than Pt[1]. It is expected to be used as cathode catalyst in proton exchange membrane fuel cells (PEMFCs). However, selective dissolution of Co from the Pt-Co alloy catalyst is a serious problem in the application, which causes degradation of PEMFCs performance[2]. Thus, dealloying treatments are important in order to reduce the selective dissolution. The methods of dealloying are mainly divided into two forms: chemical leaching and electrochemical leaching. In this study, Selective dissolution behavior of Co during chemical leaching has been investigated using Pt-Co binary alloy thin films.

Experimental

Pt-Co binary alloys and pure Pt thin films were vapor-deposited on glassy carbon by physical vapor depoition (PVD). The deposited thin film samples were vacuum-encapsulated in a silica glass tube at 2.0×10^{-5} Torr, and homogenized at 600 ^{o}C for 24 h. The sample surface was dry-polished by sputtering with glow discharge optical emission spectroscopy (GD-OES) to eliminate oxide layers formed during the heat treatment. Three different alloys, Pt_{51}-Co_{49} (Pt-49at%Co), Pt_{43}-Co_{57}, Pt_{28}-Co_{72} and Pt_{24}-Co_{76}, were used, the chemical composition of which was determined by X-ray diffraction. .

Electrochemical measurements were performed at 25^{o}C in a two-compartment Teflon cell using aerated 0.5 M H_2SO_4 solution. The thin film samples were used as working electrode, the geometric surface area of which was 0.13 cm^2. A double junction KCl-saturated silver/silver-chloride electrode (SSE) was used as reference electrode and a gold wire was used as the counter electrode. The samples were immersed in 0.5 M H_2SO_4 for 24 h. The rest potential was monitored during the immersion test, and the dissolved Co ions in the test solution were quantitatively evaluated by inductively coupled plasma mass spectroscopy (ICP-MS) after the immersion test.

Results and discussion

The changes in the rest potential, E_{rest} of the Pt and Pt-Co alloys made by PVD during the 24 h immersion test is shown in Fig.1. The E_{rest} for pure Pt was very stable at 0.798 V. The E_{rest} for Pt_{51}-Co_{49} and Pt_{43}-Co_{57} showed a slightly lower than that of Pt at the initial stage of immersion and finally became 0.785 and 0.796 V respectively. Their values were very close to that of pure Pt, indicating that a Pt-enriched layer formed by selective dissolution of Co in the initial stage of immersion suppresses further selective dissolution of Co. However, the E_{rest} for Pt_{28}-Co_{72} and Pt_{24}-Co_{76} was much lower than that for Pt_{51}-Co_{49}, Pt_{43}-Co_{57} and Pt. The final potentials for Pt_{28}-Co_{72} and Pt_{24}-Co_{76} were 0.677 and 0.617 V, respectively. It implies that selective dissolution of Co is not suppressed by the Pt-enriched layer formed by immersion.

The dissolved Co ions per geometric area for Pt_{51}-Co_{49}, Pt_{43}-Co_{57}, Pt_{28}-Co_{72} and Pt_{24}-Co_{76} determined by ICP-MS were 2.38, 2.93, 20.0 and 45.5 μgcm^{-2}, respectively. It can be seen that the amount of the dissolved Co ions (Δm) decreases by increasing the Pt amounts. These results are in good agreement with those of the rest potential. The relationship between Pt contents in Pt-Co binary alloy and the amount of dissolved Co ion is plotted in Fig. 2. The amount of the selective dissolution of Co dramatically changes between 28 and 43 at% in Pt content. The gray plots show previous results of bulk Pt-Co binary alloys investigated by Hoshi et al[3]. This figure revealed that Pt-Co binary alloy thin films and bulk Pt-Co binary alloys have a similar tendency for selective dissolution of Co. In this study, it was found that the threshold level of Pt contents for suppressing the selective dissolution of Co for nano-scale Pt-Co binary alloy is between 30 at% and 40 at%.

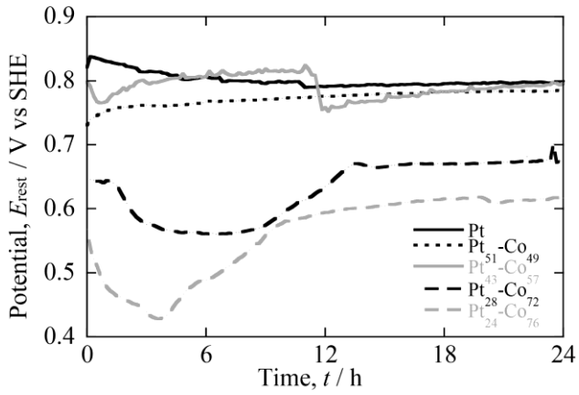

Fig.1 Change in rest potential of the physical vapor deposited pure Pt and Pt-Co binary alloy thin films during the immersion test.

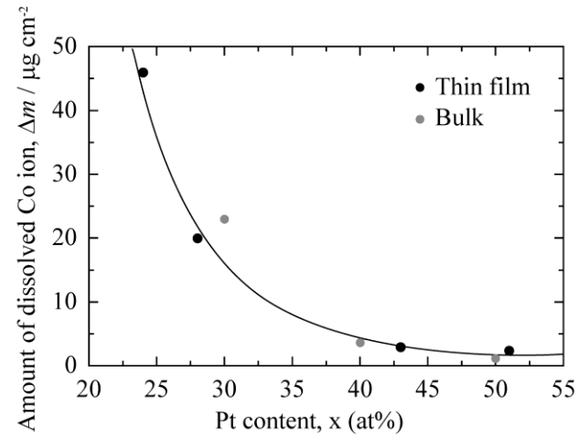

Fig.2 The relationship between the amount of dissolved Co from Pt-Co binary alloy thin films

Reference

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