The Spectroscopic Study on the Chemical State at Pd/Mg Interface

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The chemical state of interface between Pd and Mg layers has been investigated by XPS and NEXAFS methods. Since it is thought that the hydrogen storage ability strongly depends on the chemical state of the interface, we focus on the interface of the Pd–Mg. It is found that the different phase from bulk metal or oxide exists between Pd and Mg layers prepared by both DC magnetron sputtering and vacuum evaporation methods. From XPS and NEXAFS measurements, we have revealed that Pd loses the electron and Mg picks up one in this phase. It might be thought that the Pd–Mg alloy phase exists between Pd and Mg.

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I. INTRODUCTION

The hydrogen fuel cells are focused on as the solutions for the environmental pollution and the depletion of the fossil fuel. The combustion of Hydrogen produces only water. Therefore the hydrogen is the clean energy with a low load for the environment. Furthermore it is possible to obtain the electric energy from Hydrogen in high efficiency by means of using fuel cells. Thus the hydrogen vehicle (HV) using fuel cells has been developed in the world in these years. For practical use of the HV using fuel cell, we must develop both such fuel advanced cells and the hydrogen storage technique. There are some techniques for hydrogen storage, for example, the compressed hydrogen, the liquefied hydrogen and the absorbed hydrogen into the material. In the compressed and liquefied hydrogen, the storage tank in the HV is too heavy in comparison with the amount weight of the stored hydrogen. Therefore, the hydrogen storage technique that possesses lightweight and large hydrogen storages has been developed.

Mg is the material having some properties, which are lightweight, inexpensive and 7.6w% of hydrogen storage capacity. There is a problem, however, the Mg absorbs and desorbs the hydrogen at the temperature of more than 600 K. Yoshimura et al. have reported that the Mg thin film covered with Pd prepared by DC magnetron sputtering method can absorb and desorb the hydrogen at room temperature and under ambient pressure [1]. When the thin film is prepared by vacuum evaporation method, the hydrogen storage ability of the sample is not shown under some conditions [1]. Thus, it is thought that the hydrogen storage ability depends on the preparation method of the Mg thin layer. Especially, it indicates that the Pd–Mg interface influences the hydrogen storage ability. However, the chemical state of the Pd–Mg interface is not clarified in the difference of the preparing method for samples. In order to progress the hydrogen storage capability, thus, it is very important to reveal the chemical state of the Pd-Mg interface.

To progress the hydrogen storage capability, we suggest increasing the joint area at the interface. When a nanoparticle is used, it is possible to increase the joint area per ambient volume. Moreover, there are advantages for using nanoparticle, i.e. increasing the specific surface area, progressing the hydrogen diffusion rate and improving the performance for the hydrogen dissociation catalyst.

In this paper, we reveal the chemical state change between Pd and Mg at the interface by X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) measurements. To reveal the properties of each nanoparticle, as a first step, we study the sample that is the interface of the Pd layer/Mg nanoparticle.

II. EXPERIMENTAL

Table I shows the details of the formation of the samples prepared by several methods. The notations “sputtered”, “evaporated” and “NP” denote the preparation methods of the DC magnetron sputtering, the vacuum evaporation and the nanoparticle deposition methods, respectively. The sample for XPS measurement was prepared the double-layered structure of the Pd (evaporated)[1 nm]/Mg NP[approximately 1 monolayer] in order
TABLE I: The formations of specimen prepared by several methods.

|          | XPS                                      | NEXAFS                                              |
|----------|-----------------------------------------|-----------------------------------------------------|
|          | Pd (evaporated)/Mg NP/Pd (evaporated)/Mg NP/Ni substrate |                                                     |

1. Pd (sputtered) [4 nm]/Mg (sputtered) [40 nm]/Ni substrate
2. Pd (evaporated) [4 nm]/Mg (sputtered) [40 nm]/Ni substrate
3. Pd (evaporated) [4 nm]/Mg NP [0.1 nm]/Mg (sputtered) [40 nm]/Ni substrate

FIG. 1: AFM image of Mg NP deposited on Si substrate and size distribution with standard deviation.

The formations of specimen prepared by several methods.

The Mg nanoparticles were fabricated by the gas evaporation method using He gas and were deposited on Ni substrate [2, 3]. Moreover, the Pd atoms were deposited on the substrate by the vacuum evaporation method. The deposition was conducted under vacuum condition. The size and the deposition amount of Mg nanoparticles were controlled by He partial pressure and deposition time, respectively. The samples for NEXAFS measurement were prepared by the methods described before in order to reveal the chemical state fabricated by the different prepared methods. The Pd of the samples 1, 2 and 3 were prepared by the DC magnetron sputtering, the vacuum evaporation and the nanoparticle deposition methods.

The diameter of Mg nanoparticles was estimated by Atomic Force Microscope (AFM; NanoScope III-a, Veeco Inst.) observation. Fig. 1 shows AFM image of Mg nanoparticles deposited on Si substrate. This AFM measurement was carried out by tapping mode under atmospheric condition. The diameter of Mg nanoparticles has been estimated by the height value of AFM observation because the AFM observation has the high resolution in vertical direction compared with horizontal one. The average diameter of Mg nanoparticles is 3.3 nm.

The XPS measurement was carried out by using MgKα X-ray and Concentric Hemispherical Analyzer (PHOBOS 100-5ch; SPECS). The base pressure was around 1.0×10⁻⁸ Pa. The binding energy scale of the XPS measurements was calibrated with Mo 3d₃/₂ photoelectron peak of the sample holder at 228.0 eV. The Pd L₃- and Mg K-edges NEXAFS measurements were carried out at BL-10 of the SR center in Ritsumeikan University by total electron yield (TEY) and fluorescence X-ray yield (FY) methods under high vacuum condition (≈7×10⁻⁶ Pa) [4]. The TEY and FY methods are sensitive for the bulk and the surface, respectively. The incident X-ray energy was calibrated with the first peak of the NEXAFS spectrum for MgO powder (purity: 99%) and PdO powder (purity: 99%) at 1309.5 eV and 3176.0 eV, respectively.

III. RESULTS AND DISCUSSIONS

A. XPS measurement

Figure 2 shows Pd 3d XPS spectrum. To define the peak positions of Pd bulk and PdO components, the standard samples are measured. The XPS spectra are deconvoluted by using those standard peak positions. As a result, there is the component that is not assigned to the components of Pd bulk and PdO. There is no influence...
of the atmospheric impurities, namely C, N, O and other elements. Because those samples are measured under in situ conditions. In spite of in situ condition, the PdO component is measured in this study. The surface of the Pd evaporation source is covered with the oxide Pd. It is impossible to remove all PdO although we have tried to remove the oxide layer by the pre-evaporation under vacuum condition. Thus it indicates that the PdO mixes in the prepared sample. Therefore, it is thought that the peak located near 336.2 eV shows the component of the Pd–Mg interaction, as shown in Fig. 2. The peak position of the Pd–Mg interaction shifts to the higher binding energy side compared with the peak position of Pd bulk. This peak shift shows that Pd loses the electron. Therefore, Mg picks up the electron from Pd. In the Mg XPS measurement, it is thought that the peak position of the Pd–Mg interaction shifts to the lower binding energy side compared with the peak position of Mg bulk. But the peak shift was not shown in the Mg 2s XPS measurement. On the other hand, Yoshimura et al.

B. NEXAFS measurement

Figure 3 shows Pd L$_3$-edge NEXAFS spectra obtained by FY method. The Pd bulk and PdO were measured as the standard NEXAFS spectra. Figure 3(b) is the close-up of the region between 3165.0 eV and 3185.0 eV in Fig. 3(a). For samples 1-3, there are almost the same shapes about all NEXAFS spectra. The peak positions for the samples 1-3 are different compared with that for Pd bulk and PdO. The phase other than Pd and PdO exists. The MIX layer is that the Pd and Mg are deposited by DC magnetron sputtering method at the same time. The Pd–Mg MIX phase, namely the entire sample is like Pd–Mg interface, are prepared. The absorption-edge position for the MIX shifts to higher energy side compared with that for the Pd bulk. Similarly, the energy position of the samples 1-3 is higher than that of Pd bulk. Thus, it might be thought that the Pd–Mg alloy phase exists in the sample 1-3. But the peak position originated from MIX is observed at higher energy side compared with PdO. It might be thought that this large peak shift depends on the rate of the amount of Pd and Pd–Mg alloy. In future, revealing whether the Pd–Mg alloy phase exists between Pd and Mg or not is necessary.

Figure 4 shows Mg K-edge NEXAFS spectra obtained by TEY method. TEY method possesses a high sensitivity for the surface chemical state. In samples 1-3, the Pd–Mg interface exists more superficial than Mg bulk layer. Figure 4(b) is the magnification of the region between 1298.0 eV and 1308.0 eV in Fig. 4(a). The absorption-edge position of the MIX shifts to lower energy side compared with Mg bulk. Therefore, the Mg provides the electron to the Pd. For the samples 1-3, a little shift is observed at the absorption-edge. For these reasons, the chemical state other than Pd and PdO exists between Pd and Mg. It has possibility that this state is the Pd-Mg alloy phase. The future plan is to verify that this state is the Pd–Mg alloy phase through XRD and XPS Mg 2p measurements.

IV. CONCLUSIONS

We have investigated the chemical states for the samples prepared by the methods of DC magnetron sputtering, vacuum evaporation and nanoparticle deposition, by XPS and NEXAFS measurements. Judging from the results of XPS and NEXAFS, there is the chemical state other than Pd and PdO. It has possibility that this state is the Pd-Mg alloy phase.
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