Abnormal Hydrogen Absorption/Desorption Properties of Nanoporous Pt with Large Lattice Strains

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Hydrogen absorption/desorption properties of nanoporous Pt fabricated by dealloying were investigated. At high pressure (> 1.3 MPa), the nanoporous Pt released hydrogen during hydrogen pressurization; in contrast, it absorbed hydrogen up to 3.5 atom% during hydrogen depressurization, which have not been seen in current metal/hydride systems including nanoparticles. First-principles calculations suggested that the abnormal hydrogen absorption/desorption properties are due to the relaxation/preservation of the lattice strain in Pt hydride. [doi:10.2320/matertrans.M2010403]

1. Introduction

Nanoporous metals have recently been generating recent research interest[1] although the formation of nanoporosity itself has been known for a long time.[2] Nanoporous structures have distinctive properties that have not been observed in conventional nanostructured materials. Moreover, the extraordinarily large surface area per apparent volume is useful for catalytic[3] and sensing[4] applications. The authors have found that the nanoporous Pd exhibits different hydrogen absorption properties from the Pd nanoparticles owing to the surface effects.[5]

Recently, it has been reported that Pt nanoparticles with a diameter of 2–3 nm absorb hydrogen, whereas bulk Pt does not.[6,7] In this Rapid Publication, we describe the abnormal hydrogen absorption/desorption properties of nanoporous Pt, which is produced by dealloying, with a ligament size of ∼3 nm. High H_2 pressure (> 1 MPa) leads to dehydrogenation, which is opposite to the hydrogenation behavior in hydrogen-absorbing materials including advanced nanoparticles. First-principles calculations on the formation energy of Pt hydride are performed to determine the origin of the abnormal hydrogen absorption/desorption properties.

2. Experimental

Nanoporous Pt was fabricated by electrochemical dealloying of a $Pt_{0.2}Cu_{0.8}$ alloy sheet in 1 M H_2SO_4 for 12 h under the potentiostatic condition at $+1.1$ V vs a saturated calomel electrode at room temperature.[8,9] Figure 1(a) shows the microstructure of the dealloyed nanoporous Pt. The ligament size of the nanoporous Pt was ∼3 nm. The lattice contraction and expansion in the nanoporous Pt are shown in Fig. 1(b). As shown in Fig. 1(b), large lattice strains of approximately
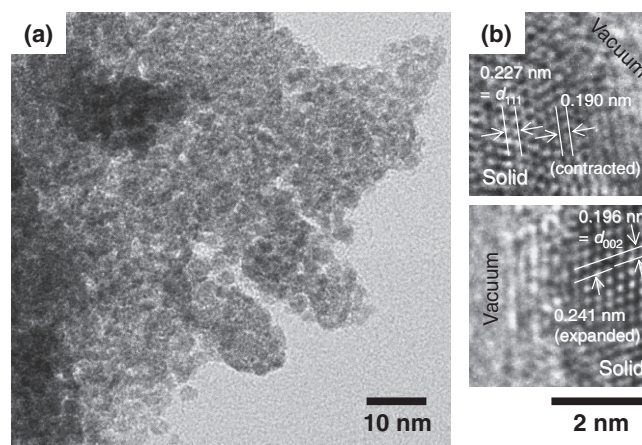

Fig. 1 (a) Transmission electron microscopy image of the dealloyed nanoporous Pt. (b) High-resolution transmission electron microscopy images of the dealloyed nanoporous Pt. Complex disordered structures with marked lattice contraction and expansion are found near the surfaces.

18% were found near the surfaces. Note that the nanoporous Pt had complex disorder structures with marked lattice contraction and expansion. The significant disorder is due to the very small ligaments.[5,10] The X-ray diffraction (XRD) profile (Fig. 2) of the nanoporous Pt before PCT measurement had a broadened peak, which suggests that the ligament and pore sizes are very small and that the crystal lattice of Pt is significantly disordered. Elemental analysis by energy-dispersive X-ray spectroscopy detected no residual Cu after dealloying. After pretreatment of the samples in vacuum for 5 h at 373 K for activation, a pressure-composition isotherm (PCT) was measured by a JIS H 7201 method[11] at 298 K where the volumetric technique is employed under fully isothermal condition.

3. Results

PCT of nanoporous Pt is shown in Fig. 3. The H absorption in the pressure range of 0.01–0.1 MPa was enhanced

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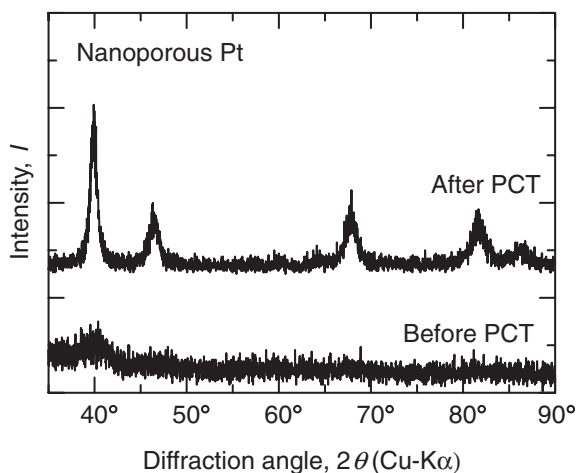*3Graduate Student, Kyoto University

Fig. 2 X-ray diffraction patterns of nanoporous Pt before and after PCT measurement.
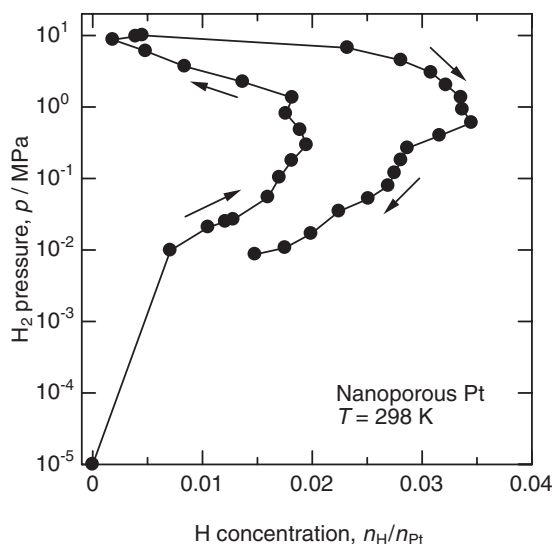

Fig. 4 Relationship between the formation energy of PtH (ΔE) and the lattice strain in Pt (y) calculated by first-principles calculations. In the strain-remaining case, PtH has the same strain as Pt. In the strain-relaxed case, the strain in PtH is relaxed.

Fig. 3 Pressure-composition isotherm for the nanoporous Pt. Note that the nanoporous Pt releases H during H_2 pressurization at high pressure; in contrast, it absorbs H during depressurization.

where the H_2 pressure is nearly constant. Recently, the absence of plateau region has been found for Pd nanoparticles.[6,12] Also, Pt nanoparticles showed a monotonic relationship between the H_2 pressure and the concentration.[6,7] The hydrogenation during pressurization and the dehydrogenation during depressurization are common to conventional hydrogen-storage materials and advanced nanoparticles, irrespective of the presence or absence of plateau region. However, the nanoporous Pt exhibited the dehydrogenation during pressurization and the hydrogenation during depressurization at high H_2 pressure. Thus, the hydrogen absorption/desorption properties of the nanoporous Pt are quite different from those of not only the conventional hydrogen-storage materials but also advanced nanoparticles.

4. Discussion

The hysteresis in PCT curves is often affected by irreversible changes or lattice defects such as dislocations.[13,14] On the other hand, lattice strain effect on hydrogenation on Pd nanoparticles[15] and epitaxial Nb films[16] has been pointed by Langhammer et al.[15] and Allain and Heuser[16] respectively, although the present abnormal PCT (Fig. 4) has not been reported so far. The present nanoporous Pt has the remarkably disordered structures with lattice contraction and expansion. The large lattice strain is likely to be responsible for the abnormal hydrogen absorption/desorption properties. To investigate the strain effect on the hydride formation, first-principles calculations were conducted within the generalized gradient approximation proposed by Perdew et al.,[17] using the CASTEP code. The electron-ion interaction was described on the basis of ultrasoft pseudopotentials for H and Pt with a cutoff energy of 400 eV. Brillouin zone integration was performed with a grid of $12 \times 12 \times 12$ special k-points. It is known that Ni and Pd form stable hydrides (NiH_x and PdH_x)[18,19] with a face-centered-cubic crystal structure; hence, the crystal structure of Pt hydride (PtH) was assumed to be of the NaCl type. The formation energy of Pt hydride can be calculated as

compared with that in the range less than 0.01 MPa, showing that the nanoporous Pt reacted with H in the pressure range of 0.01–0.1 MPa. The H concentration was nearly constant during H_2 pressurization in the pressure range of 0.5–1.3 MPa. Surprisingly, the nanoporous Pt released the hydrogen during H_2 pressurization in the pressure range of 1.3–9.8 MPa. After the release of hydrogen during pressurization, the H concentration increased with increasing H_2 pressure from 9.8 MPa to a maximum pressure of 10 MPa. After the maximum pressure of 10 MPa was achieved, the H_2 pressure was reduced for depressurization. Surprisingly again, the H concentration increased with decreasing H_2 pressure from 10 to 0.6 MPa. Finally, the H concentration decreased with decreasing H_2 pressure in the range less than 0.6 MPa. Thus, at high H_2 pressure, the nanoporous Pt released hydrogen during H_2 pressurization; in contrast, it absorbed hydrogen during H_2 depressurization. In general, the PCTs of conventional hydrogen-storage materials show the plateau region
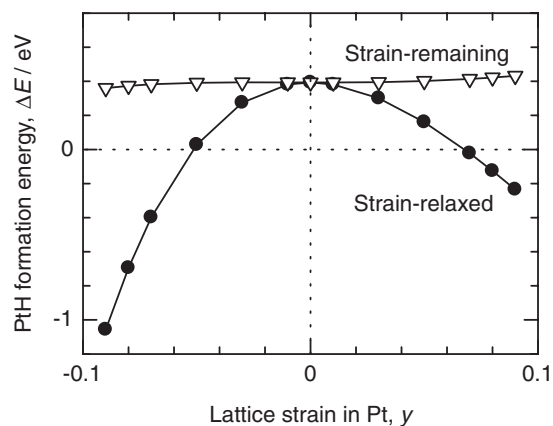
$$\Delta E = E_{total}(PtH) - E_{total}(Pt) - 1/2\,E_{total}(H_2), \quad (1)$$

where ΔE is the formation energy of the Pt hydride, and $E_{total}(Pt)$, $E_{total}(PtH)$, and $E_{total}(H_2)$ are the total energies of Pt, PtH, and gaseous H_2, respectively. After the lattice constants (or interatomic distances) with no strain were determined by the geometrical optimization of the primitive cells of Pt and PtH, lattice strain from -9 to $+9\%$ was introduced by changing the lattice constant of the primitive cells. Considering the strain, the formation energy of PtH from the strained Pt, ΔE, can be calculated as

$$\Delta E = E_{total}(PtH, x) - E_{total}(Pt, y) - 1/2\,E_{total}(H_2), \quad (2)$$

where x and y are the strains in the primitive cells of PtH and Pt, respectively. In this work, the formation energy of Pt hydride from the strained Pt has been calculated in two cases: the strain-remaining case where the lattice strain in PtH is kept unchanged during hydrogenation, and the strain-relaxed case, where the lattice strain in PtH is relaxed during hydrogenation. In the strain-remaining case, PtH have the same strain as Pt ($x = y$); on the other hand, in the strain-relaxed case, the strain in PtH is fully relaxed during hydrogenation ($x = 0$). Figure 4 shows the relationship between the formation energy of Pt hydride ($= \Delta E$) and the strain in Pt ($= y$). When the lattice is not strained ($y = 0$), the formation energy of Pt hydride is positive. This agrees with the fact that Pt hydride is not formed in bulk Pt. In the strain-remaining case, where the strain remains unchanged during Pt hydride formation, the formation energy of Pt hydride does not depend on the strain and it is positive in the strain range investigated, indicating that the no Pt hydride is formed when the lattice strain is not relaxed. On the other hand, when the strain in Pt hydride, irrespective of whether it is positive or negative, is relaxed (the strain-relaxed case), the formation energy of Pt hydride decreases monotonically with increasing strain. It is worth noting that the formation energy of Pt hydride is negative when the strain of 6% in expansion and 5% in contraction is relaxed. This indicates that the stable Pt hydride is formed by the relaxation of lattice strain.

The PCT curve in Fig. 3 indicates that nanoporous Pt absorbs hydrogen during H_2 pressurization in the range of 0.01–0.1 MPa, but it releases hydrogen during hydrogen pressurization in the range of 1.3–9.8 MPa. This fact indicates that Pt hydride is generated in the pressure range of 0.01–0.1 MPa; however, it is unstable at a higher H_2 pressure. Another abnormal behavior observed is that the hydrogen is again absorbed during hydrogen depressurization in the range of 0.6–10 MPa, suggesting that Pt hydride is formed during hydrogen depressurization. Interestingly, the maximum amount of hydrogen absorption during H_2 depressurization surpassed that during H_2 pressurization. Therefore, the lattice strain in Pt hydride is likely to be relaxed during H_2 depressurization. Figures 5(a) and 5(b) shows microstructures of the nanoporous Pt after the PCT measurement. Note that the ligaments coarsened to about 20 nm and that the lattice strain was fully relaxed; one may presume that the relaxation of lattice strain is related to the coarsening during the PCT measurement. The XRD profile with sharp peaks (Fig. 2) also indicated the coarsening after the PCT measurement.
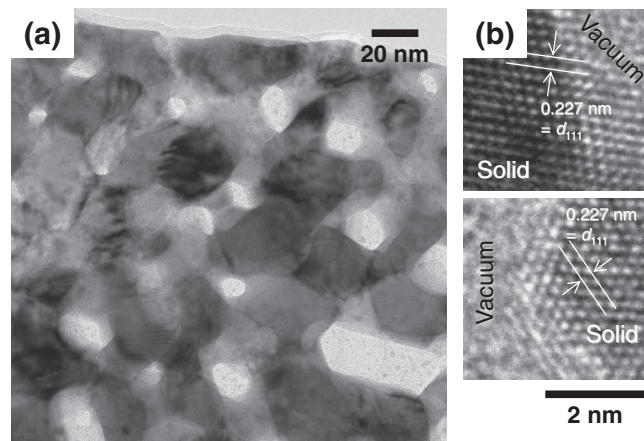

Fig. 5 (a) Transmission electron microscopy image of the nanoporous Pt after the PCT measurement. The ligaments coarsened to about 20 nm. (b) High-resolution transmission electron microscopy images of the nanoporous Pt after the PCT measurement. Lattice strain was fully relaxed after the PCT measurement.

The nanoporous structure is coarsened by thermal treatment[8,20,21] and acid treatment.[22] On the other hand, the present results showed that coarsening occurs at an ambient temperature without acid and electrochemical treatments. Recently, Di Vece et al.[23] demonstrated the coarsening of a Pd nanocluster film by hydrogen exposure. They attributed the coarsening to the difference in sublimation energy between Pd and its hydride. In the present study, however, sublimation hardly occurs at the high hydrogen pressure of 10 MPa. The other possible reason for enhanced surface diffusion is excessive vacancies. The nanoporous Pt absorbed hydrogen in the range of 0.01–0.1 MPa and the Pt hydride was formed, but it decomposed into Pt and H during hydrogen pressurization in the range of 1.3–9.8 MPa. During the decomposition, the H site is apt to be replaced by a vacancy because the mobility of H is much higher than that of Pt, resulting in excessive vacancies. Furthermore, the surface diffusion may be enhanced by depressurization.[24] Thus, the coarsening occurs during hydrogen depressurization, which makes the Pt hydride stable. *In situ* characterization such as XRD during hydrogenation will help further understanding.

5. Conclusions

Nanoporous Pt released hydrogen during hydrogen pressurization; in contrast, it absorbed hydrogen during hydrogen depressurization. The abnormal hydrogen absorption/desorption properties of nanoporous Pt are suggested to be due to the relaxation/preservation of the lattice strain in the Pt hydride. Although the abnormal PCT behavior itself is not good for hydrogen storage, the present result indicates the considerable effect of the hydrogen absorbed in nanostructured Pt materials. There will be much room for study on the hydrogenation of nanoporous Pt.

Acknowledgement

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