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Characteristics of the absorption and the emission of hydrogen in palladium nanoparticles encapsulated into graphite at 1.0 MPa hydrogen pressure

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Abstract

Palladium nanoparticles encapsulated into graphite (Pd–graphite intercalation compound: Pd–GIC) were produced from two kinds of graphite, natural graphite (average flake size: 270 μm) and kish graphite (average flake size: 15 μm). Hydrogen storage properties of Pd–GIC have been investigated by means of differential scanning calorimetry (DSC) between 473 and 573 K at 1.0 MPa hydrogen pressure. It is found from the DSC measurement that Pd–GIC can absorb and emit hydrogen.

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Keywords: Graphite intercalation compound; Hydrogen storage; Palladium; Encapsulated nanoparticle; Differential scanning calorimetry

1. Introduction

The architecture of environmental-friendly material processing is desired intensively to cope with various environmental issues on exhaustion of energy sources, waste emissions, and so on. Especially, the development of materials related to energy storage and energy transformation is an urgent subject on the advanced materials science and technology.

Hydrogen as a clean energy source has received considerable attentions in recent years. The technique for hydrogen storage is one of the most important subjects for clean and sustainable energy system with hydrogen because of its high combustibility. Hydrogen storage alloys can absorb hydrogen with more safety and higher density than the storage of hydrogen as compressed gas or liquid hydrogen. The hydrogen storage alloys, however, usually change their volumes during absorption and emission of the gas. They sometimes, therefore, disintegrate themselves and reduce their hydrogen capacity after long cycle usage [1–4]. In order to avoid the disintegration, the encapsulation of the powder

of hydrogen storage alloys with metal films has been proposed [1,5–7].

Meanwhile, we have succeeded in producing quasi two-dimensional palladium nanoparticles encapsulated into graphite (Pd–graphite intercalation compound: Pd–GIC) [8–11]. Then, it was found that those Pd nanoparticles indicate some peculiar properties, such as catalysis [10,12] and magnetism [11,13], which differ from those of the bulk palladium. It is well known that the bulk palladium can store the hydrogen. Since no information on the hydrogen storage properties of Pd–GIC has been given so far, we should elucidate the behavior of Pd–GIC in hydrogen atmosphere. In addition, the production of the above Pd–GIC [8–11] was carried out by using natural graphite, but the effect of graphite-types on the GIC stage structures has not been understood yet. There are many sorts of graphite with various specifics, e.g. flake size, bulk density, surface area, and so on. They can be sometimes obtained as by-products in steelmaking processes.

In the present work, we have produced Pd–GIC by using two kinds of graphite as the host intercalation materials, natural graphite and kish graphite. Then, the hydrogen storage properties of Pd–GIC have been investigated by means of differential scanning calorimetry (DSC) between 473 and 573 K at 1.0 MPa hydrogen pressure.

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Table 1
Average flake size, bulk density and BET surface area of the host graphite

	Average flake size/ μm	Bulk density/ g cm^{-3}	BET/ $\text{m}^2 \text{g}^{-1}$
Natural graphite	270	1.4	0.52
Kish graphite	15	5.8	0.33

2. Experimental

In order to produce Pd–GIC, two kinds of graphite are used here; one is natural graphite (Graphitwerke Kropfmühl, 99.95%, average flake size: 270 μm) and the other is kish graphite supplied by Nippon Steel Chemical Co., Ltd. (average flake size: 15 μm). Average flake size, bulk density and BET surface area of the host graphite are shown in Table 1. The procedure of Pd–GIC preparation is almost the same as shown in the literature [9]. The precursor (PdCl₂–GIC) is obtained by the following procedure; PdCl₂ mixed with host graphite is sealed in a glass ampoule in chlorine atmosphere, and is heated at 600 °C for 1 week. PdCl₂–GIC production is confirmed by XRD (RINT2500V, RIGAKU). Pd–GIC is synthesized by the reduction of PdCl₂–GIC in a solution of lithium diphenylide in THF at room temperature for 1 week. An outline of Pd–GIC preparation procedure is shown in Fig. 1.

The behavior of the absorption and the emission of hydrogen in Pd–GIC are investigated by DSC in high H₂ gas atmosphere. The DSC of Pd powder and of natural graphite is also carried out in order to compare the above DSC measurement with that of Pd–GIC. The weight of each sample for DSC measurement is 15 mg. At 1.0 MPa hydrogen pressure, the temperature rises from room temperature to 573 K, and then the temperature changes cycles eight times for Pd–GIC (three times for Pd powder

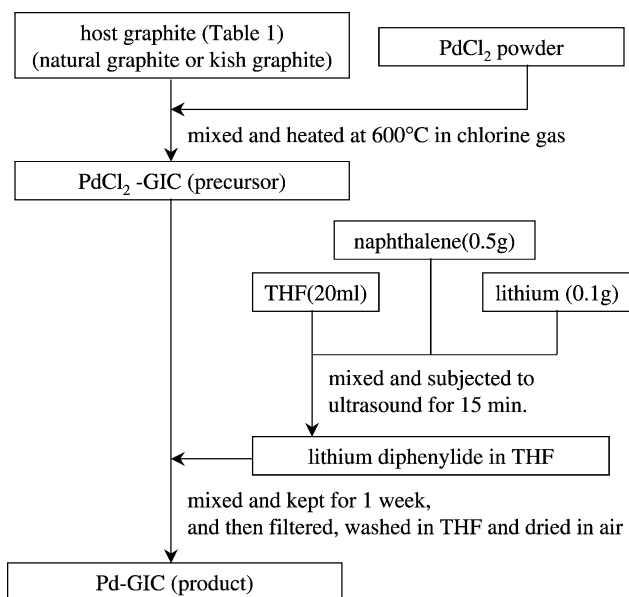


Fig. 1. Outline of the procedure of Pd–GIC preparation.

and natural graphite) between 473 and 573 K. The heating and cooling rate is 10 K min⁻¹. Before and after the DSC measurements, Pd–GIC, whose host graphite is natural graphite, was studied by TEM (Hitachi 9000) at 300 kV.

3. Results and discussion

XRD patterns of the PdCl₂–GIC (precursor) and the reduced Pd–GIC (product) are shown in Figs. 2 and 3. The host graphite used is natural graphite in Fig. 2, and kish graphite in Fig. 3, respectively. From the analysis of the XRD patterns in Fig. 2, we found that the precursor obtained from the natural graphite has the seventh stage structure (Intercalation layer distance: $I_c \cong 2.67 \text{ nm}$) of PdCl₂–GIC, while the second stage structure ($I_c \cong 1.10 \text{ nm}$) of PdCl₂–GIC exists in the precursor from the kish graphite. The lower stage structure of PdCl₂–GIC means that the more amounts of PdCl₂ molecules are intercalated in the graphite layers. Thus, it is found that more PdCl₂ molecules are stored in the kish graphite than the natural graphite.

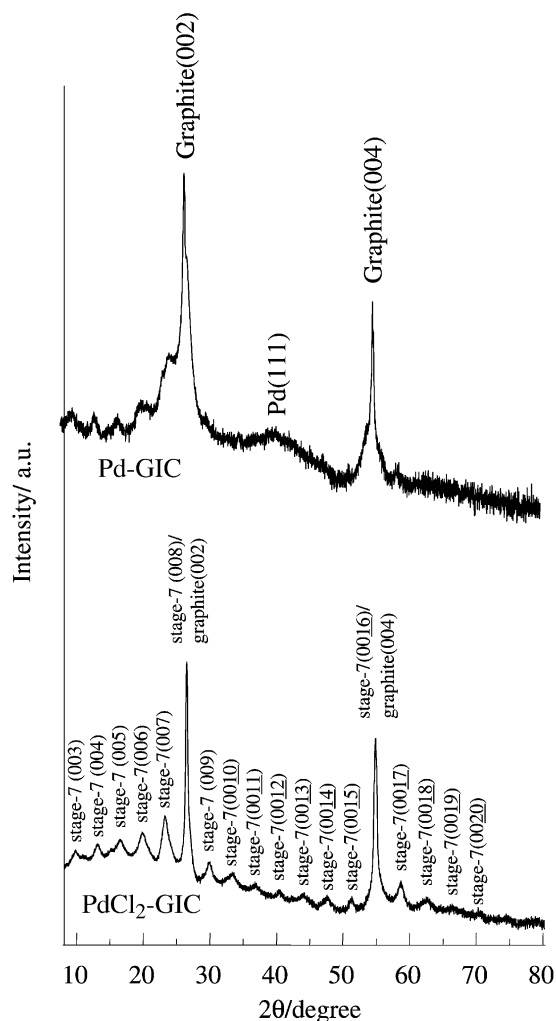


Fig. 2. XRD patterns of the PdCl₂–GIC precursor and of the reduced Pd–GIC. The host graphite used is natural graphite.

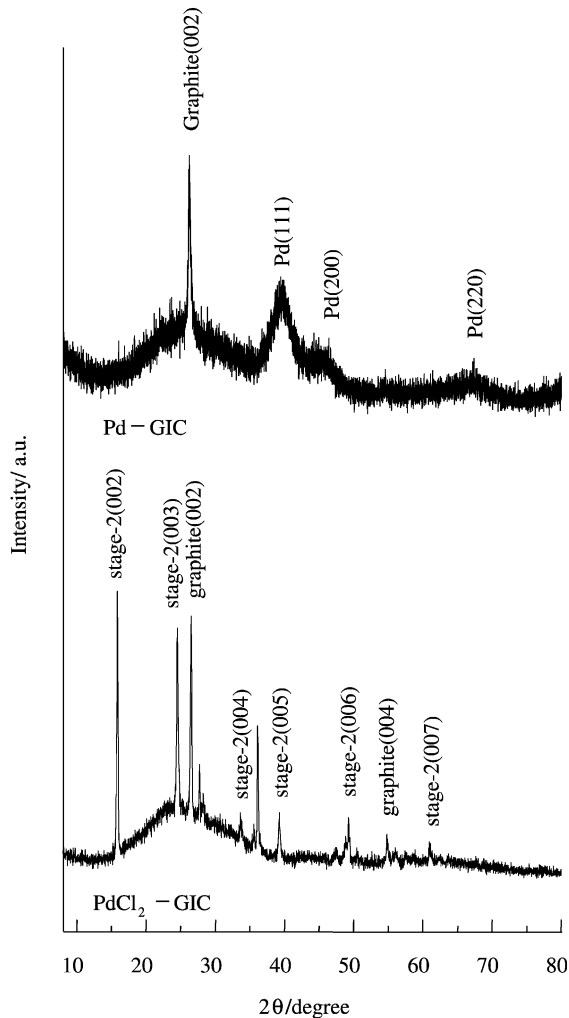


Fig. 3. XRD patterns of the PdCl_2 -GIC precursor and of the reduced Pd-GIC. The host graphite used is kish graphite.

This result stems from that the flake size of the natural graphite is larger than that of kish graphite. Then, the PdCl_2 could penetrate easily into the molecular layers in kish graphite compared to those in the natural graphite. No peaks indexed as PdCl_2 are observed in the pattern of the precursors. As can be seen in Fig. 3, XRD patterns of the products (Pd-GIC) contain the peaks indexed as graphite and palladium, indicating the success of synthesis of Pd-GIC.

Figs. 4 and 5 show the experimental results of DSC for Pd-GIC at 1.0 MPa hydrogen pressure in the temperature region between 473 and 573 K. The host graphite used is natural graphite in Fig. 4, and kish graphite in Fig. 5, respectively. The results of the DSC curves for Pd powder and natural graphite are given in Figs. 6 and 7 which were obtained at the same conditions as those for the above Pd-GIC. Fig. 6 represents sharp heat-flow peaks, which correspond to hydrogen absorption and emission [14] of Pd during heating and cooling periods, respectively. Although no peaks are observed in Fig. 7 indicating that natural graphite does not absorb and emit hydrogen in

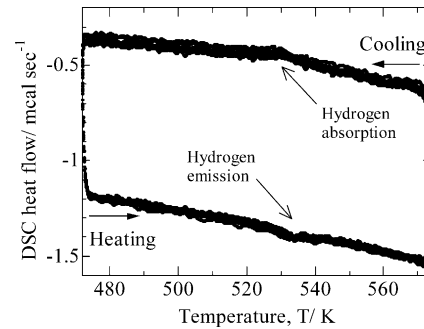


Fig. 4. Differential scanning calorimetry of Pd-GIC (natural graphite) at 1.0 MPa hydrogen pressure between 473 and 573 K. The heating and cooling rate is 10 K min^{-1} .

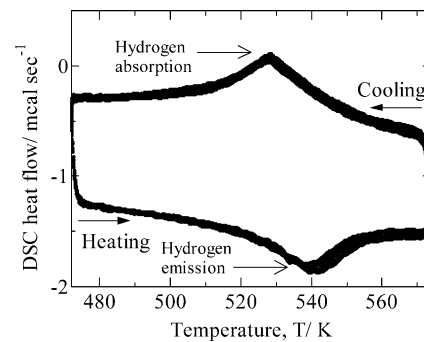


Fig. 5. Differential scanning calorimetry of Pd-GIC (kish graphite) at 1.0 MPa hydrogen pressure between 473 and 573 K. The heating and cooling rate is 10 K min^{-1} .

the temperature between 473 and 573 K, Pd-GICs in Figs. 4 and 5 show broad heat-flow peaks during heating and cooling periods. It was found from these results in Figs. 4–7 that Pd nanoparticles, which are intercalated in the graphite, absorb and emit hydrogen between 473 and 573 K.

Table 2 summarizes the total calories of heat-flow peaks observed in the above DSC measurement. As can be seen in this table, since smaller amount of Pd nanoparticles existed in Pd-GIC compared to pure Pd powder, the total heat-flow in Pd-GIC are smaller than

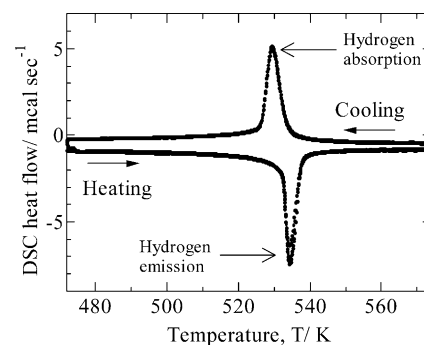


Fig. 6. Differential scanning calorimetry of Pd powder at 1.0 MPa hydrogen pressure between 473 and 573 K. The heating and cooling rate is 10 K min^{-1} .

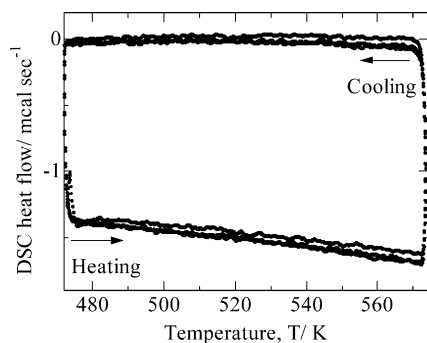


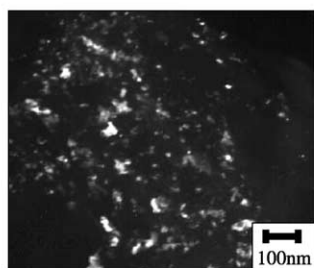
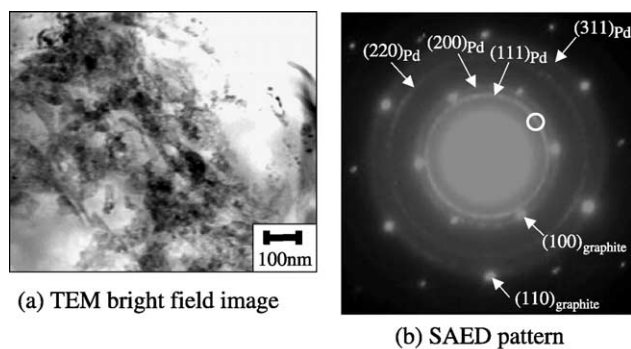
Fig. 7. Differential scanning calorimetry of natural graphite at 1.0 MPa hydrogen pressure between 473 and 573 K. The heating and cooling rate is 10 K min^{-1} .

Table 2

Total calories of heat-flow peaks in DSC measurement for Pd–GIC (natural graphite and kish graphite) and Pd powder at 1.0 MPa hydrogen pressure in the temperature region between 473 and 573 K

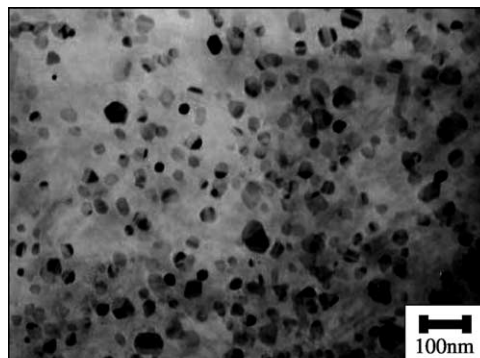
	Pd–GIC (natural graphite)	Pd–GIC (kish graphite)	Pd powder
Absorption (mcal)	$\cong 3 \text{ mcal}$	100–110 mcal	190–200 mcal
Emission (mcal)	$\cong 3 \text{ mcal}$	70–80 mcal	215–225 mcal

that of Pd powder although the former peaks amount to about half of those in the latter. In addition, the total calories of heat-flow peaks for Pd–GIC made of the kish graphite are much larger than that for Pd–GIC from



(c) TEM dark field image

Fig. 8. TEM images and SAED pattern of Pd–GIC (natural graphite) before DSC measurement. The white open circle in Fig. 8(b) corresponds to the dark field image (Fig. 8(c)).



(a) TEM bright field image



(b) SAED pattern

Fig. 9. TEM bright field image and SAED pattern of Pd–GIC (natural graphite) after DSC measurement.

the natural graphite. These results agree with the results on the stage structures, in which more PdCl_2 molecules are intercalated in the kish graphite compared to the natural graphite as described above.

Fig. 8(a) and (b) show a TEM bright field image and a SAED pattern of Pd–GIC made of the natural graphite before the DSC measurement. The spots corresponding to graphite and the rings for polycrystalline palladium can be seen in Fig. 8(b). Fig. 8(c) shows a TEM dark field image at the point indicated in the white open circle in Fig. 8(b). It is found from Fig. 8(c) that the average size of palladium nanoparticles before the DSC measurement is about 5–10 nm. This result practically agrees with the previous work [9]. Fig. 9(a) and (b) show a TEM bright field image and a SAED pattern of Pd–GIC (natural graphite) after the DSC measurement. It is found that the average size of palladium nanoparticles after the DSC measurement is about 20 nm, namely, the palladium particle size becomes bigger after the DSC measurement. Since it has been reported that the average size of palladium nanoparticles encapsulated into graphite reduced in hydrogen at $600 \text{ }^\circ\text{C}$ was about 50 nm [8], it

is considered that the palladium particle size increases because of heat treatments during the DSC measurements.

4. Conclusion

PdCl₂-GIC (precursor) and the palladium nanoparticles encapsulated into graphite (Pd-GIC) were produced by using two kinds of graphite, natural graphite (average flake size: 270 μm) and kish graphite (average flake size: 15 μm), as the host intercalation materials. We found that the precursor obtained from the natural graphite has the seventh stage structure ($I_c \cong 2.67$ nm) of PdCl₂-GIC, while that the second stage structure ($I_c \cong 1.10$ nm) of PdCl₂-GIC exists in the precursor from the kish graphite. Then, the hydrogen storage properties of palladium nanoparticles encapsulated into the natural graphite and the kish graphite (Pd-GIC) have been investigated by DSC between 473 and 573 K at 1.0 MPa hydrogen pressure. It is found that Pd-GIC can absorb and emit hydrogen, and that the size of palladium nanoparticles encapsulated in graphite increases after heating and cooling cycles.

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