Journal of Alloys and Compounds 664 (2016) 188–192

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Hydrogen absorption/desorption properties of porous hollow palladium spheres prepared by templating method

Qingquan Kong [a, *], Wei Feng [a], Xiaoxi Zhong [b], Ying Liu [c], Lixian Lian [c]

[a] School of Mechanical Engineering, Chengdu University, Chengdu 610106, PR China
[b] Sichuan Province Key Laboratory of Information Materials and Devices Application, Chengdu University of Information Technology, Chengdu 610225, PR China
[c] School of Materials Science and Engineering, Sichuan University, Chengdu 610065, PR China

ARTICLE INFO

Article history:
Received 17 October 2015
Received in revised form
20 December 2015
Accepted 28 December 2015
Available online 30 December 2015

Keywords:
Hollow
Palladium
Hydrogen absorption/desorption properties
Microstructure

ABSTRACT

In the present study, hydrogen absorption/desorption properties of porous hollow palladium spheres prepared by templating method were studied. The experimental results reveal that porous hollow Pd spheres have superior hydrogen absorption kinetics than spongy Pd. A typically pressure hysteresis behavior can also be observed in the hydrogen absorption/desorption isotherm curves. Gibbs free energy loss ΔG_{loss} correlation with pressure hysteresis of porous hollow Pd spheres is 4.3–4.8 kJ/mol, which is larger than spongy Pd and Monocrystal Pd. The special hollow structure and microstructure defects of Pd powder should be taken into account. Moreover, hydride formation enthalpy of porous hollow Pd spheres is smaller than spongy Pd and Pd black.

1. Introduction

Owing to its special physical and chemical properties, palladium is promising as a material in hydrogen related fields such as hydrogen storage, hydrogen isotopes separation, hydrogen purification, hydrogen detection and so on [1–6]. Spongy palladium powders were conventional active materials in the hydrogen isotope treatment process [7,8]. However, the low surface area and nonuniform microstructure will restrict its further application. Palladium loading on/in alumina (Pd–Al_2O_3) with high specific surface area and normatively spherical microstructure was utilized as the separation material in hydrogen isotopes separation [9]. The separation efficiency was fine, even the application of only single column. Recently, increasing researches were focused on nanostructured palladium materials according to the dramatic increase of the specific surface and their unique microstructure [10–17]. Compared to conventional palladium materials such as spongy Pd and bulk Pd, nanostructured palladium materials possessed high surface area and more surface atoms, which are beneficial to hydrogen isotopes storage and separation [18,19]. As a new type of nanostructured Pd materials, Pd particles with hollow structure or porous structure can increase their property such as electrochemical oxidation and hydrogen application due to their large surface area and unique microstructure [20–22].

Hollow spheres can be prepared by templating methods using template particles such as polystyrene beads, emulsion-templated silica beads or silica colloids [22–25]. In the former study, porous hollow palladium particles with uniform size distribution have been successfully prepared, electrochemical properties of which were tested and results reveal that it has superior ethanol oxidation ability [26]. Porous hollow Pd spheres can also be utilized as active materials in hydrogen application field. However, the hydrogen absorption/desorption properties of porous hollow Pd spheres are unclear. The properties of Pd materials may be changed when the particle size decreases to nanoscale [11]. Thus, it is necessary to clarify the hydrogen storage properties of porous hollow Pd spheres.

In this article, we report the fabrication of homogenous porous hollow Pd sphere by templating method. Moreover, hydrogen absorption/desorption properties of these resultant porous hollow Pd materials were also investigated.

* Corresponding author.
E-mail address: kongqingquan@163.com (Q. Kong).

http://dx.doi.org/10.1016/j.jallcom.2015.12.234
0925-8388/

2. Experimental

2.1. Preparation of porous hollow Pd particles

Porous hollow Pd spheres were prepared by templating method with silica colloids sphere as a template material was detailed described in the previous study [26]. Briefly, Silica colloids sphere with particle size of ~500 nm were prepared by a modified stöber method. Then Pd@SiO_2 particles were prepared by electroless plating of Pd with hydrazine hydrate as reducing regent. The prepared Pd@SiO_2 particles were corroded in 1M NaOH aqueous solution at 60 °C to remove template materials. The resultant materials were centrifuged and washed with deionized water, and then dried in a vacuum chamber. All reagent utilized in this experiment are analytical pure.

2.2. Characterization

The samples were characterized with a field-emission scanning electron microscope (FESEM, XL30SFEG) equipped with an X-ray energy spectrometer (EDS) for microstructure and elemental analyses. Transmission electron microscope (TEM) was utilized for high resolution imaging. X-ray diffraction patterns were recorded by an X-ray diffractometer (XRD, DX-2000) with Cu Kα radiation. Surface areas of porous Pd samples and spongy Pd powders were measured by a N_2 adsorption apparatus. Hydrogen absorption kinetics curve of porous hollow Pd spheres and spongy Pd powders were obtained at a pressure of 100 kPa and at 298 K. The Sieverts-type device was applied to test the hydrogen absorption-desorption properties of the porous hollow Pd spheres at 373 K, 423 K and 473 K, respectively. High purity hydrogen (99.999%) was employed in this work.

3. Results and discussion

Fig. 1 shows the XRD pattern of the prepared porous hollow Pd spheres. Only Pd peak can be detected. It reveals that the resultant Pd materials presents a highly crystallized and fcc crystalline structure. Microstructure of porous hollow Pd spheres is shown in Fig. 2. From Fig. 2a, Pd particles with hollow structure can be observed. According to TEM results, porous hollow structure of the prepared palladium particles is further confirmed (as shown in Fig. 2b). Silica colloids can be easily eroded completely in 1M NaOH aqueous solution at 60 °C [26]. Afterward, Pd spheres with hollow structure can be obtained. Moreover, the porous palladium shells are consisting of palladium nanoparticles. The porous hollow Pd particles have a high BET area of ~10 m^2/g, which is higher than conventional spongy powder (~0.31 m^2/g).

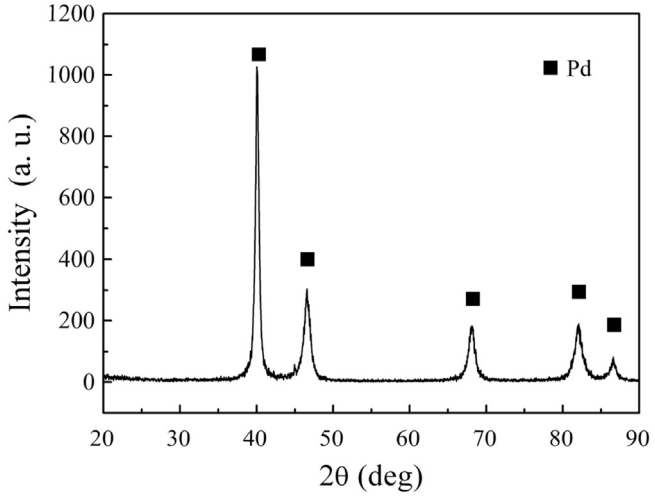

Fig. 1. XRD pattern of porous hollow Pd spheres.

Fig. 3 shows the HRTEM images and their SAED pattern of the porous hollow Pd spheres. It can be seen that the lattice spacing was approximately 0.226 nm, which is equal to (110) plane of Pd. Lattices expanded and contracted were detected in nanoporous Pd prepared by dealloying method, which may significantly influence the hydrogen storage properties of Pd materials [27]. It is obviously that none of expanded or contracted of Pd lattice can be observed in the present study. As can be seen from the inset of Fig. 3b, the SAED pattern was found to be diffraction ring indicating that the palladium nanoparticles are polycrystalline and can be indexed to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) from inside to outside reflections from face-centered cubic (fcc) Pd.

Hydrogen storage properties of Pd and Pd alloys were intensively studied [3,28,29]. Particularly, nanostructured Pd with different morphology is a promising material for hydrogen applications [13,14]. Thus, the porous hollow palladium also can be utilized to investigate their hydrogen isotope storage properties. Reaction ratio *F* of Pd materials is the complete degree of hydrogen adsorption. The hydrogen extent of reaction at *t* can be defined according to the Equation (1),

$$F = \frac{n_t}{n_{\max}} \tag{1}$$

Where n_t is the hydrogen amount in Pd at *t*, n_{max} the amount of hydrogen absorption at the equilibrium state. Hydrogen absorption kinetics curve of porous hollow Pd spheres and spongy Pd powders are shown in Fig. 4. Porous hollow Pd spheres show improved hydrogen sorption kinetics than spongy Pd powders. Due to the high surface area of porous hollow Pd spheres (~10 m^2/g), more active sites can be provided, and which is beneficial for hydrogen adsorption and dissociation. Hydrogen absorption/desorption kinetics will be improve and enhance when the grain size of metal hydride reduced to 1–100 nm [15]. Moreover, the prepared porous hollow Pd powders have special shell structure. Thus, long range diffusion distance of hydrogen atoms in solid state Pd can be shortened. It is interesting to note that the total content of hydrogen absorption in porous hollow Pd decreased slightly. The shell structure of porous hollow Pd spheres that consist of Pd nanoparticles with particle size of tens nanometers should be the main cause (as shown in Fig. 2b). Excessive refinement of Pd particles will reduce the interstitial site of hydrogen storage [12,15,16]. Consequently, total hydrogen absorption content of porous hollow Pd spheres slightly decrease.

PCT curves of porous hollow Pd spheres are shown in Fig. 5. The hydrogen content (H/Pd) increases with hydrogen pressure at 373 K, 423 K and 473 K, which shows that porous hollow Pd spheres absorb hydrogen. From Fig. 5a, a typically plateau-like region can be observed where solid solution α and Pd hydride phases βcoexist. The pressure of the plateau-like region increase as the temperature increased, which is coincided with previous report [30]. The intermediate pressure of the plateau-like region in the hydrogen absorption is larger than the equilibrium pressures for bulk Pd that only 36 kPa at 373 K [31]. PCT curves of hydrogen desorption also show the same phenomena (shown in Fig. 5b). The plateau-like region widths for the porous hollow Pd spheres became smaller with increasing temperature. Hysteresis behavior also can be observed in the PC hydrogen absorption/desorption isotherm curves (shown in Fig. 5). Gibbs free energy loss ΔG_{loss} correlation with pressure hysteresis can be calculated by equation below [30],