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The surface decoration and electrochemical hydrogen storage of carbon nanofibers

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Abstract

The tube-like CNFs with cone-shaped structure were synthesized by catalytic pyrolysis of methane. The outer surface of purified CNFs was decorated with Ni–P alloy particles having polycrystalline or nanocrystalline structure instead of amorphous structure. The low Ni–P content appeared to be more efficient to cover the outer surface of CNFs. The electrochemical discharge capacity increased with increasing the Ni–P content on the outer surface of CNFs owing to the synergistic effect between metal and carbon in the electrochemical reaction. The heat treatment contributed to the higher crystallization of surface alloy and improvement of the electrochemical capacity of the composite. © 2003 Elsevier Science B.V. All rights reserved.

1. Introduction

 AB_5 , AB_2 and Mg-based hydrogen storage alloys have been investigated extensively as electrode materials of Ni/MH batteries. The surface modification with metallic Pd, Ni and Cu has been demonstrated to be effective in improving electrochemical properties of the hydrogen storage alloys [1–3]. Currently, carbon nanoscale materials including carbon nanotubes (CNTs), carbon nanofibers (CNFs) and activated carbons have been

Corresponding author. Fax: +86-22-2350-2604. *E-mail address:* xpgao@nankai.edu.cn (X. Gao). reported to be very attractive as candidates for hydrogen storage in electrochemical reactions [4–7]. The electrochemical method for hydrogen storage on these materials in alkaline solution is more reasonable and feasible at ambient pressure even though the capacity is smaller than that in gas–solid reaction at high pressure. The acid treatment and purification of carbon nanoscale materials are shown to increase their hydrogen storage capacities [6]. However, it is well known that the electrocatalytic activity of carbon nanoscale materials in alkaline solution is relatively poor as compared with that of hydrogen storage alloy. Our previous work showed that the decoration of CNTs with metal particles can improve

the electrochemical activity of its electrode [8]. The discharge capacity of CNTs was measured and calculated after eliminating the capacity of Ni–P alloy.

In this work, the content of the Ni–P alloy on the surface of CNFs was reduced and CNFs with surface Ni–P alloy were subjected to a heat treatment. In the meantime, both CNFs and Ni–P alloy were considered as active materials to measure and calculate their discharge capacities for eliminating the disturbance of atomic hydrogen adsorbed on the surface of Ni–P alloy layer.

2. Experimental details

CNFs were prepared via catalytic pyrolysis of methane over Ni/MgO catalyst at 550 °C for 30 min. The as-prepared samples were soaked in 37% HCl acid for 1 h to remove catalyst and then rinsed with de-ionized water. The samples were then dried at 110 °C for 10 h. The carbon nanofibers were decorated chemically with metallic nickel particles using SnCl2-HCl sensitizing solution, PdCl₂-HCl activating solution and NiSO₄-NaH₂PO₂ plating solution. The detailed method was presented previously [9,10]. The composite of CNFs with Ni-P alloy particles was treated at 400 °C for 1 h in H₂ atmosphere. A transmission electron microscopy (TEM, TECNAI 20) was employed to characterize CNFs with surface Ni-P alloy. X-ray diffraction (XRD) measurements of composites were performed using a Rigaku-D/ max-2500 with Cu K_{α} radiation. The carbon content was measured and calculated according to elementary analysis (Uario EL).

Twenty mg Ni-CNFs and 200 mg carbonyl nickel powder (INCO 255) were mixed to fill the substrate of porous nickel for preparing the electrode to measure the electrochemical capacity. The carbonyl nickel powder added here is to avoid dropping of CNFs from the electrode and increase the capability of current collecting. The electrodes of carbonyl nickel powder and pure CNFs were also prepared for blank measurements, respectively. Both CNFs and Ni–P alloy were considered as active materials in calculating the electrochemical capacity. Electrochemical measurements of

the electrode were performed using a sintered nickel electrode with a large capacity as a counter electrode and an Hg/HgO electrode as a reference electrode in 6 M KOH electrolyte at room temperature in normal atmosphere. These electrodes were fully charged at 1000 mA/g and discharged at the same current density after a rest of 10 min. The discharge cutoff potential was set to be -0.4 V vs. Hg/HgO.

3. Results and discussion

The TEM images of purified tube-like CNFs are displayed in Fig. 1. The long CNFs were curved with an outer diameter of 30-50 nm and an inner hollow core of 6-10 nm. The open tips were observed clearly after eliminating the Ni catalyst. The HRTEM image showed that the graphite layers of CNFs were with an angle respected to the fiber axis, which were different from the ideal CNTs with a concentric cylinder structure. The structure of the cone-shaped CNFs was similar to that reported by several groups [11,12]. The openended graphite sheets can be expected as the major channel for the hydrogen storage [13]. In addition, poor graphitization of CNFs was found, similar to the multiwalled CNTs obtained from the thermal decomposition of organic compounds.

TEM images of CNFs decorated with Ni-P alloy (50.3 wt% carbon) are shown in Fig. 1. It revealed in the bright field that most of CNF surface was coated with smaller metallic nickel particles. The deposited electroless nickel is a metastable, supersaturated alloy consisting of P atoms trapped between the nickel atoms as discussed by Ang et al. [10]. The outer diameter of CNFs with a rough surface increased to about 50-80 nm due to the deposition of Ni-P alloy particles in a ball shape. However, the hollow core of some CNFs with Ni-P alloy particles was also observed. The mean value of carbon content was calculated to be 50.3 wt% through element analysis. The ring patterns were observed using a selected area electron diffraction (SAED) as inserted in Fig. 2b, demonstrating that the smaller Ni-P alloy particles have polycrystalline or nanocrystalline structure instead of amorphous structure.





Fig. 1. TEM (a) and HRTEM (b) images of the purified CNFs.

Moreover, it was observed in the dark field under the selected electron diffraction that the Ni–P alloy particles with fine crystallites existed along the outer surface of CNFs, like chain morphology. When the deposited Ni–P content increased to 76.3 wt% (as indicated in Fig. 3), the small Ni–P alloy particles aggregated and grew up into a big one. Some alloy particles existed off the outer



Fig. 2. TEM images of CNFs decorated with Ni–P alloy particles (Ni–P content is 49.7 wt%) in the bright field (a) and the dark field (b). The selected area electron diffraction is inserted in (b).

surface of CNFs. It was further confirmed in the dark field that the Ni–P alloy particles with fine crystallites were distributed disorderly and existed separately, different from the chain-like morphology along the outer surface of CNFs as observed



Fig. 3. TEM images of CNFs decorated with Ni–P alloy particles (Ni–P content is 76.3 wt%) in the bright field (a) and the dark field (b). The selected area electron diffraction is inserted in (b).

above. Therefore, the low content of Ni–P alloy appeared to be more efficient to cover the outer surface of CNFs.

The nano-sized metallic Ni/graphite composites prepared by arc-discharge method were found to

have largely enhanced the hydrogen storage [14]. The Ni-P alloy particles could increase the electrochemical activity of hydrogen storage for both hydrogen storage alloy and CNTs [8,15,16]. Both CNFs and Ni-P alloy were considered as active composite materials in calculating the electrochemical capacity in order to eliminate the disturbance of atomic hydrogen adsorbed on the surface of Ni-P alloy layer. The pure Ni-P alloy was also deposited on the surface of porous nickel under the same process of electroless plating to obtain the capacity of Ni-P alloy particles. It was observed that the maximum discharge capacity of the composites of CNFs and Ni-P alloy was measured to be 85.5 and 101 mA h/g for the Ni-P alloy content of 49.7 and 76.3, respectively, although the low content of Ni-P alloy was more efficient for covering the outer surface of CNFs. The capacities of the pure CNFs and Ni-P alloy were only 33 and 70 mA h/g, respectively, lower than that of the composites as mentioned above. It means that the synergistic effect between metal and carbon may contribute to the higher hydrogen storage in electrochemical reaction, similar to the hydrogen storage in gas-solid reaction of nanosized Ni/ graphite composite [14].

The CNFs decorated with Ni-P alloy (23.7 wt%) carbon) were subjected to heat treatment in H₂ atmosphere for 1 h. It was found from the XRD patterns (not shown here) that the diffraction peak at 26.2°, which corresponds to the diffraction characteristics of graphite phase, is detected for both samples before and after heat treatment. There was no dramatic change in the diffraction intensity for carbon diffraction peak. However, the crystallization of Ni–P alloy particles on the outer surface of CNFs before and after heat treatment was obviously different. The Ni-P alloy particles before heat treatment seemed to have the amorphous structure from only X-ray diffraction pattern. The selected area electron diffraction with a higher sensitivity confirmed that the Ni-P alloy particles had polycrystalline or nanocrystalline structure even though their crystallization was relatively poor. After heat treatment, the crystallization of Ni-P alloy increased and the main phase and coexisted phase with sharp peaks were assigned to the metallic Ni and Ni₃P alloy phases,

respectively. The TEM images of CNFs with Ni–P alloy after heat treatment as illustrated in Fig. 4 demonstrated that coating layer particles were adhered to the outer surface of CNFs and grown



(a)



Fig. 4. TEM images of CNFs decorated with Ni–P alloy particles after heat treatment (Ni–P content is 76.3 wt%) in the bright field (a) and the dark field (b). The selected area electron diffraction is inserted in (b).

up to 50–70 nm in diameter. The large crystal grains shown in dark field using the selected electron diffraction were formed, further supporting the higher crystallization as measured by XRD after heat treatment. In addition, it was found that the carbon content of CNFs decorated with Ni–P alloy after heat treatment was reduced from 23.7 to 20.6 wt%.

The electrochemical discharge curves of the composite of CNFs and Ni-P alloy before and after heat treatment, as well as pure CNFs are indicated in Fig. 5. The maximum discharge capacity obtained was 149 mA h/g of the composite of CNFs and Ni-P alloy after heat treatment, larger than that of the sample before heat treatment. The heat treatment in H₂ atmosphere could enhance the attachment ability to the outer surface of CNFs, which was of significance to the electric conductivity and the electrocatalytic activity of the composite electrode materials. Moreover, atomic hydrogen generated by electrolysis at metallic sites of the surface could diffuse easily through the interface into the graphite layer of CNFs. Our previous work using the cyclic voltammetry demonstrated that the produced atomic hydrogen was adsorbed preferentially at metallic sites of the electrode surface in electrochemical reaction [8,16]. The programmed temperature desorption (TPD) in gas-solid reaction at high temperature confirmed that the increased hydrogen storage indeed partly comes from the highly dispersed metal for



Fig. 5. The electrochemical discharge curves of different materials under the discharge current density of 1000 mA h/g.

nanosized Ni/graphite composite [14]. Therefore, heat treatment in H_2 atmosphere can improve the electrochemical hydrogen storage of CNFs decorated with Ni–P alloy particles.

4. Conclusions

The CNFs were synthesized by catalytic pyrolysis of methane over Ni/MgO catalyst. The graphite layers of CNFs were with an angle respected to the fiber axis, different from the ideal CNTs with a concentric cylinder structure. The ring patterns in a selected area electron diffraction demonstrated that the smaller Ni-P alloy particles decorated on the outer surface of CNFs have polycrystalline or nanocrystalline structure instead of amorphous structure. The electrochemical discharge capacity increased with increasing the Ni-P content on the outer surface of CNFs owing to the synergistic effect between metal and carbon in the electrochemical reaction. The heat treatment of CNFs decorated with Ni-P alloy particles led to higher crystallization of surface alloy particles. The maximum discharge capacities of the composites with Ni-P content of 76.3 wt% before and after heat treatment were measured to be 101 and 149 mA h/g, respectively.

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