

Electrochemical Storage of Hydrogen in Carbon Nanotubes

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ABSTRACT

The electrochemical hydrogenation property of carbon nanotubes (CNTs) was investigated. The CNTs were prepared by different methods, including chemical vapor deposition (CVD) using different catalysts (Co, Ni, etc.) or laser ablation (LA) using Co or Ni catalyst. All of the CNTs contained various amounts of residual metal catalyst. A high discharge capacity of 197 mAh/g of the CVD-Co electrode was obtained, followed by CVD-Ni (48 mAh/g) and LA (36 mAh/g) at room temperature. If the CNTs were purified by HNO₃ and similar test was conducted, it was found that the discharge capacities were dramatically reduced. When the purified CNTs were deposited with a controlled amount of metal on the surface, the discharge capacity was improved significantly. It is postulated that the electrochemical hydrogen storage by carbon nanotubes might be influenced by the catalytic effect.

Keywords: electrochemical properties, carbon nanotube, discharge capacity, catalytic effect

1. INTRODUCTION

Carbon nanotubes (CNTs) have unique mechanical, electric, and magnetic properties. The applications of CNTs include field emission display, composite, SPM tip, hydrogen storage, catalyst support for fuel cells, Li-ion battery, and son on. To study the hydrogen storage property, there are two ways to measure the amount of adsorbed hydrogen, i.e., gas-phase or electrochemical hydrogenation. Dillon et al. [1] first measured the hydrogen adsorption capacity of an as-prepared carbon soot containing only about 0.1 to 0.2wt% SWNT at 133K. Based on this result, they predicted that hydrogen adsorption capacity of pure SWNTs was between 5 to 10wt%. Generally, for physical sorption of hydrogen, a pressure of 100 bars and low temperature 77K is needed. Hydrogen adsorption by CNT is due to its large surface area [2]. Opening the caps on the end of the nanotubes [3] or increasing the spacing between the graphene sheets [4] and heat treated at temperatures higher than 1800°C [5, 6] can all increase the hydrogen storage capacity of CNT. It has been pointed that hydrogen can be stored in SWNT at room temperature [7, 8]. Metal oxide catalyst or residual catalyst may participate in hydrogen adsorption onto

carbon nanotubes [9, 10]. Tibbetts et al. studied the sorption of hydrogen with nine different carbon materials at pressures up to 11MPa and temperature from -80 to 500°C [11]. Unfortunately, very little hydrogen can be adsorbed by those carbon materials.

Until now, electrochemical method for hydrogen storage has been less extensively employed compared to physical methods. However, there have been more papers focusing on the electrochemical property of CNT, because the results can be directly used in rechargeable battery. For example, a capacity of 110mAh/g under very low discharge current density was observed for an SWNT electrode [12]. The discharge capacity of CNT can be improved if the cap is removed by acid treatment [13]. Metallic impurities, such as Co and Ni, could increase the capacity of CNT [14]. To date, the mechanism of reversible charge and discharge of hydrogen in carbon materials is not clear. It may be affected by specific surface area [15], residual metal catalyst, diameter of CNT [16], the functional group produced after acid treatment [17], charge/discharge current density, crystallinity of CNT [18], and so on. Qin et al. pointed out that for the electrode formed with MWNT and Ni powder a high discharge capacity of 200mAh/g was obtained [19]. When carbon nanotubes were decorated with metallic particles, the discharge capacity of CNT can be significantly improved [20, 21]. The electrochemical discharge capacity increased from 101 to 149mAh/g by increasing the Ni-P content on the outer surface of CNTs owing to the synergistic effect between the metal and carbon in the electrochemical reaction [22].

The purpose of this study is to offer a new idea about catalytic effect of deposited metal particles on electrochemical hydrogenation of CNTs.

2. EXPERIMENTAL

2.1 Preparation of CNTs

The carbon nanotubes were prepared by catalytic chemical vapor deposition (CVD) or laser ablation (LA) using Co and/or Ni as the catalyst. In the CVD process, a quartz tube reactor was used and C₂H₂ gas was introduced to grow carbon nanotubes on various catalysts (Co, Ni, etc.) at 750°C. For the LA process, Co or Ni was used as catalyst. All of the CNTs contained various amounts of

residual metal catalyst. Nitric acid was used to remove the residual metallic particles for all samples, and then the CNTs were soaked with $\text{Co}(\text{NO}_3)_2$ at different atomic ratios, followed by reducing in H_2 at 300°C for 30min. The salt was reduced to metallic Co or oxidized to Co_3O_4 . In addition to the above samples, some CNTs with a specified purity of 95% were also tested.

The phase structure of the samples was identified by X-ray diffraction (XRD). The diameter and surface morphology of CNTs were examined by field-emission scanning electron microscopy (FESEM).

2.2 Battery Assembly

The charge and discharge curves were measured in a test cell, which contained two pieces of positive electrode, one piece of carbon nanotube (0.02g) as the negative electrode, and polypropylene as the separator. The electrolyte was 6M KOH + 1wt% LiOH. The positive electrode material consisted of nickel hydroxide, 5wt% Co, and 5wt% CoO. Each of the positive and negative electrode material was mixed with 3 wt% PTFE to form a paste, and coated on a piece of Ni-foam. The electrode plate was cold pressed at a pressure of 100 kgf/cm^2 for 30s. The charge/discharge current and temperature were set at 10 mA/10 mA and 25°C , respectively, and the cut-off voltage was 900 mV.

3. RESULTS AND DISCUSSION

3.1 Characterization of CNTs

Fig. 1 shows the XRD patterns of as-prepared and HNO_3 treated Ni-CNT and Co-CNT prepared by CVD. After the purification treatment, although most of the metallic particles have been removed by HNO_3 , there still exists some residual catalyst. The SEM micrographs of the as-prepared CNTs show that the samples contain carbon nanotubes, amorphous carbon, metallic particles, and some nanocapsules.

3.2 Electrochemical Test

Fig. 2 shows the discharge capacities of the as-prepared and HNO_3 treated CNTs (Co-, and Ni-), and of Co-CNT decorated with 5at% Co. The maximum discharge capacity of the as-prepared Co-CNT is 200 mAh/g, equal to an H/C value of 0.74wt%. After the acid treatment, however, the hydrogen storage capacity of Co-CNT is dropped to nearly 0. After decoration with Co, the discharge capacity increases very significantly, and the cyclic stability is improved compared with the as-prepared sample. The discharge capacity for as-prepared Ni-CNT is quite low compared with that of Co-CNT. However, they have the same behavior, i.e., the discharge capacity is

decreased after removing the metal catalyst. Although Ni is a good catalyst for hydrogen dissociation in alkaline solution, the catalytic effect of Ni seems not as good as Co for the CNT electrode.

When the commercial CNTs with a purity of 95% were tested, the discharge capacity was also very low, as shown in Fig. 3. After decoration with Co, the discharge capacity was increased markedly. The maximum discharge capacity reaches 231mAh/g when 10at% Co has been deposited to the CNTs. This phenomenon can also be observed in CNTs prepared by different methods. Fig. 4 shows the discharge capacities of an SWNT electrode prepared by laser ablation with a purity of 70%. The maximum discharge capacity of as-prepared sample is only 25mAh/g. It increases dramatically to 150mAh/g after decoration with 10at% Co. The discharge capacity of the

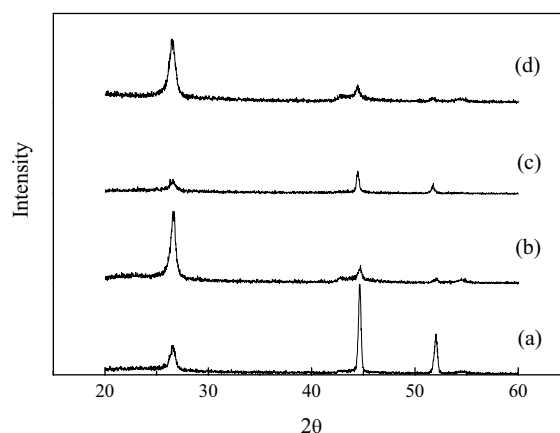


Fig. 1 XRD patterns of Ni- and Co-CNT prepared by CVD. (a) as-prepared Ni-CNT, (b) acid treated Ni-CNT, (c) as-prepared Co-CNT, and (d) acid treated Co-CNT.

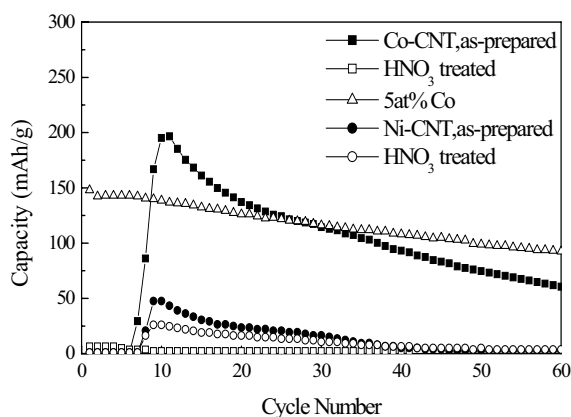


Fig. 2 Discharge capacities of Co- and Ni-CNT electrodes.

modified electrode increases with the Co content.

The results of the above electrochemical tests are summarized in Table 1. It is concluded that CNTs of higher purity or after acid treatment have lower discharge capacity.

4. CONCLUSION

Several kinds of CNT were used as the negative electrode material in alkaline solution, and their hydrogen storage capacities were measured by electrochemical method. The CNTs of high purity or after acid treatment exhibit lower hydrogen storage capacity. Decoration with Co on CNTs is effective to enhance the electrochemical hydrogen storage capacity.

5. ACKNOWLEDGMENTS

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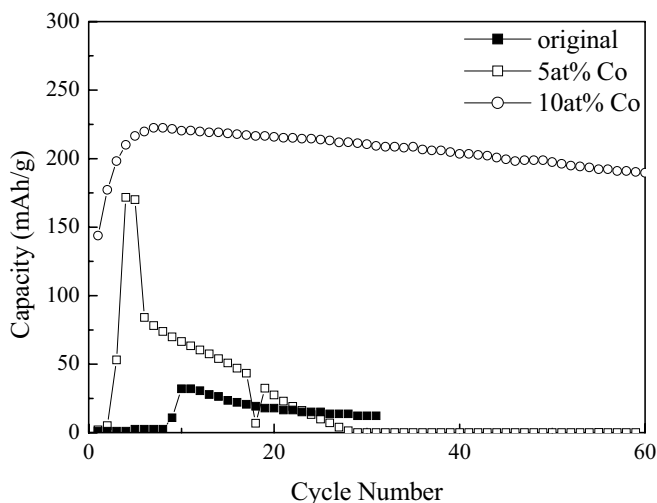


Fig. 3 Discharge capacities of commercial CNTs with a purity of 95%.

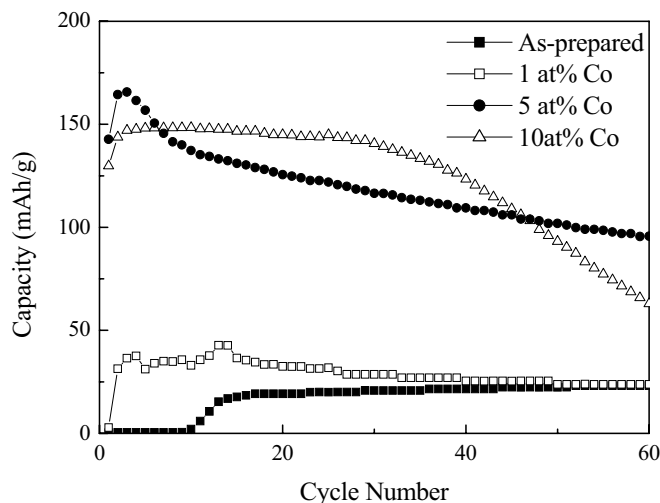


Fig. 4. Discharge capacities of CNTs prepared by LA with a purity of 70%.

Table 1 Discharge capacities (mAh/g) of the CNT samples.

Sample	As-prepared	Decorated with Co			HNO ₃ Treated
		1at%	5at%	10at%	
Co-CNT	197	-	143	-	7
Ni-CNT	48	-	-	-	26
Commercial	-	-	172	231	32
LA-CNT	36	43	166	148	-

Note: 100mAh/g = 0.37 wt% H.

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