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# Effect of carbon nanotubes purification in the performance of a negative electrode of a Ni/MH battery

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ABSTRACT

Multiwall carbon nanotubes (MWCNT) with a diameter of 30–50 nm was added to the negative electrode of a Ni–MH battery in order to study the effect of its purification treatment on the electrochemical performance. Three different reflux assisted digestion methods were analyzed. MWCNT were structural characterized before and after purifications by means of different techniques such as HRTEM, EDS, SEM, XRD and FTIR. Subsequently they were incorporated into the working electrode to evaluate the electrochemical performance by charge/discharge cycling and rate capability.



## 1. Introduction

The science and technology related to hydrogen storage in carbon nanotubes (CNTs) has been studied for several years. Studies [1,2,3] show that the adequate CNTs aggregate to a Ni/MH negative electrode can improve its electrochemical properties, exhibiting a good hydrogen storage capacity, high rate capability, charging efficiency, durability and low impedance [4]. The benefits have been attributed to the large reaction surface and low internal resistance as well as the strong resistance to CNTs oxidation which can improve performance in cycles when introduced into the electrodes.

Among the studies are those made by Yi et al. [1,2] where CNTs with different diameters were synthesized by chemical vapor deposition (CVD), purified and added to Ni/MH working electrode (WE). The maximum capacity obtained was 425.9 mAh/g with 20–40 nm diameter CNTs, and later a discharge capacity of 519.1 mAh/g was achieved by annealing at 800 °C. However the charge and discharge current densities were very small in the test.

Tsai et al. [5], developed a method to produce a new material called buckypaper with an alloy of $MmNi_5$ and MWCNT. The high flexibility and good contact with the alloy provide high electrical conductivity, revealing that it can be a versatile replacement for the conventional anode of Ni/MH, thus reducing significantly the cost and weight. Chen et al. [6] obtained CNTs 20–30 nm diameter by catalytic decomposition of methane over a $LaNi_5$ alloy. The obtained CNTs were purified in HCl and added to the active material, showing 267 mAh/g discharge capacity.

Although the experiments demonstrated that CNTs are a good choice as replacement of other carbon components, they also reveal large differences [7], since the quality of a nanotube sample may be influenced by the number of walls, tube defects and even the sample purity. These are factors

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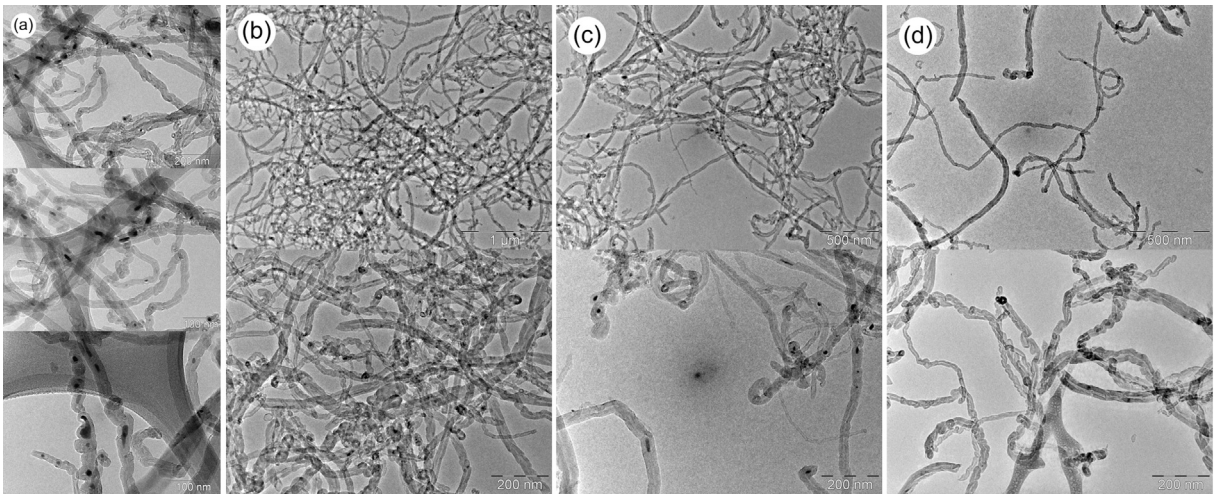


**Fig. 1 – HRTEM images of MWCNT (a) as received, (b) in $H_2SO_4$, (c) in $NH_4OH$:$H_2O_2$, (d) in HCl:$H_2O_2$.**

which may interfere with the sorption processes and the capillary properties, losing the unique properties of carbon nanotubes [8].

Thus, to achieve the full potential of the carbon nanotubes, it is necessary to develop an easy and effective purification procedure to remove impurities such as amorphous carbon, carbon nanoparticles and metal particles that may be present. That procedure would also allow the opening of the ends which are usually closed.

The objective of this study is to analyze different CNTs purification processes and determine how they influence the electrochemical performance when they are added to a Ni/MH negative electrode.

## 2. Experimental

The CNTs were produced by the Cheaptubes American Company, using chemical vapor deposition (CVD). These ones have been characterized, purified and added to the anode of a laboratory Ni/MH battery.

### 2.1. *Characterization of CNTs*

The "as received" and purified CNTs were microstructural characterized in a Philips CM200UT high resolution transmission electronic microscope (HRTEM). The presence of metal impurities was checked by energy dispersive spectroscopy (EDS) coupled to the HRTEM, and the carbon impurities were detected with infrared spectroscopy in a Perkin Elmer Spectrum 400 FTIR. X-ray diffraction was measured with a Philips PW3700 diffractometer. The CNTs-added electrodes were analyzed in FEG NovaNano 230 scanning electronic microscope (SEM).

### 2.2. *Purification of CNTs*

The "as received" MWCNT were put in a reflux system at 75 °C for 3 h and 80 mL of three solutions, $H_2SO_4$ (3 M), $NH_4OH$:$H_2O_2$ (3 M:30%) and HCl:$H_2O_2$ (3 M:30%) mixtures. After that, the samples were filtered and washed repeatedly by distilled water until the pH value of the filtrated product was the same as that of the distilled water. Finally, the sample was dried for 24 h at 105 °C.

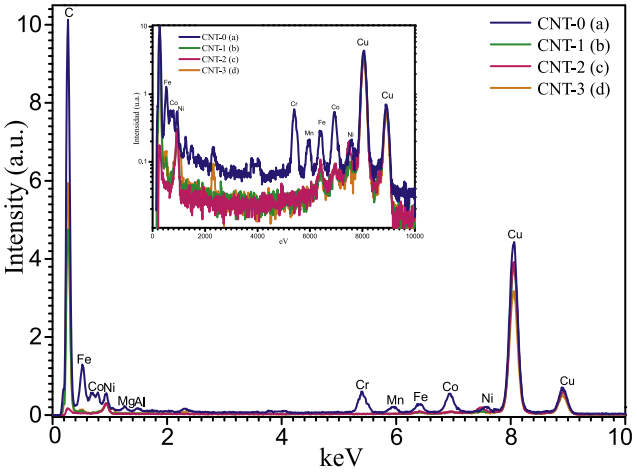


**Fig. 2 – EDS spectra of MWCNT (a) as received, (b) in $H_2SO_4$, (c) in $NH_4OH$:$H_2O_2$, (d) in HCl:$H_2O_2$.**

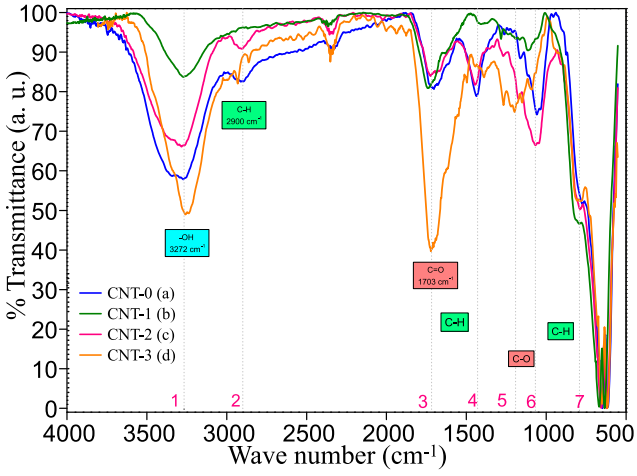


**Fig. 3 – FTIR spectra of MWCNT (a) as received, (b) in $H_2SO_4$, (c) in $NH_4OH$:$H_2O_2$, (d) in HCl:$H_2O_2$.**

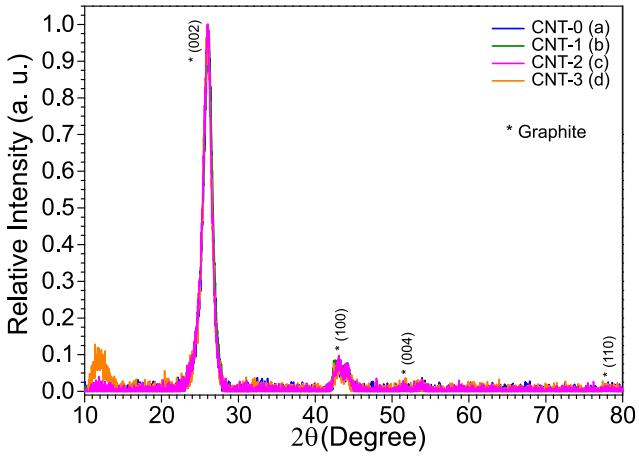


**Fig. 4 – XRD of MWCNT (a) as received, (b) in $H_2SO_4$, (c) in $NH_4OH$:$H_2O_2$, (d) in HCl:$H_2O_2$.**

### 2.3. *Preparation of the working electrodes*

After purification, the CNTs were mixed with $LaNi_{3.8}Co_{0.3}Mn_{0.3}Al_{0.4}$ powder with particle size between 44 and 74 μm [9], and Carbon Teflon (Carbon Black Vulcan XC72 + PTFE) as mechanical support and electric conductor. The mass radio was 1:10:10 respectively. The mixture was pressed together with a Ni mesh as current collector at 200 MPa. The working electrode obtained had an 11 mm diameter.

### 2.4. *Electrochemical characterization*

An open cell with a three-electrode system (Ni mesh as CE and Hg/HgO as RE) was used to measure the electrochemical properties in a 6 M KOH aqueous solution as electrolyte, at room temperature. Charge/discharge cycling was studied at 0.5 C current rate, charge time was 20% plus the nominal equivalent capacity and discharge cut-off potential was −600 mV. The rate capability test was made between 0.1 C and 5 C.

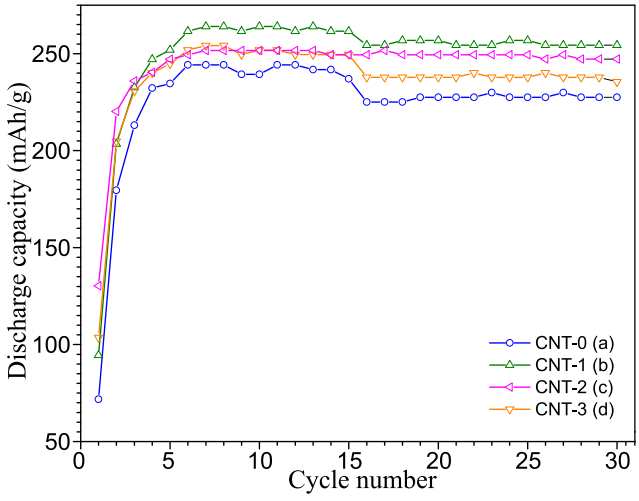


**Fig. 5 – Discharging curves of working electrode made with alloy-MWCNT (a) as received, (b) in $H_2SO_4$, (c) in $NH_4OH$:$H_2O_2$, (d) in HCl:$H_2O_2$.**

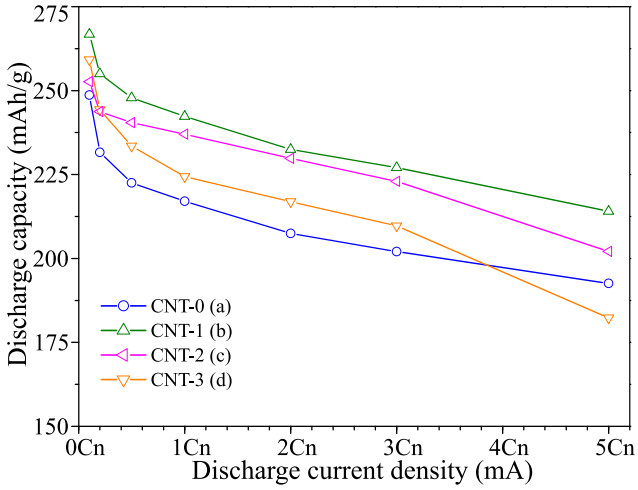


**Fig. 6 – Rate capability of working electrode made with alloy-MWCNT (a) as received, (b) in $H_2SO_4$, (c) in $NH_4OH$:$H_2O_2$, (d) in HCl:$H_2O_2$.**

## 3. Results and discussion

Fig. 1 shows the HRTEM images of purified and unpurified nanotubes. The initial sample (a) can be seen as structures made up of graphene sheets rolled up on themselves as 30–50 nm diameter nanometer cylinders, and with the presence of bamboo like sections with closed ends in many cases. Various defects are also observed, which distort significantly the CNTs curvature, typically produced by the presence of pentagons, octagons or heptagons. Those are embedded in the graphite hexagonal network [10]. Furthermore, the presence of a large amount of carbonaceous residues adhered to the walls and metal particles embedded in the interior of the tubes are observed as contaminants.

These observations call for the need of a purification process to help remove sorbed material, to open the closed ends and eventually contribute to the disappearance of the bamboo structure necks that could interfere with the flow of hydrogen when the CNTs is applied to a Ni/MH negative electrode.

The micrographs of Fig. 1(b) and (c) show the purified nanotubes, where the treatments leave cleaner samples. These results were confirmed by EDS analysis (Fig. 2) where there is a decrease in the signals of the metals detected in relation to unpurified nanotubes (CNTs-0).

The treatment carried out with sulfuric acid (CNTs-1), in addition to removing metals, shows conservation of the CNTs structure and length (Fig. 1(b)). The sorbed waste on the walls was removed. This observation is confirmed by the disappearance of the infrared spectrum bands 2 and 4 (Fig. 3), which can be associated with amorphous carbon impurities and hydrocarbon fragments as employed for CNTs synthesis [11].

The purification by mixture of ammonium hydroxide/hydrogen peroxide (CNTs-2) preserves the nanotubes structure (Fig. 1(c)), as in the treatment carried out with sulfuric acid, but shows nanotubes shorter than CNTs-1. These last results are consistent with the X ray diffractograms (Fig. 4), where the sharpness peak located at the angle $2\theta$ 25.5° indicates that the graphite structure of the CNTs was oxidized without

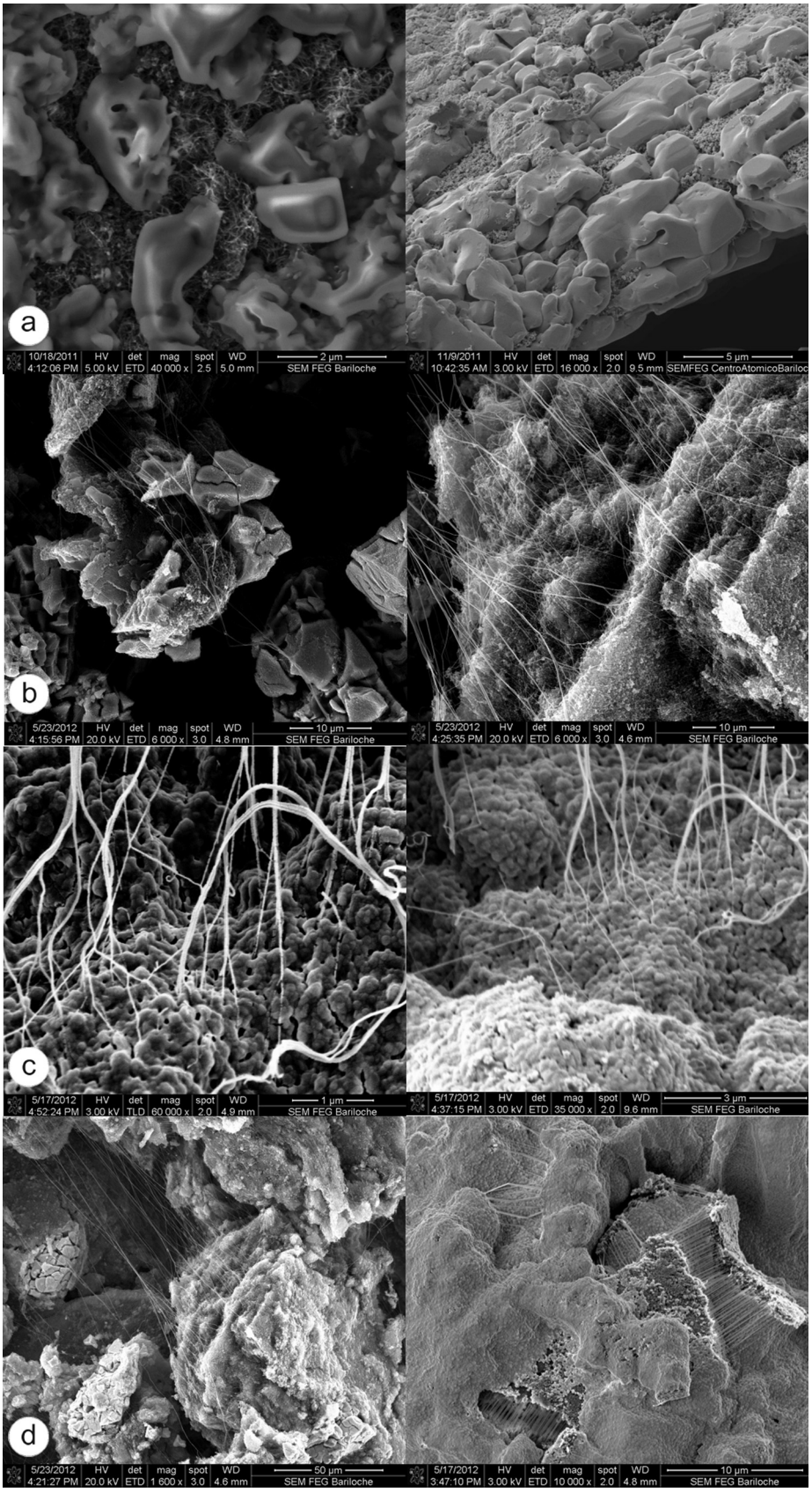


**Fig. 7 – Working electrode made with alloy-MWCNT (a) as received, (b) in $H_2SO_4$, (c) in $NH_4OH$:$H_2O_2$, (d) in HCl:$H_2O_2$.**

significant damage, since any reduced crystallinity on the CNTs peaks produces X-ray diffraction broader than standard one and moves them to lower angles [12]. Furthermore, the micrographs of Fig. 1(c) also show that some of the sorbed and embedded residues are still present in the nanotubes.

The treatment carried out with hydrochloric acid/hydrogen peroxide (CNTs-3) presents shorter nanotubes and a partially degraded structure (Fig. 1(d)). Fig. 4 diffractograms show that although treatment did not affect the main peak ($2\theta = 25.5°$), there appear peaks for smaller angles. This phenomenon may depend on the nanotubes being associated together due to the modifications made by such treatment [13].

The electrochemical results allow us to differentiate the electrodes made with treated and untreated nanotubes. The charge/discharge cycling (Fig. 5) shows that the electrode prepared with unpurified nanotubes has the lowest discharge capacity, whereas the electrode CNTs-1 added has the largest capacity, achieving 264mAh/g, value that is up to 14.2% higher than the electrode CNTs-0 added. While the electrode prepared using the CNTs-3, has the lowest discharge capacity of the purified nanotubes, it is higher than the electrode with unpurified nanotubes added, indicating that all purification treatments have a positive effect that may vary in range.

The rate capability results (Fig. 6) show that the discharge capacity at high rates becomes differentiated; revealing that the electrode CNTs-1 added has the best performing features. These results show that the electrode prepared with CNTs-1 is the most suitable for instantaneous high demand applications, such as in the case of the HEV.

SEM observations of the electrodes conformation show that when untreated nanotubes (Fig. 7(a)) are aggregated, they do not have greater interaction with the other components of the electrode. It is also shown that the purified nanotubes (Fig. 7(b)–(d)) interact with carbon teflon and CNTs-1 (Fig. 7(b)) also in particular interact with the alloy, which may improve electronic conductivity between the particles after activation of the metallic alloy.

## 4. Conclusions

The purification treatments made to carbon nanotubes positively influenced the electrochemical results of the electrodes CNTs added. The electrode ensembled with sulfuric acid purified CNTs was able to increase the maximum discharge capacity by 14.2% compared with the electrode containing only the metallic alloy. Furthermore, the electrode made with purified CNTs showed better performance at high rates in the rate capabilities studies. These results are consistent with the purity analysis, which showed reductions in the amount of metals and carbon residue sorbed on the walls of the tubes.

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