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

*L.A. Benavides**, *D.J. Cuscueta, H. Troiani, A.A. Ghilarducci, H.R. Salva*

Centro Atómico Bariloche – CNEA, Instituto Balseiro – UNCu, CONICET, Av. Bustillo 9500, 8400 San Carlos de Bariloche, Argentina

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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

* *Corresponding author*. Tel.: +54 9294 415536694.
E-mail addresses: lis@cab.cnea.gov.ar, lisbenavides@unicauca.edu.co (L.A. Benavides).
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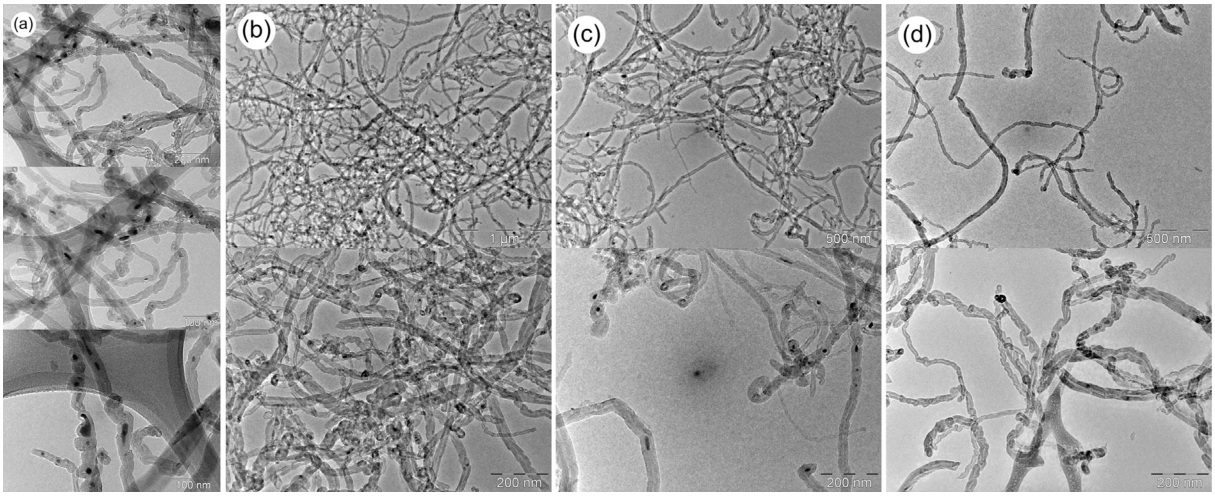

Fig. 1 – HRTEM images of MWCNT (a) as received, (b) in H_2SO_4, (c) in $NH_4OH:H_2O_2$, (d) in $HCl:H_2O_2$.

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.

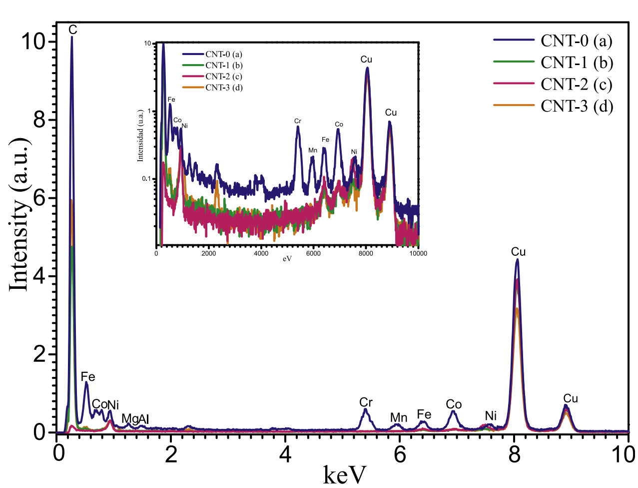

Fig. 2 – EDS spectra of MWCNT (a) as received, (b) in H_2SO_4, (c) in $NH_4OH:H_2O_2$, (d) in $HCl:H_2O_2$.

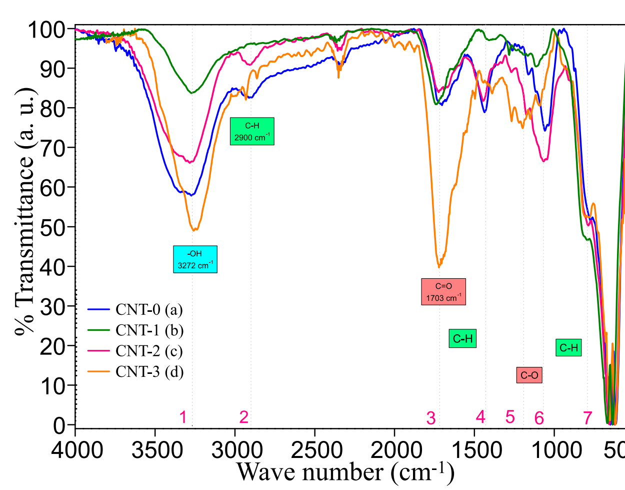

Fig. 3 – FTIR spectra of MWCNT (a) as received, (b) in H_2SO_4, (c) in $NH_4OH:H_2O_2$, (d) in $HCl:H_2O_2$.