

Electrochemical studies of hydrogen evolution, storage and oxidation on carbon nanotube electrodes

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Abstract

Carbon nanotube films produced on a Si(1 0 0) substrate without any metal catalyst were used as electrodes in galvanic cells. The electrochemical mechanism of hydrogen evolution, storage and oxidation was studied using cyclic voltammetry and galvanostatic polarisation. Cyclic voltammetry showed that hydrogen is easily produced on the carbon nanotube surface, but a significant overvoltage was observed for hydrogen oxidation. The kinetics of hydrogen evolution influenced the quantity of hydrogen stored in the nanotube, which increased with increasing discharge currents.

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1. Introduction

Carbon nanotubes (CNTs) combine unique chemical and physical properties which have attracted the interest of numerous researchers for applications such as supercapacitors [1,2], chemical sensors [3] and energy storage devices [4]. One of the most exciting application fields for CNTs is hydrogen storage. The storage of hydrogen in a light element like carbon could lead to the formation of power supplies for mobile applications with higher energy densities.

Dillon et al. [5] reported for the first time excellent hydrogen storage properties of single walled carbon nanotubes (SWCNTs). Thereafter, many research groups started to carry out hydrogen storage experiments [6–11]. Most of the studies on hydrogen storage in CNTs were conducted by temperature-programmable desorption measurements [5–8] and electrochemical methods [9,11]. From the literature results it is quite difficult to reach a common conclusion for maximum adsorption capacity. The variation of hydrogen storage capacity may arise due to the differences of CNTs used (SWCNT or multi walled carbon nanotubes), purity, chirality of tubes, tube diameter, bundle appearance and possible presence of metals used as catalysts in the

synthesis procedure. Furthermore, metals able to interact with hydrogen can also be introduced during the activation process [12]. Besides the debate of hydrogen storage capacity, there are other important tasks to be achieved such as the understanding of the mechanism for hydrogen storage. We describe here studies on the electrochemical absorption and desorption of hydrogen in SWCNTs produced without metal catalyst addition on a Si(1 0 0) substrate.

2. Experimental

CNT films were produced by using a new route [13] with amorphous hydrogenated carbon nanoparticles as precursors, without metal catalyst addition. The CNTs are formed by low-velocity spraying of carbon particles onto a heated Si(1 0 0) substrate, when the deposition temperature is sufficiently high to enable self-assembling processes. Electrochemical characterisation of the obtained materials was performed in a classical three-electrode cell. The silicon substrate was dipped in concentrated hydrofluoric acid to remove silicon oxide from the rear surface and washed with deionised water. The working electrode was prepared by adhering the rear surface of the silicon substrate onto carbon paper using a carbon-based conductive paste. The carbon paper and the silicon substrate were covered with an insulating paint, leaving exposed only the surface onto which CNTs

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were deposited. The total area of the working electrode exposed to the electrolytic solution was about 0.4 cm^2 . A platinum rod and a saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. The cell was filled with a $1 \text{ M H}_2\text{SO}_4$ aqueous solution. Milli-Q water was used for all solutions and rinsing. High purity nitrogen was used to flush the solutions before and during the experiments. The electrochemical cell was connected to a Solartron 1286 potentiostat/galvanostat for cyclic voltammetry with a scan rate of 10 mV s^{-1} and to a Maccor 4000 for galvanostatic polarisation. Each experiment was repeated five times to determine reproducibility.

3. Results

The material used for the electrochemical characterisations appears in a scanning electron microscope (SEM) image (Fig. 1) as a mat of ropes $50\text{--}60 \text{ nm}$ in diameter and several micrometers in length. The RAMAN scattering exhibits a low frequency band with the typical position and bunched shape of SWNTs [13], suggesting that the film consists primarily of bundles in which the SWNTs are interlaced.

Reverse scan voltammetry was carried out by reversing the direction of the scan rate at a certain switching potential. Fig. 2 shows the voltammograms obtained by changing the switching potentials from 0.08 to 0.05 V with step of 0.01 V . A sharp cathodic peak, related to hydrogen evolution, appeared at about 128 mV versus Ag/AgCl. The discharge reaction is as follows:



where H^\bullet denotes the hydrogen adatom intermediate. Molecular hydrogen can be formed both by adatom recombination

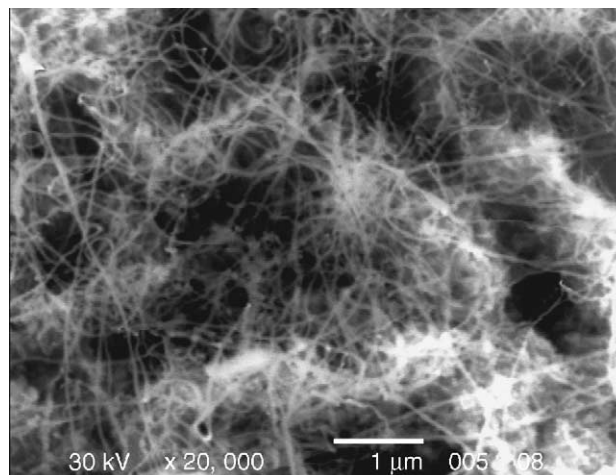
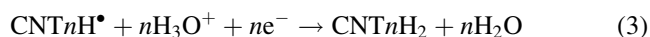


Fig. 1. SEM micrograph of the CNT film used for the electrochemical characterisations.

(the Tafel–Volmer route, Eqs. (1) and (2)) or following the Heyrovsky–Volmer route (Eqs. (1) and (3)).



The electrochemical process is characterised by a fast kinetics as one may deduce from the low overpotential (ca. 70 mV). On the other hand, the peak related to hydrogen oxidation is quite broad, extending over a large voltage range (from 0.08 to 0.4 V). This result may be related to a slow hydrogen oxidation kinetics. The quantity of hydrogen oxidised, proportional to the peak area, was seen to increase when decreasing the switching potential as a result of larger amount of hydrogen produced and stored in the CNTs during the cathodic sweep.

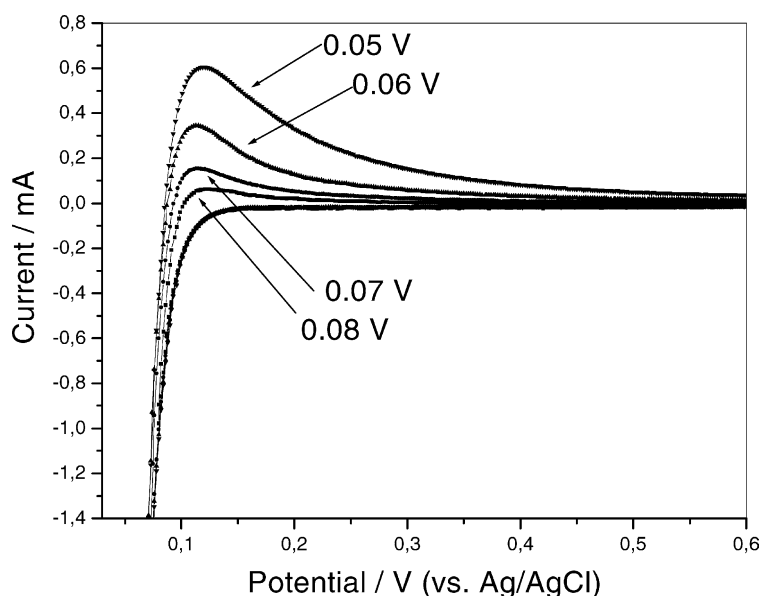


Fig. 2. Cyclic voltammograms carried out by reversing the direction of the scan rate. The switching potential is reported in the figure: temperature 20°C .

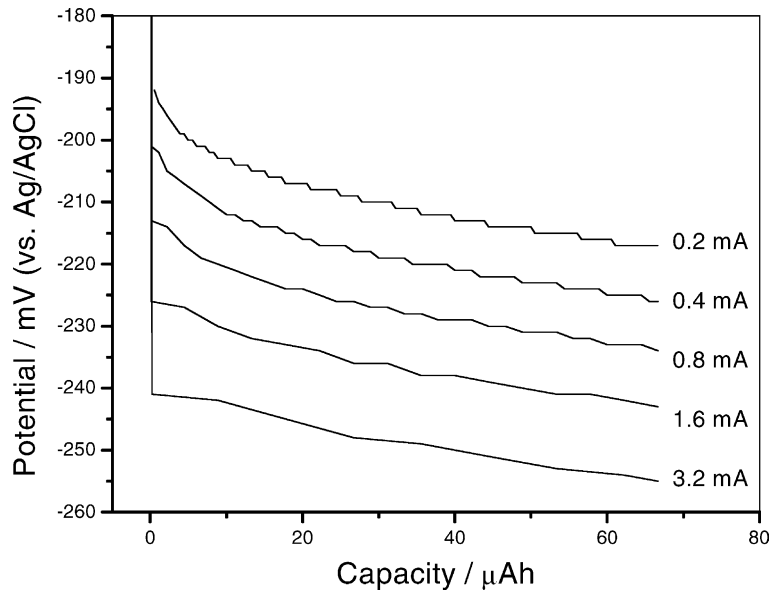


Fig. 3. Selected voltage profiles for the CNT electrode at 20 °C at various charging currents ranging from 0.2 to 3.2 mA.

To study the kinetics of hydrogen evolution a fixed amount of electricity, 66.66 μAh, was passed through the electrode using discharge currents ranging from 0.2 to 3.2 mA. Fig. 3 shows the voltage profiles for selected discharge cycles. The potential of the electrode decreased gradually during discharging and its polarisation was relatively low even for the discharge current of 3.2 mA. To obtain the kinetic parameters the method suggested by Allen and Hickling for plotting data registered at low overpotential has been used [14]. The classical Tafel equation can be rewritten as

$$i = i_0 \exp\left(\frac{-\alpha n F \eta}{RT}\right) \left[1 - \exp\left(\frac{-n F \eta}{RT}\right)\right] \quad (4)$$

or

$$\log \left[\frac{i}{1 - \exp(-n F \eta / RT)} \right] = \log(i_0) - \frac{\alpha n F \eta}{2.3 RT} \quad (5)$$

Fig. 4 is a plot of overpotential (η), measured at the end of the discharge versus $\log[i/(1 - \exp(-n F \eta / RT))]$ (the current density was determined using the geometric area of the electrode). The value of the exchange current extrapolated at $\eta = 0$ was 0.29 mA cm⁻². The high value of the estimated exchange current density makes these CNTs a good electrocatalyst for the hydrogen evolution reaction. A transfer coefficient of $\alpha = 1.5$ was determined from the curve slope. Assuming low coverage of adsorbed hydrogen, the only mechanism which will give rise to a transfer coefficient of

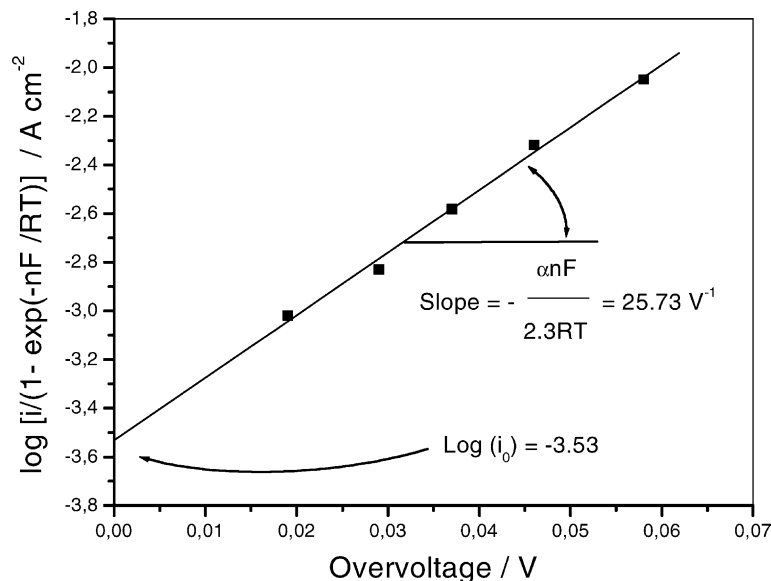


Fig. 4. Modified “Tafel plot” for hydrogen evolution on CNT electrode. Data were taken from Fig. 3.

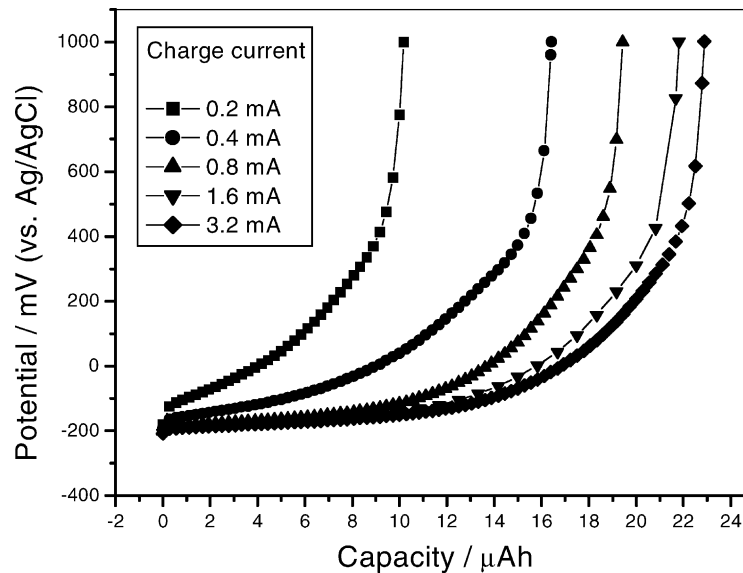


Fig. 5. Selected discharge voltage profiles for the CNT electrodes charged at various current ranging from 0.2 to 3.2 mA. The electrodes were discharged at a constant current of 0.2 mA: temperature 20 °C.

1.5 at low overpotential is the discharge followed by a rate-determining electroodic desorption [15]. From this result it follows that the hydrogen adatom formation (Eq. (1)) is fast and hydrogen evolution follows the Heyrovsky–Volmer route (Eq. (3)).

The effect of the discharge current on the quantity of hydrogen stored in the electrode was also studied. After the discharging process the hydrogen stored in the electrode was oxidised at a fixed charge rate (0.2 mA). Fig. 5 shows the voltage profiles for selected charge cycles. The charge plateau detected for the CNT electrode was very similar to the charge curve of metal hydrides. The plateau of charge potential was observed at approximately -0.2 V versus Ag/AgCl.

The quantity of hydrogen oxidised in the charge step increases by increasing the discharge current used for hydrogen evolution. This result can be related with an increased hydrogen adatom concentration, over the equilibrium concentration, with increased discharge currents.

The kinetics of the hydrogen oxidation was investigated by oxidizing at different charge currents the hydrogen intercalated on the electrode. Hydrogen was produced by passing a fixed amount of charge (0.24 C) at a fixed charge rate (2.0 mA). Fig. 6 shows that the Faradaic yield (the amount of hydrogen oxidised over theoretical amount generated) decreases by increasing the charge current. Practically, it was not possible to oxidise the hydrogen stored in the

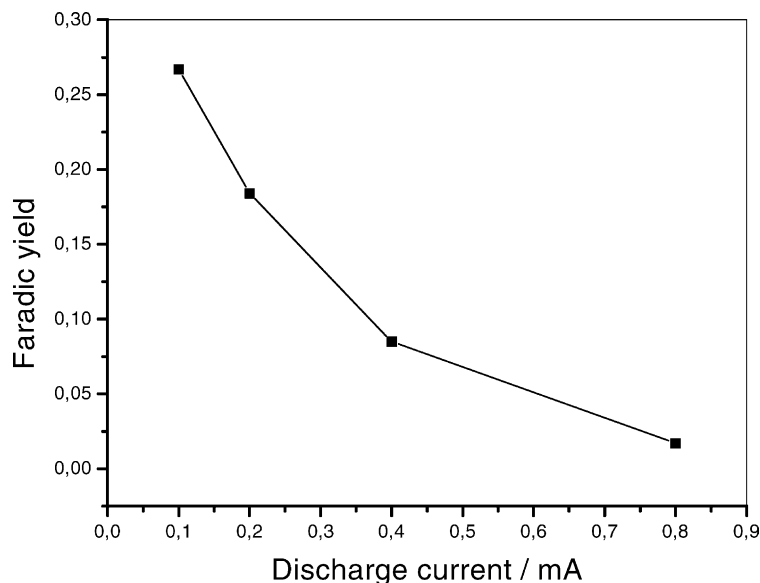


Fig. 6. Faradic yield as a function of the discharge current for a CNT electrode charged at 2 mA for 2 min: temperature 20 °C.

electrode using currents as high as 0.8 mA. This experiment confirms that hydrogen oxidation on CNTs is a kinetically unfavorable process.

4. Conclusions

Kinetic studies have shown that hydrogen can be easily generated with low overvoltage on CNTs. The high value of the exchange current density makes CNT electrodes a good candidate to replace expensive noble metals used as catalysts in acid electrolyzers. But high overvoltage for hydrogen oxidation makes CNTs inadequate for use as catalysts in fuel cell applications. The hydrogen storage capability was strongly affected by the discharge rate used to generate hydrogen. At high discharge rates hydrogen adatoms may greatly contribute to the total amount of hydrogen stored in the electrode.

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