

The electrochemistry of carbon nanotubes : I, aqueous electrolyte

Citation for published version (APA):

Niessen, R. A. H., Jonge, de, J., & Notten, P. H. L. (2006). The electrochemistry of carbon nanotubes : I, aqueous electrolyte. *Journal of the Electrochemical Society*, 153(8), A1484-A1491.
<https://doi.org/10.1149/1.2205184>

DOI:

[10.1149/1.2205184](https://doi.org/10.1149/1.2205184)

Document status and date:

Published: 01/01/2006

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.



The Electrochemistry of Carbon Nanotubes

I. Aqueous Electrolyte

R. A. H. Niessen,^{a,z} J. de Jonge,^b and P. H. L. Notten^{a,b,*}

^aPhilips Research Laboratories, 5656 AA Eindhoven, The Netherlands

^bEindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

The energy storage potentials of many different carbon nanotube (CNT) materials are investigated electrochemically. The electrochemical response of all the investigated materials is rather featureless during charging and discharging and does not show any phase transitions or clear redox responses. The maximum discharge capacity, ~130 mAh/g, is measured for an as-produced single-walled carbon nanotube material. Measurements indicate that the electrochemical activity of the matrix material, used to manufacture composite electrodes, should also not be ignored. Highly pure CNTs yield a substantially lower response, indicating that the CNTs itself can only account for a small part hereof. The measured response of CNT materials is related to a number of processes, including the irreversible oxidation of carbonaceous material, the reversible oxidation/reduction of residual metal catalyst or carbonaceous impurities, and an electrostatic charging component. Steady-state impedance measurements, cross-correlated with cyclic voltammetry, show that (dis)charging of the electrical double layer can be directly linked to this electrostatic charging component. Characterization of highly pure CNT materials shows that more than 90% of the total charge was stored in this way. Only about 25% of the total amount of charge could be explained in this way for the as-produced materials. Based on the overall results it is highly unlikely that a significant amount of hydrogen can be stored in CNT material and that the exact amount of charge that can be reversibly stored in CNT material heavily depends on its morphology and the level of purity.
© 2006 The Electrochemical Society. [DOI: 10.1149/1.2205184] All rights reserved.

Manuscript submitted November 30, 2005; revised manuscript received March 29, 2006. Available electronically June 5, 2006.

The large empty spaces inside single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs), coupled with their large geometric surface areas, provides sufficient potency on a chemical level to study the energy storage characteristics of CNT materials. It was hypothesized that the hollow cores of nanotubes would be excellent sites for the storage of small molecules, like hydrogen. Furthermore, if the main aim is to develop a novel storage material with high capacity, low-mass, and high-stability CNTs seem to be an excellent class of materials to achieve this as they are chemically stable and have a low mass density.

A vast amount of research has been performed on the energy and hydrogen storage characteristics of CNT materials. Focusing on the storage of hydrogen in CNTs, this research can generally be divided into two parts, based on the hydrogen storage method used. The first method stores hydrogen via the gas phase: Here, the CNT material is exposed to a H₂ atmosphere, mostly at elevated pressures and temperatures, and the ad- or absorbed amount is determined using a Sieverts-type of device. H₂ molecules are thought to be adsorbed at the exterior surfaces of CNTs or absorbed into the interstitial spaces between CNTs.¹ The second possibility, and the one described in this study, is storing hydrogen electrochemically. Here the CNT material is employed as the working electrode in an electrochemical three-electrode setup and hydrogen is expected to be electrochemically ad- or desorbed.

Many researchers have studied the electrochemical hydrogen storage characteristics of CNTs over the past years. Nützenadel et al.^{2,3} found reversible hydrogen storage capacities of up to 170 mAh/g for unpurified arc discharge produced samples, containing only a few percent of SWNTs. For purified SWNT samples Rajalakshmi et al.⁴ found that the discharge capacity had increased to 800 mAh/g, with only relatively small variations in capacity with varying discharge currents. Based on a theoretical model, Lee et al.⁵ calculated that (10,10)-SWNTs could have storage capacities of up to 4500 mAh/g. More recently, work done by Gao et al.,⁶ Züttel and Zhang et al.⁸ was published which showed hydrogen storage capacities around 200 mAh/g for both MWNTs and SWNTs. However, all these CNT materials were synthesized using transition metals and well-known hydride-forming materials as catalysts.

Although different groups carried out electrochemistry-based hydrogen storage research on CNTs, a suitable mechanism, able to

explain the measured response, was never given. Even unambiguously showing that it was hydrogen that was “stored,” or that the stored energy could be related to other processes, was never really confirmed. Furthermore, the hydrogen storage capacities deduced from the electrochemical data showed a huge spread and did not seem to be clearly dependent on the purity of the material or the type of CNT investigated.

When electrochemically characterizing CNT materials in an alkaline environment and a cathodic current is applied, water is reduced at the CNT/electrolyte interface. During this process hydrogen atoms may adsorb at the surface of the CNTs, similar to the case for a conventional hydride-forming compound. As the exact charge-transfer mechanism remains unclear at the moment, it is generally approximated by⁹



It is also possible that the adsorbed hydrogen at the CNT surface instantly recombines to molecular hydrogen, forming gas bubbles at the surface of the electrode. As both the reduction and oxidation reaction are accompanied by charge transfer (see Reaction 1), the amount of hydrogen that possibly adsorbs and desorbs can be determined by measuring the electric charge transferred.¹⁰

The main aim of this contribution is to shed some light on the processes that can account for the electrochemical responses measured at CNT electrodes. To this end a wide variety of CNT materials was investigated. Based on selected characteristic responses, obtained by means of a variety of electrochemical methods, a clearer picture will be generated that is able to link the energy storage characteristics of CNT to very basic chemical processes.

Experimental

CNT materials were obtained from various manufacturers including Iljin Nanotech (Korea), MER Corp. (USA), University of Montpellier (France), IMRE (Singapore), Shell Global Solutions (The Netherlands), Philips Research Aachen (Germany), Carbolex (USA), and Dresden University of Technology (Germany). These materials included as-produced (a.p.), purified and aligned samples of SWNTs, MWNTs, and carbon nanofibers (CNFs), produced with a variety of techniques, including chemical vapor deposition (CVD), arc discharge (AD), and laser ablation (LA). Additionally, some of these samples were chemically purified in-house before being electrochemically investigated. As a large amount of different chemical treatments were utilized, each consisting of many individual steps, they are not discussed.

* Electrochemical Society Active Member.

^z E-mail: rogierniessen@philips.com

The CNT materials were electrochemically analyzed in the form of cylinder-shaped pellet electrodes (8 mm \varnothing and ~ 0.2 mm thick). These electrodes were prepared by cold pressing a powder mixture consisting of 10 mg of CNT material and 75 mg of silver powder at 3 bar for 2 min. Ag powder was used as a matrix material as it is electrochemically inert in the potential region explored when studying the electrochemical behavior of CNT material. After pressing, the pellet was weighed to correct for possible loss of material in the mold. Hereafter, the pellet was placed on the tip of a silver electrode holder after which a shrink sleeve, which was placed around the electrode, was heated with warm air. This caused the sleeve to shrink around the pellet and the silver rod, attaching the two to each other firmly. The remaining part of the sleeve was cut off in order to make the pellet accessible for the electrolyte. The shrink sleeve used is comprised of a synthetic material that is electrochemically inert under the conditions applied.

A range of different analysis techniques thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) surface analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM, etc.) was employed to characterize the CNT samples before they were investigated electrochemically. As only the analysis results of the TGA and BET methods are treated in this contribution, the exact specifications are given. TGA measurements were performed using a Mettler Toledo TGA/SDTA 851 $^{\circ}$ (STAR $^{\circ}$ software). The experiments were performed in the temperature regime of 25–1100 $^{\circ}$ C, utilizing a heating rate of 1 $^{\circ}$ C/min and using a 50/50 vol % O $_2$ /Ar mixture. The BET measurements were performed with the NOVA Data Analysis Package (v1.10). The adsorbate used was nitrogen and the bath temperature was 77.40 K. The initial pressure (P_0) was 772 mmHg.

Electrochemical measurements were performed using a three-electrode setup of which the specifications were given in previous work.¹¹ Galvanostatic measurements were performed using a Maccor M2300 battery tester (Maccor, Tulsa, OK). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were done on an Autolab PGSTAT30 (Ecochemie B.V., Utrecht, the Netherlands). EIS measurements were conducted at equilibrium voltage conditions using a stimulus of 5 mV root-mean-square and scanning the frequency from 50 kHz to 1 mHz. EQUIVCRT was used to analyze the EIS data. Unless stated otherwise, the cutoff voltage applied during all galvanostatic experiments was set to 0 V vs Hg/HgO and all potential values are given vs Hg/HgO (6M KOH).

Results and Discussion

Galvanostatic behavior.— An electrode consisting of AP-produced SWNTs (Iljin Nanotech) was charged with a current density of -200 mA/g. Hereafter, the current was switched off for 1 h in order to let the potential relax to its equilibrium value. Subsequently, the electrode was discharged using a current density of $+200$ mA/g until the potential reached the cutoff potential. At this point the current was switched off again. Figure 1 shows the electrode potential vs the transferred amount of charge during charging (a) and discharging (b).

It is evident that when the electrode is charged, the potential decreases slowly and continuously to more negative values. Eventually, at a charge capacity of about 150 mAh/g, the potential stabilizes at about -1.1 V. At this point hydrogen gas bubbles were visually observed, indicating the onset of the hydrogen evolution reaction. From the overall charging response it can be deduced that close to 150 mAh/g of charge could be stored in the material, the rest being irreversibly lost due to hydrogen gas evolution. The subsequent discharge shows a rather featureless potential response up until the cutoff potential and close to 130 mAh/g of charge could be reversibly extracted. As it is rather difficult to determine where hydrogen evolution exactly starts during charging, it is not straightforward to calculate a precise value for the charge capacity. Additionally, during hydrogen evolution it is still possible that a small part of the current is used to add more charge to the SWNT material itself.

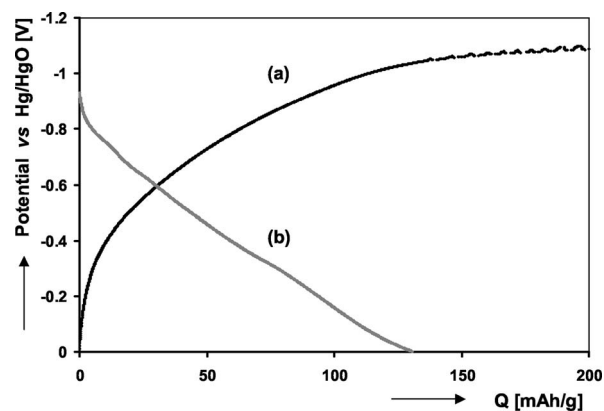


Figure 1. Electrochemical response of a composite electrode containing 10 mg of a.p. SWNT material, manufactured by means of AD (Iljin Nanotech), mixed with 75 mg of Ag. The (a) charging and (b) discharge behavior, using a current density of 200 mA/g, are shown.

Because of these complicating factors, only the discharge capacities can yield valid information about the amount of energy stored in a particular CNT material.

A featureless potential response, as depicted in Fig. 1 for a SWNT electrode, was observed during galvanostatic charging and discharging of all the measured CNT materials (SWNTs, MWNTs, CNFs). The only distinction that could be made between these materials was that the amount of charge inserted/extracted from the material could differ slightly, depending on the actual morphology of the sample measured. Overall, the highest discharge capacities were measured for a.p. SWNTs, amounting to ~ 130 mAh/g. Strikingly, discharge capacities of commercially purified SWNTs were, generally, about 5 mAh/g. Table I shows a summary of the gravimetric storage capacities, as well as other measured characteristics referred to later in this contribution, of all investigated CNT materials. In this table the uncertainty for each of the values is also included. These are based on the measuring error induced by the analysis method and the spread in the separate samples.

No plateau-like responses were ever observed during the charging or discharging of the CNT material. However, a plateau-like behavior was reported in work carried out by Rajalakshmi et al.,⁴ Gao et al.,⁶ and Qin et al.¹² Careful examination of these studies reveals that redox responses originating from the matrix material were falsely attributed to hydrogen storage in the CNT material. The oxidation and reduction of the copper compacting powder was measured by Rajalakshmi et al.⁴ Gao et al. and Qin et al. studied the hydrogen storage properties of MWNTs, using either nickel as compacting powder in the electrode preparation or Ni-coated MWNTs.^{6,12} In both contributions the measured redox response was attributed to hydrogen storage in MWNTs, leading to storage capacities of 450 and 500 mAh/g, respectively. However, the reported blank measurements on pure Ni essentially showed oxidation and reduction responses at exactly the same potentials as the Ni-coated MWNTs, only less intense. Based on this observation, it is more than likely that the measured redox responses are linked to the oxidation/reduction of Ni and not to hydrogen storage.

In order to prove that pure Ni can account for these effects, galvanostatic measurements were performed on a pure Ni electrode consisting of 200 mg of Ni (Aldrich, $\varnothing 0.8$ μ m), a composite electrode consisting of 10 mg of AD-produced a.p. SWNT material (MER Corp.) mixed with 200 mg of Ni, and a composite electrode containing 10 mg of the same a.p. SWNT material mixed with 200 mg of Ag. Figure 2 shows the potential responses of these electrodes during galvanostatic discharging using a current of $+0.2$ mA. The response of the pure Ni electrode [curve (a)] reveals a sloping plateau at around -0.7 V, which is nearly identical to the response found by Qin et al. for a MWNT/Ni composite electrode. As ex-

Table I. Specifications and experimentally determined parameters for all investigated CNT materials.^a

Material	Manufacturer	Manufacturing method	Residual catalyst (wt %) ± 0.5 wt %	Storage capacity (mAh/g) ± 2 (mAh/g)	BET surface area (m ² /g) ± 5 m ² /g	C _{dl} (V) (F/g)
a.p. SWNT	Iljin Nanotech	AD	22	130	100	25–65
Temp-treated SWNT	Iljin Nanotech	AD	30	110	80	20–45
HCl-treated SWNT	Iljin Nanotech	AD	15	107	ND	ND
Comm. Pur. SWNT	Iljin Nanotech	AD	2	3	175	5–15
a.p. SWNT	Carbolex	AD	13	35	185	45–70
a.p. SWNT	Univ. Montpellier	AD	15	64	ND	ND
a.p. SWNT	MER Corp.	AD	24	60	200	25–55
HNO ₃ -treated SWNT	MER Corp.	AD	4	72	220	35–65
a.p. SWNT	Univ. Dresden	LA	14	45	250	20–30
Aligned MWNT	Philips Research Aachen	CVD	4	53	ND	ND
a.p. MWNT	IMRE	CVD	11	11	260	15–35
HNO ₃ -treated MWNT	IMRE	CVD	1	22	350	20–40
a.p. CNF	Shell Global Solutions	CVD	2	55	25	10–30
HNO ₃ -treated CNF	Shell Global Solutions	CVD	1	10	70	25–40
Aligned MWNT	Shell Global Solutions	CVD	5	25	ND	ND

^a The storage capacity (obtained at a 200 mA/g discharge) and (potential-dependent) C_{dl} were determined electrochemically. Moreover, the uncertainty for each of the measured quantities is given in italic font. The values for C_{dl} indicate a range and were rounded up/down to the nearest 5 F/g. Some characteristics were not determined (ND) for some samples.

pected, the SWNT/Ni composite electrode reveals a very similar curve [curve (b)]. This indicates that this response is dominated by the electrochemical oxidation of the Ni matrix and only to a minor extent by that of the SWNT material. Pourbaix has shown that Ni is electrochemically active in 6 M KOH solutions at potentials between 0.8 and 0 V.¹³ Based on the data provided, the plateaus observed in curves (a) and (b) must therefore be attributed to the oxidation of Ni to Ni(OH)₂.

The small difference between curves (a) and (b) results from the response of the a.p. SWNT material. By using an inert matrix material in the composite electrode (i.e., Ag), the electrochemical response of the SWNT material can easily be measured [see Fig. 2, curve (c)]. This again results in a featureless discharge curve, characteristic for these types of materials (see also Fig. 1). Furthermore, subtracting the amount of charge extracted from the pure Ni electrode [curve (a)] from that of the SWNT/Ni composite electrode [curve (b)] yields approximately the value given by curve (c).

In order to unravel the energy storage mechanism responsible for the characteristic CNT response shown in Fig. 1, specific electrochemical measurements can be utilized. Basically, energy can be electrochemically stored via two main processes: (i) Via a redox

reaction, coupled with charge transfer. In this process the electrode material is either oxidized or reduced at the solid/electrolyte interface, resulting in the consumption or release of electrons. Essentially, electrical energy is converted into chemical energy, and vice versa. (ii) Via electrostatic charging/discharging of a capacitive element. In this process, usually associated with materials that have a very large surface area, charge is stored electrostatically across the solid/electrolyte interface. Here, no charge transfer takes place. This process is actually identical to the storage of charge across the plates of an electronic capacitor.

Using the appropriate electrochemical techniques it is possible to estimate to what extent charge is stored via a redox reaction, electrostatically, or a combination of both. In order to establish whether or not a charge-transfer mechanism plays a role in the electrochemical energy storage of SWNTs, it is investigated whether a Tafel-like behavior (indicative of charge transfer) can be measured.¹⁴ Figure 3 depicts the potential responses of an a.p. SWNT material (AD-produced, Carbolex) when charging at different current densities. A characteristic featureless shape is observed during charging, as was already shown in Fig. 1 for a different SWNT sample. If the logarithm of the applied current is plotted vs the measured potential at

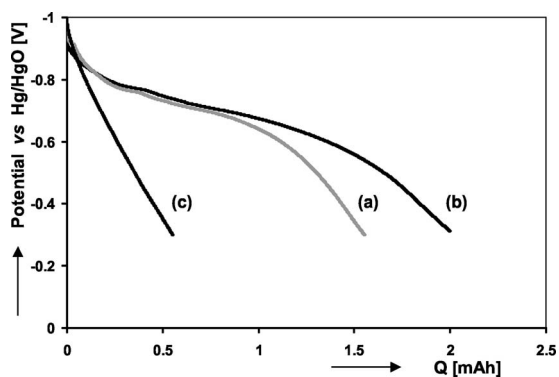


Figure 2. Galvanostatic discharge curves of a (a) pure Ni electrode, (b) a SWNT/Ni composite electrode, and (c) a SWNT/Ag composite electrode. The applied discharge current was +0.2 mA and the cutoff potential was set to -0.3 V. The a.p. SWNT material was obtained from MER Corp. and produced with AD.

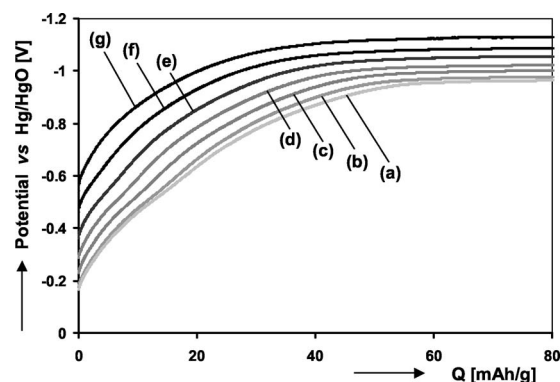


Figure 3. Galvanostatic charging curves of 10 mg a.p. SWNT material, produced means of AD (Carbolex), mixed with 75 mg of Ag. The current densities used were (a) 2, (b) 4, (c) 10, (d) 20, (e) 50, (f) 100, and (g) 200 mA/g.

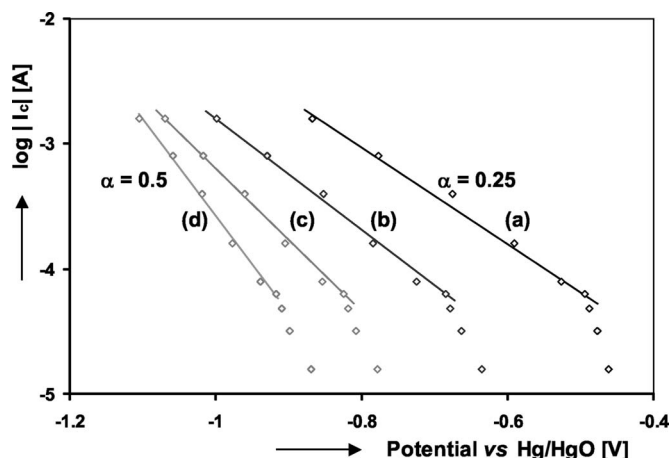


Figure 4. Tafel behavior of the a.p. SWNT material shown in Fig. 3. Tafel plots are shown for (a) 10, (b) 20, (c) 30, and (d) 40 mA/h/g. Additionally, the calculated values for α are shown for the extreme cases.

specific energy storage capacity values (Q), a Tafel plot can be constructed. This plot is shown in Fig. 4 for Q values of 10–40 mA/h/g.

It is evident that the SWNT material clearly exhibits Tafel behavior for the higher current densities used. Deviation from this linear dependence, at low current density, results from the fact that the back reaction cannot be neglected anymore ($\eta < 60$ mV). The observed Tafel behavior indicates that in this case a charge-transfer reaction is definitely occurring and also significantly contributing to the overall energy storage of this material. It is interesting that α slowly changes from about 0.25 at 10 mA/h/g to approximately 0.5 at 40 mA/h/g. This points to that fact that the kinetics of the charge-transfer reaction is changing from asymmetric to fully symmetric.¹⁵ However, the exact reason explaining such a behavior cannot be given at this moment. This will require additional research.

Galvanostatic intermittent titration technique.— The isotherms of the CNT materials were determined electrochemically by means of galvanostatic intermittent titration technique (GITT). The electrode was charged by applying 50 current pulses of 1.5 min, using a current density of -200 mA/g. 50 pulses were found to be sufficient to completely charge the electrode and reach the stage at which hydrogen gas bubbles were produced. After each current pulse the current was switched off for 1 h, so the potential could relax to its equilibrium state. After GITT charging, the electrode was discharged using GITT employing the same parameters, with the only difference that a current density of $+200$ mA/g was used.

Figure 5 shows the obtained equilibrium data for both charging [curve (a)] and discharging [curve (b)]. Additionally, the galvanostatic charge (c) and discharge (d) curves of this sample are shown, also using a current density of 200 mA/g. It can be seen that these are nearly identical to those shown in Fig. 1. During galvanostatic discharging, no cutoff potential was set. Comparing both the equilibrium and the galvanostatic data, it is clear that the shapes of the curves are very similar. During charging the equilibrium potential gradually decreases until a constant potential is reached after the storage capacity reaches a value close to 150 mA/h/g.

During GITT discharging [see curve (b)] a featureless curve can be seen up to a potential of -0.2 V, equal to that of the galvanostatic discharge up to 0 V [see curve (d)]. However, upon continued discharging a sloping plateau is revealed in both the GITT curve (between -0.2 and 0 V) and the galvanostatic curve (between $+0.1$ and $+0.4$ V). A very similar response was also seen by Jurewicz et al. for activated carbon and was attributed to overoxidative modification of the carbon.¹⁶ This shows that this process, of which the equilibrium potential extends from -0.2 to at least 0 V, cannot be

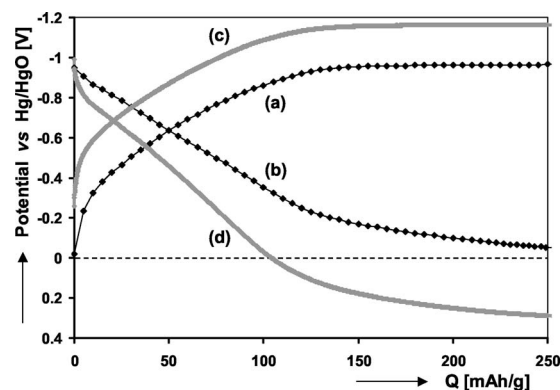


Figure 5. Equilibrium voltage curves during (a) charging and (b) discharging of an AD-produced SWNT material (10 mg of SWNT mixed with 75 mg of Ag). Additionally, the galvanostatic charge (c) and discharge (d) responses are shown for the same sample. In all cases a current density of -200 mA/g was used for charging and $+200$ mA/g for discharging.

related to hydrogen extraction. This hypothesis was also confirmed by experimental data, which showed that this process could also be measured when investigating a CNT sample that was not yet electrochemically charged (not shown here). Additionally, these measurements showed that this process was of irreversible nature. Moreover, O_2 formation cannot explain this response as this process only occurs at potentials more positive than $+0.2$ V. Disregarding hydrogen gas formation and the process related to oxidation of the CNT material itself leaves only the responses up to about 120 mA/h/g unexplained. Although galvanostatic measurements and GITT experiments both show similar responses in this region, neither technique can provide a clear indication of what type of process is taking place. In this next section, CV is used in an attempt to obtain a clearer picture.

Cyclic voltammetry.— In order to understand what part of a particular CNT material gives rise to which current response, CV was performed on different samples consisting of key components also present in the a.p. material (i.e., metal catalyst, CNT material obtained after partial purification of a.p. material (i.e., heat-treated), and commercially purified CNTs). Overall, the samples presented in this section give a very good indication of which fraction is actually (electro)chemically active and which one does not contribute to the measured electrochemical response. For the sake of clarity only one type of CNT material is presented. As the AD-produced SWNT material obtained from Iljin Nanotech showed the most promising electrochemical response, this material is presented here.

The four key materials of which the CV responses are compared include:

Unpurified a.p. SWNTs.— This material contains about 50–60 vol % CNTs. The main impurities present in this material are residual metal catalyst (22 wt %) and carbonaceous impurities. XRD showed some graphite and TEM analysis indicated large quantities of amorphous carbon and carbon shells around the bulk of the residual catalyst. Additionally, the material contains close to 4 wt % of smaller fullerenes (C_{60} , C_{70}).

Heat-treated SWNTs.— This material was obtained by heating the a.p. SWNT material at 350°C for 1.5 h. This was done in an O_2/Ar atmosphere (50/50 vol %). The result of this heat-treatment is the combustion of a significant part of the amorphous carbon impurities. Especially the carbon shells, encapsulating the metal catalyst in the a.p. material, are removed during this purification step. The result is that almost all metal impurities are electrochemically accessible. Close to 30 wt % of the material consists of metal impurities.

Metal fraction.— This sample consists of a mixture of metals identical to the metal catalyst fraction present in the a.p. SWNT material. The sample consisted of a mixture of Fe, Ni, and Co powders (2:3:3

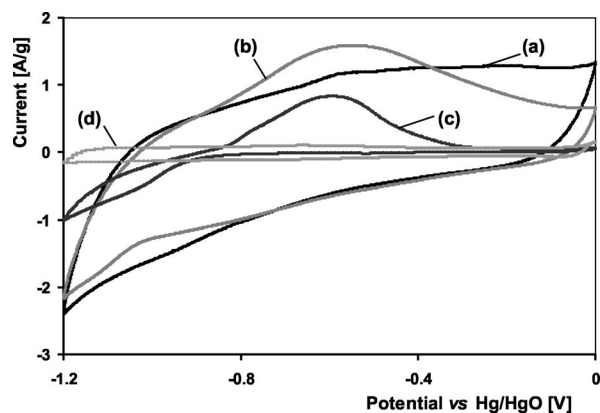


Figure 6. CVs of different fractions of SWNT material with Ag matrix material, showing (a) a.p. SWNTs, (b) heat-treated SWNTs, (c) metal catalyst fraction, and (d) commercially purified SWNTs. A scan rate of 5 mV/s was used and all voltammograms were normalized to enable direct comparison.

on weight basis). However, the particle size of the powders used (300 nm) was larger than the cluster size of the metal impurities in the SWNT material (50–100 nm). This mixture was heated at 350°C for 1.5 h in an O₂/Ar atmosphere (50/50 vol %). This was done in order to mimic the heat-treatment of the purification procedure.

Commercially purified SWNTs.— This material is obtained after extensive purification of a.p. SWNT material. The precise purification procedure is not known but involves several acid treatments and partial oxidation steps. The material contains only 2 wt % of residual catalyst. The main carbonaceous impurity is graphite (XRD analysis). The final product is reported to contain close to 80–90 vol % of SWNTs.

For all these samples at least five consecutive CV scans were made using a scan rate of 5 mV/s and scanning between 0 and –1.2 V. For each sample, a stable CV was obtained after the second scan. These scans are depicted in Fig. 7, in which the current values are normalized to 10 mg of active electrode material, enabling direct comparison.

Curve (a) in Fig. 6 shows the CV response of the a.p. SWNT material. The voltammogram shows that when changing the potential of the electrode in negative direction (charging), a gradually increasing negative current is measured. Although the highest reduction current is measured at around –1.2 V, hydrogen evolution was experimentally observed, indicating that a substantial part of the measured current can be attributed to this process. Like in the galvanostatic experiments presented earlier, almost no discontinuities or features can be observed during the charging process. When the scan is reversed at –1.2 V, a gradually increasing oxidation current is observed which reaches a plateau current in the potential region between –0.6 and 0 V. Very close to 0 V the current seems to increase once more, probably due to the electrochemical process related to the oxidation of the carbon material. The overall response shown in curve (a), although looking distinctly capacitive in nature, can be explained in part by focusing on the response induced by the metal catalyst fraction. Frackowiak and Beguin already indicated that pseudocapacitive electrochemical responses could result from very small (transition) metal clusters dispersed on carbon material.¹⁷ The remaining metal clusters in the a.p. SWNT material are indeed nicely distributed and of similar small size. In order to check the influence of the residual metal catalyst the a.p. material was heat-treated, resulting in the fact that almost all metal is directly electrochemically accessible. The corresponding voltammogram is depicted as curve (b) in Fig. 6, revealing not a predominantly featureless response as for the a.p. material [curve (a)] but showing redox responses on top of a featureless background. These are mea-

sured during reduction between –1.0 and –1.2 V and during oxidation between –0.7 V and –0.4 V. As most metal impurities are electrochemically accessible in this material (verified by TEM and SEM, not shown here), it is likely that the measured redox responses originate from the reduction/oxidation of Fe, Ni, and Co species.

This hypothesis is verified by curve (c), showing the response of the metal fraction only. Although the exact oxidation state and cluster size of the metal impurities in the a.p. material can never be duplicated, the mixture shows a distinct reduction and oxidation response at exactly the same potentials as the heat-treated material. This indeed suggests that the metal fraction accounts for a substantial part of the measured electrochemical response shown in curves (a) and (b).

Removing practically all the metal catalyst and the bulk part of the carbonaceous impurities, effectively only leaving the SWNTs, results in a very poor electrochemical response [curve (d)]. This curve shows a featureless CV, very similar to the “block” response of an ideal capacitor.¹⁸ Compared to the a.p. SWNT material [curve (a)], the measured current is over 1 order of magnitude lower, indicating very poor energy storage characteristics for purified SWNTs.

In conclusion, the electrochemical response of a.p. SWNT material can mainly be attributed to residual metal catalyst and some redox behavior of carbonaceous impurities. This is in line with the evidence found in Fig. 4, indicating that charge is stored in the material via a charge-transfer reaction. The response of commercially purified SWNTs, however, appears to be completely capacitive, indicating electrostatic energy storage only.

Electrochemical impedance spectroscopy.— EIS measurements were conducted to identify the processes giving rise to the electrochemical response measured during galvanostatic or CV experiments. Although these impedance measurements were performed on many CNT materials, only a few selected materials are presented in this section in detail. These include a.p. SWNTs and commercially purified SWNTs from Iljin Nanotech and HNO₃ purified MWNTs from IMRE. These materials were chosen as their responses revealed specific characteristics which can be used most efficiently in explaining the different types of charge storage involved when electrochemically investigating CNT materials. Of the remaining materials the experimentally determined parameters (C_{dl} and BET surface area) are shown in Table I.

All EIS measurements were done under steady-state conditions at potentials between 0 and –1.2 V, at 50 mV intervals. The experiment was started at an electrode potential of 0 V. In order to obtain steady state, the electrode potential was fixed for 1 h at this potential. Hereafter, the EIS measurement was performed. Subsequently, the electrode potential was changed stepwise to a more negative value and again fixed for 1 h before the next EIS experiment was conducted. This procedure was repeated until a potential of –1.2 V was reached. At this point the electrode was discharged with the same small potential steps and the impedance was again measured at each of these potentials.

A.P. SWNTs.— For an a.p. SWNT material (Iljin Nanotech) the experimentally obtained impedance data when charging the electrode is shown in Fig. 7. In this figure selected measurements are presented for the sake of clarity. All impedance plots shown consist of a single, large semicircular response in the intermediate- and low-frequency range. The diameter of this circle diminishes in size at very negative potentials (–1.1 to –1.2 V). In the high-frequency range some small effects can be observed which can be related to porosity effects.¹⁹ As this high-frequency part is not of particular interest when considering the electrochemical energy storage characteristics, it is not treated in this study. By modeling the experimental data with the simplified EQC shown in the inset in Fig. 7, values for the charge-transfer resistance (R_{ct}) and the double-layer capacitance (C_{dl}) can be determined at each potential. The values obtained for C_{dl} , during charging and discharging, are plotted vs potential in Fig. 8.

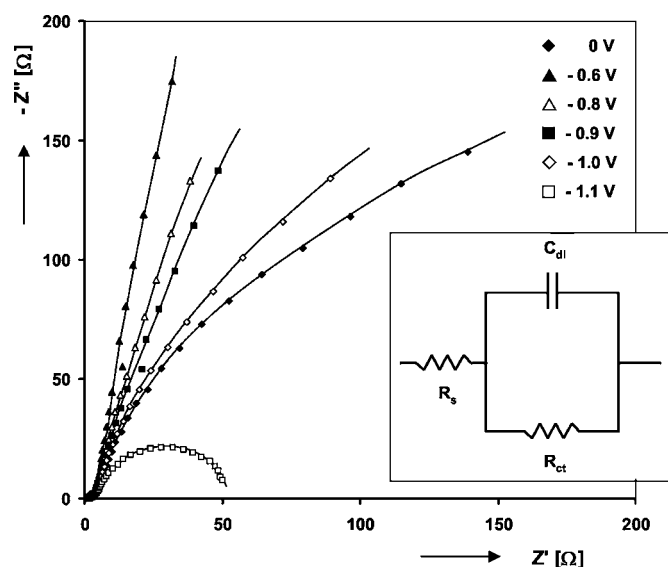


Figure 7. Impedance spectra of 10 mg a.p. SWNT material (Iljin Nanotech) mixed with 75 mg of Ag. Data is shown of measurements performed at (◆), 0 (▲) - 0.6, (△) - 0.8, (■) - 0.9, (◇) - 1.0, and (□) - 1.1 V. Inset the equivalent circuit used to model the impedance data.

The C_{dl} values shown in Fig. 8 closely match those that can be calculated based on the BET surface area of this material, which was analyzed to be around $100 \text{ m}^2/\text{g}$. Straightforward calculation shows that using $35 \text{ } \mu\text{F}/\text{cm}^2$ as an average value for the specific double-layer capacitance ($C_{dl,spec}$) of SWNT material in an aqueous electrolyte²⁰ and the mentioned BET surface area, a C_{dl} value of 35 F/g is expected. This value is close to the C_{dl} values obtained via EIS, which are shown in Fig. 8. The $C_{dl,spec}$ value used is based on a substantial number of different CNT materials investigated by Emmenegger et al., showing that $C_{dl,spec}$ ranges from 10 to $60 \text{ } \mu\text{F}/\text{cm}^2$, depending on the morphology of the material. Additionally, it was experimentally determined that the contribution of the silver matrix material (see Experimental section) to the measured C_{dl} is negligible (not shown here).

Now that C_{dl} has been determined for a whole range of potentials, the corresponding double-layer charging or discharging current can be calculated and subsequently compared to the experimentally obtained CV (see Fig. 6, curve a). The calculated double-layer cur-

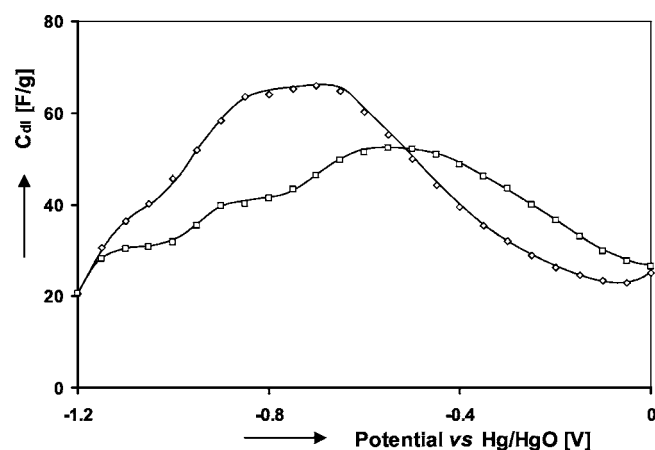


Figure 8. Plot showing the value of C_{dl} vs potential for the a.p. SWNT material shown in Fig. 7 for both (◇) charging and (□) discharging.

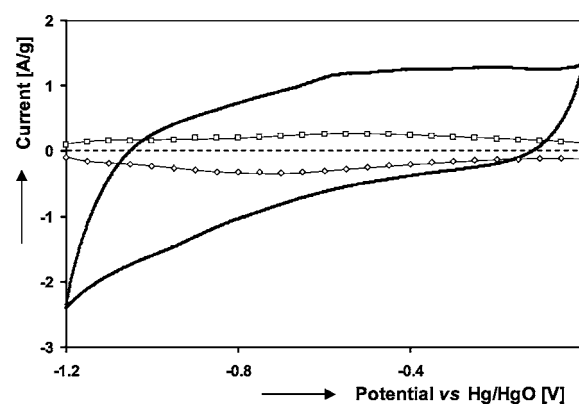


Figure 9. CV of the a.p. SWNT material shown in Fig. 7 obtained at a scan rate of 5 mV/s (bold continuous line). The calculated double-layer charging current, during (◇) charging and (□) discharging of the SWNT material is also plotted.

rent (I_{dl}) at a certain potential is equal to the product of the double-layer capacitance (C_{dl}) at that potential and the scan rate (ν) at which the CV is performed (see Eq. 2)²¹

$$I_{dl}(E) = C_{dl}(E)\nu \quad [2]$$

In this manner the double-layer charging and discharging current can be distinguished from the faradaic current, which is directly coupled to the amount of charge stored via a charge-transfer reaction. For this approach the results of the steady-state impedance experiment are combined with the results of the dynamic CV experiment. However, if the assumption remains valid that C_{dl} is the same in dynamic and static conditions (at the same potential) this method can prove highly useful.

Figure 9 shows the measured CV plot of the same material obtained at a scan rate of 5 mV/s (bold continuous line). Additionally, the calculated I_{dl} during charging and discharging are depicted in this figure (open symbols). It is evident that when comparing these currents, charging and discharging of the double layer cannot be neglected. Near a potential of -0.8 V , the double-layer current accounts for over one-third of the total current response in the CV plot. Apparently, a quite significant part of the energy is stored electrostatically, whereas the remainder is the result of faradaic processes (electrochemical charge transfer). This shows that this electrostatic process contributes significantly to the overall energy storage properties of these a.p. SWNTs.

Commercially purified SWNTs.— Above it was shown that the electrochemical response of an a.p. SWNT material could be attributed, for a substantial part, to the electrostatic charging of the double layer. As this material is comprised of not only SWNTs (50 vol %) but also metal catalyst and carbonaceous impurities, it is hard to estimate which fraction accounts for the electrostatic part and which for the faradaic part. Commercially purified SWNTs (Iljin Nanotech), containing close to 90 vol % CNTs, were therefore investigated by impedance experiments.

The EIS results were again used to calculate the charging and discharging current of the electrical double layer. These results are shown in Fig. 10, together with the corresponding CV ($\nu = 5 \text{ mV/s}$). Apart from some minor differences, the calculated double-layer current is indeed almost identical to the measured CV plot at all potentials. The differences can be explained by oxidation of the carbon near 0 V (as explained above), hydrogen gas evolution in the potential region between -1.0 and -1.2 V , and redox responses linked to oxidation/reduction of metal remaining catalyst at around -0.7 V (see Cyclic voltammetry section).

This observation must lead to the conclusion that even the low current measured in the CV is not caused by an actual electrochemi-

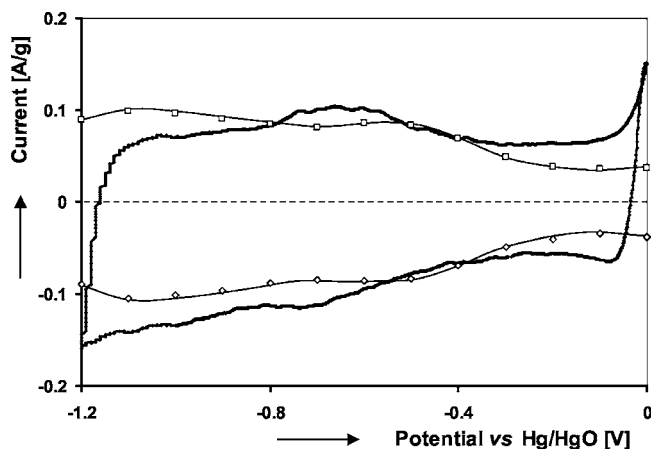


Figure 10. CV of a commercially purified SWNT material (Iijin Nanotech) obtained at a scan rate of 5 mV/s (bold continuous line). The composite electrode consisted of 10 mg of SWNT and 75 mg of Ag. The calculated double-layer charging current during (\diamond) charging and (\square) discharging is also plotted.

cal reaction (faradaic) but merely by the charging and discharging of the electrical double layer. This unambiguously shows that SWNTs, of which the purified material mainly consists, are only able to store energy electrostatically and not electrochemically. Like for the a.p. SWNT material the validity of the calculated electrostatic storage can be checked. Using $C_{dl,spec} = 10 \mu\text{F}/\text{cm}^2$, based on work done on purified SWNTs by Frackowiak et al.²² and the measured BET surface area of this material ($175 \text{ m}^2/\text{g}$), C_{dl} can be calculated. The determined value (17 F/g) is equal to those experimentally determined in the potential region of -0.4 to -1.2 V .

Purified MWNTs.— Until this point only the electrochemical response of SWNT materials has been explained in detail. It was shown that the response could be attributed to the electrostatic charging of the double layer and the faradaic response linked to the oxidation/reduction of the (metal) impurities. That this reasoning also holds for the other materials investigated (MWNTs and CNFs) is shown by taking a closer look at the response of a MWNT material.

CV and EIS measurements were performed on a HNO_3 -purified MWNT material (IMRE). This material consists of solely CNTs, contains a very low amount of residual catalyst ($\sim 1 \text{ wt } \%$) and only a minor amount of carbonaceous impurities. Figure 11 shows the

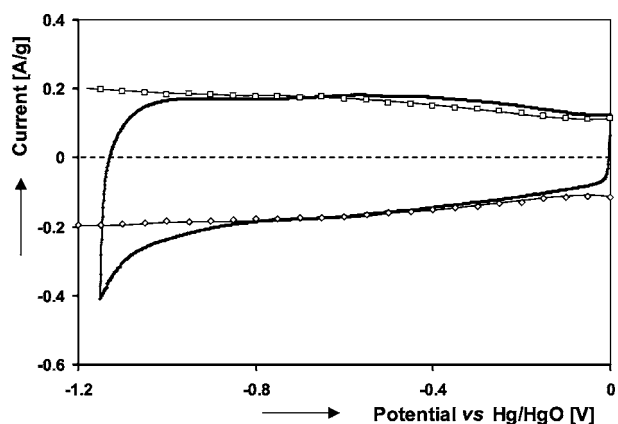


Figure 11. CV plot of a composite electrode consisting of 10 mg of HNO_3 purified MWNT material (IMRE) and 75 mg of Ag. The scan rate used was $\nu = 5 \text{ mV/s}$ (bold continuous line). The calculated double-layer charging currents during (\diamond) charging and (\square) discharging are also shown.

CV of this material using a scan rate of 5 mV/s and cycling between 0 and -1.15 V . The voltammogram is highly symmetrical when comparing the reduction and oxidation currents. This symmetrical shape shows that all charge stored in the material can be released with a very high coulombic efficiency ($\sim 95\%$). This was also confirmed using galvanostatic experiments (not depicted here). The reduction response near -1.1 V can again be linked to hydrogen gas formation. The overall shape of the CV curve is very similar to that what would be expected for purely capacitive behavior.

Focusing on the calculated double-layer current, which is depicted in Fig. 11 both for charging (\diamond) and discharging (\square), it is evident that the electrochemical response of this MWNT material is completely dominated by electrostatic (dis)charging of the double layer. There is no experimental evidence of any significant, reversible faradaic contribution. Like for the a.p. SWNT and commercially purified SWNT materials, the BET surface area ($350 \text{ m}^2/\text{g}$) can be used to calculate the expected value for C_{dl} , resulting in a value matching that experimentally determined.

The double-layer capacitance of this material, in the potential range of 0 to -1 V , is $25\text{--}40 \text{ F/g}$. This very large capacitance, and the fact that all energy can be released with a very high coulombic efficiency, shows that this MWNT material might be advantageously used in the field of electrochemical double-layer capacitors. Although significant, the energy storage and release related to these materials is, however, still substantially lower than that reported for polypyrrole-coated MWNTs (up to 300 F/g)^{22,23} and traditional RuO_2 pseudocapacitors (well over 100 F/g)²⁴ in acidic media.

Conclusions

The electrochemical energy storage properties of a wide variety of CNT materials, produced via different methods, were investigated. Additionally, some of these samples were chemically treated in-house before being electrochemically investigated. From all the measured electrochemical responses, only a small selection was presented in this contribution.

Galvanostatic measurements showed that the general electrochemical response of all these materials, during charging and discharging, is rather featureless and does not show any phase transition or clear redox responses. The maximum discharge capacity of all investigated materials was $\sim 130 \text{ mAh/g}$ for a.p. SWNT materials, which is generally what is reported in most of the literature dealing with this subject. Surprisingly, the commercially purified SWNT materials that were investigated showed very low discharge capacities (generally less than 10 mAh/g).

Measurements indicated that the electrochemical activity of the matrix material, used to manufacture composite electrodes, should not be ignored. It was shown that the response of electrochemically active matrix materials (Ni) was falsely attributed by a number of other researchers in the past to the ability of the CNT material to store hydrogen. Therefore, only electrochemically inactive matrix materials were used in the current study (Ag). Interestingly, Tafel plots did indicate that part of the measured response of a SWNT electrode could be linked to a charge-transfer reaction, as a clear linear dependency was measured.

To evaluate the equilibrium behavior of the CNT materials, GITT was performed. The resulting isotherms revealed curves identical in shape to those obtained from galvanostatic experiments, with the only exception that a sloping plateau emerged at around -0.2 V during the discharge. Based on literature and extensive experimentation, this plateau was attributed to the irreversible oxidation of the carbon material.

In addition to the galvanostatic experiments CV was performed. As commercially purified SWNTs showed a substantially lower response, as compared to their a.p. counterpart, it is believed that the CNTs are only able to account for a small part of the measured response. Analysis on a number of characteristic SWNT samples showed that the measured response of a.p. SWNTs materials is related to a number of processes. Among these are hydrogen gas for-

mation, irreversible oxidation of carbonaceous material, reversible oxidation/reduction of residual metal catalyst or carbonaceous impurities, and a significant electrostatic charging component.

Impedance measurements, obtained at steady state, were cross-correlated with CV data. This showed that the electrostatic storage of energy could be linked directly to (dis)charging of the electrical double layer. Highly pure CNT materials, like commercially purified SWNTs and MWNTs, showed that more than 90% of the total charge was stored electrostatically. However, about 25% of the total amount of charge could be explained in this way for the a.p. SWNT materials, the remainder being caused by the processes mentioned above.

Overall, it can be concluded that it is very unlikely that a significant amount of hydrogen can be stored in CNT material and that the measured responses are due to electrostatic charging of the double layer and the oxidation/reduction of (metal) impurities. The exact amount of charge that can be reversibly stored in CNT material heavily depends on its morphology and the level of purity.

Acknowledgments

The authors thank M. Ouwerkerk, P. Kalisvaart, and Z. Jiang for many interesting and stimulating discussions. Furthermore, H. Stil, J. Zhang, O. Jost, and P. Bachmann are acknowledged for providing some of the CNT samples.

Eindhoven University of Technology assisted in meeting the publication costs of this article.

References

1. A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, *Nature (London)*, **386**, 377 (1997).
2. C. Nützenadel, Ph.D. Thesis, University of Fribourg (1999).
3. C. Nützenadel, A. Züttel, D. Chartouni, and L. Schlapbach, *Electrochem. Solid-State Lett.*, **2**, 30 (1999).
4. N. Rajalakshmi, K. S. Dhathreyan, A. Govindaraj, and B. C. Satishkumar, *Electrochim. Acta*, **45**, 4511 (2000).
5. S. M. Lee, K. S. Park, Y. C. Choi, Y. S. Park, J. M. Bok, D. J. Bae, K. S. Nahm, Y. G. Choi, S. C. Yu, N. Kim., T. Frauenheim., and Y. H. Lee, *Synth. Met.*, **113**, 209 (2000).
6. X. P. Gao, Y. Lan, G. L. Pan, F. Wu, J. Q. Qu, D. Y. Song, and P. W. Shen, *Electrochem. Solid-State Lett.*, **4**, A173 (2001).
7. A. Züttel, Ch. Nützenadel, P. Sudan, Ph. Mauron, Ch. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaff, and T. Kiyobayashi, *J. Alloys Compd.*, **330-332**, 676 (2002).
8. H. Zhang, X. Fu, Y. Chen, S. Yi, S. Li, Y. Zhu, and L. Wang, *Physica B*, **352**, 66 (2004).
9. A. K. M. Fazle Kibria, Y. H. Mo, K. S. Park, K. S. Nahm, and M. H. Yun, *Int. J. Hydrogen Energy*, **26**, 823 (2001).
10. A. Züttel, P. Sudan, Ph. Mauron, T. Kiyobayashi, Ch. Emmenegger, and L. Schlapbach, *Int. J. Hydrogen Energy*, **27**, 203 (2002).
11. R. A. H. Niessen and P. H. L. Notten, *Electrochim. Acta*, **50**, 2959 (2005).
12. X. Qin, X. P. Gao, H. Liu, H. T. Yuan, D. Y. Yan, W. L. Gong, and D. Y. Song, *Electrochem. Solid-State Lett.*, **3**, 532 (2000).
13. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd ed., p. 333, National Association of Corrosion Engineers, Houston, TX (1974).
14. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., p. 103, John Wiley & Sons, New York (2001).
15. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., p. 97, John Wiley & Sons, New York, (2001).
16. K. Jurewicz, E. Frackowiak, and F. Béguin, *Electrochem. Solid-State Lett.*, **4**, A27 (2001).
17. E. Frackowiak and F. Béguin, *Carbon*, **39**, 937 (2001).
18. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed. p. 18, John Wiley & Sons, New York (2001).
19. E. Karden, Ph.D. Thesis, Aachen University of Technology (2001).
20. Ch. Emmenegger, Ph. Mauron, P. Sudan, P. Wenger, V. Hermann, R. Gallay, and A. Züttel, *J. Power Sources*, **124**, 321 (2003).
21. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., p. 233, John Wiley & Sons, New York (2001).
22. E. Frackowiak, K. Jurewicz, K. Szostak, S. Delpoux, and F. Béguin, *Fuel Process. Technol.*, **77**, 213 (2002).
23. E. Frackowiak, K. Jurewicz, K. Szostak, S. Delpoux, and F. Béguin, *Chem. Phys. Lett.*, **347**, 36 (2001).
24. B. E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic/Plenum Publishers, New York (1999).