The electrochemistry of carbon nanotubes: I, aqueous electrolyte

Citation for published version (APA):

DOI:
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:

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Download date: 07. Oct. 2019
The Electrochemistry of Carbon Nanotubes

I. Aqueous Electrolyte

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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.

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The CNT materials were electrochemically analyzed in the form of cylinder-shaped pellet electrodes (8 mm Ø 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 851e (STAR² software). The experiments were performed in the temperature regime of 25–1100°C, utilizing a heating rate of 1°C/min and using a 50/50 vol % O₂/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 (P₀) was 772 mmHg.

Electrochemical measurements were performed using a three-electrode setup of which the specifications were given in previous work.⁴ Galvanostatic measurements were performed using a Macor 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 (6 M 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.

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.,⁶ Gao et al.,⁶ and Qin et al. 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.⁶ 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. 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 likely than likely that hydrogen resp.
served in curves
Galvanostatic discharge curves of a
/H2O851
curve
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terial in the composite electrode
response of the a.p. SWNT material. By using an inert matrix ma-
dation of Ni to Ni
response of the SWNT material can easily be measured
/tween 0.8 and 2 V.13 Based on the data provided, the plateaus ob-
electrochemically active in 6 M KOH solutions at potentials be-
extent by that of the SWNT material. Pourbaix has shown that Ni is
the electrochemical oxidation of the Ni matrix and only to a minor
characteristic for these types of materials
produced with AD.

The small difference between curves (a) and (b) results from the response of the a.p. SWNT material. By using an inert matrix ma-
terior 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 ma-
characteristic for these types of materials (see also Fig. 1). Furthermore,
subtracting the amount of charge extracted from the pure Ni ele-
response of the SWNT material can easily be measured [see Fig. 2, curve (c)]. This again results in a featureless discharge curve, charac-
teirod SWNT composite electrode. The electrochemical re-
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 electro-
chemical 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 inter-
face, 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 el-
ment. 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, elec-
statically, or a combination of both. In order to establish whether or not a charge-transfer mechanism plays a role in the electrochemi-
energy storage of SWNTs, it is investigated whether a Tafel-like behavior (indicative of charge transfer) can be measured.14 Figure 3
picts the potential responses of an a.p. SWNT material (AD-produced, Carbolex) when charging at different current densities. A charac-
teristic featureless shape is observed during charging, as was already shown in Fig. 1 for a different SWNT sample. If the loga-
mith of the applied current is plotted vs the measured potential at

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Manufacturing method</th>
<th>Residual catalyst (wt %) ±0.5 wt %</th>
<th>Storage capacity (mAh/g) ±2 (mAh/g)</th>
<th>BET surface area (m²/g) ±5 m²/g</th>
<th>Cdl (V) (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.p. SWNT</td>
<td>Iljin Nanotech</td>
<td>AD</td>
<td>22</td>
<td>130</td>
<td>100</td>
<td>25–65</td>
</tr>
<tr>
<td>Temp-treated SWNT</td>
<td>Iljin Nanotech</td>
<td>AD</td>
<td>30</td>
<td>110</td>
<td>80</td>
<td>20–45</td>
</tr>
<tr>
<td>HCl-treated SWNT</td>
<td>Iljin Nanotech</td>
<td>AD</td>
<td>15</td>
<td>107</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Comm. Pur. SWNT</td>
<td>Iljin Nanotech</td>
<td>AD</td>
<td>2</td>
<td>3</td>
<td>175</td>
<td>5–15</td>
</tr>
<tr>
<td>a.p. SWNT</td>
<td>Carbolex</td>
<td>AD</td>
<td>13</td>
<td>35</td>
<td>185</td>
<td>45–70</td>
</tr>
<tr>
<td>a.p. SWNT</td>
<td>Univ. Montpellier</td>
<td>AD</td>
<td>15</td>
<td>64</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>a.p. SWNT</td>
<td>MER Corp.</td>
<td>AD</td>
<td>24</td>
<td>60</td>
<td>200</td>
<td>25–55</td>
</tr>
<tr>
<td>HNO₃-treated SWNT</td>
<td>MER Corp.</td>
<td>AD</td>
<td>4</td>
<td>72</td>
<td>220</td>
<td>35–65</td>
</tr>
<tr>
<td>a.p. SWNT</td>
<td>Univ. Dresden</td>
<td>LA</td>
<td>14</td>
<td>45</td>
<td>250</td>
<td>20–30</td>
</tr>
<tr>
<td>Aligned MWNT</td>
<td>Philips Research Aachen</td>
<td>CVD</td>
<td>4</td>
<td>53</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>HNO₃-treated MWNT</td>
<td>IMRE</td>
<td>CVD</td>
<td>1</td>
<td>22</td>
<td>350</td>
<td>20–40</td>
</tr>
<tr>
<td>a.p. CNF</td>
<td>Shell Global Solutions</td>
<td>CVD</td>
<td>2</td>
<td>55</td>
<td>25</td>
<td>10–30</td>
</tr>
<tr>
<td>HNO₃-treated CNF</td>
<td>Shell Global Solutions</td>
<td>CVD</td>
<td>1</td>
<td>10</td>
<td>70</td>
<td>25–40</td>
</tr>
<tr>
<td>Aligned MWNT</td>
<td>Shell Global Solutions</td>
<td>CVD</td>
<td>5</td>
<td>25</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

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

Figure 2. Galvanostatic discharge curves of a (a) pure Ni electrode, (b) a SWNT/Ni composite electrode, and (c) a SWNT/Ni 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.
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 mAh/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 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 the calculated values for $Q$ slowly change from about 0.25 at 10 mAh/g to approximately 0.5 at 40 mAh/g. This points to that fact that the kinetics of the charge-transfer reaction is changing from asymmetric to fully symmetric. However, the exact reason explaining such a behavior cannot be given at this moment. This will require additional research.

*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 from IJin 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 (30/50 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 (2:3:3:1).
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-like 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. 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 measured 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. 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-like, 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 (Cdl 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. 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 (Rct) and the double-layer capacitance (Cdl) can be determined at each potential. The values obtained for Cdl during charging and discharging, are plotted vs potential in Fig. 8.
The $C_d$ 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 m²/g. Straightforward calculation shows that using 35 µF/cm² as an average value for the specific double-layer capacitance ($C_{dl,spec}$) of SWNT material in an aqueous electrolyte and the mentioned BET surface area, a $C_d$ value of 35 F/g is expected. This value is close to the $C_d$ 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 µF/cm², 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 $C_d$ is negligible (not shown here).

Now that $C_d$ 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 current ($I_d$) at a certain potential is equal to the product of the double-layer capacitance ($C_d$) at that potential and the scan rate (ν) at which the CV is performed (see Eq. 2).

$$I_d(E) = C_{dl}(E)\nu$$

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 $C_d$ 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 $I_d$ 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 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 (ν = 5 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-
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 ~130 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. SWNTs and MWNTs, showed that more than 90% of the total 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.

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