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Carbon Composite Electrodes

Composite Carbon Nanotube/Carbon Electrodes for Electrical Double-Layer Super Capacitors**

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Electrical double-layer capacitors (EDLC), denoted as supercapacitors, can have very high power densities (orders of magnitude higher than that of batteries) and reasonable energy densities (only one order of magnitude lower compared to that of practical batteries).[1,2] The most important type of EDLCs relates to carbon electrochemistry. They comprise large-surface-area activated porous carbon electrodes.

As only electrostatic interactions should exist between the electrodes and the solution species with no involvement of redox reactions, electroadsorption/desorption cycles of EDLC systems are highly reversible, with practically no capacity fading.[1–8] Therefore there are many designs of power sources that couple batteries and EDLCs in which the energy should be provided by the battery and high power by the capacitor.

One of the most promising carbon materials for EDLC electrodes are the non-graphitizable amorphous carbon materials[4] (that is, they cannot be converted into graphite by further high-temperature treatment). Such carbon materials are produced from materials such as biomass (such as wood or nutshells), non-fusing coals, and many thermosetting polymers (such as poly(vinylidene chloride), PVDC). These carbon precursors retain a solid phase during carbonization, and the limited mobility of the formed crystallites leads to the formation of a rigid amorphous structure that consist of randomly oriented graphene layers.[5] The loss of volatiles and the retention of a rigid and complex molecular structure during the carbonization of many non-graphitizable carbon materials can lead to a highly porous structure without the need for further activation ($>600\,\text{m}^2\,\text{g}^{-1}$ for PVDC).[4,6]

Another family of carbonaceous materials that is attracting a lot of attention in recent years is carbon nanotubes (CNTs, both single- and multiwall structures).[9] Owing to their unique structure (graphitic layers) and morphology, CNTs have been explored as candidate electrode materials for energy storage and conversion devices, which may overcome the drawbacks of conventional activated, high-surface-area carbon materials (for example, limited electrical conductivity and mechanical strength).[1,4]

A major challenge in incorporating CNTs in composite electrodes is to overcome the high entanglement of the tubes and to reach an efficient nanotube separation and dispersion, which is a hard task because of the tendency of CNTs to form bundles owing to the extremely high van der Waals attraction (ca. $450\,\text{eV}\,\mu\text{m}^{-1}$) between the individual tubes.[10]

Herein we propose that combining CNT and activated high surface area carbon in an integrated composite structure should form ideal electrode material for EDLC. We present a straightforward and reproducible method for the synthesis of large-surface-area carbon/CNT composite materials for EDLC electrodes. CNTs are uniformly dispersed in solution containing polymer or polymerizable species, and a polymer–CNT composite is formed. The polymeric matrix is then carbonized and activated by mild, controlled oxidation. The method is universal and suitable for many types of polymeric species and CNTs. The CNTs are not damaged by the carbonization and activation processes.

We were able to clearly demonstrate the positive influence of CNTs dispersed in the activated carbon matrices on the mechanical and electrical stability of EDLCs electrodes upon many thousands of cycles. The crystallinity and the associated electromechanical properties of the CNTs, which are well maintained after the carbonization and activation of the composite active mass, enable the new composite materials to exhibit much higher stability compared to the conventional EDLC electrode materials produced from the activated carbonized polymers, and demonstrate much better electrochemical performance upon cycling (the novelty of this work compared to any previous attempt to develop CNT–carbon composites for EDLC is described in the Supporting Information). An example of a process of the composite electrode preparation and their characterization is described below. More examples are described in the Supporting Information.

Imaging of the activated carbon matrices formed by high-resolution scanning electron microscopy (HRSEM) and transmission electron microscopy (HRTEM) shows that the CNTs are well-dispersed in the carbon matrix (Figure 1) thus forming a network of CNTs, which functions as electrochemically inert conductive additive. The amorphous material demonstrates high porosity (Figure 1e), and the CNTs crystal structure was not affected by the activation process at high temperatures (Figure 1f). Furthermore, Raman spectroscopy, which is widely used for analysis of composite and nanostructures of carbonaceous materials,[11,12] demonstrates differences in the I_G/I_D peak ratio between the PVDC-based activated carbon and the PVDC/CNT-based activated carbon composite material (Supporting Information, Figure S1). The ratios between the intensities of the G and D bands were 0.8

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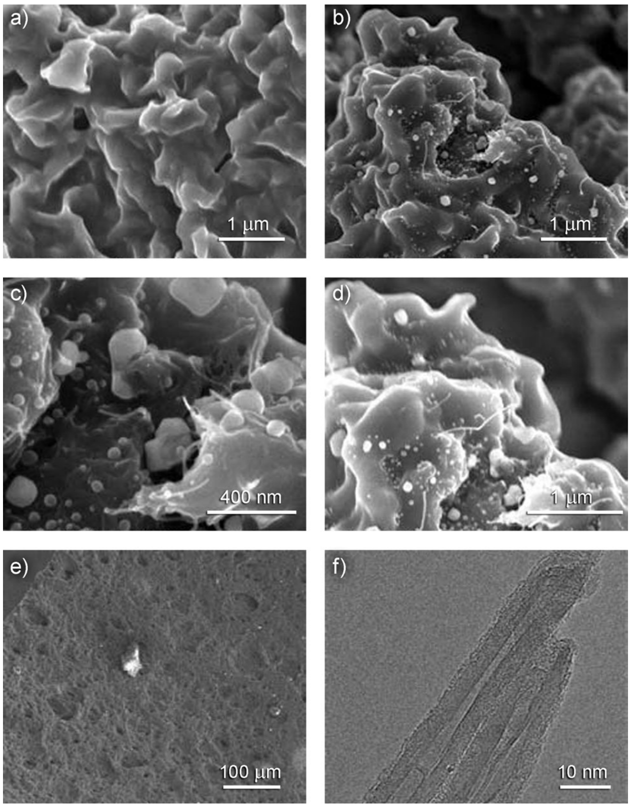

Figure 1. Electron microscopy images of the carbon materials. a,e) HRSEM of the carbonized PVDC based carbon (no CNTs). b–d) Carbonized CNT/PVDC based composite; the CNTs are separated and dispersed in the amorphous carbon matrix. f) HRTEM of CNTs extracted from a carbonized and activated carbon composite; the crystallinity of the CNTs is maintained even after the prolonged activation process.

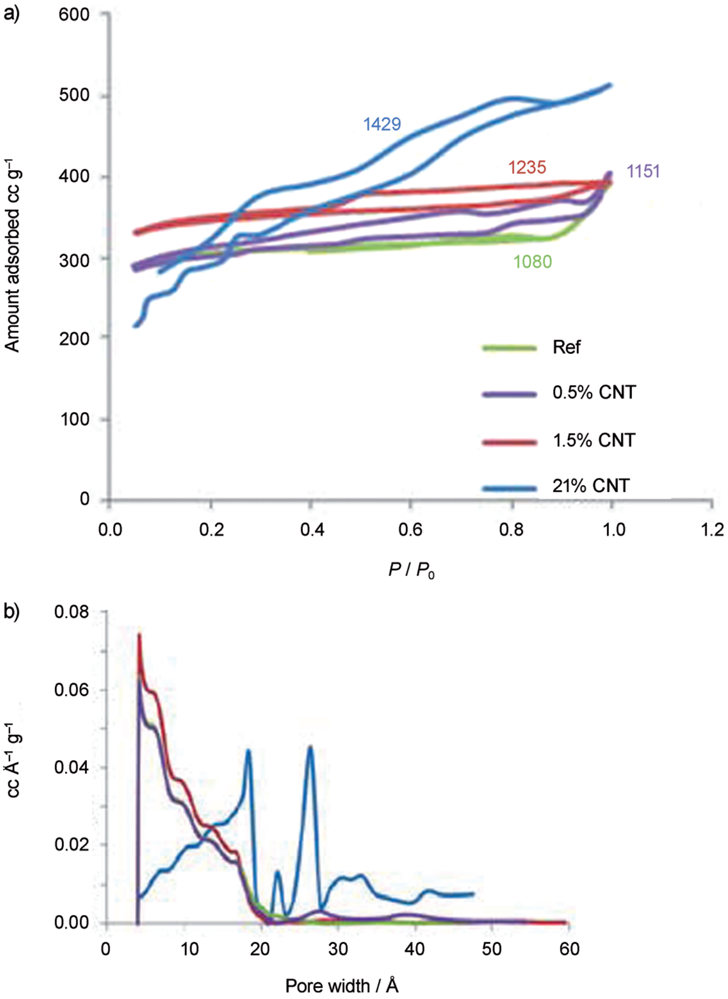

Figure 2. a) Adsorption isotherms of nitrogen related to activated carbonized PVDC, and to activated carbonized composites with different CNTs concentration. The calculated specific surface areas (BET model) are marked therein. b) Pore size distribution of the various activated carbon materials analyzed from the N_2 adsorption behavior based on the DFT model.

and 0.93 for the carbonized polymer (no CNT) and the carbonized CNT/polymer composite containing 21 % CNT by weight, respectively, which strengthens the conclusion that the CNTs maintain their crystal structure in these composite electrodes.

Typical results from measurements of N_2 adsorption into the carbonaceous materials are presented in Figure 2 a (adsorption isotherms) and Figure 2 b (pore size distributions). The relevant specific surface areas of the various materials are marked therein.

As the composite materials contain a higher percentage of CNTs, their surface area after activation is higher (1080, >1200, and $>1400\,\mathrm{m^2\,g^{-1}}$ for carbon without CNTs and composites containing >1 and $>20\%$ CNT by weight, respectively). This observation is attributed to the enhancement of activation kinetics in the presence of CNTs (Supporting Information). Furthermore, a high enough percentage of CNT in the composite material leads to an impressive mesoporous structure of the activated matrices (Figure 2 b), which should facilitate their electroadsorption/desorption kinetics.

Electrochemical performance evaluation of the activated carbon materials produced herein was performed in aqueous 6 M KOH solutions. Electrodes comprising the carbonaceous materials were charged and discharged galvanostatically 50000 times. The EDL capacitance and the electrode impedance were evaluated every 10000 cycles using cyclic voltammetry and electrochemical impedance spectroscopy (EIS), respectively. To demonstrate possible differences between the various carbonaceous materials, we used high current densities for both charge and discharge ($5\,\mathrm{A\,g^{-1}}$). Indeed, the electrochemical measurements showed pronounced differences between electrodes comprising the composite CNT/activated carbon and electrodes for which the active mass was activated carbon without CNTs (Figure 3 a–d). As can be clearly seen in Figure 3, the CNT/carbon composite material demonstrated impressive stable behavior. It was possible to cycle capacitors comprising electrodes containing the CNTs at high rates for many thousands of cycles (50000 demonstrated in Figure 3 c) with negligible capacity fading, while similar experiments with electrodes comprising the same activated carbon without CNTs demonstrated pronounced capacity fading (Figure 3 a). The impedance spectral studies of the CNTs containing electrodes

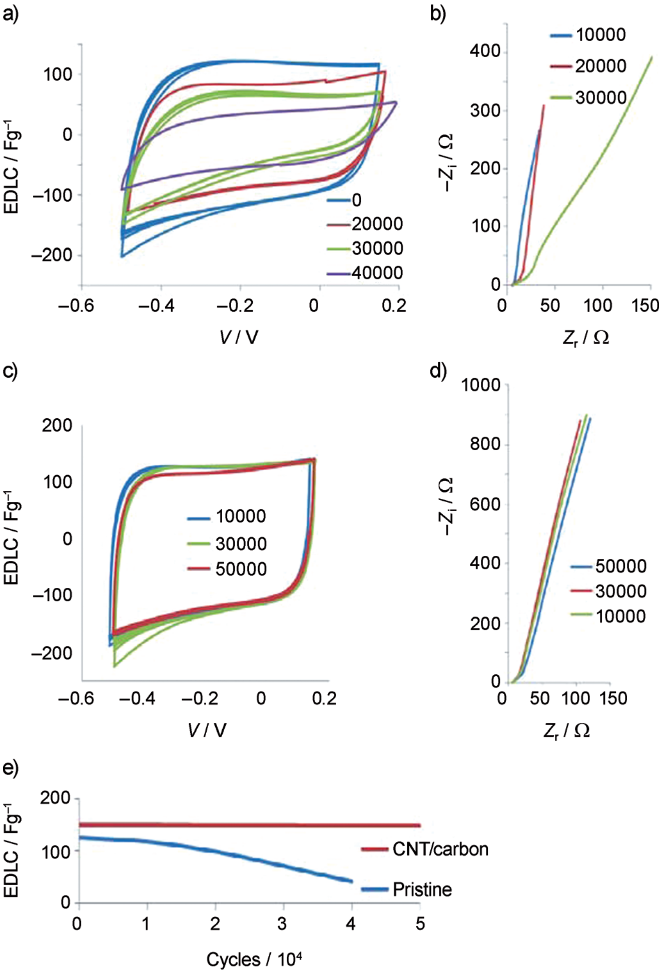

Figure 3. Cyclic voltammograms and EIS measurements of the carbon electrodes in 6 M KOH aqueous solutions after prolonged periodic galvanostatic cycling. The relevant numbers of galvanostatic charge/discharge cycles before each of these measurements are marked in the charts. The content of CNTs by weight in the composite electrodes was 1.5 %. a,b) Responses of the carbonized activated polymer-based carbon electrodes without CNTs. c,d) Same measurements for the composite carbon electrodes that contained CNT (ca. 1.5 % by weight). a, c) voltammetric response, b, d) EIS response. e) Capacity vs. cycle number curves of typical electrodes (cycle scale of 10^4 units).

(Figure 3 d) also indicates a "healthy" stable capacitive behavior during 50 000 cycles and more, while similar data from electrodes that did not contain CNTs reflected unstable behavior even after 30 000 cycles (see the change in the impedance spectra upon cycling in Figure 3 b).

A rigorous analysis of these impedance spectra is beyond the scope of this manuscript, but they can be used at the qualitative level, as the differences between Figure 3 b and d are so spectacular. It is amazing to realize that the presence of around 1.5 % CNT by weight have such a pronounced impact on the stability of the activated carbon electrodes during prolonged cycling.

Yushin et al. demonstrated the recovery of capacity after re-mixing of electrodes, suggesting that mechanical electrode degradation is mostly responsible for the capacity fading of composite activated carbon electrodes.[14] Accordingly, we suggest that the pronounced mechanical stability demonstrated herein may be attributed to the presence of CNTs and its positive effect on the binder-active material contacts and the mechanical integrity of the composite active mass upon prolonged cycling.

Furthermore, it was possible to fabricate monolithic activated composite electrodes, based on PVDC, with high CNT concentrations (> 20 %) and high specific surface areas (> 1400 $m^2 g^{-1}$; Figure 2). Such electrodes have stable capacity of more than 200 $F g^{-1}$ during many thousands of cycles in aqueous KOH solutions (see a typical electrochemical response in the Supporting Information). The enhanced electrosorption performance is attributed to the presence of mesopores in the active material of the electrode. These mesopores are created upon re-coagulation of the carbon-coated CNTs. The formation of this mesoporous structure required a high concentration of CNTs (ca. 20 %), with PVDC (Figure 2) and PAN (Supporting Information, Figure S5).

It should be noted that similar positive effects of CNT in activated carbon composites could be demonstrated with carbon materials that were produced from other polymers (Supporting Information). The possibility to prepare such composite electrodes from precursors that includes CNT and the monomer would be highly interesting, so the first step in the synthesis is preparation of matrices of well-dispersed CNTs in the monomer following polymerization, carbonization, and activation steps.

In summary, we have demonstrated a straightforward method for the synthesis of CNT/porous carbon composite electrodes with a uniform distribution of CNTs and a high surface area of the carbon material. We have shown that the crystal structure of the CNTs was not badly affected by the high-temperature activation process. We also developed monolithic CNT/activated carbon composite electrodes (no need of binder or current collector).

We have tested the electrochemical performances of these composite electrodes in prototype EDLCs and demonstrated their superior properties, such as high rates and high stability. It is clear that the presence of well-dispersed multiwall carbon nanotubes in matrices of high-surface-area activated carbon materials enhance the mechanical stability of the electrode remarkably, even with a low concentration of CNTs. Furthermore, by incorporation of a high concentration of CNTs into the active material (ca. 20 % w/w), a mesoporous structure becomes favorable and thus a further improvement of the electrosorption performances is demonstrated.

Experimental Section

CNTs were purchased from NanoAmor, and were dispersed in poly(vinylidene chloride) (PVDC) homopolymer according to the following process. The CNTs were dispersed in NMP (a polar co-solvent, excellent for slurries) according to the procedure described elsewhere.[10] The PVDC polymer was dissolved in a NMP/THF mixture (THF/NMP/PVDC 1:1:0.83 w/w). The concentration of the CNT in the composites were determined by dispersing different concentrations of CNTs in the NMP before dissolving the polymer in the solvents mixture. After 2 h of stirring under 80 °C, the syrup was cast and dried before carbonization.

Carbonization was carried out under a flow of nitrogen according to a procedure published before.[13] Activation was carried out under flow of CO_2 (a mild oxidizer) at 900 °C during one hour. The carbon materials were pulverized in a ball mill until all the carbon material became a uniform powder. The pulverized carbon materials were substantially stirred overnight with 25 % PVDF in NMP, and spread by a doctor blade onto current collectors (e.g. graphoil or stainless steel). Additionally, thin film composite electrodes with higher CNTs concentration were fabricated. For instance, CNT dispersed in THF with 1 % Pluronic-127 as a surfactant were mixed with the polymer and NMP at a weight ratio for THF/NMP/PVDC/CNT of 4:4:3:0.02. This mixture was spread onto glass substrates to form monolithic composite precursor layers (after evaporating the solvents), which were then carbonized and activated.

Electrodes were cut to the desired size and were dried overnight and were measured in T-type cells that served as test supercapacitors. 6 M KOH (aq.) electrolyte solution was used. Galvanostatic charge–discharge cycling was performed on a multichannel computerized equipment (BT2000 Arbin Instruments). Cyclic voltammograms and electrochemical impedance measurements were carried out with cycled electrodes (for example every 10000 cycles) using equipment from Bio-Logic Inc.

HR-TEM and HRSEM measurements were carried out with a JEOL-JEM-2011 (200 kV) electron microscope and by FEI Helios 600 system focused ion beam (FIB), respectively. Thermal analysis was carried using TGA-MS, TGA Q500 combined with Mass spectrometer, model Thermostar, Pfeiffer Inc. The TGA procedure is similar to the carbonization procedure and included dwells in 190 °C and 300 °C.

Gas adsorption properties of the activated carbon samples were analyzed by means of N_2 adsorption isotherms at 77 K taken by Autosorb-1 MP (Quantachrome, Florida USA). The specific surface area was calculated using the BET model. The pore size distribution was calculated by the DFT model. Raman spectra were measured with a JY Horiba spectrometer using a He/Ne laser (632.817 nm). Experiments were performed at room temperature (25 ± 4 °C). We focused on the 1000–1900 cm^{-1} spectral region, which is the most informative for carbon materials.

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