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# Thin CNT-based Films Deposited with the Layer-by-Layer Technique for Supercapacitor Applications

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## Abstract

A Layer-by-Layer (LbL) approach is used to form ultra-thin films from functionalized multi-walled carbon nanotubes (MWNTs) to serve as porous electrodes in electrochemical energy storage devices like supercapacitors. The MWNT-membrane-MWNT assemblies are tested in aqueous electrolyte, ionic liquid and polymer electrolyte for evaluation purposes. The deposition parameters of the MWNT layers greatly influence the properties of the thin film electrodes and can be easily tailored to specific requirements. This allows a maximum flexibility for the characteristics of the supercapacitors, demonstrating the great potential of this approach.

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## 1. Introduction

There has been considerable effort to implement carbon nanotubes (CNTs) as electrode material in electrochemical devices, such as fuel cells [1-3], Li-ion batteries [4-6] and supercapacitors [7-9]. Based on the outstanding electronic and mechanical features of single CNTs, many attempts have been undertaken to make use of these properties most beneficially in CNT-based network structures. Considering electrochemical applications, they promise to offer porous and electrical conductive films with good ion access to a large surface area and chemical resistivity. When considering supercapacitors, there is a strong competition with Li-ion secondary batteries. While electrochemical capacitors come with high-power density, they considerably lack in energy densities [10]. To close

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this gap, capacities and voltage windows of supercapacitors have to be further increased. The latter drawback is reduced by using ionic liquids (IL) as electrolytes which are stable up to 2.1 V in cathodic and anodic direction each, providing a 4.2 V stability window [11]. Boosting capacities is possible by adding surface redox reactions at the electrode-electrolyte interface, which are referred as pseudo-capacities. As transition metal oxides, such as ruthenium oxide are expensive [12,13], Faradaic reactions of surface functional groups are a promising approach.

The Layer-by-Layer (LbL) approach uses opposite charged CNTs to form multilayer thin films on any surface charged substrate by dipping it alternately into the negatively and positively charged dispersion [17]. The charges located on the shell of the CNTs originate from a change in ionization of functional groups attached to the shell when dipped into water. The functional groups also offer the possibility of Faradaic reactions and hence, the exploitation of pseudo-capacities. Commonly used membranes from cellulose nitrate are well suited to serve as substrate, which makes this technique also highly versatile. Also, by dipping the membrane into the CNT dispersions, the electrodes – separator assembly can be made in one single step by this method. This study investigates the suitability of the LbL method for preparation of CNT electrodes in supercapacitors and their performance in different electrolytes. The tested electrolytes were KOH, Ethyl-3-methylimidazoliumtetrafluoroborate (EMImBF<sub>4</sub>) and a mixture of EMImBF<sub>4</sub>/PVA (2:1) to which the membranes were exposed before electrode deposition. This selection covers the most commonly used types of electrolytes, as there are aqueous electrolytes for high power densities, ILs for a broad voltage window and a IL/polymer solid electrolyte to reduce packaging effort [18].

## 2. Experimental Details

### 2.1. Preparation of the separator for polymer-electrolyte

A thin Millipore filtration membrane with average pore diameter of 0.46 µm was dipped in a well-stirred solution of 1- EMImBF<sub>4</sub>, PVA and DI-water (2:1:10). The soaked membrane was slowly dried at 4°C to avoid any pinhole generation within the polymeric filler. After deposition of the electrodes, the assembly was heated up to 80°C to soften the PVA and form a good connection between electrolyte and electrodes.

### 2.2. Preparation of the electrodes

MWNTs were COOH-functionalized by reflux in a bath of concentrated sulfuric and nitric acid (3:1) for 4 h at 75°C. To generate amide groups on the MWNTs shell, the previously carboxylated tubes were chlorinated in thionyl chloride for 6 h at 75°C. The acid was removed by distillation and replaced by a mixture of anhydrous toluene and ethylene diamine (1:1) and once again refluxed for 24 h at 75°C.

The MWNT-COOH were dispersed in pure DI-water by sonication with a Hielscher UP400S, whereas 0.03 mg·ml<sup>-1</sup> CTAB were added for the dispersion of the MWNT-NH<sub>2</sub>. A cellulose nitrate membrane was soaked with a mixture of DI-water, PVA and EMImBF<sub>4</sub> (10:1:1) and dried at 50°C to evaporate the water.

To deposit the CNTs, the prepared membrane was alternately dipped into both types of CNT dispersions with extensive rinsing in DI-water three times for three minutes each between the steps. The membrane was masked at the edge regions to avoid CNT adsorption which could result in electrical shortcuts. Collectors were prepared by sputter deposition of 150 nm Pt on both electrodes at a back pressure of 3 µbar in an atmosphere of pure argon in the deposition chamber and a plasma power of 200 W, respectively.

### 2.3. Characterization

Electrochemical measurements were done using a potentiostat PGU 10V-1A-IMP-S. To determine the condition of highest zeta-potential of the dispersions, an Acoustic Spectrometer DT-1200 was used, scanning the amount of surface charges depending on the pH value. Layer thickness was obtained from a FRT MicroProf 100 chromatic white light (CWL) sensor which offers the possibility to measure contact-free the layer thickness on a large area.

### 3. Results and discussion

For preparation of the dispersions, the CNTs were functionalized with  $\text{NH}_2$  amine groups and  $\text{COOH}$  carboxylic groups, respectively. The first ones get protonated in water to  $\text{NH}_3^+$ , while the latter ones are ionized to their conjugate base. The charging is pH dependent, but it was shown by zeta-potential measurement, that for conditions of pH 7 the absolute surface charges of both types of functional groups are +31 mV and -41 mV, respectively. According to the standard set by the American Society for Testing and Materials, the corresponding surface charge density is high enough to ensure a good layer attachment [19]. Therefore, pure deionized (DI) water without addition of ionic surfactants could be used. Between the dipping steps, the membrane was repeatedly washed in DI-water to rinse off all excess tubes. After each dipping and washing step, a new monolayer of CNTs was adsorbed on top of the substrate. Two successively adsorbed layers each from a positive and negative dispersion form a bi-layer (BL), which concludes the dipping cycle. The process is shown schematically in Fig. 1(a).

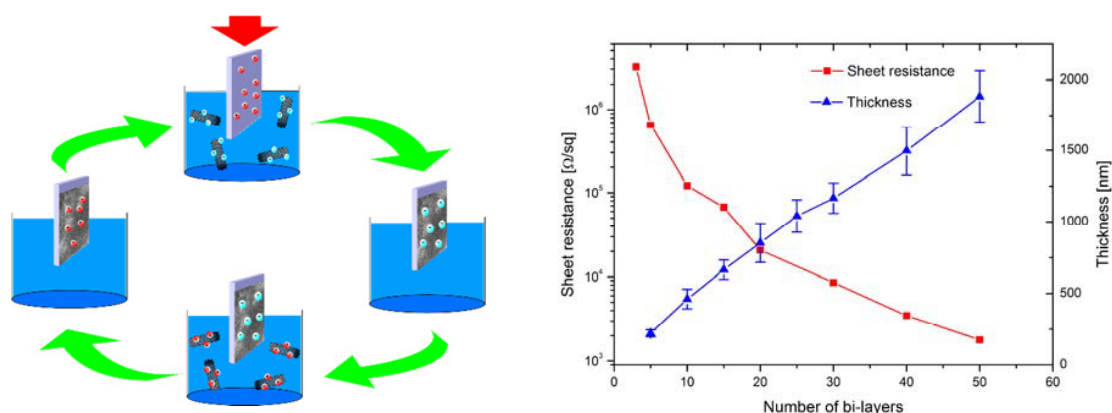


Fig. 1. (a) Illustration of the LbL technique, (b) Correlation of bi-layer number with film thickness and sheet resistance.

Theoretically this could be continued until any targeted number of layers is attached [20], but for practical reasons the maximum number of cycles was limited to 50 in this study.

The actual thickness of a nanotubes film after five dipping cycles is about 240 nm, as can be seen in Fig. 1(b). This makes 24 nm per monolayer which is twice the thickness of a single Multi-Walled Nanotube. The electrical sheet resistance in such thin films is with 1100  $\Omega/\text{sq}$  relatively high, as has been evaluated by van-der-Pauw measurements and also shown in Fig. 1(b). This is due to the limited number of electrical pathways. Starting from a 5 BL film, the sheet resistance decreases drastically with increasing film thickness. For films of approximately 20 BL and more, the slope of the resistance characteristics becomes linear, which fits with the observations made by Zhou *et al.* for CNT films made by filtration [21]. To use the samples as supercapacitors and to ensure an efficient charge transfer, 150 nm thin collectors were applied on top of the electrodes by sputter deposition of platinum. The collectors were contacted via platinum wires for all further electrochemical measurements. The complete device had an overall thickness of around 100  $\mu\text{m}$  and a diameter of 2.2 cm, respectively.

Typical electrochemical analysis was done by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The voltammogram traces allow a calculation of capacitances and reveal the low frequency behavior of the device, as there are cathodic and anodic limits of the electrolyte, diffusion processes and leakage resistance. The excitation for EIS measurements were done with an amplitude of 10 mV, which allows treating the current versus voltage curve as pseudo-linear. Spectroscopy offers a good possibility to determine the different components of the equivalent circuit. From the complex plane impedance plot, the frequency dependent components

can easily be determined. An important parameter for the supercapacitor performance is the equivalent series resistance (ESR) which directly influences the power density according to  $P_{max} = V_i^2 / (4 \cdot ESR \cdot m)$  ( $V_i$ : initial voltage,  $m$ : mass per unit area [ $\text{g} \cdot \text{cm}^{-2}$ ]). The ESR is defined as the real part of the impedance at 1 kHz [9]. This value is easily obtained from the EIS data.

The results of the measurements in KOH are shown in Fig. 2.

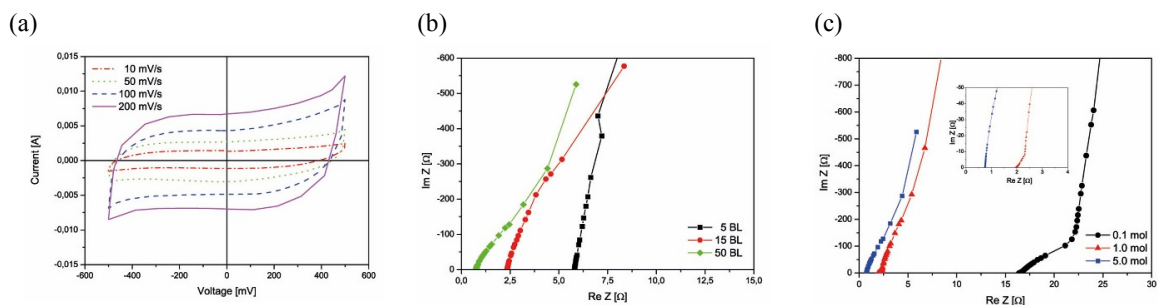


Fig. 2. Results of the electrochemical investigations of supercapacitors in KOH

The voltammogram is quite typical for samples with mainly capacitive behavior (see Fig. 2(a)). It shows a nearly rectangular shape with rounded edges which are due to the finite charging time of the capacitor. The capacitance is a function of the scanning velocity and is calculated from  $C = I \cdot (dU/dt)^{-1}$ . The Nyquist plot in Fig. 2(b) shows the dependency of the overall sample resistance  $R_s$  from the electrode thickness. Since the resistance of the electrolyte remains constant, the increased in  $R_s$  for thinner electrodes is due to the higher sheet resistance of the CNT network for low deposition cycle numbers. This corresponds well with the results obtained by van-der-Pauw measurements, shown in Fig. 1(b). An important parameter on double layer capacitance is also the concentration of the electrolyte. For low concentrated KOH,  $R_s$  becomes considerably higher since less charge carriers are available. Also, Fig. 2(c) shows a large diffusive component for a 0.1 mol solution which indicates an increased charge transfer resistance within the pore structure. This means that the response time of the capacitor now depends on the pore resistance.

Equivalent measurements were also done for EMImBF<sub>4</sub> as a representative for IL electrolytes and, as a third experimental run, the performance of LbL-made electrodes in supercapacitors with gel electrolyte was tested.

Table 1 lists the evaluated performance parameter of the investigated devices. Maximum energy density is given by  $E_{max} = C \cdot U^2 / 2 \cdot m$ .

Table 1. Characteristic parameters of uncharged supercapacitors with 50 BL electrodes. Energy and power density were determined by using the capacitances measured by CV. The mass of the electrodes was  $0.6 \text{ mg} \cdot \text{cm}^{-2}$

	KOH	EMImBF <sub>4</sub>	EMImBF <sub>4</sub> /PVA (2:1)
C [ $\text{F} \cdot \text{g}^{-1}$ ]	52,5	37,5	42,5
$R_s$ [ $\Omega$ ]	0,58	4,3	10,99
$R_f$ [ $\Omega$ ]	–	–	0,53
Power density [ $\text{kW} \cdot \text{kg}_{\text{cell}}^{-1}$ ]	517	279	86
Energy density [ $\text{Wh} \cdot \text{kg}_{\text{cell}}^{-1}$ ]	10,5	30	34

As the capacitance of supercapacitors is a function of the applied voltage, the values given in Table 1 are only valid for fully charged devices.

#### 4. Conclusion

In summary, we demonstrated that through the LbL technique ultrathin CNT electrodes with precisely controlled thickness can be realized. The process is easy to handle, and generates CNT-based porous network structures that are well suited for use in electrochemical devices. The deposition is highly reproducible and is potentially applicable to a wide range of substrates such as polymers which are often incompatible for high temperature synthesis techniques. As a second major outcome, the separator has been modified to serve as multifunctional membrane to minimize the encapsulation effort. The cellulose nitrate fibers offer a mechanical robust matrix which is filled with a solid electrolyte. The surface charges of this assembly match again perfectly with the need of the LbL technique for a charged substrate. The results for energy and power densities, obtained with non-optimized cell design, are highly promising as they can be improved by optimizing the pore geometries and therefore the efficiency of the electrodes. As an additional benefit of the LbL approach, the functional groups of the CNTs, necessary for the deposition process, can be used to boost the capacitance by undergoing reversible redox-reactions, forming pseudocapacitances. We successfully fabricated supercapacitors that are assembled with less effort, mechanically flexible, but robust and only 160  $\mu\text{m}$  thick. This offers a wide area of potential applications, e.g. as energy storage device in combination with energy harvesters providing peak power output for wireless sensor systems.

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