

CARBON NANOTUBES - SMART MATERIAL OF THE FUTURE: EXPERIMENTAL INVESTIGATION OF THE SYSTEM RESPONSE

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Abstract. *The electromechanical characterization of carbon nanotube (CNT) papers, which are immersed in an aquatic electrolyte, is the main focus of this paper. The experimental set up consists of an ordinary three electrode cell, filled with the liquid electrolyte and using the CNT paper as working electrode. The in plain strain of the paper is measured and its quasi static and dynamic response to various electrical potential excitations has been investigated in a series of experiments. Additionally, the influence of different electrolytes, pre-stresses and types of carbon nanotubes (SWNT vs. MWNT) was studied.*

1 INTRODUCTION

One essential component of all smart structures is the actuator, which will induce strain into a system in order to change its shape or to compensate disturbing vibrations. These actuators incorporate materials that usually convert electrical energy into mechanical energy. Besides many materials of minor importance there are two major groups that are commercially available. One of these are piezoceramics that expand/contract when applying an electrical field and the other one are shape memory alloys, that change crystal configuration with temperature. Disadvantages of these species are the required high voltages and currents and the high density of the actuation material.

Actuators based on carbon nanotubes (CNT) have the potential to overcome these drawbacks¹⁻⁴. They are working at a few volts and the density of the raw material is as low as 1.33 g/cm³. Moreover, active strains of up to 1% can be achieved - due to the CNTs dimensional changes on charge injection. In order to do so, the nanotubes have to be arranged and electri-

cally wired like electrodes of a capacitor, and then immersed in an electrolyte. Ever since the actuation mechanism of CNT was first described by Baughman⁵ several groups of researchers have made attempts to get a deeper understanding of the actuation effect and to overcome the major limitations on the way to production of these actuators.

2 STATE-OF-THE-ART

Most contributions on the characterization of CNT based actuators, that have been published so far, can be subdivided in two categories: those with electrochemical and those with electro-mechanical focus. The contributions of the first group explore the possibilities of using aquatic electrolytes⁶⁻⁹ and ionic liquids¹⁰, mainly using cyclic voltammetry. The second group focuses more on the electromechanical aspects like dynamics of the system^{9,11,12}, control laws for driving voltages¹³ and comparison with other actuation materials like polyaniline¹⁴ and other conducting polymers¹⁵. However, a full description of the dynamic model for in-plane actuation is still missing just like an intense experimental investigation of the systems response.

There are three types of experiments evaluating the active strain, that were carried out so far: measurements of individual nanotubes¹⁶, measurement of in-plane strain of bucky-paper^{13,17} (including measurements of active strains in fibers¹⁸) and measurement of strain in thickness direction of a bucky-paper^{12,19}. The advantage of in-plane measurements are especially the comparatively high displacements that can be achieved, so that the signals do not have to be low pass filtered, which might manipulate the dynamics of the system. Compared to the measurement of individual nanotubes the in-plane strains are much closer to later applications.

This paper contributes to filling the gap in the area of quasi static and especially dynamic experimental investigations of nanotube based in plane actuators.

3 EXPERIMENTAL DETAILS

3.1 Macroscopic CNT Structures

The CNT structure used for all following investigations is based on so called "bucky-papers", which is a paper of statistically directed nanotubes made by vacuum filtration. These bucky-papers were prepared by several steps. Purified SWNTs²⁰ have been purchased from Carbon Nanotechnologies Incorporated, Houston, USA. This material was synthesized by gas-phase decomposition of CO over Fe catalyst (HiPco method) and the purity of this single wall carbon nanotube batch was denoted by the producer of more than 85%. About 30 mg of SWNT material was dispersed in 30 ml 1% solution of sodiumdodecylsulphate (SDS) as a surfactant and then processed by three step ultrasonication. First the solution was sonicated for 30 minutes with a Branson Sonifier Cell Disruptor B15, energy output level 3, pulsed of 50% duty cycle and a 1/2 inch horn. The second step was carried out by the same apparatus settings except from a smaller 1/8 inch horn. Finally, the resulting solution was sonicated for 60 minutes in an Bandelin ultrasonication bath to improve the dispersion of the SWNTs. This dispersion was

vacuum filtered over a polytetrafluorethylene membrane with a pore size of about $0.35\mu\text{m}$ and a diameter of 47 mm by Schleicher & Schuell MicroScience GmbH. At first 50 ml ethanol was given to the filter in order to open the pores, followed by the SWNT-dispersion and finishing with deionized water to remove SDS. The resulting bucky-paper was carefully peeled off the membrane filter in the wet state and disrobed on a polytetrafluorethylene foil covered with a lantern slide. Drying for 48 hours at room temperature results in an slightly flexible, easy to handle bucky-paper with a thickness of about $50\mu\text{m}$ and a surface resistance $\ll 10\Omega/\text{cm}$ (see figure 1).

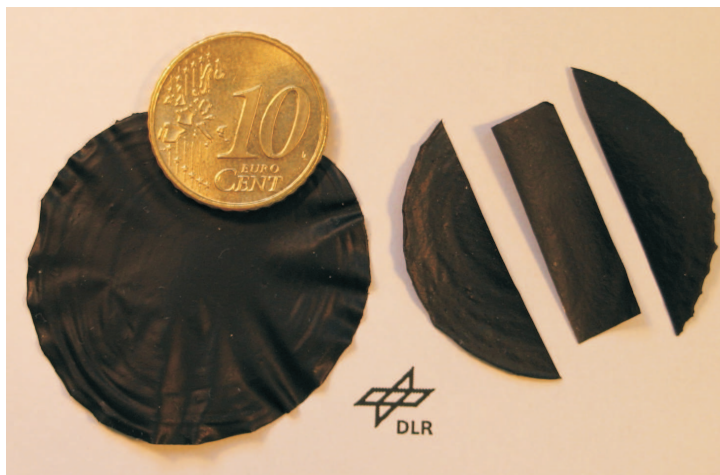


Figure 1. Bucky-Paper after production (left); Sample for electromechanical analysis (right).

The indicated specimen made of MWNT were basically produced using the same steps described for the SWNT, above. The raw material was obtained from FutureCarbon GmbH, Bayreuth, Germany. The bucky-paper made of this material showed a surface resistance of about $12\Omega/\text{cm}$.

All chemicals that were used are highest grade. Aqueous solutions were prepared using deionized water.

3.2 Experimental Setup

A conventional three-electrode cell was used for all experiments. The schematic set up for all quasi steady measurements is shown in figure 2.

The counter electrode was a Pt ribbon, the reference electrode was Ag/Ag^+ . The SWNT (or MWNT) bucky-paper was employed as working electrode, connected via a Pt wire to the electrical feedthroughs. The potentiostat was a 1030PC.T. Potentiostat/Galvanostat by Jaissele Elektronik GmbH, Waiblingen, Germany. Output of this device is the potential at the working electrode in V as well as the current that is flowing between working and counter electrode. This current is given as a proportional voltage, where 1000mA corresponds to 10V. The input (the

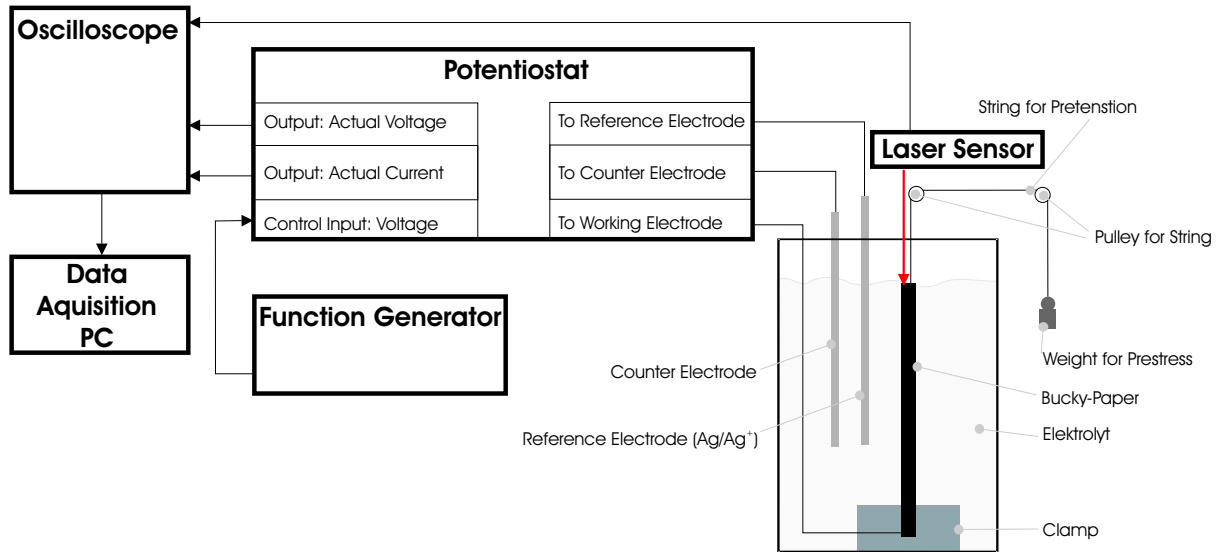


Figure 2. General experimental setup for quasi static measurements. In case of dynamic measurements the oscilloscope, computer and function generator are substituted by the FFT-analyzer.

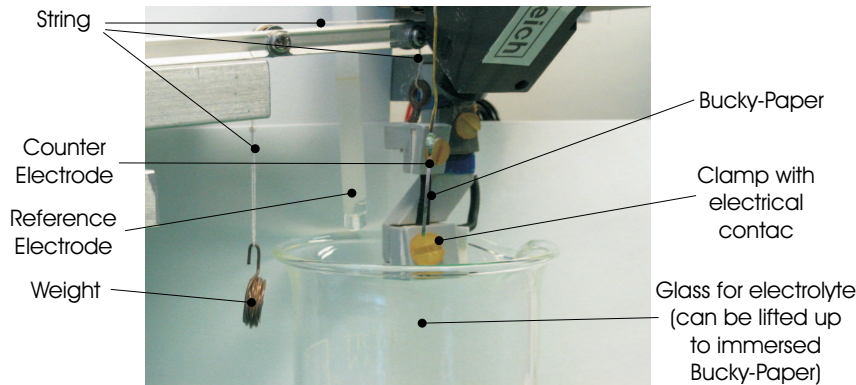


Figure 3. Experimental Setup.

voltage that should be applied in the cell) for the potentiostat was given by a function generator Yokogawa F120, the active displacements were measured by a laser-triangulator Micro-Epsilon Opto 1605-0,5 with a measuring range of 0.5 mm. Output of this laser is a voltage signal from -10V to +10V. A given voltage has to be multiplied with the factor of $25\mu \frac{m}{V}$ in order to derive the displacement of the laser in meter. The output from the potentiostat (voltage and current) as well as the displacement was recorded using an oscilloscope Tektronix TDS 3014, which was connected via GPIB with a PC, reading the data from the oscilloscope with a LabView program. The displacement signal had to undergo further processing, since some drift was found in the signal (as it can be also seen in experimental results for cyclic excitations in the literature¹⁴), which assumed to be due to quelling of the bucky-paper in water. Since this effect can be described as a linear term, superposed to the rest of the signal it was counteracted by adding a

linear term with opposite sign to the signal, resulting in a periodic output signal without drifting. Due to this drift it was also not possible to derive the original displacement at zero voltage, so the minimum was set to zero, resulting in a signal from zero on up. This signal was divided by $-l_0$ in order to derive the strain ε , which also goes from zero on up.

Dynamic measurements of the Transfer functions were carried out by means of an Ono-Sokki CF-5220 multi purpose FFT-analyzer, which is a two channel device. For measuring the spectra swept sine signals were used.

The bucky-papers used as working electrode had a size of $3 \times 18 \times 0.05 \text{ mm}^3$. They were standing upright in the electrolyte, being clamped on the upper and lower side of the paper. The clamp on the lower side incorporates the platinum wire for the electrical contact. The upper clamp was used to bring some pre-stress to the specimen - either by a spring or by a constant force through a string going around some pulleys with a counter weight on the other side (see figure 2). The pre-stress is necessary to keep the bucky-paper from bending. The laser triangulator measures the displacement of this upper clamp. The strains are measured in the direction of the longest dimension, so that $l_0 = 11 \text{ mm}$.

4 EXPERIMENTAL RESULTS

At first the prepared bucky-papers were analyzed by means of cyclic voltammetry in order to get the capacity (as it is done in literature^{5, 10, 21}) and the electrochemical stability window of the system. Thereafter, electromechanical investigations of the in-plane strain of the bucky-paper were performed. Rectangular voltage steps were given to the system in order to investigate the step response of the system. In a next step the dynamic response of the system was investigated.

4.1 Cyclic voltammetry (CV)

All systems that were analyzed (different bucky-paper and electrolytes) were investigated by means of cyclic voltammetry. This test is defined in such a way, that the voltage that was given to the system follows a slow ramp of about 60 mV/s . The resulting plots are shown in figure 4. The general characteristic of this curve shows three regions: The middle region is dominated by straight lines (which are located above zero for $\Delta U/\Delta t > 0$ and below zero for $\Delta U/\Delta t < 0$) with little slope. As soon as the voltage surpasses a certain level (in the positive and the negative end of the middle region) there is a rapid growth in current to be seen. The voltages that mark the boundaries of the middle regions are marking the electrochemical stability window of the systems. Beyond these voltages non reversible chemical reactions (e.g. electrolysis) take place. As it can be seen in figure 4 there are differences in the size of this window. Especially for those systems with iod and bromine ions, there is a much earlier start of electrolysis at the anodic side ($+0.25\text{V}$ for bromine and $+0.7\text{V}$ for iod), which can be seen in the rapid increase of the curves. Apart from this, the electrochemical characteristics look much similar.

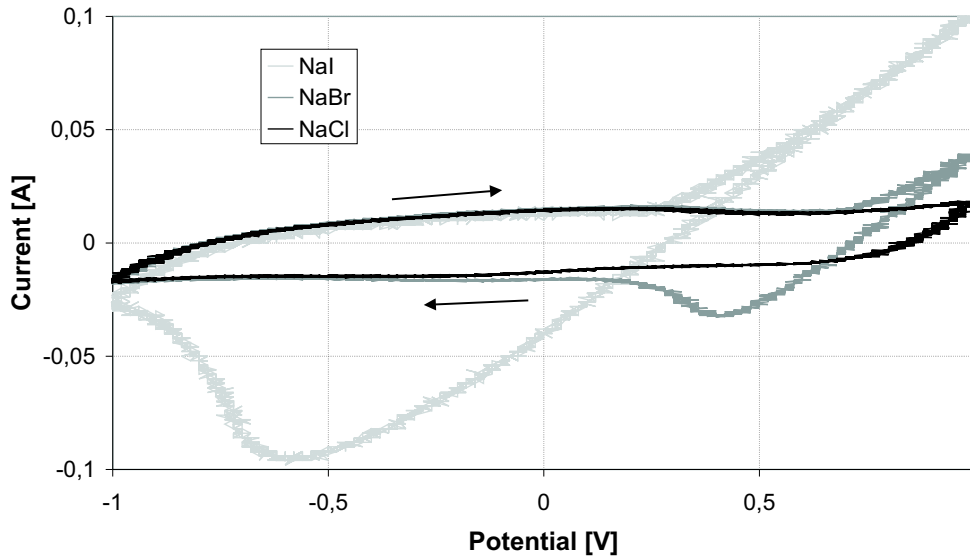


Figure 4. Cyclic voltammetry at a scan rate of 60 mV/s for the following electrolytes: NaCl, NaBr and NaI.

4.2 Quasi static electromechanical characterization

In order to characterize the electromechanical response of the system, a series of experiments was carried out, exciting the system with a voltage step of different amplitudes. It could be shown that constant voltages (within the electrochemical stability window) lead to constant displacements - with two restrictions. First, the bucky-paper quelling has to be stopped (which is going towards zero with time - several minutes) and second, the system is relatively slow (time constant of several seconds) and so it has to be waited for the system to reach the desired state. For voltages beyond the electrochemical window the strains that will be achieved at a constant voltage are not necessarily constant any more but rather rapidly growing. The strain developed in this region is much likely irreversible, which would mean, that this type of strain development cannot be used in technical applications. Resulting from this general observation a plot of strains over voltage for quasi static conditions can be established, which is shown in the following figure 5. The curve can be subdivided into three regions according to the curves slope. In region I there is a negative slope, in region II the slope is close to zero and in region III the slope is positive. For a description in formulas this subdivision is helpful. The complete curve is the basis for all further investigations. It gives a global characteristic of the system which can be quantitatively compared for different systems. In order to create these curves a test procedure has to be defined. Our test procedure takes one singular point of the system as a basis for the investigation. This point is the voltage of minimum strain U_0 . As system input a voltage step starting at U_0 was used. The system response for all these experiments was written down as voltage/strain over time plot like seen in figure 6a. Since preliminary analyses have shown a minimal strain at a voltage of about $U_0 = 0.3V$, the steps, that were used as input, were always starting at $0.3V$ (e.g. $[0.3 \text{ to } -0.8][0.3 \text{ to } -0.7] \dots [0.3 \text{ to } 0.7][0.3 \text{ to } 0.8]$). The voltage range was

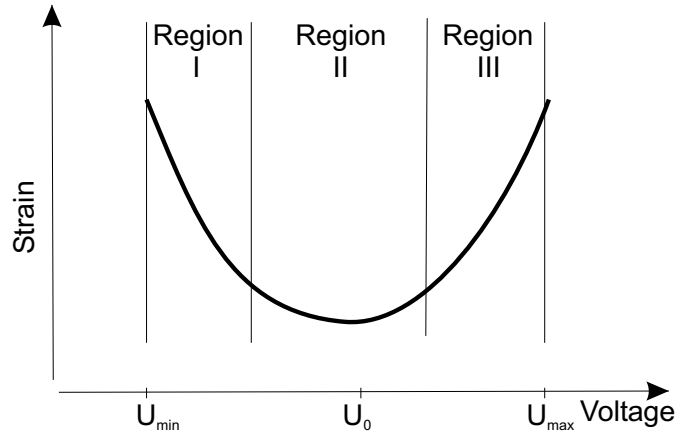


Figure 5. General correlation between strain and voltage; subdivision into three regions; including limits of the electrochemical stability window (U_{min} and U_{max}).

chosen in a way, that the electrochemical stability window was not exceeded.

Maximal strains ε_{max} of these responses were plotted over the potential, that was applied as a step starting from 0.3V. The resulting curves are shown in figure 6 b. It can be seen, that the

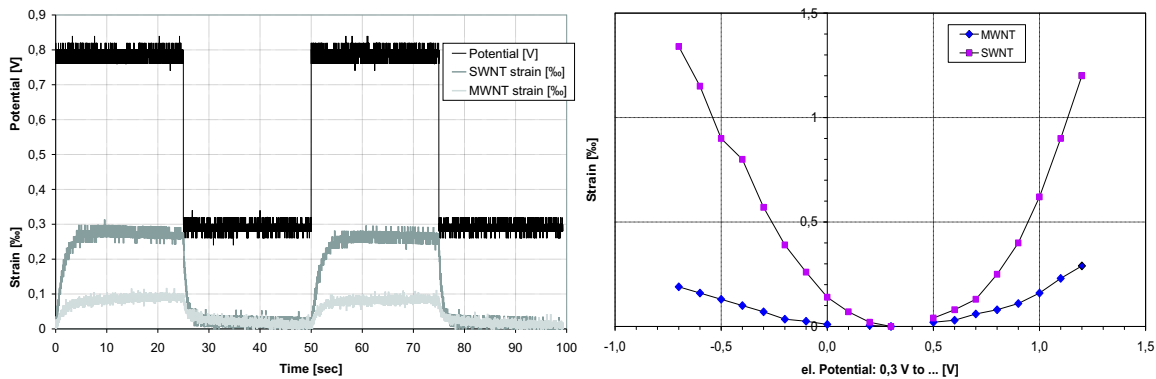


Figure 6. Comparison between SWNT and MWNT samples. Electrolyte: NaCl. a) Strain over time at voltage step: 0.3 V - 0.8 V; b) Strain vs. potential.

SWNT specimen reaches much higher active strains than the MWNT specimen. The quality of a bucky-paper and a complete system can be measured with these strain over potential plots. The following comparisons were carried out: Different pre-stress levels and methods, variation of electrolyte concentration, different ions in aquatic electrolyte and different bucky-papers.

The investigation on the influence of the pre-stress on the systems behavior is crucial for the whole experimental set up. Two versions to apply the pre-stress were tried: The use of a spring and the use of a counterweight using string and pulleys. The first one is introducing additional stiffness into the system and with this changing the results dramatically. The weights did not change the maximal strains or strain rates of these quasi static experiments. The size of the weights was varied between 2 g and 10 g, but a influence on the results could not be shown.

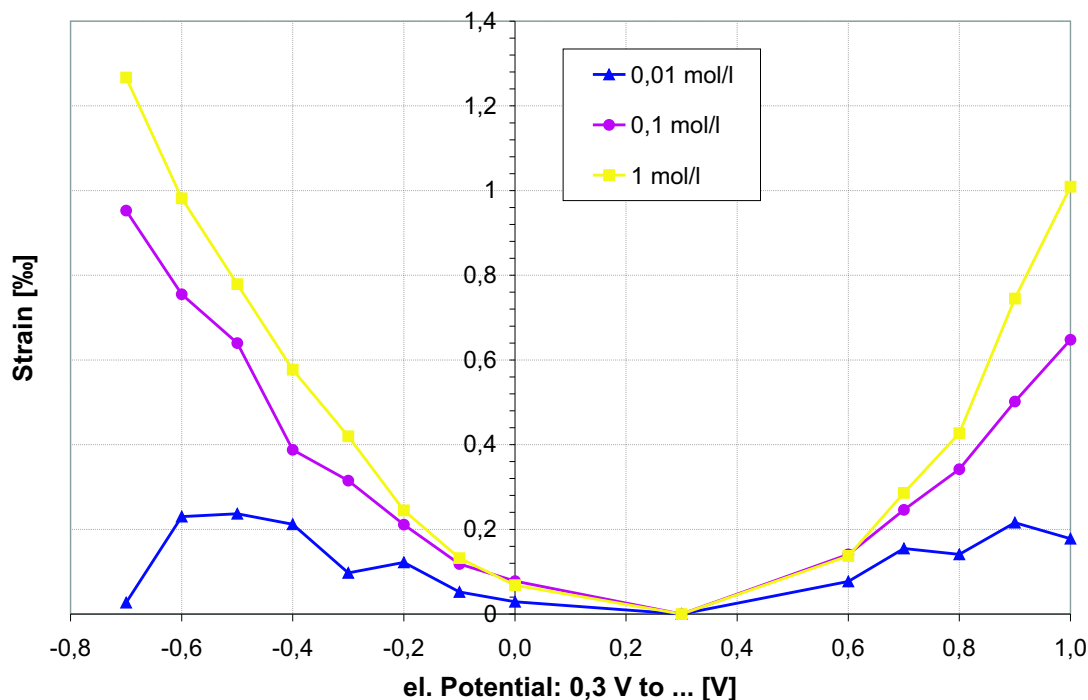


Figure 7. Strains at different NaCl concentrations. The overall strain performance of this bucky-paper is low, which is due to high resistance of the paper.

For the aquatic electrolyte NaCl the concentration was varied from 0.01 M to 1 M. The maximum strain that could be reached increased with the ion concentration (see figure 7). For higher concentrations (1 M - 4 M) there was no further increase found. This seems obvious, since with lower ion concentration there are less ions available for the actuation of the bucky-paper.

One very interesting outcome of the investigation is the influence of different ions on the strain and the strain rate. Different aquatic solutions were tested. The anions that were looked at are Cl^- , CHO_2^- , $\text{C}_2\text{H}_3\text{O}_2^-$, NO_3^- , Br^- and O_4P^- , keeping Na^+ as cations the same each time. All these experiments with different ions were carried out with the same bucky-paper sample, which was rinsed between two experiments in deionized water. The concentration was 1 M (except for the $\text{Na}_3\text{O}_4\text{P}$, which was 1/3 M). The results in figure 8 show, that there is no direct influence of the ion size on the derived strain. It is not clear, whether ions that were still in the bucky-paper could not be rinsed out completely and might have caused this lack of sensitivity for other electrolytes.

One further investigation concerned different qualities of bucky-papers. In the course of production there were certain quality criteria. One was the resistance of the specimen. bucky-paper with different resistance were tested. The strain that was generated decreased with increasing resistance. As a result of this interrelation it is strongly recommended to have low resistance of the bucky-paper material or an additional electrical contacting possibility.

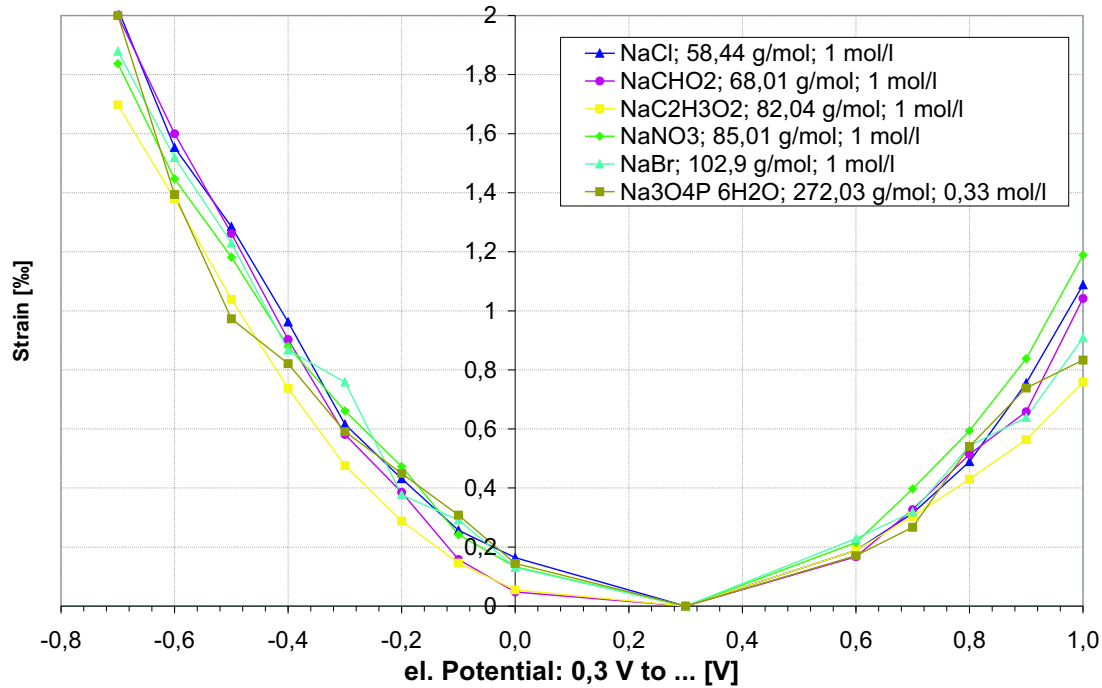


Figure 8. Results for different anions.

4.3 Dynamic characterization of the Actuator system

In order to analyze the dynamics of the system the frequency response function (FRF) of the system was determined. The electrical excitation for the system was a voltage sweep sinus with $U = -0.2V \pm 0.1V$ which represents the region I of the behavior (see figure 5) and $U = +0.6V \pm 0.1V$, which is located in region III of the general system response. The electrolyte that was used is 1M NaCl aquatic solution. The frequency range for these experiments was set to 0 to 0.8 Hz and 2 Hz respectively. Higher frequencies do not give any essential further information. The system outputs that were analyzed were current and displacement. The bode diagram is shown for current/voltage (figure 9), displacement/voltage (figure 10) and displacement/current (figure 11).

For the electrical system (figure 9) a characterization by means of electrical components is being used. In the region of $f < 0.1$ Hz for region I and $0.01 \text{ Hz} < f < 0.1$ Hz for region III the characteristic of a capacitor can be found. The gain is rising (constant in logarithmic scale) and the phase shift is approaching $+90^\circ$. This explains, why CNT actuators are often compared with capacitors. For frequencies $f > 0.7$ Hz and especially $f \gg 0.7$ Hz the gain comes to a constant level and the phase shift approaches 0° . This is the dynamic character of an Ohmic resistance. This means that for high frequencies the system acts like a resistance.

The description of the transfer function for system input voltage and system output displacement (figure 10) is not quite that easy to interpret. Strains are decreasing with increasing

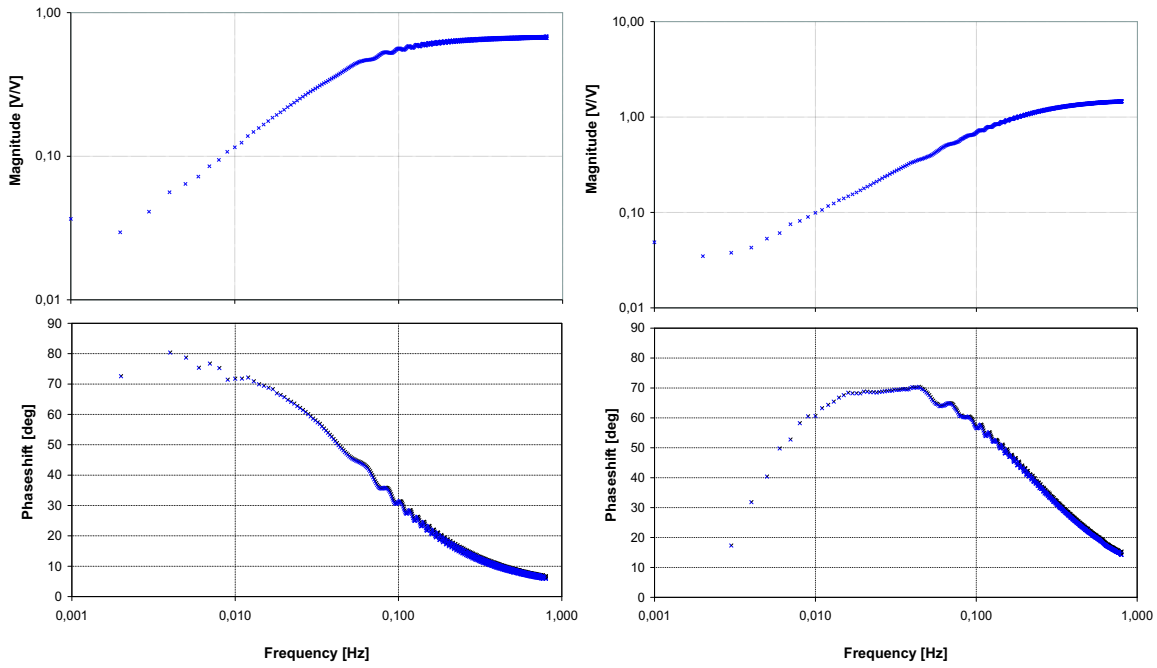


Figure 9. Dynamic response of CNT based actuator system; system input: voltage, system output: current; Left graphs: region I ($U = -0.2V \pm 0.1V$). Right graphs: region III ($U = +0.6V \pm 0.1V$).

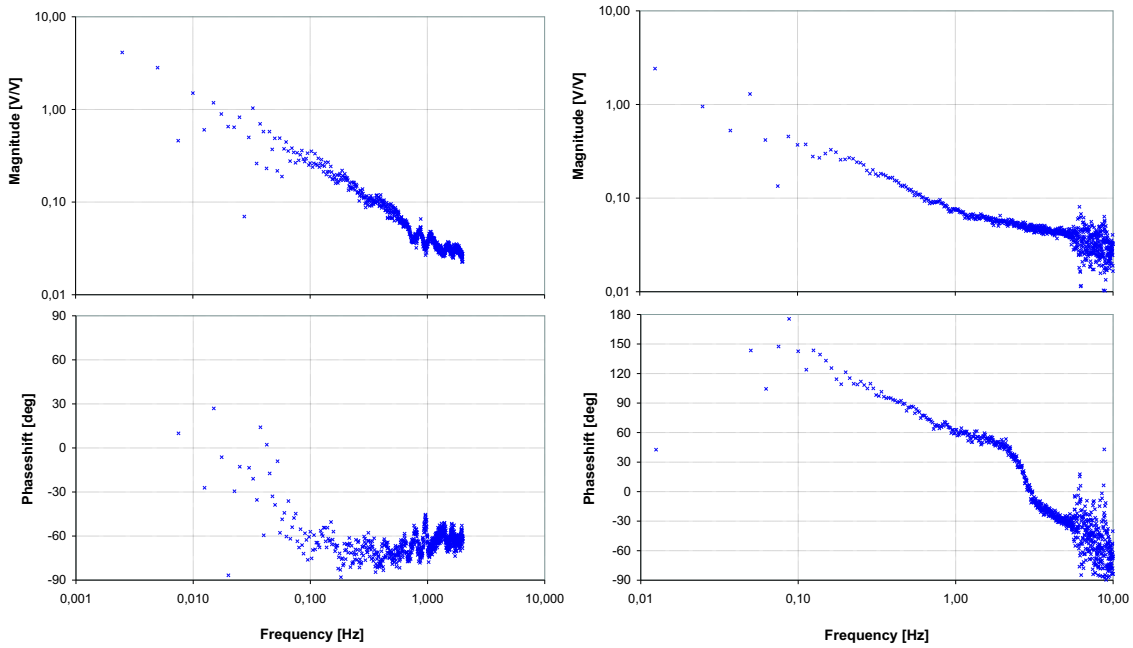


Figure 10. Dynamic response of CNT based actuator system; system input: voltage, system output: displacement; Left graphs: region I ($U = -0.2V \pm 0.1V$). Right graphs: region III ($U = +0.6V \pm 0.1V$).

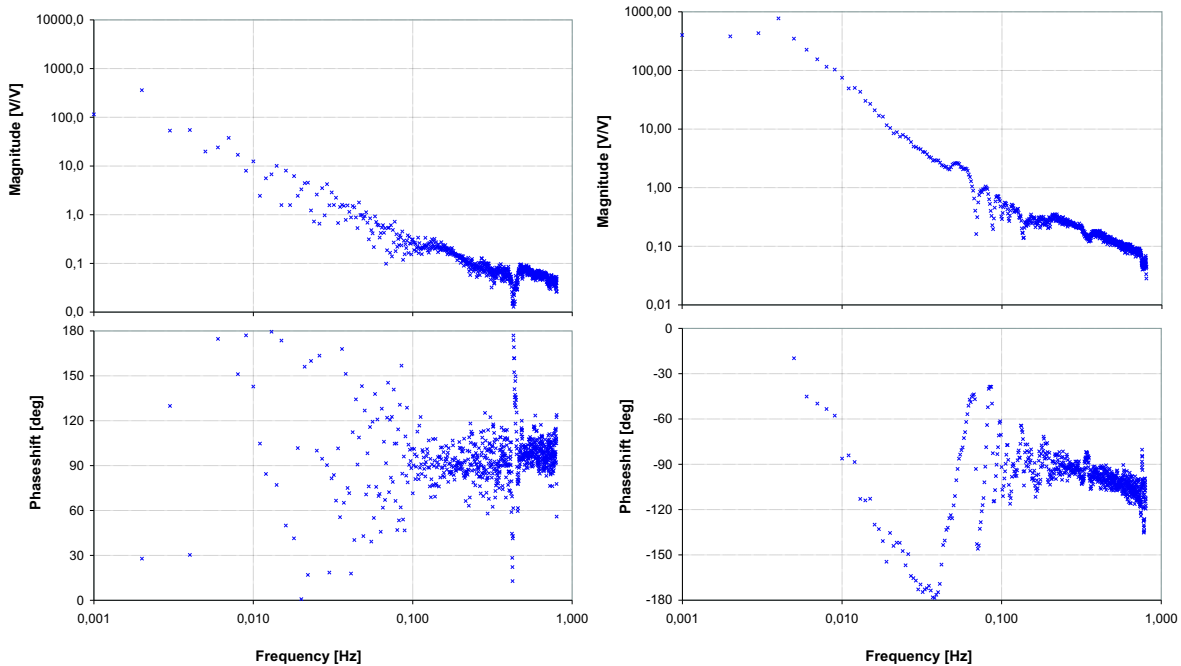


Figure 11. Dynamic response of CNT based actuator system; system input: current, system output: displacement; Left graphs: region I ($U = -0.2V \pm 0.1V$). Right graphs: region III ($U = +0.6V \pm 0.1V$).

frequency - which has been stated before.⁵ The double logarithmic axis scaling make the curves look like straight lines.

A more interesting insight into the system can be given, when the transfer function for the system with current as input and displacement as output is being looked at. The resulting FRF and phase shift is shown in figure 11. The double logarithmic scaling of the axis leads to a straight line with negative gradient - just as for an integrator. The phase shift up to $f < 0.1$ Hz does not seem to follow an obvious order. For higher frequencies there is a tendency towards a phase shift of $+90^\circ$ for region I and -90° for region III. Those characteristics in region III for gain and phase shift are those of an integrator. Assuming that there is also an integrator behavior between charge and current, the conclusion can be drawn, that there is only a proportional transfer function between charge and strain for a given region. These correlations are similar for region I, with the only difference, that the phase shift is $+90^\circ$, which is due to the negative gradient of the strain voltage curve in region I.

5 CONCLUSIONS AND OUTLOOK

Several experiments exploring the quasi static and especially dynamic behavior of nanotube based in plain actuators are carried out.

5.1 Quasi static Operation

In series of experiments the strain characteristics at different voltages is studied in detail. It could be shown that at a potential of around 0.3 Volts there is a minimum of strain. Higher and lower potentials, respectively, cause the bucky-paper to expand. For each voltage (within the electrochemical stability window) there is a maximum strain ε_{max} that can be found after a certain rise time. The correlation between voltage and strain is parabolic. It is shown that this correlation can be well reproduced and gives a measure for strain generation capability of a given CNT-structure in combination with a given electrolyte. A test procedure was defined by which these curves are to be established.

As far as high strains are concerned there is one rule, that has to be applied: the Ohmic resistance of the CNT structure has to be as little as possible. Apart from that, electrolytes are being searched for, that have a large electrochemical stability window. The use of CNT based actuators outside this window is uncertain due to non reversibility.

5.2 Dynamic Operation

The dynamic response of the system was investigated by means of a FRF. The analysis was carried out for regions I and III, respectively. For both regions similar characteristics could be shown. The electrical FRF shows characteristics like a capacitor for lower frequencies and like an Ohmic resistor for higher frequencies. The electromechanical FRF shows, that amplitudes are decreasing for higher frequencies. For current as system input and displacement as system output, there is a characteristic in region III for gain and phase shift which looks like that of an integrator. Assuming that there is also an integrator behavior between charge and current, the conclusion can be drawn, that there is only a proportional transfer function between charge and strain for the given region.

5.3 Steps that have to be taken

There are several steps that have to be taken before CNT based actuators can be applied in technical applications.

A sufficient formalism has to be found to describe the systems behavior.

Especially the macroscopic CNT structure has to be improved a lot. The superb structural properties of individual nanotubes have to be transferred to macroscopic structures. Ways that lead this way are the production of CNT fibers²²⁻²⁴ or the reinforcement of single-walled carbon nanotube bundles by intertube bridging²⁵.

Another step towards the realization of a CNT based actuator is the incorporation of solid state electrolytes. This has been demonstrated in literature^{26,27}, but has to be examined in detail. Questions that have to be answered are, which electrolytes are most appropriate and how can they be handled easily in an efficient way.

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