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Carbide-derived carbon-based
electromechanical actuators



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I. LIST OF ORIGINAL PUBLICATIONS

- I. J. Torop, M. Arulepp, J. Leis, A. Punning, U. Johanson, V. Palmre, A. Aabloo, Nanoporous carbide-derived carbon material-based linear actuators, *Materials*, **3** (2010) 9–25.
- II. J. Torop, F. Kaasik, T. Sugino, A. Aabloo, K. Asaka, Electromechanical characteristics of actuators based on carbide-derived carbon. In: Proc. of SPIE Vol. 7642, 76422A: Electroactive Polymer Actuators and Devices (EAPAD) 2010; San Diego, USA; March 7.–11. 2010
- III. J. Torop, V. Palmre, M. Arulepp, T. Sugino, K. Asaka, A. Aabloo, Flexible supercapacitor-like actuator with carbide-derived carbon electrodes, *Carbon*, **49** (2011) 3113–3119.
- IV. J. Torop, M. Arulepp, T. Sugino, K. Asaka, A. Jänes, E. Lust, A. Aabloo, Microporous and mesoporous carbide-derived carbons for electro-mechanical actuators, *submitted to Materials Letters*.
- V. J. Torop, T. Sugino, K. Asaka, A. Jänes, E. Lust, A. Aabloo, Nanoporous carbide-derived carbon based actuators modified with gold foil: Prospect for fast response and low voltage applications, *Sensors and Actuators B: Chemical*, **161** (2012) 629–634.

Other papers in related field:

- VI. V. Palmre, J. Torop, M. Arulepp, T. Sugino, K. Asaka, A. Jänes, E. Lust, A. Aabloo, Impact of carbon nanotube additives on carbide-derived carbon-based electroactive polymer actuators. *Carbon (In press)*.
- VII. V. Palmre, E. Lust, A. Jänes, M. Koel, A.-L. Peikolainen, J. Torop, U. Johanson, A. Aabloo, Electroactive polymer actuators with carbon aerogel electrodes. *Journal of Materials Chemistry*, **21** (2011) 2577–2583.
- VIII. V. Palmre, D. Brandell, U. Mäeorg, J. Torop, O. Volobujeva, A. Punning, U. Johanson, M. Kruusmaa, A. Aabloo, Nanoporous carbon-based electrodes for high strain ionomeric bending actuators. *Smart Materials & Structures*, **18** (2009) 095028.

2. AUTHOR'S CONTRIBUTION

In Paper **I** author performed all experiments and participated in preparation of manuscript. In Paper **II** author participated in experimental work and he is mainly responsible for the preparation of manuscript. The author is responsible for majority of research in all phases (including planning and conducting of experiments, data analysis, preparation of illustrations and writing manuscripts) of Papers **III–V**.

3. ABBREVIATIONS AND SYMBOLS

APS	average pore size
C	capacitance
CC	constant current
CCCP	combined constant current and constant potential
CDC	carbide-derived carbon
CDC/gold	gold-foil-modified actuator
C_m	gravimetric specific capacitance
CNTs	carbon nanotubes
CP	conjugated polymer
CPC	carbon-polymer composite
CV	cyclic voltammetry
DMAc	N,N-dimethylacetamide
EAP	electroactive polymers
EDL	electrical double-layer
EDLC	electrical double-layer capacitor
EIS	electrochemical impedance spectroscopy
EMIBF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate
EMITf	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
HRTEM	high-resolution transmission electron microscopy
I_c	constant current
IEAP	ionic electroactive polymer
IL	ionic liquid
IPMC	ionic polymer-metal composite
MEMS	microelectromechanical systems
PANI	polyaniline
PC	propylene carbonate
PEDOT	poly(3,4-ethylenedioxythiophene)
PPy	polypyrrole
PTFE	polytetrafluoroethylene
PVdF-HFP	polyvinylidene fluoride-co-hexafluoropropylene
S_{BET}	specific surface area
SWCNTs	single-walled carbon nanotubes
TEABF ₄	tetraethylammonium tetrafluoroborate
V_c	constant voltage
V_{tot}	total volume of pores
V_μ	volume of the micropores
δ	displacement
ε	strain

4. ABSTRACT

This thesis introduces experiment series carried out for carbide-derived carbon (CDC) based actuator devices in order to study relations between porosity parameters onto generated strain of actuators. In linear actuator configuration the effects based on charge induced volumetric expansion of electrolyte impregnated CDC electrodes were investigated. Test cells with different electrolytes were assembled and electromechanical response was characterized. Dry-type bending actuators which had three layer configuration of two polymer supported carbonaceous electrodes and thin polymeric membrane between them were developed and analyzed. In addition to electromechanical characterization, electrochemical measurements were simultaneously carried out to describe energy consumption of both CDC-based actuators.

Studies revealed that linear actuators based on high specific surface area CDC were suitable for short range displacement applications whereas actuation response was proportional to charge inserted and total displacement was approximately 1% of total electrode thickness. Despite the low displacement values, the linear actuators were capable to generate forces above 100 N, specific capacitance of CDC was found to be 120 F/g, and charge conversion efficiency reached up to 80%.

CDC-based bending actuators developed during this study had two features by their nature when voltage is applied: (i) the synthesized device is a bending-type electromechanical actuator, and (ii) this device is also an electrochemical capacitor, providing opportunity to store a considerable amount of charge. The gold-foil-modified laminated actuators can work in open air at low voltages (0.25–3 V). Their operating frequency is between 5 mHz and 50 Hz, and the maximum strain calculated from transducer displacement is 2.2%. The gravimetric capacitance of CDC in actuator electrodes was found to be 120 F/g at 1 mV/s sweep rate of the applied triangle voltage.

CDC-based bending type actuator device is expected to provide a useful means for creating low voltage, smart actuation systems where displacement range is well defined and controlled, and which will facilitate integration of electroactive printable solutions. Other potential applications of proposed soft, light-weight, flexible and low voltage driven actuators include artificial muscles, and hybrid actuator/energy conversion devices.

5. INTRODUCTION

A major goal in soft polymeric electromechanical actuator research is to develop a device that operates rapidly with high displacement at low voltage applied, and has low energy consumption at the same time. Current technologies based on electromotors and pneumatic actuators make the final product often too noisy, heavy and too complicated. For that reason a notable demand exist for soft, simple and miniature actuation devices in many technological solutions. For robotics and medical applications the desired actuation source should guarantee steady operation in different environments.

Electroactive polymers (EAP) offer unique possibilities and are perfect candidates for such actuators [1–5]. They are lightweight, silent, and require low voltages [6–7] to generate large deformations. However, some critical issues need to be resolved to engage them in future technologies. Since 1992 [8], ionic electroactive polymer actuators (IEAP) based on ionic conductive membrane covered with metallic plates, and different polymer supported carbon materials in combination with ionic liquid containing membranes have been extensively studied [7, 9]. Their working principle relies on electronically conductive layer and electrolyte interaction during charging, which causes volume changes of polarized electrodes [1, 2, 6, 10]. When an electric field is applied to the device, it drives the motion of counterions and the entrained solvent, leading to swelling or relative contraction when these ions enter or leave regions of the electrode layer. The actuation of IEAPs is mainly initiated by the migration of ions to the oppositely charged electrodes causing (local) volume changes. The charging may (conjugated polymers) or may not (carbon materials) be accompanied by oxidative-reductive processes of the electrode matrix/material itself [11–14].

IEAPs include conjugated polymers (CPs) [12, 15, 16], carbon nanotubes (CNTs) [14, 17, 18], and ionic polymer-metal composites (IPMCs) [2–6, 19, 20]. These materials present several advantages, including the capability of large bending deformation even at low ($\sim 1\%$) intrinsic strains of the electroactive layer. Materials can be driven with low voltages (1–5 V), making them well suited for several applications especially interfacing with biology and low voltage electronics [19].

However, there are some issues with these actuator materials that are not completely solved. The main problems are the complexity of the manufacturing process, insufficient reproducibility of properties of formed actuators, short lifetime, and insufficient control as well as guidance of the actuator movement. It has been reported that the displacement depends mainly on the total charge used and not on the applied voltage. Stable actuators with high speed, and with relatively high power are still a challenge.

6. BACKGROUND AND CONCEPT

In this chapter typical electroactive materials are discussed. Fundamentals for electromechanical actuation generation are explained. Bottlenecks, which limit wide breakthrough of these materials in many fields are dissected and pointed out. Advantages of carbide-derived carbon in electrochemical capacitor applications are described by means of charge induced volumetric expansion and strain generation for bending actuators.

6.1 Common materials used for electroactive actuators

Electroactive polymer actuators offer promising approach to meet the increasing demand of low voltage, energy efficient, smart and silent actuation systems. Electromechanical actuation is the conversion of electrical energy into mechanical motion or work. The electroactive effect of soft ion-conductive films was first described in concept of ionic conductive separator (Nafion) in-between two thin, flexible metallic plates. Pt-coated Nafion strip (in Li^+ form) was immersed in deionized water and after applying 2 V the aforementioned device curved [8].

In principle, electromechanical actuators can be divided into three major categories by the active electrode material used in actuator electrodes. The first category is carbon materials, including activated carbons, templated carbons like carbide derived carbon, carbon aerogels, carbon nanotubes and graphene [21, 22, I–V]. The actuation mechanism of these active materials is based on principle of charging of electrical double-layers (EDL) in polymer supported carbon matrixes. These carbon materials usually have large specific surface area and porous structure to assure large number of insertion sites. The second category is redox reaction-based electroactuators using transition metal oxides such as MnO_2 or RuO_2 in electrode layers. RuO_2 and MnO_2 have fast and reversible redox reaction at surface of active material particles. Metal oxides have usually high resistance, therefore oxide powders in electrode layer are often modified with pure, SWCNTs, or CNTs. Oxide-based electrode layers can be covered also with highly conductive noble-metal layers [23, VII]. The third category is conductive polymers with polypyrrole (PPy), polyaniline (PANI), or poly(3,4-ethylenedioxythiophene) (PEDOT) being typical examples [24–27]. Conductive polymers have several advantages for instance low cost and variety of synthesis routes, sufficient stability in air and high conductivity. Polymer supported actuator with PANI and CNTs have shown great cycle life and larger tip deflection compared to pure CNT electrodes [28].

Several types of carbon based electroactive materials are widely known. Carbon nanotubes, fullerenes and graphene-like structures are some of the attractive candidates for actuators. It was serendipitously discovered by Aida and coworkers that single-walled carbon nanotubes (SWCNTs) are additives that induces gelation of imidazolium cation-based ionic liquids (ILs) [29]. The

prepared gel was called "bucky gel", and this discovery led to intense research of CNT and IL mixtures. The gelation can be evoked reproducibly by grinding CNTs dispersed in imidazolium-based ionic liquids with an agate mortar and pestle or by sonicating the CNT-dispersed ILs [30]. During Raman spectroscopy studies scientists did not observe any chemical disruption of CNT mixtures prepared by abovementioned methods. TEM observation of the gel after rinsing IL with water revealed that the CNT bundles are exfoliated to give finer bundles. It is thought that interaction between CNTs is lost by cation- π and/or π - π interactions between the IL and CNTs. The bucky gel is a unique elastic material that displays both ionic and electronic conductivity. This unusual feature has so far produced several electrochemical applications [14, 18, 29].

Carbon based actuators, including CNTs, CDCs, or activated carbons predicate on two main actuation mechanisms. The first principle is based on the electronic conductivity of carbon material. Actuators of such type need high electrical potential (field) for actuation [31]. Actuation occurs due to carbon-carbon interaction change due to high electrical field. Another principle is diffusion of ions and ion pairs induced by applied low potential. These transducers usually combine carbon materials with polymer matrix and some ionic conducting media. They seem to have much more possible applications in the near future [14, 32].

Guangli *et al.* made the first example of an actuator based on a nanostructured carbon material. The actuator consisted of branched carbon nanotubes embedded within the pores of a microporous alumina template membrane and graphitic carbon used as the electroactive material. Electrochemical Li^+ intercalation caused this nanotube-containing membrane to flex, and electrochemical de-intercalation causes the membrane to relax to its original position [33].

CNTs have been one of the most intensively studied carbon materials in actuator applications [13, 14]. The first actuator made of CNTs was a macro scale sheet of nanotubes termed bucky-gel paper [13]. This actuator produced strain due to the change in dimension of the nanotubes in the covalently bonded direction caused by an applied electric potential. The created excess charge is compensated at the nanotubes/electrolyte interface by the electrolyte ions forming a double-layer. The accumulated charge induces ion movement, which leads to a change in the dimension of the nanotube paper causing the assembly to bend. Soon after the bucky paper actuator demonstrated actuation of single-walled carbon nanotubes, in which the SWCNTs were suspended over a trench, and the edges fixed at the surface with a metal layer. The charging leads to a rearrangement of the electronic structure of the nanotubes, and to Coulombic forces, both of which result in dimensional changes [34].

Besides CNTs, several microporous- and graphitic carbons have been studied by means of dilatometry by Hahn *et al.* [35, 36]. The graphitic carbons exhibited highest volume change (up to 10–15%), whereas the expansion was observed at voltages between -2.0 and $+2.5$ V ($\Delta V = 4.5$ V). The microporous

carbons had the expansion about $\sim 5\%$ at voltages below -1.0 V and above $+1.0$ V ($\Delta V = 2.0$ V) [36]. Also, the in situ Raman spectroscopy technique was applied to study ion intercalation behavior into the carbon body [37].

The examples described above raise the interest that beside several traditional nanostructured carbons like CNTs, fullerenes and graphenes, the high surface area amorphous carbons derived from different carbide precursors could be also interesting candidates for actuators. The actuation phenomenon during charging of porous carbon was discovered while searching for appropriate materials for new alternative energy storage devices [38, 39].

Microporous amorphous carbons have non-uniform distribution of the curved graphene-like flakes [40, 41]. Carbon atoms have generally the hybridization of $sp^2/sp^3 < 10\%$, and they form a amorphous 3D network. Increased sp^2/sp^3 ratio yields higher conductivity of the CDC bulk material [42]. Due to non-uniform structure, it is quite difficult to describe porous carbon, because HRTEM images only show a very small area of samples. The so called template carbons based on metal carbides are of interest in energy storage devices beside widespread activated carbons commonly produced by thermal decomposition of organic precursor materials and successive water vapor activation, because the pore size is tunable with the synthesis parameters and by modifying the template. One representative of such template carbons is carbide-derived carbon, which is obtained by extracting the non-carbon atoms from the carbide lattice. CDCs have been investigated as promising candidates for electric double-layer capacitor (EDLC) electrode materials, for low molecular weight gas adsorbents (CH_4 , H_2 , *etc.*) and for electron emission sources [43, 44]. These materials usually possess high surface area ($1000\text{--}2000\text{ m}^2/\text{g}$), controlled micropore volumes and pore size distributions. The advanced CDC materials have high electric double-layer capacitance (130 F/g and 90 F/cm^3 in nonaqueous solution), high electric energy conversion efficiency (up to 98%), very good material stability and chemical inertness. Supercapacitors based on CDCs have shown electrode lifetimes up to 10^6 cycles [41, 42, 45].

As described above, the expansion of the carbonaceous electrodes in electrochemical capacitor applications is generally undesired, and it is a crucial factor for the lifetime of energy storage devices. Hahn *et al.* have performed dilatometric studies on porous and graphitic carbon electrodes and observed significant reversible volumetric change of the electrodes during the charging-discharging. This confirms the electroactive properties of porous carbon [36].

However, there are only a few studies about the charge induced volume changes of carbide-derived carbon electrode materials carried out to explain the relations between the porosity of CDC and generated volumetric effect [46, I–V]. In principle, the design of the ionic polymer actuators described in this thesis (both, linear and bending) is comparable to supercapacitors. Thereby, relying on association by similarity, the electroactive mechanism of nanoporous carbon electrodes is related to electric double-layer formation during charging of the porous carbon material, and the dimensional change of the actuator is the consequence of charge injection in carbon nanopores during the electric double-

layer charging. It is also reported that particular gas evolution (faradic process) on the micropores could be a reason of the carbon actuation process, but using TEABF₄ salt in propylene carbonate solution or ionic liquids (EMITf and EMIBF₄) the electrochemical reactions are marginal in the voltage range of 0 to 3.0 V [39, 41, 47].

6.2 Electrochemical origin of porous carbon material-based actuators

When the porous carbon-based electrode is immersed into an electrolyte solution or electrolyte is introduced into the porous carbon material, charge is accumulated at the interface due to the presence of mobile electronic and ionic charge carriers. The interfacial region is the spatial region in which the properties vary between those of the bulk phases. In this assumption the interface is taken to be an infinitely thin, two-dimensional plane which represents the formal boundary between the two phases [48]. The interfacial region between the electrode and the electrolyte is commonly appointed as the electrochemical double-layer, even it may be thought to consist of more than two layers [49].

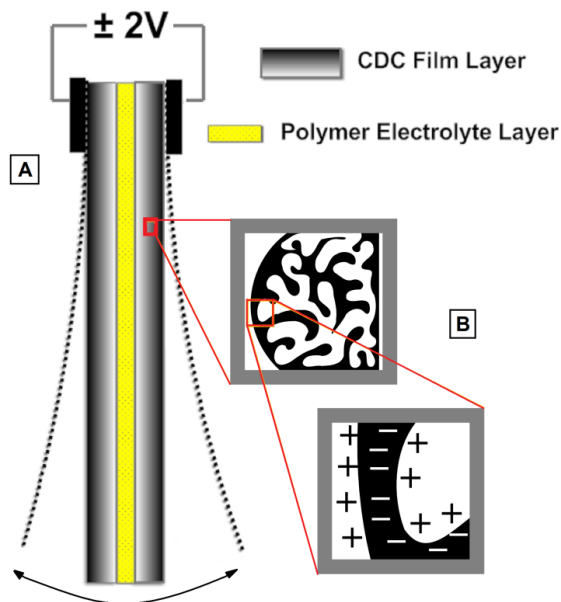


Figure 1. Schematic depiction of CDC actuator (A), and simplified notation of electrical double-layer formation inside porous media of CDC when voltage is applied.

Charge induced electromechanical actuation is a combination of charge injection during electrical double-layer charging of high surface area carbon, and ion migration/accumulation induced by charge distribution [46]. Aforementioned effects result in the more expressed expansion of the negatively polarized electrode compared to the positively charged electrode [35]. EDL charging is expected to be a fast process where the main limitation is the electronic conductivity of the carbon-based electrode. On the contrary, ion migration is affected by pore size distribution of porous carbon, and ionic conductivity of porous separator [49, III, IV].

In 1853 H. Helmholtz described the first model for electrical double-layer theory [50]. The proposed model supposed that the electrical double-layer consists of two parallel layers of counter charges. This simple and often used model assumes that no charged species can cross the interface regardless of the potential of the electrode. The electrode is thus said to be ideally polarizable which implies that it behaves like an ideal capacitor without the leakage of charge across the interface. Helmholtz's model suggests that the distance between these two layers is the diameter of charged particles and the charge in these layers is distributed uniformly all over the interface. In Helmholtz theory the electrical double-layer can be considered as a usual planar capacitor with differential capacitance, C :

$$C = \frac{\varepsilon \varepsilon_0}{l} \quad (1)$$

where ε is the relative dielectrical permittivity of environment, ε_0 is the dielectrical permittivity for vacuum, and l is the distance between capacitor plates. Helmholtz theory is in good correspondence with experimental data. However, it does not describe the dependence of differential capacitance and charge density on the temperature, electrolyte concentration and concentration of surface active additives in electrolyte *etc.* An expanded model of Helmholtz's theory was proposed by Gouy and Chapman [51, 52]. This theory does not take into account the interactions between charged ions and ignores dimensions of ions being applicable only in dilute solutions. The Helmholtz and Gouy-Chapman theory were integrated by O. Stern [53] who divided the electrical double-layer into two regions: Helmholtz layer, and diffuse layer where ions are in Brownian motion.

As seen in Figure 1A the design of ionic polymer actuators is comparable to electrical double-layer capacitors, often referred as supercapacitors or ultracapacitors [49]. Supercapacitors are highly capacitive devices famous for their high power densities and remarkable energy conversion efficiency up to 98% during the charging-discharging cycle [54, 55]. They consist of two high-surface area electrodes (*e.g.* porous carbon material) and an ion permeable separator between them. The porous polymer separator acts like a reservoir for electrolyte and avoids electronic conductance between the electrodes. This energy storage system based on a non-faradic process provides very fast charge

and discharge making the electric double-layer capacitors with the best candidates to meet the demand for high power and long durability. Recently, relationships between porous structures and electrochemical behavior have become increasingly important [56, 57]. Although the use of various materials as EDLCs has been investigated, the application is limited in terms of specific energy [49, 54, 55]. To enhance the specific energy and power of EDLCs, several researchers have put much effort into the development and modification of carbonaceous materials, such as controlling the pore size distribution, introducing electro-active metallic particles or electro-conducting polymers, and fabricating hybrid type cells [22, 54, 58–61].

6.3 Motivation and scope of this work

The research objects in this work are the carbide-derived carbon-based electro-active actuators, where dimensional changes are evoked during charge accumulation into porous media of CDC. The main goal is both, to develop more energy efficient actuator devices and provide actuators with controllable/predictable behavior using porous carbons with different porosity in electrode layer. Different precursor carbons were involved actuator electrode layer as tunable base material to generate gradual actuation. The electrochemical and electromechanical measurements were applied simultaneously to identify relationships between the porosity parameters of CDC and generated strain of actuators. To achieve the abovementioned goals different CDC-based actuators were prepared and investigated through the following steps:

Paper I studies the dilatometric effect of CDC-based two electrode cell actuator. Different CDC materials and electrolytes were involved, and charge induced linear (longitudinal) actuation response is described. It was found that the actuation mechanism is based on the interactions between high-surface area carbon and the ions of the electrolyte. For dilatometric experiments a specially designed test cell was developed. Linear actuators exhibited linear actuation around 1%, and showed 80% charge conversion efficiency. This paper describes the actuator setup in which the CDC electrodes were analyzed by classical electric double-layer testing routes, *e.g.* electrodes were isolated from the environment, and electrodes and solvents were kept in inert atmosphere.

Paper II focuses on synthesis aspects. Optimal ratio of CDC, ionic liquid and supporting polymer was investigated in order to get freestanding CDC-based electrode films. The developed bending type actuators were characterized by measuring blocking force, strain, response speed, and capacitance. Due to the relatively large thickness the actuators showed significant blocking force values, and were preferable for slow-response applications.

In **Paper III** CDC-based bending type actuators were demonstrated. Electromechanical and electrochemical properties were investigated by means of porosity characteristics of CDC. Three different TiC-derived microporous carbons with shifted pore size distribution due to synthesis temperature were

used in the electrode layer of the actuator. Actuators showed porosity dependent actuation response, and since the actuation is proportional to the inserted charge, the energy consumption was also dependent on the type of CDC used in the electrode layer. Besides the shape changing nature, the capacitive behavior of CDC-based actuators is demonstrated, and with restrictions the proposed actuator can be represented as a flexible supercapacitor.

Paper IV studies mesoporous and microporous carbide-derived carbon based actuators in terms of actuation response time and displacement range. The (meso)porosity influence on the charging speed (actuation speed) is investigated, and improved response times of Mo_2C -derived carbon actuators were demonstrated. The mesoporosity appears to be responsible for fast response of actuators, while total porosity affects the displacement range of actuators.

Paper V focuses on the increase of speed of TiC -derived actuators. The conductivity of CDC powder is not sufficient enough to achieve fast actuation response at a higher operating frequency range (above 50 Hz). The supporting polymer used in the electrode layer also decreases the conductivity between CDC particles. Ultrathin gold films were used on the electrode surface of CDC actuator to increase the charging speed, and therefore improve actuation response time. Remarkably low driving voltage (± 0.25 V) achieved for gold-foil-modified actuators, and good actuation response was demonstrated over large frequency range (200–0.05 Hz).

The well defined gradual actuation and improvement in energy efficiency are both important factors that limit the wide breakthrough of these materials. Therefore, gaining more information about actuator strain relations on porosity properties of CDC used in electrode layer is essential for the improvement of simple, fast and precise actuators, and to improve the energy efficiency as well.

7. THEORETICAL ASPECTS AND EXPERIMENTAL METHODS

In this chapter, a short introduction is given for the carbon material-based electromechanical actuators developed in this thesis. Specific issues for carbon materials related to electric double-layer capacitance and charge induced volumetric effects are considered. The focus is primarily on carbonaceous materials and common electrolytes used in both, in the electrode layer and in the ion-conductive membrane layer. The design aspects for linear and bending type actuators are presented. Suggested synthesis routes for the preparation of actuator devices are discussed and described in detail. Some theoretical aspects of electrochemical characterization methods used in this study are briefly introduced. The experimental setup for both type actuators is described, which exemplifies the key concepts of these actuators that can be engineered into smart materials.

7.1 Carbon-based electrode materials and common electrolytes for actuators

Carbonaceous materials are of great technological importance due to their unique properties [42, 55, 60]. Non-faradic charge storage relies on an ideal capacitive behavior of the electrochemical double-layer. Hence, the actuator concept is similar to electric double-layer capacitors the electrode materials in actuators must exhibit the characteristics of an ideally polarizable electrode as closely as possible. In order to obtain a system in which the faradic reactions are insignificant over the entire operating potential window, it is the choice of the electrode/electrolyte combination which is essential. Carbide-derived carbons satisfy all the fundamental requirements for supercapacitor electrodes [61, 62]. They have well-defined porous structure with remarkable surface area, and proper electrochemical stability. Widespread use of CDC in the supercapacitor development is particularly due to the great volumetric capacitance compared to other commercially available activated carbons [55]. Another important argument for using CDC in these applications lies in the fact, that synthesis of CDC is very well controlled and the physical architecture of the final product can be tailored to nanoscale dimensions [45, 47, 49, 58, 63]. CDC is also an excellent material for gas storage, allowing to store hydrogen 3.0 wt% at 1 atm pressure and 77 K due to its porous structure and large quantity of opened micropores [64].

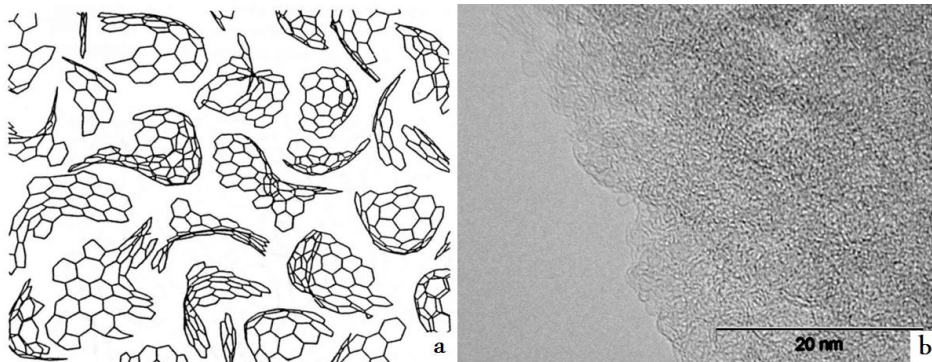


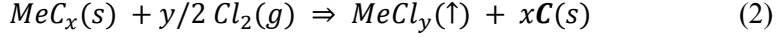
Figure 2. Suggested structure of CDC (a) [40], and High Resolution Transmission Electron Microscope (HRTEM) picture (b) of amorphous microporous carbon.

CDC is produced by selectively etching metals from carbides using chlorine at elevated temperatures. Basically, precursors are grounded metal carbides (TiC , Mo_2C , Al_4C_3 , *etc.*), but latest findings describe synthesis of CDC even from thin TiC monolithic films [41, 65]. Both described methods for carbon synthesis offer unique control over microstructure and allow fine-tuning the porosity of the final product. Generally it is understood that high electric double-layer capacitance of porous carbon is related to the high surface area, and precise pore size distribution according to the electrolyte used [47, 49, 60, 61]. Although, large pores can be produced and well controlled in a variety of materials, nanopores in the range of 2 nm and below are usually achieved only in porous carbons or zeolites [41]. Therefore, carbide-derived carbon synthesis allows the formation of highly porous carbon materials with good mechanical properties, and makes them very attractive for actuator applications since the charge accumulation in the electronically conductive porous matrix induces volumetric changes. Microstructure, pore size, pore shape, and surface termination of nanoporous CDC can be precisely controlled by changing the synthesis parameters and the composition and structure of the initial carbide precursor [63, 66].

7.1.1 Synthesis aspects and evaluation of carbide-derived carbons

Microporous and mesoporous carbide-derived carbons have been obtained by thermal chlorination. Depending on the synthesis temperature and the carbide precursor, the average pore size and the pore size distribution can be adjusted. As a general trend, higher chlorination temperatures result in more graphitic carbide-derived carbon powders with a larger average pore size [41, 58, 59].

The synthesis can be described by the general chemical reaction:



During the reaction, the metal (*Me*) is transported away from the reactor as metal chloride ($MeCl_y(g)$) together with an excess of chlorine, leaving pure carbon $xC(s)$. For aftertreatment and surface modification heating in the gas (N_2 , H_2O , CO_2 , H_2 , He/H_2 , Ar) stream is used.

The low-temperature nitrogen sorption experiments were performed at the boiling temperature of nitrogen (77 °K). The specific surface area (S_{BET}) was calculated according to the BET theory [67] up to the nitrogen relative pressure (P/P_0) of 0.2. The total volume of pores (V_{tot}) was calculated at relative pressure (P/P_0) of 0.95 and the volume of the micropores (V_μ) from t-plot, using Harkins-Jura thickness values between 5 Å and 90 Å calculated according to Equation

$$t = \sqrt{\frac{13.99}{0.034 - \log \frac{P}{P_0}}} \quad (3)$$

Average pore size (APS) is calculated according equation:

$$APS = \frac{2V_{tot}}{S_{BET}} \quad (4)$$

Table 1. Selected porosity parameters of carbide-derived carbons used for actuator preparation.

Notation of CDC material	T _{Chlorine} [°C]	S _{BET} [m ² g ⁻¹]	V _{tot} [cm ³ g ⁻¹]	V _μ [cm ³ g ⁻¹]	APS [Å]
TiC-400	400	1113	0.51	0.5	6.3
TiC-600	600	1150	0.53	0.49	9.3
TiC-800	800	1470	0.71	0.59	9.7
TiC-950	950	1843	0.94	0.72	10.2
B ₄ C-800	800	1534	0.99	0.43	12.9
Mo ₂ C-800	800	1675	1.39	0.72	16.6

T_{Chlor} – chlorination temperature; S_{BET} – BET surface area; V_{tot} – total pore volume, V_μ – micropore volume; APS-average pore size.

For morphology studies, SEM and TEM methods offer wide opportunities. SEM studies typically give information about morphology of cross-section of actuators or even independent CDC particles can be characterized. TEM provides a very clear picture of structural changes at subnanometer level, such as the degree of ordering of the graphitic layers. However, TEM images only show a very small area of samples.

7.1.2 Electrolytes for carbon material-based actuators

Ionic liquids (IL) are characterized by negligible vapor pressure, high chemical and thermal stabilities, high ionic conductivity, and broad electrochemical potential window [68]. Due to such unique properties coupled with the ability to dissolve a wide range of organic and inorganic substances, they have drawn increasing attention not only as a new class of electrolytes, but also for recyclable alternatives to conventional organic solvents for wet processes, including chemical syntheses, catalyses, liquid/liquid extractions, and so forth. Several kinds of organic and inorganic additives were found to induce gelation of ILs. The prepared gel, in which the IL is confined, is called a ionogel to express that the gel is a matrix that only contains ions. There are two common ways to prepare the gel: one method involves swelling a premade polymer with IL and the other entails a polymerizing reaction in the IL. If the polymer is insoluble in IL, a co-solvent, which dissolves the polymer, is often used, but in that case an extra process is required to evaporate the co-solvent. The polyvinylidene-fluoride-co-hexafluoropropylene (PVdF-HFP)-IL gel has been the most investigated system in order to obtain a nonvolatile polymer electrolyte for energy storage devices that might serve as an alternative to the widely used (PVdF-HFP) organic solution electrolytes.

The selection of non-aqueous electrolytes seems fairly wide at first sight, but commonly tetraalkylammonium cation based salts in organic solvents like acetonitrile, propylene carbonate, γ -butyrolactone, *etc.* are used [41, 69]. Generally, EDLCs based on non-aqueous electrolytes have to be assembled in very pure and dry conditions to avoid dissolving of electrochemically active water and oxygen in electrolyte. In this thesis the linear actuators were assembled in clean conditions similar to typical EDLC.

7.2 Actuator preparation

7.2.1 Preparation of CDC-based linear actuator

CDC powder (1 g) was mixed with a small amount of ethanol and 10% (by wt.) of PTFE (as a 60% suspension in water) to form a slurry, which thereafter was gently pressed until a wet material was formed. After evaporation of ethanol, the material was impregnated with heptane, shaped to a cylinder and rolled in the axial direction of the cylinder. The latter procedure was repeated until elastic properties appeared in the carbon sheet. Finally, the heptane was removed at ~ 110 °C, the carbon sheet was rolled stepwise down to the desired thickness, dried under vacuum at 170 °C and coated from one side with a thin (~ 2 μm) aluminum layer, using plasma activated physical vapor deposition. Electrode discs of desired size were cut from these sheets. Linear actuators were assembled from pairs of carbon electrode discs ($\varnothing$ 1.7 cm), separated with an ion-permeable separator paper from Nippon Kodoshi (Figure 3). Each actuator consisted of five electrode pairs with a total geometric surface area of

11.35 cm². The electrode assembly was placed in a sealed aluminum container. Additional mechanical pressure ($p = 48 \text{ N/cm}^2$) was applied by a spring through a special connecting rod. This rod was further used for measuring the linear movement of actuator by a laser beam [I].

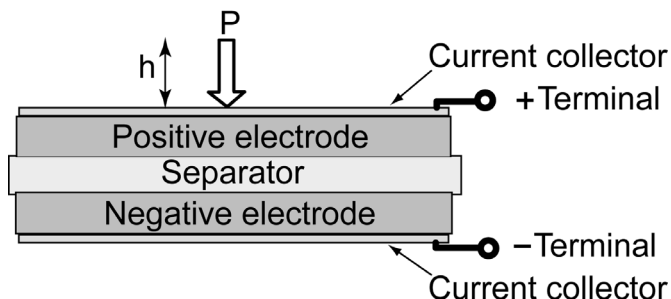


Figure 3. Simplified view of cross-section of linear actuator element.

The actuator cells were held under vacuum at 120° C for 24 h before being impregnated with the electrolyte. The electrolytes used in this study were 1.0 M tetraethylammonium tetrafluoroborate in propylene carbonate (“Honeywell Digirena ®” TEABF₄/PC, H₂O < 0.003%) and the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethane-sulfonate (EMITf, Fluka). Before evaluation, the actuator cells were kept at 60 °C for 48 h, to saturate the compact nanoporous electrode body with the electrolyte. Thereafter, continuous galvanostatic cycling between 2.7 V and 0.05 V with the current $I = 100 \text{ mA}$ was carried out, prior to performing further studies. The purpose of preliminary galvanostatic cycling is to distribute the electrolyte ions and decompose the traces of H₂O as well as to inactivate other possible impurities. Usually five cycles were needed to establish a stable actuation of the electrochemical system.

7.2.2 Preparation of CDC-based bending actuator

The simplified route for CDC-based actuator preparation is given in Figure 4. The device was obtained by hot-pressing CDC-based electrodes and IL containing polymer membrane was sandwiched between them. One of the advantages of the CDC-based three-layered composite as an actuator material is that it can be easily formed into various shapes, its properties can be engineered and it can potentially be integrated with MEMS, sensors and control devices to produce smart systems. The CDC-based simplified device conception is given in Figure 5. Forming the self-standing separator layer and electrode layers can be easily done by casting the dispersing solution and evaporating the solvent completely. This simple route offers sufficient control over the thickness of final layer.

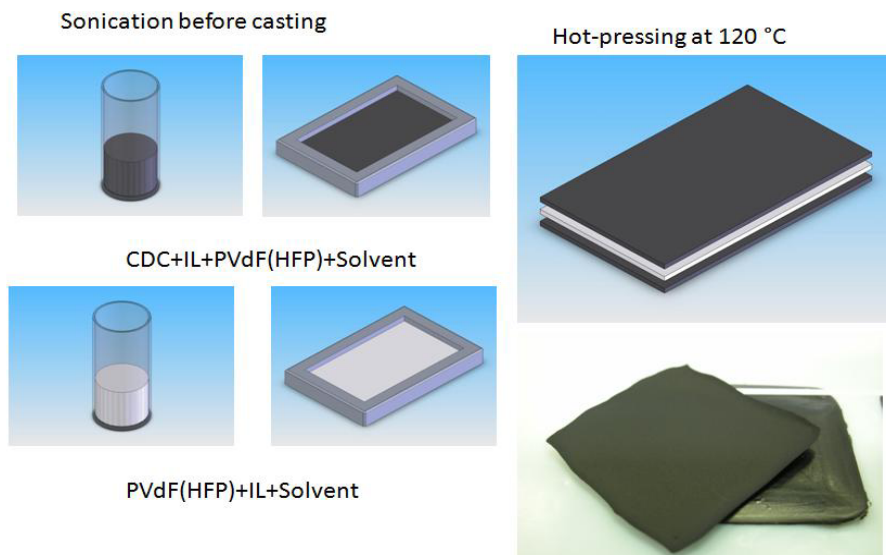


Figure 4. Simplified diagram of CDC-based actuator preparation steps and photograph of prepared electrode films.

A preparation of the electrode layer composed of 20 wt% of CDC, 48 wt% of EMIBF₄, and 32 wt% of PVdF(HFP) (Kynar Flex^{TRM} 2801) was as follows: 50 mg CDC, 80 mg of PVdF(HFP), and 120 mg EMIBF₄ were dissolved in 9 mL DMAc. The mixture was stirred at room temperature for 72 h and further was processed in an ultrasonic bath for 24 h. The electrode film was made by casting 1.6 mL CDC suspension into a Teflon mold (with dimensions 2.5 cm × 2.5 cm), thereafter the mixture was dried at 80 °C in a vacuum oven to remove residues of solvent. The electrolyte layer was prepared from PVdF(HFP) and EMIBF₄ with weight ratio of 50/50 in the film. PVdF(HFP) was dissolved in DMAc under magnetic stirring at 70 °C. After adding EMIBF₄, the mixture was stirred for two hours, and the electrolyte film was obtained by pouring the mixture into the Teflon mold and evaporating the solvent completely. Finally, the electrolyte film was sandwiched between two electrode films and hot-pressed to connect the layers. In case of gold-foil-modified (CDC/gold) actuator, the electrolyte film was sandwiched between two CDC electrode films and additional gold foils (Gold-Hammer 99.9% Au) were placed onto CDC electrode layer. Five layered actuator film was then hot-pressed to fuse the layers.

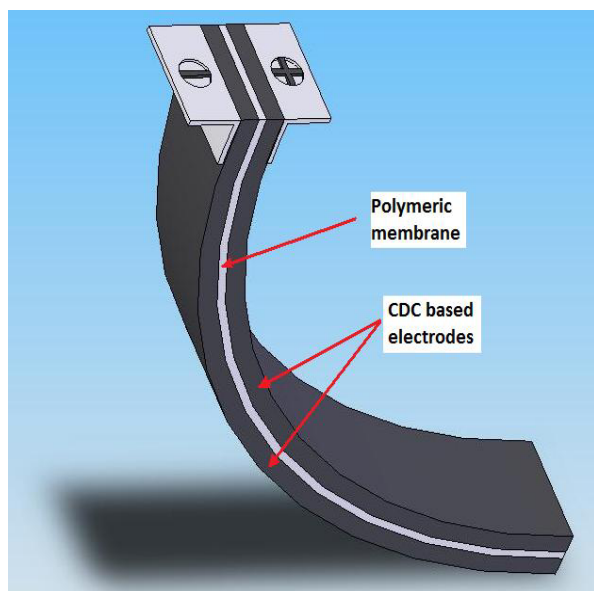


Figure 5. Architecture of supercapacitor-like bending actuator composed of solid electrolyte layer and carbide-derived carbon-based electrode layers.

8. CHARACTERIZATION OF ACTUATORS

8.1 Electrochemical characterization

Cyclic voltammetry is a commonly employed form of linear sweep voltammetry in which the voltage of an electrochemical system is changed by a constant rate, dV/dt , between two arbitrary vertex voltages. In the case of an electrode without any faradic contributions over the entire investigated potential range, the current response I is purely capacitive and follows the subsequent dependence:

$$\frac{dQ}{dt} = I = C \frac{dV}{dt} \quad (5)$$

where V is the cell voltage, I is the current, and t is the time.

The capacitance C can be calculated from current-voltage curves according to the equation:

$$C = \frac{|I^+| + |I^-|}{2dV/dt} \quad (6)$$

where I^+ and I^- are polarization currents (mA) at 0 V, dV/dt is the potential scan rate (mV/s). In symmetrical two-electrode system the gravimetric specific capacitance C_m (F/g) of carbon material can be obtained from the capacitance of the cell by:

$$C_m = 4 \frac{C}{m} \quad (7)$$

where m is a total weight of dry carbon in electrode material.

Electrochemical impedance spectroscopy (EIS) involves the study of the impedance of an electrochemical system where the current is measured as response to an applied sinusoidal voltage perturbation at different frequencies. EIS method can describe a processes involved in electrochemical test cell that are mainly associated with the transport of electrons through the electronic conductors, charge transfer on electrode-electrolyte interface and/or transport of ions through electrolyte. The total measured current is dependent on the electrical double-layer charging current, faradic reaction rate on the electrode-electrolyte interface, and on the ohmic resistances of the test cell components. EIS widely used for characterization of capacitive and resistive components of electronically conductive porous electrode materials and this method is particularly sensitive to the pore structures as they are served in porous CDC-based electrodes [49, 70].

Electrochemical characterizations of the actuators described in Paper I were performed in a sealed electrochemical cell at room temperature, by using the Solartron potentiostat 1287 with FRA analyzer. Cyclic voltammetry (CV), constant current, constant potential, and electrochemical impedance spectroscopy (EIS) experiments were carried out. The CV was performed at different

voltage sweep rates: 2, 5, 10, and 50 mV/s. The region of working voltage was varied in the interval of: 0–2.5 V, 0–2.7 V and 0–3 V. The galvanostatic measurements were performed in the current range of 10–1000 mA at voltages from 0.05 V to 3 V.

Electrochemical characterization of the gold-foil-modified actuator electrodes (Paper V) was performed in a sealed electrochemical cell in two-electrode configuration with PVdF(HFP)-based ionic liquid gel membrane, by using PARSTAT 2273 advanced electrochemical analyzer. Cyclic voltammetry and electrochemical impedance spectroscopy experiments were carried out for electrodes with diameter of 7 mm.

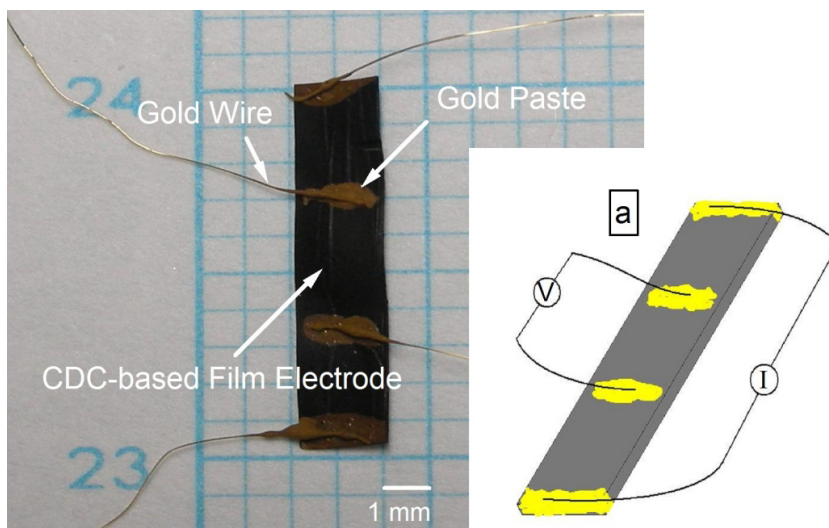


Figure 6. Experiment setup for conductivity measurements of CDC-based electrode.

The conductivity of the electrode film was measured by the four-probe DC current method. Linear sweep wave of current was applied from outer probe electrodes and the voltage was measured by inner probe electrodes Figure 6, 6a. The conductivity was estimated by the slope of the current-voltage curve. A Hokuto Denko Potentio/Galvanostat with a Yokogawa Electric model FC 200 waveform generator was used as a galvanostat mode.

8.2 Electromechanical characterization

8.2.1 Linear actuators

In order to apply to the robotics, an actuator that has a linear motion (linear actuator) is often very practical. The test cell of the linear actuator is depicted in

Figure 3, Figure 7a and 7b. It consists of two fundamental parts: the electrochemical actuator and the optical detecting mechanism. The actuator was assembled in a sealed cell. The cell incorporates a spiral spring, compressing the actuator by the force of 100 N. The optical system is mounted on the top of the cell. The mechanical coupling between the actuator and the optical system is implemented by a shifting vertical rod. The movement of the rod is transferred to the moving mirror using a steel eccentric and a lever. This mechanics magnifies the scale of movement of the actuator by 25 times. Further magnification of the scale is performed by a laser beam, reflecting from the mirror and targeted to a distant screen, as depicted in Figure 7a.

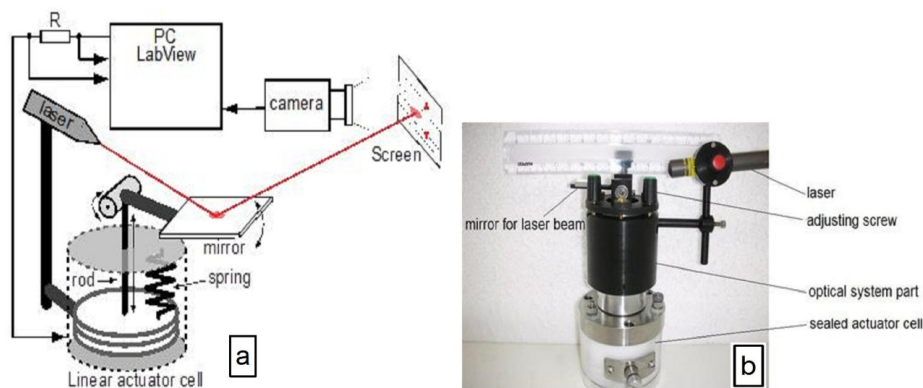


Figure 7. Experimental setup (a) and picture of linear actuator test cell (b).

The described optical system is able to magnify the scale of movement of the linear actuator by thousands of times, depending solely on the distance of the screen. In the course of the experiments, the distance to the screen was 6.25 m and the expansion of the actuator by 1 μm was detectable as a displacement of the spot of the laser beam on the screen by 1 cm. The displacement of the spot on the screen was recorded by a Firewire camera and the motion was thereafter digitalized using LabView software. Simultaneously, the electrical parameters (voltage and electric current) were recorded using a National Instruments PCI-6034 DAQ card and LabView software. The electric current was measured as a voltage drop over the low ohmic resistance R (Figure 7a).

8.2.2 Bending actuators

As described in 7.2.2, laminated bending actuators can be prepared from CDC-based electrodes while fusing membrane layer between electrode layers. Displacement measurements were carried out using 1 mm $\times$ 10 mm actuator strips clamped between gold contacts. The displacement was monitored conti-

nuously by laser displacement meter KEYENCE model LK-G3001P. The measured displacement was transformed into the strain difference (ε) of two electrode layers by using the following equation:

$$\varepsilon = \frac{2d\delta}{(L^2 + \delta^2)} \quad (8)$$

where L is the free length from gold contacts (5 mm), d is the thickness of actuator and δ is displacement of actuator.

From Figure 8, the following relation obtained:

$$(R - d/2)/(R + d/2) = (L - \Delta L_2)/(L + \Delta L_1) \quad (9)$$

where R is the curvature radius and $\Delta L_1, \Delta L_2$ the change induced length-change in each electrode by applying voltage. From above equation, the strain difference ε is given by eq. 10:

$$\varepsilon \varepsilon = (\Delta L_1 + \Delta L_2)/L = d/R \quad (10)$$

Since R is given by,

$$R = \frac{(L^2 + \delta^2)}{(2\delta)} \quad (11)$$

we can obtain Eq. (8) [12, 18].

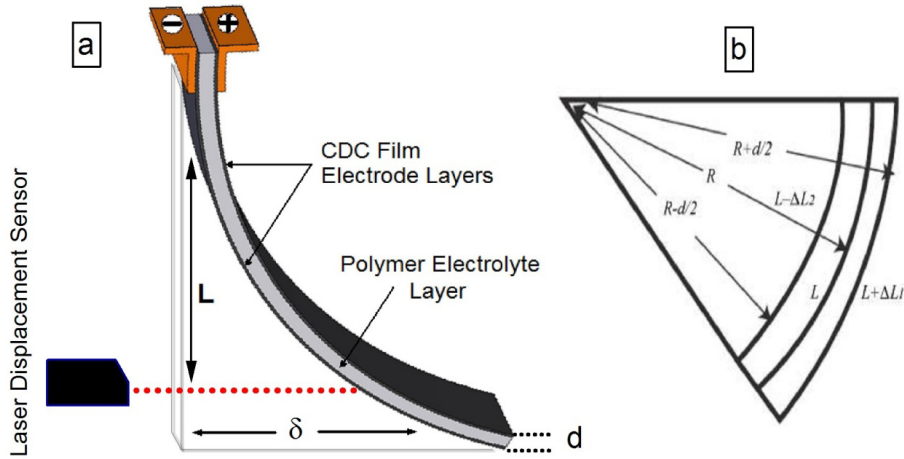


Figure 8. Schematic drawing of the displacement measurement of the CDC-based bending actuator (a). Schematic drawing for explaining the evaluation of the strain from the displacement (b) [18].

9. RESULTS

9.1 Porosity impact of CDC-based electrodes to charge induced volumetric effects

9.1.1 Linear actuators

The results presented in this section were measured in linear actuator configuration. The linear actuator devices were assembled according to instructions given in 7.2.1. In order to examine the dynamics and peak of the actuation of the linear actuators, the combined constant current and constant potential (CCCP) mode was used: after charging the actuator to a certain voltage using a constant current (I_C), a constant potential (V_C) was applied for up to 5 minutes. During the period of the constant potential, the current decreases substantially and the peak of actuation appears in few minutes. In these analyses the amperage of the constant current was varied in the range of 50 to 1000 mA.

Table 2. Notation of linear actuators used in this study.

Notation of actuator	CDC material used in electrode	Electrolyte
TEA600	TiC-600	1.0 M TEABF ₄ /PC
TEA800	TiC-800	1.0 M TEABF ₄ /PC
EMI600	TiC-600	EMITf
EMI800	TiC-800	EMITf

Figure 9a depicts the diagrams of charging the actuator EMI800 in the CCCP mode. The actuation culminates and remains stable in about 120 seconds, while the voltage reaches its stable level already in 60 seconds. This diagram is very typical, similar behavior was observed for all tested actuators. The actuation-charge diagram depicted in Figure 9b indicates that there exists a nonlinear correlation between the actuation and the electric charge of the actuator.

In case of linear actuators, the actuation amplitude was estimated using the constant current charge-discharge process. The value of the constant current I_C was 10 mA. The actuation amplitude was recorded simultaneously with charging or discharging current characteristics of the actuator. The potential of the electrodes gained some certain predefined values, *e.g.* 1.5, 2.0, 2.5 and at 3.0 V. The notations of assembled actuators are given in Table 2 and results of the measurements are given in Figure 10. The graph reveals that the four actuators function almost identically. The difference between the amplitudes of actuation is less than 20% for voltages up to 2.5 V. At higher voltages the

dissimilarity increases. At 3.0 V the difference between the actuation of TEA600 and EMI600 is almost twofold.

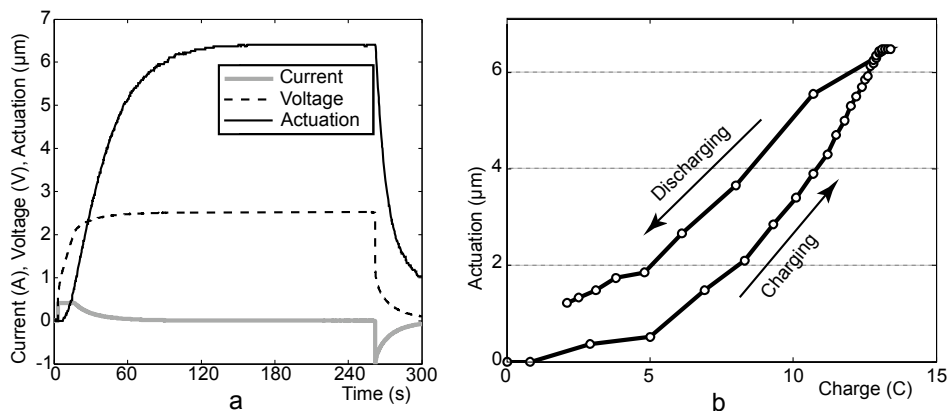


Figure 9. CCCP measurement of EMI800 ($I_C = 400$ mA, $V_C = 2.5$ V). Voltage, current and actuation vs. time (a) and actuation vs. charge (b).

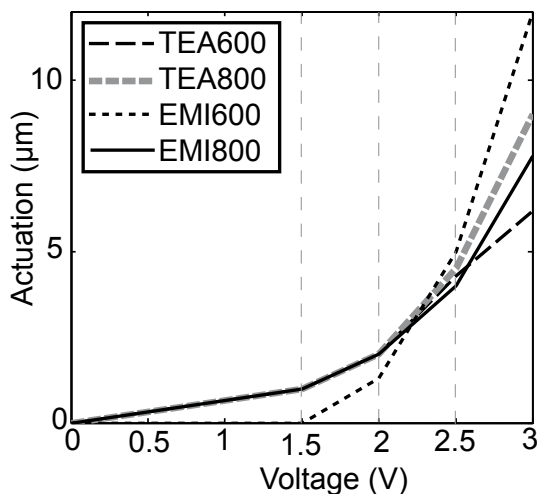


Figure 10. The actuation of the actuators at different voltages obtained at charging current $I_C = 10$ mA.

Figure 11 shows the comparison of the actuators EMI600 and EMI800. Both actuators expand slowly as the relatively low current ($I_C = 50$ mA) gives to the systems enough time to charge the double-layer of carbon electrodes. The graph given in Figure 9a indicates that EMI600 is faster than EMI800. After 200 seconds of charging, the displacement of the two systems differ about four-fold

and EMI600 require less charge for the same degree of actuation. When the charge of the actuators reaches up to 10 C, the difference between the amplitudes of actuation of the two systems is about four-fold.

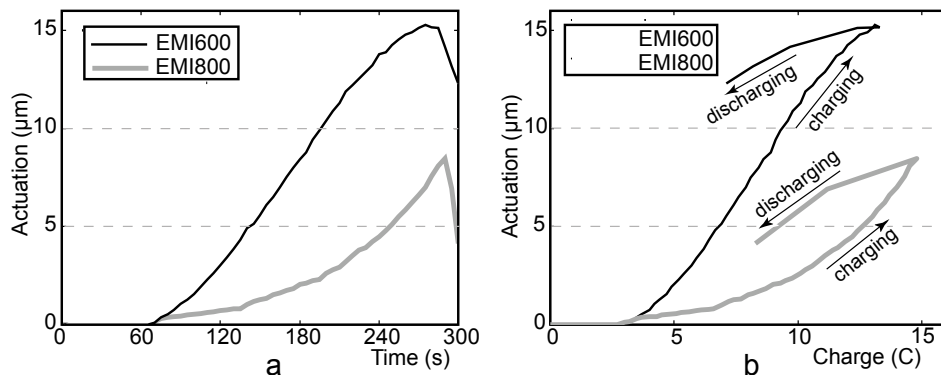


Figure 11. Actuation of EMI600 and EMI800 vs. time (a), and actuation vs. charge (b) ($I_C = 50 \text{ mA}$; $V_C = 3 \text{ V}$).

9.1.2 Bending actuators

Figure 12 shows the displacement and electric current profile of the TiC-800 CDC-based actuator at 0.1 Hz of the applied $\pm 2 \text{ V}$ rectangular voltage. Both characteristics retain their shape in time, confirming electrochemical stability of the actuator. The recorded current profile demonstrates capacitive nature of CDC based actuators. The displacement is recorded by laser sensors and snapshots A,B,C are given to illustrate the displacement behavior of bending type actuator during experiment.

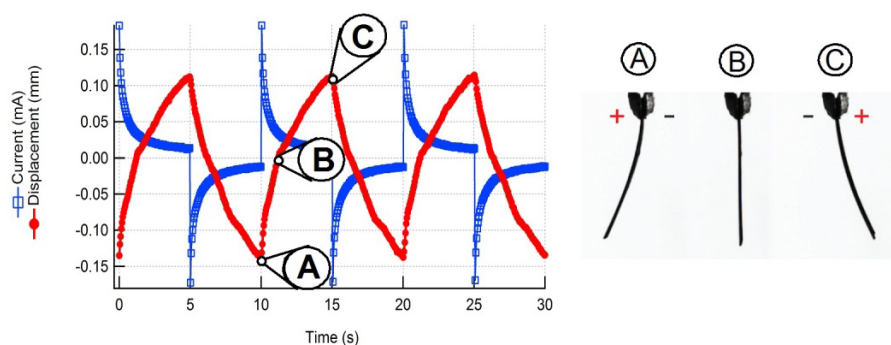


Figure 12. Typical displacement and current characteristic of actuator at 0.1 Hz frequency, when rectangular square wave voltage $\pm 2 \text{ V}$ was applied. Snapshots A,B,C were taken during actuation.

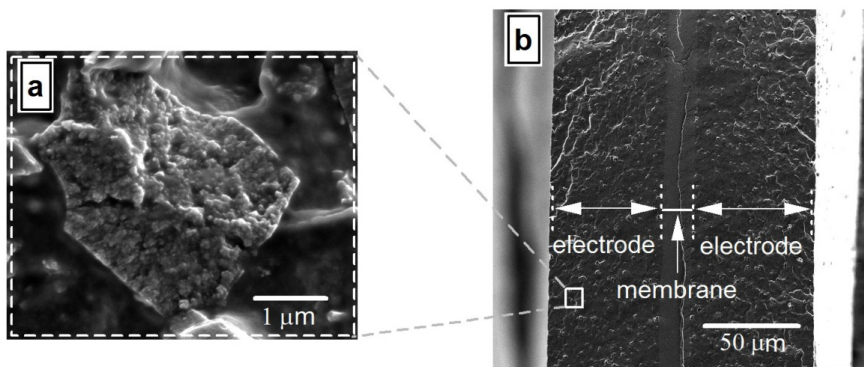


Figure 13. SEM images of cross-section of bending type actuator with CDC-based electrodes supported with polymer and ionic liquid containing polymer membrane.

In order to estimate porosity impact onto electromechanical performance of actuators the carbide-derived carbon synthesised from TiC at different temperatures were selected. Three TiC-derived carbon materials synthesized at 400 °C, 800 °C, and 950 °C, which have mainly microporous structure with narrow pore size distribution according to Table 1. As described in paragraph 6.3 the main objective of this thesis was to prepare actuators with different displacement and capacitive properties. In Figure 14, the porosity dependent electromechanical performance of TiC-derived carbon materials is demonstrated. From laser displacement recording it is seen that actuation performance is influenced by the active CDC material used in electrode layer. TiC-950-based actuators showed fast actuation response with remarkable displacement range.

To study the performance of TiC-derived carbon actuators in detail the displacement was measured and in wide frequency range. In this case the displacement is expressed in strain (ϵ) according to equation described in 8.2.2. The strain-frequency dependence of the actuator is given in Figure 15. Actuators were tested at a frequency range from 5 mHz to 200 Hz of the applied rectangular voltage of ± 2 V. Strain increases when applied frequency becomes lower. TiC-950 showed largest generated strain (0.6%) among observed CDCs. Frequency dependent displacement analyses confirmed that each CDC material has different frequency response and characteristic strain level value went the actuation reaches to the plateau. Generated strain of actuators is directly dependent on the CDC specific surface area and pore size distribution. The highest strain was observed for TiC-950 based actuators and as given in Table 1, it had the largest pore volume (0.94 cm³/g) and specific surface area (1843 m²/g) among studied carbons in Paper III.

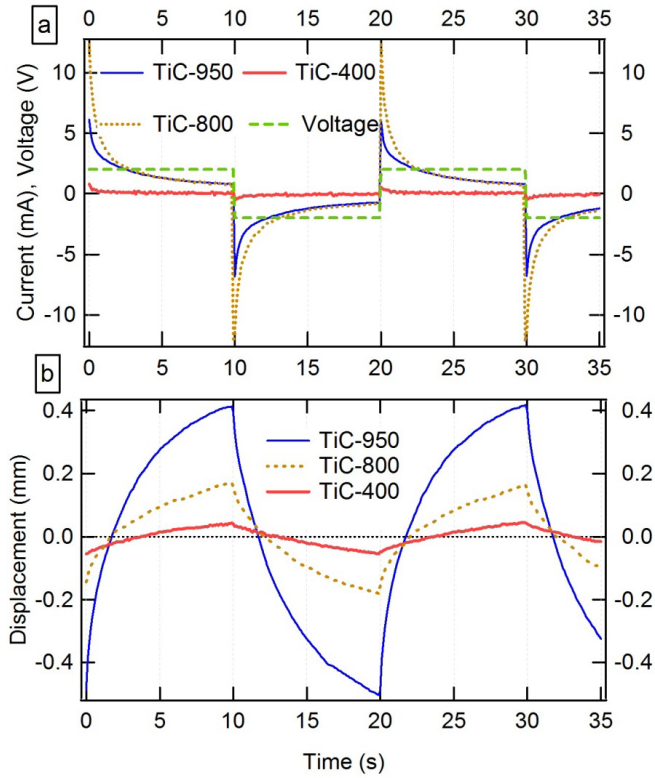


Figure 14. Performance of CDC-TiC actuators. Current profiles registered during actuation (a). Displacement of actuator devices containing CDC with different pore characteristics (b). Rectangular voltage $\pm 2V$ was applied

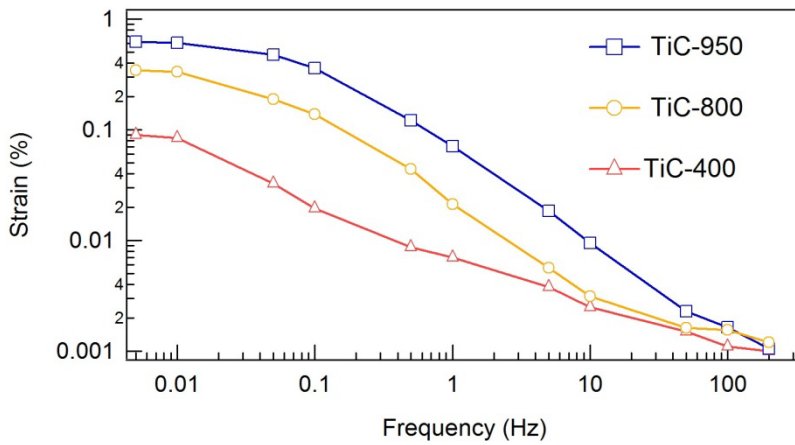


Figure 15. Frequency dependence of generated strain of CDC-based actuators.

The results described in Paper III introduce uniqueness of CDC for electroactive actuator applications by offering large variety of active materials to modify strain rate and charge consumption. In Paper IV another set of CDCs was introduced in order to examine the actuation performance of CDCs with enhanced mesoporosity content. Electrochemical and electromechanical characteristics of micro-mesoporous B_4C -, and mainly mesoporous Mo_2C -derived carbons in bending type polymeric actuators were presented, and compared with performance of TiC-600 carbons. Differences in microporous and mesoporous properties determine variations in the EDL capacitance and also the ion mobility. Therefore, various CDC can affect the displacement of actuators and offer opportunity to control the electromechanical performance of the actuator and allow turning the performance in desired direction.

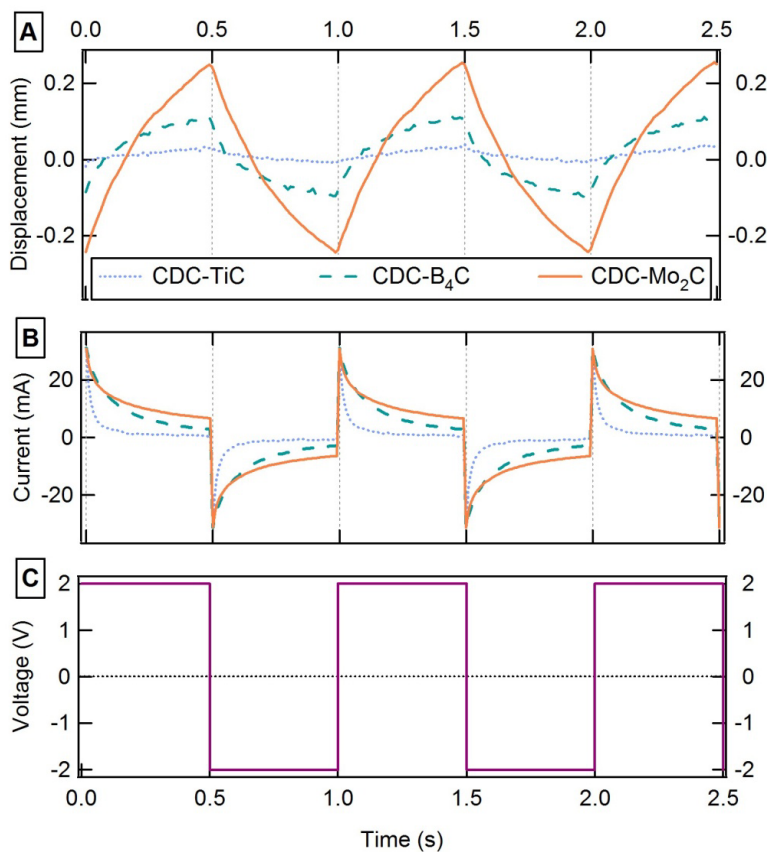


Figure 16. Charge induced electromechanical actuation response of CDC actuators consist of various carbons prepared from different precursors. (A) Displacement versus time under ± 2 V square wave voltage of 1 Hz. (B) Simultaneously registered current profiles during actuation. (C) Rectangular ± 2 V voltage profile applied to drive actuator devices.

Figure 16 shows that when square wave voltages (± 2 V) with 1 Hz frequency was applied to the CDC actuators the different displacement according to the CDC material used in electrode was achieved. The actuation amplitude of CDC-Mo₂C actuator was two times higher than CDC-B₄C reaching to the 0.5 mm peak-to-peak value, while displacement of CDC-TiC barely exceeded the noise signal. Figure 16B displays simultaneously recorded electric current profiles of the CDC-based actuators at 1 Hz. Current profiles are in good correlation with generated displacement of different carbon precursors, while larger current peaks lead to higher volumetric effects. The recorded current profiles also demonstrate capacitive nature of CDC based actuators. Both characteristics retain their shape in time, confirming electrochemical stability of the actuator.

In Figure 17 the concept of CDC-based actuator with gradual displacement behavior is demonstrated. Figure 17A shows the strain output of the mesoporous and microporous CDC-based actuators as a function of frequency between 5mHz–200 Hz at ± 2 V square wave voltage. As can be observed, the porosity has a remarkable influence on the actuation performance. Actuators where pores larger than 2 nm were appeared showed larger strain values at higher frequency region (above 5 Hz), and attained quickly to plateau value where generated strain was not affected by the excitation frequency. On the contrary, the strain values of CDC-TiC actuator were dramatically lower in high frequency region. This confirm that micropores of TiC-derived carbon are tightly packed (narrow pore size distribution), and due to absence of mesoporosity the high charging/actuation rates are unobtainable. The strain values of CDC-TiC actuator increased in lower frequency region (below 10 Hz), while other investigate carbons reached to plateau value. This indicates that maximal strain (strain at 0.005 Hz) of CDC-based actuators is related to the total porosity of CDC, and actuation response speed is proportional to the mesoporosity available in CDC-based electrode matrix. Figure 17B displays the charge consumption registered during actuation. The CDC-Mo₂C actuator showed largest charge values, and indicated that generated strain of CDC actuators is in good correlation with accumulated charge during actuation. Figure 17D shows the pore size distribution for CDCs prepared from different precursor carbides. The CDC powder derived from molybdenum carbide (Mo₂C-CDC), which showed highest strain values, had a Brunauer-Emmett-Teller (BET) surface area of 1675 m²/g, a total pore volume 1.39 cm³/g, and an average pore size of 1.66 nm according to Eq. 4.

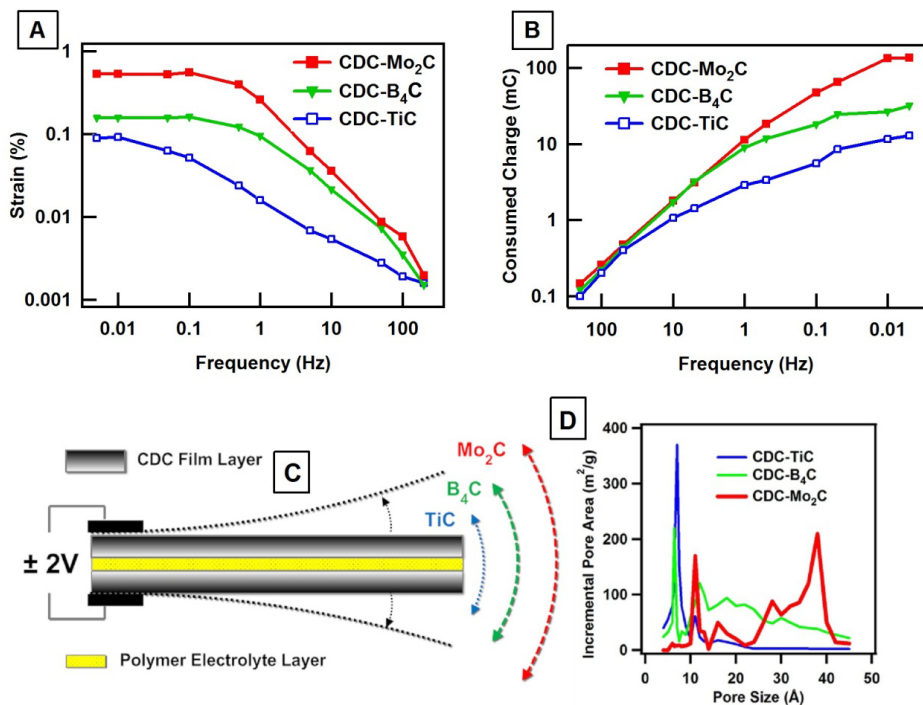


Figure 17. (A) Generated strain of CDC actuators plotted as function of frequency of driving square wave voltage ± 2 V between 5 mHz–200 Hz. (B) Charge consumption during actuation as a function of excitation frequency between 5 mHz–200 Hz at ± 2 V square wave voltage input. (C) Schematic concept of CDC-based actuator with gradual displacement. (D) Respective pore size distribution of CDCs involved.

Despite, the mesoporous Mo₂C-CDC showed quick actuation response to the voltage applied, the conductivity of CDC-based electrodes is not sufficient enough to achieve remarkable displacement at 50 Hz or higher values. To overcome the lack in conductivity of CDC an additional gold foil was applied to outer electrodes, and results were described in Paper V. The electrical conductivity of polymer supported CDC electrodes is mainly limited by highly resistive junctions between CDC grains. In electrode layer CDC grains are often separated by polymer (PVdF(HFP)), thus reducing electronic conductivity even more. Therefore, covering CDC electrodes (thickness 55 μ m) with thin (100 nm) gold foil is expected to decrease the network resistivity, and leading CDC electrodes to be more rapidly charged when voltage is applied. Thus, response time of actuator can be reduced because electrical double-layer charging inside porous matrix induces quicker volumetric changes.

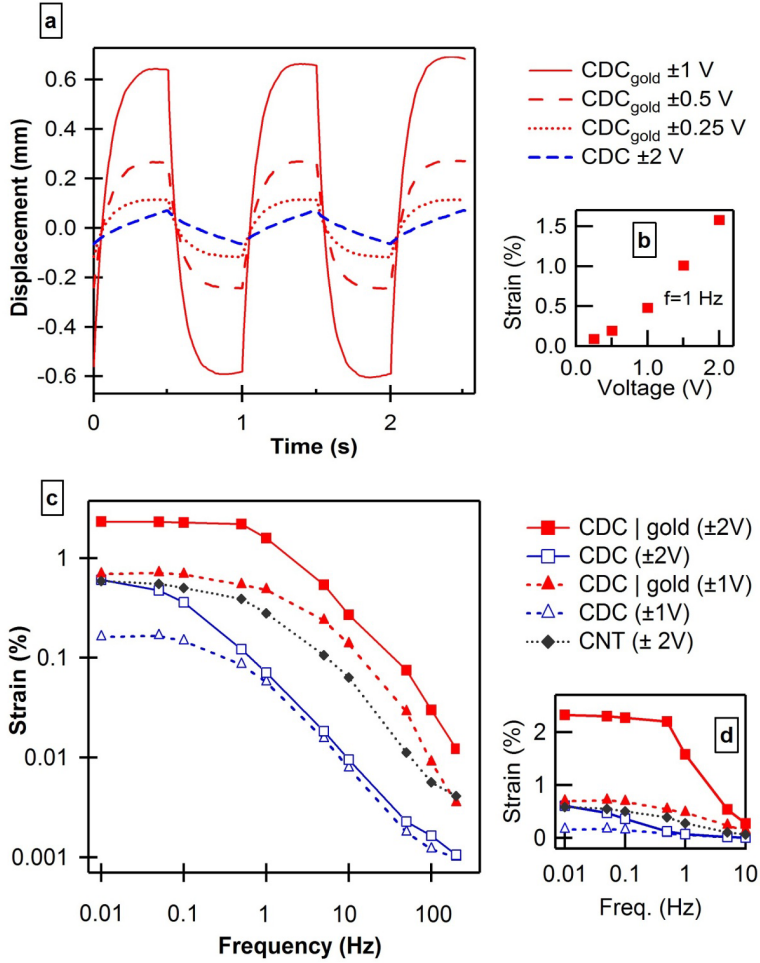


Figure 18. (a) Displacements of CDC-950 and CDC/gold actuators when different excitation voltages with frequency of 1 Hz were applied. Inset (b) represents strain as a function of applied voltage. (c) Strain of conventional CDC-based actuators and CDC/gold actuators plotted as a function of frequency. Results were obtained when ± 1 V and ± 2 V square wave voltages were applied to actuator strips. In addition to CDC actuators a typical strain vs. frequency dependence (± 2 V) of CNT actuator is given [18]. Inset (d) semi-log plot of generated strain of actuators at lower frequency range.

Figure 18 summarizes the displacement of conventional and gold-foil-modified (CDC/gold) actuators at different excitation voltages ($f = 1$ Hz), and strain respective strain values in frequency range from 10 mHz to 200 Hz. Figure 18a presents displacement behavior of actuators. The fixed excitation voltages from ± 0.25 V to ± 1 V were applied to CDC/gold actuator strip with frequency 1 Hz. Displacement of actuator strip containing only polymer supported CDC in electrode layers is provided as reference material. As seen in Figure 18a, the

peak displacement for CDC-950 actuator at ± 2 V is even lower than that of CDC/gold actuator obtained by applying ± 0.25 V to system. Figure 18b presents a strain vs excitation voltage graph for CDC/gold actuator. Strain was calculated from the peak displacement of actuator strip according to equation described in paragraph 8.2.2. At frequencies below 0.5 Hz the strain of CDC/gold actuators remain to plateau (see Figure 18). However, the magnitude of strain is strongly affected by voltage applied. It can be seen that the strain of CDC/gold actuators at applied voltages of ± 1 V was larger than respective strain values of CDC actuator without gold contact layer obtained even at voltages ± 2 V. However, discrepancy of strain values diminishes at lower frequency values. CDC/gold actuators achieved plateau value at 0.5 Hz operating frequency, which is one order of magnitude faster than that of CDC actuators. Typical strain vs. frequency dependence of CNT actuator is given as reference material [35]. In order to reveal actuation behavior at lower frequency region (below 10 Hz) strain vs. frequency dependences (semi-log plot) of CDC and CDC/gold actuators is presented in Figure 18d.

In conclusion, the displacement and strain of actuators strongly depend on the voltage applied. To compensate the relatively poor electronic conductivity of CDC, the use of gold conducting layer on the electrode surface allows reducing actuation voltage almost one order of magnitude and increase the response speed.

9.2 Electrochemical characterization of electrode material

9.2.1 Linear actuators

The linear actuators assembled in this work showed typical EDL capacitor characteristics, because the conditions for measurements were similar (*e.g.* clean electrolytes, inert atmosphere). The charge-discharge capacitances calculated from the cyclic voltammetry plots of actuators are shown in Figure 19. The specific capacitance is expressed per dry weight of carbon (F/g). The CV analyses showed a non-faradic charging behavior, and the electrical double-layer capacitance is predominant in the voltage range of 0 to 2.7 V. Generally, it is known that the specific capacitance may depend on the voltage sweep rate. The main difference between the linear actuators EMI600 and EMI800 was the carbonaceous material used in their manufacture. The actuator EMI600 was made from nanoporous TiC-600 carbon with an average pore size (APS) of 9.3 Å, whereas carbon in the actuator EMI800 has a slightly increased APS of 9.7 Å. In case of EMI600, the potential sweep rate has a large influence on the capacitance (Figure 19a). However, the specific capacitance of EMI800 is less affected by voltage sweep rate values. The observed differences in specific capacitance can be explained by different nanostructure and pore distribution of investigated carbon materials. TiC-800 has a sparse media with slightly higher

pore volume compared to TiC-600. Hence, a sparse microstructure of TiC-800 provides higher mobility of electrolyte ions and dependencies to voltage sweep rate will become obvious at higher values. Similar behaviors were observed for TEA600 and TEA800 actuators.

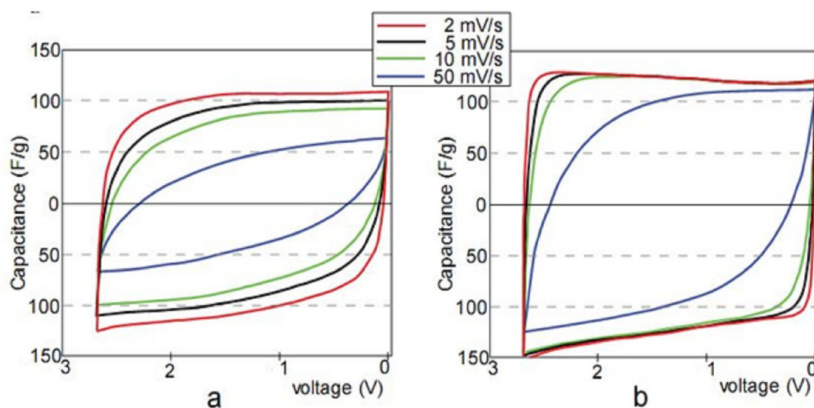


Figure 19. Capacitance vs. Voltage graphs of the actuators EMI600 (a) and EMI800 (b) recorded at different voltage sweep rates.

9.2.2 Bending actuators

CV measurements confirmed that bending type actuators can be considered as typical electrochemical capacitors, especially when small sweep rate values were applied in narrow voltage window. Figure 20 shows CV profiles of TiC-800 obtained at different scan rates.

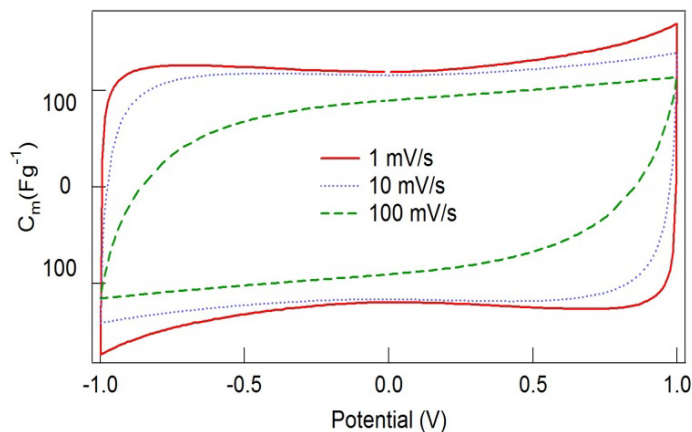


Figure 20. Specific capacitance vs. voltage of the actuator electrodes containing TiC-800 CDC measured at different voltage sweep rates.

Conductivity and capacitance data of TiC-derived carbons are summarized in Table 3. The CDC-based electrode films showed conductivities of 0.16 to 0.005 S/cm, which are relatively low as compared to those of conductive carbon nanotubes described in [4]. As discussed above a lower conductivity reduces actuator response speed and postpones the processes related to electrochemical charging processes. Carbide-derived carbon has a higher capacitance in actuator electrodes compared to CNT, except of TiC-400, where microporosity is very high and pore size distribution is too narrow for ion transport and large amount of pores are not accessible to ions of the electrolyte. The volumetric capacitance of the actuator electrodes was somewhat lower compared to the electrodes of the supercapacitor [20]. This could be explained by higher amount of binder polymer and different electrolyte used to prepare the actuator electrodes.

Table 3. Conductivity (κ) and specific capacitances per electrode volume (C_v) and per CDC mass (C_m) in CDC-based electrode films

CDC in electrode	κ (S cm ⁻¹)	C_v (F cm ⁻³)	C_m (F g ⁻¹)
C (TiC-400)	0.005	10	41
C (TiC-800)	0.16	26	119
C (TiC-950)	0.06	26	114

The conductivity studies mainly described in Paper III pointed out limitations and inspired to find solutions to increase electrode conductivity and to open up a full electromechanical potential of CDC-based actuators.

The electrochemical measurements for gold-foil-modified actuators: cyclic voltammetry and electrochemical impedance spectroscopy, were carried out in order to study the effect of additional gold foil at CDC electrodes and to characterize the electrochemical properties of actuators (Paper V).

CV curves for conventional CDC two-electrode and CDC/gold systems are given in Figure 21. Voltammograms were obtained at 100 mV/s scan rate and expressed in normalized current mode per total weight of CDC-based electrodes in two-electrode cell. For conventional CDC powder-based electrode cells the normalized capacitance and rectangular shape of voltammograms is strongly affected already at a moderate potential scan rate values. For CDC/gold electrodes CV curves display nearly rectangular shape where the absolute value of normalized current was also higher. This result indicates that the ohmic potential drop is noticeable lower and the electric double-layer charging/discharging is more efficient in case of CDC/gold electrode system rather than CDC electrodes-based cell.

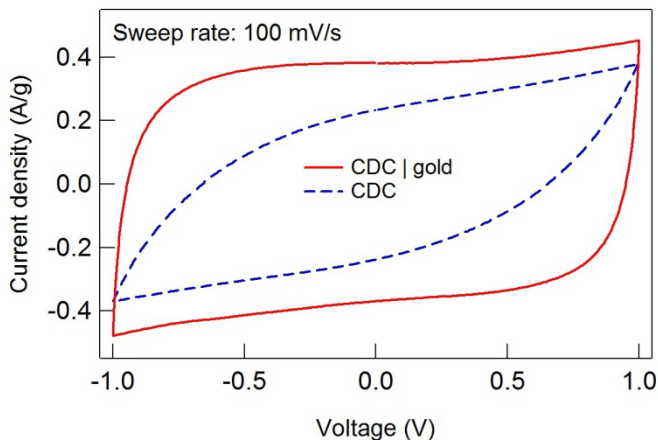


Figure 21. Current density (A/g) vs voltage (V) of CDC and CDC/gold symmetrical cells at 100 mV/s sweep rate.

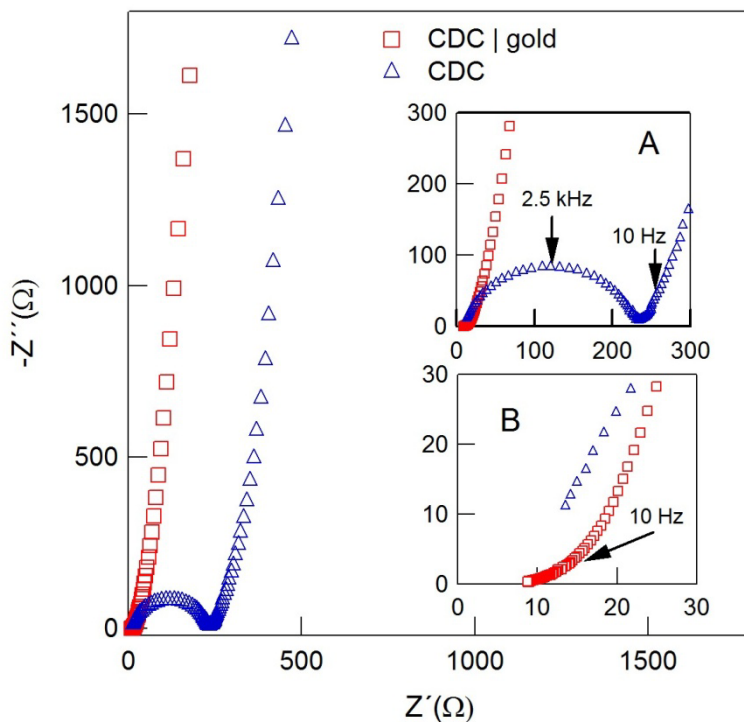


Figure 22. Electrochemical impedance spectra (Nyquist plots) of two-electrode symmetrical CDC and CDC/gold electrode cells at 0 V open circuit potential using sinusoidal signal of 5 mV in the frequency range between 100 kHz and 5 mHz. Measurements were performed on a symmetric two-electrode cell with a thickness of 55 μm per electrode and 15 μm per ionic liquid gel membrane. The insets (A) and (B) show an enlarged views of the higher frequency region.

According to the data presented in Figure 22, Figure 23A and 23B, CDC based electrodes and CDC electrodes modified with gold foil showed fairly conventional behavior of porous electrode systems [49, 62, 70], and both cells approached a vertical line at low frequencies (Figure 22). However, Nyquist plot for conventional CDC symmetrical two-electrode system shows a depressed semicircle in the high frequency region and this high frequency impedance loop is related to the electronic resistance between CDC grains. The vertical shape of Nyquist plots at lower frequencies ($f \leq 0.05$ Hz) indicates a nearly capacitive behavior with adsorption limited step [49]. The impedance response of CDC electrodes modified with gold foil is thus typical for double-layer charging of highly conductive porous electrodes.

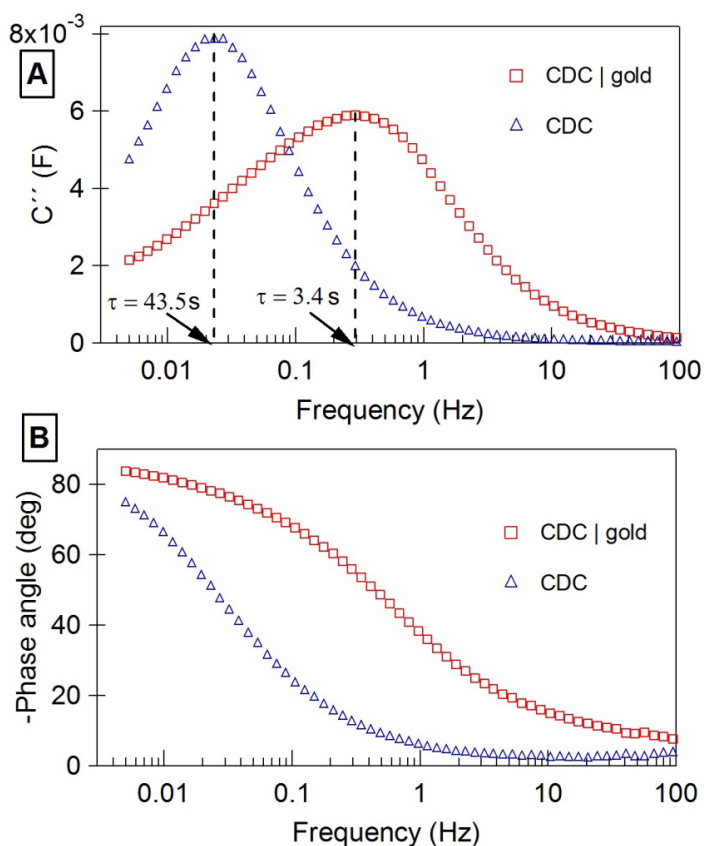


Figure 23. Imaginary capacitance vs. frequency dependencies (A) and Bode phase angle plots (B) for CDC and CDC/gold symmetrical two-electrode cells.

10. CONCLUSIONS AND SUMMARY

Carbide-derived carbon materials were used for preparation of electro-mechanical actuators in both, linear and bending type devices. Among the studied carbons were TiC-, B₄C-, and Mo₂C-derived highly porous carbons with specific surface area from 1113 m²/g to 1843 m²/g. The impact of porosity was studied in terms of electromechanical performance (*e.g.* displacement range and response speed). Linear actuators studied in this thesis were based on electrodes commonly used in electrochemical capacitor applications, and commercially available separator material. For preparation of bending type actuator electrodes and membrane layer a simple tape casting method is proposed.

For actuator characterization the electromechanical measurements were carried out simultaneously with electrochemical measurements. Relations between porosity parameters of CDC onto displacement performance and energy consumption were investigated. Experiments with three different porosity TiC-derived carbons revealed that generated stress and strain of actuators were directly dependent on the specific surface area and pore size distribution of CDC used in electrode layer. On the other hand, the porosity of TiC-derived was determined by the synthesis conditions (*e.g.* chlorination temperature). Abovementioned unique property makes CDC an attractive base material for actuator applications.

In linear type actuators the effect of volume change of CDC-based electrodes was found to be around 1% of total thickness of disk-shaped device in two-electrode-cell configuration. It was also pointed out that CDC-based actuator device required preload to observe reversible expansion/contraction. This indicates that some processes responsible for actuation in bending type actuators *e.g.* mass transport is depressed in the linear actuator configuration. However, in bending type actuators even 1% volume change in electrode thickness will result in large deflection of the two-electrode device.

Bending type actuators made from various microporous (CDC-TiC), micro-mesoporous (CDC-B₄C), and mainly mesoporous (CDC-Mo₂C) carbon materials showed both, different displacement performance and energy consumption according to the amount of mesopores introduced in the electrode layer. The highest bending displacement as well as energy consumption during actuation was observed for Mo₂C-derived carbon and the lowest values for TiC-derived carbon. CDC-TiC had very confined and narrow pore size distribution below 1 nm, compared to other studied carbide-derived carbons.

To study the influence of improved conductivity CDC-based electrode layers on the performance of actuator displacement the TiC-derived carbon electrodes were modified with a gold layer. The gold foil was hot-pressed on the outer surface of electrode based on TiC-derived carbon. The electrochemical and electromechanical study revealed that compared to uncovered electrodes a remarkable improvement in the response time was achieved and noticeable displacement of actuators was registered at ± 0.25 V driving voltage.

The studies have pointed out that actuators with gradual displacement/strain characteristics can be prepared from wide selection of precursor carbides available to determine the porosity of the final carbon material and therefore influence the performance of the CDC actuators. This unique property together with their facile preparation method, flexibility, remarkable specific capacitance, and low driving voltage enable the CDC-based actuators application in many areas such as artificial muscles, and hybrid actuator/energy conversion devices.

I I. SUMMARY IN ESTONIAN

Karbiidset päritolu süsinikmaterjalidel põhinevad elektromehaanilised täituriid

Käesolevas töös kasutati karbiidset päritolu süsinikmaterjale (CDC) valmistamiseks nii painduvaid kui ka lineaarsel liigutusel põhinevaid elektromehaanilisi täituriid. Vaatluse all olid erinevatest lähtekarbiididest (TiC, B₄C, Mo₂C) laias temperatuurivahemikus sünteesitud ja peamiselt mikropoorse struktuuriga süsinikmaterjalid eripinnaga vahemikus 1113–1843 m²/g. Uuriti poorsuse mõju süsinikmaterjalidest valmistatud aktuaatori elektromehaanilistele parameetritele nagu liigutusulatus ja liigutuse kiirus ning kirjeldati seoseid antud parameetrite vahel.

Töös kirjeldatud lineaartäituriid põhinesid klassikalise elektrokeemilise kondensaatori arendustegevuses kasutatavatel süsinikelektroodidel ja laialt levinud separaatormaterjalil. Painduvate täituriidmaterjalide valmistamiseks kirjeldatakse antud töös koostameetodit, kus valmistatakse eraldi nii elektroodmaterjal kui separaatormaterjal. Koostatud täituriidanalüüsiks kasutati paralleelselt elektromehaaniliste mõõtmistega elektrokeemilisi uuringuid. Samaaegselt olid vaatluse all aktuaatormaterjalide liigutusulatus ja energiatarve. Erinevused liigutusulatuses kui ka energiatarbes olid tingitud elektroodkihi kasutatava süsinikmaterjali poorsuse parameetritest.

Kolme erineva titaankarbiidist pärineva süsiniku elektromehaanilised uuringud näitasid, et elektroodkihis kasutataval süsinikmaterjalil on pooride jaotusest ja eripinnast tulenev omadus mõjutada täituriid liigutusulatust. Samas võimaldab karbiidset päritolu materjalide sünteesimeetod lihtsal viisil kontrollida just lõpp-produkti pooride jaotust ja poorsusest tulenevat eripinda. Üldmainitud sünteesiaspektid muudavad karbiidset päritolu süsinikmaterjali atraktiivseks baasmaterjaliks elektromehaanilistele täituriidte, arendamiseks välja täpse liigutusulatusega täituriidmaterjale ja tõstmaks nende kasutegurit.

Lineaartäituriid valmistamiseks kasutati süsinikmaterjalina titaankarbiidist 600 °C ja 800 °C juures sünteesitud pulbreid, kusjuures esimene omas märgatavalt kõrgemat mikropoorsust ja mõnevõrra väiksemaid nanopooride mõõtmeid kui teine. Saadud pulbrite baasil valmistati elastsed kiled, mis omakorda kaeti õhukese alumiiniumi kihiga. Spetsiaalselt disainitud mõõterakus mõõdeti materjalide liigutusulatust, liigutuse kiirust, täpsust (reprodutseeritavust) ning nende parameetrite sõltuvust rakendatud pingest ja voolutugevusest. Leiti, et liigutuse ulatus lineaarsete täituriidte puhul moodustab ligikaudu 1% elektroodide paksusest, sealjuures peavad süsinikelektroodid reprodutseeritavate tulemuste saamiseks olema eelnevalt kokku surutud. Uuringute käigus hinnati ka klassikalisi superkondensaatori parameetreid, kasutades tsüklilist voltamperomeetriat, elektrokeemilist impedantsspektroskoopiat ja galvanostaatilisi mõõtmisi ja samaaegselt registreeriti materjali paisumisest tulenevaid ruumalalisi efekte. Hinnati ka süsinikmaterjalidest valmistatud kilede lineaarse liigutuse ning materjalis salvestunud laengute hulga vahelisi seoseid mitmekihilistes süsteemides.

TiC-st, B₄C-st ja Mo₂C-st sünteesitud süsinikpulbritel põhinevatel painduvatel täituriitel leiti, et elektrilise pinge rakendamisel tekitatava liigutuse ulatus ja materjali kuju muutumise kiirus kasvavad vastavalt suurenevale mesopooride hulga elektrilisele. Suurimad liigutuse amplituudid registreeriti Mo₂C-st valmistatud süsinikelektroodidel ja väikseimad TiC-st 600 °C juures sünteesitud süsinikpulbril põhineval täituriil. Viimati nimetatud süsinikmaterjal omas väga kitsast mikropooride jaotust alla ühe nanomeetri piirkonnas.

CDC süsinikmaterjalide elektronjuhtivus ei ole piisav arendamiseks kiire liigutusega (üle 50 Hz) täitureid. Parandamiseks juhtivust elektroodkihis pressiti täituriite pinnale täiendavad kuldelektroodid. Tegemist oli 100 nm paksuse ja väga elastse kuldfoliumiga, mis tõstis oluliselt süsinikelektroodide pinna juhtivust, kuid samas säilitas painduvale komposiitmaterjalile vajaliku elastsuse. Kuldfoliumiga modifitseeritud täituriite elektrookeemilised ja elektromehaanilised mõõtmised kinnitasid tähelepanuväärset kasvu liigutusulatuses ja sealjuures täheldati tööpinge langust kuni 0,25 voldini. 0,25 V oli piisav pinge väärtus, mille rakendamisel registreeriti makroskoopilisi muutusi täituri materjali kujus.

Käesoleva töö raames läbiviidud katsed näitasid, et karbiidset päritolu süsinikmaterjalid on sobilikud elektromehaaniliste täituriite rakendustes, kus eeldatakse suurt täpsust ja piisavat kontrolli materjali liigutusulatuses üle. Täituriite liigutusomadusi, samuti ka energiatarvet saab modifitseerida, kasutades elektroodkihis erineva poori jaotuse ja eripinnaga karbiidset päritolu süsinikmaterjale. See unikaalne omadus koos materjalide lihtsa valmistamismeetodiga, täituri suure paindeulatuse, madala tööpinge ja täituri elektroodide suure erimahtuvusega pakub kasutusvõimalusi mitmetes rakendustes nagu näiteks tehislühased või hübriidsed elektromehaanilised täituriid ja energia muundamise seadmed.

12. REFERENCES

1. Y. Bar-Cohen, (Ed.) *Electroactive Polymer (EAP) Actuators as Artificial Muscles*, SPIE Press, 2nd ed., Washington, 2004.
2. M. Shahinpoor, K.J. Kim, *Smart Mater. Struct.* 10 (2001) 819–33.
3. K.J. Kim, M. Shahinpoor, *Smart Mater. Struct.* 12 (2003) 65–79.
4. M. Shahinpoor, K.J. Kim, *Smart Mater. Struct.* 13 (2004) 1362–1388.
5. M. Shahinpoor, K.J. Kim, *Smart Mater. Struct.* 14 (2005) 197–214.
6. K. Asaka, K. Oguro, *J. Electroanal. Chem.* 480 (2000) 186–98.
7. S. Tadokoro, M. Konyo, K. Oguro, Modeling IPMC for design of actuation mechanisms, in *Electroactive Polymer (EAP) Actuators as Artificial Muscles* (Y. Bar-Cohen Ed.), SPIE Press, 2nd ed., Washington, (2004) 385–427.
8. K. Oguro, Y. Kawami, H. Takenaka, *J. Micromachine Soc.* (1992) 5 27–30.
9. S. Nemat-Nasser, C.W. Thomas, Ionomeric polymer-metal composites, in *Electroactive Polymer (EAP) Actuators as Artificial Muscles*, (Y. Bar-Cohen Ed.), SPIE Press, 2nd ed., Washington, (2004) 171–230.
10. A. Punning, M. Kruusmaa, A. Aabloo, *Sensor. Actuator. A-Phys.* 133 (2007) 200–209.
11. Q.-X. Zhou, L.L. Miller, J.R. Valentine, *J. Electroanal. Chem.* 261 (1989) 147–64.
12. Q. Pei, O. Inganäs, *J. Phys. Chem.* 96 (1992) 10507–10514.
13. R.H. Baughman, C. Cui, A.A. Zakhidov, Z. Iqbal, J.N. Barisci, G.M. Spinks, G.G. Wallace, A. Mazzoldi, D. DeRossi, A. Rinzler, G.O. Jaszinski, S. Roth, M. Kertesz, *Science* 284 (1999) 1340–1344.
14. K. Mukai, K. Asaka, T. Sugino, K. Kiyohara, I. Takeuchi, N. Terasawa, D.N. Futaba, K. Hata, T. Fukushima, T. Aida, *Adv. Mater.* 21 (2009) 1582–1585.
15. T.F. Otero, *Artificial Muscles in Handbook of Conducting Polymers: Conjugated Polymers Processing and Applications* (eds T. Skotheim, J.R. Reynolds,) 3rd edn, CRC Press, Boca Raton, 2007.
16. E.W.H. Jager, E. Smela, O. Inganäs, *Science* 290 (2000) 1540–1545.
17. J. Li, W. Ma, L. Song, Z. Niu, L. Cai, Q. Zeng, X. Zhang, H. Dong, D. Zhao, W. Zhou, S. Xie, *Nano Lett.* 11 (2011) 4636–4641.
18. T. Fukushima, K. Asaka, A. Kosaka, T. Aida, *Angew. Chem. Int. Ed.* 44 (2005) 2410–2413.
19. F. Carpi, E. Smela, *Biomedical Applications of Electroactive Polymer Actuators*. Chichester: Wiley-VHC; 2010.
20. S. Nemat-Nasser, Y. Wu, *J. Applied Phys.* 93 (2003) 5255–5267.
21. J.-H. Jung, J.-H. Jeon, V. Sridhar, I.-K. Oh, *Carbon* 49 (2011) 1279–1289.
22. V. Presser, M. Heon, Y. Gogotsi, *Adv. Funct. Mater.* 21 (2011) 810–833.
23. B.J. Akle, M.D. Bennett, D.J. Leo, K.B. Wiles, J.E. McGrath, *J. Mater. Sci.* 42 (2007) 7031–7041.
24. J. Foroughi, G.M. Spinks, G.G. Wallace, *Sensor. Actuat. B-Chem.* 155 (2011) 278–284.
25. Q. Pei, O. Inganäs, *Adv. Mat.* 4 (1992) 277–278.
26. G.M. Spinks, L. Liu, D. Zhou, G.G. Wallace, *Adv. Functional Mat.* 12 (2002) 437–440.
27. H. Gao, J. Zhang, W. Yu, Y. Li, S. Zhu, Y. Li, *Sensor. Actuat. B-Chem.* 145 (2010) 839–846.
28. T. Sugino, K. Kiyohara, I. Takeuchi, K. Mukai, K. Asaka, *Carbon* 49 (2011) 3560–3570.

29. T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, *Science* 300 (2003) 2072–2074.
30. T. Fukushima, T. Aida, *Chem. Eur. J.* 13 (2007) 5048–5058.
31. I. Wen, P. Chen, Z. Liang, B. Wang, C. Zang, *Carbon* 48 (2010) 1064–1069.
32. I. Takaeuchi, K. Asaka, K. Kiyohara, T. Sugino, N. Terasawa, K. Mukai, T. Fukushima, T. Aida, *Electrochim. Acta* 54 (2009) 1762–1768.
33. C. Guangli, S.A. Miller, E.R. Fisher, C.R. Martin, *Material. Anal. Chem.* 71 (1999) 3187–3191.
34. S. Roth, R.H. Baughman, *Curr. Appl. Phys.* 2 (2002) 311–314.
35. M. Hahn, O. Barbieri, R. Gallay, R. Kötz, *Carbon* 44 (2006) 2523–2533.
36. M. Hahn, O. Barbieri, F.P. Campana, R. Kötz, R. Gallay, *Appl. Phys. A* 82 (2006) 633–638.
37. P. Ruch, M. Hahn, F. Rosciano, M. Holzapfel, H. Kaiser, W. Scheifele, B. Schmitt, P. Novák, R. Kötz, A. Wokaun, *Electrochim. Acta* 53 (2007) 1074–1082.
38. M. Hahn, O. Barbieri, M. Campana, R. Gallay, R. Kötz, Charge-induced dimensional changes in electrochemical double-layer capacitors. In *Proceedings of 14th International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices*, Deerfield Beach, FL, USA, 6.–8. December, 2004.
39. F.P. Campana, M. Hahn, A. Foelske, P. Ruch, R. Kötz, H. Siegenthaler, *Electrochem. Commun.* 8 (2006) 1363–1368.
40. P.H. Harris, *Carbon Nanotubes and Related Structures*, Cambridge University Press: Cambridge, UK, 1999.
41. Y. Gogotsi, *Nanomaterials Handbook*. Boca Raton FL: CRC Press. 2006.
42. Y. Gogotsi, *Carbon Nanomaterials*. CRC/Taylor & Francis, 2006
43. R. Dash, J. Chmiola, G. Yushin, Y. Gogotsi, J. Laudisio, J. Singer, J. Fischer, S. Kucheyev, *Carbon* 44 (2006) 2489–2497.
44. M. Lätt, J. Leis, M. Arulepp, H. Kuura, E. Lust, Latest developments in carbide derived carbon for energy storage applications. In *The 16th International Seminar on Double Layer Capacitors & Hybrid Energy Storage Devices*, Deerfield Beach, FL, USA, 4.–6. December, 2006.
45. A. Jänes, H. Kurig, E. Lust, *Carbon* 45 (2007) 1226–1233.
46. M.M. Hantel, V. Presser, R. Koetz, Y. Gogotsi, *Electrochem. Commun.* 13 (2011) 1221–1224.
47. E. Lust, A. Jänes, M. Arulepp, *J. Electroanal. Chem.* 562 (2004) 33–42.
48. S. Trasatti, R. Parsons, *Pure Appl. Chem.* 55 (1983) 1251–1268.
49. B.E. Conway, *Electrochemical supercapacitors. Scientific fundamentals and technological applications*. New York: Kluwer Academic Publishers/Plenum; 1999.
50. H. Helmholtz, *D. Gesetze, Pogg. Ann.* LXXXIX (1853) 211.
51. L.G. Gouy, *J. Phys.* IV 9 (1910) 457–468.
52. D.L. Chapman, *Philos. Mag.* 24 (1913) 475–481.
53. O. Stern, *Z. Elektrochem.* 30 (1924) 508–511.
54. E. Frackowiak, F. Beguin, *Carbon* 39 (2001) 937–950.
55. M. Arulepp, J. Leis, A. Kuura, M. Lätt, E. Lust, A.F. Burke, *J. Power Sources* 162 (2006) 1460–1466.
56. J.S. Huang, B.G. Sumpter, V. Meunier, *Angew. Chem. Int. Ed.* 47 (2008) 520–524.
57. C. Largeot, C. Portet, J. Chimola, P.L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* 130 (2008) 2730–2731.

58. A. Jänes, T. Thomberg, E. Lust, *Carbon* 45 (2007) 2717–2722.
59. J. Leis, M. Arulepp, M. Käärik, A. Perkson, *Carbon* 48 (2010) 4001–4008.
60. F. Beguin, E. Frackowiak, *Carbons for Electrochemical Energy Storage and Conversion Systems*, CRC Press, New York, 2010.
61. P. Simon, Y. Gogotsi, *Nat. Mater.* 7 (2008) 845–854.
62. A.F. Burke *J. Power Sources* 91 (2000) 37–50.
63. T. Thomberg, A. Jänes, E. Lust, *Electrochim. Acta* 55 (2010) 3138–3143.
64. R.K. Dash, J. Chmiola, G. Yushin, G. Laudisio, J. Singer, J. Fischer, Y. Gogotsi, *Carbon* 44 (2006) 2489–2497.
65. J. Chmiola, C. Largeot, P.L. Taberna, P. Simon, Y. Gogotsi, *Science* 328 (2010) 480–483.
66. Y. Gogotsi, A. Nikitin, H. Ye, W. Zhou, J.E. Fischer, B. Yi, *Nat. Mater.* 2 (2003) 591–594.
67. S. Brunauer, P.H. Emmett, E. Teller, *J. Am. Chem. Soc.* 60 (1938) 309–319.
68. T. Torimoto, T. Tsuda, K. Okuzaki, S. Kuwabata, *Adv. Mater.* 21 (2009) 1–26.
69. R. Kötz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483–2498.
70. A. Jänes, E. Lust, *J. Electrochem. Soc.* 153 (2006) A113–A116.

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Juhendatud lõputööd

Friedrich Kaasik, magistritöö materjaliteaduses, 2011
Pille Rinne, magistritöö materjaliteaduses, 2012

Uurimisvaldkonnad

Ioonsete elektroaktiivsete materjalide arendustegevus. Karbiidset päritolu süsinikmaterjalidel põhinevad elektromehaanilised täituriid.

DISSERTATIONES TECHNOLOGIAE UNIVERSITATIS TARTUENSIS

1. **Imre Mäger.** Characterization of cell-penetrating peptides: Assessment of cellular internalization kinetics, mechanisms and bioactivity. Tartu 2011, 132 p.
2. **Taavi Lehto.** Delivery of nucleic acids by cell-penetrating peptides: application in modulation of gene expression. Tartu 2011, 155 p.
3. **Hannes Luidalepp.** Studies on the antibiotic susceptibility of *Escherichia coli*. Tartu 2012, 111 p.
4. **Vahur Zadin.** Modelling the 3D-microbattery. Tartu 2011, 149 p.