In situ measurements with CPC micro-actuators using SEM

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ABSTRACT

Comparative measurements of carbon-polymer composite micro-actuators based on room temperature ionic liquid electrolyte were carried out *in situ* (1) in vacuum using a state-of-the-art scanning electron microscope, (2) in an oxygen-free atmosphere under ambient pressure, and (3) under ambient environment. The fabricated micro-actuators sustained their actuation performance in all three environments, revealing important implications regarding their humidity-dependence. SEM observations demonstrate high stroke actuation of a device with sub-millimeter length, which is the typical size range of actuators desirable for medical or lab-on-chip applications.

Keywords: carbon-polymer composite, CPC, carbide-derived carbon, CDC, actuator, artificial muscle

1. INTRODUCTION

Ionic electroactive polymers (IEAP) are materials which change their size and shape due to ion flux under electric stimulus and due to their similar behavior to biologic or human muscles this kind of materials are often referred to as artificial muscles. They are unique materials and highly suited candidates for lightweight actuators [1,2] as they do not need rotating axes and require low voltages to generate large deformations, i.e. actuation. IEAPs comprise of electrolyte-containing membrane, laminated between two conductive layers, serving as electrodes. The working principle of IEAPs relies on the interaction of the electronically conductive layer and electrolyte ions during charging, causing volume changes of polarized electrodes. The electric field between the electrodes drives the motion of ions and the entrained solvent, leading to swelling or relative contraction when these ions enter or leave regions of the electrode layer [3,4].

Until now, the most extensively studied IEAP materials are ionic polymer-metal composites (IPMCs) and the first papers analyzing IPMCs appeared in the early 1990s [5,6]. The early IPMCs were based on aqueous electrolyte and therefore worked only in aqueous environment. During the last 25 years the choice of membrane materials, electrolytes, and electrode materials has been significantly widened, eventually reaching to IEAP materials working in dry environment [7]. The first actuators with carbonaceous electrodes appeared in 2005 [8,9], where the electrode material was composed of bucky-gel – a gelatinous mixture of singe-wall carbon nanotubes (SWCNTs) and room temperature ionic liquid (RTIL). The results with bucky-gel electrodes has encouraged the researcher to use all kinds of carbon allotropes for the preparation of carbonaceous electrodes: various carbon nanotubes and their composites, carbon nanofibers, graphene and its derivatives, microporous carbon materials (for example carbide-derived carbons (CDCs) and carbon aerogels) as well as the possible combinations of these materials have been tested [10]. In the scope of the current paper we investigate the actuators with electrodes consisting boron carbide-derived nanoporous carbon referred to hereinafter as CPC (carbon-polymer composite) actuators.

Commonly, CPC actuators consist of three layers: two laminated electrode layers and a separator membrane between them. Electrodes are composed of porous carbons with a high specific surface area, polymer binder, and RTIL as the electrolyte. The membrane is made of porous polymer containing with RTIL. The main construction

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and the working principle of CPC is similar to those of the supercapacitors; yet, the only difference between these two devices is the optimization of the mechanical and electrochemical properties of the laminate and the fact that supercapacitors are completely sealed from their surroundings by a metal casing while CPCs are open to their environment. In the case of supercapacitors, any mechanical response and self-deformation is unwanted, while the whole concept of actuators lies in their ability to controllably perform bending operations. The rigidity and inflexibility of the supercapacitors is accomplished by using tight compression and sealing of the electrode-separate-electrode stack and mitigation of pore swelling via the appropriate combination of the pore size of the nanoporous carbon with the small mobile ions of the electrolyte introduced into porous electrodes. In the case of CPC actuators, the membrane is flexible and the electrodes are made stretchable, introducing a much larger amount of polymer binder. The cations and anions of the electrolyte barely fit into the nanopores of the chosen carbon material to promote expansion and contraction of the whole CPC actuator structure.

The CPC actuators explored in the current paper are composed of boron carbide-derived carbon (B_4C-CDC) as an active electrode material, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) RTIL as an electrolyte and polyvinylidene fluoride-co-hexafluoropropylene (PVdF(HFP)) as electrode and a separator binder. The B_4C-CDC has comparable characteristics studied by Jänes et al [11]. The actuators were prepared using layer-by-layer casting and subsequent hot-pressing. This type of CPC actuator is capable achieving up to 3 % of strain in 60 s with the maximum cell voltage of ±2.8 V applied. The fabrication as well as electrical, electrochemical and electromechanical properties of the actuators of this type are thoroughly described in [12,13].

Performing long-term experiments with the CPC actuators, we noticed that sometimes the results were not reproducible. For some unknown reasons, the consumed electric current and the mechanical output of the samples varies within a wide range. The phenomenon was especially conspicuous when the samples were used after a longer delay. Contrary to all expectations, the performance of the actuators varied widely without a clear reason. Finally, to our surprise we noticed that the electromechanical properties of the carbonaceous IEAP materials depend on the weather and the season.

Our laboratory is located in northern Europe, in the northern part of the temperate climate zone and in the transition zone between maritime and continental climate with differences between the minimal temperature in winter and the maximal temperature in summer of up to 60 ^{o}C . Similarly, the relative humidity (RH) varies between almost dry in winter and 100% RH in summer. Since the experiments are carried out in laboratories without a high level of humidity regulations, and as similar CPC materials are known as humidity sensors [14], we found that relative humidity most seriously affects the CPC actuator performance.

In general, one would expect that the ionic conductivity of the membrane and electrodes changes noticeably with humidity; in fact, it is well-known that humidity has a large influence on the viscosity (and electrochemical performance) of ionic liquids. Surprisingly, the humidity-dependence of the IEAP actuators has not received much attention in the scientific community so far. Naturally, there exist some reports, describing the humidity-dependence of the aqueous IPMC [15,16]. Yun et al. reported that the actuation performance of electro-active paper for a durable biomimetic actuator is sensitive to humidity and reduces drastically with reducing the relative humidity level [17]. Liu et al. claimed that change of environment humidity has no observable effect on the actuator response for the IPMC with vertically aligned carbon nanotubes [18]. On the contrary, Yeo-Heung et al. argued that the carbon nanofiber actuator, based on a solid polymer electrolyte, after absorbing a small amount of moisture shows improved actuation performance [19].

In the scope of the current paper we show that even a slight change of humidity affects noticeable the electromechanical properties of the carbonaceous IEAP materials. We performed similar measurements in dry ambient environment, under vacuum, and in dry oxygen-free environment. In our experiments under environmental conditsion, the RH was around 6 %. Achieving that low stable relative humidity intentionally is a complicated procedure and is achievable only in special climate chambers. The recorded parameters - the current-voltage characteristics and the generated mechanical strain difference of the actuators show significant differences in these variable environmental conditions mentioned. Experimental data show remarkable change of the electromechanical properties of CPC as well as the rate of change.

A convenient equipment to produce a high vacuum with the option of recording the structural changes is a state-of-the-art scanning electron microscope (SEM). The field of sight of SEM system dictated the dimensions of the actuator studied: its length was only 1.5 mm. Thus, on the other hand, the experimental data demonstrate the feasibility of microscopic IEAP devices capable working without encapsulation under vacuum as well as in air. The electromechanical response of the actuators in ambient air was recorded by an optical microscope, equipped with an optical camera and the appropriate microscope adapter.

2. EXPERIMENTAL

1.1 Materials

RTIL 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) and polyvinylidene fluoride-co-hexafluoropropylene (PVdF(HFP)) polymer were purchased from Sigma-Aldrich. Solvents 4-methylpentan-2-one (MP) and 4-methyl-1,3-dioxolan-2-one (propylene carbonate PC) were also obtained from Sigma-Aldrich, while N,N-dimethylacetamide (DMAc) was purchased from Fluka. Carbide-derived carbon (CDC) obtained by chlorine treatment of boron carbide (B_4C) was purchased from a former company called Y-Carbon. All materials were used as received without any further purification.

1.2 Fabrication of CPC

Actuator material was prepared as described in [12,13] using the layer-by-layer casting method.

Electrodes consist of 35 wt% PVdF(HFP), 35 wt% $EMIBF_4$ and 30 wt% B_4C-CDC. First, the polymer pellets were dissolved in DMAc. Concurrently, $EMIBF_4$ and B_4C-CDC powder were mixed in DMAc and treated with an ultrasonic probe Hielscher UP 200 S for 5 min with 50% power and 0.5 Hz duty cycle. Thereafter polymer solution was added to B_4C-CDC/RTIL mixture and treated with ultrasonic probe about 5 min applying the same regime. The mixture recieved was poured out to poly(1,1,2,2-tetrafluoroethylene (PTFE) mold and dried in ambient atmosphere for 12 h.

The separator membrane was prepared from the $EMIBF_4$ and PVdF(HFP) (50/50 wt%), dissolved in a 24 wt% of PC dissolved in MP at 70 ºC, stirred with a magnetic stirrer overnight, and then poured into PTFE mold and dried for 12 h.

In order to prepare even and homogeneous membranes, the molds should be placed in a fume hood, on top of a massive object, and accurately leveled. The lower surface of the fabricated membranes is more even than the top one, as this dries in contact with the bottom of the mold. Therefore, for the next step – hot pressing – the orientation of the samples is important. Finally the electrodes and membrane have been hot pressed together with hot-press HillsBorough B 70175 at 80 °C for 10 s. The compression force applied is crucial and requires some experience: pressing too hard will result in short-circuit of the electrodes through membrane, while too slight pressure applied will not compact the electrodes enough to achieve good adhesion.

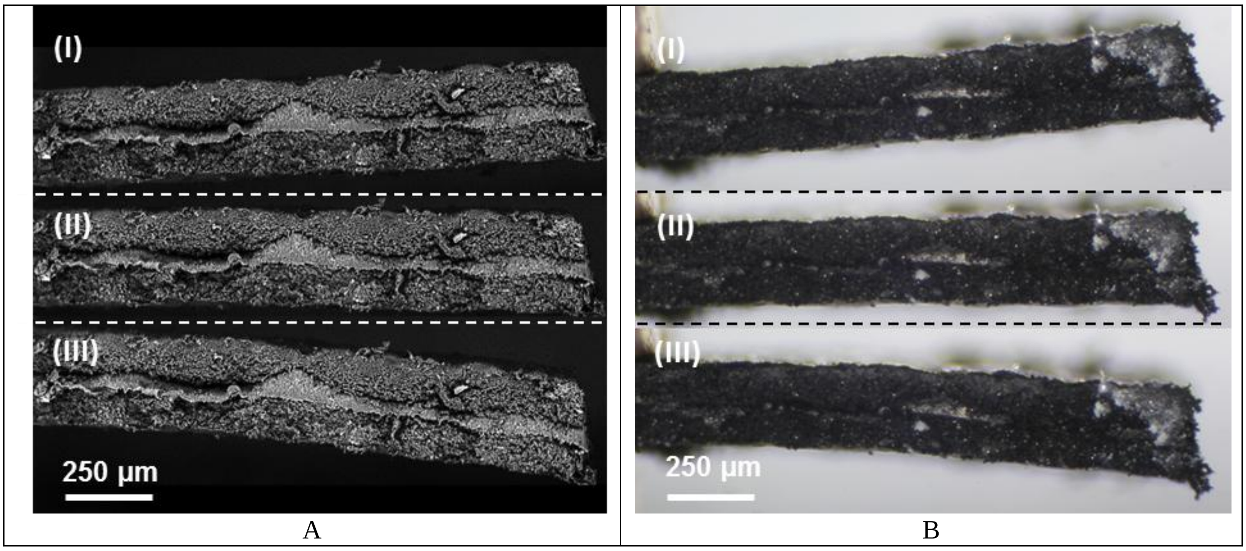
2.3. Electromechanical response in three different environments.

In order to compare the electromechanical properties of CPC actuator, comparable experiment have been conducted in 3 different environments:

1. Under high vacuum conditions using SEM equipment. The equipment used for the experiments was the SEM Hitachi TM 3000 with electrical feed-through to the observation chamber;
2. In an ambient air. During the short period of time of the measurements the atmospheric pressure was 1036 mbar, RH 6.3%, temperature 23 ºC)
3. In oxygen-free glove box using pure nitrogen (H_2O >0.5 ppm, O_2 > 1ppm)

The measurements with the samples were driven using an Ivium potentiostat.

The micrographs for the actuator in its initial state and for two opposite bending directions are presented in Figures 1 and 2. As seen in Figure 1, the total thickness of the used CPC actuator sample is 270 µm. Thickness of the electrodes is ~105 µm and the thickness of the membrane is ~60 µm. The initial mass of the actuator was 1.76 mg. The actuator with the dimensions of 1700×700 μm^2 was cut with a sharp blade, therefore the edges are rough. The contact clamps (not seen in the pictures) were made of 50 µm thick gold sheet, therefore the blocked area of the sample, fixed between the contacts is only 200 µm long. The images reveal that the unevenness of the membrane does not affect on its uniform bending.



A B

Figure 1. A) SEM micrographs; B) optical micrographs. A and B are made from the same actuator strip in initial state and bent to two opposite directions (I, II, III).

Analysis of data for measured images of the actuators shows that in the bent state, the edges of the actuators form nearly perfect circular arcs. The exact comparisons, given in Figure 3 and Table 1, reveal that though the symmetries of bending are slightly asymmetric, the peak-to-peak tip displacements and strains calculated according to $r = \frac{L^2+\partial^2}{\partial}$ [20] are equal within the accuracy of the measurements. The bending follows the principle given in [21] and thus the tip of the actuator moves along a circle with center at $^1/_3$ length from the fixed contacts.

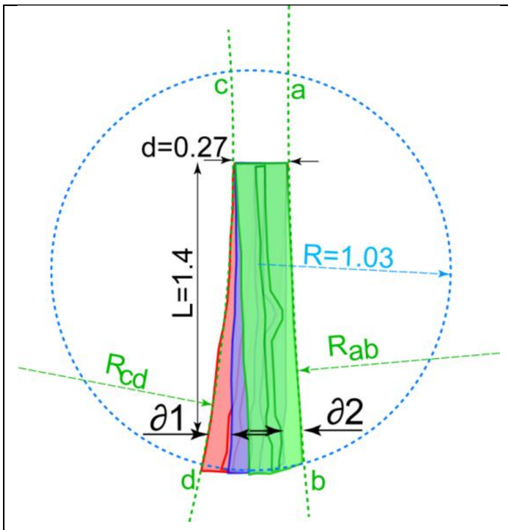


Figure 2. Measures of the actuator.

	Vacuum	Ambient air
Tip displacement to the left ∂ 1 (mm)	0.116	0.1
Tip displacementto the right ∂2 (mm)	0.066	0.08
∂1+∂2 (mm)	0.183	0.183
strain1	0.032	0.018
strain2	0.027	0.023
Radius bending to the left R_{cd}	8.12	8.56
Radius bending ti the right R_{ab}	22.8	15.0
D (mm)	0.27	0.27
L (mm)	1.4	1.4

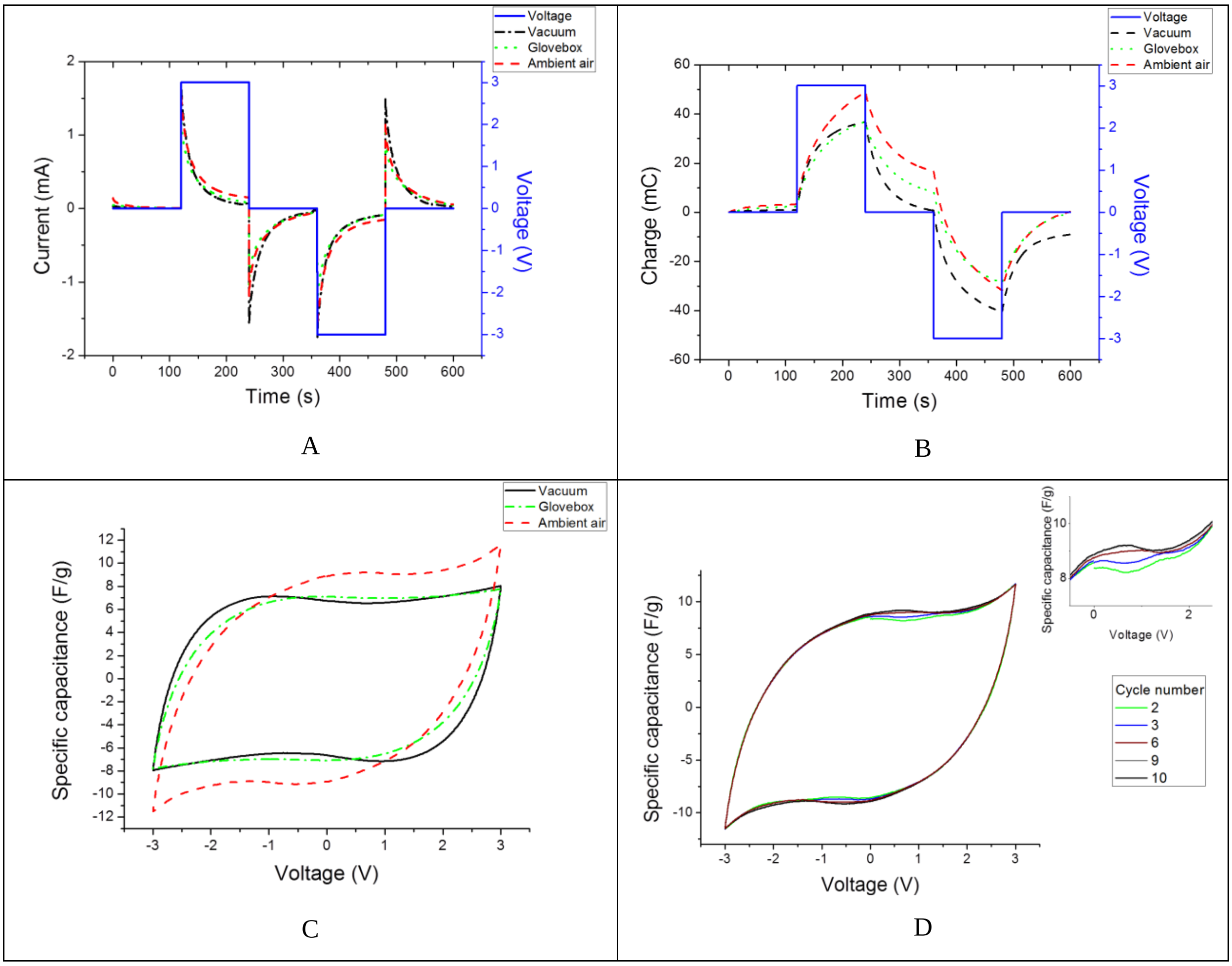
2.4. Voltage-current characteristics in 3 environments.

The measurements were conducted in the following order:

1. In order to avoid contamination of the SEM vacuum chamber, the sample was kept under vacuum at below 1 mbar overnight. For drying and degassing the sample, the same procedure was followed before conducting experiment inside glove box.
2. The sample was lead to SEM chamber as fast as possible, and the vacuum chamber of SEM was depressurized.
3. The ±3 V square wave voltage signal was applied to the actuator while the bending of actuator has been recorded using camera, resulting with the images given in Figure 1. Simultaneously, the input voltage and electric current were recorded by the potentiostat. It must be pointed out that recording

an image with SEM takes about 40 seconds. For this time the actuator should have obtained it’s static state, otherwise the image will be feculent. This requirement dictates the timing of the rectangular voltage signal. The recorded voltages and currents are presented in Figure 3A. The charge values accumulated by the actuator calculated as an integral of electric current with respect to time is given in Figure 3B

4. Thereafter the potentiostat was used in the cyclic-voltammetry mode using scan rate 10 mV/s and the resulting cyclic voltammogram (CV) graph is given in Figure 3C. After 10 cycles the vacuum chamber of SEM system was lead to the normal air pressure, while recording the voltammogramms was not interrupted. The resulting transition to ambient air conditions resulted as voltammogram, given in Figure 3D shows that CPC reacts to air instantly. The CV data show that during 20 min of ventilation the CPC material already obtains the new state, stabilizing finally after 2 h.
5. The optical micrographs of the sample (given in Figure 1B) were recorded under an optical microscope equipped with a standard SLR camera Canon EOS 6D and an appropriate ocular adapter.
6. In order to dry the sample carefully, the electrical measurements inside of the glove box were conducted after keeping the sample in vacuum at below 1 mbar overnight. For technical reason we were not able to make micrographs of good quality in the glove box.



A

B

C

D

Figure 3. A) Voltage and electric current in 3 different environments; B) Voltage and accumulated charge calculated in 3 environments; C) CV characteristics in 3 environments, scan rate was 10 mV/s. D) CV transition from vacuum to ambient air at scan rate 10 mV/s.

From data given in figures 3 A-C it can be seen that in these environments the studied current and charge have different behavior. Current consumption in glove box and under vacuum are really comparable but different from data compared to ambient air. Both charging and discharging consume more current (charge) in ambient air than that in vacuum or glove box. Conditions are more clearly pronounced in figure 3B, where consumed charge is presented. In ambient air actuator needs a lot more charge to bend as much as in vacuum. Also the discharging part in glove box is not reaching to its initial level, as soon as in Figure 3B. In Figure 3C the cyclic voltammograms are different depending on the used environment. The reason for these phenomena must be related to humidity. We see that in Figure 3D the conditioning of an actuator takes more time in air and it is known that used ionic liquid and CDC both are hydrophilic and like to adsorb water. In fact, it is well-known that humidity affects the ionic conductivity and viscosity of ionic liquids significantly. The minor differences in glove box and under vacuum are much smaller and must be caused by the differences in moisture levels still present inside the CPC actuator stack (in the SEM, the ultralow pressure ensure removal of even smallest amounts of water from the samples, while the ambient pressure in the glove box does not).

3. CONCLUSIONS

CPC micro-actuators based on RTIL electrolyte are capable for operation under moderate vacuum conditions where data were obtained using in situ SEM. The developed CPC actuators are composed B_4C-CDC as an active electrode material, $EMIBF_4$ as the electrolyte and PVdF(HFP) as electrode binder and separator. The actuators were prepared using layer-by-layer casting and subsequent hot-pressing. Low vapor pressure, non-flammable character and wide electrochemical window make RTIL favorable solvent-free electrolytes for ionic actuators working under wide range of environmental conditions. The fabricated micro-actuators sustained their actuation performance under moderate vacuum, enabling to use SEM for electromechanical characterization. SEM observations demonstrate high stroke actuation of a completed device with sub-millimeter length, which is the typical size range of actuators desirable for medical or lab-on-chip applications.

The change in ambient water content in environment above the surface of the laminate causes the water sorption. The resulting volumetric effect causes measurable deformation of the actuator even when the input contacts are short-circuited. Comparison of data given in Figure 2 and Table 1 shows that the peak-to-peak tip displacements and strain differences are equal in air and under vacuum, the symmetries of bending is slightly asymmetric.

Based on data collected we have demonstrated that even a slight change of the humidity of the environment affects the electrical properties, as well as the bending performance, of the CPC actuators. For that reason we recommend scientific reports analyzing the electromechanical properties of any IEAP device could be accompanied with exact description of the ambient environment – atmospheric pressure, relative humidity, and temperature.

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