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**Back-relaxation of carbon-based ionic electroactive polymer actuators.**

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Abstract

Back-relaxation - a phenomenon, where the ionic electro-active polymer actuator in its excited state decays back towards its initial shape - is commonly associated with the aqueous IPMC and explained with leak of water. Regardless of the absence of the fluent liquid, the dry actuators with electrodes made of carbon and ionic liquid as electrolyte, exhibit similar side effect. We show that by means of their long-term transient spatial actuation, moment of force, and back-relaxation, the behavior of the carbon-based actuators is comparable to the water-based IPMC actuators.

INTRODUCTION

Ionic electroactive polymers (iEAP) are a separate class of electroactive polymers, where the displacement of ions inside the material causes its shape change. Commonly, the iEAP material is a laminate consisting of some porous polymer between conductive surfaces serving as electrodes. The structure is swollen with some liquid, capable to dissociate into the opposite charged ions - electrolyte. The voltage applied between the electrodes, makes the ions moving following the electric field. This results with the bending of the laminate.

Perhaps the first and most distinguished iEAP is the ionic polymer-metal composite (IPMC) [1]. The term IPMC commonly refers to a material where an ionic polymer is used for the membrane, while the material of the electrodes is not prescribed. Supposedly the best known type of IPMC stands of the water-swollen nafion covered with platinum electrodes. When an electric field is applied between the electrodes, the positive hydrated cations move in the fixed network of negative ions of the polymer towards the negative charged surface, causing expansion of the polymer at one face and shrinkage at the opposite face. Figuratively, while one face of IPMC withers and shrinks, the opposite face becomes swollen with water and ions. As the result, the polymer network bends towards the shrinking face.

In recent years, the concept of iEAP has been significantly broadened. The list of the electrolytes is replenished by the ionic liquids, and the conductivity of the electrodes is attained using non-metallic materials – oxides or allotropes of carbon. Moreover, the ionic polymer, as membrane material, may be replaced by some specific porous non-ionic polymers.

One of the iEAP materials, where all the aforementioned replacements have been taken, is the Carbon-polymer composite (CPC). This concept means a type of ionic electromechanically active structure consisting of two carbon electrodes separated by an ion-permeable polymer film. The role of the separator is to act as a reservoir for the electrolyte and to avoid electronic conductance between electrodes [2]. Unlike in the case of IPMC, it is not an ionic polymer. The whole CPC structure – separator membrane and electrodes – contains ionic liquid as electrolyte. In the sense of assembly, as well as the working principle, this structure is similar to electric double-layer capacitors (EDLC). Their difference is based on the optimal congruence of the surface area of pores and the transport of the electrolyte [3]. When voltage is applied between the surface electrodes, due to a combination of different charging and ionic effects, the CPC laminate bends, i.e. behaves as an iEAP actuator. The rumors tell that the idea of CPC actuators is originated by the researchers of EDLCs complaining about their bulging supercaps...

It is well-known that the actuation of IPMC is accompanied with a spillover effect – back-relaxation [1,4,5]. Back-relaxation is a phenomenon where the actuator, excited with a DC voltage, instead of holding its bent state, decays back towards its initial shape. This behavior is commonly treated as a shortcoming of iEAP actuators, decreasing their ability to deliver a constant peak force and hindering their exact control. There have been several attempts to slower the rate of back-relaxation by choosing an opportune combination of separator, electrodes or mobile ions [4,6]. The dispute over the physical mechanism of back- relaxation of IPMC still continues, but one of the prevalent theories explains the effect with flow of the water molecules out of the ion-exchange membrane [7].

While the phenomenon of back-relaxation of aqueous IPMC is well-known and versatile explained, the similar behavior of the other iEAPs is commonly suppressed. In most cases the attentive reader can detect the back-relaxation only from the illustrative graphs describing the tip displacement of the actuators [8]. The reason of the confidentiality may lie in the absence of a plausible explanation of back-relaxation of the so-called dry actuators. While the back-relaxation of the aqueous IPMC can be easily explained with the leak of water out of the membrane, this explanation is unsuitable in the case of non-fluent electrolyte.

The objective of the current work is to demonstrate that the phenomenon of back-relaxation of CPC actuators exists regardless of the absence of the fluent liquid, and regardless of the membrane or electrode material. It appears that even without poring on the physical mechanisms of actuation and back-relaxation, by means of their transient spatial actuation and transient moment of force, the long-term behavior of the wet IPMC and dry carbonaceous actuators is just similar.

Representation of bending

The early studies of the iEAP actuators assume that the shape of an actuator forms a uniform arc of a ring and characterize the bending amplitude of the actuators with the tip displacement only. This representation may reflect the true behavior in the case of small displacements only. The careful examination shows that on most occasions the bending is more intensive close to the input contacts while sometimes the curvature of the free end does not deviate at all.

In order to characterize an actuator in detail, we express its curvature along the sample with respect to the distance from the input contacts. This representation is not limited with the bending amplitude and allows comparing the quantity of bending and the electrical signals at any point s of the sample.



FIGURE 1. Vector representation of the shape of actuators.

The concept of the vector representation is given in Fig. 1. The camera image of the actuator is adjusted until the actuator forms a contrast line. The line representing the shape of the actuator is divided into vectors of equal lengths, assuming that within every vector the curvature is constant. The coordinate-dependent shape of the actuator is characterized by a number of angles ( in Figure 1) between the vectors. Each next angle is measured with respect to the previous one, while the angle of the first vector may be arbitrary. Since the bending is smooth, it is possible to interpolate the result along the coordinate and to obtain a continuous curve of the actuator. The images may be processed by some appropriate software or even manually with the ruler and protractor. Applying the procedure for the sequential images of a video gives a 3-dimensional evolution of curvature along the actuator in time.

A proper lighting greatly simplifies the image processing. When the direction of the camera is set transverse to the actuator and the stage is illuminated from the background, the image of the actuator consists of a single contrast line. Additional illumination from the sides will further improve the image by eliminating the effects of parallax and reflections from the sides even when the sample twists.

The length and total number of the vectors is a trade-off between the accuracy of the result and the resolution of the camera. It is self-evident that more vectors represent a complicated shape better. However, as the width of the actuator is finite, but the recorded image consists of discrete pixels, the relative error of detecting the angle depends on the width of the actuators image measured in pixels.

Bending moments

In the scope of current paper the inertia and mass of the actuator are ignored and each time step is treated as an independent static problem. The total bending moment inducing the curvature is the sum of the three components: electrically induced bending moment , the moment produced by the own weight of the actuator , and the moment straining the actuator towards its initial shape - back-relaxing bending moment ,as depicted in Fig. 2. The weight of the actuator may be leaved out by holding the actuator edgewise.



FIGURE 2. The moments bending the actuator.

Commonly the iEAP materials are fabricated in the form of a homogeneous sheet, while the actuators of arbitrary shape are sliced later. Without setting any limitations to the shape of the actuator, its bending moment can be directly derived from the curvature according to the Euler-Bernoulli law:

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| --- | --- | --- |
|  |  | (1) |

where is the modulus of elasticity and I(s) is the coordinate-dependent second moment of area. For rectangular cross-section, the second moment of area is expressed as

|  |  |  |
| --- | --- | --- |
|  |  | (2) |

where and are the thickness and the coordinate-dependent width of the sample respectively.

In the simplest case the homogeneous rectangular actuator is set up edgewise. In that configuration, the second moment of area is constant, the moment caused by the weight of the actuator in the plane of bending is zero, and the total bending moment reflects exactly its curvature, yet in a different scale.

Electromechanical model

An electromechanical model describing the amplitude of bending dependent on the distance from the input contacts along the coordinate s, is introduced in [9]. According to that concept the quantity of bending of an IPMC actuator at any time and any point is defined by the charge carried over between the electrodes at that point by that time. The amount of charge is determined by the transitory voltage that in turn is uneven due the electrical resistance of the electrodes. The electrical constituent of the model, depicted in Figure 3, resembles a sophisticated lossy RC transmission line. The conductivity of the electrodes of the iEAP material is represented by a series of resistances of the opposite electrodes and , while the capacitance , and the loss parameters and form the impedance of the material.



FIGURE 3. Electrical model of an iEAP actuator.

The propagation of voltage along this RC line is described by a Sobolev type PDE [9], similar to those describing for instance the diffusion in porous media.

The solution of the PDE for the Heaviside step input voltage is given by the following infinite sum [10]:

|  |  |  |
| --- | --- | --- |
|  |  | (3) |
|  |  |

where R=Ra+Rb, L is the length of the sample,

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| --- | --- | --- |
|  |  |  |

and

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| --- | --- | --- |
|  |  |  |

The resistances of the electrodes and , the capacitance , and the conductivities and are defined as per unit length along the coordinate s.

The complicated time-evolution of the voltage distribution along the iEAP device is defined by the measurable parameters: by impedance of the material, by the dimensions of the sample, and by time. For an initially completely discharged line, the charge is expressed via voltage as

|  |  |  |
| --- | --- | --- |
|  |  | (4) |

The paper [9] demonstrates that for a short time the correspondence between the curvature and charge is proportional. According to the equation (1) we can write that the relation between the bending moment and charge is linear, defined by the coefficient :

|  |  |  |
| --- | --- | --- |
|  |  | (5) |

In [9] the validity of this electromechanical model is proved by comparing the transient voltage, simulated according to the equation (3) with the transient voltages measured from the electrodes of a real sample, and by comparing the charge, simulated according to (4) with the bending of the actuator.

back-relaxing bending moment

The objective of the current paper is to elaborate from the phase where the paper [9] discontinues, i.e. when the phenomenon of back-relaxation becomes noticeable. Assuming that the electrically induced bending moment is proportional to the charge simulated according to the equation (4), the difference between the experiment and simulation gives the desired component of back-relaxation.

From the Euler-Bernoulli law (1) we get that the curvature is proportional to the summarized bending moment:

|  |  |  |
| --- | --- | --- |
|  |  | (6) |

or

|  |  |  |
| --- | --- | --- |
|  |  | (7) |

Since in the scope of this paper, α, and I are constants, it is convenient to group them into a single coefficient denoting the proportionality between the curvature and charge:

Now (7) obtains the form:

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| --- | --- | --- |
|  |  | (8) |

EXPERIMENTAL

The experiments were carried out with the actuators cut from the three different iEAP materials:

The **iEAP-A** is the 0.25mm thick Musclesheet™ IPMC provided by BioMimetics Inc. in 2005. This material is the conventional wet IPMC with nafion membrane and platinum electrodes. It contains water; the cations introduced were Li+. Although it is intended for continuous work in aqueous environment, the short-run measurements were carried out in air. This material is soft, gains its maximal actuating amplitude within a fraction of a second, and relaxes back in about 10 seconds. The conductivity of the platinum electrodes is good and due to the aqueous electrolyte the conductivity W is also noticeable. Its working voltage should not exceed its electrochemical window – about 1.7V in the case of the Li+ cations.

The **iEAP-B** is a typical carbon-polymer composite (CPC). Its membrane is made of a non-ionic polymer – PVDF, while the conductivity of the electrodes and the capacitance of the device is achieved by the carbide-derived carbon. The whole laminate contains ionic liquid (EMIBF4) and is fabricated by hot-pressing. It is much stronger than the other two, but slow – it gains the ultimate bending amplitude in a few minutes and relaxes back up to half an hour. Its maximum working voltage (2.8V) – is defined by the ionic liquid used. The details and fabrication of iEAP-B are presented by Torop et al in [2].

The **iEAP-C** is an intermediate between the others. Its membrane is nafion and electrolyte is an ionic liquid EMITf, but the electrodes are made of carbide-derived carbon and covered with thin gold leaf. So, by means of the membrane it is IPMC, but by means of the electrodes it is CPC. The uppermost gold layer guarantees the excellent conductivity of the electrodes, while the carbonaceous backbone of the electrodes adds rigidity to the whole laminate. It gains its maximum amplitude in a few seconds and relaxes back in about 10 minutes. Detailed description of fabrication and properties of iEAP-C is available in [11], referred to as the Carbon(1).

Measuring the electrical parameters , and seems to be easy using an electrochemical potentiostat. However, the parameters exceed the ranges of the ordinary electrochemical equipment. The technique suggested in [9] - analyzing the electric current corresponding to the step voltage - works only when the conductivity of the electrodes in the direction of the thickness is very good, i.e. in the case of the iEAP-A only. Therefore determining of the coefficient as well as the electrical parameters , , and was carried out in three phases:

1. The resistances of electrodes and were measured using 2-point or 4-point sensing method.
2. The rest of the electrical parameters - , and - were obtained by fitting the equation (3) against the measured voltage along the actuator.
3. The assumption that for a short time the back-relaxing moment is inconsiderable () helps to determine the electromechanical coefficient by fitting the initial rising slope of the experimentally recorded bending against the charge, simulated according to the equation (4).

The fitting was performed using the differential evolution algorithm. The parameters of the three samples cut from the three iEAP materials are given in the Table 1. The electrical parameters are defined as per unit length along the coordinate s.

TABLE 1. Parameters of the materials.

|  |  |  |  |
| --- | --- | --- | --- |
|  | iEAP-A | iEAP-B | iEAP-C |
| Dimensions | 45x3x0.25 | 14x1x0.35 | 28x5x0.2 |
|  | 11.5 | 2000 | 2 |
|  | 0.008 | 0.009 | 0.035 |
| *G* | 0.001 | 0.0002 | 0.046 |
| *W* | 0.1 | 0.0075 | 0.044 |
|  | 27.6 | 27.8 | 1.6 |

RESULTS

The edgewise positioned actuators with the input contacts at one end were subjected to the input voltage defined by the Heaviside step function. The amplitudes of the voltage were close to the maximum voltage, but certainly less than the electrochemical window of that particular material. The bending responses of the actuators were recorded by a CCD camera. The image processing was performed later according to the technique described hereinabove.

The obtained curvatures of the three samples are depicted in Figure 4A. The graphs reveal that the long-term bending and relaxing of the totally different materials is very similar, though in different time scales. All samples perform a swift bending forward, whereas the amplitude is higher close to the input contacts and the bending close to the tip is delayed. The twitch is followed by a slow, approximately exponential decay backwards. We never had enough patience recording with the camera until they reached their steady states.

The graphs presented in Figure 4B are the charges simulated according to the equation (4). Again, the graphs are similar with each other in different time scales. The electrochemical capacitance of the actuator is charged until the steady state, where the decay along the coordinate s is defined by the ratio of the resistance of the electrodes and the conductivity (see Figure 3).

The difference of the previous two surfaces is presented in Fig. 4C. The (scaled dividing by EI) back-relaxing bending moment MB straining the actuator towards its initial shape grows roughly exponentially depending on the charge. In the regions where the transferred charge was larger, the moment of back-relaxation is also stronger.

|  |  |  |  |
| --- | --- | --- | --- |
| **A** – curvature |  |  |  |
| **B –** charge |  |  |  |
| **C** – |  |  |  |
|  | iEAP-A (IPMC) | iEAP-B (CPC) | iEAP-C(CPC) |

FIGURE 4. Back-relaxation of the iEAP actuators. Each column depicts one of the three iEAP materials. Row A – measured curvature; row B – simulated charge; row C – scaled moment of back-relaxation. For better look the angles of view are different in the third row. The graphs at the origin of the position axis are not defined because the values of the curvatures and moments are assigned to the midpoints of the vectors.

DISCUSSION

Now we have measured one parameter of the actuators – the true transient summarized moment, bending it forward followed by releasing backwards, and simulated another parameter – the charge carried over, associated with the electrically induced bending moment ME . Without any further discussion about the physical processes causing the bending and relaxing, their difference appears to be similar in the case of all three different iEAP materials. This resemblance calls into question if the major cause of the back-relaxation of IPMC is the leakout of water. The effect can be explained simply with the slow distension of the polymer network in the case of all iEAP materials.

The moment bending the actuator backwards appears to be a function, exponential with respect to time and the charge carried over. Nevertheless, the simple exponent with respect to time does not explain all characteristic curves of the back-relaxation graphs. A deductively obtained function, impressively fitting with the experimental data contains the integral of charge with respect to time:

where C1 and C2 are the material-dependent constants.

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References

1. Bar-Cohen, Y., Electroactive Polymer (EAP) Actuators as Artificial Muscles - Reality, Potential, and Challenges (2nd Edition), SPIE Press, Bellingham (2004).
2. Torop, J., Palmre, V., Arulepp, M., Sugino, T., Asaka, K., and Aabloo, A., 2011. “Flexible supercapacitor-like actuator with carbide-derived carbon electrodes”. *Carbon*, *49*(9), pp. 3113-3119.
3. Must, I., Kaasik, F., Põldsalu, I., Johanson, U., Punning, A., and Aabloo, A., 2012. “A carbide-derived carbon laminate used as a mechanoelectrical sensor”. *Carbon*, *50*(2), pp. 535-541.
4. Nemat-Nasser, S., Zamani, S., Tor, Y., 2006. "Effect of Solvents on the Chemical and Physical Properties of Ionic Polymer-Metal Composites". *Journal of Applied Phys*ics, 99, p. 104902.
5. Bao, X., Bar-Cohen, Y., and Lih, S. S., 2002. “Measurements and Macro Models of Ionomeric Polymer-Metal Composites (IPMC)” In EAPAD Conference.
6. Kim, D., Kim, K. J., Nam, J., Palmre, V., 2010. “Electro-chemical operation of ionic polymer–metal composites”. *Sensors and Actuators B: Chemical*, 155(1), pp. 106-113.
7. Nemat-Nasser, S. and Wu, Y., 2006. “Tailoring the Actuation of Ionic Polymer-metal Composites”. *Smart Materials and Structures*, 15(4), pp. 909-923.
8. Oh, I. K. and Jung, J. Y., 2007. “Biomimetic Nano-composite Actuators Based on Carbon Nanotubes and Ionic Polymers”. *Journal of Intelligent Material Systems and Structures*.
9. Punning, A., Johanson, U., Anton, M., Aabloo, A., Kruusmaa, M., 2009. “A Distributed Model of Ionomeric Polymer Metal Composite”. *Journal of Intelligent Material Systems and Structures*, 20, pp. 1711-1724.
10. Punning, A., Jalviste, E., 2009. “Analytical Solution for Voltage-Step Response of Lossy Distributed RC Lines”. *IEEE Transactions on Microwave Theory and Techniques*, 57(2), pp. 449 – 457.
11. Palmre, V., Brandell, D., Mäeorg, U., Torop, J., Volobujeva, O., Punning, A., Johanson, U., Kruusmaa, M., and Aabloo, A., 2009. “Nanoporous carbon-based electrodes for high strain ionomeric bending actuators”. *Smart Materials and Structures*, 18, p. 095028.