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

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Abstract

Ionic electromechanically active polymers (IEAP) is one of two main classes of electroactive materials, where actuation is primarily caused by the displacement of ions inside the laminate. Perhaps the first and most distinguished IEAP is ionic polymer-metal composite (IPMC). In recent years the range of IEAP materials has been significantly extended by means of materials used for electrodes (e.g. nanoporous carbon, carbon nanotubes, etc.), separator membrane, as well as the electrolyte (e.g. ionic liquid). At first glance, all IEAPs seem similar in construction and bending behavior – but their actuation mechanisms can be significantly different.

Already since the very first reports about IPMC, the authors have described the „back-relaxation“ effect – an IPMC actuator excited with a DC input will slowly relax back towards its initial state. This effect appears clearly in slow driving signals and interferes the exact control of the actuators. Although one prevalent theory explains the effect with flow of the water molecules across the ion-exchange membrane, the dispute over the physical mechanism of back- relaxation of IPMC still continues.

We demonstrate that regardless of the absence of the fluent liquid, the IEAP actuators with electrodes made of carbon exhibit similar back-relaxation. It appears that the long-term behavior of carbon-based actuators and water-based IPMC is similar by means of their nonuniform transient spatial actuation, and nonuniform transient moment of force. Although the physical mechanisms of the actuation and back-relaxation of the different materials may be different, the resulting descriptive model fits to all of them and supposedly facilitates the long-term control of the actuators.

INTRODUCTION

 Ionic electroactive polymers (IEAP) is 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. Electric field applied between the electrodes, makes the ions moving between the electrodes. The effect is expressed as bending of the laminate.

Perhaps the first and most distinguished IEAP is the ionic polymer-metal composite (IPMC) [BarCoheni raamat]. 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 [Torop], but 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, similarly to the already familiar IPMC. 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[IndrekCarbon]. 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 distending supercaps...

It is well-known that the actuation of IPMC, is accompanied with a spillover effect – back-relaxation [XX,XX]. 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 [XX,XX]. 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 [NasserWu].

While the phenomenon of back-relaxation of aqueous IPMC is well-known and versatilely explained, the similar behavior of the other IEAPs is commonly suppressed. In most cases the attentive reader can detect the back-relaxation solely from the illustrative graphs describing the tip displacement of the actuators. One of the exceptions is reported by [Oh-Jung] as a distinctive property of the IEAP actuators with the electrodes consisting of multi-walled carbon nanotubes. 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 into 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 relaxation

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Bending moments

For characterization of the force or curvature output of the actuator, one needs to have an overview of bending moment distribution of the beam. Depending on the configuration of the beam e.g. simply supported, cantilevered, clamped at both ends, the bending moment distribution can be totally different. In this paper, the actuator, with a cross-section of a rectangle, is set up in cantilevered configuration. In that way, the corresponding bending moment can be directly derived from curvature according to the Euler-Bernoulli law:

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where E is the modulus of elasticity and I is the second moment of area. For rectangular cross-section, the second moment of area is expressed as , where b and h are width and height of the cross-section of the sample respectively.



It must be noted that in the scope of current paper the inertia and mass of the actuator are ignored and we treat each time step as an independent static problem. The weight of the actuator is neglected by holding the actuator edgewise. Hence, the total bending moment, inducing the curvature, is the sum of EIBM and BRBM.

The described methodic does not pose any restrictions to the shape of the actuator, it works as well when the second moment of inertia is not constant along the sample e.g. the sample is tapered, or its cross-section differs from rectangular. In our case the summarized bending moment of the time-dependent behavior of the sample presented in Fig. 1. reflects exactly its bending depicted in Fig. 6., yet in a different vertical scale.

Electro-mechanical model

In order to characterize the BRBM in terms of electrical input, we have to define electromechanical relation for EIBM. The sophisticated approach that considers distribution of curvature is published in [DM]. It declares that the bending of an IPMC actuator at any time and any point is caused by the charge carried over between the electrodes at that point by that time. The amount of charge is determined by the inhomogeneous transitory voltage that in turn is uneven due the electrical resistance of the electrodes. The electrical constituent of that model depicted in Fig. X 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 Ra and Rb, while the capacitance C, and the loss parameters G form the impedance of the material.



An advantage of this model is the existence of analytical solution for Heaviside step function. Hence, it is possible to compare the model against actual response e.g. by placing additional sensing electrodes along the actuator. The solution for Heaviside step input voltage is given by the following infinite sum:

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where L is the length of the sample,

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and

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It turns out that the complicated time-evolution of the voltage distribution on the line is defined solely by the measurable parameters: by impedance of the material, by the length of the sample, and by time. For a completely discharged line, the charge is expressed via voltage as

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As an illustrative example, the simulated transient behavior of voltage and charge of the actuator depicted in Fig. 1., are given in Fig. 11.

EXPERIMENTAL

The experimental part of the current paper is carried out using three different IEAP materials: **A**, **B**, and **C**.

The material **A** is a conventional wet IPMC with nafion membrane and platinum electrodes. It contains water; the cations introduced were Na+. Although it is intended for continous work in water environment, the measurements of short duration were passed in air. This material is soft, gains its maximal actuating amplitude in less than a second and relaxes back in about 10 seconds. Its working voltage should not exceed its electrochemical window – about 1.7V. The actuator presented in Fig. 1 is a typical example of this IEAP material.

The material **B** is a so-called carbon-polymer composite (CPC). Its membrane is made of a non-ionic polymer – PVDF, while the capacitance of the electrodes is contributed by the carbide-derived carbon. The whole laminate contains ionic liquid (EMIBF4) and is fabricated by hot-pressing. It is slow, gaining its ultimate bending amplitude in 60 seconds and relaxing back up to 600 seconds, but is much stronger than the other two. Its working voltage - up to 2.8V – is defined by the ionic liquid used. For details please refer to [doi:10.1016/j.carbon.2011.03.034].

The material **C** is an intermediate between the others. Its membrane is nafion and electrolyte is and ionic liquid EMITf, but the electrodes are made of carbide-derived carbon and covered with 15 um of gold. So, by means of membrane it is IPMC, but by means of electrodes it is CPC. The uppermost gold layer guarantees the good conductivity of the electrodes that in turn determines the speed and strength of this material. It gains its maximum amplitude in a few seconds and relaxes back in a few tens of seconds. Detailed description of fabrication and properties of **C** is available in [doi:10.1088/0964-1726/18/9/095028], referred to as the Carbon(1).

All three actuators placed in cantilever configuration were subjected to the input voltage defined by the Heaviside step function. The corresponding response was investigated by a CCD camera and the curvature was extracted as described in section (bla). The curvatures for different IEAP actuators are indicated in Figure x. Once more, the experiment showed the justification of relating charge with EIBM, but only in some narrow region in the beginning of the input signal. To cover the full actuation process, one has to consider the back-relaxation present in case of all of the three IEAP actuators.

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| **MS** | **CPC** | **Kullaga IPMC** |

For characterizing the relaxation in terms of the bending moment BRBM, it is necessary to determine several electrical and mechanical parameters. The linear behavior between charge and EIBM is here denoted by the coefficient, which together with Euler-Bernoulli relationship gives:

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In this paper the E, I, and is not separated and considered as combined constant. Hence, for more convenient manipulation between charge and curvature, the constant is introduced.

The determination of the parameters was carried out in three stages:

1. The resistance of electrodes R was measured using 4-point sensing method.
2. The rest of the electrical parameters C, G and W were obtained by fitting the model against measured voltage between electrodes along the IEAP actuator.
3. The electro-mechanical parameter was determined from equation (1) assuming BRBM=0 in first few seconds of the actuation.

The simulated and measured voltages of material **B** are depicted in Fig X. The determined parameters for all three samples are shown in table 1.



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|  | **A** | **B** | **C** |
| Dimensions  | 45x3x… | 14x1x… | 28x5x… |
| R | 11,51 | 2509 | 2 |
| C | 0,00826 | 0,0088 | 0,035 |
| G | 0,001 | 0,000128 | 0,046 |
| W | 4,302 | 0,0075 | 0,0435 |
|  | 10 | 7,848 | 1,68 |

Plugging in the parameters above allows us to extract the curvature of relaxation (BRBM/EI), which is given here:

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| **MS** | **CPC** | **Kuld IPMC** |

Acknowledgments

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References

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Annex A

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**Notes:**

**Graphics:**

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