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Electro-mechanical actuator with muscle memory†

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Electro-mechanical memory (EMM) is a type of actuator material that incorporates memory and control in the material itself. Thus its actuation can be manipulated, stored, read, and restored independently. We demonstrate here a realization of such a material by combining ionic actuation with shape memory polymer properties. The ionic actuation function and amplitude can be tuned or completely switched off by uniaxial mechanical programming. The shape transformations are reversible, and states can be selectively restored by exposure to pre-programmed temperature levels. Programming at two different temperatures is used to demonstrate storage and later recall of multiple shapes and actuation responses. Upon recall, the EMM's function and actuation amplitude are recovered and the restored states can also be cycled thousands of times using low voltage inputs. We analyse the dependence of the electrical actuation on the amount of mechanical programming, and the mechanism behind the behaviour.

Introduction

Memory and physical movement are the leading characteristics of intelligent behaviour in living systems. Recent developments in polymer actuators[1] have achieved reversible muscle-like movements with a variety of mechanisms and stimuli.[1–3] One way to make them "smarter" is to incorporate memory of environmental history and previous actuator states into the material itself. Here, we briefly introduce the separate capabilities of ionic polymers and shape-memory polymers and demonstrate an electro-mechanical memory (EMM) material with programmable electrical actuation.

Ionic electroactive polymers (EAPs) are a class of "smart" materials which can perform both sensing and actuation at low voltages.[4–7] This low voltage operation, combined with flexibility and a Young's modulus close to those of biological tissues, make them interesting for biomedical applications (stents, steerable catheters and actuators for microsurgery in confined spaces).[8–10] Ionic EAPs can operate in air,[4] in vacuum,[11] or in liquid media.[8] When ionic polymers are combined with metal electrodes (Fig. 1), large bending actuation can be induced by small electric fields; these ionic polymer metal composites (IPMCs) have found use as actuators in fields such as biomedicine and robotics.[12] The IPMCs can even sustain a bent shape due to hysteresis from chain rearrangements.[13] This is a type of temporary memory, which is erased however with larger amplitude actuation.

With few exceptions,[6,14] however, IPMCs do not respond to multiple stimuli and tend to perform a single action for a single defined stimulus.[15–17] Recently, there have been attempts to introduce multiple responses in ionic polymer actuators, such as electrochromism and sensing,[6,17–19] but both responses are triggered by the same stimulus, thus lacking independence.

Shape memory polymers (SMPs) on the other hand can be programmed to memorize and revert to a number of different shapes using temperature and mechanical stress.[20–22] These are chemically or physically cross-linked polymers, which can be mechanically deformed, yet regain their original shape upon heating above the transition temperature.[22] Attempts were made to use programmed bending, achieving partial thermal recovery of the original shape.[14] SMPs were also used to freeze more permanently the temporary bent shapes previously observed from IPMC hysteresis. Recently, the importance of incorporating multi-functionality in shape memory polymers was highlighted.[23–25] Responses to multiple stimuli make shape-memory polymers smarter.

A material which can independently and reversibly store and restore its actuation response, such as an electro-mechanical memory (EMM) – is still an outstanding challenge in the field. Such a smart material would display a "memory" of previous environmental conditions and find applications in novel programmable devices, dynamic coding[26] and secure message transmission. More prosaic applications include toys, such as

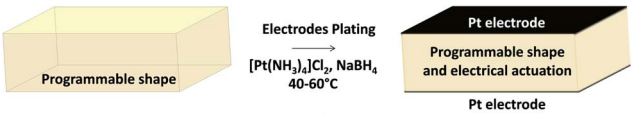

Fig. 1 Fabrication of IPMC by chemical reduction of platinum salt. A detailed synthetic procedure is given in the Experimental section.

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† Electronic supplementary information (ESI) available: Fig. S1–S6 include characterization of ionic and shape-memory properties of the EMM material, schematics of measurement configurations, and ESI Video 1 showing EMM's real time actuation response. See DOI: 10.1039/c4tc00904e

artificial fish, which are already life-like in their swimming behaviour,[27] but can be made even smarter by programming responses into the actuator material. While this could be accomplished by separate sensors, memory, and voltage controllers, having both functionalities in the same material would eliminate the need for signal transmission and control between multiple devices.

We introduce an EMM material which combines the desirable features of both IPMC actuators and SMPs. The EMM material is an actuator which has knowledge of its thermal history, and whose ionic response can be tuned continuously from full amplitude to an intermediate or switched off state and back again in a completely reversible fashion. A number of shapes can be programmed with different stable actuation characteristics.

Experimental

Materials

Protonated Nafion 117 (Dupont Inc, Wilmington, Delaware) was annealed at 140 °C for 30 minutes prior to the IPMC synthesis. Sodium borohydride and tetraammineplatinum(II) chloride hydrate 98% ($[Pt(NH_3)_4]Cl_2$) were purchased from Sigma-Aldrich. The thickness of the Nafion material is 183 μm and the tensile modulus is between 64 and 249 MPa according to the relative humidity and the water content.

Synthetic procedure

A modified procedure of platinum salt reduction, at the surface of a protonated Nafion 117 membrane, was followed to obtain the tri-layer structure (shown in Fig. 1).[28] First, the membrane surface was roughened by sand paper scratching followed by ultrasonic washing in HCl 1 mol L^{-1} and in DI water for 10 minutes each. The exchange of protons by platinum ions was then performed by immersing the membrane for one night in 0.1 mol L^{-1} $[Pt(NH_3)_4]Cl_2$ aqueous solution stabilized with 5% ammonium hydroxide (approximately 3 mg of Pt salt were adsorbed per cm^2 of membrane for Nafion 117). The membrane was then rinsed by stirring in 50 ml of water at 40 °C for 30 minutes and four times 2 ml of sodium borohydride solution (5 wt%, $NaBH_4$aq) was added every 30 minutes for two hours while the temperature was continuously increased to 60 °C. 20 ml of $NaBH_4$aq were then added to the solution and the solution was stirred continuously at 60 °C for another two hours. A grey layer of Pt particles was observed at the surface of the film. To finish the process, the membrane was rinsed with water and immersed in HCl 0.1 M for 12 hours. To obtain the tri-layer configuration of an IPMC, the edges of the film were cut exposing the non-metallized middle ionic layer.

Methods

Shape memory characterization. The samples were dried under vacuum for two days to reach a low water content to avoid the contraction of the material during heat programming and actuation due to the water evaporation, leading to an over-programmed material (≈2%). Indeed, if the material is in hydrated state before the programming, it will dry during the heating ramp and have a negative strain before the stretching process. A Dynamic mechanical analyser (Q800, TA Instruments) was used to characterize the shape memory effect. The experiments were conducted in a tensile mode with a heating ramping rate of 5 °C min^{-1}, cooling ramp was not controlled. The sample was heated up to the switching temperature. A shape was programmed for pure Nafion material at a switching temperature of 100 °C.[21] The strain-controlled mode programming is performed by uni-axial stretching at a strain rate of 10% min^{-1} to a target strain at this temperature, followed by cooling at constant strain to 45 °C. The stress was then released. All strain recovery experiments were carried out under stress free conditions (a static force of 0.01 N was used). The recovery experiments were conducted heating the materials to target temperature (105 °C) for 120 minutes. The shape memory materials are characterized by their fixity and recovery rates defined by the following eqn (1) and (2):

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100 \quad (1)$$

$$R_{r,tot} = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m} \times 100, \quad (2)$$

where ε_m, ε_u, ε_p are respectively the strain after maximum stretching, after release of stress and after the recovery. R_f and $R_{r,tot}$ are functions of the number of programming/recovery cycles N performed on the material (Fig. 2b). R_f shows the ability of the material to be programmed and $R_{r,tot}$ quantifies the recovery compared to the original length or shape.

Combined displacement and conductance measurements. Conductance measurements were carried out with a Keithley nanovoltmeter 2182A, contacting the electrode with two probes spaced out by 5 mm. The displacement response was stimulated by applying a square wave potential of ±2 V at a frequency of 0.5 Hz, and recorded by a laser displacement sensor (ILD 1401-5, Micro-Epsilon) fitted to a computer. The displacement amplitude was measured at a position 2 mm away from the contact where the actuator was clamped. In the un-programmed state, the transverse displacement amplitude, 2 mm away from the fixed contact, was 41 μm. By programming, the bending amplitude was decreased from 41 to 0 μm between 0 to 100% programmed strain, at which point the EMM no longer actuated. The electrical conductance was initially 1.25×10^{-1} Ω^{-1} for the undeformed sample, and decreased significantly when the material was stretched, reaching 10^{-7} Ω^{-1} for 100% strain.

Results and discussion

Programming/recovery of the EMM, synthesis described above, was accomplished in the temperature range 60–110 °C, with a potential of just ±2 V required for bending electrical actuation. The electrical actuation amplitude can be linearly modulated with programming strain up to 70%, and completely switched off for strains ≥100%. The recovery of the actuation amplitude is possible even from completely inactive states (see Video V-1†). We have investigated the cycling of the shape memory

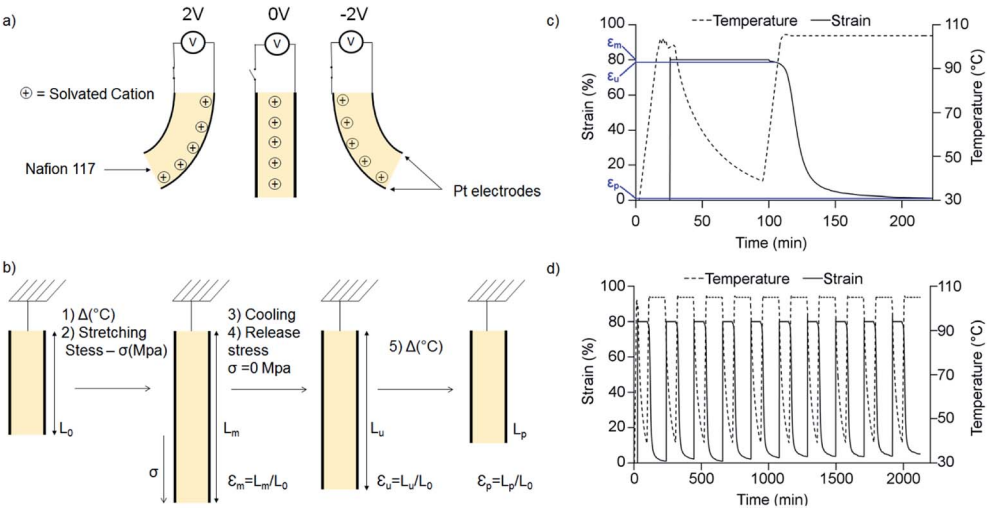

Fig. 2 (a) Actuation principle of IPMC materials, small voltage potentials applied to the electrodes can cause the charged mobile ions (here positive) to move away from one electrode to the other. Shrinking of the polymer matrix near one electrode and swelling near the other results in stresses that cause the material to bend. (b) Shape memory programming and recovery. The materials is heated to its switching temperature, stretched and cooled before releasing the stress, recovery is subsequently brought about by heating the materials above the switching temperature. L_0 is the original length of the sample, L_m the elongated length, L_u the length after the stress release and L_p the recovered length, (c) shape memory properties of the IPMC materials for an 80% stretched sample on the first cycle and (d) over 10 cycles.

properties and have achieved >10 shape-memory cycles with little degradation in performance for a sample programmed to 80% strain.

First, an IPMC actuator was synthesized from an ionic polymer, Nafion®,[29] in which actuation is triggered by an electric field applied between two metal electrodes. This induces movement of the mobile cations (electrophoresis) within the ionic polymer matrix made of immobile negatively charged chains (Fig. 2a). The electrophoretic transport of solvent (water) associated with mobile cations creates two layers in the material with opposite volume changes, one swelling and one shrinking, causing the material to bend.[12] In general, for cation exchange membranes, the actuator will bend towards the shrinking anode as water is displaced towards and swelling the cathode.

Nafion (117H^+ form, Dupont Inc, Wilmington, Delaware) was used to provide memory properties to the EMM material, since it has recently been shown to be capable of memorizing multiple shapes at different temperatures.[20,21] We created electrodes on the surface of Nafion by an electroless deposition technique (See Experimental section).[28] Using a dynamic mechanical analyser, we programmed multiple shapes by heating the material at temperatures above 60 °C, stretching it, and cooling to a lower temperature. To create a multi-temperature memory effect, the programming can be continued by stretching further at that temperature (above 60 °C) and further cooling, and so on, until finally we cool to room temperature, before releasing the programming stress. The original shapes are restored, from final strains of >100%, when the material is heated back to the respective programming temperatures (Fig. 2b).

We studied how the shape memory programming would affect the ionic induced actuation functionality and whether such large deformations would be reversible in IPMCs. Investigating the bending of programmed EMMs under electrical fields, we discovered two distinct regimes of actuator behaviour (Fig. 3a). Mechanical programming of the material can be used to completely switch off, or simply attenuate, the ionic actuator function.

Various exact strains were mechanically programmed into the EMM material at 100 °C in air using a dynamic mechanical analyser. The shape memory effect is achievable both in air and aqueous media, however, ionic actuation is only reproducible with a well-hydrated material. Therefore, the samples were then soaked in water for 24 hours at room temperature, to ensure the material had reached the maximum water uptake (the number of water molecules per sulfonic acid group is $\lambda = 22.5$ (ref. 30)) which is the source of ionic conductivity inducing the bending during the operation of the EMM material. The linear elongation due to water swelling was small, ≤2% in the programmed strain direction. We also verified that the swelling does not destroy any of the shape-memory programming. Upon heating back the material between 60 and 105 °C under water or in air, we obtained full recovery of the shapes at their respective programming temperature.

Fig. 2c presents the quantification of shape memory properties for a sample stretched to 1.8 times its original length (1 cycle). Fig. 2d shows the shape-memory cycling performance for the same strain over 10 cycles, after which the material is only about 7% longer than the original (93.6% recovery rate after 10 cycles). The fixity (R_f) and recovery (R_r) rates were measured to determine programming cyclability and mechanical reversibility of the EMM material. R_f was found constant (99.1%) for all conditions and independent of the number of cycles. R_f = 99.1% means a programmed sample experiences a spontaneous shape/length change of less than 1% upon release of the programming stress. $R_{r,tot}$, for a sample stretched to 80% strain

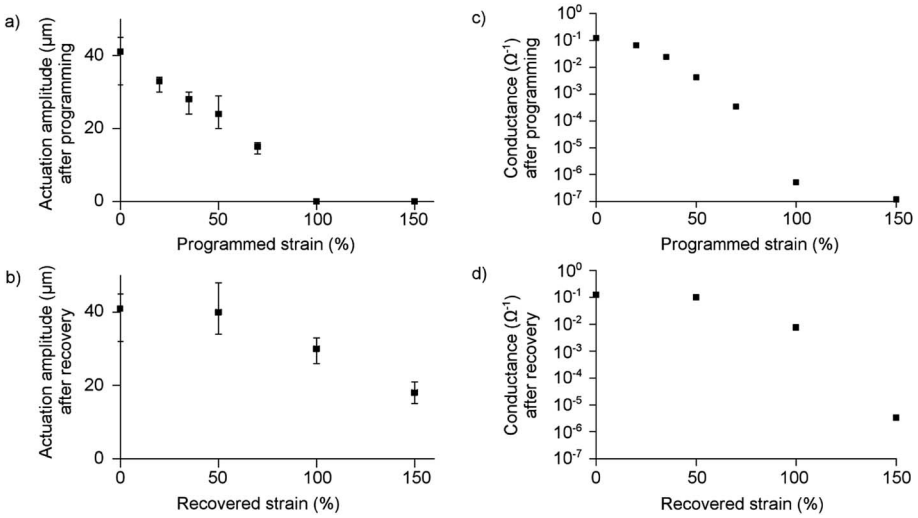

Fig. 3 Electro-mechanical memory: correlation between electrical actuation and electrodes conductance in programmed and recovered sates (a) electrical actuation in different stretched states at 2 mm away from the contact under a ±2 V square signal at 0.5 Hz, (b) actuation amplitude after the recovery from different programmed strain, (c) conductance after programming and (d) after the first recovery of actuation.

at 100 °C, was 98.6% after the first cycle, 96.3% after the fifth and 93.6% after the tenth cycle. Fig 2d also shows it can withstand tens of shape-memory programming cycles without significant loss of performance. These high numbers for shape-memory recovery and cyclability are comparable to those achieved with pure Nafion.[20] For a physically cross-linked polymer, such a small creep is expected, which decreases the recovery rate with the number of cycles. Cyclability would be improved with chemically cross-linked polymers, which we are in the process of synthesizing. The shape memory properties for different programmed strains are reported in Fig. S1.†

The bending response from ionic actuation was quantified with a displacement laser sensor (see Experimental section and ESI Fig. S2†). Fig. 3a shows that the amplitude of the bending actuation response can be tuned, and its decrease is linearly proportional to the amount of programmed strain. Above a critical strain of ~70%, however, the response becomes non-linear, and for strains above 100%, no electrical actuation was observed. Thus the mechanical programming can act as both a variable attenuator and as an on-off switch. Upon heating, the material can also act as a thermal history sensor, since the deformation stresses are reversed sequentially at their programmed temperatures, and the electrical actuation properties of the EMM material are restored. The restoration is complete even for the first cycle for samples programmed up to 50% strain and only partial for 100% and higher strains (Fig. 3b). Fig. 4 illustrates the ability to program the actuation of the EMM material, with material pre-programmed with two shapes (50% and 100% strain) at 70 °C and 90 °C, respectively. Under the same applied voltage of ±2 V, the 100% strained material shows no actuation; after exposure to 70 °C, the thermal recall leads to partial restoration of actuation, and after exposure to 90 °C, full restoration of the initial actuation amplitude is achieved. (See also ESI Video V-1†)

We hypothesize that the mechanism for this variable attenuation and reversible switching property is related to the conductance of the electrode surfaces.[31] When the magnitude of the programming strain increases, cracks are created on the surface of material perpendicular to the stretching direction (Fig. S5†), leading to a decrease in conductance. When the material shape is recovered, the fractured regions of the electrodes reconnect and the conductance is then recovered. A lower conductance of the electrodes results in higher voltage drop and locally lower electric fields in the EMM. These fields are unable to trigger sufficient ionic movement to produce mechanical deformation for bending actuation in programmed state of the material.

Combined amplitude (Fig. 3a and b) and electrical conductance (Fig. 3c and d) measurements were performed on the electrodes of the material after programming and recovery.

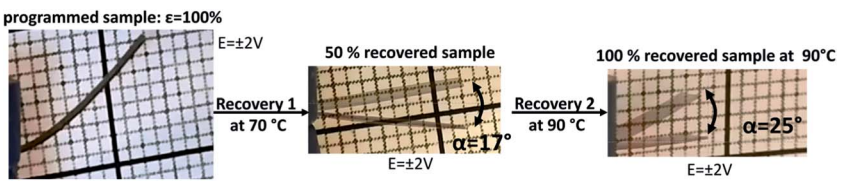

Fig. 4 Electro-mechanical memory: illustration of the electrical actuation in programmed states at 100% strain (no actuation), 50% recovered state (amplitude spans 17 degrees) and after full recovery (25 degrees).

Fig. 3c shows the hypothesized drop in conductance corresponding to the drop in actuation amplitude with strain (Fig. 3a). These changes mirror each other and are completely reversible for strains up to 50%. For strains of 100 and 150% restoration of its functionalities is only partial. Fig. 3d shows that the partial recovery of the ionic actuation for sample programmed to strains over 100% is due to a partial recovery of the conductance as well. This irreversible behaviour for high strain programming is likely due to creep of the polymer chains and corresponding residual strain in the electrodes.

The matching shapes of both amplitude and electrode conductance, with a proportional gradual decrease, and the same strain position for their non-linear drop-offs, supports our hypothesis that the changes in actuation amplitude and conductivity are likely due to a percolation to non-percolation transition of cracks in the electrodes perpendicular to the electrode length (Fig. S5†).

Conclusions

Ionic actuators, and specifically IPMCs, are among the best developed technologies for soft actuators. The current EMM material introduces a memory functionality, which can be triggered by the independent application of temperature, to recall a previous performance of the actuator, achieving a sort of artificial "muscle memory". EMMs also combine attractive, independently controlled functionalities: low-voltage operation with moderate energy densities (5×10^{-3} J cm^{-3}) on one hand, similar to IPMCs, and high strain (>100%) and high energy density (2 J cm^{-3}) actuation, typical for shape-memory polymers.

The EMM is quite versatile in cycling performance, and the ionic actuation mode can be used with or without shape-memory programming (Fig. S3†). The ionic actuation can be cycled hundreds of thousands of times underwater and under appropriate humidity, and for >2000 cycles under low humidity in air (due to evaporation of water).[19] The SMP function can be used to program the actuator size/shape, its mode of operation, and to provide readout of its environmental history. For the moment, this function can be cycled a few dozen times with only modest performance degradation.

The EMM, in addition to actuator and memory, also has a sensory function. Its actuation amplitude, though not optimized for this application, is a dynamic readout of the history of environmental conditions to which the system has been exposed. The ionic actuator can be cycled for many thousands of times and operate independently of the SMP function.

There are a wide range of EMM materials that could be synthesized from available ionic polymers that exhibit shape memory properties.[20,32] Their compatibility with ionic liquids is attractive for aerospace applications, where they can achieve higher strains at lower voltages compared to piezoelectric ceramics that require mechanical amplification of their maximum (0.2%) achievable strains.[1,33]

EMM materials can also self-deploy fully functioning actuator structures that had been previously folded for compact storage. Shape memory materials have only been used previously for achieving such self-deployable static structures.

In summary, we have described an EMM material with actuation modes controlled by two different stimuli (electricity and temperature). Shape memory programming can be used to tune or switch (on/off) the material's ionic actuation independent of the electrical stimuli. In this paper, we focus on the novelty of this independent modulation of the ionic actuation, how it can be used for sensing-based alteration of function, and for reading the temperature history of the material. It is worth noting, however, that this material is also capable of sensing stresses and converting them to electrical signals, as well as harvesting small amounts of energy in this manner.[19,34]

Such actuators, having memory of their state, sensing their environment, potentially harvesting energy, and delivering a programmed response bring us one-step further in achieving life-like behaviour with artificial materials.

Abbreviations

EMM	electro-mechanical memory
IPMC	ionic polymer metal composite
EAP	electro-active polymer
SMP	shape-memory polymer

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