Thickness dependence of curvature, strain, and response time in ionic electroactive polymer actuators fabricated via layer-by-layer assembly

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Ionic electroactive polymer (IEAP) actuators containing porous conductive network composites (CNCs) and ionic liquids can result in high strain and fast response times. Incorporation of spherical gold nanoparticles in the CNC enhances conductivity and porosity, while maintaining relatively small thickness. This leads to improved mechanical strain and bending curvature of the actuators. We have employed the layer-by-layer self-assembly technique to fabricate a CNC with enhanced curvature ($0.43 \ mm^{-1}$) and large net intrinsic strain (6.1%). The results demonstrate that curvature and net strain of IEAP actuators due to motion of the anions increase linearly with the thickness of the CNC as a result of the increased volume in which the anions can be stored. In addition, after subtracting the curvature of a bare Nafion actuator without a CNC, it is found that the net intrinsic strain of the CNC layer is independent of thickness for the range of 20–80 nm, indicating that the entire CNC volume contributes equivalently to the actuator motion. Furthermore, the response time of the actuator due to anion motion is independent of CNC thickness, suggesting that traversal through the Nafion membrane is the limiting factor in the anion motion. © *2011 American Institute of Physics*. [doi:10.1063/1.3590166]

I. INTRODUCTION

Development of stimuli responsive materials has attracted considerable interest from the materials research community. In one key example, there have been substantial efforts to develop soft, light, and efficient electromechanical actuators capable of generating a large mechanical strain to be used in several potential applications such as biomimetic devices and micro-robotics. Electroactive polymers (EAPs) are soft, flexible, and low-density materials that exhibit reversible mechanical deformation by electric fields. The electromechanical response of EAPs is due to either electrostatic force (dielectric EAPs) or displacement of ions inside the polymer (ionic EAPs (IEAPs)). IEAPs are particularly attractive because they have lower density, higher resilience, and higher strain and lower operating voltage compared to other types of electroactive materials.[1–3]

Compared to electroactive ceramics (EACs), dielectric EAP, and shape memory alloys (SMAs), IEAPs are significantly more efficient by generating larger strain under application of smaller voltage. The mechanical strain generated by soft, elastic IEAPs under application of few volts (≤ 4 V) can be up to two orders of magnitude larger than that generated by fragile and rigid EACs under application of several hundred volts.[4,5] IEAPs also have significantly higher resilience and lower density compared to SMAs.[6] These properties, together with high flexibility, make IEAPs quite a favorable material for soft actuators.[4,7]

The IEAP actuators with the largest actuation typically consist of two conductive network composite (CNC) layers formed on the surfaces of an ionomeric membrane containing an electrolyte. Motion of ions of different size and charge through the ionomeric membrane and CNCs and their accumulation at the oppositely-charged electrodes generates stress, which in turn causes mechanical strain. Motion of ions toward or away from each electrode is due to attractive or repulsive forces between the electrically charged electrode and the ions and can be reversed upon modulating the polarity of the electric field.

Previous studies have demonstrated that the actuation behavior of IEAPs depends on the properties of CNC layers.[3,8,9] CNCs are designed to act as reservoirs for electrolyte (aqueous or ionic liquid) solution. The mobility of ions through the CNC layer, in the presence of an electric field, depends on several factors such as size, length, conformation, and number of nano/micro-channels as well as the interaction of ions with the nano/micro-channels and of course the strength of the electric field. The mobility of the ions defines attributes of CNC layers and can ultimately define the characteristics of IEAP actuators. Most of these attributes can be tuned and optimized by variation of the composite materials, fabrication technique, and thickness of the CNC layers. The ratio between the size of the ions and the diameter of the nano/micro-channels is also of significant importance and can be tuned by choice of proper electrolyte.[10] Several research groups have modified the properties of different components of IEAP actuators to enhance their performance. For instance, Akle *et al*. formed CNCs from composites of RuO_2 particles and gold flakes at different

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ratios and studied the effects of porosity and conductivity on the performance of actuators. It was shown that the higher porosity of the CNC layer enhances mechanical strain.[3] Kim *et al.* studied the mechanical behavior of IEAP actuators consisting of ionomeric membranes with different thicknesses and verified that thicker ionomeric membranes result in generation of larger forces.[11] Bennet *et al.* embedded precious and nonprecious metals via electroless plating into CNCs and have shown that both categories of metals can be used in forming CNC layers; yet precious metals, primarily gold or platinum, are advantageous as they eliminate the oxidation problem and do not require further processing steps such as a co-reduction process or deposition of an ultra-thin protective layer.[12] Use of aqueous electrolytes limits the operating voltage of actuators to values below the voltage of water hydrolysis. Bennett *et al.* have shown that use of ionic liquids can eliminate this issue.[13,14]

The fabrication method of the CNC is clearly influential on the properties of the actuator. Several methods have been used to form CNC layers on ionomeric membranes to fabricate IEAP actuators. Plating is a traditional method and has been employed by several research groups to form CNC layers on Nafion.[1,6,15–17] In this method, metal penetrates into the membrane and forms a polymer-metal interfacial area, which is responsible for high electrical capacitance of these composites. The high density of such composites limits the electrolyte up-take, which generally results in smaller and slower strain response. Painting and spin coating are alternative methods for directly forming the CNC on the membrane. Akle *et al.*[18,19] developed a highly effective method for fabricating electrodes with large polymer-metal interfacial area. In this method, a mixture of metal and Nafion polymer are painted directly onto the Nafion membrane and then hot-pressed into the surface.

We have previously shown that higher strain and bending curvature can be achieved by employing the layer-by-layer (LbL) technique to form CNC layers.[20,21] In that prior work, we stapled the Nafion membranes to a thin polycarbonate frame to hold the Nafion rigid and achieve more homogeneous film deposition. However, it was observed that frequently the AuNP solution would degrade and form aggregates after the deposition of 10–15 bilayers; this necessitated regularly changing the solutions and increases the production effort and cost. Here, glass frames with the Nafion secured by double-sided tape have been used rather than staples and eliminates this problem, resulting in formation of uniform and homogeneous CNCs for deposition of >100 bilayers. An SEM image of a 40-bilayer AuNP surface is shown in Fig. 1.

In this work, we investigate a series of IEAP actuators consisting of CNCs with different thicknesses, fabricated via the LbL assembly[22,23] technique with the newer glass frames. Control over the thickness of the CNC is achieved directly through the number of deposited bilayers of the composite material on the ion exchange membrane. We used spherical gold nanoparticles (AuNPs) in forming the CNC to enhance both porosity and electrical conductivity and have quantified the actuation radius, intrinsic strain, and response time of the resultant actuators with different thickness CNCs.
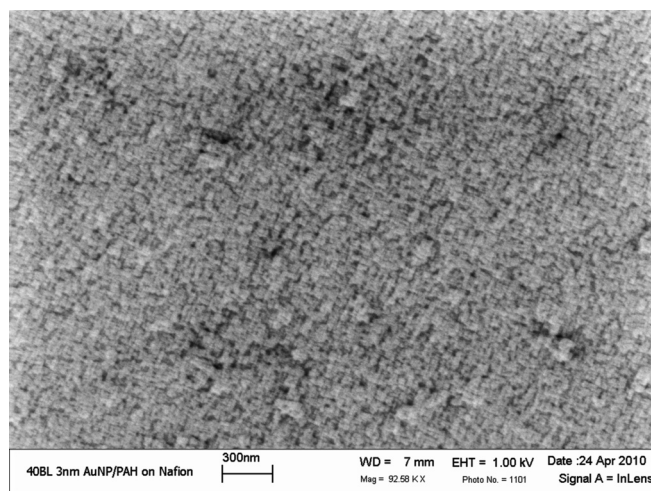

FIG. 1. SEM image of 40 bilayers of (PAH/AuNPs) on Nafion.

II. MATERIALS AND TECHNIQUES

Commercially available Nafion film of 25 μm thickness (Ion Power, Inc.) was used as the ionomeric membrane in all IEAP actuators investigated in this work. Nanocomposites of the polycation poly(allylamine hydrochloride) (PAH) (Sigma Aldrich) and anionic functionalized gold nanoparticle (AuNP) (~3 nm diameter, Purest Colloids, Inc.) were grown on both sides of the Nafion membrane via LbL deposition of the ionic species. The substrates were alternately immersed for 5 min each in aqueous solutions of PAH at a concentration of 10 mM at pH 4.0 and AuNP at a concentration of 20 ppm at pH 9.0 with three rinsing steps for 1 min each in de-ionized water after each deposition step. Glass frames were used to support the membrane in the solutions during the deposition process. After deposition of the PAH/AuNP CNCs on the Nafion membrane, the films were soaked with 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf) (Sigma Aldrich) ionic liquid to approximately 40 wt. %. Gold leaf electrodes of 50 nm thickness were then hot-pressed on both sides of the membrane to form IEAP actuators. Other ionic liquids can also be used as sources of mobile ions; however, IEAP actuators with EMI-Tf have shown the highest strain response.[20] The IEAP actuators were then cut into approximately 1×6 mm^2 strips for testing. The thicknesses of CNCs consisting of different numbers of bilayers were measured using a Veeco Dektak 150 profilometer.

III. RESULTS AND DISCUSSION

As shown in Fig. 2, the thickness of the CNC with respect to the number of deposited bilayers exhibited a linear growth of approximately 2 nm/bilayer. Because the CNCs are fabricated on both sides of the ionomeric membrane, twice the CNC thickness is added to the thickness of the membrane to obtain the total thickness of the ionic polymer-metal composite (IPMC). The thicknesses of different samples are presented in Table I.

As we have shown previously,[24] ionic liquid bending actuators under constant applied voltage exhibit first a motion toward the anode followed by a motion toward the
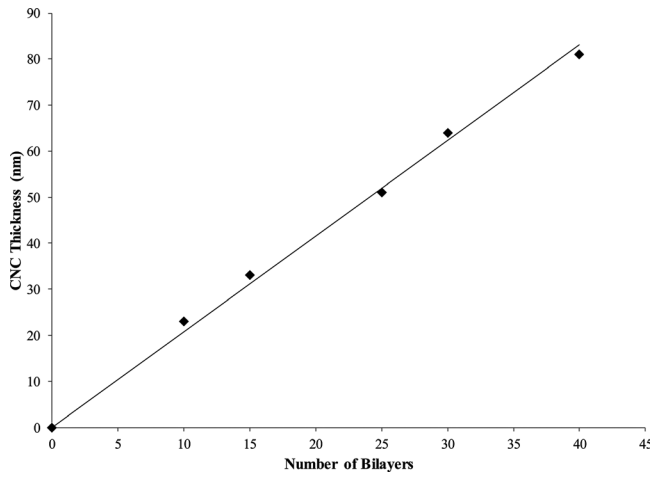
FIG. 2. CNC thickness vs number of bilayers. The trend line indicates linear increase in thickness.
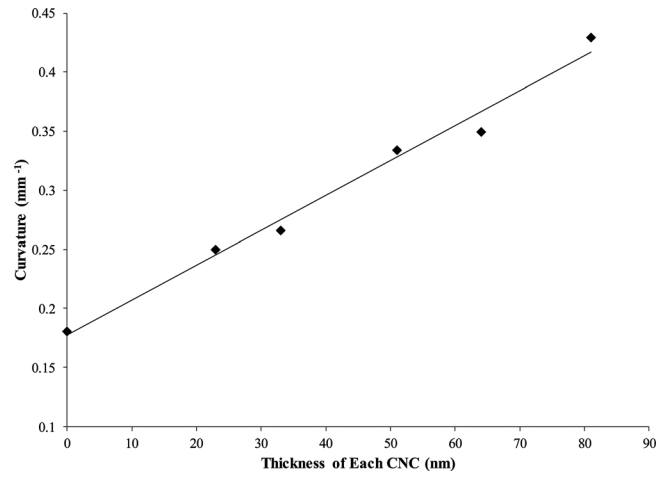

FIG. 3. Curvature (Q) increases linearly with the increase in the thickness of CNC. The curvature of an actuator consisting of 80 nm thick CNCs exhibited a 72% increase in comparison to the actuator consisting of 20 nm CNCs. Data are taken under application of 4 V step function.

cathode. This is interpreted as a fast motion by the ionic liquid cations followed by a slower motion of the anions. In the devices discussed here, the faster bending has a fairly small amplitude (with a time constant of ∼0.2 s) until the device has undergone several cycles of actuation, while the slower motion (time constant ∼1.5 s) toward the cathode remains fairly constant during this conditioning process. In this paper, we will focus our discussion on the slower motion toward the cathode. The faster response will be discussed in more detail in a separate publication.

The responses of IEAP actuators to an electrical signal of 4 V were monitored and recorded using a charge-coupled device (CCD) video camera. The actuation radius of each actuator as a function of time was determined from the optical images and used to calculate the actuation curvature (Q). Fig. 3 shows the maximum actuation curvature toward the cathode (generated by anions) as a function of CNC thickness for actuators with different numbers of bilayers comprising the CNC, including the case of bare Nafion (no CNC). The curvature increases linearly with the thickness of the CNC at a rate of 0.0029 mm^{-1}/nm. The increase of actuation curvature as a function of thickness is due to the motion of a larger number of ions into the thicker CNCs, as thicker CNCs are capable of containing more electrolyte and hence more ions accumulate at each electrode in the presence of an electric field due to this higher capacitance. Accumulation of a larger number of anions results in a larger volume imbalance between the electrodes; this in turn causes a larger mechanical deformation and thus curvature. The largest actuation curvature

(0.43 mm^{-1}) corresponds to the sample consisting of 40 bilayers. The curvature of the 40-bilayer device is 2.4 times larger than that of the actuator without a CNC, confirming the role of CNC layer in increasing the ion density and thus bending curvature.

In the case of symmetric cantilever actuators with length significantly larger than width and width significantly larger than total thickness, the application of electric field across the thickness of the actuator will cause longitudinal expansion or contraction in the CNC layers; this produces mechanical bending. For a free cantilever bimorph actuator, the extensional force (F) and external moment (M) are zero, and only pure bending occurs during the actuation.[25] The intrinsic strain (ε) within the CNC layer can be obtained from Eq. (1), using the thickness and elastic modulus of each layer along with the radius of curvature.

$$\varepsilon = \frac{Y_m\left[\left(\frac{2t_m^3}{3}\right)+2t_m\left(t_c+\frac{t_i}{2}\right)^2+t_m^2(2t_c+t_i)\right]+Y_c\left[\frac{2t_c^3}{3}+t_c\frac{t_i^2}{2}+t_c^2 t_i\right]Y_i\left[\frac{t_i^3}{12}\right]}{rY_c\left(t_i t_c+t_c^2\right)} \tag{1}$$

where Y is the modulus, t is the thickness, and r is the radius of curvature, and the subscripts m, c, and i correspond to metal, CNC, and ionomeric membrane, respectively.

To quantify the generated intrinsic strain, the elastic modulus of each layer was characterized along the direction of the actuator surface, using a setup specifically designed to measure the elastic modulus of soft materials. Details of the setup and procedures are presented in our previous work.[20] Briefly, the elastic modulus of the Nafion film with 40 wt. % EMI-Tf was measured first (= 50 MPa). Then the elastic modulus of the specimen with CNC deposited on the Nafion membrane was characterized from which the elastic modulus of the CNC layer is deduced (= 739 MPa). The elastic modulus of the five-layer IEAP actuator swollen with EMI-Tf was also measured from which the elastic modulus of the gold electrode was deduced (= 20 GPa)

TABLE I. Thickness of different components of variety of actuators.

Sample	CNC (μm)	IPMC (μm)	Actuator (μm)
Bare Nafion	0.000	25.000	25.100
10 BL	0.023	25.046	25.146
15 BL	0.033	25.066	25.166
25 BL	0.051	25.102	25.202
30 BL	0.064	25.128	25.228
40 BL	0.081	25.162	25.262

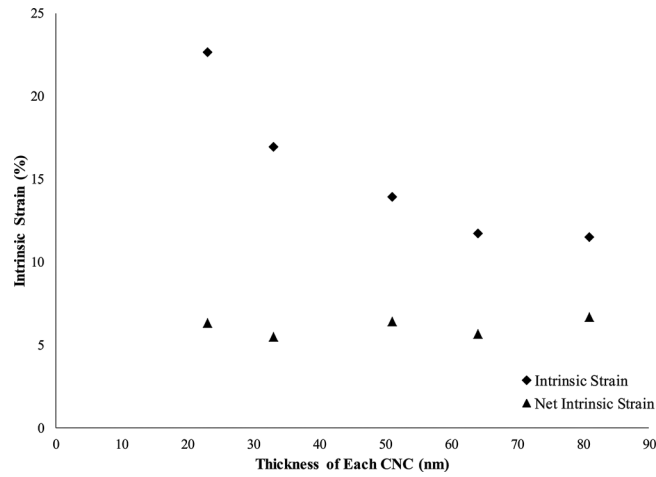Bare Nafion has thickness of 25 μm and each metal electrode is 50 nm thick

FIG. 4. Normalized intrinsic strain and net intrinsic strain due to the CNC layer as a function of CNC thickness. Samples consisting of thinner CNCs exhibited a larger intrinsic strain, but the net intrinsic strain due to the CNC layer after subtracting the contribution from bare Nafion is a fairly constant value. Data are taken under application of 4 V step function.

The actuator consisting of 10 bilayers (thinnest CNCs) exhibited largest intrinsic strain as derived from Eq. (1) compared to other actuators consisting of thicker CNCs. Presented in Fig. 4 is the calculated intrinsic strain as a function of CNC thickness. The mechanical intrinsic strain generated under 4 V was obtained to be 22.65% (45.3% peak to peak) for the 10-bilayer actuator and 11.48% (22.96% peak to peak) for the 40-bilayer actuator. In comparison, the intrinsic strain of an IEAP actuator based on a 3 μm thick RuO_2 CNCs is 3.3% (6.6% peak to peak) under the same voltage. The considerably enhanced strain of the actuators investigated in this work is due to successful formation of uniform and thin CNCs. Such CNCs contain less metal, which lowers the modulus, and uniform structure, which facilitates effective mobility of ions and also increases electrolyte up-take. It is important to note that the actuator without a CNC still exhibits non-negligible curvature. To determine the true intrinsic strain of the actuators, this contribution to the curvature should be removed. Thus the net intrinsic curvature due

to the CNC layers for each actuator was derived by subtracting the curvature of the bare Nafion actuator from that of the other actuators. The net curvature was then used to calculate the net intrinsic strain due to the CNC; this was found to be a fairly constant value. The net intrinsic strain has an average value of 6.1% as shown in Fig. 4. The independence of the net intrinsic strain on the CNC thickness indicates that the additional CNC material contributes equally to the bending response over the measured thickness range of 20 to 80 nm.

The radius of curvature r is used with Eq. (2) to obtain the net strain as a function of the thickness h of the actuator. The net strain of an actuator differs from the intrinsic strain of an actuator as the former corresponds to the overall strain generated in the actuator as a whole, whereas the latter is the strain generated in the CNC layers only. The net strain is independent of all intrinsic properties of the actuator such as materials, moduli, and composite structure and only depends on the thickness and radius of curvature. In the other word, it is the strain of any bent structure of a given thickness and arbitrary properties. The net strain increases as the thickness of the actuator (i.e., CNC layer) increases; which is due to the significant increase in the bending for a relatively small increase in the thickness of the actuator as a result of the facilitation of the accumulation of charge at the electrodes by the CNC. Fig. 5 illustrates the change in the net strain as a function of the thickness of CNC layer.

$$\varepsilon(\%) = \frac{h}{2r} \times 100 \tag{2}$$

The speed of the actuators was also characterized as a function of CNC thickness. The strain generated by each actuator was normalized with respect to the maximum strain and plotted as a function of time. Comparing the normalized strain of different actuators versus time revealed that the response times of all actuators are approximately the same with respect to their normalized strain, suggesting that time required for anions to travel through the CNC layer is negligible compared to that for travel through Nafion. In Fig. 6, the normalized strain for two of the actuators is shown as a function of time. Data points were fitted with $\varepsilon = \varepsilon_{max}(1-exp(-t/\tau))$ where t is time
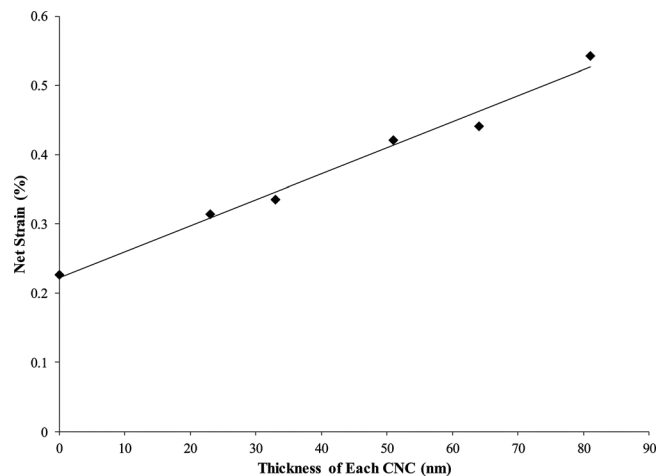

FIG. 5. Net strain increases with the increase in the thickness of the CNC. This strain is obtained using the net thickness of the actuator, as shown in Table I, and the corresponding radius of curvature under application of 4 V step function.
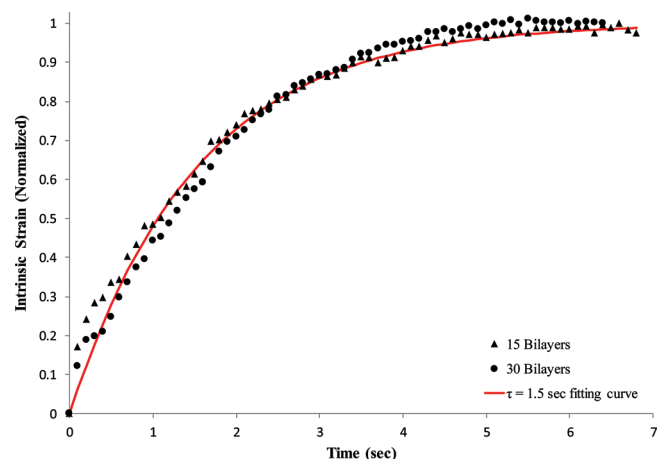

FIG. 6. (Color online) Response time of actuators consisting of 15 and 30 bilayer CNCs. It was observed that the change in normalized strain of actuators as a function of time is independent of the thickness of actuators.

and τ is the time constant, which yields $\tau = 1.5$ s. It should be noted that the independence of the response time for anion motion on CNC thickness observed here is different from the results of Ref. 21 for the fast, cation motion in which we observed that the response time increased significantly with increased CNC thickness. The difference is presumably due to the ability of the cations to move much more quickly through the Nafion membrane such that the time for traversal of the CNC becomes the rate-limiting step for the cations.

IV. CONCLUSION

CNCs consisting of different numbers of bilayers of PAH and AuNPs were fabricated via the LbL self-assembly technique and used to form IEAP actuators. The resultant actuators exhibited significantly large strain compared to other types of actuators. It was observed that actuators with thicker CNC layers are capable of generating larger bending. The maximum curvature of the actuators due to anion motion was found to increase linearly with the thickness of the CNC layer; this is the result of larger ion storage volume in thicker CNC layers. After accounting for the curvature observed in an actuator with no CNC layer, the net intrinsic strain of the CNC was found to be $\sim6.1\%$ independent of thickness, indicating that the entire CNC volume contributes equivalently to the actuator motion. The response time for actuation due to anion motion was also found to be relatively independent of CNC thickness, with a time constant of 1.5 s, suggesting that the time required for anions to travel through CNC is negligible compared to the time required for traveling through the Nafion membrane. The improved actuation curvature and strain achieved in this work are results of successful fabrication of thin and uniform CNCs.

ACKNOWLEDGMENTS

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