Influence of conductive network composite structure on the electromechanical performance of ionic electroactive polymer actuators

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The influence of the nanostructure of the conductive network composite (CNC) on the performance of ionic electroactive polymer (IEAP) actuators has been examined in detail. We have studied IEAP actuators consisting of CNCs with different volume densities of gold nanoparticles (AuNPs) and the polymer network. Varying the concentration of AuNPs in CNC thin films was used as a means to control the CNC–ion interfacial area and the electrical resistance of the CNC, with minimum effect on the mechanical properties of the actuator. Increasing the interfacial area and reducing the resistance, while maintaining porosity of the composite, provide means for generating motion of more ions into the CNC at a significantly shorter time, which results in generation of strain at a faster rate. We have demonstrated that cationic strain in actuators with denser CNCs is improved by more than 460%. Denser CNC structures have larger interfacial areas, which results in attraction/repulsion of more ions in a shorter time, thus generation of a larger mechanical strain at a faster rate. Also, time-dependent response to a square-wave voltage was improved by increasing the AuNP concentration in the CNC. Under 0.1 Hz frequency, the cationic strain was increased by 64% when the AuNP concentration was increased from 4 to 20 ppm.

Keywords: ionic electroactive polymer actuator; functional thin film; conductive network composite

1. Introduction

Smart polymers have attracted considerable experimental and theoretical interest from the materials research community. In recent years, there have been significant efforts to understand the mechanism [1–3] and improve performance of smart polymers in actuators, sensors, super-capacitors and fuel cells [4–6]. Smart polymers are particularly attractive for their lower density, higher resilience and higher strain and lower operating voltage compared to smart alloys and ceramics [7,8].

Ionic electroactive polymer (IEAP) actuators are a class of smart structures, based on polymers, which exhibit mechanical response to external electrical stimulus. The mechanical response is due to the force generated by a volume imbalance between the two sides of the actuator, which results from transport of ions of different size and charge through the device and their accumulation at the oppositely-charged electrodes. Motion of the ions

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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 by inverting the polarity of the external electric field [9,10].

Typically, high performance (large actuation) IEAP actuators contain an ionic polymer–metal composite (IPMC) that consists of two conductive network composite (CNC) layers formed on the surfaces of an ionomeric membrane (very often Nafion®) containing an electrolyte [11,12]. Figure 1a shows a schematic diagram of an IEAP actuator. The CNCs are added to the ionomeric membrane to act as reservoirs for electrolyte (aqueous or ionic liquid). Thus, they have a significant interface and interaction with the ions in the electrolyte, and their properties directly influence the mobility of ions in the IPMC. The mechanical response of most ionic liquid-containing IEAP actuators to an external electric field can be divided into two separate steps in opposite directions [13]. The fast response is typically smaller in magnitude and is generated by cations that rush toward the cathode rapidly once the voltage is applied and cause the actuator to bend toward the anode. Depending on the thickness of the IPMC and the CNC–ion interfacial area, the fast response can have a time constant as low as 0.18 second [14]. The slow response is generated by motion of anions.

Figure 1. (a) Schematic of an IEAP actuator (not to scale). (b) Overlaid photographic images of an IEAP actuator responding to a 4V step voltage; electrode on the left side is anode.
(or ion clusters with net negative charge). It is larger in magnitude and consists of bending of the actuator toward the cathode, canceling the fast response completely. Figure 1b shows the response of an IEAP actuator, consisting of 20-bilayer CNCs (AuNP concentration of 20 ppm) and 25 µm Nafion, to a 4 V step voltage. There are applications in which fast cationic response is preferred, yet a large magnitude of bending is also desired. Operating the actuator at a fast enough frequency, the anionic response can be eliminated. The magnitude of bending can be maximized through optimization of the CNC layers. Most electrical and mechanical properties of the CNC layers, such as conductivity, volume density, porosity and pore size, can be optimized by variation of the composite materials, fabrication technique and thickness of the CNC [15]. The speed and extent of response of ions to an external electric field depends on several factors including the CNC-ion interface area and the conductivity of the CNC layer. Previous studies have demonstrated the great influence of CNC layers on the electromechanical behavior of IEAP actuators; moreover, it is well known that the dynamics of mobility and diffusion of ions in IPMC and their interaction with CNC layers has a vital rule in defining the electromechanical properties of ionic devices [4,5,16].

We have previously shown that higher strain and bending curvature can be achieved by employing the layer-by-layer (LbL) technique with gold nanoparticles (AuNPs) to form porous CNC layers of desired physical properties [14,17]. One of the main advantages of using the LbL technique is the ability to construct electrically conductive, porous CNCs while keeping the thickness in the nanometer range [18–20]. Such ultra-thin composites do not interfere with the desired mechanical properties of the Nafion membrane. That is, the modulus is not changed by a significant amount, while the CNC–ion interface is dramatically increased and mobility of ions through the CNC is facilitated. Moreover, IPMCs with porous CNC layers have larger electrolyte uptake capacity due to the porosity. Previously, we have shown that the thickness of the CNC is highly influential on the performance of IEAP actuators [21]. In that prior work, we demonstrated that increasing the thickness of the CNC results in larger strain and bending curvature, which are the results of the increased electrolyte uptake, without significantly increasing the overall thickness or modulus of the IPMC.

In this work, we investigate the motion of ions in a series of IEAP actuators consisting of CNCs with different AuNP densities fabricated via the LbL assembly technique and demonstrate that the cationic response can be maximized by tuning the nanostructure of CNC layers. Control over the density of the CNC is achieved directly through varying the concentration of AuNPs in the aqueous immersion solution. We have quantified the sheet resistance, anionic strain, cationic strain and frequency dependence of the cationic strain of the resultant actuators with different density CNCs, and have also characterized charging and discharging of the actuators.

2. Experimental
Commercially-available Nafion membranes of thickness 25 µm (Ion Power, Inc.) were 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 nanoparticles (AuNPs, ∼3 nm diameter, Purest Colloids, Inc.) were deposited on both sides of the Nafion membrane via LbL deposition. 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 AuNPs at 2, 4, 10 and 20 ppm concentrations at pH 9.0 with three rinsing steps for 1 min each in deionized water after each deposition
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step. The resultant thin films had a thickness of approximately 2 nm/bilayer. Glass frames were used to support the membrane in the solutions during the deposition process to eliminate frame–solution chemical reactions. After deposition of the PAH/AuNP CNCs on the Nafion membrane, the membranes were soaked with 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-Tf) (Sigma Aldrich) ionic liquid to approximately 40 wt %. Gold leaf electrodes of thickness 50 nm were then hot-pressed on both sides of the membrane to form IEAP actuators. Ionic liquids were used rather than aqueous electrolytes as they eliminate the operating voltage limitations associated with hydrolysis of water in aqueous electrolytes [22,23]. EMI-Tf, a widely studied ionic liquid, was used as the sole source of free ions in actuators studied in this work because IEAP actuators containing EMI-Tf have shown the highest strain response [14]. The IEAP actuators were then cut into approximately 1 × 6 mm² strips for testing. The thicknesses of CNCs fabricated by different AuNP concentration were measured using a Veeco Dektak 150 profilometer. The surface resistance was measured using a Jandel four-point-probe measurement system equipped with a cylindrical probe head. Actuation motion was monitored and recorded at the rate of 30 fps by a charge-coupled device (CCD) camera mounted to an in-house fabricated probe station. A step voltage was derived from an HP 6218A and square waveforms were generated using an HP 3312A function generator. Current flow was measured and recorded using a FRA2 µAutolab type III potentiostat. Strain was calculated by two different methods, depending on the extent of bending. In the case of large bending, the radius of curvature r (deduced from the recorded images) and thickness h of the actuators were used along with:

\[ \varepsilon(\%) = \frac{h}{2r} \times 100. \]  

(1)

In the case of small, vibration-like, bending the tip displacement \( \delta \) (deduced from the recorded images) and free length of actuator \( L \) were used with [10]:

\[ \varepsilon(\%) = \frac{\delta h}{L^2} \times 100. \]  

(2)

The strain calculated with these two methods is the net strain, depending only on the geometry of the structure, and it is not modified by any of the intrinsic properties of the actuator such as materials, moduli, composite structure etc.

3. Results and discussion

3.1. IPMC characteristics

Electrical conductivity and ionic permeability of CNC thin films largely depend on the concentration of the metallic component and the size of pores formed in the structure of the nanocomposite, respectively. Decreasing the concentration of AuNPs, as shown in the scanning electron microscopy (SEM) images of Figures 2a–b, results in formation of a nanocomposite structure with lower gold densities per layer. Films with reduced AuNP density have low electrical conductivity yet larger pores. Although the pore size is increased in samples with lower AuNP concentration, the total number of ions that move into the CNC under applied voltage is expected to be low due to the reduced electrode surface area. As a result, the response of ions to electric field is limited and so is the generated strain. On the other hand, increasing the AuNP concentration results in formation of closely packed metallic structures, which is more effective in establishing a distributed electric
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Figure 2. SEM images of CNCs containing (a) 2, (b) 4, (c) 10 and (d) 20 ppm concentration of AuNPs.

Field to attract/repel ions and hence generate strain. Figures 2c–d shows SEM images of CNCs consisting of a higher concentration of AuNPs. The porosity of the composite allows ions to easily move through the nanocomposite, while the high concentration of AuNPs provides large gold–ion interfacial area. It is important to note that pores that are too small (on the order of the size of the mobile ions) will also reduce performance of the actuators by limiting the mobility of ions. An optimum structure has large enough pores to easily allow transport of ions and a dense enough electrically conductive structure to maximize CNC–ion interface and thus increase participation of ions in the actuation process.

Taking into account the approximate two-dimensional geometry of the IPMCs, with thickness significantly smaller that width and length, the sheet resistance of IPMCs containing different volume ratios of AuNPs was measured using the four-point-probe method. The measurements were carried out under 20–120 mV, using very low current flow (10–100 nA) to compensate for the relatively high resistance of the thin films. As expected, we found that the sheet resistance decreased as the concentration of colloidal gold was increased. This is due to the increased interconnectivity of the conductive particles. Figure 3 shows sheet resistance for IPMCs containing different concentrations of AuNPs. It is clear from these data that at relatively low concentration of AuNPs, the sheet resistance of the IPMCs is approximately equal to that of bare Nafion (no CNC), since the nanoparticles are too separate to allow electron transport between them. The insulating PAH polymeric network does not have a significant contribution to electrical conductivity of the thin film.

3.2. Mechanical response to electric field

In IPMC-based actuators, the largest portion of the strain is generated within the CNC layers. Fast motion of EMIm+ cations toward the cathode quickly generates a relatively small strain and causes the actuator to bend toward the anode. This quick and small cationic strain is then canceled by the slow moving Tf− anions or anionic complexes that are more effective in generating strain and bend the actuator toward the cathode. Given the larger
Van der Waals volume of EMI$^+$ cations, compare to Tf$^-$ anions, it is believed that charge clusters of negative net charge (e.g. Tf$^-$–EMI$^+$–Tf$^-$) are present in the electrolyte [24] and participate in the actuation process, which causes anions to be more effective in generating strain. Figure 4 shows the cationic and anionic strains generated by actuators consisting of CNCs based on 4, 10 and 20 ppm AuNP concentrations, in response to a step voltage of 4 V. Actuators consisting of CNCs based on 2 ppm AuNP concentration did not exhibit measureable strain. The cationic strain is quiet small since EMI$^+$ cations are not as effective as Tf$^-$ anions in generating strain, yet they show an increasing trend as the AuNP concentration is increased in the CNC. Since bending due to cationic motion is limited by the time required for anions to generate opposite strain, the larger cationic strain generated by CNCs with higher AuNP concentration (denser nanostructure) indicates that EMI$^+$ cations move quicker in denser CNCs. Although denser CNCs have higher capacitance, they also have significantly lower resistance which reduces the time required (time constant $\tau = RC$) for charging. Moreover, the larger CNC–ion interface in the denser CNCs reduces the screening of electric field by ions that have already moved into the CNC at any given time. Therefore, in the dense CNCs, during the first few seconds that the electric field is applied, a large number of EMI$^+$ cations respond to the electric field and participate in actuation process. Thus, the generated strain is larger compared to that in less dense CNCs for the same duration of time, which is the time before the cationic strain is canceled by anionic strain. As is shown in Figure 4, the magnitude of cationic strain for actuators with AuNP concentration of 20 ppm is more than 460% larger than that of actuators with AuNP concentration of 4 ppm. It is also evident from the same figure, that anionic strain is fairly constant for different samples, implying that all samples get fully charged by the same
Figure 4. Strain due to cations and anions as a function of AuNP concentration. Anionic strain is fairly constant, whereas cationic strain exhibits an increase with increasing AuNP concentration.

amount after significant time, also suggesting that there are approximately equal amounts of ions in each sample.

To further scrutinize the effect of the CNC density on the charging process, we measured the current flow during charging and discharging of the actuators as a function of time, to compare the charging/discharging times for actuators with different density CNCs. The mobility of ions within the IPMC can be modeled by complex resistor–capacitor (RC) circuits [13] in which the charging/discharging time constant depends on the product of the corresponding capacitance and internal resistance of different types of ions in the system. As shown in Figure 5, charging and discharging time constants are shorter for denser CNCs and the time constant is increased as the density of CNC is reduced. The observation that denser CNCs charge and discharge at a faster rate is in agreement with experimental strain measurements.

3.3. Frequency dependence of cationic strain

The frequency dependence of the electromechanical strain of the actuators was characterized under 4 V square-wave to study the influence of the density of AuNPs in the CNC layers on the time-dependent performance of actuators. Actuators with different CNC densities were subjected to a range of frequencies and mechanical strain was deduced from either radius of curvature or the tip displacement (where the radius of curvature was insufficient to measure). Since the bending is quite small under 1 and 10 Hz frequencies, the tip displacement was recorded, instead of radius of curvature, and was used along with the thickness and free length of the actuator to calculate the strain using Equation (2).
It is important to note that strains generated at all these frequencies are cationic strain as, in this set of actuators, anionic strain begins to dominate at a time longer than 10 seconds from application of electric field. Figure 6 shows the peak-to-peak cationic strain of actuators with different CNC densities in response to a 4 V step voltage at a range of frequencies. The strain is increased for lower frequencies as the cations are given more time to accumulate at the electrodes. Also, denser CNCs show larger strain at any frequency, again suggesting that denser CNCs charge at a faster rate. At 0.1 Hz frequency, cationic strain is increased by 64% when the AuNP concentration is increased from 4 ppm to 20 ppm.

4. Conclusion
We have successfully controlled and varied the AuNP concentration in CNC thin films with minimum thickness fluctuation and minimum effect on mechanical properties of the IPMCs. Varying the AuNP concentration in the CNC provides a means to control resistance and the CNC-ion interfacial area, which in turn influences the charging/discharging rate and the bending magnitude, respectively. Actuators with higher concentration of CNC exhibited faster charging/discharging rates and generated larger cationic strain. The larger cationic strain in denser CNCs is due to faster charging in such systems, which results in accumulation of more cations at the cathode before the cationic strain is canceled by anionic strain in the opposite direction. Such systems can be used in applications where fast response and optimum strain are desired. We presume there is an upper limit for the concentration of AuNPs, above which the performance of the actuator is no longer improving.
Figure 6. Cationic strain of actuators with different AuNP concentration in response to a 4 V step voltage at different frequencies. Cationic strain increases with increasing AuNP concentration and decreasing frequency.

At this limit, the CNC is expected to be closely packed thus increasing the concentration will not contribute to the conductivity of the CNC.

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References


