High electromechanical responses of ultra-high-density aligned nano-porous microwave exfoliated graphite oxide/polymer nano-composites ionic actuators

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High elastic energy density and high-efficiency ionic electromechanical actuators were prepared from aligned activated microwave exfoliated graphite oxide (A-aMEGO)/polymer nano-composites, and the electromechanical performance was characterized. The elastic modulus and elastic energy density of the ionic actuators can be tuned over a wide range by varying the polymer (poly (vinylidene fluoride/chlorotrifluoroethylene) [P(VDF-CTFE)]) concentration in the nano-composite actuators. The A-aMEGO/P(VDF-CTFE) nano-composite actuators with 35 wt.% of polymer content exhibit an elastic energy density higher than 5 J/cm\textsuperscript{3} and an electromechanical conversion efficiency higher than 3.5\%, induced under 4 V. The results show the promise of high-density highly aligned graphene electrodes for high-performance ionic electromechanical transduction devices.

\textbf{Keywords:} nano-porous activated microwave exfoliated graphite oxide (aMEGO); actuator; self-assembly; elastic modulus; elastic energy density

1. Introduction

Materials that can generate large strain with a high force level under an applied electrical signal are of great importance for applications such as artificial muscles, precise motion and position control, and micro-electromechanical systems (MEMS) [1–9]. The significance of these materials is especially more evident when they can generate large electro-actuation strain under a few volts, making them appealing for direct integration with advanced microelectronics and thus performing complex functions. In designing actuator devices from these materials, one has to pay special attention to not only the strain magnitude but also the force level the device can exert. In other words, generation of a large strain does not necessarily translate into high device performance. For instance, ionic polymer actuators such as gels and soft polymers that contain a high fraction of water can generate strains >50\% under a few volts. Nevertheless, a major constraint of these gel...
actuators for practical applications is their extremely low elastic modulus (<1 MPa) [10–12].

Our previous studies have revealed that a class of aligned activated ‘nano-porous’ microwave exfoliated graphite oxide (A-aMEGO) actuators with controlled nano-morphology can generate an electroactuation strain of more than 50% under a few volt electrical excitation [13]. The A-aMEGO actuators were fabricated by the aid of a modified self-assembly procedure and by using poly (tetrafluoroethylene) or poly (vinylidene fluoride/chlorotrifluoroethylene) (P(VDF-CTFE) as the polymer matrix in the system and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) solution in acetonitrile (AN) as the electrolyte. The principal actuation mechanism of these A-aMEGO actuators, as schematically illustrated in Figure 1, was believed to be due to the ingestion and/or depletion of the mobile ions in the nano-pores to compensate the changes in the electronic charges on the A-aMEGO electrodes under the external voltage. Due to a very high degree of alignment (orientation) of the aMEGO sheets and nano-pore sizes that match the sizes of mobile ions, this process caused changes in the inter-sheet spacing that resulted in the unique large anisotropy of the electroactuation strain in A-aMEGO actuators. Namely, the large strain was induced along the direction of the average surface normal to the graphene sheets, while in the directions perpendicular to that, the strain was more than 10 times small.

As was investigated in the aforementioned study, the electromechanical performance of the A-aMEGO/polymer nano-composite devices depends on several parameters, including voltage, scan rate, electrolyte type, polymer type, and concentration. Specifically, to improve the force generation capability of these devices, the elastic modulus of the nano-composites has to be improved since following Hooke’s law, the stress generated is proportional to the elastic modulus of the actuator material. It was shown that the nano-composite actuators with 10 wt.% P(VDF-CTFE) exhibited an elastic modulus of 67.5 MPa without actuation that reduced to about 9 MPa at 56.6% actuation strain under 4 V. As a result, the actuators showed an electromechanical conversion

![Figure 1](image_url)

Figure 1. (a) An illustration of ionic electroactuation in graphene sheets where the ingression of the mobile ions (blue circles, cations here) into the interlayer space upon the application of an external voltage generates large strain when the interlayer spaces are comparable to the mobile ion sizes. e⁻ represents the electron charges on the cathode (graphene sheets). (b) Schematic of the nano-morphology of highly oriented aMEGO sheets of an ionic actuator employing the actuation mechanism in (a), generating large electroactuation strain along the z-direction (‘thickness direction’).
efficiency about 1.5%, not as high as expected considering the large electroactuation strain and reasonably high elastic modulus of the nano-composites in the non-actuated state.

In the present study, we investigate the influence of the polymer matrix concentration in the nano-composites on the electromechanical response of the actuators. By increasing the polymer matrix concentration (reducing the volume content of the voids, which were originally occupied by electrolyte in the micro-, meso-, and macro-pores), the elastic modulus of the A-aMEGO/polymer can be improved. Therefore, although the strain level would decrease by an increase in the polymer content, elastic energy density and electromechanical efficiency of the actuator device may be improved. For this purpose, 10, 20, 35 and 50 wt.% of P(VDF-CTFE) copolymer was incorporated into the A-aMEGO/polymer nano-composites and the corresponding electromechanical performance were characterized. The results show that the electroactuation and force generation capabilities depend critically on the polymer concentration, and the electromechanical performance of the composite actuator show an optimum state at 35 wt.% P(VDF-CTFE) with an electromechanical conversion efficiency of more than 3.5%, very high among ionic electroactive polymer actuators.

2. Experimental and characterization

The synthesis of ‘nano-porous aMEGO’ is presented in detail in Ref. [14]. A modified vacuum-assisted self-assembly method was employed to fabricate the highly aligned nano-porous aMEGO sheets [13,15,16]. During the filtration process, nano-porous aMEGO and P(VDF-CTFE) layers are pulled toward the Anodisc surface and stacked successively on top of each other. In this study, 10, 20, 35 and 50 wt.% polymer was incorporated into the nano-composites.

To fabricate the ionic actuators, the A-aMEGO/P(VDF-CTFE) composites were swelled by a 2 M solution of [BMIM][BF₄] (Iolitec) in AN. Square-shaped A-aMEGO/P(VDF-CTFE) (40–60 μm thick) were cut and placed in an electrolyte bath at room temperature. After the nano-composites were completely infiltrated by the electrolyte (~30 min), the electroactuation and cyclic voltammetry (CV) performance were characterized. The electroactuation strain in the ionic A-aMEGO/P(VDF-CTFE) nano-composites was characterized in a configuration reported in the previous study [13]. For the actuation characterization, two A-aMEGO/P(VDF-CTFE) nano-composites of 2 × 2-mm lateral size and 0.05 mm thick (along the z-direction, Figure 1(b)) were bonded to the bottom of a Teflon sample holder filled with [BMIM][BF₄]/AN electrolyte. The Teflon sample holder has two square dishes of 2.2-mm diameter and 1-mm depth connected by a 1-mm-wide channel for the ion conduction between the two nano-composite electrodes. The two nano-composites served as two electrodes, and two tungsten pins with flat heads of 1.5-mm diameter were used as the current collectors, which were pressed lightly to the top surfaces of the two nano-composites. The positions (both lateral and vertical) of the tungsten electrodes were precisely controlled by micro-manipulators. The electroactuation strains in both the cathode and the anode were characterized using a fiber optic displacement sensor (MTI 2100 Fotonic) that has a resolution of 25 nm. The capacitance of the ionic A-aMEGO/P(VDF-CTFE) nano-composite actuators was measured with a potentiostat (VersaSTAT 4, Princeton Applied Research).

The Young’s moduli of the ionic A-aMEGO/ P(VDF-CTFE) nano-composites along the thickness (the z-direction in Figure 1(b)) under no applied voltage were measured using the Derjaguin–Muller–Toporov model from the data acquired with the nano-mechanical characterization mode (peak force tapping) of a Bruker Icon atomic force
microscope (AFM). The operation principle relies on the interaction of the modulated tip with the sample surface [17–19]. The elastic modulus of the nano-composite actuators under different applied voltages was characterized by measuring the change of the electroactuation strain under load along the z-direction (Figure 1). In this measurement, a load (0.025, 0.25, and 0.5 MPa) was applied to the composite sample and the thickness change due to the electroactuation was measured.

3. Experimental results and discussions

The electroactuation strain in the cathode of the ionic A-aMEGO/P(VDF-CTFE) nano-composites with [BMIM][BF4]/AN electrolyte was characterized under different voltage at a 50-mV/s scan rate. The strain magnitude was calculated from the following:

\[
\text{Strain} = \left( \frac{\text{Final thickness} - \text{Initial thickness}}{\text{Initial thickness}} \right) \times 100
\]  

(1)

Figure 2(a) represents a typical thickness electroactuation strain hysteresis loop of the nano-composite actuator (along the z-direction Figure 1(b)) with 10 wt.% of P(VDF-CTFE), measured at the cathode under 4 V. Figure 2(b) summarizes the cyclic

Figure 2. (a) An electroactuation cycle for A-aMEGO/P(VDF-CTFE) nano-composite containing 10 wt.% polymer as an example. Arrows indicate the strain direction. (b) Electroactuation strain on the cathode for the A-aMEGO/P(VDF-CTFE) nano-composites investigated at different applied peak voltages and 50-mV/s scan rate. (c) CV curves for A-aMEGO/P(VDF-CTFE) nano-composites at 50-mV/s scan rate at different polymer concentrations.
Electroactuation thickness strain of the A-aMEGO/P(VDF-CTFE) nano-composites of different P(VDF-CTFE) wt.% in the composites, measured at the cathode under different voltages. Similar to previously observed trend, the strain value in the thickness direction increases almost linearly with the voltage and reaches the maximum value at 4 V. However, the strains perpendicular to the thickness direction were negligible and had a sign opposite to that of the thickness strain. Such large electroactuation strain anisotropy is caused by the unique nano-morphology of the highly oriented nano-pores of the aMEGO sheets. Another evident trend in Figure 2(b) is the reduction of the strain value with increased polymer concentration in the composites. For instance, under 4 V, the strain is 56.6% for the nano-composite containing 10 wt.% polymer, its value drops to 43.2% for the nano-composite with 20 wt.% of P(VDF-CTFE), and it further decreases to 20.3% for the composite containing 50 wt.% polymer. This is understandable since the elastic modulus of the composite film increases with the polymer content due to the replacement of voids filled with ionic liquid inside the pores in the original composite with a much stiffer polymer matrix. In addition, the increased polymer in the nano-composites causes a reduction of the mobile ion mobility in the composite matrix, which reduces the excess mobile ion concentration in the electrodes under a given voltage and scan rate as shown in the CV curves in Figure 2(c). Although the strain magnitude decreases by increase in the polymer content, nevertheless, the increased elastic modulus improves the device performance in terms of force generation capability, elastic energy density, and electromechanical conversion efficiency, as will be discussed in the following.

The charge/discharge behavior of the A-aMEGO/P(VDF-CTFE) nano-composites was characterized using CV experiments under 4-V peak voltage and 50-mV/s scan rate. As depicted in Figure 2(c), the CV curves for the nano-composites are nearly rectangular, which is the indication of non-Faradaic charge transfer in A-aMEGO-based electrodes similar to the previous observations [13]. The CV curves also reveal that the specific capacitance for the composites decreases with the polymer concentration. This is comprehensible since by addition of the polymer matrix, the mobility of the mobile ions is reduced. Hence, the amount of the excess mobile ions stored in the porous electrodes under a given voltage and scan rate decrease, which is reflected in the specific capacitance values.

As mentioned earlier, strain generation is not the sole parameter in defining the electromechanical performance of an actuator device; the elastic energy density and electromechanical conversion efficiency are also critical parameters. The elastic energy density is used to characterize an actuator material’s strain and stress generation capability [1–3,20]. The strain by the electroactuation that changes the nano-composite thickness from the initial thickness \( l_0 \) to \( l \) under an applied voltage \( V \) can also be generated by applying a force \( F \) along the thickness direction \( (F = \sigma A) \), where \( \sigma \) is the stress and \( A \) is the nano-composite area that does not change with the applied voltage or stress due to the large elastic anisotropy of the A-aMEGO/polymer nano-composite. The total mechanical work \( W \) done by the external force, divided by the nano-composite initial volume \( (\text{Vol} = A \times l_0) \), is the elastic energy density stored in the nano-composite actuator. For materials with large strain, the mechanical stress is \( Y \times e \) where \( Y \) is the elastic modulus and \( e \) is true strain \( e = \ln(l/l_0) \). The work \( W \) done by the external force \( F \) is as follows:

\[
W = \int_{l_0}^{l} F \, dl
\]
Dividing $W$ by $\text{Vol} = A \times l_0$ yields [2,21,22] the following:

$$U_m = \int_{l_0}^{l} Y(x) \ln(x) \, dx$$  \hspace{1cm} (3)$$

which is the elastic energy density of the ionic A-aMEGO/P(VDF-CTFE) nano-composite actuators. The elastic energy density derived here is the total elastic energy density generated in the actuator, which is, in general, different from that delivered to an external load.

For the purpose of elastic energy density calculations, the elastic modulus $Y$ of the A-aMEGO/P(VDF-CTFE) nano-composites along the $z$-direction when the composite actuators were not actuated was characterized by an AFM using a tapping method [21,23]. Afterwards, the elastic modulus of the nano-composite actuators under different applied voltages was characterized by measuring the reduction of the induced strain under load along the $z$-direction. In this measurement, a load (a fixed weight) was applied to the composite sample and the thickness change due to the electroactuation was measured. Using the relation that the strain under a load (stress) is

$$S(\text{strain}) = S_0 - \frac{\text{load}}{Y}$$  \hspace{1cm} (4)$$

where $S_0$ is the strain generated under 4 V in the absence of the load and $Y$ is the elastic modulus at strain $S$, the elastic modulus $Y$ at $S$ can thus be deduced when $S$ is not far from $S_0$.

Figure 3(a) represents the strain data at the cathode side under 4 V for nano-composites with different polymer content under different applied loads. As expected, increasing the load value reduces the electroactuation strain. The data from this measurement were used to deduce elastic modulus (using Equation (4)) of the nano-composites in the actuation state under 4 V, which are presented in Figure 3(b). The results show that the elastic modulus of the nano-composites decreases with the actuation strain.

To deduce the elastic energy density of the nano-composite actuators from Equation (3), the dependence of the elastic modulus with the actuation strain ($Y(x)$) is deduced from the two data points in Figure 3(b) by assuming that the elastic modulus is a linear function of the

Figure 3. (a) Strain under different (0.025, 0.25, and 0.5 MPa) applied load. The error bars are not shown to have a clean graph. (b) Elastic modulus for A-aMEGO/P(VDF-CTFE) nano-composites at different polymer concentrations with and without electroactuation (at 4 V).
strain \( Y = Y_0 - a \times \text{Strain} \), where \( a \) is a coefficient that is determined from the two data points in Figure 3(b). The elastic energy density of the nano-composite actuators with different polymer content thus derived is presented in Figure 4(a), which shows that the elastic energy density increased with the polymer content and reaches a maximum for the nano-composites with 35 wt.% P(VDF-CTFE), which is >5 J/cm³. On the other hand, the nano-composites with 50 wt.% P(VDF-CTFE), due to the reduction of the strain, show an elastic energy density of 2.2 J/cm³. The input electric energy density is deduced from the CV curves in Figure 2(c), and the ratio of elastic energy density and the input electric energy density yields the electromechanical conversion efficiency, which is presented in Figure 4(b). The nano-composites with 35 wt.% of P(VDF-CTFE) exhibited an electromechanical conversion efficiency of 3.7%, owing to the combined effect of a higher actuator elastic energy density and reduced input electric energy density compared with the nano-composites with 10 and 20 wt.% P(VDF-CTFE).

It should also be noted that the elastic energy density deduced in Figure 4(a) is the total stored electric energy density in the actuator device, which is different from that of the actuator delivers to an external load. For example, under 0.5-MPa load, the A-aMEGO/P(VDF-CTFE) with 10 wt.% polymer shows an electroactuation strain of 50%, which translates to a work density of 0.25 J/cm³, which is different from the intrinsic elastic energy density presented in Figure 4(a). The result indicates that the work that an electroactuator delivers to a load will depend on the load condition.

As depicted in Figure 4(a), the elastic energy density increases by increasing polymer concentration. This can be attributed to the increase in the elastic modulus of the nano-composite with P(VDF-CTFE) content. Nevertheless, the increase in the energy density reaches a maximum value at 35 wt.% polymer and afterwards its value diminishes. Since the energy density is a function of both elastic modulus and strain, and given that usually an increase in one results in a decrease in the other, this observation is expected. Although the nano-composites with 50 wt.% polymer exhibit the highest modulus amongst all, however, this does not compensate the significantly reduced strain value for this specific composition and hence the elastic energy density is reduced. Very similar behavior was observed for the efficiency of the nano-composite, with the highest efficiency for the sample with 35 wt.% polymer. This again is related to the highest elastic energy exerted by this sample per unit value of the consumed electric energy, calculated form the CV
curves. The elastic energy density and efficiency values for A-aMEGO/P(VDF-CTFE) nano-composites are among the highest for ionic actuators performing under voltages lower than 4 V. The high performance features of the A-aMEGO actuators render them potentially valuable systems for MEMS applications.

4. Conclusions
In this study, the electromechanical performance of A-aMEGO/P(VDF-CTFE) nano-composite ionic actuators was investigated and optimized by varying the polymer concentration in the composites. Under 4-V applied voltage, the nano-composites with 10 wt. % polymer exhibited the highest strain of 56.6% and the lowest elastic modulus of 67.5 MPa, whereas the nano-composites with 50 wt.% polymer showed the lowest strain of 20.3% and highest elastic modulus of 218.0 MPa. Similar trend was observed under 3 and 2 V. The actuation mechanism was due to ingress and/or depletion of excess mobile ions into/from the nanometer-sized pores of the aligned graphene sheets in response to the external applied voltage. The trade-off of the actuation strain and elastic modulus with the polymer content in the nano-composites results in a maximum elastic energy density for nano-composites with 35 wt.% polymer content, which also exhibits the highest electromechanical conversion efficiency of 3.7%, among the nano-composites studied.

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