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Characterization of the Blocking Force Generated by Buckypaper Composite Actuators

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CHARACTERIZATION OF THE BLOCKING FORCE GENERATED BY BUCKYPAPER COMPOSITE ACTUATORS

By

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ABSTRACT

Lightweight composite actuators with large bending displacement and high blocking force have great potentials for various engineering applications. Carbon nanotube thin film or Buckypaper-based composite actuators (BCAs) have been developed and tested in an open air environment to demonstrate their use as electromechanochemical actuation devices. The actuator is a bimorph structure fabricated with Nafion, a solid electrolyte layer capable of ion diffusion, sandwiched between two buckypaper (BP) electrode layers. Actuation mechanisms were studied, revealing that ionic current flow is the major actuation mechanism. To further improve actuation performance, Nafion doping has been studied. LiCl and Imidazolium (IL) solutions have been used to dope the Nafion and both cases have demonstrated substantial increases of BCA displacement. With the dimensions of the BCA held constant (30 mm × 5 mm × 0.07 mm), a non-doped BCA with a 3 V stimulation input at 200 mHz only can generate a total bilateral displacement of up to 0.09 mm; but LiCl-doped and IL-doped BCAs can produce ×100 and ×150 more displacement than that of the non-doped BCAs, respectively. The effect of driving voltages and frequencies with respect to displacement and blocking force generation of IL-doped BCAs were characterized. BCA thickness variation was introduced to evaluate the effect of the BCA structure on actuation performance. The improved BCAs have achieved a maximum strain and stress of 0.1% and 0.175 MPa, respectively. This is comparable to other polymer-based actuators. Finally, a preliminary model of BCA blocking force estimation was proposed to predict and further optimize the BCA actuation properties. The predicted results of the model are in agreement with the experimental data.
CHAPTER 1

INTRODUCTION

An actuator, by definition, is a servomechanism that supplies and transmits a measured amount of energy for the operation of another mechanism or system [1]. An actuator is typically a mechanical device that takes energy, usually created by air, electricity, or fluid, and converts it into some form of motion. More importantly, it can also be used to apply force. That force induced motion can accomplish anything from blocking to clamping and ejecting.

Actuators are widely used for industrial applications in our everyday lives. They can be used to effectively functionalize motors, pumps, switches, and valves. Figure 1 shows some examples of common actuator systems.

![Figure 1: Common Actuator systems: (a) Natural Muscle, (b) Hydraulic, and (c) Pneumatic [2] [3].](image)

As shown in Figure 1, common actuator systems include some form of energy transformation or conversion. Natural muscle provides up to 1000 Joules of work per gram of glucose consumed [4]. The brain sends electrical signals to each muscle via the neurometer junction. The operation of muscles depends on chemically driven reversible hydrogen bonding between two polymers, actin and myosin. The actuation energy is provided by a chemical-free energy of a reaction involving adenosine triphosphate (ATP) hydrolysis. The release of Ca\(^{2+}\) ions is responsible for turning on and off the conformational changes associated with muscle striction [4].

In hydraulic actuation systems, high pressure liquid (hydraulic fluid) is transmitted throughout the machine to various hydraulic motors and cylinders. The fluid is controlled by
control valves and distributed through hoses and tubes. As demonstrated by most tractor backhoe-loaders, shown in Figure 1(b), they are capable of very high power densities [3].

Pneumatic actuation systems, shown in Figure 1(c), are based on the use of gas as the medium for power transmission, generation, and control. The energy stored in compressed air is used to drive mechanisms. To control the air flow and pressure, various compressors and pumps are used. Pneumatic actuators are generally preferred over hydraulic actuators because hydraulic oil and devices can prove costly; it also requires major efforts to check for leakage if problems arise [2]. Conversely, the air used to power pneumatic actuators is free.

There are also lesser known actuation systems. Some materials with actuating properties are known as smart materials. Existing smart materials, such as piezoelectric ceramics, electro-active polymers, and shape memory alloys, have various limitations that hinder them from practical applications [5]. One of the major limitations is the excess of voltages and currents that are required to generate strain or deformation. The materials are either brittle, heavy, or have a small range of actuation strain. Of all the smart materials, carbon nanotubes (CNTs) are the strongest and most flexible nanostructured materials known due to their unique C-C covalent bonding and seamless nanoscaled hexagonal network. The combination of both high electrical conductance and large surface area possessed by CNTs provide unique opportunities to create a composite material with even greater actuation capabilities in addition to multifunctional properties uncommon to other materials.

Carbon nanotube thin film or Buckypaper-based composite actuators (BCAs) have been developed and tested in an open air environment to demonstrate their use as electromechanochemical actuation devices. As shown in Figure 2 (a) and (b), the actuator is a bimorph structure fabricated with Nafion, a solid electrolyte layer capable of ion diffusion, sandwiched between two buckypaper (BP) electrode layers. Actuation mechanisms were studied, revealing that ionic current flow is the major actuation mechanism [6].
Unlike hydraulic and pneumatic actuators, electricity is used to drive mechanical deformation in BCAs via ion flow. Figure 2 (a) shows that a BCA bends towards the anode. Being that anions are in a naturally fixed position within the Nafion structure and cations are mobile, cations are majorly responsible for actuation movement. During electrical stimulation, with a suddenly applied potential, both the fixed anions and mobile counter-ions are subjected to an electric field, with the counter-ions being able to diffuse toward one of the electrodes [7]. This capability allows cations to become excited and move towards the cathode. Subsequently, when a copious number of cations overload the inner cathode surface, mechanical expansion is provoked substantially on one side of the BCA. As a result, the composite undergoes an initial bending deformation. This is due to the composition of the backbone ionomers in Nafion and the nature of counter-ions. Figure 2 (b) more closely shows the path in which ions travel during electrical excitation. More specifically, it also shows that H\textsuperscript{+} ions are the driving sources of swelling and subsequent cathodal expansion.

Purchased from DuPont, Nafion NRE – 212 is the electrically conducting polymer membrane used as the medium between two Single-wall nanotube (SWNT) BP strips. This polymer was chosen for its proven ion mobility and environmental stability. SWNTs were purchased from Thomas Swan and used in the fabrication of BP sheets. SWNTs are an ideal material to make electrodes (BPs) because of its unusually high aspect ratio as well as its electrical, mechanical, and chemical characteristics [8]. Electrical conductivity, thickness and area density of the SWNT buckypaper are 400 S/cm, 15 µm, and 20-30 g/m\textsuperscript{2}, respectively. As shown in Figure 3, Nafion was sandwiched between two BP layers and hot-pressed at 250°F while exposed to a pressure of 120 psi for 10 minutes.
Figure 3: BCA Fabrication Process.

Figure 3 also shows that a Nafion liquid solution was spread onto the BP and Nafion to help completely fuse the strips and form a composite. Compared to other electroactive polymer and CNT-based actuator fabrications [9] [10] [11] [12] [13], the BCA manufacturing process is much simpler and less expensive.

Figure 4 shows the test setup required to measure BCA bending displacement. An Agilent Model 33220A function generator is used as the DC Power Source. Voltage settings range from 0-30 V. All selected voltages are capable of being set at frequencies from 1 μHz to 20 MHz. The Agilent model used primarily functions as a cyclic voltmeter. If 10 V is chosen to manipulate the sample, a square wave potential of +/- 10 V is applied. It essentially promotes bimorph type movement by oscillating applied voltage.
Figure 4: Test setup of BCA displacement measurement

Figure 4 also shows that an MTI Microtrak II laser displacement sensor is used to record the actuation deformation. It is capable of recording up to 16 mm of total displacement. Displacement beyond this point is out of measurement range and cannot be recorded. This high resolution laser displacement sensor is designed to monitor the small displacement generated by a CNT actuator. As shown in Figure 5, the high resolution laser sensor can successfully measure BCA displacement.

![Graph showing SWNT BCA bending displacement at 3 V and 200 mHz](image)

Figure 5: SWNT BCA bending displacement at 3 V and 200 mHz

Figure 5 shows that during 3 V and 200 mHz excitation, the BCA can generate 0.09 mm of total bending displacement. It also shows that the BCA is susceptible to performance drifting or ion instability.
Furthermore, we need to measure blocking force generation of BCAs. The magnitude of force that the BCA can generate will determine application potential for all BCAs, such as morphing structures and driving devices. Figure 6 reveals the concept behind blocking force by fixing a rigid object against a moving actuator or BCA.

![Diagram of blocking force measurement concept using BCA and rigid load-cell.](image)

Figure 6 shows an enlarged BCA generating a potential force F against the rigid load-cell at 3 V. If no load-cell was present, 0.09 mm of displacement would be generated, as shown in Figure 5. Since the load-cell is present and rigid, an equal but opposite counter-force P is experienced by the BCA, causing the generated displacement to alternatively become 0 mm. However, the energy is not lost; it is simply transformed into a quantifiable amount of force that is blocked by the rigid load-cell. This measured counter force is the blocking force that the BCA can potentially generate.

In this research, a systematic characterization of the displacement, material, and force properties of BCAs has been conducted. BCA performance characterization also included the effects of input voltage and frequency variation; improvements of actuation performances through Nafion-doping; and the effect of BCA geometry as well as preliminary model development of blocking force.
CHAPTER 2

PROBLEM STATEMENT

Scientists dedicated to the specialization and study of smart structures have been trying to overcome limitations involving strain and/or force generation by smart materials [14]. Of all the smart materials, carbon nanotubes are the strongest and most flexible molecular material known due to the unique C-C covalent bonding and seamless nanoscaled hexagonal network. Though nanoscale properties are impressive, successfully replicating its superb properties in the macroscale may prove to be a challenge. We have studied BCAs for potential light weight morphing structure and actuation device applications [6] [15] [16]. The BP sheets are made by using a filtration system developed at HPMI [17] [18]. By using BP as the electrode layer and reinforcing material for BCAs, 5 of the 9 requirements for lightweight actuators have been achieved for creating a working actuator with adequate actuation performance. Table 1 shows a comparison of BCA properties with actuator requirements.

Table 1: Comparison of BCA Capabilities with desirable Actuation Characteristics of Lightweight Actuators

<table>
<thead>
<tr>
<th>Good Actuator</th>
<th>BCA at HPMI</th>
</tr>
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<tbody>
<tr>
<td>Low power consumption</td>
<td>✔️</td>
</tr>
<tr>
<td>Lightweight</td>
<td>✔️</td>
</tr>
<tr>
<td>High electrical conductivity</td>
<td>✔️</td>
</tr>
<tr>
<td>Durable</td>
<td>✔️</td>
</tr>
<tr>
<td>Repeatability</td>
<td>✔️</td>
</tr>
<tr>
<td>Good mechanical properties</td>
<td>✔️</td>
</tr>
<tr>
<td>&gt;50% Strain generation</td>
<td>X</td>
</tr>
<tr>
<td>High Frequency Response</td>
<td>✔️</td>
</tr>
<tr>
<td>Force &gt; 0.5 N</td>
<td>X</td>
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<table>
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<tr>
<td>High electrical conductivity</td>
<td>✔️</td>
</tr>
<tr>
<td>Low durability</td>
<td>X</td>
</tr>
<tr>
<td>Repeatability</td>
<td>✔️</td>
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<tr>
<td>Poor mechanical properties</td>
<td>X</td>
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<tr>
<td>&lt;7% Strain generation</td>
<td>X</td>
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<tr>
<td>~40 Hz excitation maximum</td>
<td>✔️</td>
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<tr>
<td>Force &lt; 7 mN</td>
<td>X</td>
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</table>
Table 1 also shows the shortcomings of current BCAs. The lack of BCA durability shortens performance life-cycle time. Low BCA mechanical properties limit its performance potential. BCA strain generation and subsequent blocking force exertion could also stand for improvement.

### 2.1 Low Material Durability

In the nanoscale, a single CNT is extremely durable because of its strong and perfect molecular structure. In the macroscale, when many CNTs are dispersed together and filtered to make buckypaper (BP), BP properties are significant reduced. BP has a brittle characteristic that prevents excessive deformation. MWNT BP is even more brittle than SWNT BP due to much smaller aspect ratios. Once a crack or fracture has occurred in the BP, it usually leads to significant performance degradation. To effectively utilize the CNT actuation potential, a composite needs to be created to ensure sufficient durability for actuation applications.

Voltage limitations are also present. To exhibit movement, a large amount of voltage is usually required. When too much voltage is applied, the BP sample burns and reduces material properties. For instance, high voltages (|V| > 10V) are usually avoided to prevent bubbling generations due to electrolyte burning. Such tiny bubbles on the surface of a working CNT BP strip due to electrolyte burning can lead to delamination and/or cracking, hence significant reduction of the voltage output into the actuating system will further degrade sample performance [19].

### 2.2 Poor Mechanical Properties

BCAs require an electrolyte in order to function properly. Electrolytes allow ion transfer to take place and stimulate both C-C bond deformation within BP and swelling within the electrolytic polymer. The electrolyte chosen is called Nafion, which is a relatively weak polymer film material. However, the mechanical properties of the Nafion membrane are suspect in restricting potential bending displacement generation and mechanical properties of BCAs. The experimental stresses generated by current BCAs are subsequently insufficient.
2.3 Insufficient Strain Generation

A good actuator is capable of >50% strain generation as demonstrated by most pneumatic, hydraulic, and natural muscle actuators. BCAs are currently capable of ~0.1% strain generation on average, depending on the input voltage and frequency. Governing factors of strain generation need to be analyzed in order to determine the best technique for realizing actuation performance enhancement. It is believed that subjecting ionic doping methods to the ionic membrane (Nafion) may prove successful in promoting larger strains \[20\]. A more deformable or thin CNT network (BP) may also be desired to obtain higher strain values. Studies concerning strain enhancement methods have yet to be conducted in order to determine how much influence that ionic doping can have on BCA strain generation potential.

2.4 Insufficient Stress and Force Generation

The baseline requirement for actuator performance is solely dependent on the application or function for which it is intended to perform. However, for an actuator to be considered for most applications, it should be capable of outputting a force greater than 0.5 N \[21\]. Figure 7 shows that a pneumatic actuator is capable of about 1 MPa of stress generation while sustaining large strains.

Figure 7: Stress and Strain actuation comparison for various actuation devices \[22\].
Figure 7 also shows that Ionic polymer membrane composite actuators (IPMCs), which like BCAs, incorporate CNTs are also capable of the same amount of stress, if not more. IPMCs generally incorporate platinum (Pt) particulates by Pt electrode sputtering or plating [23]. Platinum is used as the electrode material for its high electrical conductivity. In this particular case both Pt and M-CNTs were used to combine property performance enhancement. The Blue area highlighted in Figure 7 represents the performance potential that a BCA may be capable of. Studies have not yet been conducted to determine how much force a BCA can generate. Though different test methods have been used, it should be noted that there is no standard method for measuring blocking force [4].
An actuator is a mechanical device used for moving or controlling a mechanism or system. Actuators have been around for many years and are used every day. Some commonly known actuators include hydraulic and pneumatic actuators. Such actuators tend to be very cumbersome and involve many parts; hence a substantial amount of energy is required to run these mechanisms. A more efficient and lightweight actuator is in need. Analyzing and demonstrating the true potential of BCAs is an attempt to develop this new desired actuator type. A good actuator should be able to generate high displacement values at minimal applied voltages, high range frequencies and output substantial amounts of force. If lower voltages are achieved for significant displacement, less energy is consumed. This is important for many aerospace applications and other portable devices. High range frequencies are desired for actuators in the aerospace industry. If aircrafts can utilize energy as birds do, a considerable amount of money can be saved on fuels and less air pollution would be expected. Since birds use little energy to fly at great distances, the aircraft actuator wings should ideally require low amounts of electricity to power [20] [24]. Biomimetic studies have shown that a bird’s wing beat can be as low as 2.5 Hz and as high as 12.3 Hz depending on the bird’s mass and wingspan [24]. A computer generated image from DARPA of a futuristic actuator application is shown in Figure 8.
Figure 8: Computer generated image of a futuristic actuation based flight mechanism for advanced aerospace applications.

If a large scale actuating wing that has the ability of achieving high frequency and large displacement actuation is developed, a bird-like high-performance aircraft could potentially be achieved. CNT BPs have high electrical conductivity, large surface area and are lightweight; hence they have the potential for developing high-performance actuators.
CHAPTER 4

OBJECTIVE

The objective of this research is to further exploit and improve the potential actuation properties of BCAs. Maximizing BCA strain generation and force output while minimizing the BCA energy consumption are major goals. The objectives and research tasks are detailed as follows:

- Study mechanisms and models of displacement and blocking force
- Characterize BCA displacement generation:
  - Effect of electrolyte doping
  - Effect of voltage
  - Effect of Nafion thickness change
  - Effect of frequency
- Characterize ionic liquid-Doping effect on Nafion:
  - Mechanical properties
  - Ionic conductivity
- Characterize the force generation of various BCAs:
  - Effect of Nafion thickness change
  - Effect of voltage change
- Validate blocking force model
- Reveal governing factors for the force generation
CHAPTER 5
LITERATURE REVIEW

Nanotubes have the highest current density capability of any known material, measured as high as \(10^9\ \text{A/cm}^2\) [25]. Due to its high current-carrying capabilities, high conductance and nanoscale, it is an ideal candidate for future nano-electronics [26]. Particularly, CNTs have the potential to make high-performance electrodes because of its unusually high aspect ratio as well as its electrical, mechanical, and chemical characteristics [27].

5.1 Carbon Nanotube Actuation

The ideal actuator material would operate at low voltage and at least match the performance of skeletal muscle: typical 20% strain; 0.35 MPa stress generated; and 10% \(\text{s}^{-1}\) strain rate [14]. Several low voltage actuator materials, including gels and conducting polymers, are capable of meeting and even exceeding the first two requirements, but only high voltage electrostrictive elastomers come close to matching the strain rate of natural muscle [28]. Carbon nanotubes (CNTs) also demonstrated the potential for developing high-performance actuators.

5.1.1 CNT Artificial Muscle

Dr. Ray Baughman and his team at UT Dallas have developed an actuator capable of surpassing the functionalities of a human muscle [29]. The artificial muscle is composed of CNT networks. The actuator elongates 10 times that of natural muscle at a rate 1,000 times faster. The frequency of a human muscle is about 20-40%/s while the abilities of this artificial muscle approach 30,000%/s [29]. It is also capable of 15% lateral contraction and operates at extreme temperatures. There are not many smart materials that are functional in temperatures as low as -196°C and as high as 1,538°C [29]. However, the amount of power required to run this actuator is 5kV [29]. If it is truly meant to be an artificial muscle, it should be able to be powered by at most a standard AA battery. In addition, the force output generated is not significant enough for physical weight bearing movement to take place.
5.2 Electro-active polymers

At Inha University, a cellulose based electro-active paper (EAPap) has been discovered as a smart material. It is distinguished for its lightweight, biodegradable, low price, large bending displacement, low power consumption, and piezoelectric abilities [30]. EAPap actuators are made with regenerated cellulose paper. Very thin (100 nm) gold electrodes are vacuum plated on both sides of cellulose paper. Figure 9 shows the general design of the EAPap actuator.

![Figure 9: Schematic diagram of the cellulose EAPap. [30]](image)

As shown in Figure 9, a large bending displacement is produced when an electric field is applied across the thickness direction of the paper [30]. The actuation principle of EAPap actuators is associated with the combined effects of piezoelectricity and ion migration. Unfortunately, the actuation performance is sensitive to environmental conditions. The force output and frequency bandwidth are also limited, as shown in Figure 10. Hybrid EAPap that is coated with conducting polymer has been studied to improve its bending displacement and blocking force [30]. To increase the frequency bandwidth and blocking force, carbon nanotubes have been mixed into the cellulose [30]. The 10% CNT loading improved the stiffness and conductivity of the EAPap.
As shown in Figure 10, increasing the applied electric field from 0.05V to 0.3V improved the bending displacement from 0.69 to 3.3 mm. The magnitude of displacement is directly proportional to the applied electric field. Though acceptable displacement was generated, results are inconsistent due to environmental influences.

The displacement was reduced from 4.8 to 0.13 mm on decreasing the humidity level from 90%RH to 50%RH [30]. The possible reason may be due to the cellulose electrolyte being sensitive to moisture. It is undesirable to have an actuators performance dependent on the relative humidity.

5.2.1 Bucky Gel Actuator

The University of Tokyo reported that the first dry actuator could be fabricated through layer-by-layer casting, using ‘bucky gel’. Bucky gel, as shown in Figure 11, is a gelatinous room-temperature ionic-liquid containing a 10% loading of SWNTs. The ionic liquid used is an Imidazolium solution with C$_3$H$_4$N$_2$ cations and BF$_4^-$ anions within. The gel used allows for reasonable flexural rigidity along with large bending displacement potential [31]. It is fabricated by hot-pressing the prepared electrode and electrolyte layers together. The actuator has a bimorph configuration with a polymer-supported bucky gel electrode layer. This allows for quick and lasting actuations in dry environments at low applied voltages.
Figure 11: Schematic illustrations of the actuator strip composed of a polymer-supported ionic-liquid electrolyte layer sandwiched by bucky-gel electrode layers, and experimental setup for cantilever bending of displacement measurement (a) and force measurement (b) [31].

Similar to Figure 11, the bending response is considered to take place by the dimensional changes of both electrodes in response to alternative voltages. When a voltage is applied between two electrode layers, cations and anions in the gel electrolyte layer are transferred to the cathode and anode layers, respectively. This forms an electric double layer with negatively and positively charged nanotubes. It is suspected that these ion transports result in swelling of the cathode layer and shrinkage of the anode layer. This causes the actuator to bend towards the anode side. As shown in Figure 12, the generated strain and curvature of the bucky gel actuator were measured and analyzed.
By comparing the area of the charging current profile for each actuator strip, it was determined that the amount of SWNTs in the electrode layer may have influenced the actuator performance. The curvature curve shows that the actuator bent towards the anode side quickly when applying the voltage. The curvature of thinner actuator strips was larger and faster than that of thicker one. Ultimately, the larger force was generated by the thicker bucky gel electrode layer. Unfortunately, the highest measured force generated was less than 0.04 N; much less than expected as shown in Figure 12 (c).

This low-voltage driven solid-state actuator shows a maximum stress of 4.7 MPa and a maximum stain of 1.9% [31]. These results are comparable with other similar low-voltage driven solid-state electroactive polymer actuators. The advantage of the bucky gel actuator is its good actuation performance and the ease in fabrication.

### 5.3 Ionic Polymer Metal Composite Actuator

This actuator type is an electro-active polymer, typically comprised of a pair of electrodes attached to opposite surfaces of an ion exchange membrane [20]. Similar to BCAs, the principle of IPMC actuation has been explained by the immigration of hydrated cations [20].

The IPMC is fabricated by first casting an ionic polymer membrane such as Nafion. The Nafion is then treated using a chemical oxidation-reduction reaction method to help create an electrode surface that will surround it. The IPMC fabrication procedures are shown in Figure 13.
Figure 13: Nafion casting procedure and IPMC fabrication process [20].

Figure 13 also shows that Li$^+$ cations are selected to replace the original H$^+$ cations via ion exchange. The ion exchange process has been carried out to improve IPMC performance [20]. After creating the IPMC actuator, force characterization tests were conducted. Figure 14 shows a schematic of the blocking force test setup.

Figure 14: Schematic diagram of blocking force test setup [20].
As seen on Figure 14, a bending beam load cell is used to record the blocking force generated by the IPMC actuator. The blocking force is mainly dependent on the thickness, width, and length of the IPMC [20]. Figure 15 shows the blocking force associated with various actuator geometries.

![Figure 15: Blocking force with varying IPMC length (a), width (b), and thickness (c) [20].](image)

The blocking force exhibited at various actuator lengths while keeping width and thickness constant is shown in Figure 15 (a). The shorter lengths exhibit the larger blocking force. This is because short actuators are generally stiffer than long actuators in these cases. The blocking force of varying actuator widths while keeping length and thickness constant is seen in Figure 15 (b). Increasing actuator width directly increases the magnitude of generated blocking force. This has proven true because additional width provides an increase in actuator stiffness. It also presents a larger surface area for improved electrical excitation potential. Figure 15 (c) shows

\[ F = (wt^2/L)^c \]

(w) Width  
(t) Thickness  
(L) Length  
(F) Force  
(c) constant

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\[ F = (wt^2/L)^c \]

(w) Width  
(t) Thickness  
(L) Length  
(F) Force  
(c) constant
that increasing the actuator thickness while keeping length and width constant prove to be the most effective way of increasing the generated blocking force. A large IPMC blocking force of 6.4 gf was achieved using an actuator with a thickness of 1.05 mm. Increasing the thickness directly increases the actuator stiffness, which in turn helps to exhibit larger generated force. The results exemplify the effects of geometrical changes on force generation. An actuator with a short length, large width, and large thickness may prove to be the most viable option for a high force generation application.

### 5.4 Blocking Force Estimation Model

To further analyze the governing factors involved in cantilever-style bending actuator force generation, each actuator component must be modeled. Figure 16 shows a diagram of a cantilever-style bending actuator, displaying various material property components [31].

![Diagram of cantilever-style bending actuator displaying various material property components](image)

Figure 16: Diagram of cantilever-style bending actuator displaying various material property components [31].

The diagram in Figure 16 also shows that the strain experienced by each electrode is generated in the opposite directions; this is what causes the actuator to bend. $E_1$ and $E_2$ are the moduli of the electrode (BP) and electrolyte (Nafion), respectively. Also, $h_1$ and $h_2$ are the thickness values of
the electrode (BP) and electrolyte (Nafion), respectively. These components are important because they help to determine the magnitude at which the BCA can deform.

5.4.1 Curvature

Measuring the generated curvature value of an actuator is a widely practiced method to determine the magnitude of BCA deformation [7] [31]. Since during electrical stimulation, the BCA bends as if it were a cantilever beam, a cantilever beam mechanics model can be used to calculate BCA curvature.

5.4.1.1 Cantilever Beam Mechanics Model

The inverse of curvature is known as the radius of curvature. In solid cantilever beam mechanics, the curvature of a beam is calculated using Equation (5.1) [7]:

\[
\text{Curvature} = \frac{1}{R} = \frac{1 + \left(\frac{dy}{dx}\right)^2}{\frac{d^2y}{dx^2}}
\]

(5.1)

Where the parameters are defined in Figure 17. If a beam was bent at a certain magnitude or distance, it would form the shape of what would be a segment of a circle. The radius of that segment can be determined by finding the distance from the origin of the circle to the neutral axis (N) or \(\frac{1}{2}\) the BCA thickness. By using the components displayed in Figure 17, the curvature generated by the BCA can be determined.

![Diagram of key components involved in curvature calculation methodology][7]

Figure 17: Diagram of key components involved in curvature calculation methodology [7].
Similarly, modeling of BCA curvature can be achieved by using both the components in Figure 17 and Equation (5.1). The major assumption by using cantilever-beam mechanics to solve for curvature is that the beam is a homogenous material, such as metals and polymers. It does not account for the variations in material modulus and subsequent thickness in composite based actuators as shown in Figure 16.

5.4.1.2 Composite Actuator Model

In order to properly account for the BCA being a composite actuator using two different materials with two different moduli, another equation has been introduced to accurately calculate the actuators generated radius of curvature. The alternative method of calculating the radius of curvature generated by an actuator can be achieved using Equation (5.2). The measured displacement $\delta$ was transformed into the curvature ($1/R$) by using the following equation on the assumption that the cross-sections are plane at any position along the actuator and that there are no distortions of the cross-sections [31]:

$$\frac{1}{R} = \frac{2\delta}{L^2 + \delta^2}$$  \hspace{1cm} (5.2)

Where (R) is the curvature radius and (L) is the free length of the actuator strip as shown in Figure 11.

5.4.2 Moment of Inertia

By definition, moment of inertia is the term given to rotational inertia. It is also known as the rotational analog of mass for linear motion. It is essentially a dynamic relationship derived for rotational motion.

5.4.2.1 Cantilever Beam Mechanics Model

Given a rectangular cross-section, like that of the BCA, the area moment of inertia can be calculated by the following Equation (5.3):

$$I = \frac{wt^3}{12}$$  \hspace{1cm} (5.3)
Where I is considered the area moment about the free length of the actuator, w is the actuator width and t is the total beam thickness [7]. The classical cantilever beam model (5.3) assumes that there are homogeneous and isotropic material properties throughout the entire actuator.

5.4.2.2 Composite Actuator Model

With reference to the diagram of key BCA material components shown in Figure 16, the area moments of inertia of the BP layers (I₁) and Nafion layer (I₂) are given by:

\[
I_1 = \frac{2w(t_{\text{Nafion}}/2 + t_{\text{BP}})^3}{3} - \frac{2w(t_{\text{Nafion}}/2)^3}{3} 
\]

\[
I_2 = \frac{2w(t_{\text{Nafion}}/2)^3}{3} \quad (5.4)
\]

\[
I_2 = \frac{2w(t_{\text{Nafion}}/2)^3}{3} \quad (5.5)
\]

The variables t_{BP} and t_{Nafion} are considered to be BP and Nafion thickness, respectively. As used for Bucky-Gel electrodes [31], Equation (5.4) and (5.5) can also be used to estimate the potential area moment of composite actuators.

5.4.3 Strain

By definition, strain \( \varepsilon \) is the geometrical measure of a deformation ratio representing the relative displacement of a material or sample. In this case, the amount of extension or compression along the BP electrodes is relatively small due to low voltage induction.

5.4.3.1 Cantilever Beam Mechanics Model

The modulus and thickness of the actuator are critical variables for actuator performance. The equivalent stiffness EI of the actuator can be calculated by using Equation (5.6):

\[ EI = E_T \times I_T \quad (5.6) \]

Where variables \( E_T \) and \( I_T \) are the total actuator modulus and area moment of inertia, respectively. The actuators max strain \( \varepsilon \) can be calculated by using Equation (5.7):
Variables $t$ and $\rho$ are the actuators’ total thickness and maximum radius of curvature, respectively. Equation (5.7) assumes that through thickness properties are uniform.

### 5.4.3.2 Composite Actuator Model

The following equation is used to account for the flexural rigidity $EI$ of the whole actuator \( [31] \):

$$EI = E_{bp} I_{bp} + E_{Nafion} I_{Nafion} \quad (5.8)$$

Provided that the radius of curvature $R$, and the numerical values of the other parameter in Figure 16 are known, the generated strain $\varepsilon$ is given by the following Equation \([31]\):

$$\varepsilon = \frac{EI}{RE_{bp} wt_{bp} (t_{bp} + t_{Nafion})} \quad (5.9)$$

### 5.4.4 Blocking Force

Blocking force (F) can be treated as the external force needed to block the bending displacement of the actuator tip \([31]\). Additionally, the force $F$ is the final force measured upon activation of the BCA to ensure maximum blocking force potential has been met.

#### 5.4.4.1 Cantilever Beam Mechanics Model

The maximum moment resisting movement of the beam occurs at the rigid clamp with the maximum stress occurring according to Equation (5.10).

$$M = \frac{EI}{R} \quad (5.10)$$
Where \( M \) is considered the moment about a rigidly clamped beam, \( R \) is the radius of curvature, \( I \) is the area moment of Inertia and \( E \) is Young's Modulus for the material used [32]. Since the majority of the actuator strip length serves only to increase the moment at the rigid clamp, various modifications of the simple actuator strip structure are used to reduce the actuator strips mass.

The generated blocking force \( F \) of the actuator can be calculated by using Equation (5.12):

\[
F = \frac{M}{L}
\]  
(5.12)

The variable \( M \) is the moment about the free length \( L \) of the actuator [7]. Equation (5.12) shows that the blocking force \( F \) generated by the actuator is strongly dependent on the induced moment of the actuator via current-induction and also the length of the actuator. This also implies that more force can be generated by decreasing the length of the actuator.

5.4.4.2 Composite Actuator Model

The generated blocking force \( F \) of the composite actuator can also be given by the following equation [31]:

\[
F = \frac{E_{BP} \cdot W \cdot \alpha_{BP} (I_{BP} + I_{Nafion})}{L} 
\]  
(5.13)

In Equation (5.13), it is assumed that the radius of curvature is extremely large \((1/R = \infty)\). It can also be inferred from Equation (5.13) that the tip force is inversely proportional to the actuator length. The force model described by Equation (5.13) can be applied to calculate the blocking force that can be generated at the tip of the actuator.

There are various types of CNT based composite actuators that are currently being studied [8] [14] [20] [25] [26] [28] [29] [30] [31] [33]. The BCA sandwich structure is unique in the sense that most researchers used dispersed nanotubes in resins or gels to create their composite materials. Since nanotubes are generally randomly aligned in the BP, it promotes a relatively even distribution of nanotubes throughout the actuator to maximize CNT loading (%) and
minimize electrical impedance. Alternate CNT actuators risk losing good CNT contacts, which in turn, increase electrical impedance.

Since the goal is to maximize generated blocking force using the least amount of power, different approaches need to be studied to improve BCA actuator performance. For instance, using various Nafion thicknesses as shown in Figure 18 can potentially improve performance. In addition to the 2 mil thick Nafion polymer membranes, 3.5 mil, 5 mil, and 7 mil membranes are also commercially available. The corresponding product models are NRE-212, NM-1135, NM-115, and NM-117, respectively. These membranes are tested in BCAs to determine their impact on force and displacement.

![Figure 18: Schematic of various Nafion thicknesses for BCAs.](image)

Using a thicker Nafion membrane as shown in Figure 18 to create the composite actuator should inherently increase the mass and stiffness properties. High force generation requires a large mass at a high acceleration. Unfortunately, it is believed that if the Nafion is too thick, the magnitude of generated deformation may be limited along with a decrease in bending acceleration. However, it may prove more beneficial to increase actuator mass while maintaining substantial levels of bending acceleration by using higher voltages.
6.1 Key Governing Factors

There are several proposed explanations about how BCAs actually function. According to Dr. Ray Baughman, the electrochemical double-layer charge injection in nanotubes is believed to induce actuation via quantum mechanical and electrostatic effects that dominate for small and large degrees of charge injection, respectively [8]. This double layer charge injection shown in Figure 19, is a non-Faradaic process in which changing the charge on the carbon atoms results in changes of C-C bond lengths [8]. The excess charge on the nanotubes is compensated at the nanotube electrolyte interface by ions (cations or anions). The nanotubes act as double-layer capacitors (ECDL) that are charged and discharged during actuation cycles [8]. Hence, it is believed that CNT actuation performance is governed by both the expansion and contraction of BP electrodes and the mobility of the ions used with the respective electrolyte membrane.

![Figure 19: Charge distribution throughout a BP actuator strip during actuation [8].](image)

It is also believed that since an electrolyte is required to promote ion mobility, an optimal utilization of the Nafion polymer network is vital to exhibiting exceptional actuator performance.
Inside the Nafion polymer chain exists a network of fixed anionic clusters along with mobile cations [34]. Once an electric potential is applied at a given frequency, the H\(^+\) cations are then attracted to the electrode carrying negative potential. The conglomeration of H\(^+\) ions and water molecules within the Nafion structure cause subsequent swelling in areas where the electrode is negatively charged. In this case, the size and number of ions present dictate the magnitude of the response. It is possible that both Nafion swelling and C-C bond expansion induced by electrical excitation can promote mechanical deformation of BCAs.

### 6.1.1 Selection of Electrolyte

An electrolyte is required to functionalize a CNT based actuator. In previous studies [15], salt water (NaCl solution) was the electrolyte used for ion migration. To increase actuator functionalities, ionic polymer membranes were used in order to promote dry environment actuation. Nafion, polypyrrole, aerogel, and cellulose are among the electrolytes most recently studied for CNT actuation [20][29][30]. In previous studies, Nafion could be characterized as an electrolyte that allows for dry environment actuation but can also be limiting because of its poor mechanical and electrical properties. It allows for ion storage and migration but does not allow for a quick/ responsive migration [34]. Other ionic polymer membranes were studied for CNT actuator applications. Among them are Bucky gel and cellulose, which were previously discussed. The mechanical properties of the electrolyte and electrodes used may also inhibit its performance. The stiffer the electrodes are, the less inclined they may be to generate high amounts of displacement.

### 6.1.2 Effect of actuator dimension

The dimensions of the actuator have a significant influence on their performance. When the actuator’s dimensions are made to be long and thin, it has the potential of generating substantial magnitudes of bending displacement as discussed before [20]. Inversely, short and wide actuators usually produce less deformation. Short and wide actuators can however, output more force than its geometrical counterpart. Further analysis needs to be conducted to determine the most optimal dimensions for the actuators desired applications.
6.1.3 Effect of selected frequency ranges

The frequency range at which displacement occurs is important to the overall functionality of an actuator. If an actuator is desired to mimic the movements of a dragon fly, high frequency responses should be desired. Recent studies have shown that higher displacements are generated at low frequencies [30]. The time it takes the ions to completely migrate to the opposing electrode is greater than the allotted time at high frequencies. It also requires more power to increase the generated displacement at high frequencies.

6.1.4 Limitation of Applied

Previous experimentation [15] [16] [17] has shown that the maximum allowable voltage for a BCA is about 7 V. MWNT BCAs have a maximum allowable voltage of 10 V. It is known that as voltage input increases, the generated displacement also increases. If the maximum allowable voltage is increased, strain generation would also increase. Although low voltage actuation is desired, 20-25 V would make for a better voltage maximum. However, subjecting the BCA to such high voltages could lead to overwhelming amounts of material heat induction and burn electrolytes in use. Using thicker Nafion membranes for BCA fabrication may possibly extend operable voltage limitations. Also, coating the BP with a conductive polymer may prove to enhance its durability and extend its voltage limitations.

6.1.5 Effect of Humidity and Temperature

The level of humidity and temperature that the actuator is exposed to may influence its performance [30]. Nafion is currently the electrolyte of choice for dry environment actuation; however, Nafion is also sensitive to its surroundings. If the humidity is high, it is perceived that the actuator performance will be enhanced. Performance suffers in drier, colder environments due to loss of water molecules within the Nafion membrane.

6.1.6 Effect of Electrical contact quality

It is extremely important that the contact points between the BP and power source are consistent and efficient in transmitting all the power that is intended. A path of least resistance should be followed in order to effectively charge the actuator. Copper tape is currently being used as the
medium between the electric wires and BP to transmit energy. The high electrical conductivity of copper allows the energy to be transferred with the least amount of resistance. The desired size and location of the contact also needs to be studied. A small copper strip may be sufficient in transferring charges, but a larger contact may prove useful in exposing more charges to the BP surface. It may be more beneficial to the enhancement of an actuators performance if the contact was properly located at one end of the actuator, in between both edges of the actuator strip. Should 50% of the actuator be exposed to contacts or would only 10% be sufficient? These concerns should be investigated and addressed in order to promote optimal actuator performance.

6.1.7 Manufacturing Challenges

During our BCA actuator fabrication as shown in Figure 3, before combining the BP and Nafion membrane, a Nafion solution is layered on the two sheets of BP. Approximately nine drops are spread out to increase the interfacial bonding before hot pressing the composite structure. Additional experiments need to be composed to demonstrate consistency of sample quality in terms of BP/Nafion interfacial bonding, Nafion/CNT contact and electrical and mechanical properties.
CHAPTER 7

CHARACTERIZATION OF DISPLACEMENT

7.1 Test Setups and Actuation Characterization

7.1.1 Test Setups

A test setup as shown in Figure 20 was used to measure the displacement at the tip of the actuator when sets of voltages and frequencies were applied to the BCA samples from the function generator. The actuator is held between two pieces of copper tape attached to plastic slides. Positive and negative functional wires are then attached to the ends of the copper tapes. Once attached, it is then clamped to keep the sample secured. The clamp that holds the slides together is mounted to a breadboard from ThorLabs. The breadboard has a Plexiglas enclosure with a door mounted on top of it to prevent air flow from disturbing the results. Lastly, the breadboard is mounted on top of the Iso-Plate Passive Isolation System to dampen the setup from vibrations in the room.
Figure 20: Displacement test setup with the clamps to mount the BCA and laser sensor to measure deformation.

The function generator is then set to a desired frequency and voltage input. The pattern that is received can be square waves, sine waves, or pulse waves. A square wave voltage pattern is chosen in this study. The MicroTrak laser sensor is aimed at the tip of the BCA to record deflection during operation.

Again, as shown in Error! Reference source not found., at a 3 V and 200 mHz input, a CA is capable of generating ~0.09 mm of total bending displacement. Though actuation takes place, the magnitude of deformation is not significant. It is evident that ionic manipulations are necessary. The same setup will be used to determine if ion-doped BCAs are capable of the same performance or better.

### 7.2 Doping Experiments

In past experiments, Na+ salt water solution was used as the electrolyte for ion mobility between BP electrodes. Currently, an ionic polymer membrane known as Nafion is used to promote ion mobility in dry environments. H+ ions are built into the Nafion network and are major factors in
driving BCA actuation. It has been demonstrated that other ions may be used instead of hydrogen ion to generate larger displacement [6] [16]. Lithium Li+ is a potential candidate for outperforming the H+ ions within the Nafion structure.

### 7.2.1 Lithium Chloride Doping

The multitude of Hydrogen ions located within the Nafion structure presents undesirable limitations. Since Lithium ions have a higher energy density than Hydrogen, along with superior ionic properties, ion replacement was studied. This was done in order to replace the hydrogen ions with Lithium ions. To do this, Nafion doping has to take place. Figure 21 shows the LiCl-Doped BCA fabrication process.

As seen in Figure 21, the Nafion was arbitrarily doped in LiCl solution (0.5 M in anhydrous tetrahydrofuran) from Sigma Aldrich. It was doped for three hours prior to sandwiching and pressing the composite actuator structure. Once fabrication was complete, the actuator was then tested to determine the level of functionality. Figure 22 shows the measured displacement of a LiCl-doped BCA during 3 V excitation at 200 mHz.
As seen in Figure 22, the total generated displacement of the LiCl-doped BCA is about 9 mm. The magnitude of deformation is improved by a factor of ×100, compared to the non-doped pristine Nafion BCA. It is now evident that ionic manipulations are necessary for generating large deformations. Figure 23 shows a comparison of the properties present in Hydrogen and Lithium.

As seen in Figure 23, a Lithium ion (Li+) is shown to have a larger covalent radius than a Hydrogen ion. The covalent radius of a Lithium ion is 9.7 pm larger than that of the Hydrogen ion [35]. This is relevant because the size of the ions can dictate the magnitude of deformation.
during actuation. When charged, the cations are attracted to the negatively charged electrode. Since larger ions generally require more space within the Nafion, substantial swelling is induced.

A combination of properties provided by Lithium ions makes them a more viable option for ion transport within the Nafion structure. By doping the Nafion in a lithium solution such as LiCl solution, lithium ions are added to the already hydrogen ion enriched Nafion structure to improve actuation performance.

The superiority of Lithium over Hydrogen ions in BCA applications can be quantified by understanding ionic flow patterns within the Nafion structure. Figure 24 shows a magnified image of ion flow within the Nafion polymer membrane during actuation.

As seen in Figure 24, Nafions’ clustered network is modeled to show the dimensions of ionic flow pathways in addition to the direction of ion flow during actuation. Since the Nafion is doped in LiCl solution, both Lithium and Hydrogen ions are randomly present throughout the Nafion morphology. The Lithium ions (green) are large relative to the Hydrogen ions (red). It is believed that the Lithium and Hydrogen ions work together to promote larger deformations in BCAs. The size and mobility of Hydrogen ions allow them to move quickly throughout the channels of the Nafion network. The large mass and volume of the Lithium ions allow them to...
compliment the Hydrogen ions by way of causing additional swelling within the Nafion structure during actuation. We believe that both the number and size of the ions present within the Nafion structure dictate the magnitude of deformation during actuation. By adding more large ions to the Nafion structure, the charge density is increased and better performance was achieved as shown in Figure 22.

### 7.2.2 Ionic Liquid Doping

It is now confirmed that utilizing only the Hydrogen ions already present within the Nafion structure to generate strain is insufficient for achieving high-performance actuation. Since Lithium ions are larger in size and induce significant swelling which translates into improved bending deformation. The following question is now proposed: if the size of the cation is larger than Li\(^+\), will it promote greater displacement? An Imidazolium (IL) solution has been introduced in order to confirm the culprit of performance increase. The ionic liquid (Product #91508) used in this project was purchased from Sigma Aldrich. This material is the liquid used to “dope” the BCAs. Its chemical name is 1-Butyl-3-methylimidazolium tetrafluoroborate. The molecular structure is made of \(\text{C}_{8}\text{H}_{15}\text{BF}_{4}\text{N}_{2}\). The primary anion will be \(\text{BF}_{4}^-\). This will prove if cation size is a major governing factor in BCA actuation performance. In order to replace the hydrogen ions with IL ions, Nafion doping first has to take place. Figure 25 shows the IL-Doped BCA fabrication process.

![Figure 25: IL-Doped BCA fabrication process.](image)
As seen in Figure 25, before doping the Nafion an additional step is taken to ensure that an increased amount of IL ions are introduced to the Nafion structure. The Nafion is placed in an oven at 110ºC with a vacuum pressure of 25 psi for 3 hours. This should increase the probability of the Nafion absorbing more IL ions. After dehydration, the Nafion is submerged into the IL solution and kept in the oven at 110 ºC for 3 more hours.

After the Nafion was done soaking, it was removed from the oven and placed between Teflon sheets to protect it from the outside atmosphere. This prevents water molecules in the air from being absorbed by the Nafion. Next a piece of buckypaper was placed on each side of the Nafion. This sample was placed between two pieces of freshly cut Teflon film and then placed in the hot press that has been preheated to 110 ºC. The pressure applied by the hot press was 70 MPa for 10 minutes. Each sample was then removed from the press and cut to the desired size. Multiple samples can be cut from each 6 cm by 6 cm sheet.

Once fabrication is complete, the BCA is believed to have absorbed the ions from the IL solution. The effects of IL doping will be tested to determine the level of functionality improvement of the resultant BCAs. Figure 26 shows the measured displacement of an IL-doped BCA during 3 V excitation at 200 mHz.

Figure 26: IL-Doped BCA bending displacement at 3 V and 200 mHz.

As seen in Figure 26, the total generated displacement of the IL-doped BCA is about 13.4 mm. Compared to the non-doped BCA, the magnitude of deformation is now improved by a factor of ×150. Also, no drifting takes place, meaning performance is more stable. In reference to the
LiCl-doped BCA, the magnitude of deformation is improved by a factor of \( \times 1.5 \). Hence, we can see that cation size is a governing factor for generating large bending deformations.

The superiority of IL ions over both Hydrogen and LiCl ions in BCA applications can be quantified by understanding ionic flow patterns within the Nafion structure. Figure 27 shows a magnified image of IL ion flow within the Nafion polymer membrane during actuation.

![Figure 27: Ionic flow within the IL-Doped Nafion polymer membrane during actuation.](image)

As seen in Figure 27, Nafions’ clustered network is modeled to show the dimensions of ionic pathways in addition to the direction of ion flow during actuation. Since the Nafion is doped in IL solution, both C\(_8\)H\(_{15}\)N\(_2\) cation chains and Hydrogen ions are randomly present throughout the Nafion morphology. The C\(_8\)H\(_{15}\)N\(_2\) cation chains (yellow) are relatively much larger than the Hydrogen ions (red). It is believed that the C\(_8\)H\(_{15}\)N\(_2\) cation chains and Hydrogen ions work together to promote larger deformations. The size and mobility of Hydrogen ions allow them to move quickly throughout the channels of the Nafion network. The large mass and volume of the C\(_8\)H\(_{15}\)N\(_2\) cation chains allow them to compliment the Hydrogen ions by way of causing the majority of the swelling within the Nafion structure during actuation. It can be said that along with increasing ion size, the number of ions present within the Nafion structure also dictate the magnitude of deformation during actuation. By adding more ions to the Nafion structure, the charge density is increased and superior performance is now expected. Based on the improved
performance demonstrated in Figure 26, the IL-Doping method has been selected for further characterization in the following studies:

7.3 Effect of Voltage

Theoretically, increasing the applied voltage directly increases the charge affinity between the BP electrodes and ion mobility. When high voltages are applied, actuation performance generally improves in a linear [31]. However, too high a voltage can damage BCA samples and cause confines in movement due to large current-induced heating. In previous experiments, there have been limitations presented involving the introduction of high voltages onto the BCAs. Previously, when applying large voltages above 3 V, material heating took place. Though most heat is present near the electrical contact point, the ion interaction is not yet known. Since IL-Doping is now used to activate superior BCA performance, there are other variables to consider during excitation. In order to characterize the effect of voltage on IL-doped BCA displacement generation, further analysis is required. Since the magnitude of BCA bending displacement has significantly increased, the laser displacement sensor is no longer in measurable range. Instead, graphing paper is used as a visual reference to measure BCA displacement and curvature. Figure 28 shows an actual image of the IL-doped BCA during 3 V excitation at 200 mHz.

![Figure 28: Actual images of IL-Doped 2 mil BCA bending displacement at 3 V and 200 mHz.](image)

As observed in Figure 28, the total generated displacement of the IL-doped BCA is measured to be about 13 mm. It is also observed in Figure 28 that the BCA bends slightly more in one direction than the other. For large bending, the BCAs radius of curvature should be considered
and calculated for performance evaluation. By selecting 3 points on the BCA at max displacement, two slopes can be estimated. Equation (5.1) can then be used to calculate the maximum generated curvature of the BCA at 3 V. The calculated radius of curvature is ~164.27 mm.

To further characterize the effect of voltage, the BCA is additionally tested at 5 V, 7 V, and 10 V. Figure 29 shows actual images of the IL-doped BCA during 10 V excitation at 200 mHz.

![Figure 29: Actual images of IL-Doped 2 mil BCA bending displacement at 10 V and 200 mHz.](image)

As observed in Figure 29, the total generated displacement of the IL-doped BCA is measured to be about 30 mm. It is also observed in Figure 29 that the BCA bends significantly more in one direction than the other. It is not yet known why the dominating one-sided response takes place during actuation.

To fully characterize the effect of voltage increase on the curvature and displacement generated by the IL-doped BCA, an experimental relationship was developed. Figure 30 shows the measured displacement and curvature generated by the IL-doped BCA during 3 V, 5 V, 7 V, and 10 V excitation at 200 mHz.
As seen in Figure 30, the IL-doped 2 mil BCA generated displacement increases linearly with applied voltage. There is an average of 4.5 mm increase in displacement per 1 V input from 3 V to 10 V. The resulting performance begins to conclude that BCA performance is majorly dependent on voltage input. Also, BCA generated curvature decreases linearly. Additionally, it is evident that there is no longer a 10 V limit of electrical excitation potential. However, it is possible that a limitation still exists >10 V. More studies should be conducted to determine what the limit may be.

To further validate the relationship between voltage input and BCA generated bending displacement, a thicker Nafion membrane is introduced to confirm performance similarities. Figure 31 shows an actual image of the 3.5 mil IL-doped BCA during 10 V excitation at 200 mHz.
As observed in Figure 31, the total generated displacement of the IL-doped BCA is measured to be about 26.4 mm. It is also observed in Figure 31 that the BCA bends significantly more in one direction than the other. This one-sided performance favorability is in agreement with the IL-doped 2 mil BCA.

To characterize the effect of voltage increase on the curvature and displacement generated by the IL-doped BCA, an experimental relationship was additionally developed for IL-doped 3.5 mil BCAs. Figure 32 shows the measured displacement and curvature generated by the IL-doped 3.5 mil BCA during 3 V, 5 V, 7 V, and 10 V excitation at 200 mHz.

![Figure 32: Effect of voltage increase on curvature and displacement of IL-Doped 3.5 mil BCA at 200 mHz.](image)

As seen in Figure 32, the IL-doped 3.5 mil BCA generated displacement increases exponentially with applied voltage. There is roughly an average of 5.3 mm increase in displacement per 1 V input from 5 V to 10 V. The resulting performance also indicates that BCA performance is in fact dependent on voltage input. Also, BCA generated curvature decreases exponentially.

To finalize characterization of the effect of voltage increase on the curvature generated by both 2 mil and 3.5 mil IL-doped BCAs, an experimental relationship was developed. Figure 33 shows a comparison of the measured curvature generated by both 2 mil and 3.5 mil IL-doped BCAs during 3 V, 5 V, 7 V, and 10 V excitation at 200 mHz.
Figure 33: Comparison of measured curvature generated by both 2 mil and 3.5 mil IL-doped BCAs during 3 V, 5 V, 7 V, and 10 V input at 200 mHz.

As seen in Figure 33, the large deflection generated by the IL-doped 2 mil BCA allows for smaller curvature values than the 3.5 mil BCA counterpart. This relationship may be due to the increased thickness of the Nafion membrane within the BCA. Generally, if presented with two beams made of the same material and one beam is thicker than the other, if fixed at one end and equal in length; when applying an equal force to each one, the thicker beam will bend less than the other. This is the case because the overall structural rigidity of the thick beam is increased. Therefore this relationship is reasonable. It is also evident that as input voltage increases, the curvature gap between the 2 mil and 3.5 mil BCA decreases. This could mean that as voltage is increased, the difference in Nafion thickness within the BCA is negligible in reference to displacement generation.

To further study the performance of IL-doped BCAs, comparative displacement generation relationships of different BCAs are developed. Figure 34 shows the effect of voltage on generated displacement comparison between IL, LiCl, and Non-doped BCAs from 0 V to 10 V at 200 mHz.
As seen in Figure 34, increasing applied voltage positively influences measured displacement up to only 5 V for the LiCl-doped BCA. After 5 V, the LiCl-doped BCAs may become oversaturated, causing a reduction in performance. It is also evident that the LiCl-doped BCAs may be more susceptible to current induced heating at high voltages. The IL-doped 3.5 mil BCA surpasses the displacement of the LiCl-doped 2 mil BCA after 6 V. To summarize Figure 34, the IL-doped 2 mil BCA proves to generate the greatest displacement. Conversely, the Non-doped BCA generates the least amount of displacement. More importantly, the data concludes that IL-doping helps to achieve superior BCA performance. Hence, further characterizations will only be conducted for IL-doped BCAs.

### 7.4 Effect of Nafion thickness change

It has previously been determined that Nafion thickness increase takes away from the magnitude of generated displacement. The added stiffness makes the actuator harder to bend; especially at low voltage. It is suspected that it takes more time for ions within the ionic-polymer (Nafion) to reach the attracting electrodes. Using the laser displacement setup, we were able to characterize the displacements of the BCAs with different thicknesses when given a potential of 3 V at 200 mHz as shown in Figure 35.
Figure 35 shows that the 2 mil, 3.5 mil, 5 mil, and 7 mil BCA’s generated 13.4 mm, 4.1 mm, 2.1 mm, and 1.1 mm deformation respectively. As expected, the actuator with the smallest thickness and lowest stiffness displaced the most. Increasing thickness exponentially reduces displacement. The 3.5 mil BCA shows respectable displacement for its thickness while the 5 mil and 7 mil actuator show a drastic decrease in the magnitude of generated displacement. Though 5 mil and 7 mil BCAs achieve small displacements at 3 V, increasing the voltage input may significantly improve performance.

7.5 Effect of Frequency

When operating the BCA at 200 mHz, it was studied that larger displacement was achieved using higher driving voltages as discussed in Section 7.3. This is true because increasing the driving voltage directly increases the amount of current used to excite the ions within the BCA. Further excitation of the ions contributes to the possible magnitude change of ion mobility and velocity. It is believed that at higher frequencies, it gives less time for ions within the ionic-polymer membrane (Nafion) to reach the attracting electrodes, hence leading to less deformation. Using the laser displacement setup, we were able to characterize the displacements of the BCAs when supplied with potentials from 1 V to 14 V at 1 Hz frequency. The results are shown in Figure 36.
Figure 36: Effect of IL-doped 2 mil BCA driving voltage on generated displacement @ 1 Hz.

As seen in Figure 36, the 2 mil BCA displacements are in fact dependent on both voltage and frequency input. When supplying voltages from 1 V to 14 V, the displacement increases from 0.35 mm to 5.5 mm, respectively. Though the BCA follows the same trend of displacement increases due to driving voltages at 1 Hz, the magnitude of displacement is much larger at 200 mHz, compared to Figure 34. This is the case because at 1 Hz, the ions within the Nafion are not given enough time to travel from the cathode side of the electrode (Buckypaper) to the anode side.

It is believed that the distance that the ions need to travel between electrodes requires ample time to compromise. The resulting BCA displacement needs to be quantified at higher frequencies to validate this theory. Figure 37 shows the effect of IL-doped 2 mil BCA frequency input on generated displacement at 3 V.
As seen in Figure 36, increasing frequency exponentially decreases BCA generated displacement. When increasing frequency from 1 µHz to 10 Hz, the displacement is drastically reduced from 23 mm to 0.092 mm, respectively. It should be noted that the IL-doped BCA generated displacement at 3 V and 10 Hz is equal to that of the Non-doped BCA operated at 3 V and 200 mHz.

Ultimately, a low frequency input is desired for generating large bending displacements. In this study, BCAs generated displacement at 1 µHz allows for maximum displacement to take place at any given voltage. This gives mobile ions enough time to travel to the opposing electrode location within the Nafion.
CHAPTER 8
CHARACTERIZING IL-DOPING EFFECT ON NAFION

8.1 Effect of Ionic Liquid Doping on Nafion Properties

To further understand why IL-doping improves BCA displacement performance, an analysis of material properties must first be conducted. This includes studying the effect of Nafion-doping on mechanical properties at various thicknesses of Nafion and BCAs. The change in Nafions’ ionic conductivity after doping must also be analyzed and understood.

8.1.1 Mechanical Properties of Nafion

Using a Dynamic Mechanical Analyzer (DMA Q800) provided by TA Instruments Incorporated, tensile tests were conducted. Tensile tests were conducted on the various states of Nafion during the Nafion doping process. The first state is the pristine state, in which the Nafion was used as received. This state was used as the control status. The second state is the post-oven state. This state was tested to determine if dehydrating the Nafion makes the Nafion stiffer. The third state was the post-doping state. This state was tested to determine the effect that Nafion doping has on Young’s modulus. The fourth and final state is the post-pressing state. This state should represent the final state of Nafion after BCA fabrication is complete. If the material properties of Nafion in its final state are known, its measured values can be considered for more accurate BCA modeling estimations. The Young’s modulus of BCAs will also be tested to determine the influence of BP material properties on the entire BP-Nafion composite (BCA) itself.

DMA tests were conducted at each state of the IL-doping Nafion manufacturing process to determine the change in Young’s modulus for each Nafion thickness. Figure 38 shows the DMA tensile test results of 2 mil, 3.5 mil, 5 mil, and 7 mil Nafion membranes.
Figure 38: Effect of Nafion doping on the Young's modulus of (a) 2 mil, (b) 3.5 mil, (c) 5 mil, and (d) 7 mil thickness Nafion samples.

As shown in Figure 38, all Nafion thicknesses follow the same property changing trends during each state of the Nafion doping process. Nafion modulus significantly decreases from the pristine state to the pressed state. Figure 39 more clearly shows the effect of each state of the doping process on mechanical properties for each Nafion thickness.
Figure 39: Nafion thickness effect on the Young's modulus of (a) pristine, (b) post-oven, and (c) post-doped Nafion processing states. (d) The comparison of Young’s modulus at BCAs final state.

Since the Nafion pressed state is also considered Nafion’s final state for BCA functionality, all Nafion thicknesses have comparable modulus values at this state. During Nafion’s pristine state, the 5 mil Nafion has the highest modulus. Figure 39 shows that the 2 mil BCA has the highest measured Young’s modulus compared to its counterparts. As BCA thickness increases, BCA modulus decreases due to low modulus of Nafion compared to buckypaper electrode layers. Since Nafion is softer than BP, when it is thicker, the composite material as a whole becomes softer based on the Rule of Mixture [36] [37].

It is believed that the Nafion doping process changes its mechanical properties due to wetting % variation [4]. The Nafion wetting % is related to the amount of H₂O present in the Nafion material. Between each state of the Nafion doping process, the Nafion was weighed using
an Adventurer™ OHAUS scale. Figure 40 shows the resulting effect of Nafion processing on the mass and thickness variation.

![Graph showing the effect of Nafion processing on mass and thickness.](image)

Figure 40: Effect of Nafion processing on their mass and thickness.

It can be seen in Figure 40 that thicker BCAs generally have a larger mass. The mass increase amounts to about 0.01 g per 1 mil of Nafion thickness used in BCA fabrication. The average standard deviation of mass change for all BCAs during processing is about 0.016 g.

Between each state of the Nafion doping process, in addition to recording the mass of each Nafion, the dimensions were also collected. Knowing the mass and volume of each Nafion allows for density to be calculated. Figure 41 shows the resulting effect of Nafion processing on density.
It is evident in Figure 41 that all values follow the same density change trend during Nafion processing, except the 3.5 mil Nafion after doping. The average standard deviation of density change for all BCAs during processing is ~0.3887 g/cm\(^3\) to ~0.5348 g/cm\(^3\).

### 8.1.2 Ionic Conductivity of Nafion

Using an Hioki 3532-50 LCR HITESTER for conductivity analysis, the through-thickness impedance of the Nafion can be determined. A diagram of impedance testing procedures using the LCR HITESTER is shown in Figure 42.
Figure 42: Impedance testing procedures for Nafion samples

More specifically, Figure 42 shows that at a set length of 30 mm between conductive electrodes, the impedance of ion flow can be recorded. Figure 43 shows the resulting impedance analysis at the various states of Nafion samples. This is done to determine the effect of doping on Nafion impedance and thickness.

The general trend shown in Figure 43 is that the impedance increases as Nafion thickness increases. The Nafions’ pristine state has the lowest impedance. It is also evident that the impedance values of Nafion after being doped are relatively consistent for all Nafion thicknesses.
To calculate the ion conductivity of Nafion at each state using the Nafion impedance $Z$ collected from the LCR Hi TESTER, Equations (8.1), (8.2), and (8.3) are used:

$$Z = \rho \frac{L}{w\times t} \quad (8.1)$$

$$\rho = \frac{1}{\vartheta} \quad (8.2)$$

$$\vartheta = \frac{1}{\left(\frac{Z \times w \times t}{L}\right)} \quad (8.3)$$

Variable $L$, $t$, and $w$ are Nafion samples’ length, thickness, and width, respectively. It is evident that larger values of Nafion width $w$ and thickness $t$ make the Nafion susceptible to a decrease in ionic conductivity. Variables $\rho$ and $\vartheta$ are the Nafion resistance and ionic conductivity, respectively. Figure 44 shows the resulting ionic conductivity analysis at the various states in Nafion-doping. It shows the effect of doping on Nafions’ ionic conductivity and thickness.

![Figure 44: Effect of Nafion doping on ionic conductivity.](image)

The general trend shown in Figure 44 is that ionic conductivity decreases as Nafion thickness increases during processing. Ionic conductivity is the highest and most consistent for pristine Nafion with respect to all Nafion thicknesses. It is believed that pristine Nafion has the highest ionic conductivity because there are an abundant amount of small and mobile hydrogen ions within. Unfortunately, it is believed the ion size in pristine Nafion is too small to cause large
deformation during BCA actuation. Figure 44 also shows that Nafion has the lowest ionic conductivity after being exposed to the oven because there are fewer ions available within the Nafion membrane due to vacuum-oven induced evaporation. It should be noted that tests were conducted at 5 V and 1 MHz; results may vary at different voltages.

A Nafion sample in its doped state is more conductive than Nafion in its post-oven state. Unfortunately, it is less conductive than Nafion in its pristine state. This is the case because there are an abundant amount of both small and large ions within. The larger ions may have a diffusion limitation due to their size. However, even though the larger ions may move slowly within the Nafion, larger deformation is achieved during BCA actuation as shown before. Fundamentally, it is believed that ionic conductivity is dependent on ion size [20] [35].
CHAPTER 9

CHARACTERIZATION OF BLOCKING FORCE

9.1 Actuator Operation

In this study, various test setups and data collection methods were studied to characterize the generated blocking force of BCAs.

9.1.1 Test Setup

As shown in Figure 45, first, the BCA is clamped with conducting copper contacts. The clamped BCA is then placed under a microscope. Under a microscope, the movement of the wire can be measured before (control) and after BCA actuation. The tip on the BCA should be positioned against the midway point of the load-cell pin. This will ensure that the BCA does not slip of the load-cell pin during actuation. The force test setup is shown in Figure 45 with a close-up of the actuator positioning against the wire.
Figure 45: Force test setup with close up of the actuator against the wire.

Under the microscope shown in Figure 45, the location of the wire was measured before and after BCA actuation. To determine the total range of movement, an initial image of the untampered tip should first be captured. The focus of the microscope should then be adjusted onto the load-cell pin tip as shown in Figure 46a.

Figure 46: Diagram showing top view of actuator before actuation (a) at 0 V. After actuation (b) at 3 V, the pin is moved distance of \( y_{\text{max}} \).
After the initial image is captured, the initial location of the pin can be determined by counting the quantity of pixels between the wire tip and a fixed point. Once the initial pin location is established, a pre-determined voltage should then be applied to the BCA for generating force to be exerted onto the load-cell pin. Figure 47 shows the variables to consider when applying a point-load at the midway point of a beam (load-cell pin).

![Figure 47: Variables to consider when applying stress at mid-length of a beam.](image)

The voltage range selected for force characterization ranges from 0.5 V to 3 V. To ensure that both maximum displacement and force are exerted onto the load-cell pin. A direct current (DC) is used rather than a set frequency input. Once the BCA ceases to bend the pin any further from its original state, it is considered to have reached its maximum blocking force potential against the pin. A final image of the pin is then captured for analysis. The final pixel generated distance is measured between the wire tip and fixed point. Both initial and final pixel measurements can be used to calculate the total pin displacement generated by the BCA:

\[ Y_{\text{max}} = y_f - y_i \]  

(9.1)

According to Equation (9.1), by subtracting the final distance of the pin \( y_f \) from the original distance of the pin \( y_i \), the total deflection of the wire \( y_{\text{max}} \) can be calculated. The results are then compared to the amount force required to bend the pin. The wire has a modulus (E) of 34.22 GPa and the length (L) is 12.05 mm. The area moment of inertia (I) about the fixed end of the load-cell pin is \( 2.043 \times 10^{-16} \) m\(^4\). This data allows for BCA blocking force to be calculated.
Then, the blocking force is calculated using Equations (9.2) and (9.3):

\[
Y_{\text{max}} = \frac{5PL^3}{48EI} \quad (9.2)
\]

\[
P = \frac{Y_{\text{max}} \times (48IE)}{5L^3} \quad (9.3)
\]

Using the mechanical properties of the pin and resulting \(Y_{\text{max}}\), Equation (9.2) and (9.3) can be used to calculate the BCA force generation, in Newtons. As shown in Equation (9.1), the displacement \(Y_{\text{max}}\) is the difference in distance between initial position of the pin and the position after the BCA pushes the pin. An example of the actual before and after BCA generated pin displacement is shown in Figure 48.

![Figure 48: Wire position change: (a) before and (b) after the BCA generated pin displacement.](image)

After measuring the total deflection of the pin movement shown in Figure 48, the force produced by the actuator can be calculated. At 5 V, the experimental deflection is 0.449 mm. The calculated blocking force is 6.023 mN. The overall effect of BCA thickness on BCA generated force at 3 V is shown in Figure 49.
Figure 49 shows that the 2 mil, 3.5 mil, 5 mil, and 7 mil BCAs generated 2.790 mN, 6.294 mN, 6.810 mN, and 4.897 mN blocking forces, respectively. According to the data presented in Figure 49, the 3.5 mil and 5 mil BCAs generate the largest force at 3 V. The 2 mil BCA force is lowest due to both its small thickness and lack of stiffness. The 7 mil BCAs may require either more voltage to compensate for the increased thickness.

To convert the force to stress in MPa, the area of contact between the actuator and the wire is plugged into Equation (9.4). This area is based on the assumption that the area of contact between the BCA and the wire is a rectangle. The dimensions of this rectangle are assumed to be the thickness of the actuator (71 µm) by the diameter of the wire (0.05 mm). The approximate cross-section m² of the BCA to load-cell pin area is estimated to be $~1.8*10^{-8}$ m².

$$Pa = \frac{N}{m^2} \quad (9.4)$$

For a 2 mil BCA operated at 3 V, the force exerted is 3.3 mN. The subsequent stress is calculated to be $~185,000$ Pa or 0.185 MPa. The overall effect of BCA thickness on BCA generated stress values at 3 V is shown in Figure 50.
Figure 50 shows that the 2 mil, 3.5 mil, 5 mil, and 7 mil BCAs generated 0.110 MPa, 0.180 MPa, 0.144 MPa, and 0.106 MPa respectively. The 7 mil BCA, being the thickest and stiffest, yielded the least stress. The 3.5 mil BCA generated the highest stress at 3 V. Again, the 7 mil BCA may require more voltage input to compensate for increased thickness.

Using the force setup and Equations (9.1), (9.2), (9.3), we were able to develop a preliminary characterization of the blocking forces that BCAs can produce at different thicknesses. The 5 mil BCA generated the highest force while the 3.5 mil BCA generated the highest stress.

### 9.2 Effect of Nafion Thickness on Actuation Performance

To summarize the effect of thickness on BCA generated displacement and force, further analysis was conducted. Figure 51 shows the difference in BCA generated displacement and force with respect to the thickness of the Nafion at 3 V.
Figure 51: Effect of IL-doped BCA thickness on force and displacement generation @ 3 V (DC).

At 3 V, BCA displacement decreases as the Nafion thickness increases. Excluding the 7 mil BCA, at 3 V, BCA force generation increases as the Nafion thickness increases. It is evident in Figure 51 that as the thickness of Nafion increases, the BCA generated displacement decreases and force increases. When 7 mil Nafion is used to fabricate the BCA, more than 3 V may be required to increase performance. In this study, the force consistently peaks when using the 3.5 mil Nafion in BCAs.

### 9.3 Effect of Voltage Change

Increasing the applied voltage should directly increase the charge affinity between the BP electrodes and ion mobility. When high voltages are applied, actuation displacement performance generally improves. To determine if BCA blocking force increases in a similar fashion due to voltage induction, further studies were conducted.

#### 9.3.1 Blocking Force Estimation

Using the load-cell pin to gather data for BCA force generation as shown in Figure 45 is only a preliminary test method for determining total BCA generated blocking force. To estimate BCA generated blocking force, the free displacement (without any blocking) generated by the BCA must first be recorded. In this study, the BCA generated free displacement is the maximum displacement achieved when the desired voltage is applied for 1 minute. Once free displacement measurements are collected, they can then be compared and collaborated with BCA generated
force data previously gathered from the pin setup. The tests were conducted at 0.5 V, 1 V, 1.5 V, 2 V, 2.5 V, and 3 V (DC) input settings consistently for each BCA thickness using the 2 mil, 3.5 mil, and 5 mil Nafion respectively. Unfortunately, when operating BCAs at high voltages the force setup’s range is not sufficient. BCA generated free displacement data was gathered using the same input voltages and additionally including 5 V, 7 V, and 10 V (DC) in order to estimate BCA generated blocking force at higher voltages. The relationships between BCA generated force and free displacement at various input voltages are shown in Figure 52, with the assumption that deformation and blocking force have a linear relationship.

![Figure 52: Blocking Force vs. deformation model of 2 mil BCA from 0.5 V to 10 V (DC).](image)

The relationships in Figure 52 show that the deformation values generated by the BCA are simply transformed into a quantifiable amount of force that is blocked by the semi-rigid load-cell. As seen in Figure 52, each line represents both BCA generated blocking force and free displacement at a given input voltage. From 0.5 V to 3 V, there is a gap between the y-axis (force) and the data collected. This is the case because the load-cell pin used in the force setup prevents the BCA from achieving maximum deformation; instead, a measurable amount of force was induced. If no gap was present, the BCAs would have achieved a maximum blocking force. At 3 V (orange line), using a direct current (DC), a 2 mil BCA can generate 23 mm of total free displacement. Using the same input setting, it can also generate 3.397 mN of blocking force by
completely blocking the maximum free deformation. The equations shown in Figure 52 represent the force-deformation relationship for each case. They also represent the actuation performance expected by 2 mil BCAs at each voltage from 0.5 V to 10 V. If displacement (x) is set to equal zero, an estimate of maximum blocking can be achieved. Since the force setup could not be used to measure the BCA force generation at 5 V, 7 V, and 10 V, the BCA generated free displacement data was used instead to estimate 2 mil BCAs blocking force at those voltages. In summary, the force and displacement relationship plots help estimate what the BCA generated blocking force would be at different deformation status for each voltage input selection from 0.5 V to 3 V. Figure 53 more clearly shows the effect of voltage increase on the blocking force and stress generated by the 2 mil BCA (DC).

As seen in Figure 53, both force and stress generation increases linearly with voltage input increase. There is about a 1 mN and 0.02 MPa cumulative increase in BCA force and pressure generation per 1 V input, respectively. The same tests were conducted for the 3.5 mil and 5 mil BCAs to determine both the effects of voltage and thickness increase on BCA generated blocking force. Figure 54 shows the relationship between BCA thickness and voltage input on BCA generated blocking force and stress.
As seen in Figure 54, the 3.5 mil BCA generates the highest overall blocking force and stress. The 5 mil BCA generates the highest force at 3 V. The 5 mil BCA also generates the least amount of stress. This is due to the increase in force exposed contact area or cross-section. Assuming that the 5 V, 7 V, and 10 V projected BCA blocking force estimation data is adequate, the same projections are also conducted for the 3.5 mil and 5 mil BCAs to determine both the influence of voltage and thickness increase on BCA generated blocking force at higher voltages, based on the equations shown in Figure 52. Figure 55 shows the relationship between BCA thickness and high voltage input on projected BCA generated blocking force and stress.

As seen in Figure 55, it is projected that the 5 mil BCA can generate a blocking force of up to ~42.1 mN at 10 V. This is about a 50% increase in force compared to the 3.5 mil BCA at 10 V.
Similarly, after 3 V, the 5 mil can generate a stress of up to \(~1.124\) MPa at 10 V. This is about a 53\% increase in stress compared to the 3.5 mil BCA at 10 V. It can be seen that thicker BCAs require higher voltages to generate more force. According to Figure 55, thicker BCAs require at least 3 V or more to generate larger stress values. Based on the experimental input voltage ranges chosen from 0.5 V to 3 V, the 3.5 mil BCA consistently generated the largest blocking forces from 1.25 mN to 6.3 mN, respectively. Table 2 shows how BCA performance in study compares with other actuators [4].

Table 2: Comparison of BCA properties with performance of other actuators.

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<td>0.8 MPa</td>
<td>700 MPa</td>
<td>65 MPa</td>
<td>100 MPa</td>
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<td>(\mu) sec</td>
<td>sec to min</td>
<td>(\mu) sec</td>
<td>(\mu) sec</td>
<td>(\mu) sec</td>
</tr>
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<td>3 g/cc</td>
<td>6 g/cc</td>
<td>7.5 g/cc</td>
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<tr>
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<tr>
<td>Fracture toughness</td>
<td>large</td>
<td>large</td>
<td>large</td>
<td>low</td>
<td>large</td>
<td>medium</td>
</tr>
</tbody>
</table>

As seen in Table 2, BCAs generate relatively low blocking force compared to smart memory alloy (SMAs) and piezo-single crystal actuators. The BCA performance more closely matches that of Electro-static silicone elastomers and polymer electrostriction actuators. More importantly BCAs use significantly less voltage to generate acceptable amounts of blocking force. Though BCAs do not generate large blocking force, they use the least amount of energy to generate small forces. BCAs can still be considered for low force, low voltage applications. It should be noted that all experiment were conducted with BCAs having the same length and width. It is believed that if the length of the BCA is shortened and the width increased, more BCA force generating potential can be exploited.
9.4 Model Validation

Equations (5.12) and (5.13) were both used to estimate BCA blocking force. The blocking force models developed for actuator induced cantilever-style bending behavior and force generation have been verified [7] [31]. Figure 56 shows the results estimated by the blocking force actuator model compared to the experimental results in this study.

![Figure 56: Blocking force modeling validation.](image)

After calculations were conducted using Equations (5.12) and (5.13), it was determined that both equations were in fact the same. Derivations show that Equation (5.13) represents actuator performance more specifically in terms of material properties and dimensions, but since most of those properties are already included in solving for the moment generated by the BCA, both equations represented the same exact values of BCA force generation. Equation 5.12 is still useful because the governing factors of BCA performance are more clearly revealed. It can be seen in Figure 56 that the blocking force model estimations are comparable to the experimental values. Furthermore, the model can potentially be used for high voltage force generation estimations.
CHAPTER 10
CONCLUSION

The goal of this research is to measure and improve the performance of BCA actuation, special focus is put on BCA blocking force measurement. In this study, we explored the effects of Li\(^+\) and IL doping on both deformation and blocking force generation for BCA actuators of different thickness under different stimulation voltages and frequencies.

The results show that doping the Nafion with IL solution significantly improves performance. This was determined by measuring and comparing the displacement generated by non-doped, LiCl-doped, and IL-doped BCAs. While the Li-doped BCA generated \(\times100\) more deformation than that of the non-doped BCA, the IL-doped BCA generated both \(\times150\) and \(\times1.5\) more deformation than those of the non-doped and Li-doped BCAs, respectively. It is believed that this is the case because adding larger cations results in larger anodal expansion or swelling.

Since the IL-doped BCA shows better performance, further experiments were conducted to determine how Nafion property changes governed performance improvement. Nafion doping involves three main material states. DMA tests were conducted on Nafion’s pristine (non-doped), post-oven, and post-dope and press states to evaluate Young’s modulus change among all states. Pristine Nafion had the highest Young’s modulus of 202.2 MPa. After subjecting the Nafion to oven treatment, the Young’s modulus was reduced to 120.1 MPa. The modulus of the Nafion was further reduced to 21.38 MPa once exposed to doping and pressing steps. These drastic changes in material stiffness may have been due to the instability of new ions introduced and loss of H\(_2\)O molecules.

The effect of Nafion thickness on BCA modulus was studied. The BCA made using 2 mil Nafion recorded the highest Young’s modulus of 341.4 MPa. The 3.5 mil, 5 mil, and 7 mil BCAs measured 240.4 MPa, 71.46 MPa, and 61.18 MPa for their moduli, respectively. The thicker BCAs have achieved a lower Young’s modulus because of the lower modulus provided by Nafion compared to that of BP layers. Though Nafion doping changes its Young’s modulus drastically, mass and density changes have proven to be minor. However, the ionic conductivity values of Nafion are governed by the doping process. In the order of steps during Nafion doping, pristine Nafion had the highest measured conductivity of 0.011 S/cm, post-oven Nafion had the
lowest ionic conductivity of 0.003 S/cm, and post-doped Nafion conductivity measured to be about 0.006 S/cm. The larger ions present within Nafion after doping may have a diffusion limitation due to their size. Though Nafion doping has shown to improve BCA performance, ionic conductivity may not be the sole governing factor. Nafion doping still provides the larger ions necessary for large BCA generated displacement.

Actuation characterization results show that blocking force and bending deformation increases almost linearly and sometimes exponentially with voltage input increase. Blocking force testing procedures for activated BCAs consisted of placing a thin load-cell pin with known mechanical properties under a microscope for the BCA to bend through unidirectional force generated from applied potential. The microscope is used to measure the exact load-cell pin displacement caused by BCA activation. Once the pin displacement is determined, a beam equation is used to determine the magnitude of force instilled by the BCA.

The blocking force test was conducted at voltages ranging from 0.5 V to 3 V for 2 mil, 3.5 mil, and 5 mil BCAs. Studies show that for 2 mil and 3.5 mil BCA samples, the blocking force linearly increases with higher voltage input. The blocking force generated by 5 mil and 7 mil BCAs exponentially increases when input voltages are increased from 3 V to 10 V. Thicker BCAs can generate more blocking force. This is due to an increase in ion carrying capacity. It is also due to having larger mobile cations available to help produce substantial swelling within the Nafion. Even though BCA deformation decreases when using thicker Nafion membranes, the blocking force generation increases.

Preliminary blocking force estimation modeling results are in good agreement with the experimental results. The results show that Nafion thickness is a key parameter for BCA force generation. The characterization also indicates that with only a 3 V voltage setting, the BCA can achieve 0.3 MPa stress. This performance is comparable to that of skeletal muscle. Optimization of BCA dimension and geometry for blocking force generation need to be further studied.
REFERENCES


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