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Multi-Component Single-Substrate Conducting Polymer Actuation Systems and Fabrication Techniques

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ABSTRACT

Conducting polymer materials can be employed as actuation elements, length sensors, force sensors, energy storage devices, and electrical components. Combining the various functionalities of conducting polymers to create single-substrate, integrated systems remains a challenge, as chemical and electrical insulation barriers, adhesion techniques, and the possibility of scaling need to be taken into consideration. Here fabrication techniques for combining multiple conducting polymer components by means of electrically insulated, mechanical attachments are developed. Electrochemically synthesized polypyrrole substrates were coated with thin films of polystyrene, Parylene, and polyimide. The isotonic actuation performance of each coated film was evaluated in comparison to non-coated films, with an observed decrease in peak-to-peak maximum strain output near 95% (polystyrene and Parylene), 20% (vacuum, 0.8 Pa), 50% (curing at 110°C) and 20% (localized polyimide deposition). The chemical barrier properties of each manufacturing technique were evaluated by exposing the coated polypyrrole substrates to an oxidative chemical vapor deposition of Poly(3,4-ethylenedioxythiophene) (PEDOT). Vapor-deposited PEDOT made the insulation layers of polystyrene and Parylene conductive at thicknesses up to four microns. Spin-coated films of polyimide, greater than ten microns thick, maintained electrical insulation properties after PEDOT depositions. Conducting polymer film-to-film attachments using each manufacturing technique were attempted, with polyimide working successfully when employed under a specific deposition, drying, and curing protocol, as discussed. Three dimensional conducting polymer actuation systems composed of actuators, length sensors, and energy storage devices were constructed on flexible, single substrates. These results build a foundation upon which scalable, self-powered, polymer actuation systems can be developed.

Keywords: Conducting Polymers, Actuators, Strain, Energy Storage, Polypyrrole

1. INTRODUCTION

Mammalian skeletal muscle is a highly integrated, multifunctional system composed of actuation elements, length and force sensors, localized energy storage and delivery components, along with a supporting neuromuscular system that allows muscle to be controlled over a range of frequencies, to a high degree of precision. Conducting polymers are one possible candidate for replicating the integrated compositional structure and functions of muscle, due to their inherent multifunctional nature. Conducting polymer actuators produce moderate strains [1] and high stresses [2]. Conducting polymer length sensors can measure similar strain ranges over a broad range of frequencies [3]. Conducting polymer supercapacitors can store energy, and deliver power to the subcomponents of an actuation system, while remaining flexible and scalable [4]. While these subcomponents have been studied significantly on an individual basis, the challenge remains to combine the subcomponents to create coupled actuation systems, whereby different conducting polymer elements (actuators, sensors, supercapacitors, etc.) are fabricated and operate simultaneously.

Combining these conducting polymer subcomponents onto single substrates requires the consideration of several important mechanical, electrical, and chemical properties. For example, actuators that are coupled to length sensors need to operate concomitantly, yet remain compliantly attached such that both systems function optimally. Supercapacitors that provide power to actuators and length sensors need to be flexible and scalable, such that they can be distributed next to the system to which they provide energy.

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Furthermore, subcomponents should be combined in such a way that they can be effectively scaled, laterally, longitudinally, or radially. These requirements impose significant challenges in developing fabrication techniques to combine conducting polymer actuation systems.

Several manufacturing techniques have been investigated as possible methods of combining conducting polymer components. These techniques include plasma-aided polystyrene depositions, Parylene depositions, and spin-coated polyimide techniques. Each technique has been evaluated with respect to the decrease in actuation performance resulting from the processing steps. The feasibility of maintaining electrical insulation after exposing coated conducting polymer actuators to a layer of Poly(3,4-ethylenedioxythiophene) (PEDOT), deposited through oxidative chemical vapor deposition, has also been evaluated. Advanced interconnection fabrication methods have been developed based on the successful implementation of polyimide as an insulator and mechanical adhesive.

2. SYNTHESIS OF CONDUCTING POLYMERS

Polypyrrole was chosen as the main conducting polymer to be used for actuation, length sensors, and supercapacitor elements. Polypyrrole substrates were polymerized according to a recipe developed by Yamaura [5, 6], with slight modifications [7, 8]. All depositions occurred in a solution of 0.05 M tetraethylammonium hexafluorophosphate (Sigma), 1% vol/vol water, and 0.05 M pyrrole (Sigma) in propylene carbonate. Pyrrole, being sensitive to light, oxygen, temperature, etc., was freshly distilled before deposition and sealed in airtight, light-free containers at -20 °C before use. All other chemicals were used as received, unless otherwise noted. Polypyrrole films were grown on cylindrical glassy carbon crucibles produced by HTW Hochttemperatur-Werkstoe GmbH. The counter electrode used during depositions was a 0.5 mm sheet of copper foil (Mc-Master-Carr), whose surface area was at least two times the size of the working electrode (i.e. glassy carbon crucible). Films were deposited galvanostatically at current densities near 0.5 A/m². The temperature was maintained at -40 °C during depositions. Deposition times were typically 10 h, resulting in film thicknesses near 20 µm. Films were air-dried, passively for 12 hours following deposition and then sealed in air-tight containers until use. An example glassy carbon crucible electrodeposition of polypyrrole is shown in Figure 1.



Figure 1: Example depositions of polypyrrole deposited onto a glassy carbon crucible (left) and a 100 mm Ti/Au-plated silicon wafer (right). The resultant polypyrrole films are smooth, and have comparable conductivity values.

In certain procedures, polypyrrole was grown on Ti/Au plated silicon wafers (Figure 1), using the same concentrations and environmental conditions as stated above. The wafers were treated prior to electrodeposition with titanium (10 nm) and gold (50 nm) through sputter coating (AJA Orion 5). The use of silicon wafers was explored as a means of obtaining geometrically acceptable polypyrrole substrates to which conventional micro-electro-mechanical-systems (MEMS) manufacturing processes could be applied.

3. POLYMER-POLYMER INSULATION AND MECHANICAL ATTACHMENTS

One approach to depositing insulation layers between different components made of conducting polymer is through the plasma-aided deposition of polystyrene. Polystyrene coatings can conform to surfaces of various geometries, especially

thin films in which surface variations are small enough such that no shadowing effects occur. Polystyrene films have the potential to act as insulators between layers of conducting polymer materials.

Several polystyrene coatings were performed on polypyrrole substrates. Initially, polystyrene conformed well to the polypyrrole substrates. No electrical conductivity was observed on the coated side of conducting polymer films following deposition. The polypyrrole films, however, lost their moisture content and became mechanically brittle after being exposed to vacuum environments for extended periods of time (10 to 60 minutes) and heat exposure during polystyrene depositions. In addition, while polystyrene initially conformed well to polypyrrole film surfaces, after a 48 hour period, the outer layers of polystyrene began to peel off. A photo of a 1 μm coating of polystyrene and the effects of peeling is shown in Figure 2.

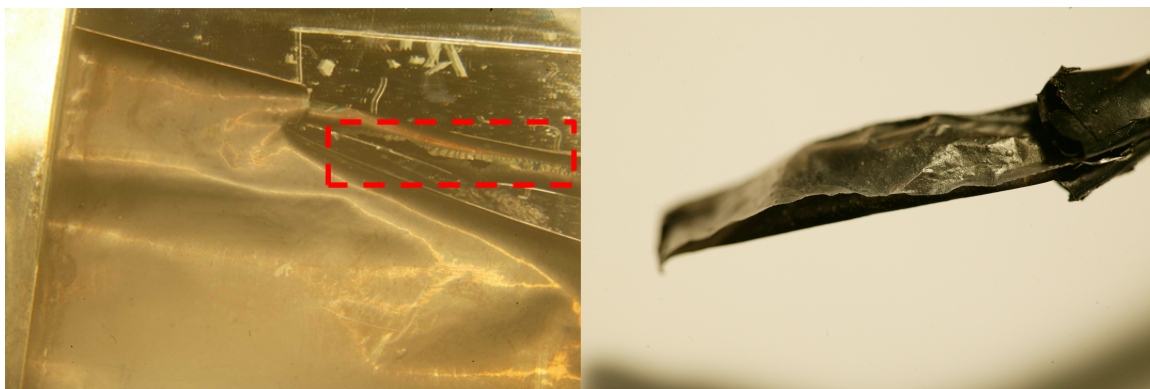


Figure 2: Plasma-aided polystyrene deposited onto free-stranding polypyrrole film (left). Cracking and peeling of the polystyrene is visible along the ridge in the photo (dotted box). Parylene-coated polypyrrole sample (right). Although Parylene initially conformed well to polypyrrole surfaces, after cooling and drying, Parylene coatings could be peeled away.

Parylene was also tested as an interfacial material because of its ability to resist solvents and maintain electrical insulation. Parylene depositions are similar to polystyrene in that they subject polypyrrole films to heat and vacuum environments. Parylene, however, can also be deposited up to higher thickness. Greater thicknesses ultimately lead to more flexibility in controlling the insulation properties. Polypyrrole films that were grown on silicon wafers and subsequently Parylene coated (Paratech Lab Top Coater, Parylene N, 3 g, 3 hours) yielded consistently thick films ($\sim 4 \mu\text{m}$) that were electrically insulating. After such depositions, Parylene-coated films were significantly less brittle than films that had been deposited with polystyrene. The same issues involving separation after drying, however, occurred with Parylene coatings as well (Figure 2), usually after a period of 24 hours.

As an alternative approach to vaporized deposition under vacuum, polyimide was spin-coated onto polypyrrole substrates and cured at low temperatures (90 to 110 $^{\circ}\text{C}$), forming a soft, flexible film. All polyimide films were spin coated using a Solitec Spin Coater for times ranging from 60 to 90 s at speeds between 500 and 4000 RPM, according to a custom calibration curve. The speeds and times yielded film thickness between 1 to 30 μm .

While polyimide adhered to polypyrrole films after soft-curing, initially the insulation layers showed significantly poorer performance than that of polystyrene and Parylene. One cause of poor insulation was the fact that polypyrrole is porous, and after spin coating polyimide resin onto polypyrrole substrates, the polyimide began to seep through the polypyrrole films. If left for a sufficient period of time (~ 15 minutes), the uncured polyimide coatings would seep completely through a 20 μm film. This seepage caused curdling during the curing process as well, yielding cured surfaces that did not adhere well, and were not electrically insulating. Such curdling is shown in Figure 3, where a two sheets of polypyrrole were attached, using a polyimide interface, waiting 15 minutes before curing.

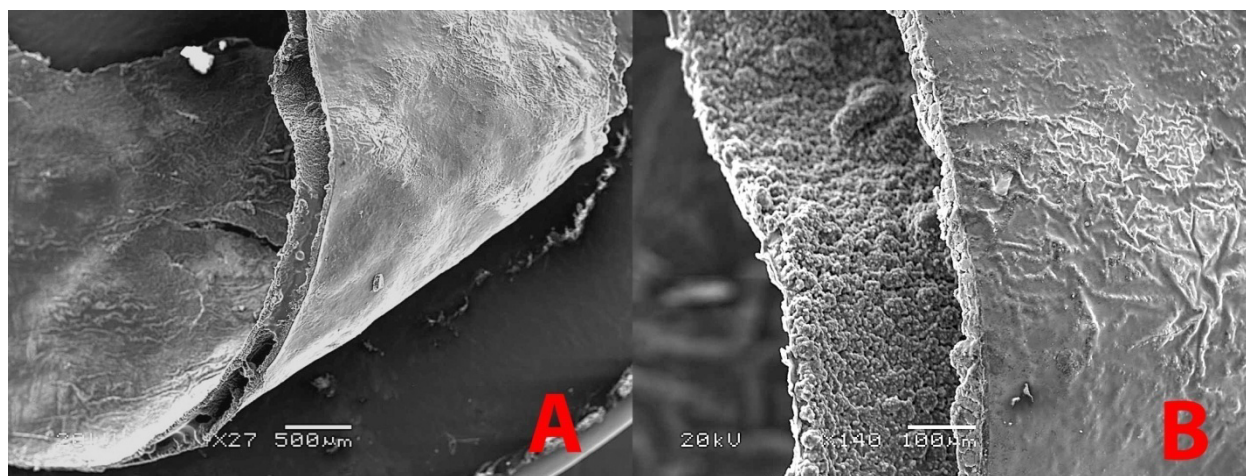


Figure 3: Two free-stranding polypyrrole films surrounding a layer of polyimide. The polyimide did not attach the two films together, but dried in a curdling manner on each respective surface. The poor attachment properties between the polypyrrole substrates can be attributed to the moisture content of the polypyrrole films and seepage. (B) is a close-up view of (A). (SEM micrographs from Jeol 6060).

To reduce seepage and promote adhesion, modifications were made to the polyimide deposition protocol. First, it was determined that increasing the drying time of the polypyrrole film, following electrodeposition, led to less seepage. In addition, the underlying substrate was reduced in thickness (thinner Si wafers) in order to promote equal drying on both the top and bottom of the substrate. Finally, polyimide films were cured within 60 s of resin application, reducing the overall seepage time. Figure 4 shows an example of two polypyrrole films, firmly attached by an interfacial layer of polyimide using this modified protocol.

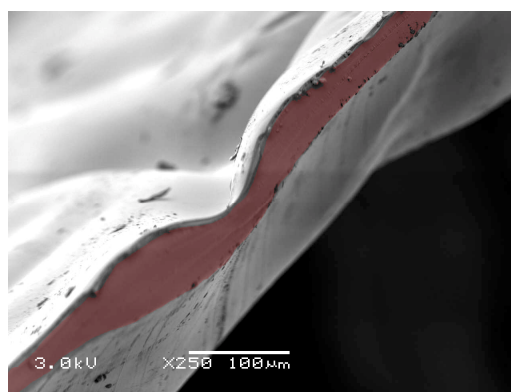


Figure 4: Two free-standing polypyrrole films attached by a thin layer of polyimide. With sufficient drying, mechanical attachments between polypyrrole films are possible. (SEM micrograph from Jeol 6060).

The thermal-mechanical behavior of polyimide during curing also affected the quality of the final coated polypyrrole films. Polyimide shrinks during curing, thereby generating stresses between the polyimide-polypyrrole interface and deforming the final shape of the combined films. This problem can be mitigated by curing polyimide in gradations. For example, if a thick (greater than 5 μm) insulation layer of polyimide is required, polyimide can be spin coated onto a silicon substrate, soft cured, and then attached to a polypyrrole substrate with a thin layer of polyimide adhesion (1 to 2 μm). An additional possibility is to apply polyimide to localized regions of the polypyrrole substrate, and thereby limit any material stress that would otherwise act across an entire substrate. Both methodologies, thin adhesion layers and localized polyimide depositions, were employed to create multicomponent conducting polymer actuation systems.

4. INTER-COMPONENT ELECTRICAL INSULATION

One method of creating integrated, conducting polymer actuation systems is to add a vapor deposited layer PEDOT on top of an insulated, polypyrrole film [9]. Such fabrication geometries enable two conducting polymer layers to function in parallel, while remaining electrically insulated from each other. After investigating possible electrical insulators for conducting polymer films (Section 3), each insulator was subject to the deposition of PEDOT, through oxidative chemical vapor deposition (oCVD), to test whether or not the insulation layer could maintain electrical isolation. With oCVD, very thin films of PEDOT can be patterned onto substrates in a conformal manner, according to previously described methods [10]. PEDOT layers can then be used as sensors, or as energy storage electrodes.

In the oCVD process, the vapor deposition of PEDOT often penetrates into the substrate upon which it is deposited, especially if such a substrate is porous. To examine the feasibility of multi-layer polypyrrole-PEDOT actuation systems, polypyrrole substrates were grown through electrodeposition, dried, and coated with insulation layers of polystyrene, Parylene, and spin-coated polyimide. After depositing the insulation layers, each film was subsequently coated with PEDOT through oCVD. The conductivity between the two layers of conducting polymers, after the deposition of PEDOT, was then measured.

Figure 5 shows three different polypyrrole insulated substrates coated with PEDOT. In each of the three cases, PEDOT coated permanently onto the surfaces of the insulating layer. Less evident from the photos, however, is the penetration depth of the PEDOT through the insulator layer. Table 1 shows the effects of PEDOT depositions with respect to the resistance between layers of conducting polymers (PEDOT and polypyrrole) when separated by a layer of insulation.

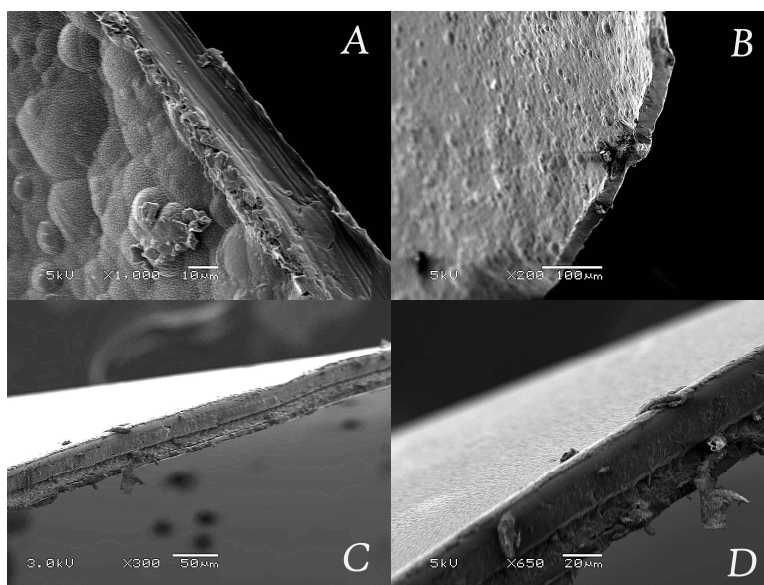


Figure 5: PEDOT coated samples of polypyrrole, insulated by (A) polystyrene, (B) Parylene, (C) polyimide, and (D) polyimide. In (A), the PEDOT settled on the polystyrene substrate in globular formations. In (B), (C), and (D), the PEDOT depositions were smoother.

Table 1: Summary of possible electrical insulators and adhesives for multi-component conducting polymer systems

Insulation Type	Film thickness	Resistance across interface before PEDOT deposition	Resistance across interface after PEDOT deposition
Polystyrene	500 nm to 1 μ m	20 M Ω	< 100 Ω
Parylene	2 to 5 μ m	10 M Ω - OPEN	~1 k Ω
Polyimide	1 to 10 μ m	2 M Ω - OPEN	OPEN

In each case, prior to PEDOT deposition, the insulating surfaces were non-conducting. After PEDOT depositions, however, the resistance between layers decreased significantly, except when polyimide was deposited in thick layers. The penetration depth of the PEDOT was estimated to be between 5 and 7 μm through a polyimide substrate, according to the deposition conditions, as can be discerned from Figures 5 (C) and (D).

5. FABRICATION EFFECTS ON ACTUATOR PERFORMANCE

In order for conducting polymer actuation systems to function optimally, the processing techniques used to combine subcomponents should have minimal effect on the performance of the overall system. To investigate these effects, the peak-to-peak strain of polypyrrole actuators was measured before and after each processing step. Figure 6 shows the comparison of an untreated polypyrrole actuator with respect to the different processes involved in polystyrene, Parylene, and polyimide processing. The results of Parylene and polystyrene coated actuators have been omitted, as both resulted in strain reductions of nearly 95%. Results in Figure 6 show that extended vacuum exposure degraded the performance of the polypyrrole actuator by 20%. Vacuum environments, used for both polystyrene and Parylene depositions, would therefore reduce actuation performance significantly. Heat treatment at 110 $^{\circ}\text{C}$ also reduced strain output by 50%. Polyimide coated actuators also showed large reductions in strain. For example, a polypyrrole actuator with 20 μm coating of polyimide showed a reduced strain output of 90%. If polyimide was applied locally, however, only to sections of the actuator by which mechanical attachments were made, strain output was significantly higher. For the case of a 20 mm actuator with two, 2.5 mm polyimide connections, the strain output was only reduced by 20%.

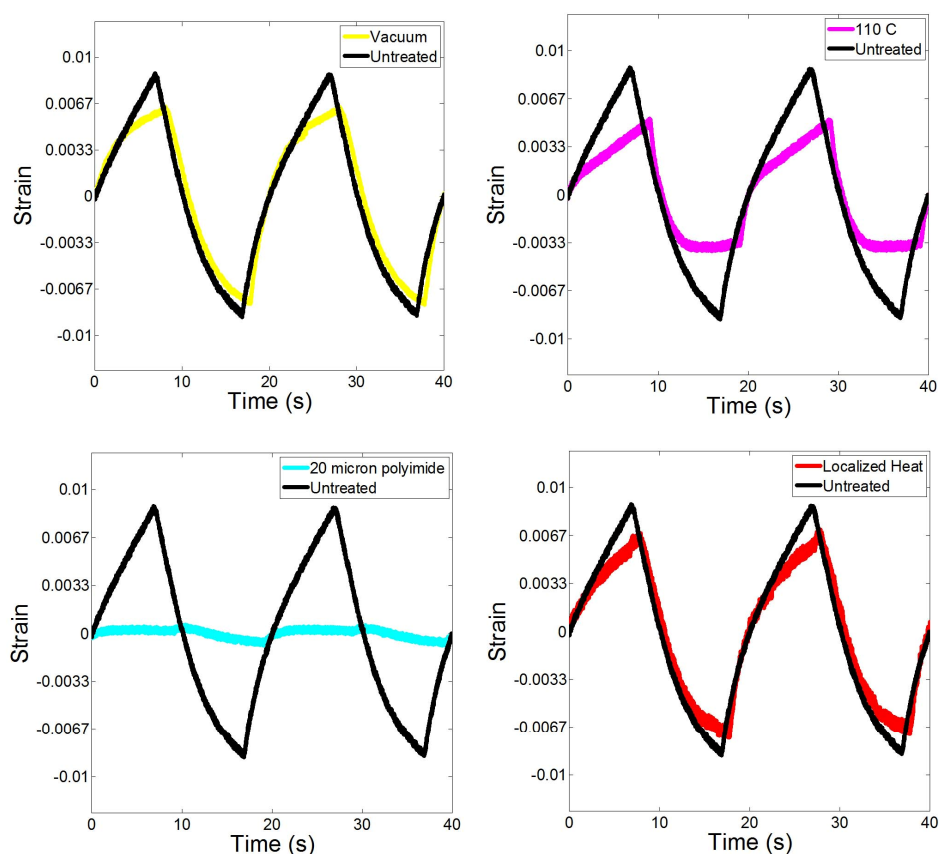


Figure 6: Strain comparison of polypyrrole actuators when subject to different fabrication conditions. All actuators had an original length of 20 mm. Vacuum treatment was carried out at 0.8 Pa for 1 hour. Heat treatment was carried out at 110 $^{\circ}\text{C}$ for 10 minutes. A 20 μm polyimide backing was applied along the entire length of the actuator. For localized heat, two polyimide strips were connected to the outer 2.5 mm ends of a 20 mm polypyrrole actuator.

6. MULTI-COMPONENT FABRICATION

Of the possible candidates developed for creating multi-component conducting polymer actuation systems, polyimide provides the highest degree of electrical insulation, while causing the lowest reduction in strain output. Furthermore, while Parylene and polystyrene offer electrical insulation, they cannot be used as adhesives. As such, polyimide was further explored to combine different conducting polymer subcomponents in the fabrication of multi-component conducting polymer actuation systems.

To build these actuation systems, polypyrrole was electrochemically deposited, as discussed in Section 2. Subcomponents were then cut to shape by means of laser ablation. Conducting polymer actuators and length sensors were made from thin strips of un-modified conducting polymer films. Conducting polymer energy storage devices were fabricated, according to a protocol previously discussed [3]. Attachments between components were performed using thin layers of polyimide, applied locally to the different subcomponents at their attachment locations. Localized heat was applied using a heating iron, set at 110 °C.

Figure 7 shows one possible configuration for a conducting polymer actuation system, whereby an actuator, length sensors, energy storage and electronics are arranged in a serial fashion. The simultaneous operation of these subcomponents [3] renders the possibility of creating more complex systems in which components are integrated in series, parallel, and stacked configurations. The final working substrate, which is both flexible and scalable, points towards a means of fabricating large-scale, conducting polymer actuation systems.

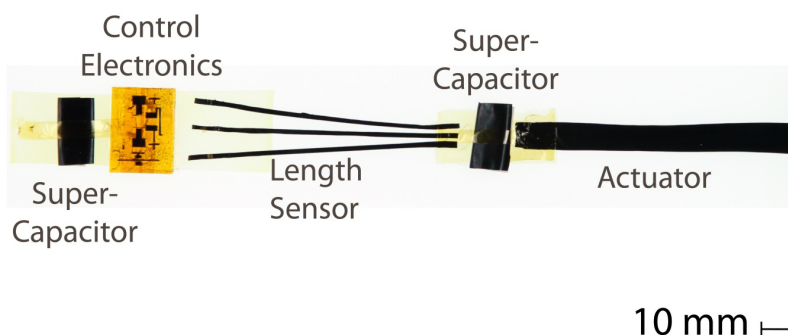


Figure 7: Multi-component conducting polymer actuation system. A polypyrrole actuator, length sensors, supercapacitors, and transistors are connected in series. Polyimide films provide both mechanical attachment and electrical insulation between components.

7. DISCUSSION AND CONCLUSION

The fabrication techniques developed here offer a stepping-stone by which conducting polymer actuation systems can be built. While polystyrene and Parylene provide limited insulation properties in the fabrication of multi-component systems, their long-term adhesion properties and inability to prevent PEDOT penetration preclude them from being employed on a larger scale. Polyimide can be used as an adhesive and insulator, granted that underlying polypyrrole films are dried significantly before being processed. Localized heating offers an additional alternative to bulk polyimide processing, as localized attachments mitigate part of the strain reduction that results from polyimide coatings. While multifunctional conducting polymer actuation systems have been developed and tested, a significant area of future research will look at shrinking the size of each sub-component, enabling the automatic attachment and insulation between components, and the ability to scale such systems in an effort to build complex geometries with unique actuation properties.

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