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# Conductivity Trends of PEDOT-PSS Impregnated Fabric and the Effect of Conductivity on Electrochromic Textile

Yujie Ding, Michael A. Invernale, and Gregory A. Sotzing\*

Department of Chemistry and the Polymer Program, University of Connecticut, 97 N. Eagleville Road, Storrs, Connecticut 06269-3136

**ABSTRACT** A stretchable e-textile was fabricated by simply soaking Spandex fabric in a conductive polymer aqueous dispersion, PEDOT-PSS. The resulting conductive fabric had an average conductivity of 0.1 S/cm. Subjecting the fabric to more than one soaking step increased the conductivity of the fabric up to ca. 2.0 S/cm resulting in a 33 % faster switching speed. This simple methodology is not limited to Spandex (50 % nylon/50 % polyurethane). Several other fabric compositions were investigated for their conductivity via this process, including 100 % cotton, 60 % cotton/40 % polyester, 95 % cotton/5 % Lycra, 60 % polyester/40 % rayon, 100 % polyester, and 80 % nylon/20 % Spandex, listed in order of decreasing hydrophilicity. Those fabrics with higher water uptake resulted in higher conductivities upon soaking in PEDOT-PSS. Electrochromic polymers coated on the fabric could be switched between their different colored states, even upon stretching of the Spandex. SEM revealed that the electrochromic polymer coated on the substrate separated under stretching, uncovering the color of the base conducting fabric. It was found that the PEDOT-PSS was not a film on the Spandex but rather homogenously dispersed nanoparticles within the fabric matrix forming a percolated network.

**KEYWORDS:** conductive polymer • stretchable electrode • electrochromic • PEDOT-PSS • conductive textile

## INTRODUCTION

In recent decades, a new research trend in the area of smart fibers and fabric has emerged, focusing efforts on enhancing the functional properties of textiles. Wearable technology, usually electronic-based, is one of the many attempts to add new features to traditional fabrics (1). As an example, strain gauges, biomotion detectors, and wearable displays have been reported by impregnating various kinds of electronic devices into garments using fabrics developed by SmarTex (2). On the fashion end, Philips and Levis have integrated mobile phones, LEDs, and music players into their prototype clothing. Nokia also has a prototype snow jacket with a mobile phone incorporated. However, this method of imbedding a device in fabric could result in bulky, not-everyday-friendly clothing. Functional electronic textile, in order to be successful, would need to be lightweight, have the feel of a fabric, be comfortable to wear, and yet be easy to care for (3, 4). To address this problem, many researchers are seeking an approach to obtain a truly conductive textile that feels and folds like normal fabrics but also supports the functions of smart textile, thus integrating the devices into the base fabrics themselves. Conducting polymers, because of their light weight, processability, relatively high conductivity, stability, and flexibility, are well-suited for the fabrication of conductive textiles (5). Very recently, our group reported a fabric electrochromic device prototype made using conductive

polymer impregnated Spandex (6). Electrochromism is a phenomenon wherein a material changes color when undergoing a redox switch between its oxidized and reduced states. Conducting polymers represents a relatively new generation of electrochromic materials with significant potential for the same reasons they are sought for as conductive coatings. Additionally, electrochromic materials can afford easy and tunable color variation (7–9). Our previous work (10–12) on precursor polymers allows us to coat and pattern any substrate by spray-coating or other solution-based casting method. Oxidative conditions will then convert these precursors to conjugated polymers (13–16). The ease of processability makes them ideal choices for wearable electrochromic devices. The resulting color-changing fabric has potential in fabricating adaptive camouflage, wearable displays, textiles, and fashion wear.

The conductive Spandex we used for the all-organic electrochromic fabric prototype was fabricated by simply soaking commercially available Spandex in a PEDOT-PSS solution. The fact that the coating does not affect the mechanical properties of the substrate allows for them to be used as flexible and deformable substrates. CP composite conductive textiles have been reported elsewhere. Wallace and co-workers reported an *in situ* polymerization of polypyrrole or polyaniline onto normal synthetic fibers that render a “normal-fabric-like” conductive fabric with reasonable conductivity (17–25). Kotov et al. (26) imbedded single-wall carbon nanotubes in cotton threads with a simple dipping process. The resultant conductive cotton fabric served as wires to light an LED. However, due to the black color of the carbon nanotubes and dark color of polyaniline or polypyrrole impregnated fibers, these materials are un-

\* Corresponding author. Tel: 860-486-4619. Fax: 860-486-4745. E-mail: sotzing@mail.ims.uconn.edu.

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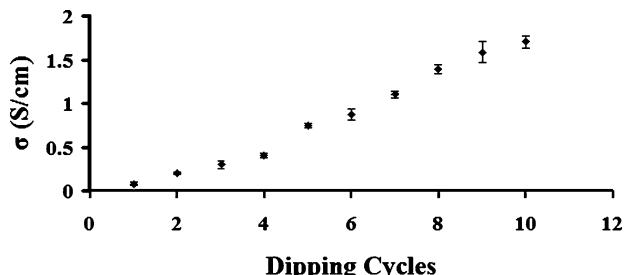


FIGURE 1. Conductivity increase for PEDOT-PSS-soaked Spandex across multiple dipping cycles.

likely candidates for the use in color functional electrochromic textile as one will not be able to perceive a significant color change in the reflected light. Our method provides a light blue color to the conductive fabric, allowing for perception of the electrochromic color change on the surface of the fabric.

Herein we present a systematic study on the methodology of making conductive Spandex fabric by physically soaking it in a commercially available PEDOT-PSS dispersion. The resultant PEDOT-PSS-soaked Spandex substrate is light blue and retains the stretchability of the original substrate. Parameters such as doping, annealing, and the effect of stretching have been evaluated with respect to the fabric's conductivity. The effect of the conductivity on electrochromic switching was also investigated, as well as how the color perceived could be modulated by stretching. Other types of fabric, apart from Spandex, were also evaluated in order to assess saturation limits of PEDOT-PSS within the base materials.

## RESULTS AND DISCUSSION

**Fabrication of the Conductive Spandex.** The optimum conditions for soaking were found to be 5 min in a PEDOT-PSS dispersion doped with 2 wt % d-sorbitol (ca. 14% increase of conductivity compared to the pristine sample; see the Supporting Information for details). On the basis of previous work, it was found that fabric electrodes whose conductivities were as low as 0.05 S/cm were able to switch the electrochromic material. Further, if the conductivity was greater than 0.1 S/cm, the conductive substrates could also electrochemically convert precursor polymer to the conjugated, electrochromic material (6). Repetitive soaking/drying cycles, referred to as “dipping cycles,” increased the conductivity in a quasi-linear fashion (Figure 1). This increase began to taper above dipping cycles. Furthermore, conductive material was visibly flaking from the substrate at and beyond 10 dipping cycles so no further dipping cycles were attempted. The maximum conductivity achieved during this process was 1.71 S/cm. The conductivities in Figure 1, while not as high as thin films of PEDOT-PSS, still allowed for the fabric to function as electrodes. A double-concentration PEDOT-PSS solution was obtained by evaporating 50% of the water by mass. A single dipping cycle with this higher concentration of PEDOT-PSS was found to enhance conductivity from 0.060 S/cm to 0.175 S/cm. This result was expected, as the concentration of conducting polymer in the

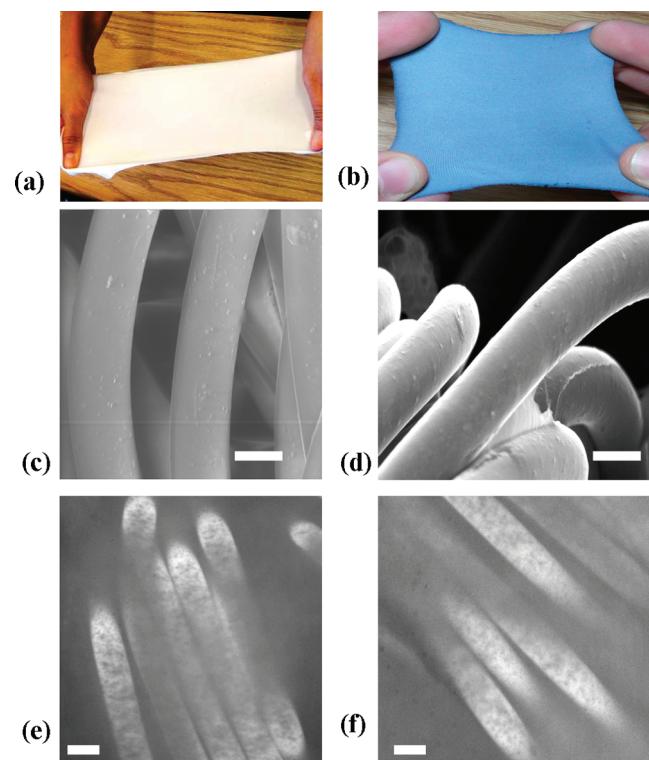


FIGURE 2. Stretchable Spandex fabric (a) before soaking and (b) after soaking with PEDOT-PSS. Scanning electron microscope images of this fabric (c) before and (d) after soaking. Polarized microscope images for the fabric (e) before and (f) after soaking. All scale bars are 10  $\mu$ m.

evaporated solution is enhanced, allowing more conductive material to be absorbed by the fabric.

The Spandex fabric turned from its original white to a light blue color upon soaking. It retained the feel and texture of the original Spandex (Figure 2). Scanning electron microscopy (SEM) was used to examine the PEDOT-PSS coated fabric for potential aggregates and nonuniformity. The surface is smooth and no apparent boundary of the substrate fiber with PEDOT-PSS can be seen. Few polymer aggregates could be seen between the bundles, as compared to those observed in the case of *in situ* polymerized polypyrrole on textiles (27). To understand how the PEDOT-PSS particles are distributed inside the threads, confocal microscopy was used to examine the soaked fabric. Because a fluorescent whitening dye was used in the process of the Spandex manufacturing, it was expected that when excited, PEDOT-PSS particles will appear in the fluorescence image as dark shadows. However, no particles were observed. Polarized microscopy was also employed (Figure 2) and no significant difference could be observed between the pristine and soaked fabric. The black spots seen in both images could be attributed to the holes that could be also observed from SEM images on the thread surface. These holes are much larger than PEDOT-PSS particles, which have an average size of 25–75 nm (28). These results, along with cross-sectional analysis of soaked fabric, indicate that the PEDOT-PSS was distributed evenly throughout the Spandex material. We did not have a film of PEDOT-PSS, but were rather dealing with a uniformly dispersed conductor, as in a percolated system.

Subsequent dipping cycles were therefore increasing the particle loading in the insulating Spandex material, which resulted in increased conductivity, as expected.

Many studies have been carried out on the annealing effect of sorbitol-doped PEDOT-PSS films. Although the question of why the dopants increase the conductivity is still controversial, it is suggested that annealing will not result in a significant change in conductivity unless films are heated above 150 °C (29, 30). Therefore, we annealed several samples of the PEDOT-PSS soaked Spandex at 150 and 200 °C for 2 min. The reasons for the short annealing time are: (a) research has shown that a short period of time is enough to bring about the enhancement in conductivity (30) and (b) longer heating times will jeopardize the mechanical property of the base fabric, which turns brittle and less elastic (and can exhibit browning, in some cases) after the annealing process. Unlike their film counterparts, annealing conductive fabrics does not increase the conductivity of the fabric.

The stability of PEDOT-PSS films is also well-studied. The conductivity of the films decreases gradually during storage. It was reported that the decrease slowed down when stored in dry nitrogen atmosphere than those stored in oxygen and humid environments. The stability of the conductive textiles agrees with earlier reports on sorbitol-doped PEDOT-PSS films (29). The conductivity of Spandex samples decays much slower when they are stored in a desiccator (50% loss after 5 days), as compared to those stored in air (70% loss after 5 days; see the Supporting Information).

**Stretchability.** The Spandex used in the conductive textile can be stretched up to 200% of its original length and recover completely when released. The conductive fabric retained its mechanical properties and thus was also stretchable. First, we tested if simply stretching the fabric will have any effect. A piece of conductive fabric was stretched to a desired length and mounted on the conductivity setup. As shown in Figure 3, the conductivity increased with increasing elongation while measured in the stretched state. Hysteresis was measured for this conductivity; it showed little effect for 20% elongation. The stress-strain curve mimicked this result. For an 80% elongation, however, a significant hysteresis was observed for both conductivity and stress-strain. Note that films of PEDOT-PSS could not undergo such stresses and retain their conductivity because of mechanical failure. Therefore, the PEDOT-PSS has to exist in the Spandex as homogenously distributed nanoparticles.

When the spandex was stretched to the same degree three times and released to its original length, the final conductivity was lower than its original value. The more it was stretched, the more it decreased: 12.5% loss in conductivity for a stretch to 1.2×, 38.1% loss for a 1.5× stretch, and 65.2% loss for a 2× stretch. A possible explanation of this phenomenon is that when the fabric was stretched for the first time, the PEDOT-PSS coating/filling was aligned, the PEDOT-PSS particles were closer to each other and thus charge-hopping became easier. When the force was removed, the continuity of the PEDOT-PSS filling was somewhat broken and it became more difficult for charges to flow

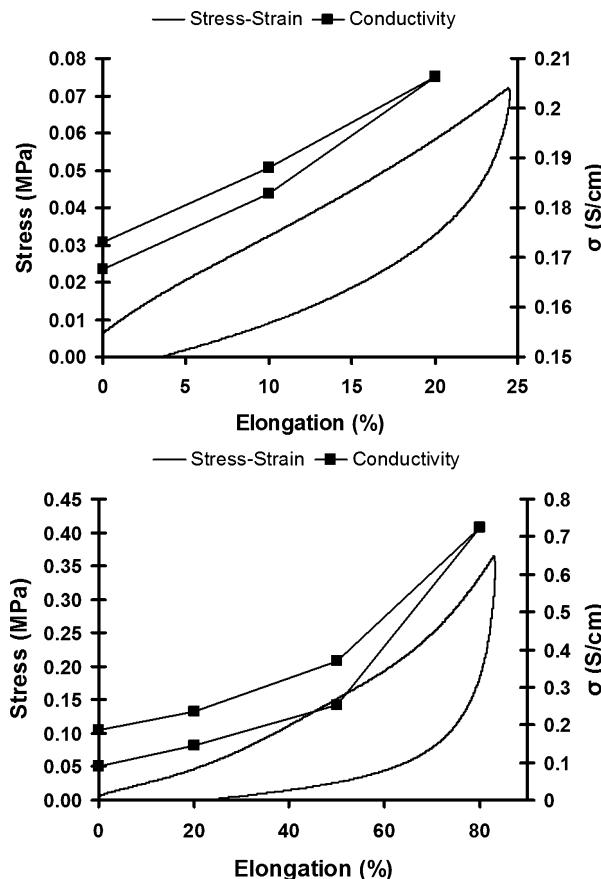


FIGURE 3. Top: Hysteresis for conductivity and stress-strain for a spandex electrodes at an elongation of 20%. Bottom: Hysteresis for conductivity and stress-strain for a spandex electrodes at an elongation of 80%.

in the matrix. Larger stretching resulted in more severe damage to the continuity and lower conductivities. We hypothesized that carrying out a dipping cycle while the Spandex was stretched may eliminate this decrease when the textile was exposed to a similar stress. Therefore, we soaked a set of Spandex in PEDOT-PSS under 50% stretching while a control group was soaked normally (all other conditions were kept the same). Results showed that the pieces soaked while stretched had, on average, 10.4% lower conductivity than the control group. However, both groups have similar losses in conductivity after repeated stretching at 50% (25.4% loss for the control group versus 26.9% loss for the soaked-while-stretched group).

The reason for this hysteresis can be explained by way of contact resistance. Because the Spandex is a woven structure, apart from the resistivity of the individual fibers, there is a contact resistivity between each thread. It has been proven (4) that the contact resistance decreases with increasing applied load. Therefore, when the fabric was stretched, contact resistivity decreased and the conductivity of the fabric increased. After several stretches, the tightly woven matrix became loose and the resistivity at the overlapping point went up, which resulted in decreasing conductivity of the fabric. Soaking while stretched could not prevent the fabric from loosening when stretched again and hence could not avoid the conductivity loss. Moreover, the

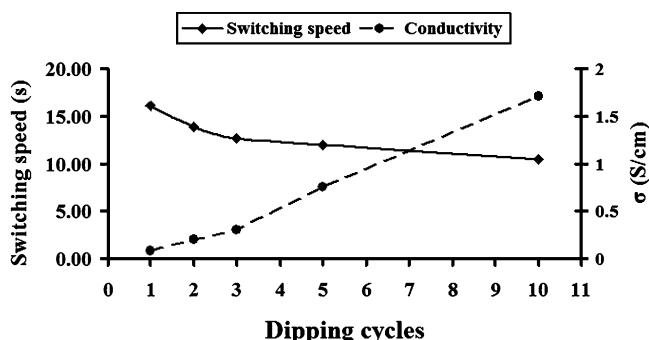


FIGURE 4. Switching speed of the electrochromic polymer (diamonds) and the conductivity of its base substrate (circles) for  $2\text{ cm}^2$  area electrodes as a function of dipping cycles.

long period of stretching during soaking also increased the contact resistivity between threads and therefore led to a lower initial conductivity as compared to the control group. These results are also consistent with percolation behavior. As the volume decreases perpendicular to the fiber axis, it is expected that the conductivity would increase. Slight variation in the redistribution of nanoparticles in the fiber composite could lead to hysteresis.

**Effect of Conductivity on Electrochromism.** It is reasonable to expect that higher conductivity will result in a faster switch for the electrochromic material. Figure 4 shows the switching speed achieved for fabrics assembled into devices that were subjected to 1, 2, 3, 5, and 10 dipping cycles. When the conductivity of the PEDOT-PSS-soaked fabric increased, the switching time of the electrochromic devices decreased, from 16.04 to 10.47 s, for 10 dipping cycles. There was no significant change in switch speed at conductivities beyond 0.25 S/cm, however, as going an order of magnitude higher in conductivity only provided a 2 s faster response speed. All electrodes used were  $2\text{ cm}^2$  in area. Moreover, it was possible to convert the precursor polymer electrochemically when the conductivity of the Spandex was greater than 0.1 S/cm.

It was demonstrated that the electrochromic material is still fully functional when the substrate was stretched (6). Apart from the conductivity factor, stretching itself affects the morphology of the spray-coated electrochromic polymer films. As seen in Figure 5, stretching resulted in gaps in the electrochromic polymer film, thus exposing the PEDOT-PSS-soaked fibers underneath. The fibers, on the other hand, showed no color change (separation) or continuity problems upon stretching, again confirming the result of a percolated network of PEDOT-PSS particles. The intensity of the red color diminished because of the exposure of the blue underneath, and returned to its original state when released.

**Other Fabric Compositions.** As long as a fabric absorbs water, aqueous PEDOT-PSS dispersions should be able to impregnate the fabric matrix, resulting in a conducting textile. The conductivity of the textile will depend on a variety of factors, including the style of the weave, porosity, and hydrophilicity of the material. As shown in Figure 6, seven different fabrics: 100% cotton, 60% cotton/40% polyester, 95% cotton/5% Lycra, 60% polyester/40% rayon, 100% polyester, 80% nylon/20% Spandex, and 50% nylon/

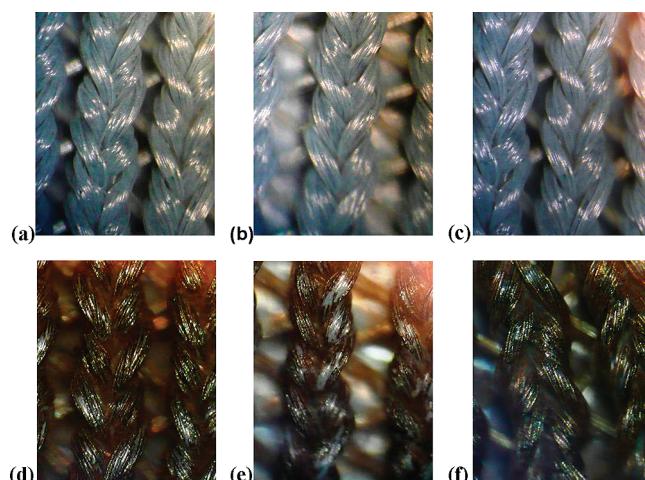
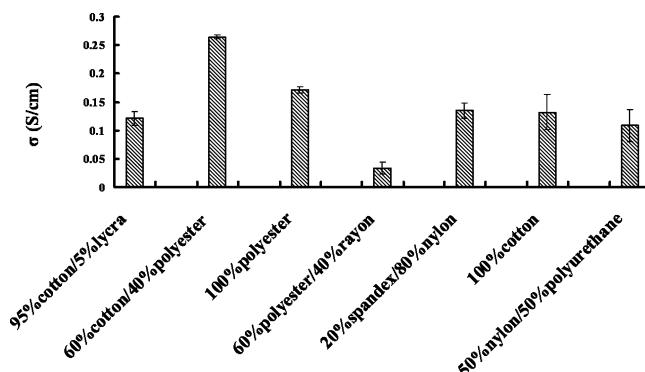


FIGURE 5. Optical microscope images ( $20\times$ ) of (a–c) conducting fabric and (d–f) electrochromic polymer coated fabric. (a, d) Before stretching, (b, e) under ca. 20% stretching, and (c, f) after relaxation to its original state.



Textile type	Water absorbed (mg)
95% cotton/5% lycra	299.36
60% cotton/40% polyester	310.21
100% polyester	207.5
58% polyester/40% rayon	287.66
20% spandex/80% nylon	177.84
100% cotton	326.73
50% nylon/50% polyurethane	163.77

FIGURE 6. Top: Conductivity of various textiles soaked with PEDOT-PSS. Bottom: Water absorbed by different fabrics.

50% polyurethane (the Spandex used above), were soaked in the sorbitol-doped PEDOT-PSS solution for 5 min and were dried in air for equal periods of time before measuring their conductivity. All fabrics turned from white to light blue and retained their original mechanical properties. The ability of the fabric to absorb water was measured by soaking the fabrics in distilled water and weighing. As shown in Figure 6, the fabric with the highest conductivity—60% cotton/40% polyester—absorbs one of the highest amounts of water. The same relative order of mass uptake was observed for soaking in PEDOT-PSS. Other fabrics with high conductivity, such as 100% polyester and 100% cotton also have high water mass uptake. On the other hand, 20% Spandex/80% nylon and 50% nylon/50% polyurethane have medium to high conductivity with relatively low mass uptake. The 60% polyester/40% rayon has very low conductivity despite having a

287.66 mg water absorbance. This could be explained by moisture regain of the different textiles. Rayon has a relatively high moisture regain value: 11.0 compared to 7.0 of cotton, 4.5 of nylon, and 0.4 of polyester (31). Therefore, although rayon absorbs more PEDOT-PSS with water, after drying, the high moisture regain value results in more water entering the textile from the atmosphere than the other dried fabrics. As described earlier, humidity is detrimental to the conductivity of the fabrics and thus results in a lower conductivity value. Similarly, 100% cotton had lower conductivity than 60% cotton/40% polyester, although it absorbed more water because of its much higher moisture regain value than polyester.

Spandex-based electrodes and devices achieved switching speeds of ca. 15 s. To understand the effect of fabric conductivity on switching speed across multiple fabric types, we also chose the highest (60% cotton/40% polyester) and lowest (60% polyester/40% rayon) conductivity fabrics for device assembly. It was found that for an equal area device ( $2\text{ cm}^2$ ), the switching speed for the highest conductivity fabric was ca. 10 s and that for the lowest was ca. 20 s. This is consistent with previously observed trends (6).

## CONCLUSION

We have reported a simple method for preparing electronically conductive fabric by soaking in a PEDOT-PSS dispersion. Secondary doping with d-sorbitol enhances the conductivity of the fabric, whereas annealing has no significant effect. The nature of the Spandex substrate enables the conductive fabric to be stretchable and flexible. When stretched, the conductive Spandex could switch the electrochromic material coated on it; switching speed increases with increasing conductivity. Therefore, one would expect that a fully stretchable ECD based upon these fabrics would switch faster while in the stretched state. The PEDOT-PSS was confirmed as a homogenously dispersed system throughout the Spandex matrix, as stretching did not result in delamination or breaks in the conductivity or discontinuity in the blue color. The coated electrochromic material did exhibit breaking upon stretching, consistent with what is expected from a film. However, the fact that the electrochromic functioned while the Spandex was stretched confirms that there was no discontinuity in the PEDOT-PSS. This simple methodology was applied to various textiles, as well, each with varying conductivities according to their absorption characteristics. There is a growing interest from academia and the industrial world to develop real, wearable displays and truly integrated fabric electronics; the work herein is essential toward the strengthening of such efforts.

## EXPERIMENTAL SECTION

**Materials.** Acetonitrile (ACN) and dichloromethane (DCM) were purchased from Thermo-Fisher and distilled over calcium hydride before use. Lithium trifluoromethane sulfonate (LITRIF), propylene carbonate (PC), polyethylene glycol diacrylate (PEG-DA), and dimethoxyphenylacetophenone (DMPAP) were purchased from Sigma Aldrich and used as received. Copper tape was purchased from Newark. The Lycra Spandex was generously donated by Lubrizol. ORGACON S300 type PEDOT-PSS

dispersion was procured from Agfa, 1.3 wt % PEDOT-PSS in water. d-Sorbitol and ferric chloride were purchased from Thermo-Fisher and used as received. The various fabric compositions were purchased from JoAnn Fabrics.

**Instrumental.** Keithley 224 Programmable Current Source and 196 System DMM were used for conductivity measurements. Samples were air-dried and measured by a four-probe colinear array conductivity measurement set up; the setup was built according to literature designs (32). Current was applied to the outer leads while measuring a voltage drop across the inner leads. The formula used to calculate conductivity from these measurements is  $\sigma = s/twR$  where  $\sigma$  = conductivity,  $s$  = distance between leads (constant for all four leads),  $t$  is sample thickness,  $w$  is the length of the leads (constant for all four leads), and  $R$  is the measured resistance (calculated from  $V = iR$  for an applied current,  $i$ , and a measured voltage,  $V$ ). When a sample's thickness " $t$ " is larger than the distance between the probes " $s$ ", it is considered to be a bulk sample. When " $t < s$ ", it is considered as a thin film. In our system, the thickness of the fabric (0.4 mm) is much smaller than " $s$ ", and therefore we considered it as a thin film sample. Microscopic characterization was carried out by Nikon Metaphot microscope. Electron microscopy was performed using an AMRAY 1810 SEM and IXRF Systems Inc. 500 Digital Processing Confocal images were taken by Andor Spinning Disk Confocal & TIRF Microscope.

**Conversion of Precursor.** Electrochemical conversions and chronocoulometry were carried out with a CHI 400A potentiostat. Solution conversions were carried out in 0.1 M LITRIF/ACN solutions, with respect to a nonaqueous  $\text{Ag}/\text{Ag}^+$  reference electrode, calibrated to 0.455 V vs NHE. Chemical conversions were accomplished by use of a 0.1 M ferric chloride/acetonitrile solution. See the Supporting Information for the chemical structure of the electrochromic, as well as a schematic for precursor conversion.

**Conductive Fabric Preparation.** Fabrics were immersed in ORGACON solution with 2 wt % d-sorbitol for varying times, as noted throughout. They were soaked under normal lab conditions (ca. 20 °C and ca. 40% relative humidity) and were dried in air. Samples were stored in a desiccator, except where noted. Conductivity was measured by using the four probe method. All values were averaged over three samples.

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**Supporting Information Available:** Additional materials (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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