POLYMER BASED ENERGY STORAGE AND THERMAL MANAGEMENT ON TEXTILE DEVICES

Wesley A. Viola
University of Massachusetts Amherst

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POLYMER BASED ENERGY STORAGE AND THERMAL MANAGEMENT ON TEXTILE DEVICES

A Dissertation Presented

by

Wesley Viola

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 2023

Department of Chemical Engineering
POLYMER BASED ENERGY STORAGE AND THERMAL MANAGEMENT ON TEXTILES

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Wesley Viola

Approved as to the style and content by:

________________________________________
Trisha Andrew, Chair

________________________________________
John Klier, Member

________________________________________
Wei Fan, Member

________________________________________
Yanfei Xu, Outside Member

________________________________________
Russell Tessier, Acting Department Head
Department of Chemical Engineering
ACKNOWLEDGEMENTS

Thank you to David Bilger, Peiyao Zhao, Linden Allison, Evan Patamia, Ruolan Fan, Zohreh Homayounfar, and Kwang-Won Park and the rest of WELab for engaging discussions and community over many tea times. Thank you to Alex Curtiss and Oscar Zabala for help with the thermal textile project. Thank you to Trisha Andrew for giving me the freedom to explore a variety of topics and guiding me to prioritize, problem solve, and to always consider the audience. I am grateful for my house and housemates – Jeffrey Gertler, Catherine Tremblay, Schuyler Lockwood, and Teal Brechtel – especially for our memorable if not turbulent covid pod. Thank you to my friends – Alex, Oscar, Anh, Shane, Kate, and Jason for putting up with me. Thank you to my family who inspired my scientific curiosity early on and always emphasized the value of education. Thank you to Teal Brechtel (and Sokee) for helping to grow my sense of self-love and empathy. Thanks to my landlords Seth Isman and Erika Hollister for allowing me to start a garden in the beautiful Pioneer Valley. I am very grateful for all the memories!
ABSTRACT

POLYMER BASED ENERGY STORAGE AND THERMAL MANAGEMENT ON TEXTILES

February 2023

WESLEY VIOLA, B.S. TUFTS UNIVERSITY
Ph.D. UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Trisha Andrew

Humans developed textiles to manage thermal energy transfer with the environment and support homeostasis in a wide range of climates. With the anticipation of wearable technologies to transform healthcare via early, pre-symptomatic detection of illness, there is now a demand for electrical energy storage to support such on-body devices. Finding energy materials to merge seamlessly with textiles is basic requirement to ensure widespread adoption of wearable health monitors.

Here we use a vapor deposition process to conformally coat ordinary fabrics with the doped conjugated polymer poly(3,4 ethylenedioxythiophene) (PEDOT-Cl), a soft material which possesses electronic and redox capabilities. We demonstrate PEDOT-Cl electrode threads that may be directly sewn into garments to form supercapacitors which meet the needs of low-power biometric sensors. Towards optimizing PEDOT-Cl material properties for such electrochemical applications, we then show control over two electrode-performance dependent properties: film porosity and crystallinity. By tuning the reactant ratio of EDOT monomer and iron oxidant, we introduce interface-extending porosity in the films which enhances short time scale (~minutes) charging kinetics. We
then show that the in-situ growth temperature of the polymer film, which has been shown to improve crystalline order, limits the self-discharge of the polymer electrodes. A proposed mechanism is presented, by which ion channels/planes in the PEDOT-Cl crystal influence long time scale (~hours) charging kinetics.

We shift our attention from electrodes (electron conducting) to electrolytes (ion conducting), often the origin of low temperature performance issues in energy storage devices. Here we formulate an aqueous LiCl mixture at the eutectic concentration and demonstrate excellent performance down to -70°C. Temperature-dependent conductivity of the 25 wt% LiCl-H₂O mixture is characterized, which shows high ionic conductivity – 1 mS/cm at -70°C, at least 1000x higher than conventional organic electrolytes in this temperature range. A low-temperature polymer gel electrolyte is then presented, forming a textile supercapacitor which efficiently powers an LED at -70°C.

Finally, motivated by the energy and climate crises, we revisit the design of the textile for its original function – thermoregulation – to investigate sustainable ways of supporting thermal homeostasis amidst environmental extremes. We take inspiration from polar-dwelling animals that suppress thermal emission and harvest solar heat to reduce metabolic energy needs via radiative energy management. In the wings of certain moths and butterflies, melanin microstructures interact with light to control heat. The high optical density of melanin enables broadband light absorption and efficient light interference effects to suppress thermal emission. The polar bear has similarly evolved melanin-enriched skin for photothermal capture. This effect is enhanced by its fur made of pigment-free, hollow fibers that forward-scatter light inward and inhibit heat diffusion outward. We develop a bilayer textile which combines such light and heat control
elements. The bottom nylon fabric is vapor coated with PEDOT-Cl, an optically dense organic conductor with high visible light absorption and low thermal emission. The top fabric is made of spun-bonded polypropylene fibers (Agribon AG-19) and acts as a semi-transparent insulator, transmitting ~85% of visible light to the photothermal PEDOT-Cl-nylon layer. Under moderate illumination of 130 W/m² (ca. 0.1 sun), this textile maintains the wearer’s thermal comfort down to 4.1 °C – an additional heating effect of 10°C relative to a typical cotton T-shirt that is 30% heavier. Under full wintertime sunlight (650 W/m²), the garment supports thermal homeostasis in extreme conditions as low as -28°C. As the energy and environmental crises progress, reinventing textiles with polymer-enabled light and heat control will prove increasingly useful.
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CHAPTER 1
INTRODUCTION

1.1 MOTIVATION

Besides other factors like social collaboration, humans have been particularly successful at adapting to new environments and changing situations due to the development of technology, particularly as a means of controlling energy in its different forms. The use of fire provided light, warmth, and a way to cook food; agriculture harnessed the energy of photosynthesizing plants; clothing and textiles supported thermal homeostasis, extending the livable environmental window.

The last century saw electricity become the most useful energy form to society, with the build-out of electricity generation and power distribution systems being called the “greatest engineering achievement of the 20th Century” by the National Academy of Engineering. (1) Besides powering modern infrastructure, electrical energy is the power source of information technology which has greatly enhanced collaborative networks. For processor and sensor hardware to shrink and disappear into ubiquitous objects for consumer, industrial, and agricultural use, so too must energy systems. In this race, microprocessors have the edge: historically, Moore’s law has proved true, with integrated circuits becoming exponentially more powerful in a smaller footprint. (2) Energy storage devices have seen only incremental gains and suffer many practical challenges such as charge capacity, flexibility, and fire safety. (3)

The lack of suitable power delivery is a major barrier to the development to a host of wearable technologies – health and environmental monitoring, motion track, sleep evaluation - which promise to transform healthcare via early, pre-symptomatic detection
of illness.(4) For widespread adoption of such devices, performance metrics matter only insofar as how the end-user experiences the physical form factor, flexibility, and aesthetics of a wearable device. Polymer energy materials have emerged as a competitive choice, having the appropriate properties to merge with the soft materials from which textiles are traditionally made.

Conjugated polymers are one class of materials possessing electronic and redox capabilities more commonly seen for inorganic materials like lithium, nickel, and copper.(5) Upon polymer oxidation, mobile charge carriers are formed which, in the solid-state physics community, are termed polarons and bipolarons and are characterized by unique interactions between the mobile electrons and the dynamic polymer crystal distortions which follow wave propagations.(6) Typically, the more ordered or crystalline the conjugated polymer, the more easily charge carriers are conducted and the more closely the polymer approximates metallic behavior. As of now, the most conductive conjugated polymers are still at least 100 times less so than metals like copper.(7)

Poly(3,4-ethylenedioxythiophene) (PEDOT) is the conjugated polymer with the greatest tendency, due to planar pi-conjugated and an electron donating monomer structure, to form highly crystalline films that are persistently conductive or “doped” (a term borrowed from semiconductor physics, more precisely “oxidized” due to charge transfer).(8) For this reason, it has been used in various energy applications including charge storage as a redox-active electrode(9) and harvesting as a transparent top layer conductor.(10) As an energy material, it is desirable for its earth-abundant raw components, flexible mechanical properties, biocompatibility, and ease of processing.(11)
PEDOT is most commonly coated from aqueous solution as a macromolecular salt (most commonly as poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)).(12) Recently, under the umbrella of reactive vapor deposition (RVD) including other vapor phase chemistries such as initiated chemical vapor deposition (iCVD) for free radical polymerizations, oxidative chemical vapor deposition (oCVD) of PEDOT has seen attention which, as a solvent-free system eliminating surface tension effects, is particularly suitable to forming thin, conformal coatings on topologically complex substrates. (13) Figure 1a shows the oCVD reactor where the EDOT monomer and iron (iii) chloride oxidant are vaporized and the resulting PEDOT-Cl polymer (Figure 1b) is deposited on the inverted substrate stage. Whereas traditional physical vapor deposition (PVD) proceeds at ultralow pressures (~ 1 μTorr) resulting in line-of-sight coatings, oCVD uses relatively high pressures (~1 Torr) with mean free path lengths less than 1 mm resulting in non-line-of-sight coatings, i.e. conformal coverage over features around 1 mm (Figure 1c,d). This length scale is typical of textiles which, unlike the planar substrates of traditional electronic circuitry, vary in feature size from the thread, yarn, to weave level.
Figure 1. Oxidative chemical vapor deposition overview. (a) Custom built chamber operates at moderately low pressures (~1 Torr) in which monomer (ethylenedioxythiophene [EDOT]) and oxidant (iron (III) chloride) are heated to form vapors that intersect and react at the inverted substrate stage. Vapor deposition yields conformal coatings on wool fibers – (b) uncoated and (c) coated. (d) Neutral poly(3,4-ethylenedioxythiophene) (PEDOT-Cl) – shown as \(n\) repeat units - is doped (oxidized) to form a radical polaron unit – shown as \(m\) repeat units - that carries charge along the polymer backbone.

Due to inherent redox properties and flexibility, PEDOT-Cl is a promising electrical energy storage material for powering wearable electronics, which is rapidly advancing to bring unprecedented functionalities – health monitoring, motion tracking, sleep evaluation – into everyday objects. The irony is that the first wearable – the textile – has not evolved in how it performs its original energy management function: thermoregulation. Thousands of years later, textiles are still woven from fibers into thick structures that manage heat.
transfer by inhibiting diffusive heat loss. With increasing environmental and economic pressures to find more sustainable ways of living in a rapidly changing climate, we circle back to leverage novel materials and revisit the design of one of the oldest and most basic technologies. In Chapter 4, we explore how the electronic properties of PEDOT-Cl may be harnessed to selectively manage electromagnetic (radiative) energy transfer with the environment, in a manner similar to how some animals living in extreme environments support energy-intensive thermal homeostasis.

1.2 THESIS ORGANIZATION

This thesis is organized into four major chapter which follows the development of PEDOT-Cl for energy harnessing textiles. Chapter 2 begins with the application of vapor deposited PEDOT-Cl threads for sewable, textile-integrated supercapacitors. Chapter 2 continues with two published studies on the optimization of the vapor deposition process aiming to control two electrode performance-dependent properties: film porosity and crystallinity. We show that the reactant ratio of EDOT monomer and iron oxidant may be used to introduce interface-extending porosity in the films which enhances short time scale (~minutes) charging kinetics. We then show that the in-situ growth temperature of the polymer film, which has been shown to improve crystalline order, limits the self-discharge of the polymer electrodes. A proposed mechanism is presented, by which ion channels/planes in the PEDOT-Cl crystal influence long time scale (~hours) charging kinetics.

Chapter 3 presents published work on the development of ultralow (-70°C) temperature energy storage, enabled by an aqueous eutectic LiCl electrolyte. Temperature-dependent
conductivity of the 25 wt% LiCl-H2O mixture is characterized, which shows high ionic conductivity – 1 mS/cm at -70°C, at least 1000x higher than conventional organic electrolytes in this temperature range. A low-temperature polymer gel electrolyte is then presented, forming a textile supercapacitor which efficiently powers an LED at -70°C.

The project presented in Chapter 4 switches focus toward utilizing PEDOT-Cl coatings in radiative energy management for supporting thermal homeostasis and mitigating fossil-fuel intensive heating in cold climates. Taking inspiration from arctic-adapted animals, we leverage optical polymer materials to design a radiative heating textile as the first wearable mimic of the absorber-transmitter structure of the polar bear skin and fur. While retaining familiar textile qualities, the bilayer design suppresses radiative dissipation of body heat and maximizes radiative absorption of visible-NIR light. Due to a faithful imitation of the light harvesting structure and function of polar bear pelt, the garment achieves a significantly greater heating performance than other nominal mimics which either lack a transmitter or sacrifice solar utilization for thermal insulation. Under moderate illumination of 130 W/m² (ca. 0.1 sun), this textile maintains the wearer’s thermal comfort down to 4.1 °C – an additional heating effect of 10°C relative to a typical cotton T-shirt that is 30% heavier. Under full sunlight, the garment supports thermal homeostasis in extreme conditions as low as -28°C.
CHAPTER 2

VAPORE-DEPOSITED CONJUGATED POLYMERS FOR WEARABLE ENERGY STORAGE DEVICES

2.1 INTRODUCTION

Improved wearable energy storage is essential to the development of many emerging on-body health monitoring and consumer technologies. In such applications, device performance metrics matter only insofar as how the end-user experiences the physical form factor, flexibility, and aesthetics of a wearable device. The development of flexible and lightweight electrodes on suitable substrates is thus key to realizing widespread adoption of next-generation electronics.

Conjugated polymers are a competitive material choice, possessing the appropriate flexibility, processability, and charge capacity for wearable energy storage devices. Being soft materials, conjugated polymers have the necessary mechanical properties to flex and deform, readily adapting to body movements, as well as resisting delamination on flexible substrates. While possessing desirable mechanical properties, conjugated polymers are also amenable to a variety of processing techniques including screen printing, inkjet printing, and vapor deposition. (14–16) Without the surface tension limitations common in solution processed techniques, vapor deposition of conjugated polymers specifically achieves robust, conformal coatings on ordinary textiles for seamless integration of wearable devices with ordinary garments. With both good device metrics and the unmatched pliability and feel of natural fabrics, such wearable devices have the potential for widespread adoption.
In this chapter, we will discuss the development of such a wearable energy storage device – a sewable thread-based supercapacitor using vapor-deposited polymer coatings – and studies into the how conjugated polymer material properties may be optimized for energy storage applications by varying oxidative chemical vapor deposition (oCVD) parameters.

2.2 GARMENT INTEGRATED MICROSUPERCAPACITORS FOR POWERING WEARABLE ELECTRONICS

2.2.1 METHODS

All chemicals were purchased from Sigma-Aldrich or TCI America and used without further purification. Field-emission scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed using a Magellan 400.

Films of p-doped PEDOT-CI were directly deposited on stainless steel threads using a previously described reaction chamber and process parameters.\(^{(17, 18)}\) Briefly, 3,4-ethylenedioxythiophene (EDOT) (95%, TCI America) was used as the monomer and iron(III) chloride (FeCl\(_3\)) (97%, Sigma-Aldrich) was used as the oxidant. EDOT was heated to 90 °C and was delivered into chamber through a Swagelok SS-4JB needle valve. The needle valve was open for a quarter turn. Argon gas was used to maintain the total pressure in the chamber of 300 ± 10 mTorr, and the substrate stage temperature was strictly maintained at 120 °C during deposition. Film deposition rate and the thickness were controlled by the FeCl\(_3\) evaporation rate, which was monitored by a quartz crystal microbalance (QCM) sensor located inside the chamber. The ratio of the actual film thickness measured post-deposition to the real-time QCM reading during deposition was recorded as the “tooling factor.” The actual film growth rate was kept at 2 nm/s. As the
desired film thickness was reached, the vacuum was maintained until the substrate stage was cooled below 60 °C. The resulting films were immersed in methanol for 15 min to remove trapped iron salts and other reaction byproducts. The PEDOT-Cl films thus obtained were stably p-doped, as previously established.

PEDOT-Cl-coated stainless steel threads were characterized by three-electrode cyclic voltammetry (CV) measurements using a WaveNow potentiostat. A reference electrode of Ag/AgCl in KCl and counter electrode of platinum wire were used, and the PEDOT-Cl coated thread served as the working electrode. Alligator clips were used to grip the PEDOT-Cl-coated threads and place them into the electrolyte solution. The electrolyte was 0.5 M aqueous Na₂SO₄ or 0.5 M aqueous H₂SO₄.

The polymer gel electrolyte was prepared by slowly adding poly(vinyl alcohol) (PVA, 1 g) (89 000–98 000, 99%, Sigma-Aldrich) to a stirred 1 M aqueous H₂SO₄ solution (10 g). The mixture was heated at 90 °C under vigorous stirring for 2 h. Solid-state devices were prepared by casting this polymer gel electrolyte onto sewn electrodes and drying in air.

Alternatively, two–three drops (ca. 0.05 mL volume per drop) of ethylmethyl imidazolium tetrafluoroborate (EMIMBF₄) ionic liquid was dropped over the surface of the sewn MSC.

Solid-state MSCs were characterized by two-electrode CV and galvanostatic charge/discharge measurements using a WaveNow potentiostat. The two separated threads of the MSC served as the two electrodes. Alligator clips were used to grip the PEDOT-Cl coated threads from the surface of the textile MSC.
2.2.2 RESULTS

Figure 1 shows the schematic illustration of the RVD chamber and the substrate holder designed to uniformly coat every exposed surface of fiber/yarn substrates with persistently p-doped PEDOT-Cl. The substrate holder allows up to 32 feet of fibers/yarns to be coated in a single deposition run. One of the key factors for maximizing the capacitance and energy density is a high mass loading of the electrochemically active material. In solution-processed devices, the mass loading is often impeded by poor adhesion of the electronic material (which causes thick films to flake off) or limited pathways for ion transport within thick films of unoptimized morphology. Here, a high mass loading is achieved by depositing PEDOT-Cl on stainless steel threads via RVD. Moreover, the high surface area of the stainless steel threads allows increased contact with ions from the electrolyte.
Figure 2. RVD of PEDOT-Cl and electrochemical characterization of PEDOT-Cl-coated stainless steel threads. (a) Schematic illustration of the RVD chamber. (b) Chemical structure of PEDOT-Cl created by RVD, after solvent rinsing. (c) Photographs of a pristine and PEDOT-Cl-coated stainless steel thread. (d,e) SEM images of a pristine two-ply stainless steel thread. (f,g) SEM images of a PEDOT-Cl-coated two-ply stainless steel thread. (h) SEM image of a PEDOT-Cl-coated microfibril from the surface and (i) buried core of a two-ply stainless steel thread. (j) EDX images of a PEDOT-Cl-coated stainless steel thread corresponding to the SEM image in (g).

Figure 1c shows the magnified (4×) optical images of a pristine and PEDOT-Cl-coated two-ply stainless steel thread. Non-line-of-sight deposition leads to uniform coating of PEDOT-Cl around the thread, which maximizes the mass loading of the electroactive material. Figure 1d–g displays the cross sections of microfibril bundles without and with PEDOT-Cl coating. The two images resemble each other at this length-scale, confirming
the conformal coating on each microfibril without bridging polymer films formed in between, which contributes to the mechanical ruggedness of the coating. The SEM images in Figure 1g and EDX images in Figure 1j further reveal the efficiency of the deposition on such a rough surface with an extremely high surface area. The EDX images reveal that the coating is not limited to the surface. Instead, PEDOT-Cl films are also deposited on the microfibril surfaces that are buried inside the stainless steel thread. Iron is a major component of stainless steel, whereas C, O, and S elements are contributed by PEDOT-Cl. Figure 1h,i shows the cross section of a PEDOT-Cl-coated microfibril exposed at the surface of the thread and a microfibril buried deep in the core region. The coating is 5 μm thick at the surface and 1 μm thick in the core region.

Figure 2 shows cyclic voltammograms measured with a three-electrode setup in aqueous 0.5 M Na₂SO₄ or 0.5 M H₂SO₄ using a 1 cm-long PEDOT-Cl thread as the working electrode (platinum wire counter, Ag/AgCl reference). The near rectangular voltammograms are maintained up to 100 mV/s in both electrolytes. PEDOT-Cl-coated thread capacitances per unit length at different scan rates are summarized in Figure 2c. Capacitances of 15 and 12 mF/cm are achieved at a scan rate of 5 mV/s in Na₂SO₄ and H₂SO₄, respectively. The scan rate has a relatively mild effect on the length capacitance. At a fast scan rate of 100 mV/s, an appreciably high length capacitance of 8.5 mF/cm is retained in both electrolytes.
Figure 3. Cyclic voltammograms of PEDOT-Cl-coated stainless steel threads in (a) aqueous Na$_2$SO$_4$ and (b) H$_2$SO$_4$ obtained using a three-electrode setup. (c) Capacitance per unit length of PEDOT-Cl-coated stainless steel threads calculated from (a,b).

Figure 3 illustrates the process to create textile MSCs. Minimizing the spacing between electrode fingers is critical to obtaining a miniaturized device with reduced ion conduction lengths and maximized charge storage capabilities. The difficulty in reducing this interspace comes from the fuzziness of threads. As shown in the magnified photograph in Figure 1c, microfibrils of the stainless steel thread randomly stick out and tend to contact with microfibrils of a neighboring electrode, causing a short circuit. To address this issue, a stretchable textile is used as the substrate. For the sewing process, the substrate textile is pre-stretched and six interdigitated electrode fingers are alternatively sewn. We take advantage of the dimensions of the knit structure of the backing textile to confine the electrodes: the length of each electrode finger and the interelectrode spacing of the sewn MSCs are simply set by the length and width of the knit pattern of the stretchy textile backing. The neighboring electrodes are separated by two threads of the substrate textile. Each electrode is composed of two PEDOT-Cl-coated stainless steel threads stacked to form a 3D architecture, with a length of 5 mm, width of 0.6 mm, and height of 1.2 mm, presumably leading to significantly increased areal capacitance. A PVA/H$_2$SO$_4$ gel
electrolyte is then dropcast to cover all electrodes. The gel electrolyte also serves as an insulating cladding to prevent contact between electrodes. Before the electrolyte completely solidifies, the prestretched substrate is released such that the PVA gel wrinkles (thus preventing folding-induced microcracks) and a compact, pliable device is formed. An ionic liquid electrolyte, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), is also explored as an alternative approach. The positive and negative electrodes are then connected by buslines. The photograph in Figure 3b shows an MSC (without gel electrolyte) after the textile is released. The overall size of a device is 6 mm in length, 5 mm in width, and 1.2 mm in height.

Figure 4. Fabrication and electrochemical characterization of textile MSCs. (a) Schematic illustration of the device fabrication sequence. (b) Photograph of a textile MSC with sewn electrodes (electrolyte is not shown). CV curves of textile MSCs with (c) PVA/H₂SO₄ gel electrolyte and (d) EMIMBF₄ ionic liquid electrolyte. (e) Comparison of the areal capacitances obtained from textile MSCs with different electrolytes calculated from the CV curves in (c,d). The area of the entire device is taken into consideration. (f) Galvanostatic charge/discharge curves of a textile MSC with PVA/H₂SO₄ gel electrolyte.

Figure 3c,d shows cyclic voltammograms of the textile MSC with the PVA/H₂SO₄ gel electrolyte and EMIMBF₄ electrolyte. Areal capacitances at different scan rates are
summarized in Figure 3e, where the entire device area is taken into consideration. With the PVA/H₂SO₄ gel electrolyte, the areal capacitance is 80 mF/cm² at a scan rate of 2 mV/s, 60 mF/cm² at a scan rate of 5 mV/s, and maintained at 26 mF/cm² when the scan rate is increased to 300 mV/s. With EMIMBF₄, an areal capacitance of 50 mF/cm² at a scan rate of 5 mV/s can be obtained. Figure 3f displays the galvanostatic charge/discharge curves of a textile MSC with the PVA/H₂SO₄ gel electrolyte, which shows the characteristic triangle shape arising from the pseudocapacitive behavior of PEDOT-Cl supercapacitors. The inset shows the enlarged graph revealing a negligible voltage drop, indicating low internal resistance within the device.

Figure 4 displays the device resilience to harsh mechanical distortions. The galvanostatic charge/discharge measurements are conducted while the device is bent at either 90° or 180°, twisted or fully rolled up. The charge/discharge traces are exactly similar to the traces obtained for a flat device. Such high tolerance to extreme mechanical distortions is particularly important for wearable charge storage technologies, which are subjected to constant movements and deformations.
Figure 5. (a) Pictures of the textile MSC subjected to various mechanical distortions. (b) Galvanostatic charge/discharge curves measured as the device was bent, twisted, or rolled up. The charge/discharge curves of the deformed device resemble that of a flat device. (c) Cycle stability of the textile MSC measured at a fast scan rate of 7 mA/cm$^2$. (d) Areal Ragone plot comparing the textile MSC reported here to other state-of-the-art flexible MSCs.

PVA/H$_2$SO$_4$ gel electrolyte is tested at a high rate of 7 mA/cm$^2$ and shown in Figure 4c. The capacitance of the device is surprisingly and reproducibly recoverable: after the first 4000 cycles, 71% of the initial capacitance is retained, which is recovered to 93% after a 12 h no-operation period. After another 4000 cycles, the capacitance again shows a 71% capacitance retention, which can be recovered to 93% after another 12 h rest period. This recoverable behavior is confirmed by multiple measurements on 12 different devices (the measurement for each device was repeated three times). One possible reason for this behavior is the redistribution of unbalanced charges in the solid-state device during the 12 h rest period.
Figure 4d compares the performance of selected, state-of-the-art flexible MSCs to those of the textile MSCs reported here. The energy density metric is particularly important for wearable MSCs. The devices reported here have energy densities of more than 1 order of magnitude higher than those of previously reported textile MSCs,\(^{19}\) as well as those of paper \(^{20}\) or plastic substrate-based MSCs.\(^{22–24}\) Normalized to the weight of the entire device (including the textile backing, PEDOT-Cl-coated thread electrodes and ionic liquid electrolyte), the textile MSC produces an energy density of 0.1 mWh/g per individual device (scan rate 5 mV/s).

Ideally, individual MSCs with optimized performance need to be connected in series or in parallel to tailor the voltage and current output required for varied, practical applications. To reduce energy losses arising from mismatched device parameters, the individual device performance needs to be highly reproducible. Reproducibility requires coating uniformity and strict control over device parameters, such as overall device area, electrode dimensions, and electrode spacing. The performance of MSCs is sensitive to the device architecture, including the dimensions of electrodes and spacing between electrodes. Normally, lithography and/or shadow-masking are/is required to micropattern electrodes. Analogous textile-based devices at microscales are difficult to obtain by hand-sewing. We take advantage of the dimensions of the knit structure of the backing textile to confine the electrodes: the length of each electrode finger and the interelectrode spacing of the sewn MSCs are simply set by the length and width of the knit pattern of the stretchy textile backing. In this way, multiple MSCs with reproducible performance can be easily embroidered on any textile that is knit in the same pattern as the common jersey cloth used here. Figure 5 shows two MSCs connected in series to produce twice the voltage output, in
parallel to yield twice the current output, and in a combination of series and parallel to afford twice the voltage and current output. All data are collected at the same scanning rate of 1 mA/cm².

Figure 6. Galvanostatic charge/discharge curves at a current density of 1 mA/cm² for (a) two MSCs in a series connection, (b) two MSCs in a parallel connection, and (c) four MSCs in series and parallel connections. The galvanostatic charge/discharge curves of a single device are shown for comparison. (d) Picture of four MSCs sewn on a commercial cotton jersey T-shirt
2.2.3 CONCLUSION

Despite remarkable progress in creating wearable and/or garment-integrated heart rate monitors and biosensors, portable power sources that can be practically integrated with these devices are not known. In-plane, interdigitated MSCs hold the greatest promise to be integrated into wearable electronics because of their miniaturized footprint, as compared to conventional, multilayered supercapacitors, and batteries. Constructing MSCs directly on textiles, while retaining the fabric’s pliability and tactile quality, will provide uniquely wearable energy storage systems. However, relative to plastic-backed or paper-based MSCs, garment-integrated MSCs are underreported. The challenge lies in creating high capacitance fiber or textile electrodes that can be turned into MSCs.

Here, we report a facile vapor deposition and sewing sequence to create rugged textile MSCs. Conductive threads are vapor-coated with a stably p-doped conducting polymer film and then sewn onto a stretchy textile to form 3D, compactly aligned electrodes with the electrode dimensions defined by the knit structure of the textile backing. The resulting solid-state device has an especially high areal capacitance and energy density of 80 mF/cm\(^2\) and 11 \(\mu\)Wh/cm\(^2\) with a polymer gel electrolyte and an energy density of 34 \(\mu\)Wh/cm\(^2\) with an ionic liquid electrolyte, sufficient to power contemporary iterations of wearable biosensors. Further, series- and/or parallel-connected integrated charge storage circuits can be readily elaborated on commercial garments. The proof-of-concept MSC reported here opens a new window for the facile fabrication of lightweight, high-energy density textile-based MSCs that are highly tunable, are mechanically robust, and can be easily integrated into wearable power supply systems.
2.3 POROSITY IN VAPOR DEPOSITED POLYMER FILMS AND CORRELATED IMPACT ON ELECTROCHEMICAL PROPERTIES

2.3.1 METHODS

Films of persistently p-doped poly (3,4-ethylenedioxythiophene) (PEDOT-X) were directly deposited on 25 μm-thick polyimide films via oCVD, using a previously described reaction chamber and process parameters (Figure 1). Briefly, 3,4-ethylenedioxythiophene (EDOT) (95%, TCI America) was used as the monomer and iron (III) chloride (FeCl$_3$) (97%, Sigma Aldrich) was used as the oxidant. EDOT was heated to 90°C and was delivered into chamber through a Swagelok SS-4JB needle valve. The needle valve was open for a quarter turn. Typically, the oxidant flux was 1.5 times higher than the monomer flux. A significantly lower monomer rate resulted in a non-uniform film over a 5 × 5 inch$^2$ substrate, while a significantly higher monomer rate sacrificed the conductivity of the resulting PEDOT-X film. Argon gas was used to maintain the total pressure in the chamber of 300 ± 10 mTorr and the substrate stage temperature was strictly maintained at 150°C during deposition.

Film deposition rate and the thickness were controlled by FeCl$_3$ evaporation rate, which was monitored by a quartz crystal microbalance (QCM) sensor located inside the chamber. Both the flow rate of the EDOT monomer and the oxidant contributed to the QCM reading. Due to the different positioning of the QCM relative to the substrate stage, the film growth rate at these surfaces is not equivalent but proportional by some factor. The ratio of the actual film thickness measured post-deposition to the real-time QCM reading during deposition was recorded as this ‘tooling factor’, which was found to be 0.5. QCM thickness readings were then corrected by this factor. The actual film growth rate was kept
at 2 nm/s. As the desired film thickness was reached, the vacuum was maintained until the substrate stage was cooled below 60°C. Because of the iron (III) chloride oxidant used, chloride counterions were present in the as-deposited films, which likely underwent anion exchange upon rinsing. The as deposited films were immersed in either 0.5 M H₂SO₄ or HCl for 15 min to remove trapped iron salts and other reaction by-products. Films obtained using this method remained p-doped even after rinsing/drying. Polymer films rinsed with HCl retained a chloride counterion after rinsing and are referred to as PEDOT-Cl. Polymer films rinsed with H₂SO₄ contained an ill-defined mixture of chloride, sulfate, hydrogen sulfate counterions and are referred to as PEDOT-X.

Free-standing films were obtained by vapor depositing onto poly(tetrafluoroethylene) (PTFE) substrates, carefully peeling off the resulting monolithic films from the PTFE and immersing in 0.5 M H₂SO₄ for 15 min to rinse out residual iron salts.

Morphologically uniform 10 μm thick films could be created on a variety of substrates over a total lateral area of up to 10 cm × 10 cm (limited by the size of the substrate stage). The maximum film thickness reported here, 10 μm, is not determined by an innate material or process characteristic but, rather, by the practical fill capacity of the electrical furnace used in our chamber to vaporize FeCl₃. Use of a larger furnace with higher fill capacity should allow access to thicker films. Electrochemical Analysis of vapor-Deposited PEDOTX. The volumetric capacitance was characterized by three-electrode cyclic voltammetry measurements by using a Wavenow potentiostat from Pine Instruments. A platinum wire was used as the counter electrode, Ag/AgCl in 1 M KCl as the reference electrode, and 0.5 M aqueous H₂SO₄ as the electrolyte.
Calculations. The volumetric capacitances of PEDOT-X electrodes were calculated from three-electrode CV measurements using Equation 1.

\[
C_{\text{electrode}} = \frac{\int j \, dV}{2\nu \Delta V} \left[ \frac{F}{cm^3} \right] (1)
\]

where \(j\) is current density normalized to the volume of PEDOT-X film, \(V\) is voltage, \(\nu\) is scan rate, \(\Delta V\) is voltage window.

2.3.2 RESULTS

The reactive vapor deposition of persistently p-doped poly(3,4 ethylenedioxythiophene) (PEDOT-X) is carried out in a custom-built reactor (Figure 1(a)). Vapor-phase oxidative polymerization of the electron rich monomer, 3,4-ethylenedioxythiophene (EDOT), effected by an iron (III) chloride oxidant yields in situ conducting polymer growth (Figure 1(b)). Process parameters such as chamber pressure, monomer/oxidant flux, substrate stage temperature, and deposition time can be actively tuned during deposition to optimize polymer molecular weight, film uniformity and electrical conductivity. Higher oxidant flux, relative to monomer flux, is typically employed to promote p-doping concomitantly with film formation.
Figure 7. Reactive vapor deposition of persistently doped polymer films. a, Illustration of reactive vapor deposition chamber. b, Vapor phase chemistry and structure of doped conducting polymer film. Iron (III) chloride serves to both polymerize EDOT and to oxidize PEDOT (supplying a chloride counterion), forming persistently p-doped PEDOT-Cl. An acid rinse removes metal salts and results in counterion exchange to an ill-defined extent.

Aggregates of the excess iron (III) chloride oxidant and iron (II) chloride by-products are uniformly dispersed throughout the bulk of the polymer film during growth. These aggregates are dissolved out of the film during a post-deposition acid rinse (26) in
aqueous sulfuric acid (Figure 2), leaving behind empty 100–200 nm-sized nanopores. The simultaneous removal of elemental iron and appearance of a porous nanostructure can be seen in the EDX and SEM characterizations of the polymer film before and after rinsing. Since oxidant aggregates are uniformly dispersed throughout the bulk of the film, this nanostructure extends the full 10 μm thickness of the porous PEDOT-X films.

Figure 8. Controlled porosity in vapour deposited PEDOT-X. a-c, Films deposited at low oxidant flux and high monomer flux. Crosssection scanning electron micrographs (SEMs) of as-deposited (a) and acid rinsed (b) films with corresponding energy dispersive X-ray (EDX) spectra (c) showing removal of iron residues. d-f Films deposited at high oxidant flux and low monomer flux. Cross-section SEMs of as-deposited (d) and acid rinsed (e) films with resulting porous morphology and corresponding EDX spectra (f) showing removal of iron residues.

Polymer morphology may be controlled by adjusting the ratio of EDOT monomer to iron (III) chloride oxidant during the vapor deposition process. Real-time control of the reactant ratio, enabled by the chamber’s internal QCM sensor, gives rise to dense polymer films at high relative monomer flux and very porous films at high oxidant flux. With a
minimal loading of iron (III) chloride, the dense films lack nanostructure and, as expected, retain their morphology following rinsing.

In electrochemical applications, the morphology of active electrode materials plays a significant role in the kinetics of redox-driven charging. The ability to tune the nanostructure of our PEDOT-X films allows for optimization of this process, as porous channels efficiently shuttle ions through the bulk. Electrochemical characterizations of the dense and porous films demonstrate this interdependence between film morphology and electrochemical performance (Figure 3). Using a three-electrode cyclic voltammetry, we show the dense PEDOT-Cl film shows sluggish charging kinetics as the infiltration of ions is impeded, while the porous film maintains highly rectangular profiles even at rates of 1000 mV/s.
Figure 9. Electrochemical correlation to changes in film porosity. a,b, Three-electrode cyclic voltammetry of dense (a) and porous (b) PEDOT-Cl films (after acid rinsing). c,d Scan rate dependence of volumetric capacitance of porous and dense films. Log-log plot (d) with labelled i–v relationships.

Further analysis of the charging kinetics may be done by examining the relationship between electrochemical current and scan rate (Figure 3(c)). Log-log plots of this data show that for dense films, current closely scales with the square root of the scan rate ($i \sim v^{0.58}$), indicative of diffusion-limited kinetics (Figure 3(d)).(27) With the introduction of porous channels that facilitate ion diffusion, the charging current of the porous films is closer to being directly proportional to scan rate ($i \sim v^{0.75}$), indicating nearly full redox accessibility of the electroactive polymer film even at high charging rates.
The influence of mass loading on the volumetric capacitance of vapor-deposited, porous PEDOT-Cl films is investigated using three-electrode cyclic voltammetry in aqueous sulfuric acid electrolytes. In comparing among films of varying thickness, capacitance normalized by volume of the active layer is a more meaningful quantity since it is an intrinsic property that, in the absence of transport limitations, will be constant for varying material thicknesses. Volume normalized cyclic voltammograms of 0.2 μm, 1 μm and 10 μm thick PEDOT-Cl films on polyimide are mostly similar to each other (Figure 4(a)), meaning that the porous, vapor deposited PEDOT-Cl films maintain their electrochemical behavior even at high mass loadings. Calculated volumetric capacitance values (three-electrode setup) for 0.2 μm, 1 μm and 10 μm-thick films at a 2 mV/s scan rate are 173 F/cm³, 189 F/cm³, and 182 F/cm³, respectively. Similar volumetric capacitances are observed for thin versus thick PEDOT-Cl films even at high scan rates (Figure 4(b)), suggesting that both electron and ion transport is optimized in these films.
Figure 9. Porous PEDOT-Cl thickness study. a, Three-electrode cyclic voltammograms of 0.2 μm, 1 μm and 10 μm-thick porous PEDOT-Cl films on polyimide in 0.5 M H2SO4 aqueous electrolyte at scan rate of 100 mV/s with current normalised to volume of film. b, Scan rate dependence of volumetric capacitance of 0.2 μm, 1 μm and 10 μm-thick PEDOT-Cl films (three-electrode measurement). c, Nyquist plots of the impedance of symmetric PEDOT-Cl electrodes, in comparison to platinum electrodes. Inset: magnification for the high-frequency region for 10 μm-thick PEDOT-Cl. d, Impedance phase angle versus frequency for symmetric PEDOT-Cl electrodes of varying thickness. e, X-ray diffraction spectrum of a 10 μm-thick PEDOT-Cl film deposited on polyimide. f, Sheet resistance and conductivity of PEDOT-Cl films of varying thickness.
Electrical impedance spectroscopy performed in aqueous sulfuric acid electrolytes using two PEDOT-Cl coated polyimide substrates as electrodes provides deeper insight into the internal resistances operating within the vapor-deposited film. Near-vertical lines are observed in Nyquist plots for PEDOT-Cl films of varying thickness, similar to a platinum electrode control (Figure 4(c)). A semicircle is not observed at high frequency, even for thick films, confirming minimal charge exchange resistance and efficient ion diffusion in 10 μm thick vapor-deposited PEDOT-Cl. Impedance phase angle analysis (Bode plot, Figure 4(d)) also reveals similar ion transport impedances for thin and thick electrodes. The corresponding time constants (read from the inverse of the characteristic frequency at which −45° is reached) are similar for PEDOT-Cl electrodes of different thicknesses, confirming efficient ion transport through the polymer bulk. This series of experiments prove that thick, vapor-deposited PEDOT-Cl films act as high-performance electrochemical electrodes without the need for a metal charge collector.

The X-ray diffraction (XRD) spectrum (Figure 4(e)) of a 10 μm thick porous PEDOT-Cl film on polyimide shows a sharp diffraction peak at 2θ = 6.48. The corresponding d value of 13.6 Å matches the (100) axis of crystalline PEDOT-Cl (29), revealing the lamellar packing of PEDOT-Cl chains normal to the surface, even in highly porous films. Charge transport should be maximized within crystalline domains (30) and, therefore, these PEDOT-Cl films are expected to display high electronic conductivities. Indeed, the sheet resistance of porous PEDOT-Cl films on polyimide linearly decreases from 91 to 2 Ω/square with increasing film thickness (Figure 4(f)). High conductivities above 500 S/cm are maintained even as film thicknesses are increased from 0.2 to 10 μm. Such high conductivity values confirm that thick, porous films nonetheless retain
continuous polymer networks, ensuring that high electronic conductivities are maintained along with high porosity.

In sum, the combined presence of crystalline PEDOT-Cl domains (that promote charge transport) and uniformly distributed nanopores throughout the polymer bulk (that promote electrolyte penetration and ion transport deep within the film) result in concomitant optimization of both ionic and electronic charge carriers, despite their disparate transport mechanisms. This claim is confirmed by the nearly rectangular cyclic voltammograms observed for 10 μm thick PEDOT-Cl films on polyimide at a high scan rate of 1 V/s.

2.3.3 CONCLUSION

Reactive vapor deposition creates thick films of electroactive conjugated polymers that are highly conductive and can act as sole-component electrodes for electrochemical charge storage devices. The unique, porous yet crystalline film structure created by a combined reactive vapor deposition/acid rinse sequence is critical for enabling efficient charge and ion transport in electroactive materials. Here we demonstrate tunable control of this nanostructure and correlate it to electrochemical properties of the resulting films. Analogous to solution processed nanocarbon and transition metal oxide/dichalcogenide electrodes, the nanoscale porosity in vapor deposited polymer films allows for increased polymer/ electrolyte contact and rapid ion transport, leading to thickness independent volumetric capacitances, which is not a common feature of most conducting polymer-based electrode materials.
The results of this report are significant to all electrochemical applications of polymers, including energy storage, biosensors, OECTs, and desalination membranes. The real-time control of porosity demonstrated here also suggests the ability to introduce a porosity gradient by varying the oxidant flux over the course of the deposition. This may have implications in material design for certain electrochemical technologies, e.g. polymeric actuators, where gradient structures play an important role in modulating mechanical responses.(31)

Further, design principles established by the supramolecular chemistry community can be exploited to exquisitely direct the size, shape and orientation of the pores within vapor-deposited polymer films. For example, by using well-defined and judiciously selected iron (III) complexes and/or clusters as the oxidant, one can direct the size, geometry and length of the oxidant aggregates that evolve during vapor deposition, which will eventually determine the nature of the pores left behind in the acid-rinsed polymer films. In this way, molecular self-organization can be exploited to create hierarchical mesostructure in soft electronic materials. These strategies will be the focus of forthcoming publications from our lab.

2.4 SELF-DISCHARGE CHARACTERISTICS OF VAPOUR DEPOSITED POLYMER ELECTRODES IN A TEXTILE SUPERCAPACITOR

2.4.1 METHODS

To create the pseudocapacitive electrodes, carbon cloth swatches (Fuel Cell Earth) were coated with PEDOT-Cl (~1 μm) as described above. Two sections of typically 0.5 × 1 cm were cut and coated with PEDOT-Cl to make up the symmetric electrodes. Two more
similarly sized pieces of cotton cloth were cut and these pieces were then sandwiched between the PEDOT-Cl coated electrodes to fashion the assembled device.

An ambient-stable gel electrolyte was made by mixing 1 g polyvinyl alcohol (PVA) (Mowiol 40–88) with 10 mL DI water, heating the mixture to 90 °C, adding 2.125 g of LiCl as a solid, and stirring the resulting mixture at 90 °C for 2 h before cooling. Once cool, the electrolyte was drop cast onto the assembled device described above, to the extent that all four fabric layers soaked up and became saturated with the electrolyte mixture. This device was then allowed to dry overnight, open to air in a fume hood. The gel electrolyte acted as both an ion conductive material and a crude binder that reliably held the four fabric layers together during the various measurement described in this work.

X-ray diffraction measurements of PEDOT-Cl-coated glass samples were taken using a Smartlab SE II (Rigaku) with a Cu-K-α radiation source. ICP-MS was taken on PEDOT-Cl-coated carbon cloth samples of varying rinse times. Polymer samples were digested in concentrated nitric acid at 65 °C for several hours before running the measurement.

Self-discharge experiments were performed by charging the sample to its final potential at 5 mV/s and subsequently measuring the open circuit potential (OCP) decay. Prior to the OCP step, samples were held at their maximum charging potential (chronoamperometry) for variable amounts of time as a pre-conditioning step. Measurements were taken in a nitrogen filled glovebox as well as in ambient. Voltage rebound experiments were performed by holding at 800 mV for 2 h, discharging to 0 mV at 5 mV/s, holding for 1 min, and then recording the open circuit voltage recovery.
Electrochemical impedance spectra were taken using an SI 1287 (Solartron Analytical) with an AC amplitude of 2 mV and a frequency range of 300 kHz to 1 Hz. Spectra of three duplicate devices were recorded and the reported charge transfer and Warburg resistances are averages of the set. Presented spectra are representative of the sets.

2.4.2 RESULTS

Thick films (∼1 μm) of persistently p-doped PEDOT-Cl were vapor deposited in a custom-built chamber. Control of the substrate stage temperature (i.e. the temperature at which the polymer grows) in oxidative chemical vapor deposition (oCVD) processes can greatly affect the morphological and electronic properties of the resulting polymer films, as discussed earlier in chapter two. Here, PEDOT-Cl was grown at high (150 °C) and low (50 °C) substrate temperatures (T_{stage}).

To investigate differences in the two materials, we characterized their electronic and electrochemical properties. Films on glass deposited at high temperatures had higher conductivities measured with a four-point probe (317 ± 19.5 mS/cm versus 98.5 ± 2.5 mS/cm, respectively). Three electrode, volumetric cyclic voltammetry (CV) scans of these films are shown in Figure 9. The significantly larger currents maintained by the 150 °C films indicate a higher specific capacitance relative to 50 °C films, suggesting greater electrochemical accessibility throughout the film. Gravimetric capacitances are found to be 149 F/g and 106 F/g for 150 °C and 50 °C films respectively. Assuming a density of 1.3 g/cm³,(32) the doping fraction (fraction of doped EDOT units), is 22 % and 16 % for 150 °C and 50 °C films respectively.
Figure 10. Film electrochemistry dependence on polymer growth temperature ($T_{\text{stage}}$). Three-electrode cyclic voltammetry of films deposited at $T_{\text{stage}} = 150 \, ^\circ\text{C}$ and $50 \, ^\circ\text{C}$ on glass.

Having characterized the growth temperature-dependent properties of PEDOT-Cl, we next sought to investigate how these materials performed in an all-textile supercapacitor, with a specific focus on their self-discharge behavior.

The textile supercapacitors were comprised of symmetric PEDOT-Cl coated carbon cloth electrodes. The electrodes, spaced apart by two uncoated cotton separators, were stacked and saturated with a nonacidic gel electrolyte (PVA/LiCl) to make a flexible, symmetric device (Figure 10a). Galvanostatic charge-discharge (GCD) curves over a range of current densities showed triangular profiles, indicating highly reversible energy storage (Figure 10a). Comparable two electrode cyclic voltammetry scans also demonstrate square-shaped capacitive charging (Figure 10c). More than 90% of the initial capacity was maintained over 20,000 GCD cycles (Figure 10b). This remarkable cycle stability is not common among conjugated polymers and is owed to the unique chemical stability of PEDOT-Cl which has been characterized in prior reports. (11, 26, 33) However, despite
demonstrating high cycle stability, PEDOT-Cl electrodes also exhibit high self-discharge rates: upon charging and switching to open circuit, 50% of the initial stored charge is lost after five hours. In this work, we sought to understand and improve this electrode property that is often overlooked in the emerging polymer supercapacitor community.

Figure 11. Supercapacitor structure and characterization of device using PEDOT-Cl electrodes grown at T\textsubscript{stage} = 150 °C. (a) Flexible, all-textile supercapacitor with symmetric PEDOT-Cl coated cotton electrodes and a polymer electrolyte. (inset) Photograph of assembled device. (b) Galvanostatic charge-discharge (GCD) curves over a range of currents normalized to device area. (c) Two electrode cyclic voltammetry. (d) Capacitance retention across 20,000 cycles of GCD performed at 2 mA/cm\textsuperscript{2}.

One mode of self-discharge identified for electric double layer capacitors (EDLCs) and transition metal oxide pseudocapacitors is charge redistribution, or the reorganization (equilibration) of charges between physical regions of high and low accessibility in the
electrode material.(34, 35) Suspecting a parallel with our PEDOT-Cl supercapacitors, which store charge in a similar manner, we incorporated a “hold step,” where the device was subjected to a constant applied potential of 800 mV following charging at 5 mV/s to allow for full charge saturation of the electrodes. Figure 11a shows typical self-discharge decays at open circuit with no hold step (black), after holding for one minute (red), and after holding for three hours (blue). The self-discharge behavior of devices constructed using PEDOT-Cl films grown at a high and low temperature were also compared. For both devices, self-discharge rates diminish with longer hold times, suggesting that charge redistribution plays a role. Also, after the first cycle, 150 °C devices show significantly better voltage retention than 50 °C devices after both one-minute and three-hour hold steps.

Figure 12. Self-discharge characteristics of textile devices with PEDOT-Cl layer grown at T_{stage} = 150 °C and 50 °C. (a) Open-circuit voltage decays of devices with varying post charge hold steps - no hold (black), 1-minute hold (red), and 3 -h hold (blue). Replots in (b) log[time] and (c) sqrt[time]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

To understand this behavior further, we replotted the self-discharge data in log time (Figure 11b) and square-root time (Figure 11c), as has been previously shown to give insight into the decay mechanism.(34) For faradaic, activation-controlled processes, voltage decays are linear in log time, while diffusion-controlled processes are linear in
square-root time. Both devices display the same qualitative trend. Initially the behavior is more characteristic of a faradaic, activation-controlled process (log dependence). This may be due to an initial irreversible oxidation of polymer segments, as has been previously reported for cycled PEDOT-Cl.\(^{(32)}\) CV scans before and after self-discharge cycling also show a profile change consistent with such an oxidation at higher potentials, with 50 °C devices showing a more dramatic change.

At longer hold times, the voltage decay becomes linear in square-root time, indicating a transition to self-discharge dominated by a diffusion-controlled process. This behavior may be akin to the diffusion-controlled charge redistribution previously identified for transition metal oxide pseudocapacitors like RuO\(_2\). In such materials, there exist “outer” regions that charge quickly and, upon switching to open circuit, dissipate into slower responding “inner” regions by a transport process linear in square-root time.\(^{(35–37)}\) The reverse is also expected when the film is equilibrated in a charged state and then discharged—outer regions should discharge quickly and, upon switching to open circuit, inner regions should slowly feed charges to the outer regions, causing a voltage rebound. Indeed, we observed this phenomenon for our PEDOT-Cl electrodes (Figure 12a), with the 50 °C film showing a more severe voltage rebound (i.e. more severe charge redistribution). These observations lead us to conclude that, in both cases, a hold step acts to fully equilibrate both the outer and inner regions of the PEDOT-Cl electrode, improving voltage retention (Figure 12b).
Figure 13. Voltage rebound and charge redistribution. (a) Voltage rebound curves of 150 °C (solid) and 50 °C (dashed) devices. (b) Illustration of charge redistribution.

Observing significant differences in the self-discharge rate between polymer electrodes grown at high and low temperature, one might expect to see a corresponding difference between impedance spectra, specifically the Warburg element, if the self-discharge is governed by a diffusion-limited process. Electrochemical impedance spectroscopy (EIS) of the two all-textile devices, fitted with a Randles circuit, indeed show this (Figure 13). Devices made with polymer electrodes grown at 50 °C exhibit significantly higher Warburg and charge transfer resistances (11.5 ± 1.5 Ω and 1.0 ± 0.04 Ω, respectively) relative to electrodes grown at 150 °C (7.6 ± 0.3 Ω and 0.29 ± 0.02 Ω, respectively). Given that the Warburg element arises from diffusion-controlled charge transport (that should follow a square-root time dependence),(38) this result is consistent with the higher rate of diffusion-controlled self-discharge observed for low temperature devices.
Figure 14. Characterizations of PEDOT-Cl grown at $T_{\text{stage}} = 150 \, ^\circ C$ (solid) and 50 °C (dashed). Impedance spectroscopy of devices with as-deposited electrodes.

With this picture of charge redistribution, the higher self-discharge rate of the 50 °C device can be understood in the context of growth temperature-dependent film properties. We believe that the key difference between the high and low temperature films is crystal morphology – this difference has been dissected in recent reports.\(^{(7, 32)}\)

The lower specific capacitance seen earlier for the 50 °C film suggests hindered ion accessibility, consistent with the self-discharge and impedance results. This correlation implies that more ordered morphologies in PEDOT-Cl result in improved ion transport behavior. At first, this seems to conflict with a recent report of another conjugated polymer, poly(3-hexylthiophene) (P3HT), exhibiting inhibited ion uptake in crystalline regions versus amorphous regions.\(^{(39)}\) Based on XRD (absence of broad features) and DSC characterizations of high and low temperature PEDOT-Cl films, we conclude that there is no significant amorphous fraction in either sample (i.e. the degree of crystallinity is the same in both samples). In this case, the entire volume of the films is paracrystalline and disorder arises as randomized (isotropic) crystallite orientation. Other reports on vapor
deposited and electrochemically polymerized PEDOT-Cl have also shown an absence of amorphous character in films, distinguishing these forms of PEDOT-Cl from other solution-processed conjugated polymers/composites, such as P3HT and PEDOT:PSS (7, 32, 40). Given the existence of ordered dopant ion planes within a PEDOT-Cl crystal (8), it is reasonable to expect more torturous (hindered) ion transport in more disordered, polycrystalline films. Such morphology-dependent ion dynamics may explain the improved electrochemical performance of high temperature grown PEDOT-Cl films observed here and highlights differences from other conjugated polymers.

2.4.3 CONCLUSION

Here we investigate the self-discharge behavior of a pseudocapacitive material, PEDOT-Cl, as it is applied to an all-textile charge storage device. We show that charge redistribution, a physical reorganization of ions within the film, accounts for a significant amount of the observed voltage losses. Variation in the self-discharge behavior was observed for polymer electrodes vapor deposited at high and low temperatures. Characterizations of the two polymer samples indicate a more disordered crystal structure for the low temperature films with correspondingly lower doping fractions and limited charge transport characteristics. We propose that self-discharge due to charge redistribution is exacerbated in these samples due to the existence of regions of low charge accessibility, possibly at the misoriented crystal boundaries. Variation in the polymer growth temperature affords control over this self-discharge property.

As a matter of practical importance for integrating flexible energy storage devices into functional systems, self-discharge of conjugated polymer-based electrodes was
studied. By controlling the charging protocol and deposition-dependent material properties, we are able to mitigate self-discharge in these textile-polymer supercapacitors. For the optimized device, more than 90% of the charge is maintained after five hours, opening the door for practical coupling of these devices into wearable garment devices and self-powered energy harvesting-energy storage circuits.
CHAPTER 3
AN AQUEOUS EUTECTIC ELECTROLYTE FOR ENERGY STORAGE WITH
AN OPERATIONAL TEMPERATURE RANGE FROM -70 TO 80 °C

3.1 INTRODUCTION

Sustainable, safe energy storage will be key to fully utilizing renewable power sources and enabling new classes of technology. One significant limitation of electrochemical energy storage is performance loss or failure at low (< -20°C) temperatures. This shortcoming impacts the efficiency of mature technologies such as electric vehicles in cold climates and limits the use of wearable electronics that are exposed to harsh weather. In more extreme environments, such as polar regions, aerospace, and other potentially habitable planets, the development of certain novel technologies which demand power delivery at -70°C and colder are even more severely limited. Clearly, a means of low temperature energy storage is needed.

The lower limit of commercial energy storage devices ranges from about -20°C to -40°C, with supercapacitors being generally more tolerant than lithium-ion batteries. Below these limits, issues arise in the ion-conducting electrolyte where increased viscosity and freezing hamper the mobility of charges. This manifests as an increased ionic resistance which either hurts the efficiency of the device or completely arrests device operation. For most electrochemical devices, the electrolyte is comprised of organic solvents and salts, so much of the work on low temperature energy storage has focused on these materials.(41–43) Propylene carbonate and acetonitrile are some commonly used examples, with low freezing points around -50°C. A common approach to extend the temperature range of the
electrolyte is to add the low-freezing solvent dioxolane. However, this is a poor electrolyte solvent (having a high viscosity and low dielectric), so custom electrode materials must be engineered to pair with it.\textsuperscript{(42)} Other efforts include developing low-freezing ionic liquid mixtures matched to activated carbons with, again, specially engineered pore distributions to accommodate bulky ions.\textsuperscript{(44, 45)}\textsuperscript{69,70} Such ionic liquids enable energy storage down to -70°C, but these exotic chemicals have a correspondingly high cost.

Aqueous electrolytes are perhaps an unlikely candidate for low temperature energy storage. Despite the growing interest in safe and low-cost alternatives to organic electrolyte \textsuperscript{(46, 47)}, these materials are little considered in the context of low temperature energy storage, likely due to the high freezing point of pure water. Here, we demonstrate that a mixture of the commodity salt lithium chloride (LiCl) and water forms an excellent low temperature electrolyte, supporting energy storage in supercapacitors as low as -80°C. The electrolyte used is a eutectic mixture of LiCl (24.8 wt%) in water with a greatly depressed freezing point of -74 °C, allowing for remarkably high conductivity (1.83 mS/cm) even at -70°C. Efficient charging of an off-the-shelf activated carbon (Kuraray) at low temperatures demonstrates the practical nature of the aqueous electrolyte which outperforms a conventional organic electrolyte below -40°C. This aqueous electrolyte is a low-cost, competitive alternative to organic electrolytes for energy storage in extreme environments.

3.2 METHODS

Electrodes were made by dip coating carbon cloth (Fuel Cell Earth) in an activated carbon (Kuraray YP-80FP) slurry. The slurry was composed of 90 wt % activated carbon
powder, 5 wt % carbon black, and 5 wt % poly(tetrafluoroethylene) (PTFE 60 wt % dispersion, SigmaAldrich). A 50/50 mixture of reverse osmosis (RO) water and ethanol were added, and the mixture was sonicated until a thin slurry was formed. Carbon cloth was dip-coated in the slurry and dried in an oven overnight at 100 °C. Carbon cloth was weighed before and after to determine a carbon loading of ∼2 mg/cm². Electrolytes used were a 24.8 wt % (7.86 mol/kg) solution of lithium chloride (LiCl; Sigma-Aldrich, >99% purity) in RO water and 0.5 m tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile. Electrodes were soaked in electrolytes overnight. A gel electrolyte was made by mixing 1 g polyvinyl alcohol (PVA) (Sigma-Aldrich Mowiol 40–88) with 10 mL RO water, heating the mixture to 90 °C, adding 2.125 g of LiCl, and stirring the resulting mixture at 90 °C for 2 h before cooling. Once cooled, the electrolyte was drop cast onto the device (same structure as above), layer by layer. This device was then allowed to dry overnight, open to air in a fume hood. Moisture loss after the drying step was recorded. Supercapacitors were made by sandwiching a cotton separator between two electrodes and saturating with electrolyte. Platinum foil contacts were used to eliminate corrosion of leads. Devices were 0.75 cm². A larger (∼8 cm²) packaged device was made to demonstrate low-temperature power capabilities.

Low-temperature measurements were taken in a custom-made chamber. A PID controller (J-KEM Gemini), taking two thermocouple inputs from inside the testing chamber, operated an aquarium pump that bubbled recycled air through liquid nitrogen and into the chamber. A heating element was also used to achieve high temperatures. More details on the chamber are provided in the Supporting Information. Temperature was held within 1.5 °C of the target during testing. Before a measurement was taken, samples were
held at the target temperature for at least 10 min. Cyclic voltammetry of the devices was taken across various temperatures at a scan rate of 5 mV/s using a WaveNow potentiostat (Pine Instruments). Specific capacitance was calculated as $C_{sp} = 4 \times \frac{C}{m}$, where $C$ is the measured capacitance of the two-electrode cell and $m$ is the total mass of the two electrodes. For the devices containing the eutectic LiCl electrolyte, the 12-h temperature hold experiment involved cooling the device to $-70^\circ$C, taking a CV measurement, holding at $-70^\circ$C for 12 h, and taking another measurement at $-70^\circ$C. Charge–discharge cycle stability measurements of these devices were taken at $-70^\circ$C and $80^\circ$C using a current of 1 A/g and 2.5 A/g, respectively. Gravimetric energy density was calculated as $E = 0.5 \times C \times V$, where $C$ is the gravimetric capacitance and $V$ is the voltage window.

Electrochemical stability measurements for the eutectic LiCl liquid electrolyte were made using a three-electrode cell with a platinum counter and working metal electrode and a Ag/AgCl reference (Chinstruments). The scan rate was 10 mV/s and the threshold for electrolyte stability was taken to be 0.6 mA/cm$^2$.

Temperature-dependent conductivity of the eutectic LiCl liquid electrolyte was determined by measuring the IR drop in galvanostatic charge–discharge tests (WaveNow potentiostat) of two activated carbon electrodes (area = $0.5 \times 1.5$cm$^2$) in the LiCl electrolyte. A charging current of 0.2 mA was used. Contact resistance was found by taking resistance measurements over varying electrode spacings and extrapolating to zero spacing. The $-80^\circ$C measurement was taken after holding for 90 min.
3.3 RESULTS AND DISCUSSION

Relative to many organic solvents, pure water has a high freezing point of 0 °C. However, the addition of salts and other solvents (i.e., road salt or alcohol) depresses this temperature by several tens of degrees. In an ideal case, freezing point depression is a colligative property: irrespective of the identity of the solute, the freezing point of the solution will proportionally decrease with solute concentration. This simple relationship holds in the dilute limit where the solute species do not interact. Of course, at sufficiently high concentrations, the solute will precipitate at moderately low temperatures, potentially forming an insulating barrier at interfaces. A phase diagram is necessary to capture transitions across a broad concentration range.

Water is an excellent solvent that forms very concentrated solutions of certain salts. Near the solubility limit (∼20 M) of some lithium salts, solutions take on a unique solvation structure and are capable of operating at high voltages.(47) These solutions, called “water in salt” electrolytes, are far more concentrated than conventional electrolytes (∼1 M). The aqueous electrolyte used in this study contains LiCl at an intermediate concentration: the eutectic (6.8 M or 24.8 wt %) where the liquid–solid transition is at its minimum, −74 °C (Figure 14).(48) Incidentally, the conductivity is greatest around this concentration.(49) Below this concentration, ice forms at relatively higher temperatures and, above it, LiCl precipitates. Both transitions are expected to hurt electrolyte performance at low temperatures.(50) Given the high concentration of charge carriers in the eutectic solution and the greatly depressed freezing point, it is expected to perform as an excellent low temperature electrolyte.
Figure 15. LiCl–H₂O phase diagram. At 24.8% LiCl, the solution forms a eutectic with a freezing point of −74 °C. Adapted from (48).

3.3.1 ENERGY STORAGE AT LOW TEMPERATURES

The eutectic LiCl electrolyte was paired with electrodes coated in an unmodified, commercial activated carbon (Kuraray YP-80FP) to evaluate its performance to support energy storage at low temperatures. Carbon electrodes were used, which eliminate possible corrosive issues in the chloride-containing electrolyte. As a point of comparison, supercapacitors containing a conventional organic electrolyte (0.5 M tetraethylammonium tetrafluoroborate (TEABF₄) in acetonitrile) were also subjected to low-temperature testing. Figure 15a,b shows charging cycles (cyclic voltammetry performed at 5 mV/s) at various temperatures of the organic and aqueous device, respectively. The organic electrolyte device performs well down to −40 °C without any significant loss of capacity. At −60 °C, below the freezing point of acetonitrile (−45 °C), charging ceases. The device containing the eutectic LiCl electrolyte performs superbly down to −70 °C, retaining 72% of the room temperature capacity (28 F/g) and fast charging kinetics evidenced by a square-shaped
profile. Zero low temperature fatigue for the aqueous device is seen at −70 °C over a 12-h hold, with charging curves taken before and after overlaying almost perfectly (Figure 15c). Surprisingly, the aqueous device even supports substantial charging (42% of room temperature capacity) at −80 °C, below the expected freezing point of the water-based eutectic electrolyte.

Figure 16. Electrochemical performance at low temperature of conventional and aqueous devices. Cyclic voltammetry (CV) of carbon supercapacitors containing (a) organic (0.5 m TEABF₄ in acetonitrile) electrolyte and (b) aqueous eutectic (LiCl 24.8 wt %) electrolyte. Charging was performed at 5 mV/s at different temperatures. (c) CV measurements taken before and after a 12-h hold at −70 °C. (d) Percent capacitance retention across a range of temperatures for the aqueous (blue) and acetonitrile (green) devices.

Since the aqueous electrolyte is nonflammable, energy storage is also possible at high temperatures - up to 80 °C without any losses. Percent capacitance retained at high and low temperatures (relative to room temperature), is presented in Figure 15d. With a conservative temperature range from −70 to 80 °C, the eutectic LiCl electrolyte can support
operation over a very broad 150 °C window. Figure 16 compares the temperature ranges of this aqueous device with conventional energy storage as well as examples of extreme conditions found on Earth and Mars. The range of the eutectic energy storage easily spans some of the coldest places on earth - a town in the Arctic where temperatures dip below −50 °C - and the hottest - such as Death Valley where temperatures reach 50 °C. The lower limit of this range is close to the coldest temperatures experienced at Gale crater on Mars. Such energy storage would require less heating to stay operational than less efficient, conventional devices.

![Temperature Ranges Diagram](image)

**Figure 17.** Comparison of the temperature windows of operation for the aqueous eutectic device and conventional energy storage as well as examples of extreme conditions found on Earth and Mars.

To look fundamentally at the eutectic LiCl electrolyte and understand the origin of its low-temperature performance, the temperature-dependent conductivity was measured (Figure 17a,b). As expected for an aqueous electrolyte, the conductivity is very high, about 180 mS/cm at room temperature. This is 1–2 orders of magnitude higher than organic electrolytes which typically have a conductivity between 1 and 10 mS/cm. (51) Even when the temperature falls to −70 °C, the eutectic is still quite conductive −1.83 mS/cm which is still in the range of organic electrolytes when measured at room temperature. This remarkable conductivity is largely why the electrolyte performs so well at low temperature.
even when paired with an industry-standard, unmodified electrode material. Below this temperature, the electrolyte is visually observed to freeze (Figure 17c) after which the conductivity falls at a much faster rate. When an Arrhenius plot of the conductivity-temperature data is made (Figure 17d), two distinct regions can be visualized. Above the eutectic freezing point, conduction occurs with low activation energy - solvated ions are diffusing in a fluid medium. Below the freezing point, the conduction still occurs but via another mechanism with higher activation energy. Likely, lithium ions are conducting via hopping within a static water network, as was shown theoretically for copper ions in frozen aqueous solutions.(52) Even in this frozen state at −80 °C the electrolyte has a conductivity of 0.19 mS/cm on par with typical solid-state ionic conductors when measured at room temperature.(51, 53, 54) This mode of conduction is responsible for the more sluggish yet significant charge storage seen earlier at −80 °C. Recently, others have observed aqueous proton batteries operating below the freezing point of the constituent acidic electrolytes.(55, 56) Here, we specifically find that proton conduction (perhaps by the Grotthuss mechanism) is not necessary to enable exceptionally high ionic conductivities and energy storage even in frozen aqueous solutions.
Figure 18. Conductivity of aqueous LiCl eutectic electrolyte at different temperatures. (a) Conductivity versus temperature and (b) magnified low temperature region with values shown. (c) Photographs of liquid and frozen LiCl electrolyte at −70 and −80 °C. (d) Arrhenius plot of temperature-conductivity data with activation energies is shown.

Clearly, aqueous electrolytes possess distinct advantages over typical organic electrolytes for energy storage applications in cold environments. A high baseline conductivity supports ionic currents at low temperatures and the unique hydrogen bonding of water solubilizes large fractions of lithium chloride, allowing for a massive freezing point depression. Still, the small electrochemical stability window of aqueous electrolytes relative to organic generally precludes their adoption into commercial energy storage devices. In the low-temperature case, however, the rates of solvent decomposition
(hydrogen and oxygen evolution) are expected to be significantly lowered since these are activation-limited processes (the reactant is the solvent). Figure 18 shows the electrochemical stability windows of the 24.8% LiCl solution at room temperature, −40 °C, and −70 °C, evaluated with linear sweep voltammetry on a platinum working electrode. From room temperature to −70 °C, the stability window of the aqueous electrolyte expands by 1 V. The voltage window reaches 3 V at −70 °C, within the range of common organic electrolytes. This is a sensible result. Given that hydrogen and oxygen evolution are activation-limited, the reaction rate constants should exhibit a very strong (logarithmic) dependence on temperature as they obey the Arrhenius equation. Furthermore, the dissociation constant of water is reduced at low temperatures, limiting the concentrations of H+ and OH− which participate in the electrolysis reaction.(57) The result is that the eutectic LiCl electrolyte can support a high-rate energy storage at low temperatures.

![Graph showing electrochemical stability](image)

Figure 19. Electrochemical stability of aqueous LiCl eutectic at different temperatures. Measurements were taken with linear sweep voltammetry at 10 mV/s on a platinum working electrode with a Ag/AgCl reference.
3.3.2 LOW-TEMPERATURE POLYMER ELECTROLYTE

While liquid electrolytes offer the highest conductivities, there are a lot of incentives to develop polymer electrolytes: adopting a leak-free, flexible, low-volatile gel material in place of a liquid could streamline both device design and manufacturing. For these reasons, we sought to translate the low-temperature performance of the liquid LiCl eutectic to a solid polymer electrolyte. A mixture of aqueous LiCl and poly(vinyl alcohol) - another very low-cost, nontoxic material - was used as a gel electrolyte in the same energy storage device as above and subjected to low-temperature charging characterizations. This polymer electrolyte enables energy storage down to −70 °C, though less efficiently than the liquid electrolyte (Figure 19a). The slower charging rates are compensated for with the greatly expanded voltage window at low temperatures (Figure 19b): at −70 °C, the voltage window for the polymer gel device is at least 2.2 V, translating to an energy density three times that of room temperature. In this sense, these devices actually perform better at low temperatures. Cycling at −70 °C shows zero fatigue over 1000 cycles, demonstrating that charge storage is reversible at low temperatures (Figure 19c). High-temperature cycling at 80 °C shows similar results. A larger scale pouch cell was made, which is shown in Figure 19d. At −70 °C, it can deliver enough power to light a yellow light emitting diode (LED) for more than a minute.
3.4 CONCLUSIONS

In this chapter, we demonstrate the remarkable performance of concentrated aqueous electrolytes for low-temperature energy storage. A eutectic mixture of lithium chloride, a commodity chemical, and water remains liquid down to −74 °C. This electrolyte possesses a remarkably high conductivity of 1.83 mS/cm at −70 °C, which is in the range of typical organic electrolytes when measured at room temperature. Such a high conductivity easily enables low-temperature energy storage in supercapacitors containing...
a completely unmodified, industry standard activated carbon. In such devices, 72% of room temperature capacitance (28 F/g) is maintained at −70 °C and, incidentally, the stability window of the electrolyte is greatly widened to 3 V. Clearly, the advantage of aqueous electrolytes - high ionic conductivity - is exemplified at low temperature, while the primary disadvantage - narrow stability window - is mitigated, making aqueous electrolytes an unexpected yet ideal candidate for low-temperature applications. A mixture of PVA and aqueous LiCl forms a gel electrolyte which retains much of the low-temperature properties of the liquid eutectic and can support powering an LED at −70 °C. The energy storage system presented here can easily operate in the most extreme conditions found on earth and does so using only low-cost, commercial, and environmentally benign materials.
CHAPTER 4

SOLAR THERMAL TEXTILES: A NATURE-INSPIRED EVOLUTION OF AN OLD COMMODITY

4.1 INTRODUCTION

Wearable technology is advancing rapidly to bring a host of novel functionalities – health and environmental monitoring, motion tracking, sleep evaluation – into everyday items. With a few exceptions, it is ironic that the first wearable – the textile – has not evolved in how it performs its original function: thermoregulation. After thousands of years, textiles are still woven from fibers into thick structures that manage heat transfer by inhibiting thermal conduction and convection from the body to the environment while maintaining breathability. With increasing environmental and economic pressures to find more sustainable ways of living in a rapidly changing climate, it is necessary to leverage novel materials and revisit the design of one of the oldest and most basic technologies.

In nature, organisms have met environmental challenges by manipulating light with optical materials for thermoregulation. Managing heat in a fundamentally different way than traditional textiles, specialized surfaces that selectively reflect, absorb, or transmit radiation across the visible and infrared (IR) spectrum allow certain animals to survive in extreme conditions. This strategy is used, for example, by reflective silver ants in the Sahara,(58) and polar bears(59) and moths(60) in the arctic circle. One commonly used material is melanin, an optically dense biopolymer comprised of light-interacting conjugated units with a high refractive index and broadband light absorption.(61, 62) Besides melanin’s role in the dynamic camouflage of cephalopods, it is also used in the thermoregulation of species of moths, butterflies, and birds that have evolved melanin-
enriched wing coatings in cold and sunny climates.\(^{(60, 63)}\) Such surfaces exhibit selective function over the visible and near-infrared (vis-NIR) spectrum, where photothermal heating takes place, and over the infrared (IR), where objects spontaneously radiate heat according to Planck’s law. The polar bear is also known for optically-enabled thermoregulation. Its pigment-free fur transmits visible light to melanin darkened skin where radiant heat is then trapped by infrared-blocking hair fibers.\(^{(59, 64, 65)}\)

Garment coatings comprised of materials like MXenes, carbon nanotubes, and silver nanowires have been pursued to approximate, though not mimic, the thermoregulation strategies found in nature.\(^{(66–70)}\) One commercialized technology – Omni-Heat by Columbia – uses aluminum dots to reflect body heat to small effect, heating slightly better than a typical cotton fabric.\(^{(71)}\) A practical challenge is robustly coating nanomaterials onto textiles, which must stand up to laundering and wear over a garment lifetime. Certain nanomaterials are also known to be toxic and biopersistent, with safety concerns given their historical lack of regulatory oversight.\(^{(72)}\) Such concerns are particularly worth addressing, considering that melanin and other polymers, such as silk, chitin and cellulose, that are used for thermoregulation by animals can perform these functions while being environmentally benign.\(^{(62, 73, 74)}\) Conjugated polymers are an alternative class of soft materials with favorable properties for wearable thermoregulation. Robust coatings of such polymers on complex surfaces characteristic of textiles are achievable with oxidative chemical vapor deposition.\(^{(25)}\) Similar to melanin, polymers like poly(3,4-ethylenedioxythiophene) (PEDOT) exhibit high optical density with electromagnetic properties arising from pi-stacked conjugated units.\(^{(75)}\) While being lightweight and flexible, conjugated polymers are also often water-swellable and possess
chemical structures that bear resemblance to those of the optically-active biopolymer melanin described above.(76)

In this chapter, we present a lightweight textile platform for light and heat management by taking inspiration from materials and structures found in nature. Our approach is to (1) adapt PEDOT as a spectrally-selective coating on textiles to mimic the thermoregulating role that melanin plays in many organisms and (2) adopt a semi-transparent upper textile layer to mimic polar bear fur and minimize heat dissipation while transmitting light to the bottom photothermal layer. A key advantage to this approach is that, unlike other thermoregulation strategies which rely on metallic or inorganic materials, the structure proposed here can be realized with all-polymer materials. Photothermal harvesting of ambient light – indoors or outdoors – allows high-power, wireless delivery of heat directly to the body without the need for bulky and underperforming wearable energy storers-harvesters like photovoltaics, triboelectrics, lithium-ion batteries, etc. A climate-controlled chamber with a skin and solar simulator is used to evaluate the heating performance relative to common garments. Exposed to a moderate light intensity of 130 W/m² (ca. 0.1 sun), this thermal textile has a temperature rating that extends 9.9°C lower than a typical cotton fabric (4.1°C/~40°F versus 14.1°C/~60°F) while weighing 30% less. A steady-state heat transfer model that considers solar absorbance and infrared emissivity is developed to understand the performance limits of a spectrally optimized absorber layer.
4.2 METHODS

4.2.1 EXPERIMENTAL

Films of PEDOT-Cl were deposited onto ripstop nylon using a custom-built reactor and process described in previous reports. Briefly, 3,4-ethylenedioxythiophene (EDOT) (95%, TCI America), was reacted with iron (III) chloride (FeCl$_3$) (97%, Sigma Aldrich) in the vapor phase at low pressures maintained at approximately 750 mTorr. EDOT was evaporated at 95°C and delivered into the chamber via a needle valve (Swagelok SS-4JB) that was typically opened a quarter turn. The volume of EDOT in the glass bulb was monitored over the course of the deposition to ensure a monomer flow rate of 5-10 sccm. FeCl$_3$ was sublimed by heating to >205°C in a Luxel RADAK II furnace. The substrate stage was heated to 150°C over the course of the deposition. Real-time film growth rate was monitored by a quartz crystal microbalance (QCM) located inside the chamber. Due to the different positioning of the QCM relative to the sample stage, a correction factor is needed to account for film growth rate variations. By measuring actual film thickness post-deposition using a Dektak profilometer, a tooling factor of 0.24 was determined. Film growth rate was kept at 2 nm/s. After the desired film thickness was reached, the sample stage was allowed to cool below 60°C under vacuum. To remove residual iron salts and oligomers, samples were immediately rinsed with dilute acid (0.5 M HCl) for 30 minutes followed by a methanol rinse.

Agribon AG-19 (140μm thickness measured with calipers) was purchased from Johnny’s Selected Seeds. Ripstop nylon (60μm), cotton terry (1000μm), and cotton jersey (310μm) were purchased from Joann’s Fabrics. Samples were cut to 5x5cm dimensions.
Agribon samples were cut to 6x6cm dimensions and supported by a 5mm thick plastic frame. Omni-Heat samples (160µm) were cut from the inside of a Columbia brand jacket.

An insulated chamber 12”x12”x9” was made with R-5 insulation board. Two silicone heaters (Tempco, 5x5cm²) were inset into a block of insulation with thermistors placed atop the skin heater and between the skin and guard heater. Manila paper was chosen as the outer “skin” surface because it has an albedo representative of human skin. Another thermistor set one inch above and one inch to the side of the skin monitored environment temperature. This thermistor was shielded with foil to measure the true air temperature under irradiance. A cooler consisting of a pump circulating chamber air through a filled 0.5 L liquid nitrogen Dewar was used. An Adafruit Feather M0 microcontroller monitored skin temperature and adjusted the environmental temperature until $T_{\text{skin}} = 33^\circ\text{C}$ using hysteresis control. The guard heater was set to maintain the same temperature within 0.3 °C as the skin heater, ensuring 1D heat transport upward. A steady state measurement was taken such that the skin temperature varied no more than 0.3 °C over the course of at least 15 minutes. Error bars provided are the standard deviation of environmental temperature during the measurement. For light conditions, a Feit 33W/300W equivalent LED bulb was used; light intensity was measured with a light meter placed in the same position as the skin heater. The spectrum was measured with a fluorimeter (Horiba Scientific). For the higher radiances, a solar simulator was used (Oriel). Measurements were taken with humidity levels in the range of 20-40%. A small thermoregulation dependence (~1°C) on humidity was observed.
A FLIR TG165 was used to measure the infrared properties of the nylon, PEDOT-nylon, and AG-19 and capture thermal images. A fabric sample was placed on a heated (60°C) 15x15 cm copper block covered with 3M Super 88 electrical tape ($\varepsilon = 0.95$) (77) and the apparent emissivity ($\varepsilon$) was measured assuming the fabric samples (<60 μm thick) reached 60°C. Transmissivity ($\tau$) was measured by covering the FLIR detector with the fabric samples, measuring the apparent temperature of the 60°C block from 6 cm away, and applying Equation 2 where $T_{\text{obj}}$ is the temperature of the fabric sample and $T_{\text{amb}}$ is the ambient temperature. (77) Transmissivity was subtracted from apparent emissivity to obtain the true emissivity. Finally, reflectivity ($\rho$) was calculated from true emissivity and transmissivity by Kirchhoff’s law. For our heat transfer analyses, we then assume that transmitted light is effectively absorbed (as it would be by the skin) so emissivity is reported and used assuming opaque samples. The optical transmission micrograph was taken using a Nikon Ti2 Eclipse with a 40x objective and a 440nm source.

$$\tau = \frac{T_{\text{obj,apparent}}^4 - T_{\text{amb}}^4}{T_{\text{obj,real}}^4 - T_{\text{amb}}^4}$$

(1)

To make the on-body radiance estimation, the human body was approximated by a vertical cylinder of height 1.7 m and surface area 1.8 m². Similar approximations have been previously made. (78) Extraterrestrial radiance values on a vertical surface on June 21st and Dec 21st in Boston, MA were obtained using the SOLPOS function (NREL). On-body radiance is then approximated as 80% of extraterrestrial radiance on the projected vertical area ($A_{xy} = 0.568$ m²) per total surface area ($A_{\text{tot}} = 1.8$ m²) as in Equation 2.
The Agribon AG-19 fabric was sewn with cotton thread and ironed to form pleated baffles. The PEDOT-nylon was then sewn to the bottom. During testing, the open ends of the baffles were covered with plastic. Washing was performed in clean water with stirring for 3 hours. Breathability was characterized by sealing textile sample discs (3.1 cm$^2$) to vials containing 3 g of Dri-Rite. Placed in a sealed chamber with a humidity of approximately 60%, the mass change of the vials was recorded at two-hour intervals. The mass gain was then divided by the surface area of the samples to obtain the water vapor transmission rate.

A solution of Gain laundry detergent was made per manufacturer's recommended usage and the textile was immersed with stirring for 15 minutes followed by immersion in fresh DI water with stirring for 15 minutes. The textile was allowed to dry for at least three hours in a hood before characterization. This procedure was repeated three times.

4.2.2 HEAT TRANSFER MODEL

To evaluate the impact of fabric optical properties on personal heating, a one-dimensional steady-state heat transfer model analysis was performed. This model is based on the control volume and energy balance analysis of heat radiation, conduction, and convection between the ambient environment and clothed human body. For simplification, the following assumptions are given:

1) The fabric is assumed to be opaque.

2) The temperature and the metabolic heat generation rate of the human skin is constant.
2) Heat convection is uniform between the ambient environment and the body.

3) The heat transfer between the clothed human body and the environment is one-dimensional transport through infinite parallel plans.

4) There is no convection between the skin and fabric.

5) Air gap thickness is small (1.4mm) and homogeneous.

6) The material optical properties are constant.

7) The environment and the skin are assumed to be the ideal black bodies.

8) The temperature of the textile is assumed to be uniform.

9) Assuming this is a steady-state heat transfer process, no heat accumulates.

10) Assuming no forced convection between fabric and environment.

11) Assuming a personal thermal comfort condition (constant $T_{\text{skin}}=33^\circ \text{C}$) and evaporative heat loss occurs.

In prior works, the natural convective heat transfer coefficient (NCHTC) was taken as a constant.\cite{71, 79} Since the temperature range in our study is significantly wider than in previous, the dependence of NCHTC on $\Delta T$ (the difference between $T_t$ and $T_e$) was included in the model. In our case, we varied NCHTC for a horizontal hot plate based on the Eqn. S1 adapted from W.H. McAdam.\cite{80}

$$h = K \times \Delta T^{\frac{1}{3}} \tag{S1}$$

The exponent $\frac{1}{3}$ is determined by the Rayleigh number (Ra) which for our system is estimated to be around $2 \times 10^9$ by Equation S2. The parameter names and values used for calculation of Ra are listed in Table S2.

$$Ra = \frac{C_p L_3 \rho_2 g \Delta T \beta}{K \mu} \tag{S2}$$
The constant K in Eqn. S1 was estimated to be 2.41 by taking $h(\Delta T=10) = 4$, which aligns with previous literature.\(^{71, 79}\) The effective length is equal to the area of the hot plate divided by the perimeter.

This model relates fabric optical and thermoregulation properties. Steady state energy (heat) balances were made at the skin surface and textile surface:

At skin surface:

$$q_{\text{gen}} - q_{\text{rad}, s}^* (1 - \rho_s) + q_{\text{rad}, t} - q_{\text{cond}} = 0$$  \hspace{1cm} (3)

At textile surface:

$$q_{\text{rad}, s}^* (1 - \rho_t) - 2 q_{\text{rad}, t} + q_{\text{rad}, e}^* (1 - \rho_e) + q_{\text{cond}} - q_{\text{conv}} + \alpha Q_{\text{light}} = 0$$  \hspace{1cm} (4)

$q_{\text{gen}}$: human metabolic heat generation rate

$q_{\text{conv}}$: convective heat flux between the textile and ambient environment

$q_{\text{cond}}$: conductive heat flux from the skin to the textile

$q_{\text{rad}, s}$: radiative heat flux from the human body

$q_{\text{rad}, e}$: radiative heat flux from the environment

$q_{\text{rad}, t}$: radiative heat flux from the textile

According to the Stefan-Boltzmann law, Newton’s law of cooling and Fourier’s law, the conductive, convective, and radiation term can be represented as,

$$q_{\text{rad}, s} = \varepsilon_s \sigma^* T_s^4$$  \hspace{1cm} (5)

$$q_{\text{rad}, e} = \varepsilon_e \sigma^* T_e^4$$  \hspace{1cm} (6)

$$q_{\text{rad}, t} = \varepsilon_t \sigma^* T_t^4$$  \hspace{1cm} (7)

$$q_{\text{cond}} = (k_s/t_s) (T_s - T_t)$$  \hspace{1cm} (8)

$$q_{\text{conv}} = 2.41 (T_s - T_t)^{\frac{1}{3}} (T_s - T_t)$$  \hspace{1cm} (9)
Based on the energy balance analysis on the controlled volume, the two unknowns, $T_e$ and $T_t$ can be solved when the input $\varepsilon_t$ and $\alpha$ vary from 0 to 1. The calculation and data visualization are completed on Matlab (version R2018b (MathWorks, Inc)). This generated a 3-dimensional plot showing the temperature map at different optical properties of the textile. Two experimental data points for nylon and PEDOT-nylon are also plotted.
Table 1. Input parameters and their nomenclature used for heat transfer model analysis.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{gen}$</td>
<td>metabolic heat generation rate per unit area</td>
<td>75</td>
<td>W/m²</td>
</tr>
<tr>
<td>$Q_{light}$</td>
<td>Solar light intensity</td>
<td>130</td>
<td>W/m²</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>Skin, $T_s$=306.15, Environment, $T_e$ Textile, $T_t$</td>
<td></td>
</tr>
<tr>
<td>$t_a$</td>
<td>Air gap thickness</td>
<td>1.4</td>
<td>mm</td>
</tr>
<tr>
<td>$k_a$</td>
<td>Thermal conductivity of air</td>
<td>0.026</td>
<td>W/m*K</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
<td>$5.67 \times 10^{-8}$</td>
<td>W/m²*K⁴</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>IR emissivity</td>
<td>Skin, $\varepsilon_s$ = 0.98, Environment, $\varepsilon_e$ = 1, Nylon, $\varepsilon_t$ = 1-$\rho_t$ = 0.65 PEDOT/Nylon, $\varepsilon_t$ = 1-$\rho_t$ = 0.48</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>IR reflectivity</td>
<td>Nylon, $\rho_t$ = 0.2 PEDOT-nylon $\rho_t$ = 0.46</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Visible light absorptivity</td>
<td>Nylon, $\alpha$ = 0.47 PEDOT-nylon, $\alpha$ = 0.91</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Properties of ambient air at 30°C and atmospheric pressure.(80)

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$, specific heat capacity</td>
<td>1.0065*10^3</td>
<td>J/kg.K</td>
</tr>
<tr>
<td>$k$, heat conductivity</td>
<td>0.026</td>
<td>W/m.K</td>
</tr>
<tr>
<td>$\eta$, dynamic viscosity</td>
<td>1.868*10^{-5}</td>
<td>kg/m.s</td>
</tr>
<tr>
<td>$\rho$, density</td>
<td>1.1649</td>
<td>kg/m^3</td>
</tr>
<tr>
<td>$g$, earth gravity acceleration</td>
<td>9.81</td>
<td>m/s^2</td>
</tr>
<tr>
<td>$\beta$, thermal expansion coefficient</td>
<td>3.32*10^{-3}</td>
<td>K^{-1}</td>
</tr>
<tr>
<td>$L$, effective length</td>
<td>1.25</td>
<td>unitless</td>
</tr>
<tr>
<td>$\Delta T$, temperature difference between air and hot surface</td>
<td>10</td>
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4.3 RESULTS

4.3.1 BIOMIMETIC SYSTEM DESIGN AND MATERIAL SELECTION

Traditionally, textiles have been made from a limited material set. Natural or synthetic fibers are spun and woven into thick fabrics that inhibit heat diffusion between the body and the environment. Perhaps due to the lack of suitable materials, traditional textile design has largely overlooked the management of radiative heat (i.e. energy carried by light). Recently, this has begun to change with, for example, the development of radiative heating textiles enabled by reflective metallic coatings\(^{71}\) and radiative cooling textiles enabled by IR transparent polyethylene fibers\(^{81}\). A performance gap still exists for more efficient personal heating in a comfortable, familiar textile format. One way forward is to not only limit dissipation of radiant body heat outward, but to also optimize absorption of ambient radiant energy inward. The power density of sunlight, for example, is sufficient \((100 - 1000 \text{ W/m}^2)\) to augment body heat \((\sim 70-120 \text{ W/m}^2)\). It is therefore unsurprising to see both directions of radiative energy management at play in adaptations of polar animals.

Two natural structures inspire the design of our solar thermal textile. The first is a type of structural coloration in some species of cold-adapted moths and butterflies that enables selective absorption of visible-NIR light and suppression of thermal (IR) emission (Figure 20a)\(^{60, 63}\). In this case, melanin is the optically active material. With an electron-dense pi-pi stacked structure, melanin behaves as a disordered organic semiconductor and has a significantly higher refractive index than most biopolymers\(^{61, 62}\). A variety of donor-acceptor units enable broadband light absorption, while a high optical density enables light interference effects (IR reflection) in melanin-enriched wing coatings. The second source of inspiration is the pelt of the polar bear which, key to the animal’s survival in the extreme
cold, simultaneously provides high thermal resistance (R) and high solar utilization (Figure 20b). The dual function arises from a specific material set and optical structure. Lacking melanin pigment, the hollow hair fibers have a low optical density and efficiently forward-scatter light, permitting photothermal capture at the melanin enriched skin while inhibiting heat loss to the environment.(59, 65) The essential optical structure of the pelt - a transmitter-insulator (transparent hair) stacked above an absorber (darkened skin) - efficiently harvests solar thermal energy to support thermoregulation in the extreme cold. While there have been reports of materials nominally mimicking polar bear fur, no garment has demonstrated this crucial optical structure nor a transmitting insulator fabric.(82–84)

To mimic such adaptations, we optically engineered a bilayer textile using polymer materials (Figure 20c). The bottom layer is a nylon fabric robustly vapor coated with the conjugated polymer PEDOT, enabling selective absorption of visible light and suppression of IR emission. In structure and function, the soft material PEDOT bears resemblance to melanin. This pi-pi stacked electronic polymer interacts strongly with light due to high free-electron density associated with long conjugated chains.(85) While PEDOT is an organic conductor, it shares the same broadband vis-NIR light absorption of melanin due to plasmon (surface electron) resonance near 1000 nm with a high optical density κ.(75) At longer wavelengths into the IR, PEDOT is a reflector (a weak emitter). Like the melanin-enriched microstructure of moth wings, a PEDOT coating can therefore be used to efficiently manage radiative heat transfer between the body and the environment. Photothermal heat generated at the PEDOT-nylon absorber is further trapped by the top layer, a semi-transparent fabric mimicking polar bear fur. This lightweight fabric (Agribon AG-19)(86) is made of low optical density polypropylene fibers that forward-scatter visible
light with about 85% transmission and more weakly transmits IR light with about 60% transmission. By confining solar thermal heat as both a diffusion and IR radiation barrier, AG-19 essentially acts like a breathable greenhouse material. Indeed, it is used in the agricultural industry for this purpose. Individual fibers are visualized in an optical transmission micrograph in Figure 1e. Fiber diameter is in the range of 9-10 microns, comparable to IR wavelengths and thus capable of strong Mie scattering.(79) As with polyethylene and other polyolefins, polypropylene is an attractive material for textiles for its potential sustainability, durability, and ultra-light weight.(81) Along with the spectrally selective PEDOT-nylon fabric, the fabric transmitter layer operates differently than traditional textiles and has the potential to provide highly efficient thermoregulation.
Figure 21. Designing a multilayer textile to mimic thermoregulation structures of animals that efficiently harvest solar thermal heat to reduce metabolic energy needs. (a) In the wings of certain moths and butterflies, melanin microstructures interact with light to control heat. The high optical density of melanin (representative structure shown) enables broadband light absorption (high $\varepsilon_{\text{vis-NIR}}$) and efficient light interference effects to suppress thermal emission (low $\varepsilon_{\text{IR}}$). (b) The polar bear has similarly evolved melanin-enriched skin for...
photothermal capture. This effect is enhanced by its fur made of pigment-free, hollow
fibers that forward-scatter light inward (high $\tau_{\text{vis-NIR}}$) and inhibit heat dissipation outward
(high thermal resistance $R$). (c) Our bilayer textile combines such light and heat control
elements. The bottom nylon fabric is vapor coated with poly(ethylenedioxythiophene)
(PEDOT) (structure shown), an optically dense organic conductor with high visible light
absorption and low thermal emission. The top fabric is made of spun-bonded
polypropylene fibers (Agribon AG-19) and acts as a semi-transparent insulator,
transmitting ~85% of visible light to the photothermal PEDOT-nylon layer. A transmission
optical micrograph showing the polypropylene fiber network. Scale bar 20 μm.

4.3.2 OPTICAL AND THERMOREGULATION CHARACTERIZATION

A one-micron thick coating of PEDOT onto nylon fabric dramatically changes the
surface optical properties due to the high optical density of PEDOT. Figure 21a visualizes
this change in photographs and thermal images. Under a commercial lightbulb, the coated
fabric absorbs more photothermal energy relative to the reflective uncoated nylon. Over an
IR source (human body), the coated fabric emits less thermal energy (appears colder) than
the high emissivity surface of the uncoated nylon. These effects are quantified in Figure
21b, where emissivity of the coated fabric (blue) and uncoated (black) is plotted against
wavelength. The uncoated nylon fabric shows a behavior typical of traditional textiles: low
emissivity (absorbance) in the visible and high emissivity in the IR. With a PEDOT
coating, this optical behavior is reversed, and the fabric behaves more like an ideal
photothermal absorber.
Figure 22. Characterizing the spectral selectivity of PEDOT-nylon fabric. (a) Photographs and infrared (IR) images comparing uncoated and coated nylon fabric interacting with a visible light source (lamp) and an IR source (human body). (b) Emissivity (absorptivity) of coated fabric (blue) relative to uncoated (black) compared against the blackbody spectra of the sun (5,504 °C) and human body (33 °C). Emissivity is calculated as 100% - ρ.

With the ability to control the optical properties of the fabric, we next evaluate the thermoregulating performance of a set of traditional and unconventional fabrics. A simple way to conceptualize this task is by considering the lowest temperature rating for which a certain textile can maintain the wearer’s thermal comfort. Warmer textiles are needed for colder environments (Figure 22a). More specifically, a textile should limit the loss of body heat (75 W/m² for an average adult at rest) to the environment so that a comfortable skin temperature (33°C) is maintained at steady state. Excluding factors like wind chill and humidity, this situation is simulated in a chamber depicted in Figure 22b. For a given textile sample, the temperature of a skin heater with a constant output (75 W/m²) is monitored by
a controller that lowers the environmental temperature until thermal comfort ($T_{\text{skin}} = 33^\circ\text{C}$) is reached at steady state. A similar chamber design was previously used to evaluate passive heating solutions,\(^{(71)}\) except here a window allows for environmental light (radiative energy) input to the textile-skin system.

Uncoated and PEDOT-coated nylon were tested, as well as a range of traditional and non-traditional textile comparators of varying weights, as shown in Figure 22c. A cotton jersey sample represents typical T-shirt material, while cotton terry is typical of heavier, warmer garments like a sweatshirt. The other optically-active textiles include commercial Omni-Heat and spun-bonded polypropylene (AG-19). The Omni-Heat fabric is tested with the reflective face up (R up) and down (R down). The AG-19 is held by a 5 mm thick plastic frame for consistency across measurements. The low temperature ratings of the textiles were measured in the environmental chamber and results for dark conditions are shown in Figure 22d. The low emissivity fabrics – PEDOT-nylon and Omni-Heat (R up) – perform similarly to the cotton jersey fabric as has been previously demonstrated.\(^{(71)}\) The thicker cotton terry and AG-19 fabrics offer more insulation and have lower environmental temperature ratings in the range of 18$^\circ\text{C}$.

Under moderate illumination of 130 W/m\(^2\), the performance of the textile samples varies more widely. While the PEDOT-nylon and Omni-Heat (R-up) fabrics perform similarly in dark conditions due to comparable thermal emissivity values, the PEDOT-nylon has a greater visible absorbance and so performs significantly better (9.6$^\circ\text{C}$ versus 11.5$^\circ\text{C}$) under illumination. Compared to PEDOT fabrics, other metal-coated textiles, like Omni-Heat, should show poor solar thermal heating due to the higher resonant frequency of most metals (typically in the UV-visible range). Individually, AG-19 also performs well
(8.2°C) but when stacked in the absorber-transmitter structure, the complementary optical functions of the PEDOT-nylon and AG-19 yield a more dramatic heating effect. The bilayer textile has a temperature rating that extends 10°C lower than the cotton jersey fabric (4.2°C/~40°F versus 14.1°C/~60°F) while weighing 30% less. With an additional layer of AG-19, the performance improves more modestly (extending to 2.9°C), suggesting that the sacrifice of solar utilization (light transmission) for thermal insulation becomes less favorable to thermoregulation.

Taking the temperature rating of the cotton jersey fabric as a baseline for the other measurements allows comparison of textile performance in both light and dark conditions (Figure 22f). While the thick, insulating cotton terry fabric shows good performance in dark conditions (+1.6°C relative to cotton jersey), it has relatively weak performance in light conditions (+1.3°C). This is representative of traditional textiles – thick, opaque insulation that limits heat dissipation outward will also limit photothermal heat transfer inward. On the other hand, the bilayer textile excels in both dark (+2.7°C) and light (+9.9°C) conditions due to the insulating yet light-transmitting AG-19 layer.
Figure 23. Characterizing the thermoregulation of traditional and novel textiles. (a) Textiles are worn to maintain thermal comfort in varying environmental conditions. (b) A chamber is used to simulate heat transfer between the body and environment and evaluate the warmth of textile samples. The “skin” surface is a heater with a constant output \( (Q_{ gen}) \) typical of an active adult metabolism. To characterize a sample, a microcontroller finds the air temperature \( (T_{ environment}) \) at which \( T_{ skin} = 33^\circ C \) (thermal comfort condition) at steady state; this is the temperature rating of the textile. Warmer textiles maintain thermal comfort at lower environmental temperatures. (c) Textile samples characterized. Fabric weight (mg/cm\(^2\)) is shown. Low temperature ratings for the textiles were measured in (d) dark and (e) light (130 W/m\(^2\)) conditions. (f) Results in d and e were baselined to (subtracted from) the cotton jersey temperature rating and stacked for comparison. Positive values indicate textiles with a greater heating effect relative cotton jersey.
4.3.3 MODELING TEXTILE THERMOREGULATION UNDER ILLUMINATION

While previous work in radiative heating textiles has studied the impact of IR surface properties, here we study the combined impact of IR and visible optical properties on personal heating in the presence of moderate light intensity. As a simple case, we focus on an absorber-only system which, due to the broad IR and visible transparency of the transmitter layer, also informs the bilayer textile design. Our steady-state heat transfer model (Methods) of the skin-textile system includes incident radiation (130 W/m²) and a natural convection coefficient that varies with the skin-environment temperature difference (Figure 23a). The results of the simulation are shown in Figure 4b and experimental data points of uncoated and PEDOT coated nylon are overlaid. The performance of the radiative heated textile is optimized at maximum solar absorbance and minimum thermal emissivity, and we note that the PEDOT coating brings the nylon fabric closer to this target. At 130 W/m², the dependence of environmental temperature on solar absorbance is roughly comparable to that of thermal emissivity; however, at greater radiance (325 W/m²), solar absorbance becomes the dominant factor.
Figure 24. Modeling the impact of optical properties on textile thermoregulation for a moderate light intensity of 130 W/m². (a) Schematic of the steady-state heat transfer model for a single-layer textile. $T_{\text{environment}}$ is calculated as a function of textile spectral selectivity given the thermal comfort condition ($T_{\text{skin}} = 33\,^\circ\text{C}$). (b) Results of the simulation. Textile thermoregulation is optimized at high solar absorbance and low thermal emissivity. Two experimental points (uncoated and PEDOT-coated nylon) are shown. c Approximation of solar radiance on a vertical body in Boston, MA. The coldest season corresponds with the maximum radiance due to reduced solar elevation; snow cover (albedo $> 90\%$) as much as doubles light exposure. The human body is taken as a vertical cylinder and incident radiance is divided by total surface area (typically 1.8 m²).

To understand realistic sunlight utilization, the human body was approximated as a vertical cylinder and normal incident radiance per total surface area (typically 1.8 m² for adults) was calculated across the year. For solar-powered personal heating, a convenient coincidence is that the coldest season corresponds with the maximum solar radiance on a
vertical body due to the reduced solar elevation. In Boston, MA, for example, the on-body radiance of direct sunlight increases from about 108 W/m$^2$ at the summer solstice to about 325 W/m$^2$ at the winter solstice. At this low angle, snow cover also becomes highly reflective and can further double light exposure to as much as 650 W/m$^2$, meaning that the available wintertime solar radiance may be about 3-6 times larger than the body heat generated by a moderately active adult (70-120 W/m$^2$). (87) The bulky, opaque nature of winter outerwear assures low utilization of this power source. On the other hand, the bilayer textile described here can harness sunlight to provide remarkable heating for its weight. Exposed to a radiance of 650 W/m$^2$, representative of wintertime sunlight at high latitudes, the textile supports thermal homeostasis down to -28°C, approaching the extreme temperature tolerance of the polar bear. (7) Indoors, a light capturing textile can support the development of passive solar architectures (88) as personal heating and design elements, as well as be powered by existing indoor light fixtures capable of the lower radiance levels modeled here. (89)

4.3.4 WEARABILITY CHARACTERIZATION

Everyday clothing is expected to be comfortable, breathable, and washable. The optically-active textiles presented herein were also evaluated for these functions. Despite being non-woven, the AG-19 transmitter fabric has many familiar textile qualities that make it suitable for garments and apparel, upholstery, and décor. The non-woven material has a similar drape to traditional woven textiles (Figure 24a) and may be sewn and ironed without damage. Advancing from the frame-supported textile presented earlier, next we demonstrate use of such materials in a self-supported garment made by sewing two layers of AG-19 and ironing pleats to form insulating baffles. PEDOT-nylon was then sewn to
the bottom to complete the solar thermal textile (Figure 24b). This textile performs similarly to the previously characterized bilayer structure and, importantly, is stable after three washing cycles using common laundry detergent (Figure 24c). Optical microscopy of the PEDOT coating across washings shows a small change in color and no damage to the mechanical stability of the films. A water vapor transmission test across an AG-19/PEDOT-nylon stack reveals that this bilayer is as breathable as other common fabrics used in the study (Figure 24d). This is unsurprising given the diffuse open mesh of the AG-19 fabric, designed to be breathable, and the hydrophilic, conformal coatings of PEDOT on nylon.
Figure 25. Practical characteristics of the solar thermal textile. (a) The non-woven AG-19 fabric has a similar drape to traditional woven fabrics. (b) Two layers of AG-19 are sewn together and ironed to make insulating baffles. The PEDOT-nylon layer is then sewn to the bottom. (c) Textile thermoregulation characterization across three washing cycles. (d) Breathability characterization shows similar water vapor transmission across the textiles tested.

4.4 CONCLUSION

Here we leverage optical polymer materials to design a radiative heating textile as the first wearable mimic of the absorber-transmitter structure of the polar bear skin and fur. While retaining familiar textile qualities, the bilayer design suppresses radiative dissipation of body heat and maximizes radiative absorption of visible-NIR light. Due to a faithful imitation of the light harvesting structure and function of polar bear pelt, the garment achieves a significantly greater heating performance than other nominal mimics which either lack a transmitter or sacrifice solar utilization for thermal insulation.(82–84) Under
moderate illumination of 130 W/m² (ca. 0.1 sun), this textile maintains the wearer’s thermal comfort down to 4.1 °C – an additional heating effect of 10°C relative to a typical cotton T-shirt that is 30% heavier. Under full sunlight, the garment supports thermal homeostasis in extreme conditions as low as -28°C.

Using similar design methods, it is also possible adapt our strategy to radiative cooling and access a reflector-emitter structure like that found on the Saharan silver ant. (58) By rejecting solar heat and dissipating thermal heat through the atmospheric window, such a structure allows adaptive living in extremely hot conditions. The material properties and vapor deposition of PEDOT can enable different kinds of optical control beyond the photothermal effect shown here. When used with specific surface geometries, the plasmon-coupled light interactions of PEDOT can also be directed to produce the high reflectivity needed for daytime radiative cooling. (90–93) The oxidative vapor deposition process used in this work is uniquely suited for such optical engineering purposes. Electronic polymer coatings of precise thickness can be conformally deposited over complex surface arrays which may, like the faceted triangular hairs that endow the silver ant with its optical thermoregulation, possess features ranging in size from sub-micron to micron. (94) The second adaption of our strategy involves designing a transparent thermal emitter layer. While the polypropylene fibers here primarily serve to transmit visible light, Mie scattering theory informs optical tuning toward high IR emittance by adjusting fiber size and geometry to achieve dielectric resonance at IR frequencies. (95)

The solar thermal textile presented here is a flexible, lightweight platform for harvesting radiative energy. Indoors, this technology can enable efficient thermoregulation by local, low-power radiant heaters (i.e. LEDs) as well as support the design of passive
solar architectures. Outdoors, a lightweight solar textile will make winterwear more comfortable and enable passively heated shelters for adaptive living in harsher climates. As the energy and environmental crises progress, reinventing textiles with polymer-enabled light and heat control will prove increasingly useful.
CHAPTER 5

CONCLUSIONS

5.1 CONCLUSIONS

Overall, the work presented in this thesis seeks to build energy materials into textiles. Specifically, we vapor deposit electronic polymers onto textiles to 1.) power the development of wearable electronics and bring new “smart” functionalities such as health monitoring and sleep analysis to ordinary clothing and 2.) enhance the original function of textiles – thermoregulation - by incorporating radiant energy management to support homeostasis amidst environmental extremes.

In Chapter 2 we first focus on designing garment-integrated energy storage units with vapor deposited PEDOT, a conjugated polymer. We demonstrate two strategies to tune the vapor deposition process for achieving optimal electrochemical characteristics in the resulting films. By affecting polymer morphology – namely large scale porosity and smaller scale crystallinity – we show control of ionic transport dependent electrode performance in textile supercapacitors. First, we control the monomer/oxidant ratio to introduce porosity in the polymer films which, when interfaced with an ion-conducting electrolyte – supports rapid, efficient charging and discharging. Second, we show that control over polymer film growth temperature can be used to improved self-discharge characteristics of energy devices, an often overlooked yet practical concern. We propose that ordering of crystals in PEDOT affects the long-time scale ionic transport involved in self-discharge processes like charge redistribution. Overall, these work progress the development of textile-integrated electrochemical energy storage by considering process parameter – material property relationships.
From Chapter 3, our work becomes more motivated by changing environmental conditions. Here we focus on the susceptibility of electrical energy storage to temperature extremes, especially low temperatures which drastically affect ionic mobility in electrolytes. We discover that aqueous lithium electrolytes formulated at the eutectic concentration – intermediate to conventional dilute and more novel water-in-salt electrolytes – can support exceptionally high ionic mobilities at low temperatures. At least 1,000x more conductive than organic counterparts, this 25 wt% LiCl-H₂O mixture has a conductivity of around 1 mS/cm at -70°C, easily capable of powering LEDs. Interestingly, we find that the electrolyte can be formulated with poly(vinyl alcohol) (PVA) to form a gel-electrolyte without significantly sacrificing low temperature performance.

Chapter 4 presents the final project, also motivated by climate change, that seeks to revisit the design of the textile to enhance the original function: thermoregulation. Here we specifically take inspiration from polar-dwelling animals that have evolved energy-saving mechanisms to supporting thermal homeostasis in extreme conditions. We design a textile that mimics the pelt of the polar bear which, key to the animal’s survival in the polar climate, simultaneously provides high thermal resistance and solar utilization. The dual function arises from a specific material set and optical structure – transparent hair fibers thermally insulate while forward-scattering light to be photothermally captured by melanin-enriched skin. We mimic this bilayer structure with a transmitting insulating fabric serving the role of the hair and a high photothermal efficiency PEDOT-nylon fabric serving as the absorbing skin. Under moderate illumination of 130 W/m² (ca. 0.1 sun), this textile maintains the wearer’s thermal comfort down to 4.1 °C – an additional heating effect of 10°C relative to a typical cotton T-shirt that is 30% heavier. Under full sunlight, the
garment supports thermal homeostasis in extreme conditions as low as \(-28^\circ\text{C}\). Overall, radiative textiles will offer a sustainable means of maintaining livability amidst simultaneous energy and environmental crises.

5.2 FUTURE WORK

The energy storage mechanism of PEDOT, a supercapacitor material, enables high efficiency charging with excellent fatigue resistance which is particularly promising for pairing with energy harvesters like triboelectrics, photovoltaics, etc. In practice, a self-charging integrated circuit will likely consist of a harvester, capacitor, and a battery, where the capacitor serves as a low-loss intermediate between the harvester and the battery. A strong future direction therefore will be to develop wearable battery materials which, to complement the energy storage behavior of PEDOT, should have energy dense, Nernst-like (fixed potential) behavior. Organic radicals polymer units like TEMPO and viologens are promising,\(^\text{(96)}\) but still suffer from low energy densities.

The natural future direction for the radiative heating textile project is toward its opposite, radiative cooling. This strategy relies on radiatively coupling warm bodies (~300K) with the coldness (~3K) of space through the atmospheric transmission window. Under clear sky conditions with no solar thermal gains, potential radiative cooling power is in the range of 100 W/m\(^2\), sufficient to cool the human body with a metabolic heat generation of similar magnitude (75-125 W/m\(^2\)). Significant progress has been made on conventional radiative coolers for building rooftops; radiative cooling textiles is a growing but still nascent field.

Using a similar optical engineering approach as for our radiative heating textile, we see a few pathways toward a cooling textile. Firstly, a transmitter fabric might also
prove useful in this application. It is common in conventional coolers to use an IR transmitter insulator, typically polyethylene, as a top layer to inhibit diffusion of heat when ambient temperatures are high while allowing the transmission of thermal radiation to the sky. With skin temperature being around 90°F, a polyethylene non-woven fabric could provide additional cooling at elevated temperatures. Secondly, conventional coolers are usually studied in ideal settings – facing directly upward with minimal obstructions toward the sky. Optimizing radiative cooling for on-body textiles has very different geometric and practical considerations. Given the majority of body area is vertical, an omnidirectional textile emitter would be at most about half coupled with the cold sky and half coupled with warm terrestrial surfaces. Practically, obstructions would be plentiful.

Whereas the radiative heating textile we present in Chapter 4 focused on spectrally selective radiative energy exchange with the environment, we believe a radiative cooling textile would serve best to be directionally selective, i.e. funneling thermal energy at high angles toward the sky while reflecting at low angles toward the terrestrial surface and potential obstructions. The heat – adapted Saharan silver ant has evolved similar directionality in its radiative cooling mechanism by enhancing upward emission with micro-hairs while suppressing exchange of heat with the hot desert surface.(58) For both extremes of the temperature spectrum, biomimetic radiative heating and cooling textiles will offer a sustainable means of adapting to a changing climate.
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