MICROSTRUCTURE-DEPENDENT ELECTROCHEMICAL PROPERTIES
OF CHEMICAL-VAPOR DEPOSITED POLY(3,4-
ETHYLENEDIOXYTHIOPHENE) (PEDOT) FILMS

by

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As members of the Master's Committee, we certify that we have read the thesis prepared by Sean Arnold, titled *Microstructure-dependent electrochemical properties of chemical-vapor deposited poly(3,4-ethylenedioxythiophene) (PEDOT) films* and recommend that it be accepted as fulfilling the dissertation requirement for the Master's Degree.

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Dedication

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2. Abstract

Conductive polymer electrodes hold exceptional promise in energy conversion technologies and bioelectronics due to their inherent mechanical flexibility and synthetic tunability of physical, chemical, and electronic properties. Solution-processing is favorable to retain low-cost but can often result in heterogeneity of physical and electronic structure due to non-conjugated side chains and polyionic dopants creating insulating domains. Such a complex landscape limits control and systematic understanding of fundamental properties including electrical and ionic transport and rates of electron transfer central to overall device efficiencies. Chemical vapor deposition (CVD) offers a promising route to simultaneously synthesize and deposit conductive polymer films at low temperatures ($<150^{\circ}\text{C}$) with controllable microstructure. Herein we use the CVD technique to synthesize and deposit different paracrystalline films of poly(3,4-ethylenedioxythiophene). Using grazing incidence wide-angle x-ray scattering, we demonstrate three different orientations of the π - π packing direction to yield thin films with face-on, edge-on, and isotropic character. These different microstructures have direct impact on the electrochemical conditioning of the redox properties of the films. We show that electrochemical properties, as defined by energy and power density, are highest for crystalline materials with edge-on orientation to facilitate ion transport while still retaining reasonable electrical conductivity.

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3. Introduction

Organic electronics provide a promising alternative to traditional semiconductor-based technologies due to biocompatibility, mechanical flexibility, and synthetically tailorable properties.¹⁻³ The organic electronics field is diverse with its most prominent subfield being organic light emitting diodes (OLEDs), which have shown notable commercial success. Aside from flexibility and potential for use in displays, organic electronics are interchangeable with many semiconducting and conductive materials for standard applications⁴ and have the potential to enable new device architectures in electrochemical systems.

3.1 Background of electrical conductivity in conductive polymers.

In organic electronics, one predominant figure of merit for evaluating the validity of different processing approaches is conductivity. Conductivities of above $2,000 \text{ Scm}^{-1}$ have been achieved for CVD PEDOT in the case of grafted, highly oriented and acid treated polymer films.⁵ Conductivity (σ) is described by the product of charge carrier mobility (μ), fundamental charge (e) and the number of charge carriers (n).

$$\sigma = ne\mu \quad (1)$$

From the equation above, two obvious approaches emerge to improve conductivities of conductive polymers. The first is to increase the mobility, which can be achieved via microstructural and morphological control through the tailoring of processing and the second is to increase the carrier density which depends largely on ionic and molecular doping.

Energy levels responsible for charge transport in conductive polymers are defined by the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the film ensemble. Specifically, conductive polymers are conjugated along their backbone which results in occupied π -orbitals and unoccupied antibonding (π^*) orbitals.⁶⁻⁸ Hole transport in conductive polymers is generally described by a localized hopping transport between π orbitals, with a dc-conductivity temperature dependence often described by the variable range hopping (VRH) model.⁹ In the

case of doped polymers, the polaron-bipolaron (PB) model is used to describe changes in charge mobility associated with increased carrier density through doping.^{10,11} The Arkhipov model suggests that low dopant concentration initially causes a decrease in mobility due to the formation of Coulombic energy wells but beyond a threshold doping level, the mobility increases super-linearly due to the overlap of those Coulombic energy wells.¹⁰ Adaptations of the Arkhipov model by Bisquert et al. have included the distinction that for carrier densities above polaron saturation, the mobility of holes will decrease due to a lessened hopping diffusivity caused by saturation of available hopping sites.¹²

3.2 Conductive polymers for electrochemical applications.

Conductive polymers are gaining significant interest for use in electrochemical applications ranging from energy storage technologies to wearable and implantable sensors due to the ease of processing and ability to synthetically control electrochemical redox properties.¹³⁻¹⁵ In addition to being low cost, one major advantage of conductive polymers over other electronic materials is a hybrid electronic and ionic charge transport mechanism. The current response in conductive polymers does not rely exclusively on electric double layer formation. Rather, carrier density can be increased in response to an electric field through volumetric doping of the material.¹² For energy storage, the hybrid electrical-ionic transport enables faster charge and discharge times compared to batteries, with higher energy densities than double layer capacitors.¹⁶ In sensors using transistor geometries, the hybrid electrical-ionic transport provides higher transconductance at moderate bandwidths over inorganic semiconductor field-effect approaches, with improved sensitivities in high ionic strength environments.¹⁷ As such there has been a growing interest in understanding the hybrid electrical-ionic mechanism and as it relates to morphological or more specifically, microstructural changes in the polymer film.¹⁸⁻²⁰

Electrochemically, the chemical capacitance (C_μ) of a p-type conducting polymer is related to the change in number of holes (p) per change in electrochemical potential (μ) as $C_\mu = e^2 \cdot dp/d\mu$.²¹ The

conductivity arising from hole transport (σ_p) is then also related to the chemical capacitance by the diffusion coefficient (D_p) of a free charge carrier (uninhibited by trap states) as $\sigma_p = D_p(E_F)C_\mu(E_F)$ given that the fermi energy (E_F) changes as a function of oxidation as carrier density increases.²² The relationship between chemical capacitance and conductivity allows a connection between observed charge transport properties and energy storage capabilities as determined by the distribution of polaronic states of varied energies.^{12,22}

3.3 Structure-property relationships of electrochemically-active conductive polymers

One major challenge for conductive polymer containing technologies is the need to understand and control the molecular-level structure-property relationships governing functionality. For conductive polymers, the design guidelines for optimizing electrical and ionic transport are somewhat contradictory. Good electronic transport necessitates well-ordered structures with good π - π overlap to promote polaron delocalization. Good ionic transport requires relaxed structures to promote ion electro-migration between chains and/or between nanoscale domains. These two competing design criteria suggest that optimal charge transfer may be achieved when neither charge nor ion transport is maximized. This work targets the investigation of electrochemical properties as a function of microstructure to qualify this hypothesis.

One of the most prominent conductive polymers in both sensing and energy conversion technologies is poly(3,4-ethylenedioxythiophene) (PEDOT) due to its high conductivity and compatibility with multiple processing methods and doping strategies. Conductivities for PEDOT of up to 5400 S cm^{-1} have been achieved through a combination of processing method, dopant selection, polymerization rate control, and post deposition solvent treatment.^{18-20,23-27} An all polymer PEDOT battery has been developed which has sufficient discharge times to switch a PEDOT electrochromic display.²⁸ Specific capacitances for PEDOT of up to 160 F/g have been demonstrated for thick films as measured by low scan rate cyclic voltammetry,²⁹ with over 400 F/g

achievable as a composite.³⁰ PEDOT coated aligned carbon nanotubes (A-CNTs) have been shown to have significantly improved volumetric charge storage capabilities with Ghaffari et al. reporting an increase in electrochemical capacitance from 3.9 to 84.0 F/cm³.^{31,32}

Microstructure control of PEDOT is especially difficult using solution processing methodologies. Once PEDOT chains are synthesized, the polymer is generally insoluble, prohibiting printing approaches. For solution-processing and printing of PEDOT, the typical approach is to include polyionic dopants – such as poly(styrenesulfonate) (PSS) – to increase both solubility and carrier density via doping. The net result is a polymeric dispersion with spatial variability of the chemical potential and anisotropic transport phenomena due to phase segregation of conductive polymer and insulating dopant.³³⁻⁴⁷ Control of PEDOT:PSS structure has led to breakthroughs in both energy conversion and sensing. PEDOT:PSS has recently been used in electrochemical thermogalvanic cells for the conversion of heat flux to electrical power.⁴⁸ These devices are highly dependent on the rate of charge transfer to redox species in solution, which is intimately connected to the microstructure^{49,50} and percolation pathways of carriers in the polymer. For sensing, controlling the microstructure of PEDOT:PSS has led to large transconductance (~20 mS) with large volumetric capacitance (113 F/cm³), with applications to bioelectronics for neural recording and stimulation.²⁷

3.4 Chemical vapor deposition of PEDOT for electrochemical applications.

Chemical vapor deposition (CVD) of PEDOT as well as other vapor phase polymerization (VPP) deposition processes have been investigated as solvent free alternatives for depositing films with well controlled microstructures and morphologies. Through the use of various oxidants, CVD of PEDOT has resulted in conductivities ranging from 1 Scm⁻¹ to 5,000 Scm⁻¹ with steadily achievable conductivities after aging of up to 2,000 Scm⁻¹.^{24,51-56}

Vapor phase polymerization (VPP) of conductive polymers provides a solvent-free alternative for depositing films with well-controlled microstructures and morphologies. An investigation by

Fabretto et al. of the effect of water vapor on VPP of PEDOT with FeCl_3 as the oxidant indicated that introduction of water vapor up to ~ 10 Torr allowed for formation of oxidatively initiated PEDOT films with conductivities up to 150 Scm^{-1} for room temperature depositions and up to 360 Scm^{-1} at 35°C substrate temperature.⁵⁶

One of the most notable approaches for PEDOT was pioneered by the seminal work of Karen Gleason using chemical vapor deposition (CVD). The mechanisms and systematic control of material properties for PEDOT and other conductive polymeric systems have been explored and described significantly in the literature by Gleason and others,^{9,24,57-60} with applications ranging from photovoltaics to fiber-based electronic devices.^{51,61} The distinction between VPP and CVD is that for the latter, the oxidant is introduced in the vapor phase rather than as a coating on the substrate. In CVD, the reaction rate is strongly linked to the conductivity and has been shown to be connected to electrochemical properties.^{24,62,63} Briefly, the polymerization of EDOT follows a chain growth mechanism between radicals in the vapor phase and adsorbed monomer at the surface, whereby the reaction propagates until termination via species such as hydrochloric acid.⁶⁴ As substrate temperature increases, the surface concentration of the monomer decreases and film formation proceeds at a slower rate.⁶⁵ Thus by controlling the substrate temperature, the microstructure of the film can also be controlled. For electrochemical applications, Zhang and Andrew demonstrated less ion accumulation during doping and de-doping of CVD PEDOT, relative to vapor phase polymerized PEDOT, which was attributed to morphological differences although microstructure was not quantified.⁶⁶

3.5 Project Overview.

The present work shows how to leverage these established deposition protocols to create PEDOT films of different microstructure, as monitored using grazing incidence x-ray scattering (GIWAXS). The following characterization is focused on three different paracrystalline films to elucidate the interconnected electrical-ionic transport properties on electrochemical behaviors. Through the

use of CVD, it is demonstrated that the systematic tuning of nanocrystallite orientation relative to the surface has a significant impact on the redox properties and the necessary electrochemical conditioning. Using energy density and power density, it is shown that one material structure does not provide optimum performance with both metrics, but rather, must be optimized to the desired functionality.

4. Experimental Methods and Data Processing

4.1 Experimental description of chemical vapor deposition of PEDOT.

All reagents were used as obtained with no further purification. CVD to form PEDOT films was achieved by room temperature evaporation of EDOT (97% Sigma Aldrich) from a monomer inlet valve in a stainless-steel deposition chamber held at 3.0 ± 0.5 Torr. The oxidant FeCl_3 (97% Sigma Aldrich) was evaporated by heating in a Knudsen cell with a constant-current resistive heating coil to a final temperature of ~ 300 °C. Substrate temperature during deposition was controlled via conductive heating of a copper stage mount brought to desired temperature prior to introduction of reactants. Films were deposited on undoped silicon (University Wafer) for conductivity, GIWAXS and FTIR analysis and ITO-coated float glass (Colorado Coatings) for XPS and electrochemical analysis. Film thickness was determined by profilometry performed on a Dektak 6M Profilometer.

Figure 1 (Left) drawing of the CVD chamber and (right) photo of the simplified version of the CVD chamber.

4.2 Variables of consideration in chemical vapor deposition of PEDOT.

Initiation of the polymerization of EDOT monomer units requires an oxidizing agent, in this case ferric chloride. The metallic salt FeCl_3 has a melting point at atmosphere of 282°C with a vapor pressure that increases above its T_m according to the Clausius-Clapeyron equation.⁶⁷ Heating of FeCl_3 in a Knudsen cell then results in vaporization of the metal salt which initiates the polymerization of EDOT at the substrate through oxidative formation of monomer radical cations.⁶⁴ It is then hypothesized in some cases that initiation of a chain growth polymerization occurs between the radical and an adsorbed monomer which will propagate to form high molecular weight films unless prevented by a terminating species such as hydrochloric acid.⁶⁸ Reactive chemical vapor deposition offers distinct processing advantages over other techniques by creating polymer films with uniform conformal surface coverage and removing the need for expensive solvent and curing steps.^{60,69} Successful CVD of polymer thin films necessitates that polymerization and deposition occur simultaneously at the substrate.^{70,71} Conformal homogeneous coverage of the substrate can be achieved via CVD of polymers even at pressures up to ambient conditions.⁷⁰ Initiation of the polymerization of EDOT monomer units requires an oxidizing agent, in this case ferric chloride.⁵³ Control over the rate of this reaction at the surface is established through adjusting the temperature of the substrate surface (Figure 2).⁷²

Figure 2 CVD chamber and proposed effect of substrate temperature on crystallinity.

Polymer CVD is typically carried out at modest vacuum levels and can be characterized by the saturation ratio of monomer vapor pressure (P_M) to the saturation vapor pressure ($P_{M,sat}$) of the monomer at the substrate surface which varies with temperature. The rate of adsorption is diminished at high saturation pressures to the extent that production rates at the film formation boundary are limited by adsorption kinetics at high temperatures.⁶⁵ The volume of monomer adsorbed on the surface (V_{ad}) as determined by the BET equation⁷³ is described by the volume of a monolayer (V_{ml}), the saturation ratio ($P_M/P_{M,sat}$) and a constant (c) which is determined by the temperature, molar constant (R) and the enthalpies of desorption (ΔH_{des}) and vaporization (ΔH_{vap}):⁶⁰

$$V_{ad} = \frac{V_{ml}c(P_M/P_{M,sat})}{(1-P_M/P_{M,sat})[1-(1-c)(P_M/P_{M,sat})]} \quad (2)$$

$$c \approx \exp[(\Delta H_{des} - \Delta H_{vap})/(RT)] \quad (3)$$

At rough vacuum levels, the saturation ratio approaches zero and the volume of monomer adsorbed becomes linearly related to the surface monomer concentration in the Henry's Law limit⁷⁴ which is then related to the enthalpy of desorption through incorporation with the Clausius-Clapeyron equation:^{60,75}

$$\lim_{P_M/P_{M,sat} \rightarrow 0} V_{ad} = V_{ml}c(P_M/P_{M,sat}) \sim [M] \quad (4)$$

$$P_{M,sat} = A \exp[-\Delta H_{vap}/(RT)] \quad (5)$$

$$[M] \sim \exp[\Delta H_{des}/(RT)] \quad (6)$$

As substrate temperature increases, the surface concentration of the monomer decreases and although propagation rates for chain growth polymerizations have a positive temperature dependence, the overall film formation rate decreases.⁶⁵ The partial pressure of HCl formed during deprotonation increases with substrate temperature which results in increased molecular weights and thus conjugation lengths due to fewer ring opening acid catalyzed reactions.⁷⁶

It has been proposed that a necessary stage for polymerization is the removal of hydrogen ions from joined monomer units by either the anion of the oxidizing agent as proposed by Gleason et al.,²⁴ by a water molecule as described by Salaneck et al.⁷⁷ or possibly by additional monomer cations when insufficient water is present. It was found by Fabretto et al. that for water partial pressures resulting in an overall chamber pressure of 4.0Torr and below, the polymerization of PEDOT did proceed for room temperature substrates with iron(iii)tosylate used as the oxidant.⁵⁶ The same effect observed in these findings are noted in the present body of work for PEDOT films deposited on room temperature substrates at 3.0Torr in that such films are green and liquid upon initial exposure to ambient conditions followed by liquid phase polymerization occurring over prolonged time at atmosphere.

At rough vacuum, there is a significant portion of reactants other than the monomer and oxidant (notably water and air) which leads to byproduct formation.⁵¹ At relatively low substrate temperatures (in this case approximately less than 40°C), reactions with an Arrhenius temperature rate dependence may still be kinetically limited by the deprotonation step resulting in high proportions of impurities and low molecular weight films.^{56,60} Increasing the substrate temperature at the film formation boundary results in increased polymerization rate but simultaneously causes a decrease in overall adsorption rate for monomer units causing a mixed trend in film growth rate.⁶⁰ For the reaction of EDOT with FeCl_3 the reaction rate increases significantly at ~40°C in the presence of both water and oxidant.^{24,77} A higher reaction rate is expected to induce changes in the microstructure of the polymer film.⁵¹

Rinsing of CVD PEDOT has been investigated to determine what steps are necessary to remove residual FeCl_3 and its hydration complexes through various solvents and acids.²⁵ It has been shown that aqueous acids successfully remove residual FeCl_3 where organic solvents such as methanol do not. The distinction has been made that acidic solutions are primarily involved in conductivity enhancement and that removal of iron byproducts is sufficiently achieved through rinsing with water.⁵⁷ For CVD films with large enough iron concentration there is significant chance

of delamination of thick films, and so prolonged rinsing is risky. Because of this, removal of iron regions and electrochemical analysis becomes infeasible for non-grafted thick films.⁷⁸ The need for rinsing steps has been eliminated in CVD deposition of PEDOT using bromine as introduced by Gleason et al.⁵² with limited conductivity enhancement (up to 380Scm^{-1}) compared to CVD with FeCl_3 performed at the same substrate temperature (80°C) and diminished conductivities ($\sim 1\text{Scm}^{-1}$) achieved in a follow up study carried out by Pistillo et al.⁵⁴. A process for CVD deposition of PEDOT using the more volatile MoCl_5 as the initiating oxidant has been developed by Parsons et al.⁵¹ which employs a nitrogen gas purging step in between sequential, alternating reactant exposures in order to reduce the formation of byproducts in between monolayer depositions; resulting conductivities of this process (performed near rough vacuum at $\sim 0.8\text{Torr}$ with substrate temperatures of $\sim 150^\circ\text{C}$) exceeded $5,000\text{Scm}^{-1}$ for non-aged samples compared with the highest reported conductivity achieved with FeCl_3 of $\sim 1,500\text{Scm}^{-1}$ (with acid rinsing and ion exchange conductivity enhancement).²⁵

Investigation of thick and thin film depositions of PEDOT by CVD with FeCl_3 for comparison with the findings mentioned above is then carried out via FTIR, XPS, GIWAXS and four-terminal sensing conductivity measurement. The implications of these findings are then used to assess the possible effects of substrate temperature on PEDOT for use in electrochemical devices by analysis of thin film behavior bearing in mind the compared and extrapolated differences for thick films.

4.3 Experimental methods of characterization.

All electrochemical measurements were performed with a CH Instruments 920D bipotentiostat with either a gold or ITO counter electrode and Ag/AgCl saturated aqueous reference electrode. Measurements were conducted in 0.1 M potassium chloride in deionized water (Millipore $\sim 18\text{M}\Omega$) at a scan rate of 100mV/s , unless otherwise noted.

Chemical analysis of PEDOT was performed using both FT-IR and x-ray photoelectron spectroscopies. X-ray photoelectron spectroscopy was performed with a Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromatic Al K α source (1486.6 eV) at a base pressure of 10^{-9} torr. Photoelectrons were collected in a hemispherical analyzer and detected with a photodiode array. The resulting XPS spectra were fit as Gaussian peaks with linear baseline correction, with a Shirley background used for the Fe Fe2p. Briefly, the S2p peak was fit with the S2p $^{3/2}$ peak at approximately 164.0eV, 164.5eV, and 165.0eV with three doublet peaks (S2p $^{3/2}$ and S2p $^{1/2}$) spaced 1.16eV apart with the S2p $^{1/2}$ peak being half the height of the S2p $^{3/2}$ peak and with the widths matched. The O1s peak was fit with three peaks at approximately 531eV, 533eV and 535eV. The Fe2p peak was fit with a Shirley background and two primary peaks at approximately 712eV and 725eV. The Cl2p peak was fit with three Cl2p $^{3/2}$ and Cl2p $^{1/2}$ doublets spaced 1.6eV apart with a 2:1 height ratio and matched widths with the Cl2p $^{3/2}$ peak at approximately 197eV, 199eV and 200eV. FT-IR spectroscopy in transmission mode using a Thermo Scientific Nicolet 6700 at a resolution of 4cm $^{-1}$ in the wavenumber range from 400-4000cm $^{-1}$ for 256 scans in transmission mode.

4.4 Discussion of chemical analysis of CVD PEDOT.

The formation of PEDOT can be verified by IR spectroscopy by monitoring the lack of a C-H bending peak at 890cm $^{-1}$ associated with the EDOT monomer.⁷⁹ The fingerprint region of PEDOT also contains absorbance information indicating the presence of C-S vibration modes from the thiophene ring, ring deformation modes as well as variable C-C and C=C bonds which correlate with the conjugation state of the macromolecule.⁸⁰ Briefly, PEDOT is known to take on two different conjugation forms depending on the degree of doping, supported by the presence of a stabilizing counterion (in this case, chloride). **Figure 3** shows the Coulombic interaction of the chloride ion of the quinoidal form, here drawn to interact with the sulfur for clarity. The two forms

are shown in **Figure 3**, termed the benzoidal (undoped) and quinoidal (doped) conjugation states, and can be monitored by FTIR spectroscopy.

Figure 3 Benzoidal vs. quinoidal conjugation states of PEDOT.

The characteristic quinoidal (doped) C=C stretch region around 1520cm^{-1} can be compared relatively to non-doped and constant relative absorbance peaks associated with PEDOT to determine the extent of doping.²⁴ For the case of thick films deposited at rough vacuum, the ratio of this peak to the constant ethylenedioxy peak at 1321cm^{-1} is seen to decrease with increasing substrate temperature keeping with the trend in sheet resistance for the same samples. Notably, the set of peaks around 1520cm^{-1} correspond to the set of stretching modes that appear in the quinoidal form of PEDOT and can be used as a handle to gauge relative amount of charge carriers in the polymer.⁷⁹ The true doping efficiency needs to be determined through correlation with chemical composition information to separate ionic inclusions caused by impurities from those that cause electron delocalization through well-defined ionic bonding with the sulfur in the thiophene ring.

Table 1 below summarizes the relative peaks for PEDOT. The formation of PEDOT can be verified by IR spectroscopy by monitoring the lack of a C-H bending peak at 890cm^{-1} associated with the EDOT monomer,⁷⁹ the C-S vibration modes form the thiophene ring, and conjugation state information of the ring deformation modes of the C-C and C=C bonds.⁸⁰ The presence of peaks $\sim 1520\text{cm}^{-1}$ correspond to the quinoidal form of PEDOT.⁷⁹

Wavenumber	Bond	Vibrational Mode	Chemical Species	Absorbance (a.u.)				Ref.
				40°C	60°C	80°C	100°C	
687 cm^{-1}	C-S	Stretching	Thiophene	0.056	0.027	0.036	0.021	64,80
838 cm^{-1}	C-S	Stretching	Thiophene	0.048	0.016	0.029	0.016	79,80
970 cm^{-1}	C-S	Stretching	Thiophene	0.075	0.027	0.041	0.021	79,80
1050 cm^{-1}	C-O	Stretching	Ethylenedioxy	0.081	0.024	0.036	0.021	64,80
1082 cm^{-1}	C-O-C	Stretching	Ethylenedioxy	0.091	0.031	0.051	0.024	79,80
1138 cm^{-1}	C-O-C	Stretching	Ethylenedioxy	0.061	0.017	0.028	0.017	80
1200 cm^{-1}	C-O	Stretching	Ethylenedioxy	0.084	0.034	0.052	0.024	64,79
			Quinoid					
1357 cm^{-1}	C-C	Stretching	Thiophene	0.054	0.025	0.041	0.016	64,79
			Quinoid					
1516 cm^{-1}	C=C	Stretching	Thiophene	0.023	0.013	0.016	0.006	79,80
3300-								
3500 cm^{-1}	O-H	Stretching	Water	0	0.086	0.023	0.013	81
3300-								
3500 cm^{-1}	O-H	Stretching	Water	0	0.019	0.071	0.011	81

Figure 4 FTIR of thick CVD PEDOT.

Total absorbance in the fingerprint region for CVD PEDOT films is seen to vary across substrate temperatures and so direct comparison is not appropriate. Quantitative comparison is done here only through peak to peak ratios after the initial background subtraction which is done linearly between the endpoints surrounding the fingerprint region from 500cm^{-1} to 1700cm^{-1} .

Figure 5 Fingerprint region of CVD PEDOT and oxidant byproducts, which may correspond to FeCl_2 , $\text{Fe}(\text{OH})$, FeS and other iron containing decomposition components.^{64,81}

Signature PEDOT absorbance features (Figure 5) occur for C-C and C=C stretching vibrations associated with the thiophene ring ($\sim 1520\text{cm}^{-1}$, $\sim 1300\text{cm}^{-1}$), C-O and C-C stretching vibrations associated with the ethylenedioxy ring ($\sim 1200\text{cm}^{-1}$, $\sim 1100\text{cm}^{-1}$), and the C-S stretching vibrations in the thiophene ring ($\sim 960\text{cm}^{-1}$, $\sim 900\text{cm}^{-1}$, $\sim 800\text{cm}^{-1}$).⁸⁰ It can be seen above that the relative amount of PEDOT associated absorbance decreases for the 80°C substrate temperature compared to 40°C substrate temperature and exhibits notably increased absorbance in regions associated with the oxidant used (FeCl_3) which may correspond to FeCl_2 , $\text{Fe}(\text{OH})$, FeS and other iron containing byproducts.^{64,81}

4.5 Two-dimensional (2D) grazing incidence wide-angle x-ray scattering (GIWAXS) measurements.

The optoelectronics properties of organic semiconductors depend highly on the extent of delocalization of charge which is largely controlled by molecular orbital overlap variation and is affected by disorder, dislocations and intermolecular orientation.⁸² Grazing Incidence Wide Angle X-Ray Scattering (GIWAXS) is used to determine nanoscale structural features of small sample size materials through appropriate selection of wavelength, incidence angle and detector geometry. Depending on the level of disorder of the crystallite, films will exhibit observable scattering peaks corresponding to two primary stacking directions of the linear polymer chains. The first of the two ordered directions in linear cyclic conjugated polymers is referred to as the lamellar stacking direction which is characterized as the distance between polymer units which are in plane with one another. The description of this stacking direction is based on its similarity to other linear polymer crystallization patterns despite the fact that --due to their high rigidity resulting from the presence of non-carbon atoms along the conjugated backbone. The other necessary stacking direction that arises in ordered cyclic linear polymers is the π - π stacking direction which refers to the fact that the π -bonds in the cyclic compounds are stacked on top of each other from chain to chain.

To quantify microstructure, GIWAXS measurements were carried out on beamline 11-3 at the Stanford Synchrotron Radiation Light Source (SSRL). The beam was kept at an energy of 13 keV and the critical angle of measurement was ~ 0.11 to 0.13° . Calibration of wavelength and sample-detector distance used a LaB6 standard sample. 2D images were corrected from intensity versus pixel position to intensity versus q -spacing using giwaxstool and nika softwares in Igor. Images were reduced to 1D plots via integration of cake segments and analyzed using the multi-peak fit package in Igor.

Figure 6 GIWAXS incoming wavevector.

Interpretation of GIWAXS requires translation of wavevectors first into scattering angles and then into the reciprocal lattice vector associated with the angle. The incoming wavevector has components in only two directions (Figure 6), but the outgoing scattered vector may have a component in three directions. The angle made with the incoming angle and the surface of the sample is significant in determination of a range of critical angles in which only the substance of interest will cause scattering, but reflectance effects will not dominate. The determination of the appropriate angle depends on the density and refractive index of the material and is calibrated experimentally. Thicker samples have larger ranges of critical angles due to longer possible penetration depths before incidence with the underlying substrate, but consistent incident angle selection is important to reduce artificial scattering distribution caused by spot size change.⁸²

Figure 7 Isotropic vs. amorphous scattering of PEDOT on ITO.

The distinction between isotropic semicrystalline polymers and amorphous ones can be readily observed via the 2D scattering profile that results from area detector GIWAXS (Figure 7). Isotropic samples demonstrate well defined rings that form radially around the origin and correlate to a lattice spacing according to the Bragg equation. Amorphous samples however exhibit a broad range of scattering vectors which rarely demonstrate meaningful change. It is often the case that there is an amorphous component to paracrystalline samples that causes background scattering which can be difficult to separate from the overall signal. Unlike substrate effects which can be removed by careful selection of the incidence angle of the incoming beam, the amorphous component is contained within the scattering region of interest.

Figure 8 Identifying orientational differences in GIWAXS.

Oriented conductive polymers are often desired to provide control over which direction of electronic transport is employed in a device. A crystalline sample will in most cases exhibit an isotropic orientation for which the scattering profile will consist of mostly uniform rings at a radius corresponding to the inverse lattice distance. For selectively processed polymers however, defined molecular orientations relative to the substrate can be achieved and will be discernible by the existence of certain peaks in only one of the two observable scattering directions— in-plane and out-of-plane. For a polymer oriented such that the face (or π -orbital overlap region) is parallel to the substrate, the associated π - π stacking scattering vector will be in the out-of-plane direction and any lamellar vectors will be in-plane. The opposite is true of edge-on orientation. Most samples above a certain thickness will adopt a somewhat isotropic orientation but can still be said to be partially ordered.

Examples of orientations are shown in Figure 8. Isotropic polycrystalline samples will exhibit rings in the two-dimensional scattering profile associated with any observable lattice spacings. Amorphous samples demonstrate one large, diffuse scattering ring created by broadening and

merging of average lattice positions as well as diminished observability of certain lattice spacing regions. The orientation the molecules within a film can be determined if separation of scattering intensity occurs along either of the two axes of a 2D scattering profile (Figure 9).

It is possible to approximate the degree of crystallinity of a polymer thin film by integration of the intensity of a baseline subtracted diffraction peak across the azimuthal angle in a reciprocal space scattering profile.⁸³ The amorphous contribution of a film varies significantly with thickness variation and processing parameters and substrate background scattering contributions are often inseparable from the polymer diffraction contributions and will be discussed in more detail below.

Figure 9 Identifying in-plane vs. out-of-plane scattering in GIWAXS.

5. Results and Discussion

As stated prior, the electrical transport properties of organic semiconductors depend highly on the extent of delocalization of charge, which is largely controlled by molecular orbital overlap variation and is affected by disorder, dislocations and intermolecular orientation.⁸² The goal of this work was to provide proof-of-concept evidence that changing the microstructure of PEDOT films impacts the electrochemical properties, specifically the electrochemical conditioning effects, at the onset in the density of states. The following work is focused on electrochemical conditioning efforts using a cell geometry whereby both the charge and the ion must be transported along the surface normal, a common geometry used in many energy conversion and storage applications such as electrochromics,^{84,85} capacitors,^{32,63,86} thermogalvanics,⁴⁸ redox-flow batteries,⁸⁷ and molecular catalysis.^{49,50} It is noted that this is different from the organic electrochemical transistor (OECT) geometry, where the electrical and ionic circuit elements are perpendicular.¹⁷ To provide comparison to this exciting area, in-plane electrical conductivity is also considered. This work is focused on the electrochemical behaviors of three relative paracrystalline systems of different orientations with respect to the substrate, namely an isotropic film, a film with the π - π stacking direction oriented perpendicular to the substrate (edge-on), and a film with the π - π stacking direction oriented parallel with the substrate (face-on).

5.1 Microstructure control and characterization

Two-dimensional grazing incidence wide-angle x-ray scattering (GIWAXS) was used to determine the interchain spacings and orientation of the films relative to the substrate. Figure 10A-C show the 2D GIWAXS detector images for three thin films of PEDOT and Figure 10D and Figure 10E show the intensity versus the out-of-plane (q_z) and in-plane (q_{xy}) wave vectors with respect to the sample surface. Intensity versus azimuthal angle (χ) taken as cake slices collected at every 10° increments relative to the surface normal are provided below in Figure 11, Figure 12 and Figure 13. Figure 10F provides the relative inter-plane spacing of the PEDOT unit cell used for peak

identification and Figure 10G provides the schematic interpretation of the orientation of the crystallite domains.

Figure 10 Two-dimensional GIWAXS plots of CVD PEDOT formed with a surface temperature of A) 30°C, B) 60°C, and C) 100°C; one-dimensional GIWAXS plots with cake slices in D) q_z (out-of-plane) and E) q_{xy} (in-plane) directions; F) plane assignments of PEDOT; and G) General descriptions of crystallographic orientations of the π - π stacking direction relative to the surface normal in conductive polymers.

Figure 11 Cake slices at 10° increments relative to surface normal for the 30°C processed film.

Figure 12 Cake slices at 10° increments relative to surface normal for the 60°C processed film

Figure 13 Cake slices at 10° increments relative to surface normal for the 100°C processed film.

PEDOT forms lamellar stacking crystallites which exhibit several scattering peaks corresponding to two primary stacking directions of the linear polymer chains as described by Figure 10F. Most pronounced is the lamellar stacking direction, referenced as the (h00) plane. Depending on degree of long range order derived from processing approaches or the inclusion of poly-ionic dopants,⁸⁸⁻⁹⁴ PEDOT films can exhibit between one and four lamellar scattering peaks along the (h00) plane.⁸⁸ The critical direction for electrical conductivity is the π - π stacking direction oriented perpendicular to the lamellar stacking direction. Typically, scattering in the π - π direction is only observed for the (020) vector; the (010) scattering vector will not be observed or is so weakly scattering that it will contribute only as indiscernible background near the low order lamellar peaks.

In Figure 10A, we observe two clear lamellar peaks corresponding to the (h00) planes located at $q \sim 0.5 \text{ \AA}^{-1}$ and $0.9 \text{ \AA}^{-1}$ and respective d-spacing values are 12.3 and 7.6 $\text{\AA}$ for the film formed at 30°C. The (020) peak at $1.91 \text{ \AA}^{-1}$ provides a π - π stacking distance of 3.3 $\text{\AA}$. In Figure 11, the relative intensities of the (100) and (020) peaks both generally decrease with increasing azimuthal angle, indicating no preferred orientation of the nanocrystallites relative to the surface normal (isotropic film).

Prior reports have shown that the microstructure of CVD PEDOT can be modified using temperature during film formation.^{62,63} Increasing the temperature to 60°C yield the film shown in Figure 10B. For this sample, it is observable that a $q_{020} \sim 1.91 \text{ \AA}^{-1}$ ($d_{020} \sim 3.3 \text{ \AA}$) and a lower full-width half maximum of the $q_{100} \sim 0.53 \text{ \AA}^{-1}$ ($d_{100} \sim 11.9 \text{ \AA}$) and $q_{200} \sim 0.87 \text{ \AA}^{-1}$ ($d_{200} \sim 7.2 \text{ \AA}$), relative to the 30°C. It is also noted that there is a peak for $q_{300} \sim 1.37 \text{ \AA}^{-1}$ ($d_{300} \sim 4.57 \text{ \AA}$). The observed increase in higher order (h00) planes, along with an observed narrowing of the lamellar peaks, has been attributed to decrease in paracrystallinity and longer range order in other thiophene systems which contributes to increased transport effects.⁹⁵ Both the 30°C and 60°C samples have higher intensities in the q_z plane, relative to the q_{xy} , as shown in Figures 11 and 12. Given that the 60°C sample is more crystalline than the 30°C sample, we reference it as more edge-on-like

relative to the sample in Figure 10A.⁶³ Finally, in Figure 10C, increasing the surface temperature to 100°C yields a narrow $q_{100} \sim 0.51 \text{ \AA}^{-1}$ ($d_{100} \sim 12.3 \text{ \AA}$) and $q_{020} \sim 1.98 \text{ \AA}^{-1}$ ($d_{020} \sim 3.2 \text{ \AA}$) indicating short-range order of the nanocrystallites, although the nanocrystallites that exist exhibit a lower paracrystalline factor. Intensity versus azimuthal angle plots in Figure 13 indicate a face-on orientation for the 100°C sample.

5.2 Effects of microstructure on redox properties.

It is well-established that the microstructure of a conductive polymer film can have impact on the relative redox properties and charge transfer, both in electrochemical systems⁵⁰ and in the solid state.⁹⁶ We are most interested in structure-property behaviors of polymer electrodes at the onset in the density of states of the polymer films and thus, focus our analysis on a small voltage window of -0.2 to 0.2 V. Wider windows and characterization of CVD PEDOT has been previously described.^{62,63} Figure 14 provides the aqueous cyclic voltammograms of the three microstructure films in Figure 10, taken immediately after deposition and rinsing to remove residual oxidant. The effects of rinsing have been previously described.²⁴

Figure 14 Cyclic voltammograms of CVD PEDOT films of different microstructure.

In Figure 14, all three films show a general capacitive behavior, with only a small oxidation peak for the first cycle at ~ 0.1 V versus Ag/AgCl. The oxidation of this peak is highly irreversible, with only a small reduction wave observed for the 30°C sample cathodically shifted by ~ 200 mV to -0.1 V. For the oxidation peak, we observe shifts in anodic potential as a function of microstructure. In Figure 14, the most crystalline film associated with the face-on orientation (100°C) has a peak onset at ~ 0.1 V, with a maximum at 0.118 V. The edge-on orientation from the 60°C deposition, which showed broader peaks in both the (100) and (020) planes relative to the face-on system in Figure 10, has a slightly more cathodic peak onset at 0.076 V and a local maximum in the oxidation peak at 0.105 V. Finally, the isotropic system (30°C) shows an oxidation onset at 0.085 V, with a local peak at 0.113 V. We note there is some evidence of shifts in redox potentials using wider voltage windows.⁸⁵ Figure 15 and Figure 16 show electrochemical conditioning using a wider potential window (-0.4 to $+0.4$ V) for ~ 130 nm films formed at 30°C and 60°C substrate temperatures, where the main reduction peaks shifts to ~ -0.2 V. This shift in reduction potential could be indicative of a change in microstructure at higher cycling windows, perhaps due to compaction of the film at reducing potentials. In some cases, we observed delamination using larger potential windows and hence for this study, these were avoided as we are most interested in the onset in density of states.

Figure 15 Electrochemical conditioning of 30°C sample using a wider potential window.

Figure 16 Electrochemical conditioning of 60°C sample using a wider potential window.

5.3 Effects of microstructure and thickness on electrochemical conditioning.

An important property of many conductive polymers is the need for electrochemical conditioning, also referred to as an electrochemical annealing or break-in effect.⁹⁷ Such a process is associated with the structural reorganization of the polymer during electrochemical doping, which can sometimes lead to changes in redox onsets and/or peak potentials that are indicative of irreversible microstructural changes. While the exact microstructural changes are beyond the scope of this work, we herein investigate the necessary degree of electrochemical conditioning required for the three above described microstructures. Figure 17 shows the electrochemical conditioning of the three films. Films were considered to be fully conditioned when i_{max} and peak shape were observed to not change with additional cycling.

In Figure 17 (top), oxidation of the face-on sample results in the formation of a small cathodic shoulder as early as the second cycle, at 0.098 V. This is consistent with the only oxidation peak observed in Figure 14. However, we observe a second, more pronounced oxidation peak at 0.118 V. Neither peak is associated with oxidation of residual FeCl_3 which has a known redox potential of ~ 0.4 V versus Ag/AgCl .⁹⁸ We further note we observed no iron in the XPS of thin film PEDOT based on the 100°C substrate temperature sample. Rather the presence of two peaks indicates a sub-population of easier to oxidize states. We note that two peaks were not observed in the cathodic wave, which remains highly irreversible, although we do observe an increase in cathodic peak current with repeated cycling. Both oxidation peaks increase in magnitude with electrochemical conditioning, although not to the same magnitude. All of the oxidation peaks shift with electrochemical conditioning to slightly higher anodic potentials.

We hypothesize that the first peak at ~ 0.1 V is associated with an undoped/unconditioned plane of high crystallinity. Upon electrochemical doping, the nanocrystallite undergoes relaxation and microstructural reorganization, resulting in a more disordered region, which has a higher oxidation potential (~ 0.118 V). Subsequent cycles then reflect that more and more crystallites

have undergone reorganization, resulting in a more pronounced increase in the 0.118 V peak with cycle number. Our results are consistent with the microstructure in Figure 10. As the π - π planes that are responsible for redox are oriented face-on relative to the surface, we speculate that underlying planes cannot be accessed (become electrochemically active) until the near-surface region has sufficiently relaxed to allow ion electro-migration to the underlying regions. Our results are also consistent with prior reports on poly(3-hexylthiophene) in water or ionic liquid environments. The relaxation of crystallite domains has been observed using electrochemical strain microscopy, which showed ordered domains as more compact and exhibit a lower anion uptake with doping relative to disordered domains.⁹⁹

Figure 17 (center) gives the edge-on orientation electrochemical conditioning. For edge-on nanocrystallites, the lamellar planes are tilted on average by 90 degrees relative to the surface. This would allow greater ion penetration into the film, consistent with higher peak current densities with cycling. We also note the reduction in the overall capacitive current density of the film relative to the face-on sample. We observe a closer peak-to-peak separation than for any of the other samples, indicating some sub-population has increased in reversibility in this sample, although the magnitude of the charge in the reductive wave is only a fraction of the oxidation wave. We also observe an increase in cathodic peak current as a function of electrochemical conditioning. A shoulder in the oxidation wave is readily detected albeit at a slightly lower potential ~ 0.085 V than the other two samples, which indicates the edge-on crystallites are easier to oxidize. We also observe a subtle increase of peak potentials to higher oxidation potentials with repeated cycling. This further supports the hypothesis of sub-populations arising from hysteresis as the diffusion front of counterions propagates through the films, with the easier to oxidize being the non-relaxed contribution (crystallites). The result is a bit surprising as it appears to be irrespective of the orientation of the crystallites. However, at low doping potentials, high-resolution X-ray diffraction techniques have shown anions enter and preferentially reside in amorphous domains

Figure 17 Electrochemical conditioning of CVD PEDOT films. Arrows indicate increasing cycle number. Sample film thicknesses are for face-on (~ 120 nm), edge-on (~ 20 nm) and isotropic (~ 120 nm).

to support charges formed in the crystallites. Only by increasing the doping fraction to above 10^{19} carriers/cm³ were anions found to significantly disrupt the π - π stacking domains irreversibly.^{100,101} We conclude that there is a preferred ion transport pathway through the polymer film, which

results in an increase in overall electroactive volume of the edge-on sample, relative to the face-on sample.

Figure 17 (bottom) shows the cyclic voltammograms of the isotropic sample during electrochemical conditioning. Here again we observe a rather large capacitive current background, consistent with the face-on sample. We note that for this particular sample, we also observe the two-populations in the oxidation wave, although it is less pronounced than for the more crystalline samples described above and the change in oxidation current is not as pronounced with electrochemical cycling.

5.4 Electrochemical energy and power density estimations.

As a possible application, we next turn to the quantification of the capacitance for the three different microstructural films. In conductive polymer electrochemistry, charge storage associated with doping is referenced as chemical capacitance^{12,86} but can also have contributions from double layer effects. We readily note that the films presented herein do not have the proper volumes necessary for energy storage applications such as supercapacitors, yet thin films are used in many applications which operate based on the same electrochemical principles of hybrid electronic-ionic charge transport, including but not limited to OECTs,^{17,89,102,103} electrochromics,^{84,85} thermogalvanics⁴⁸ and molecular catalysis.^{49,50} As a point of comparison, we first consider the energy density as a function of electrochemical conditioning. The energy density (Whr/kg) was can be estimated from cyclic voltammograms as a function of cycle number according to Equation 1:

$$\text{Energy Density}(E_f) = \sum_{n=0}^{n=f} \frac{i_n E_n \Delta t}{3.6 V \rho} \quad (7)$$

where E_0 and E_f are the initial and final potentials (V), i_n is the current indexed to the potential range, Δt is the sample interval (s) based on the scan rate, V is the volume of the film (cm^3), ρ is the density (g/cm^3), and 3.6 allows for the conversion between J/g to Whr/kg. The energy density is reflective of the total amount of energy a device can store, or more specifically, the number of

accessible redox sites providing charge per voltage sweep. Thus, collectively, the energy density is expected to also scale with thickness.

Figure 18 Cyclic voltammogram of 20 nm thick film formed at 30°C as a function of electrochemical conditioning.

Figure 19 Cyclic voltammogram of 20 nm thick film formed at 100°C as a function of electrochemical conditioning.

Figure 23 shows the estimated energy density as a function of substrate temperature, thickness and electrochemical conditioning. Corresponding electrochemical conditioning cyclic voltammograms are given in Figure 18 and Figure 19. In Figure 23, we readily observe an increase in energy density with electrochemical conditioning for thin films, as expected. We emphasize that the energy density does not scale directly with peak current density, which is more reflective of power, as described below. Additionally, we observe several important trends in thickness. First, we do not observe very pronounced electrochemical conditioning effects for thicker films. For example, the thick isotropic film (~120 nm) shows almost no change in the energy density, consistent with little change in the cyclic voltammogram in Figure 17. Second, we observe a general decrease in energy density with increasing thickness. Third, we discern little microstructure effects for thicker films. The lack of structure-property relationships with film thickness is further confirmed by considering a wider voltage window, given in Figure 20, which does show a higher energy density ~9.5 Whr/kg but little microstructure or electrochemical conditioning trend.

Figure 20 Energy density associated with the oxidation wave from 0 to +0.4 V of films of electrochemically conditioned films from -0.4 to +0.4 V.

We note that the electrical conductivity is also lower for thicker films and less dependent on microstructure. We speculate that energy density decreases with increasing thickness due to increased disorder, which is also a reasonable rationalization for lack of structure property relationships. Even for the isotropic sample we observed an increase in broadening of the GIWAXS peaks with thicker films, as shown in Figure 21.

Figure 21 Changes in GIWAXS pattern with thickness due to long-range disorder.

Figure 22 The electrical conductivity of CVD films as a function of temperature; increasing the crystallinity increases the conductivity, with the 100°C have the highest electrical conductivity.

Given that the largest changes in energy density are concentrated on the 20 nm films, we further focus our discussion on these measurements provided in Figure 24A. Figure 24A also includes the corresponding error bars, which contain uncertainty in film densities (assumed to be between 1.0 and 1.4g/cm³) and the standard deviations in film thicknesses. Regarding microstructure effects we observe the largest energy density for the face-on, most crystalline film, consistent with the large capacitive background for the 100°C discussed above. Interestingly, the energy density

for the isotropic and edge-on samples are comparable for the first five cycles in the thin films. We hypothesize that this result is due to different mechanisms. Of the two, the isotropic sample has a larger capacitive behavior over the voltage range. Alternatively the majority of the energy density of the edge-on sample is due to the integration of charge from the oxidation peak; the difference between these two phenomena is reflected more readily in the power density in Figure 24B.

Figure 23 Energy density as a function of film thickness and electrochemical conditioning.

To complement the thin film energy density measurements, the power density was calculated according to equation 2 using the variables described above.¹⁰⁴

$$Power\ Density(E_f) = \sum_{n=0}^{n=f} \frac{i_n E_n}{V \rho f} \quad (8)$$

Figure 24 A) Energy density and B) Power density of three films each ~ 20 nm thick, derived from electrochemical conditioning cycle number. In B, the inset corresponds to the anodic peak current density. Error bars contain uncertainty in film densities (assumed to be between 1.0 and $1.4 g/cm^3$) and the standard deviations in film thicknesses.

In Figure 24B, the overall power as a function of electrochemical conditioning is reflective of the ability of the ions to electro-migrate in and out of the film. From Figure 24B, it is readily apparent that the edge-on sample ($60^\circ C$) has the highest power density of 13.3 ± 5.1 kW/kg, followed by the face-on sample ($100^\circ C$) with a power density of 4.2 ± 1.6 kW/kg. The isotropic sample has the lowest power density of $\sim 3.2 \pm 1.2$ kW/kg, suggesting a more torturous pathway for ion migration. An inset of the peak current density for the anodic peak at ~ 0.118 V is provided for comparison, where the peak arises from the potential with the largest rate of charge or discharge. The current density values here are normalized by scan rate to compare the maximum ion discharge rate in terms of capacitance. This combines the effect of double layer capacitance and volumetric chemical capacitance (distinct from the capacitance determined across the range of active potentials).

6. Conclusions and Future Work

This work demonstrates that a much more precise picture of structure-property relationships is needed in electrochemical applications of conductive polymers. While we cannot speak directly to the potential- and conditioning-dependent evolution of the microstructure, comparison of the electrochemical behaviors of films with different known microstructures and orientations relative to the supporting substrate leads to the conclusion that there is a trade-off between electrical and ionic conductivity in the films that gives rise to electrochemical performance. Using the CVD technique and varying the surface temperature during film formation and deposition, we showed that the microstructure of PEDOT changes from isotropic to edge-on to face-on under optimized conditions. Electrochemical conditioning was used to understand in part the relaxation mechanism of these different orientations. Specifically, we observe the crystallites must undergo an irreversible relaxation, which shifts the oxidation potential to a higher value, regardless of the orientation of the film. However, we do observe a direct correlation between microstructure and peak anodic current density, which directly is related to power density. The edge-on films show the highest peak currents and highest power density. Overall, we emphasize that the microstructure-electrochemical property relationships cannot be ignored in future polymer electrode design, especially in the case of thin films.

Future efforts with CVD PEDOT would necessitate investigation of the effect on microstructure of electrochemical conditioning. It may also be pertinent to assess the effect of substrate grafting to control orientation and determine the effect of charge and discharge behavior for different orientations. For applications which require flexibility, it is also necessary to tune the microstructure to contain a certain amount of disorder to allow non-damaging strain to occur. Mechanical properties of PEDOT:Cl⁻ as a function of substrate temperature are also a necessary component of a proper assessment of the technological feasibility of its use in flexible systems. Conductive polymers with mid-range structural order are the strongest candidate for energy

storage applications and would likely be the most compatible microstructure for incorporation in composite super-capacitive materials. Highly ordered conductive polymers demonstrate the most well-defined oxidation behavior and would be stronger candidates for kinetically selective chemical sensing. Disordered conductive polymers exhibit the highest power density and would be best suited for fast optical switching.

7. Appendices

Figure 25 Appendix A: Anodic chronoamperometric response at 0.2V of CVD PEDOT in 0.1M TBAHFP Acetonitrile v. Ag/Ag⁺ after electrochemical conditioning via repeated cyclic voltammetry and cathodic pre-polarization at extremely reducing potentials (>0.6V).

Figure 26 Appendix B: Difference in chronoamperometric response after cathodic pre-polarization for substrate temperature extremes for CVD PEDOT in 0.1M TBAHFP in Acetonitrile v. Ag/Ag+.

Figure 27 Appendix C: Schematic for isolation of oxidation peak for power and energy density.

Figure 28 Appendix C2: Isolated peak schematic.

Figure 29 Appendix D: Spectroelectrochemistry of electrodeposited PEDOT in 0.1M TBAHFP Acetonitrile v. Ag/Ag⁺.

Figure 30 Appendix E: Change in open circuit potential over time for electrodeposited PEDOT in 0.1M TBAHFP in Acetonitrile vs. Ag/Ag+.

Figure 31 Appendix F: UV-Vis-NIR spectroscopy at various open circuit potentials of electrodeposited PEDOT in 0.1M TBAHFP Acetonitrile vs. Ag/Ag^+ .

Figure 32 Appendix G: Comparison of cyclic voltammetry and chronopotentiometry for electrodeposited PEDOT in 0.1M TBAHFP acetonitrile vs. Ag/Ag^+ with simultaneous 960nm NIR absorbance kinetic monitoring. Resolution of electrochemical behavior for certain peaks is more readily available in chronopotentiometry.

Figure 33 Appendix H: Rinsed vs. unrinsed 100°C CVD PEDOT thin film UV-Vis-NIR spectrum.

Figure 34 Appendix I: Rinsed vs. unrinsed 30°C CVD PEDOT thin film UV-Vis-NIR spectrum.

Figure 35 Appendix J: Rinsed vs. unrinsed 30°C CVD PEDOT thin film UV-Vis-NIR spectrum.

Figure 36 Appendix K: Rinsed CVD PEDOT GIWAXS analysis samples UV-Vis-NIR (cp189, cp191, cp192).

Figure 37 Appendix L: Unrinsed CVD PEDOT GIWAXS analysis samples UV-Vis-NIR (cp189, cp191, cp192).

Figure 38 Appendix M: X-ray photoelectron spectroscopy of the C 1s (left), S 2p (center) and O 1s (right) core levels of CVD PEDOT films. Films were formed at substrate temperatures of 30°C (top), 60°C (middle) and 100°C (bottom). S 2p peaks correspond to S 2p_{3/2} and S 2p_{1/2} doublets (d,e), (f,g), and (h,i). The first pair (d,e) represents the sulfur binding environment that is not doped, the second pair (f,g) represents the doped environment and the third pair (h,i) represents a non-PEDOT binding environment. O 1s peaks are labeled j, k, l and m. The j peak is the primary PEDOT related peak and the other peaks are related to byproducts and adsorbates.

Figure 39 Appendix N: X-ray photoelectron spectroscopy of Cl 2p and Fe 2p core levels of CVD PEDOT, the left shows the Cl 2p core levels for CVD PEDOT with substrate temperatures of 30°C and 60°C. Elemental analysis of PEDOT films confirmed on 2-3% Fe and 1% Cl for the 30°C and 60°C films. No residual Fe or Cl was detected in the 100°C sample.

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