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Structural, chemical and electrochemical characterization of poly(3,4-ethylenedioxythiophene) (PEDOT) prepared with various counter-ions and heat treatments

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Abstract

Electrochemical deposition of the conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) forms thin, conductive films that are especially suitable for charge transfer at the tissue-electrode interface of neural implants. For this study, the effects of counter-ion choice and annealing parameters on the electrical and structural properties of PEDOT were investigated. Films were polymerized with various organic and inorganic counter-ions. Studies of crystalline order were conducted *via* X-ray diffraction (XRD). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used to investigate the electrical properties of these films. X-ray photoelectron spectroscopy (XPS) was used to investigate surface chemistry of PEDOT films. The results of XRD experiments showed that films polymerized with certain small counter-ions have a regular structure with strong (100) edge-to-edge correlations of PEDOT chains at ~1.3 nm. After annealing at 170 °C for 1 hour, the XRD peaks attributed to PEDOT disappeared. PEDOT polymerized with LiClO₄ as a counter-ion showed improved impedance and charge storage capacity after annealing at 160 °C.

Keywords

Conducting polymers; PEDOT; XRD

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is an electrically-conducting conjugated polymer that combines excellent conductivity [1] and demonstrated biocompatibility [2]. PEDOT is chemically stable in its oxidized form, is relatively insensitive to pH changes, and can form nearly transparent thin films [1]. These unique characteristics make PEDOT a desirable material in a variety of applications, including solar cells [3], organic light emitting devices [4], and biosensors [5]. Recently, PEDOT has been used as a bioactive coating for the electrode sites of chronic neural implants and other biostimulation devices [6].

The electrical characteristics of PEDOT coatings have important consequences for neural stimulation devices. Small electrode areas are desirable for neural stimulation because they provide more spatial selectivity. However, as electrode size decreases, impedance increases and hinders charge transfer for both neural recording and stimulation [6]. Low-impedance electrodes that have been coated with PEDOT films can therefore be made smaller and can have more-acute neural specificity. In addition to low impedance, a PEDOT film delivers a large charge storage capacity (CSC) and a flat frequency dependence curve. Large CSC values indicate that PEDOT films can mediate the transfer of greater electrical charges between electrical and ionic charge carriers. Flat frequency dependence curves are important to ensure that films maintain low impedance at all relevant frequencies and to improve signal fidelity. The 300–1000 Hz range is especially important because biostimulation is most often performed with pulses in this frequency range [7].

Experiments have shown that annealed PEDOT films can have conductivities as much as three times higher than unheated films [8]. Annealing can also decrease surface roughness [9] and induce a phase transition characterized by the loss of long-range π -stacking in the PEDOT films [10]. All these experiments were performed on chemically polymerized PEDOT films. Less is known about the results of annealing electrochemically polymerized PEDOT films, which are more desirable for neural stimulation electrodes because deposition can be targeted directly to electrode sites.

A number of counter-ions have been used in the electrochemical polymerization of PEDOT, most notably LiClO_4 and PSS [7,11]. Previous work has shown that variation of the counter-ion in PEDOT polymerization changes macroscopic properties such as morphology, color, and electrical impedance [7,11]. The macroscopic differences between PEDOT samples polymerized with different counter-ions can be attributed to differences in the microstructure of the PEDOT samples [12].

PEDOT films polymerized with poly(styrene sulfonate) (PSS) and lithium perchlorate (LiClO_4) have also been used as ionic actuators that facilitate controlled drug delivery, and these counter-ions have different actuator responses. PEDOT/ LiClO_4 films actuate by transporting mobile perchlorate counter-ions, while PEDOT/PSS films have an immobile counter-ion and actuate by transporting cations. These unique actuator responses can make either LiClO_4 or PSS a more desirable counter-ion for the delivery of drugs with different charges [13]. Other considerations—such as the high surface area provided by fibrillar PEDOT polymerized with PAA and LiClO_4 —may also influence counter-ion selection [14].

The selection of a counter-ion for PEDOT deposition is an important consideration, and this selection affects both the electrical properties and morphology of a film. Thus it is valuable to systematically explore how variation of counter-ion affects the microstructure and electrical performance of electrochemically polymerized PEDOT.

In this study, we present work detailing the influence of counter-ion selection and heat treatment steps on the structural and electrochemical properties of electrochemically

polymerized films of PEDOT. X-ray diffraction (XRD) of electrochemically polymerized films of PEDOT reveals a strong edge-to-edge (100) correlation at ~1.3 nm in samples containing certain small counter-ions. X-ray photoelectron spectroscopy (XPS) shows that some sulfur oxidation takes place in the PEDOT films above 130 °C. Electrical characterization of PEDOT films polymerized on Pt/Ir ball electrodes indicates that films polymerized with large counter-ions demonstrate lower electrical impedance and higher charge storage capacity than those polymerized with small counter-ions. PEDOT films with large counter-ions show a decrease in charge storage capacity and an increase in impedance when annealed. However, annealing of films polymerized with small counterions disrupts the edge-to-edge packing, decreases the impedance, and—in some cases—increases charge storage capacity. Only PEDOT/LiClO₄ films benefit from simultaneous decreases in impedance and increases in charge storage capacity, making these films especially suitable for heat treatment. An even more dramatic improvement was manifested in the decreased saturation frequency at which PEDOT/LiClO₄ films approach their asymptotic, minimum impedances.

2. Experimental

2.1. Materials

The 3,4-ethylenedioxythiophene (EDOT) monomer was obtained from H. C. Stark, PSS was obtained from Acros Organics, and phosphate buffered solution (PBS) (10× concentration containing KH₂PO₄, NaCl, and Na₂HPO₄) was obtained from Fisher Scientific. PBS was diluted to a 1× concentration (0.15 M NaCl, 0.0057 M NaH₂PO₄, and 0.001 M KH₂PO₄). Sodium chloride (NaCl), LiClO₄, sodium phosphate (NaH₂PO₄), heparin, bovine serum albumin (BSA), hyaluronic acid (HA), poly(*d*-lysine) (PDL), *para*-toluenesulfonic acid (PTS), poly(acrylic acid) (PAA) and methylene chloride (CH₂Cl₂) were all obtained from Sigma-Aldrich. L-glutamic acid was obtained from M-P Biomedicals, tetrabutylammonium perchlorate (TBAP) was obtained from Fluka, and biotin was obtained from Pierce. All reagents except PBS—as noted above—were used as received.

Planar substrates for XRD and XPS were fabricated both from SiO₂ glass and poly(styrene) substrates sputtered with Au/Pd to a thickness of approximately 60 nm with a Hummer VI sputter system. Indium-doped tin oxide (ITO) on 25 × 25 × 1.1 mm unpolished float glass from Delta Technologies (Rs = 6 ± 2 Ω/sq, #CG-40IN-0115) was also used as substrate for some XRD and XPS trials. Pt/Ir ball electrodes were utilized for electrochemical measurements; these substrates were fabricated by flaming the tip of Teflon-coated, 90/10 Pt/Ir wire from A-M Systems with an oxygen torch.

2.2. Electrochemical polymerization

PEDOT was electrochemically polymerized on planar substrates under galvanostatic conditions from an aqueous monomer solution containing approximately 0.01 M EDOT and 0.01 M counter-ion. PEDOT films for XRD were grown at a current density of 0.5 mA/cm² for 12 min on Au/Pd-sputtered glass and indium-tin oxide (ITO) on glass. PEDOT films for electrochemical characterization were deposited at a current of 2 μA for 5 min on Pt/Ir ball electrodes. An AutoLab PGSTAT12 Potentiostat/Galvanostat (EcoChemie, The Netherlands) was used for all electrochemical polymerizations. The counter-ions used were PSS, PBS, NaCl, LiClO₄, NaH₂PO₄, TBAP, and PTS and the biologically derived counterions heparin, glutamate, HA, BSA, PDL, and biotin. Methylene chloride was used as solvent for the tetrabutylammonium perchlorate solution. Deionized water was used as solvent for all other EDOT solutions. Fibrillar PEDOT was polymerized with PAA and LiClO₄ as previously reported [14]. All samples were extensively rinsed with deionized water after deposition to wash away excess monomer and counter-ion.

2.3. Structural characterization

Structural characterization was performed *via* 2-D XRD using a Bruker D8 Discover diffractometer equipped with a HISTAR 2D wire array area detector. X-rays were generated using a fixed-tube, copper target source operated at 40 kV, 40 mA for all experiments. A 500 m monocapillary collimator was used to generate a point-focused beam. The instrument was calibrated using a NIST1976 flat plate standard or silver behenate powder as appropriate. Data were collected with a camera length of 15 cm.

XPS chemical characterization was performed using a Kratos Axis Ultra DLD X-ray Photon Spectrometer (Kratos Analytical Ltd., Manchester, UK). A Monochromatic Aluminum source was used with the C-C/C-H reference set at 285 eV.

2.4. Electrochemical measurements

Pt/Ir ball electrodes were used as the deposition substrate for electrochemical characterization of PEDOT films. Impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using an Autolab PGSTAT12. For EIS, the sample acted as the working electrode, a platinum plate as the counter electrode, a saturated Ag/AgCl electrode as the reference electrode, and phosphate buffered saline as the electrolyte. A sinusoidal AC signal with 5 mV amplitude was applied over a frequency range of 1–10⁵ Hz. Both impedance and phase angle data were collected over the frequency range. Impedance values at 1 kHz are used as a benchmark when testing PEDOT films because the frequency range of neural activity, from 300 Hz–1 kHz, is especially important in biological stimulation applications [7,15].

CV was performed with the same electrode setup. The voltage was swept from -0.6 V to 0.8 V with a scan rate of 100 mV/s. CSC values were calculated by the Autolab software.

2.5. Annealing

Planar PEDOT/NaCl samples, which demonstrated the most significant structural regularity as discussed in the results section, were annealed at temperatures up to 200 °C in both ambient and N₂ atmospheres. The structural changes of the annealed samples were investigated with XRD. When annealing in N₂ atmosphere at low temperatures, Au/Pd sputtered poly(styrene) substrates were used. For temperatures above 90 °C, Au/Pd sputtered glass substrates were used. PEDOT films polymerized on ball electrodes with PSS, heparin, LiClO₄, and NaCl as counter-ions were annealed at temperatures between 70 °C and 220 °C in ambient atmosphere ovens. Annealing was performed for 1 hour and all testing was performed after cooling and within three days of annealing.

3. Results and Discussion

3.1. Structural Analysis

The 2D XRD patterns for electrochemically polymerized PEDOT films with select counter-ions are shown in Figures 1a–1i. XRD patterns of PEDOT polymerized with NaCl, TBAP, and PTS (Figs. 1a–1c) show a distinctive low-angle peak near ~1.3 nm that is not present in background scans (Fig. 1d). The peak in the PEDOT/NaCl sample (Fig. 1a) corresponds to a first-order *d* spacing of 1.27 nm. This *d* spacing value is similar to the 1.40 nm *d*₁₀₀ (edge-to-edge) spacing of chemically polymerized PEDOT/Fe(III)Cl₃ reported by Aasmundtveit et al. [16], and the *d*₁₀₀ values between 1.30 nm and 1.40 nm for PEDOT prepared *via* chemical vapor phase deposition with various counter-ions by Winther-Jensen et al. [10]. Given its similarity to these published results, the diffraction peak observed with electrochemically polymerized PEDOT/NaCl was attributed to intermolecular edge-to-edge (100) correlations between the relatively stiff PEDOT molecules. Figure 1e shows a

diffraction pattern of PEDOT/TBAP. In this sample, the low angle (100) peak is very uniform in intensity over the observed azimuthal angle range (Fig. 2). PEDOT/PTS shows this same lack of preferred orientation (Fig. 1c). PEDOT/NaCl shows a strong preferred orientation of (100) planes whereas PEDOT/TBAP does not.

These PEDOT diffraction patterns show no indication of d_{010} or d_{001} spacings. Diffraction patterns were collected with the samples tilted about the axis of the beam to access diffraction data lying off the meridian; these data also show no indication of (010) or (001) peaks. The lack of evidence for these spacings and the minimal azimuthal variation of the PEDOT/TBAP and PEDOT/PTS (100) peaks indicate that individual PEDOT chains have a regular edge-to-edge correlation with only limited order in the other crystallographic directions. This edge-to-edge (100) correlation indicates a tendency for the chains to organize into ribbon-like structures in which a number of PEDOT chains stack edge-to-edge and remain locally parallel. The absence of other diffraction peaks indicates little or no regularity in face-to-face packing. Therefore, we propose a molecular model of PEDOT chains that are locally organized in the edge-to-edge direction but remain otherwise disordered.

In contrast to PEDOT/TBAP and PEDOT/PTS, Figures 1a and 2 show the greater azimuthal variation of the peak for PEDOT/NaCl. The PEDOT/NaCl peak has a maximum intensity along the plane perpendicular to the sample stage, which indicates that the chains prefer to organize parallel to the plane of the substrate. XRD patterns of PEDOT films polymerized with PSS and PBS do have faint peaks in the same region as the peaks seen in PEDOT/NaCl, PEDOT/PTS, and PEDOT/TBAP. These faint peaks are evidence of a preferred orientation similar to that found in PEDOT/NaCl. Despite any preferred orientation, films polymerized with NaCl, PSS and PBS have no indication of face-to-face nor backbone regularity, so the model of edge-to-edge packing between PEDOT chains that are otherwise disordered is still applicable to these films.

PEDOT samples prepared with LiClO_4 , NaH_2PO_4 , and the biologically derived counter-ions—heparin, glutamate, HA, BSA, PDL, and biotin—and fibrillar PEDOT prepared with PAA/ LiClO_4 do not show similar low angle peaks to those present in the other samples; for example Figures 1h and 1i compare the diffraction pattern for PEDOT/heparin and PEDOT/ LiClO_4 . Evidently, in these samples the larger counter-ions disrupt the lateral order of the PEDOT films.

3.2. Structural Analysis after Heat Treatment

The low angle (100) X-ray diffraction peaks from PEDOT/NaCl samples that have been annealed in ambient atmosphere are shown in Figure 3a. The (100) diffraction peak in PEDOT/NaCl decreases in intensity when annealed at 150 °C and is completely absent at 200 °C. This monotonic decrease in peak intensity with increased annealing temperature indicates that heat treatment causes a disordering in the PEDOT film. To determine whether this change was due to reactions with the atmosphere, samples were annealed at similar temperatures in N_2 atmosphere. The low angle XRD data for these samples annealed in N_2 atmosphere (Fig. 3b) are consistent with the data from the ambient atmosphere annealing: the intensity of the diffraction peak decreases monotonically as annealing temperature increases. This similarity indicates that the structural changes in the films are not caused by a chemical interaction with atmospheric gasses.

Winther-Jensen et al. reported a similar loss of intensity in X-ray diffraction peaks when PEDOT films were annealed to 140 °C [10]. It is important to note that Winther-Jensen's measurements were taken during the annealing process. Therefore, the complete loss of peak intensity at 140 °C that they reported does not conflict with our findings. Their experiments

showed that diffraction peaks reappeared with less intensity after films had cooled from 140 °C, and this finding is directly comparable to our data for PEDOT annealed to 130 °C and 150 °C and cooled (Fig. 3a & 3b).

Those PEDOT samples that showed no evidence for long-range ordering prior to heat treatment (PEDOT polymerized with heparin, glutamate, HA, BSA, PDL, biotin, LiClO₄, NaH₂PO₄, and PAA/LiClO₄) did not exhibit any XRD evidence of heat-induced ordering after heat treatments were performed.

In order to analyze the chemical changes that took place during annealing, XPS analysis of the PEDOT/NaCl samples was performed on samples annealed in both ambient atmosphere and N₂ atmosphere. The spectra for unannealed PEDOT are consistent with Spanninga et al. [17]. After annealing at 130 °C in N₂ atmosphere, changes were seen in both sulfur and oxygen spectra (Figs. 4a and 4b). The sulfur 2p spectra exhibited an increase in intensity in the small, broad peak near 168 eV. This may be an indication of sulfur oxidation in the PEDOT thiophene ring [18]. In the oxygen 1s spectra an increase was observed in the lower binding energy shoulder at ~532 eV. Similar results were seen for annealing in N₂ atmosphere. These results are not conclusive but they suggest that some sulfur oxidation is taking place. However, oxidation does not begin to occur until films reach 130 °C. Structural changes in PEDOT/NaCl samples were seen at temperatures as low as 70 °C, indicating that the structural changes observed with XRD cannot be entirely attributed to oxidation.

3.3. Electrical Characterization before and after Heat Treatment

To further investigate the affects of annealing on PEDOT films, electrical studies were performed on samples before and after annealing. EIS and CV were performed on PEDOT samples polymerized on Pt/Ir ball electrodes with four different counter-ions: PSS, heparin, LiClO₄, and NaCl. PSS and heparin were chosen for their low impedance and large CSC [1,19,20]. LiClO₄ was chosen for its previous use in neural probe coating and drug delivery investigations [13,14] and NaCl for its interesting structural properties as discussed in the previous section. PEDOT samples polymerized with PSS, heparin, LiClO₄, and NaCl were annealed at temperatures from 70 °C–220 °C. Figure 5 shows EIS impedance at 1 kHz plotted against annealing temperature, and Figure 6 shows CSC values plotted against annealing temperature. Table 1 provides a summary of electrical data for these for counter-ions.

PEDOT/PSS and PEDOT/heparin films show variations in impedance with annealing temperature comparable to the random fluctuations in the untreated films. No significant change in impedance was observed in these films in the temperature ranges examined, save a modest increase in the PEDOT/heparin samples annealed at 220 °C. CV plots of both of these samples show a 44–50% decrease in CSC when annealed at any temperature compared to the unheated sample. These results indicate that heat treatment is detrimental to the electrical performance of PEDOT films polymerized with PSS and heparin. Given the high temperatures involved, thermal degradation of the biological counter-ion heparin could have contributed to these changes in electrical performance.

However, PEDOT films polymerized with LiClO₄ and NaCl, two smaller counterions, have much higher impedances and lower CSC values before annealing than PEDOT polymerized with PSS and heparin. These results correspond well with CSC measurements reported by Winther-Jensen et al. [10]. Heat treatment of PEDOT/LiClO₄ causes a decrease in 1 kHz impedance when annealed at 70 °C–190 °C, reaching a minimum of 320 Ω when annealed at 190 °C (Fig. 5). This impedance is comparable to the 319 Ω for unheated PEDOT/PSS.

The large error bars for the impedance of unannealed PEDOT/LiClO₄ are representative of 1 kHz impedance values of 459 Ω , 711 Ω , and 1345 Ω . However, after annealing at 70 °C those films had impedances of 539 Ω , 553 Ω , and 625 Ω , respectively. The impedances of those films retain a low standard deviation (less than 50 Ω) up to 190 °C. It seems that annealing LiClO₄ films both decreases their impedance and results in a tighter distribution of electrical properties. Film stability in annealed films is a potential issue, however; 25% of films annealed between 130 °C and 190 °C failed during electrical testing.

Even more distinct than the decrease in impedance of PEDOT/LiClO₄ samples is the reduction of the frequency at which they approach their lowest impedance. All PEDOT films show similar frequency dependence in their impedance: an asymptotic, low impedance at high frequencies that increases rapidly at frequencies below a critical frequency, f_c (Fig. 7a). The value of f_c depends on counter-ion and deposition parameters. It can be arbitrarily represented by the frequency at which the impedance reaches 1000 Ω . Calculated this way, the f_c of PEDOT/LiClO₄ films decreases from 698 Hz in the unheated sample to just 14 Hz when the samples are annealed at 190 °C (Fig. 7b). For comparison the f_c of unheated PEDOT/PSS films was 3.2 Hz.

Cyclic voltammetry of PEDOT/LiClO₄ shows an increase in CSC when samples are annealed, reaching a maximum of 11.3 mC/cm² when samples are heated at 160 °C (Fig. 6, Table 1). For comparison, the polymer film with the best electrical properties in our experiments—unheated PEDOT/PSS—has a CSC value of 26.1 mC/cm². Impedance and f_c values have not reached a minimum when PEDOT/LiClO₄ is annealed at 160 °C, but they are within 15 Ω and 4.9 Hz, respectively, of their minimum values, and above 160 °C the charge storage capacity decreases significantly. Finally, these PEDOT/LiClO₄ films are stable up to 160 °C—the degradation of electrical properties described above only began at 190 °C. Therefore, 160 °C is an optimal annealing temperature for these PEDOT/LiClO₄ films.

PEDOT/NaCl samples demonstrate considerably lower impedance when annealed at 70–130 °C, with a minimum impedance of just 287 Ω at 70 °C (Fig. 5b). This value is lower than the impedance of unheated PEDOT/PSS, the benchmark for low-impedance PEDOT. The f_c values are also significantly lower in this range, having decreased from 2200 Hz to only 7 Hz when annealed at 100 °C (see Supp. 2). The CSC in this temperature range, however, is significantly lower, having decreased by more than 40% (Fig. 6). Above 160 °C, the charge storage capacity increases slightly, but the impedance when annealed above 160 °C is much higher than even that of the unheated samples. Thus, impedance of PEDOT/NaCl films can be reduced with heat treatment, but not without a significant loss in charge storage capacity.

3.4 Correlation between structural and electrical properties

The observed relationship between structural and electrical properties is quite different for each of the four counter-ions. XRD data shows that planar PEDOT/NaCl films become more disordered when annealed above 150 °C. At these temperatures, the PEDOT/NaCl films on ball electrodes demonstrate both increased impedance and decreased charge storage capacity (Fig. 5b & 6). These results suggest that regular polymer packing in unheated films supports PEDOT's ability to mediate charge transfer at the interface between ionic and electronic conduction. However, Figures 5 and 6 also show that impedance and charge storage capacity have different relationships to annealing temperature and that neither exhibits a monotonic dependence on annealing temperature. Therefore, some other structural, thermodynamic, or chemical change must also be taking place to account for the complex effects that annealing has on electrical properties.

PEDOT/LiClO₄ shows no evidence of crystallinity before or after annealing, but its electrical properties change dramatically with temperature. PEDOT/PSS and PEDOT/heparin also show no evidence of crystallinity and demonstrate some changes in electrical properties when annealed, though to a lesser extent than the other two PEDOT films. As is the case for PEDOT/NaCl, these changes in electrical properties must be attributable to some structural, thermodynamic, or chemical change. Changes in surface morphology, structural changes within the PEDOT films, and chemical changes at the polymer-substrate interface are all possible causes of the changes seen in these PEDOT films. Investigation of each of these phenomena and its affect on electrical properties could be an avenue for future research.

As demonstrated by Winther-Jensen et al., chemically polymerized films that have been annealed are unstable in their disordered state. After one month with no further heat treatments, annealed films were observed to regain their crystallinity [10]. The effect that this time-dependent return to a more stable thermodynamic state may have on electrochemically polymerized PEDOT was not studied in these experiments and could be another focus of future research.

3.4 Application of Results

The results discussed here, specifically the improvements in electrical properties seen with annealed PEDOT/LiClO₄ films, could be particularly advantageous for neural stimulation. Stimulation is most often performed in the 300–1000 Hz range and these heat treatments decrease electrode impedances to below 1000 Ω across that entire frequency range (f_c values decreased from 2200 Hz to 7 Hz for annealed PEDOT/LiClO₄). Additionally, the heat treatments applied to PEDOT/LiClO₄ films produce extremely flat impedance curves over the relevant frequency range (Fig. 7a). These flatter impedance curves can improve signal fidelity: when impedance varies across the relevant frequency range, the variations distort output signals. Heat treatment of PEDOT/LiClO₄ films could limit this problem in stimulation devices. Large CSC values are desirable as they indicate the amount of charge available for transfer from electrical to ionic current [19], so the larger CSC values of annealed PEDOT/LiClO₄ films are also advantageous. Empirical studies of this type of heat treatment for PEDOT films on neural devices could ultimately lead to smaller electrode sites that more efficiently stimulate neural tissues.

4. Conclusions

PEDOT samples electrochemically polymerized with NaCl, PTS, and TBAP contain a structural regularity associated with regular (100) edge-to-edge alignment of PEDOT chains. Heat treatment of PEDOT/NaCl between 160 °C and 220 °C causes these edge-to-edge correlations to disappear. Electrical testing indicates that the annealing also decreases impedance and increases CSC of PEDOT samples prepared with LiClO₄ as a counter-ion. In particular, annealing PEDOT/LiClO₄ to 160 °C for 1 hour decreases impedance at 1 kHz by 60%, decreases by nearly two orders of magnitude the lowest frequency at which impedance reaches 1 k Ω , and increases CSC by 25%. PEDOT/NaCl films also demonstrate a 39–42% decrease in impedance when samples are annealed in the 70 °C–130 °C range, but this decrease in impedance is accompanied by an undesirable 39–42% decrease in CSC. PEDOT polymerized with larger molecular weight counter-ions (PSS, heparin, *etc.*) do not show the structural regularity observed in PEDOT polymerized with smaller counter-ions. PEDOT polymerized with large counter-ions also do not exhibit any improvement in electrical properties when annealed.

These findings indicate that PEDOT coatings that have undergone heat treatments may be valuable for neural stimulation devices or any PEDOT application where characteristics

such as low impedance, high CSC, and flat frequency dependence curves are important. Annealing of small counter-ion PEDOT films could allow these characteristics to be fine-tuned for particular applications. Further studies will be necessary to determine the usefulness of PEDOT heat treatments for any particular device. Future research could also focus on the deposition and optimization of biological counter-ions such as those investigated here.

LiClO₄ is particularly interesting as a PEDOT counter-ion because it is smaller and more mobile than PSS. Axelsson showed that PEDOT/LiClO₄ films have a larger deflection under actuation than PEDOT/PSS films. Furthermore, PEDOT/LiClO₄ films transport perchlorate anions during actuation whereas PEDOT/PSS films transport cations from solution [13]. This difference could make PEDOT/LiClO₄ films preferable for controlled delivery of certain charged drugs. The annealing process described here can improve the electrical properties of PEDOT/LiClO₄ films to levels comparable to PEDOT/PSS. In applications such as neural stimulation devices where both drug delivery and charge delivery are important, annealed PEDOT/LiClO₄ films could prove to be an ideal solution.

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Figure 1.
2-D X-ray Diffraction data of PEDOT samples electrochemically polymerized with various counter-ions.

Figure 2. Azimuthal integration of XRD spectra for low angle (100) peaks of PEDOT/TBAP and PEDOT/NaCl.

Figure 3. XRD of PEDOT showing low angle (100) peak of PEDOT/NaCl, (a) annealed in ambient atmosphere and (b) annealed in N_2 atmosphere.

Figure 4.
XPS spectra for PEDOT/NaCl samples annealed in ambient atmosphere; (a) *sulfur (2p)* and (b) *oxygen (1s)*.

Figure 5. Magnitude of impedance at 1 kHz as a function of annealing temperature for PEDOT/PSS, PEDOT/Heparin, PEDOT/LiClO₄, and PEDOT/NaCl. Mean values for three samples are plotted, and error bars indicate one standard deviation.

Figure 6. Total charge storage capacity as a function of annealing temperature for PEDOT/PSS, PEDOT/Heparin, PEDOT/LiClO₄, and PEDOT/NaCl. Mean values for three samples are plotted, and error bars indicate one standard deviation.

Figure 7.

(a) Impedance of bare Pt/Ir, PEDOT/LiClO₄, PEDOT/LiClO₄ annealed at 160 $^{\circ}\text{C}$, and PEDOT/PSS on Pt/Ir ball electrodes. Dotted line indicates the 1000 Ω benchmark used to calculate f_c . (b) Frequency at which PEDOT/LiClO₄ samples reach 1000 Ω versus annealing temperature. Mean values for three samples are plotted, and error bars indicate one standard deviation.

Table 1

Comparison of PEDOT films polymerized with different counter-ions and annealed.

Counter-ion	Molecular weight	d_{100} spacing	1 kHz impedance and CSC before annealing	1 kHz impedance and CSC after annealing 1 hour at 160 °C
PSS	~70,000 Da	~1.3 nm	319 Ω 26.1 mC/cm ²	335 Ω 14.7 mC/cm ²
Heparin	12,000–15,000 Da		309 Ω 20.9 mC/cm ²	304 Ω 11.2 mC/cm ²
LiClO ₄	106.4 Da		839 Ω 8.6 mC/cm ²	335 Ω 11.3 mC/cm ²
NaCl	58.4 Da	1.27 nm	981 Ω 19.3 mC/cm ²	3168 Ω 12.7 mC/cm ²