

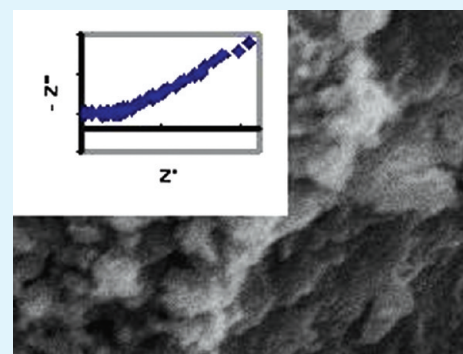
Near-Ohmic Behavior for Conducting Polymers: Extension Beyond PEDOT on Gold-Plated Platinum to Other Polymer-Counterion/Substrate Combinations

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ABSTRACT: Conducting polymers constitute a class of materials for which electrochemical and electron transport properties are a function not only of their chemical identity but also of their complex morphology. In this paper, we investigate and compare the frequency dependence behavior of the impedance of poly(3,4-ethylenedioxythiophene), or PEDOT, and that of poly(3,4-ethylenedioxyppyrole), or PEDOP, which are doped with a series of polyatomic anions during electrodeposition. We also contrast the behavior of PEDOT on Pt|Au, Pt, glassy carbon, and gold. Initial results for polycarbazole, PCz, electrodes are, in addition, included. Deposition parameters were adjusted to produce morphologically similar films for PEDOT, PEDOP, and PCz. In doing so, we have been successful in producing frequency-independent impedance behavior similar to that previously reported for PEDOT on Pt|Au. Although the impedance behavior of these polymers appears to be primarily determined by morphological features, the impact of counterion identity (beyond ionic charge transport) is also discussed. These studies suggest that choice of polymer/dopant combination and electrodeposition parameters can be manipulated to tune the impedance characteristics of electrodes, thereby optimizing them for capacitive or faradaic charge injection, or some combination of the two.

KEYWORDS: PEDOT, PEDOP, polycarbazole, impedance, Raman spectroscopy



1. INTRODUCTION

There is currently compelling evidence for the suitability of conducting polymers (CPs) for biomedical applications.^{1,2} However, the dual modes of conductivity (i.e., electronic and ionic) inherent in a CP film are predicted to result in the same frequency-reactive impedance seen for commonly used electrodes as platinum, gold and silver/silver chloride.^{3–5} From an equivalent circuit point of view, this translates to high impedance at low frequency: a phenomenon that would be detrimental to performance of the device at the frequencies required for many neuroscience applications, particularly for those which focus on neural signals and movement disorder research ($0 \text{ Hz} < f < 30 \text{ Hz}$).^{6–9} For reliable acquisition of bioelectric signals, a bioelectrode must not only avoid such impedance drawbacks, it should also exhibit minimal impedance in order to resolve small amplitude bioelectric signals from background noise.¹⁰

We have reported frequency-independent behavior in vivo for a subset of electrodes based on poly(3,4-ethylenedioxythiophene), PEDOT, deposited on a Au substrate, in the frequency range of 25 Hz to 806 Hz.¹⁰ This behavior was later reproduced using gold-on-Pt (Pt|Au) substrate electrodes in solution experiments and extended to cover the frequency range extending between from less than 100 Hz to around 100 kHz¹¹ in the case of tetrafluoroborate-doped PEDOT. Achievement of this uniquely broad range of frequency-independent impedance behavior for doped PEDOT-based electrodes provides the rationale to determine if the same

behavior can be achieved in other polymer/dopant combinations.

The frequency-independent impedance behavior for PEDOT films is postulated to result from the formation of two homogeneous layers during deposition – a compact, non-porous layer adjacent to the substrate electrode and an outer layer that is characterized by microscopic pores.¹¹ In this contribution, we compare the impedance of poly(3,4-ethylenedioxyppyrole), PEDOP, and polycarbazole, PCz, and PEDOT prepared using the same optimization criteria and probe the effect of deposition substrate on the impedance behavior of PEDOT electrodes. While the impedance behavior of conducting polymers has been extensively studied,^{12,13} there has been little direct comparative investigation of frequency dependence impedance behavior across a series of conducting polymers or substrates. The results reported here suggest that the careful choice of synthetic approach and dopant can be used to tune the impedance behavior of conducting polymer electrodes.

2. EXPERIMENTAL SECTION

Materials. Platinum (Puratronic grade) and silver (99.99%) wires, as well as hydrogen tetrachloraurate(III), were purchased from Alfa-Aesar. Sulfuric acid and acetonitrile (99.9%) were purchased from

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Fisher Scientific. The EDOP and carbazole were obtained from Aldrich. Tetrabutylammonium tetrafluoroborate, tetrabutylammonium hexafluorophosphate, poly(sodium-4-styrenesulfonate), tetrabutylammonium tosylate and tetrabutylammonium perchlorate (electrochemical grade) were obtained from Fluka Chemika or Aldrich. Acetonitrile was dried over 3 Å molecular sieve (Fisher Scientific) before use. All other chemicals were used without further purification. Adhesive polymer was obtained from Stan Rubenstein or ME Taylor Engineering, Inc. Nonporous polymer (TorrSeal) was purchased from Varian Vacuum, Inc. Aqueous solutions were prepared using 18.3 MΩ water produced with a Millipore RIO5 purification system.

Electrochemical Cell. All electrochemical reactions were carried out in a one-compartment three-electrode cell. The reference and auxiliary electrodes were Ag/AgCl (BAS RES) and platinum wire, respectively. All deposition and electrochemical characterization studies were performed using a Radiometer PGZ402 instrument controlled by VoltaMaster 4 Software. No ohmic compensation has been applied.

EIS Characterization. EIS measurements were carried out immediately after synthesis using a Radiometer PGZ 402 over the frequency range of 1×10^{-1} to 1×10^5 Hz with 20 points/decade. The system was maintained at open circuit potential for 2 mins before carrying out the EIS experiment. As was the case for PEDOT in our prior report, experiments were carried out at OCP and at 0.2 V vs OCP produced the same spectrum. The behavior for a given polymer/counterion combination in various background electrolytes (also as was the case for PEDOP in our prior report) were almost identical. All results included here are at OCP in 0.1 M KCl. A Pt wire auxiliary and a Ag/AgCl reference electrode completed the circuit.

Fabrication of Electrodes. Each platinum substrate electrode was fabricated, electrochemically cleaned, and (with the exception of the

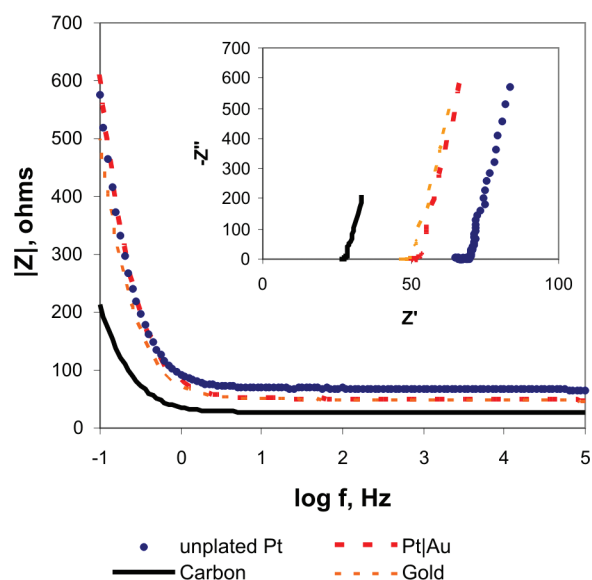


Figure 1. Impedance behavior of PEDOT/BF₄⁻ on different substrates. Electropolymerization potential: 1300 mV Vs Ag/AgCl, [EDOT] = 0.01 M; [BF₄⁻] = 0.1M; deposition time= 60 s.

PEDOT experiments of Figure 1) coated with a layer of gold as previously described¹¹ to both lower contact impedance and improve adhesion.¹⁴ (This is referred to herein as Pt|Au). The appropriate electropolymerization potential for each polymer was determined based on cyclic voltammetric measurement of the peak potential for the monomer. Optimum potentials chosen for the monomers were 1300 mV for PEDOT, 1200 mV for PEDOP and 1300 mV for PCz. Unless indicated otherwise in the figure legends or captions, deposition took place for 60 s.

Raman Spectroscopy. Raman measurements were carried out employing a Renishaw Ramascope microspectroscopy instrument equipped with a 785 nm laser (SpectraPhysics) with an output of 25 mW, a Rayleigh filter, and a 2400 line/mm grating. Instrument setup and data acquisition were controlled with Wire 2.0 software. As spectra were obtained immediately after the EIS experiments were completed, the films are assumed to be in the same oxidation state as during the EIS measurements.

3. RESULTS AND DISCUSSION

Effect of Substrate Electrode on Impedance Behavior.

In our earlier studies, the contribution of the substrate/polymer interface to the impedance behavior of the electrodes was postulated to be a minor contributor to the overall impedance. To test this aspect of the previously proposed model, we fabricated PEDOT/BF₄⁻ electrodes on Pt|Au, glassy carbon, and gold disk electrodes. The criterion for suitable films was achievement of the broadest range over which the phase angle was <2°, the range defined as “near-Ohmic” in our prior report.¹¹ As shown in Table 1, the large range characterized by

Table 1. “Near-Ohmic” Frequency Ranges for Polymers of Figures 1 and 7

	low <i>f</i> (Hz)	high <i>f</i> (Hz)	Z (ohms)	standard deviation (ohms)
PEDOT on Pt Au	5	89 000	51.7	0.6
PEDOT on Au	56	89 000	48.3	0.3
PEDOT on Pt	45	56 000	67.0	0.7
PEDOT on C	2	89 000	27.4	0.7
PCz-CIO ₄ -60s	100	71 000	6.9	0.2
PEDOP-BF ₄ -120s	36	100 000	35.9	0.5

this low phase angle (and low impedance) is maintained over the substrates tested. In Figure 1, the impedance magnitude, |Z| is plotted as a function of log *f* and the impedance plane data are shown for PEDOT grown on Pt, Pt|Au, Au, and glassy carbon. The impedance magnitude is defined as

$$|Z| = \sqrt{Z'^2 + Z''^2} \quad (1)$$

Comparison of Impedances of PEDOT, PCz, and PEDOP.

Tetrafluoroborate, BF₄⁻ was shown in our previous work to produce the widest frequency range for ohmic behavior in PEDOT-based electrodes. In Figure 2a, the impedance magnitude of PEDOT|BF₄⁻, PCz|ClO₄⁻, and PEDOP|BF₄⁻ electrodes are contrasted. All electrodes exhibit frequency independent behavior over a large range of frequency, and even below 1 Hz the magnitude of the impedance remains well below 1 kΩ for these polymers. The frequency range over which the desired low phase angle is achieved is tabulated in Table 1 for the electrodes of Figure 1.

It is obvious that PEDOT and PEDOP exhibit the desired low impedance behavior over a much wider frequency range compared to PCz when doped with tetrafluoroborate. In addition, it is clear that when films of PEDOT, PEDOP and PCz with the desired porous outer morphology are produced using the same conditions (except optimum deposition potential), PEDOP exhibits low impedance which is more similar to that of PEDOT than to PCz. The model proposed in our earlier report would suggest that the large imaginary component of the impedance at low frequency is likely due to capacitive effects caused by the differences in the penetration length of ions and or the microstructure at the smooth/porous

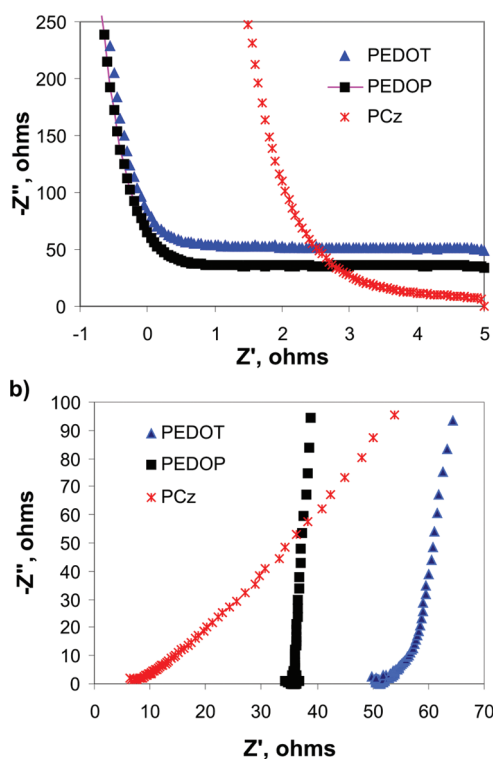


Figure 2. Comparison of ohmic impedance behavior of PEDOT, PEDOP and PCz prepared from solutions containing 0.01 M monomer and 0.1 M TBATFB. Deposition time: 120 s.

layer interface.¹¹ More extensive fitting of the data to our proposed model is currently underway.

Figure 3 shows SEM images of PEDOP and PCz electrodes grown under the conditions indicated in the figure captions. In both cases, it is possible to see the “lumpy” outer layer over a more compact layer – the morphology which produced such a broad range for PEDOT/BF₄⁻ electrodes in our earlier work.

Effects of Dopant. The Raman spectra of PEDOP doped with various counterions are shown in Figure 4 after normalization for differences in maximum intensity related to laser focusing. The films exhibit the same vibrational modes, with the quinoidal C=C stretching modes which appear at around 1600 cm⁻¹ indicating formation of the polymeric backbone.¹⁵ As can be observed from Figure 4 and as borne out by the data of Table 2, there is only a small deviation in frequency position of the PEDOP C=C and C=N quinoidal stretching modes upon changes in dopant anion. By analogy to poly(dimethoxypyrrole), shifts to higher frequency and increased apparent peak width are an indicator of changes in conjugation length of the chains,¹⁶ thus suggesting that changes in counterion identity across the series investigated here does not seem to produce major changes in conjugation length. This observation is consistent with that reported previously for PEDOT.¹¹ It has been difficult to produce films of PCz with dopants other than perchlorate that do not crack when dried. Figure 5 shows a spectrum of one of these films, in which the typical peaks are seen at around 1600 cm⁻¹ for the quinoidal C=C and C=N modes.¹⁷

It is widely accepted that the identity of the dopant, depending on its electronic properties and size, affects the conduction properties of conducting polymers.^{18,19} Panels a and c in Figure 6 display the Bode plots of the impedance spectra of PEDOP and PCz electrodes, respectively, when

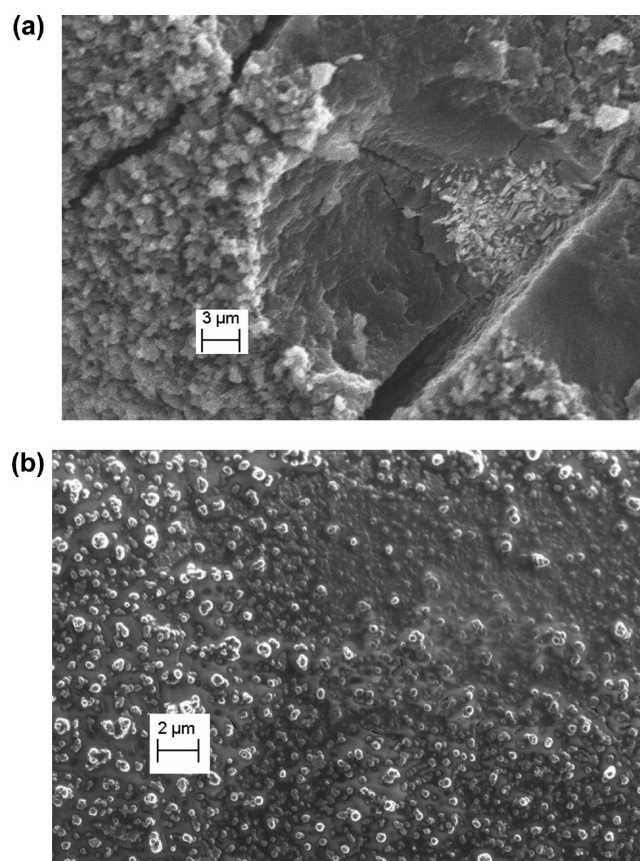


Figure 3. SEM images of (a) PCz and (b) PEDOP doped with BF₄⁻ (Solution conditions: 0.01 M monomer, 0.1 M TBATFB; deposition time 60 s.

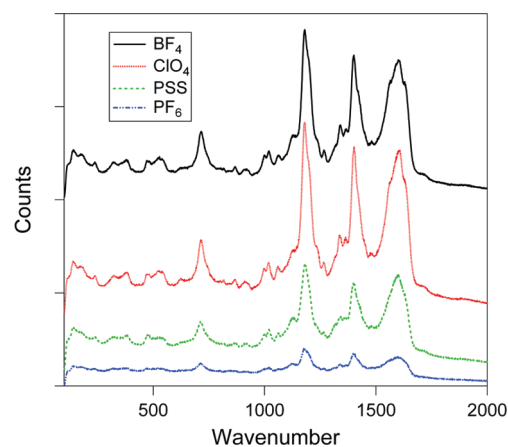


Figure 4. Raman spectra of PEDOP doped with various anions. Monomer concentration is 0.01 M, counterion concentration is 0.1 M, electropolymerization potential 1200 mV, electropolymerization time is 60 s in acetonitrile. (BF₄⁻ = tetrafluoroborate, ClO₄⁻ = perchlorate; PSS = polystyrene sulfonate, PF₆⁻ = hexafluorophosphate).

Table 2. Peak Positions for C=C Stretches for PEDOP as a Function of Counterion

counterion	peak position (cm ⁻¹)
tetrafluoroborate (BF ₄ ⁻)	1601
hexafluorophosphate (PF ₆ ⁻)	1598
perchlorate (ClO ₄ ⁻)	1608
polystyrenesulfonate (PSS ⁻)	1599

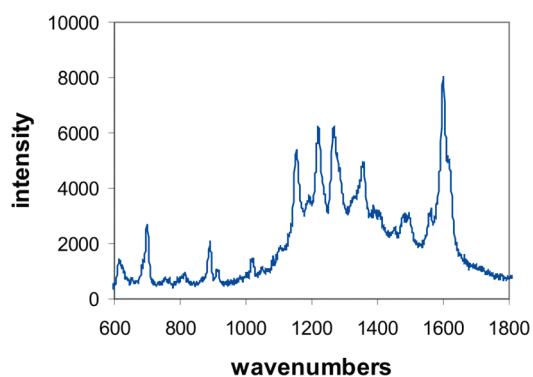


Figure 5. Raman spectra of PCz doped with perchlorate. [TBAClO₄] = 0.01M, [Cz] = 0.01 M, electropolymerization potential 1300 mV, electropolymerization time is 60 s in acetonitrile.

doped with various counterions. Two points are immediately discernible. First, it is obvious that the width of the low impedance range is highly dependent on anion for both polymers. Second, it is observed that in both cases, PSS⁻ and Ts⁻ exhibit the highest frequency-dependent impedance for most of the range probed. What might be considered the PSS⁻ monomer, tosylate (Ts⁻), leads to a smaller impedance magnitude at high frequency, but then, for PEDOP, climbs quickly to give the higher impedance. In addition, for PCz, PF₆⁻ also induces a higher impedance.

Inspection of the complex impedance plane graphs in panels b and d in Figure 6 allows for two additional observations. In several cases, the films do not present the cluster of points close to the real axis with a “capacitive tail” which were seen for the BF₄⁻ and, in the case of PEDOP, the films with PF₆⁻ and ClO₄⁻ counterions.

On the basis of the results reported by Takemura et al.,¹⁹ predicting specific interaction of the aromatic counterions and the heterolenes' π -electrons, one would expect that PSS⁻ and Ts⁻ might result in similar impedance behavior for the conducting polymers investigated here. PEDOP and PCz doped with PSS⁻ do, indeed, exhibit some similarities in their impedance behavior. It also is observed that the PSS⁻-doped polymers exhibit higher impedance compared to those doped with other anions. When these two polymers are doped with Ts⁻, comparison reveals a similar pattern both in terms of ohmicity and impedance magnitude. It is interesting that the high frequency impedance magnitude – the region more dependent on conduction along and between polymer chains – for polymers doped with Ts⁻ is more similar to that of the polymers doped with small inorganic counterions. Comparison across the inorganic counterions indicates a great deal of similarity, with a slight variation in the range over which ohmic behavior is observed for a given counterion-polymer combination. If, as postulated, this frequency independent behavior arises from a two layer morphology as we suggested previously,¹¹ this suggests that differences in anion produce

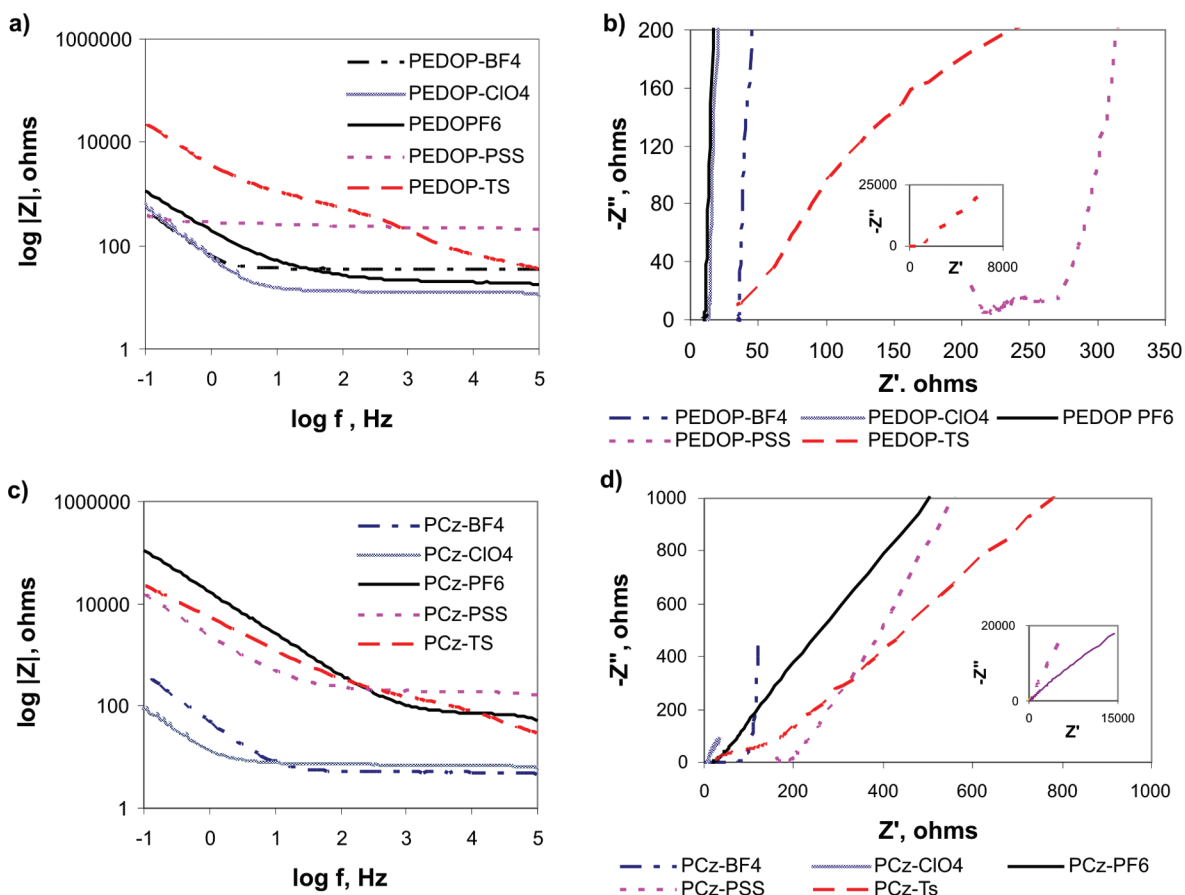


Figure 6. Effects of variation of counterion identity: (a, b) PEDOP and (c, d) PCz. Monomer concentration is 0.01 M, counterion concentration is 0.1 M, electropolymerization potential 1200 mV (PEDOP) and 1300 mV (PCz), electropolymerization time is 60 s in acetonitrile (BF₄ = tetrafluoroborate, ClO₄ = perchlorate; PSS = polystyrene sulfonate, PF₆ = hexafluorophosphate; TS = toluene sulfonate).

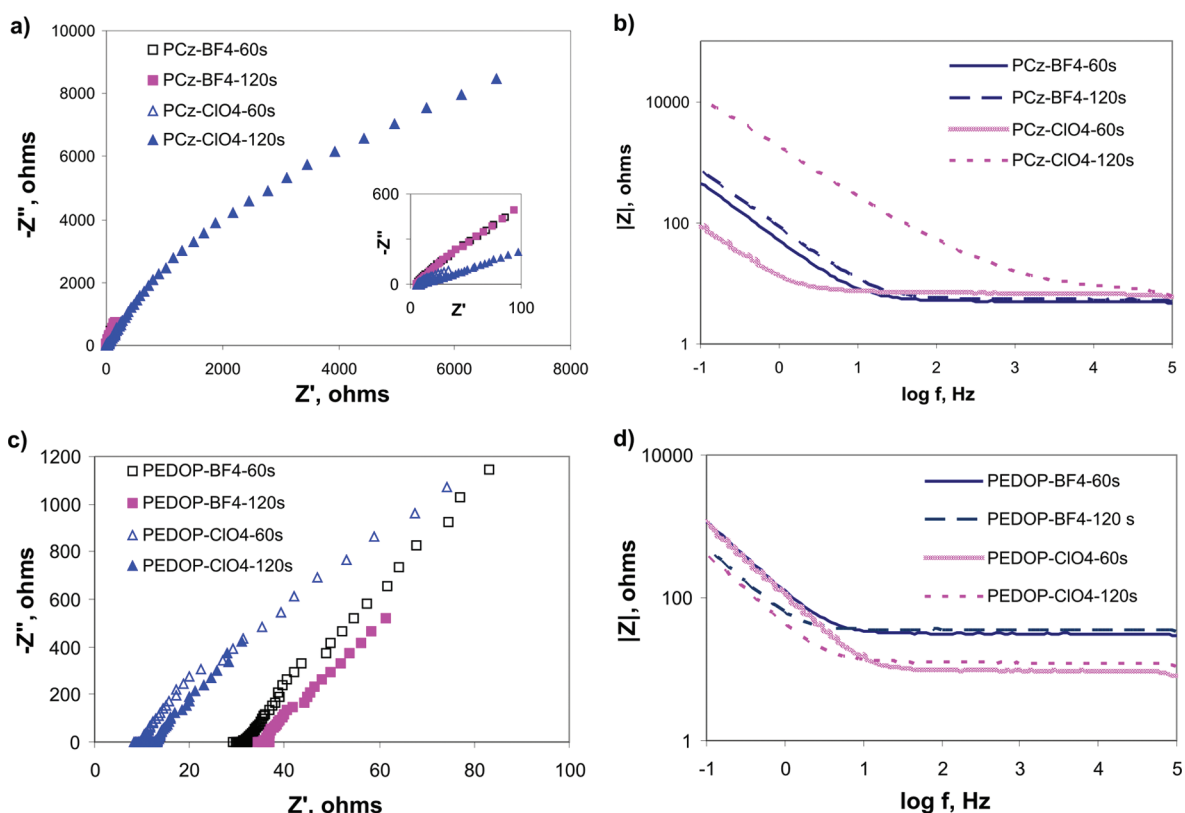


Figure 7. Impedance as a function of deposition time and counterion for PEDOT and PEDOP (~ 1.2 and ~ 2.5 μm , as determined by current passed and verified by SEM). Monomer concentration is 0.01 M, Counterion concentration is 0.1 M, electropolymerization potential 1200 mV (PEDOP) and 1300 mV (PEDOT), electropolymerization time and counterion are indicated in the legend for each curve (BF_4^- = tetrafluoroborate, ClO_4^- = perchlorate). Thickness for deposition time of 60 s was approximately 1.2 μm and for 120 s was approximately 2.5 μm .

differences in morphology of the compact layer (and thus conduction pathways available through it). Perchlorate and tetrafluoroborate appear to be the most promising counterions for PEDOP and PCz.

Effect of Heteroatom. With respect to the heteroatom identity, theoretical studies have suggested that the heteroatoms of conducting polymers have significant effects on their band gap.²⁰ Although the origin of these effects is not clear, some studies propose that the heteroatom may affect the polymers properties through the distortion of the chains and molecular packing.²¹ This proposal is supported by the results of studies showing that systematic alteration of the type of polymer backbone can be used to improve their electronic properties.²² It has been generally accepted that N-containing polymers tend to experience more distortion and thus lower conductivity.²³ However, the data of Table 1 suggest that optimization of counterion and polymerization time may result in comparable impedances to those for the sulfur-containing heterocyclic polymers.

Effects of Film Thickness on Impedance Behavior. On the basis of the proposed morphology, it might be argued that the films in which a narrower ohmic range is observed have a thinner porous layer. This would result in an impedance dominated by capacitive behavior starting at relatively high frequency. The frequency range characterized by ohmic behavior in PEDOT can be slightly extended by adjusting the thickness of the film (specifically the porous layer)¹¹ and it should be possible to optimize the relative thickness of the two layers to achieve ohmic range for PCz. Figure 7 shows the results for different deposition times for PEDOP and PCz films

doped with two different dopant anions, BF_4^- and ClO_4^- and for two different deposition times. The times were 60 and 120 s, leading to thicknesses of approximately 1.2 and 2.5 μm , based on both total current passed and on thickness estimations carried out by scanning electron microscopy. From Figure 7, it can be seen that the frequency range where ohmic behavior is observed slightly increased with an increase in the film thickness. This can be attributed to the increase in the relative thickness of the porous layer compared to the compact layer closest to the substrate, which extends the penetration length of anions from the bulk solution into the porous layer. The thickness of films which exhibit the desired behavior appears to be limited by the range over which homogeneity can be achieved.

It appears from Figure 7 that the impedance magnitude is more dependent on deposition counterion for PEDOP than on film thickness (within the optimum thickness range where these deposition times lie) for the high frequency. On the other hand, at lower frequency, where capacitive behavior dominates the impedance magnitude, the impedance becomes more dependent on film thickness than counterion. These data provide further support for the assertion in the postulated morphological model that the ohmic range is dominated by the conduction path due to solution electrolyte ions in the porous layer of the film.

Although the films investigated here are thicker than those investigated by Grzeszczuk, et al, the results reported here are consistent with their findings.^{24,25} At low frequency where capacitive behavior dominates the impedance behavior of the films, bulk solution ions have time to penetrate into the porous

layer. These findings are also consistent with their determination that electron transfer between layers in multilayer polypyrrole films dominates the behavior of the system. This behavior enforces the proposed existence of a compact layer which is minimally penetrable by bulk electrolyte ions, giving rise to the double layer capacitance at the compact/porous layer interface.

4. CONCLUSIONS

The impedance behavior of PEDOP electrodes was investigated and compared with that of PEDOT electrodes reported in earlier work, as well as initial studies for PCz. In addition, the effect of the substrate electrode used for deposition was probed. PEDOP electrodes, when doped with BF_4^- , PF_6^- , and ClO_4^- , and PCz electrodes, when doped with ClO_4^- exhibited ohmic behavior over a wide frequency range. It is worth noting that although ohmic behavior is desirable for sensing of low amplitude, low frequency signals, carried out at low or open circuit potential, it is undesirable for stimulation electrodes.²⁶

For the optimal dopant, PEDOP and PEDOT showed frequency independent impedance behavior over the range between a lower limit of 5–10 Hz and the upper limit of the instrumentation employed (100 kHz), whereas the window for polycarbazole extended over a narrower range. As was the case for PEDOT, PEDOP, and PCz films doped with PSS^- and TS^- exhibited the highest impedance magnitudes. This suggests that the effect of a small counterion size provides a greater benefit in this respect than that of the possibility of π – π interactions between deposition counterion and the conducting polymer.

Results of the investigation of the influence of film thicknesses support the previously proposed model. These studies suggested that there exists a certain distance within the film past which the moving ions from the bulk solution cannot freely travel. As such, they contribute to a double layer as they remain in close proximity with the holes (h^+) of the p-doped polymer. This acts in concert with the fact that hole transport is slower in this region as a result of decreased availability of the interchain interactions which provide alternate pathways for electronic conduction. Nevertheless, the frequency range for ohmic behavior can be slightly shortened or extended by adjusting the film thickness or more precisely the thickness of the porous layer.

Because, in theory, the two-layer morphology that is critical for this behavior can be achieved in various polymers by choosing the right counterion and electropolymerization conditions, an appropriate choice of monomer and monomer/dopant combination can be used to tune the impedance properties of conducting polymer films for use in applications which rely on capacitive vs faradaic charge injection or an optimal combination of the two. Studies are currently underway to determine the optimum overall thickness and relative compact-porous layer thickness that produces the desired resistive, capacitive, or mixed behavior for each of the polymer/substrate combinations.

The broad range over which PEDOP's impedance is frequency independent is intriguing. To date, the difficulty of synthesis and stability of the monomer²⁷ has limited research into its possible use in the design of bioelectrodes, but we anticipate that the properties described here may lead to further optimization of the synthetic routes for EDOP and the further testing of PEDOP as well other poly(3,4-alkylenedioxyppyroles).

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Notes

The authors declare no competing financial interest.

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