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Synthetic Metals xxx (2006) xxx-xxx



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A structural, electronic and electrochemical study of polypyrrole as a function of oxidation state

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8 Abstract

The electronic, structural, and chemical properties of polypyrrole doped with the hexafluorophosphate ion are investigated as a function of 9 oxidation state. These properties are found to be highly correlated; specifically, they all experience a rapid transition at approximately -0.1 V 10 versus SCE. The electronic conductivity of the film changes by two orders of magnitude through the transition potential, in the well-known doping-11 induced metal-insulator transition. Also at -0.1 V versus SCE, X_x ray diffraction and macroscopic actuation measurements reveal a structural 12 change in the polymer. Results suggest a loss of pi-stacking in the polymer crystals, and a reordering of the dopant ions in the matrix. The dopants 13 appear to exist in an isotropic liquid-like state in the highly oxidized film, changing to a channel structure at the transition point. This change in 14 structure is also consistent with the transition observed in the electrochemical impedance spectrum. The equilibrium charge on the polymer with 15 oxidation state is consistent with a constant de capacitance, however the ac impedance spectrum shows increased constant phase element behavior 16 in the reduced state. This could be due to a greater range of diffusion constants in the reduced state, which we associate with the heterogeneous 17 ion configuration. 18

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1 1. Introduction

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The conducting polymer, polypyrrole, has attracted a lot of 2 interest in recent years for its potential as a light-weight, linear 3 actuator or artificial muscle [1-4]. Electrochemical switching 4 5 of polypyrrole is capable of producing stresses 100 times that of mammalian muscle and it has been demonstrated that strains 6 [5] and specific powers [6] similar to those of muscle can 7 be achieved; however, the low strain rates (typically $\sim 1\%/s$) 8 and poor electromechanical coupling must still be improved 9 if conducting polymers are to be widely used. Despite much 10 progress in the design of polypyrrole actuators, the mechanisms 11 of actuation are still not well understood, which limits our 12 ability to further optimize their performance. The data presented 13 here help elucidate the mechanisms behind the electrochemical 14 actuation of polymers, and also have implications for the many 15 other conducting polymer applications relying on electrochemi-

2 doi:10.1016/j.synthmet.2006.04.004

cal switching, including supercapacitors [7] electrochromic devices [8].

The simplest picture of the electrochemistry of polypyrole is a distributed double layer capacitor. Electrochemical switching causes the conducting polymer chains to charge and discharge, and ions from solution move in and out of the polymer matrix to balance this charge. While the volume changes observed during switching have been widely attributed to the flux of ions [1-3,10], the full electromechanical response depends on a complex interconnection of the chemical, electrical and mechanical properties of the polymer [2,11], each of which is known to depend on the oxidation state of the polymer [12-17]. Changes in the electromechanical properties with oxidation state have been shown to dramatically affect the switching behavior of the polymer [18-21], and therefore must be taken into account in any complete model of the electrochemical and actuation behavior.

To this end, in this paper we fully characterize the electromechanical properties of polypyrrole doped with the hexafluorophosphate ion: the electronic conductivity, the structure of the polymer matrix and the electrochemical impedance are each measured as a function of oxidation state. We explore the implications of these results on the actuation behavior of polypyrrole.

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7 2. Experiment

Polypyrrole is polymerized through electrochemical oxida-38 tion of the pyrrole monomer using the method of Yamaura et 39 al. [22]. The electrolytic solution is composed of 0.06 M dis-40 tilled pyrrole, 0.05 M tetraethylammonium hexafluorophosphate 41 (TEA·PF₆) and 1 vol.% distilled water in propylene carbonate (reagents from Sigma-Aldrich). The solution is deoxygenated 43 by bubbling with nitrogen before growth. A polished, glassy 44 carbon crucible (from HTW) is used as the working electrode 45 and the counter electrode is a copper foil. The reaction occurs 46 at a constant current of 0.125 mA/cm² and a temperature of 47 -40 °C for 8 h to obtain a thickness of approximately 25 μ m. 48 All reagents are used as received, except for the pyrrole, which 49 is distilled to remove oligomers that form spontaneously in the 50 presence of light and oxygen. The distilled pyrrole is stored 51 under nitrogen in a freezer. After deposition, the polypyrrole 52 films are rinsed in pure propylene carbonate and air-dried on the 53 crucible. 54

For $\frac{de}{dt}$ conductivity and $\frac{d}{dt}$ ray diffraction measurements, 55 free-standing films approximately 1 cm wide and 3 cm long are 56 removed from the crucible and placed in a range of oxidation 57 states from fully oxidized (0.4 V versus SCE) to fully reduced 58 (-0.8 V versus SCE). The electrolyte used for this process is 59 0.05 M TEA·PF₆ in acetonitrile, which is bubbled in nitrogen 60 prior to the experiment to minimize parasitic reactions with 61 oxygen. In this study it is important for the films to be dry, 62 as the solvent also causes $X_{\overline{x}}$ ray scattering which may obscure 63 the polymer pattern. Acetonitrile has the advantage of a much 64 lower boiling point than propylene carbonate; films dry quickly 65 and can be characterized soon after cycling. The counter elec-66 trode is carbon-fiber paper and the potential was monitored using 67 a non-aqueous Ag/Ag+ reference electrode. This is only a quasi-68 reference electrode, and the potential drifted somewhat over time, therefore the reference potential was frequently checked 70 versus the standard calomel electrode (SCE). All potentials here-71 after are quoted versus SCE. All electrochemistry is performed 72 with a Solartron SI 1287 galvanostat/potentiostat. 73

The films are brought to the desired oxidation state poten-74 tiostatically. It is difficult to reduce free-standing films evenly 75 due to the increased resistance of the film in the reduced state; 76 therefore, to ensure a uniform oxidation state, the entire area of 77 the film was put in contact with an electrically conducting sub-78 strate. A working electrode consisting of the polypyrrole film 79 sandwiched in between a stainless-steel back plate covered with 80 carbon-fiber paper (TGP-H, Toray Industries Inc.) and a 70% 81 open stainless-steel mesh was created for this purpose, as shown 82 in Fig. 1. The carbon-fiber paper provides a good electrical con-83 tact with polypyrrole and the stainless steel simply provides the 84 mechanical contact between the carbon-fiber paper and the film 85 without impeding ion flow. 86

⁸⁷ The conductivity of the dry films is measured before and after ⁸⁸ potentiostatic redox with a four-point probe. Wide angle X_A ray ⁸⁹ scattering (WAXS) patterns of these films are then obtained with ⁹⁰ a Bruker AXS-D8 Advance diffractometer with a Sol-X SiLi ⁹¹ EDX detector. The source is Cu K α radiation with wavelengths ⁹² of 1.5406 and 1.5444 Å. The films are measured in transmission



Fig. 1. The working electrode configuration for even reduction of free-standing films. The polypyrrole film is sandwiched between a carbon-fiber paper covered stainless-steel back-plate and a stainless-steel mesh.

mode with the sample position fixed perpendicular to the X_{r} -ray 93 beam. The sample is placed in a vacuum chamber with Kapton 94 windows at a pressure of approximately 100 mTorr to eliminate 95 unwanted low angle scattering from air. The noise amplitude with the sample chamber under vacuum is negligible. Addition-97 ally, to increase the signal to noise, each film is folded over once 98 to get double the thickness, and at each angle, signals are aver-99 aged over 15–20 s. The WAXS patterns are normalized by the 100 thickness of the film. 101

The macroscopic changes in the dimension during switch-102 ing are investigated on a separate film from the same depo-103 sition using an Aurora Scientific Muscle Lever 300B-LR (http://www.aurorascientific.com/). The free-standing film is 105 clamped at the bottom, where electrical contact is made through 106 carbon-fiber paper, and the other end is attached to a lever 107 which applies a constant stress with a sensitive rotary motor and measures displacements down to 1/100th of a millimeter via a 109 capacitive displacement meter. The film is actuated in the same 110 acetonitrile solution using a potentiostatic square wave from 0.4 111 to -0.8 V while the length is monitored under a constant stress 112 of 1 MPa. The recorded actuation probably does not represent 113 the full volume change possible due to the large IR drop down 114 the film in the reduced state [23]. 115

The electrochemical impedance is also measured as a func-116 tion of oxidation state. Impedance spectroscopy is done with 117 a Solartron SI 1260 Impedance/Gain-phase Analyzer in con-118 junction with the SI 1287 Electrochemical Interface. The data 119 is collected and analyzed using the ZPlot software package. For 120 this measurement, a film is deposited for 30 min onto a working 121 electrode consisting of 300 nm of gold evaporated onto a silicon 122 wafer with a chromium layer to promote adhesion. Otherwise, 123 the polypyrrole deposition conditions are exactly as described 124 previously. In this configuration, the electronic resistance is 125 negligible compared to the ionic resistance; consequently the 126 diffusivity of the ions may be analyzed. After deposition, the 127 film is directly transferred to the acetonitrile solution. A cyclic 128 voltammogram is performed to relax the film and facilitate sol-129 vent exchange and then the impedance spectrum is measured 130 with an $\frac{10^{5}}{10^{5}}$ Hz model amplitude of 25 mV from 0.1 to 10^{5} Hz 131

under $\frac{de}{de}$ potentials of between 0.4 and -0.8 V. The film is stabilized potentiostatically between measurements.

134 3. Results

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135 3.1. Actuation

During the first cycle of actuation, there is an unrecover-136 able contraction of up to 10% of the original length, and an 137 irreversible loss of charge capacity in the polymer (as seen in 138 Fig. 4). Irregularities during the first electrochemical cycle are 139 quite common in polypyrrole actuators. The phenomena have 140 been collectively called the "first-scan effect" [24-26], which 141 has been attributed to polymer relaxation and solvent or ion 142 exchange. This effect will be considered further in the conduc-143 tivity and X_{r} ray diffraction studies. 144

Subsequent cycling of the polymer is stable and reversible. 145 Fig. 2 shows the stabilized actuation during a potentiostatic 146 square wave from 0.4 to -0.8 V versus SCE. During reduction, 147 the film first experiences a small contraction which may be due 148 to outflux of PF_6^- ions. The film then begins to expand at a rate 149 that is not proportional to the current. The expansion continues 150 long after the current is essentially zero, but is found to stop 151 immediately when the cell is open-circuited (not shown in the 152 figure). This result cannot be explained simply by the motion 153 of ions, solvent dragged along in the solvation shell, and osmo-154 sis. If PF_6^- is the only mobile ion as we expect, these effects 155 would all cause contraction during reduction, and even if the 156 TEA, ion were somehow mobile, the actuation would still stop 157 when the reduction was complete. When cycled to potentials 158 less negative than -0.1 V versus SCE, the film does not exhibit 159 this relaxation and in fact produces insignificant actuation even 160 though significant current flows. 161

We propose that the observed actuation behavior is caused
 by a change in interchain interactions with oxidation state rather
 than a simple swelling mechanism due to motion of ions. Spinks



Fig. 2. The actuation during potentiostatic redox in acetonitrile. The potential, the current and the strain are shown. The actuation shows only a small contraction on reduction, followed by a larger expansion which does not appear to depend on the current or the movement of ions.

et al. [4] found that the Young's modulus of polypyrrole was 165 decreased by 75% in the reduced compared to the oxidized 166 state, indicating that reduction causes a more plasticized state, or 167 decreased interchain interactions. With the film under tension, 168 this could cause an expansion during reduction. If the observed 169 expansion is caused by a decrease in stiffness, then these results 170 suggest that the stiffness is a rapidly varying function of charge 171 in the reduced state, i.e. the small amount of current flowing 172 in the fully reduced state causes a large expansion. It has been 173 shown that the conductivity increases rapidly with charge near 174 the reduced state [14], so perhaps it is not unreasonable to expect 175 rapid changes in other parameters such as the Young's modu-176 lus as well. The Young's modulus should be measured in future 177 experiments. 178

Note that these results are not typical for polypyrrole actu-179 ators in the literature. As discussed previously, the actuation 180 usually occurs in proportion to the charge [11]. The differences 181 identified in this experiment are: (1) the choice of solvent, (2) the 182 large potential range, and particularly, and (3) the long period of 183 the potentiostatic square wave. Propylene carbonate and water 184 are more common solvents for actuation. At large potentials and 185 long scans, films cycled in propylene carbonate also suffer a 186 reversal in actuation direction [27], therefore the combination 187 of long scans and wide potential ranges is likely associated with 188 this effect. 189

3.2. Conductivity

The as-grown conductivities of all of the films are fairly uni-191 form at (270 ± 25) S/cm. In this experiment, we investigate the 192 first-scan effect by comparing two sets of films at the same oxida-193 tion state. One set of films is potentiostatically reduced directly 194 from the as grown state. The second set of films is first stabi-195 lized by cycling twice with a potential square wave from fully 196 oxidized to fully reduced before being placed in the same set 197 of oxidation states. Fig. 3 shows the conductivity of these films. 198 Both sets show a sigmoidal conductivity versus oxidation state, 199



Fig. 3. The conductivity of polypyrrole films vs. potential during the first reduction from the as-grown state (circles) and after being cycled with a potentiostatic square wave from 0.4 to -0.8 V twice (triangles).

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Fig. 4. The charge on the polymer vs. potential during potentiostatic reduction from the as-grown state (circles) and after being cycled with a potentiostatic square wave from 0.4 to -0.8 V twice (triangles).

in agreement with the literature [12–14]. There is an inflection 200 point in the conductivity at approximately -0.1 V which charac-201 terizes the transition from the conductive to the non-conductive 202 state-the metal-insulator transition. The minimum conductiv-203 ity in the reduced state was measured to be (0.64 ± 0.2) S/cm, 204 considerably higher than the magnitudes quoted in the litera-205 ture [12,14], and 100 times larger than we have achieved with 206 similar films by reducing directly on the crucible. This is most 207 likely because of imperfect electrical contact with the substrate 208 during reduction. Notably, the cycled films never recovered 209 the high conductivity of the as-grown films. The charge as a 210 function of oxidation state of the films is shown in Fig. 4. It 211 is roughly linear as one would expect for a capacitor, with a 212 capacitance of approximately 0.22 F/mm³. Also shown is the 213 initial loss of charge during the first cycle. This could be part of 214



Fig. 6. The proposed unit cell for electrodeposited polypyrrole [28]. The rings are displayed edge on using rectangles. The chain length direction is b; the chains are close packed in the ring face to face direction, c; and ions are situated in channels between the chains in the a direction.

the first-scan effect, and may be related to the irreversible loss of conductivity in this cycle, and the initial contraction of the film. 215

The X-ray diffraction (XRD) patterns of the two sets of films 219 from the conductivity measurement are shown in Fig. 5. The 220 large amount of disorder inherent in the polypyrrole matrix 221 means the X_{r} ray peaks are broad Gaussians and the higher order 222 peaks are severely damped. Nogami et al. [28] provided the first 223 interpretation of this pattern; the unit cell is shown in Fig. 6. 224 The unit cell according to this model is monoclinic, with lattice 225 spacings a, b, and c equal to approximately 13.4, 7.3, and 3.75 Å, 226 respectively, and the angle, α is equal to 65°. The face-to-face 227 stacking distance is 3.4 Å and has been found to be very consis-228 tent for polypyrrole, regardless of the dopant ion. It is believed 229 that the chains are closely stacked in this direction due to pi-230 stacking in the oxidized state. Pi-stacking is a relatively strong 231 interchain interaction where unpaired electrons in the pi-orbitals 232



Fig. 5. The X-ray diffraction patterns of polypyrrole vs. potential after potentiostatic reduction from the as-grown state (a), and after being cycled twice (b). From top to bottom the potentials are: 0.4, 0.16, -0.08, -0.32, -0.56 and -0.8 V vs. SCE.

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are shared by ring molecules stacked on top of one another. Inter-233 chain coupling is thought to be important for metallic conduction 234 [29]. The amorphous peak, A = m Fig. 5 corresponds to an 235 intermolecular distance of 4.5 A. It was found to be completely 236 amorphous, even under stretching, and has been attributed to the 237 amorphous regions of the polymer [28]. The interchain spacing, 238 *a*, has been experimentally correlated to the ion size [22,30]; 239 it is thought that the ions reside in between the chains in this 240 24 direction.

Due to the poor crystallinity of the film, the peaks in Fig. 5 are
difficult to resolve, and accurate fits to the peaks are impossible.
Nonetheless, we observe certain systematic changes in the XRD

²⁴⁵ pattern with oxidation state. In both series of films:

- 246 1. The amorphous peak decreases monotonically in intensity247 with more cathodic potentials.
- 248 2. The crystal peaks do not appear to change until a transition
 249 at approximately -0.08 V.
- 250 3. At -0.08 V, the a^* peak rapidly increases in intensity and 251 broadens. It completely dominates the b^* peak which can no 252 longer be resolved at all. After this initial large increase, the 253 a^* peak gradually shrinks again.
- 4. The c^* peak begins to decrease below -0.08 V, eventually becoming the same height as the amorphous peak in the fully reduced state.
- ²⁵⁷ 5. All of the peaks appear to be smaller in the reduced state than
 ²⁵⁸ the oxidized state.

Comparison of the as-grown film at 0.4 V (a) and the cycled
film at 0.4 V (b) shows that the amorphous peak suffers a permanent decrease in intensity after the first cycle.

From these qualitative observations, we suggest the follow-262 ing transformations in the crystal structure. From 0.4 to -0.08 V, 263 the primary change in structure appears to be a decrease in the 264 intensity of the amorphous peak, while the crystalline peaks 265 are unchanged. This finding is not consistent with the amor-266 phous polymer interpretation of this peak as it is unlikely that 267 amorphous polymer would disappear, or even change greatly, 268 during reduction. However, the counter ions are leaving the 269 polymer in great numbers, and this will certainly be reflected 270 in the $X_{\mathbf{x}}$ ray scattering intensity. Based on the total charge in 271 272 the oxidized film and its volume, the ion concentration in the oxidized state is approximately 5 M. Assuming a completely 273 isotropic distribution of ions, the average radial distance between 274 ions is calculated to be 4.3 Å—very close to the observed d of 275 the amorphous peak, 4.5 Å. An isotropic distribution of ions 276 could explain the loss of intensity in the amorphous peak during 277 reduction. Conversely, if the ions were in regular lattice posi-278 tions, the crystal peaks should lose intensity during reduction, 279 which does not appear to be the case. In the fully reduced state, 280 there is some remaining intensity in the amorphous peak. There 281 should be few ions left in the film, therefore this intensity may 282 be due to amorphous regions of the polymer as put forward by 283 Nogami. Experiments with stretch-aligned films in the reduced 284 state should provide more light on the origin of this peak. 285

At -0.08 V, there is a large increase in the amplitude of the a^* peak, where we expect from the Nogami model to find the ion scattering. From the previous results, we showed that at high concentrations the ions appear to be in an amorphous configuration. At intermediate concentrations, however, the ions may take up more ordered positions in the crystals and move into the channels predicted by Nogami. This would explain the increase in intensity of the a^* peak. A similar "order–disorder" transition of the dopant ion positions has been clearly observed in the more crystalline conducting polymer, polyaniline [31]. Fig. 4 shows that further reduction after this transition causes the a^* peak to decrease monotonically in intensity as expected for a decreasing ion concentration. In the fully reduced state, the amplitude of the a^* peak is approximately the same as in the fully oxidized state which also supports the theory that the ions are not in crystalline positions in the oxidized state.

At -0.08 V, the c^* peak begins to decrease in amplitude. In Nogami's model, this peak is due to the pi-stacked rings of polypyrrole. Pi-stacking should not occur in the neutral state because there are no excess electrons to share; therefore, the decrease in amplitude of this peak upon reduction could be due to loss of pi-stacking, with an accompanying decrease in interchain order. The b^* peak is difficult to track due to considerable overlap with the other peaks, but it is also smaller in the reduced compared to the oxidized state. This peak is the characteristic intrachain repeat unit and could be decreased by changes in the order of the chain as well. As we discussed previously in the actuation section, a loss of pi-stacking could also be responsible for the changes in the macroscopic mechanical behavior at -0.1 V. This may be a link between the microscopic and macroscopic structures.

The other large change in the pattern to note is the difference between the 0.4 V film in Fig. 5(a) and (b). The reoxidized film does not recover the large amorphous peak seen in the as-grown film. This could be partly due to the initial loss of charge when a film is cycled the first time, although this is difficult to estimate quantitatively because of poor fits to the X-ray patterns. Another possibility for the change in this peak is solvent exchange. The XRD pattern for propylene carbonate is shown in Fig. 6 has a characteristic amorphous peak at 19°, the same position as the amorphous peak in the pattern of polypyrrole grown in propylene carbonate. Propylene carbonate has a boiling point of 240 °C, and a good deal remains in the air-dried films. Madden showed that there was a 20% loss of mass during vacuum drying of a previously air-dried polypyrrole film at 90 °C [32]. The remnant propylene carbonate is displaced by acetonitrile during cycling, which dries much more readily. It is clear that many organic materials have a similar amorphous spacing and care must be taken in identifying the origins of the amorphous peak.

Because the peaks are poorly resolved, we cannot comment on any shifts in the positions of the peaks which would result from an expansion or contraction of the unit cell, so we are unable to directly correlate the microscopic structure with the changes in volume of the film. For example, an expansion of 10% in the length of *a* corresponds to a shift of only 0.5° in the position of peak a^* , which is well below the accuracy of our fit to this peak position (Fig. 7). 6

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Fig. 7. The X-ray diffraction pattern of propylene carbonate shows a large amorphous peak at approximately 19° . The sharper peak at 22° is due to the sample holder.

344 3.4. Electrochemical impedance spectroscopy

The electrochemical impedance spectrum is found for oxidation states from 0.4 to -0.6 V and is shown in Fig. 8. The impedance spectrum could not be found at -0.8 V due to a large parasitic current that occurs on the gold substrate at this potential and causes delamination of the film.

The impedance of the film in this geometry is typically modeled as a distributed RC network as shown in Fig. 9 [33–36]. The model treats the polymer as an ion permeable network at the molecular scale, and is most easily understood as capacitive charging down "pores" in the polymer as shown in Fig. 9. The



Fig. 8. The electrochemical impedance of a thin polypyrrole film on a gold substrate as a function of oxidation state. The impedance is constant with oxidation state until approximately 0 V, where there is a transition to a more restricted diffusion of ions, characterized by a decrease in slope of the low-frequency portion of the spectrum.



Fig. 9. The single pore model of polypyrrole charging. R_S is the solution resistance, c_S is the unit surface capacitance, r_i is the ion resistance, and c is the unit volumetric capacitance.

electronic resistance is negligible compared to the ionic resistance in this experimental geometry therefore it is left out. The model is simplistic, but qualitatively correct and provides a good fit to the data.

From Fig. 8, we see that the high-frequency response of the 359 impedance is a skewed semi-circle in the complex impedance 360 plot. This is due to the solution resistance and the double-layer 361 capacitance on the surface, as well as the ion transport through 362 the film. The low-frequency response is a near vertical line 363 in the impedance plot, which is indicative of the volumetric 364 capacitance. The volumetric capacitance is typically modeled 365 as a constant phase element (CPE) rather than a pure capaci-366 tor to account for the dispersion of this line. From Fig. 8, we 367 can see that the impedance of the film is fairly independent of 368 potential until between 0 and -0.2 V, where it suffers a large 369 change in the slope of the low-frequency constant phase ele-370 ment behavior. This may indicate greater inhomogeneity in the 371 ionic diffusion coefficient in the reduced state as the slope of 372 a CPE is typically related to a distribution of diffusion coeffi-373 cients or the "porosity" of the film [17]. It is significant that 374 this transition occurs at the same potential as the order-disorder 375 transition observed in the $X_{\overline{k}}$ ray diffraction data. A transition 376 from an amorphous ionic distribution to a channel distribution 377 could cause such dispersion in the diffusion coefficient. It is 378 likely that in the channel conformation, the ions would see 379



Fig. 10. A relationship between the electronic, structural and chemical properties of polypyrrole during reduction.

a higher diffusion coefficient within a channel than betweenchannels.

382 4. Discussion and conclusions

- At approximately -0.1 V versus SCE we observe:
- A metal-insulator transition in the electronic conductivity of the polymer.
- A change in actuation behavior: scanning to potentials lower than -0.1 V causes a small contraction and a large expansion for small charge transfer. Less cathodic potentials cause little actuation.
- A change in the crystal structure of the polymer: observed changes may represent a transition from an amorphous ionic state to a state where the ions exist in channels between polymer chains, and a decrease in pi-stacking between chains.
- A change in the electrochemical impedance: the dispersion of the low-frequency constant phase element increases.
- The charge versus potential is approximately linear at all potentials, indicating a constant de capacitance.

These results suggest some associations between the properties which we present in Fig. 10.

During reduction, the concentration of unpaired electrons 400 on the polymer chains decreases, as does the concentration of 401 anions in the matrix balancing the charge. Unpaired electrons 402 are required for pi-stacking, which has been associated with 403 the interchain conductivity and the tough mechanical properties 404 characteristic of conducting polymers. A decrease in pi-stacking 405 with reduction thus seems reasonable and may be the cause of 406 many of the observations in this study: the decrease in the c^* 407 peak (ring face to face spacing) in the $X_{\mathbf{x}}$ ray diffraction pattern, 408 the decrease in the conductivity, and the macroscopic expan-409 sion in the film. It may also explain the decrease in Young's 410 modulus during reduction observed in [4]. The change in micro-411 scopic structure due to interchain interactions and decreased 412 anion concentration also includes a transition from an isotropic 413 distribution of anions to a channel structure. This, in turn, affects 414 the ionic conductivity as seen in the electrochemical impedance 415 spectrum. 416

More investigation is required to definitively resolve the
cause and effect relationships between the electronic, structural
and electrochemical properties; however, it is clear from the
results of these experiments that they are strongly correlated.
Understanding the associations between these inter-related polymer properties should greatly simplify the analysis and design
of these complex systems.

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