

Polypyrrole operating voltage limits in aqueous sodium hexafluorophosphate

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ABSTRACT

Actuation of polypyrrole in aqueous sodium hexafluorophosphate solution has been shown to produce relatively large strains. However little has been published on appropriate potential range of actuation in this electrolyte. This information is clearly crucial for applications. Our particular interest is in disposable applications where a relatively small number of cycles are needed, and maximum strain is desired. The electrochemical degradation as a function of voltage is investigated by cycling the film between fixed voltages and measuring the charge transfer. The experiment was done on a glassy carbon substrate in order to reduce effects of change in resistance with oxidation state, preventing actuation. The dependence of charging on voltage and the rate of reduction in the extent of charging are measured. The voltage range for effective operation of the device was found to be -0.4 V to 0.8 V versus a Ag/AgCl reference electrode in order to achieve stable performance over at least 30 minutes. The mechanisms of degradation at potentials beyond 0.8 V appear to be the substitution of hydroxyl ions in the polymer backbone, as suggested in reports on degradation of polypyrrole in other electrolytes. An observed reduction in charge transfer rate at potentials lower than -0.4 V is consistent with a reduction in ionic conductivity at highly reduced states, as has also been suggested in the literature.

Keywords: Polypyrrole, voltage range, degradation

1. INTRODUCTION

Conducting polymers such as polypyrrole have been recently used in actuator technology due to their attractive characteristics. These materials are lightweight, inexpensive and can generate large strain [1-4]. Polypyrrole and other conducting polymers can also be driven electrochemically by low operational voltages. In order to determine the range of applications that are appropriate, a key factor is the electrochemical stability of conducting polymers, which in turn will determine lifetime.

In this paper actuation of polypyrrole in aqueous sodium hexafluorophosphate is studied and the electrochemical degradation as a function of voltage is investigated. Actuation of polypyrrole in aqueous sodium hexafluorophosphate solution has been shown to produce relatively large strains (~ 6%) [5]. Our particular interest is in disposable applications where a relatively small number of cycles are needed, and maximum strain is desired.

This study involves cycling a polypyrrole film within various voltages inside an aqueous electrolyte and analyzing the film response. The dependence of polymer charging on voltage and the reduction in the extent of charging as a function of applied voltage are measured. Since conducting polymer strain is proportional to charge [6], degradation in strain and in charge transferred into the polymer are also correlated, as has been found experimentally in [7]. Therefore the results of charge measurement give direct information about the polymer induced strain in response to the voltage increase.

2. EXPERIMENT

A polypyrrole film was investigated as the working electrode in an electrochemical actuation process. The goal is to study the proper voltage range in which polypyrrole actuators can work effectively. The experimental set up consists of working, counter and reference electrodes inside an aqueous solution of NaPF_6 . The reference electrode used in this experiment is a Ag/AgCl electrode. Polypyrrole films were electrochemically deposited onto two glassy carbon substrates which are then used as working and counter electrodes.

Polypyrrole deposition was done by polymerizing the pyrrole monomer through electrochemical oxidation using the method of Yamaura et al. [8]. The electrolytic solution is composed of 0.06 M distilled pyrrole, 0.05 M tetraethylammonium hexafluorophosphate and 1 % of solution volume distilled water in propylene carbonate (from Sigma–Aldrich). The solution is deoxygenated by bubbling with nitrogen before growth. A polished, glassy carbon substrate is used as the working electrode and the counter electrode is a platinum coated glass slide. The reaction occurs at a constant current of 0.125 mA/cm^2 and a temperature of -30°C for 6 hours to obtain a thickness of approximately $10 \mu\text{m}$.

Having the glassy carbon substrate as a backing electrode for the Polypyrrole film ensures good electronic conductivity during cyclic experiment. Reversible reduction in electronic conductivity due to change in oxidation state can lead to a slowing of response [9] which can be mistaken for degradation. The use of the conducting substrate reduces the impact of this effect.

2.1 Over-oxidation

Polypyrrole as an actuator is usually used in bilayer or trilayer structures where a sequence of potential is applied to actuate the structure. Our particular interest is in actuating a trilayer back and forth for a number of cycles.

In order to investigate the rate of reduction in the extent of charging in response to different oxidation states, the following experiments were performed:

1. A fixed 0.2 V potential was applied to the working electrode for 20 minutes to bring the polypyrrole film to this oxidation state.
2. A series of square waves from 0 to 0.2 V with the cycling period of 100 seconds were applied between the working and Ag/AgCl reference electrode and the current was monitored (see Figure 1a & 1b). The amount of charge transferred during experiment 2 is calculated from these data and will be used later as a comparison to investigate charge transfer reduction.
3. At this point the incremental cycling experiment is begun:
 - a. Step 1 is repeated (0.2 V for 20 minutes).
 - b. Twenty cycles of a square wave from 0 to $v_1=0.25 \text{ V}$ are applied to the working electrode with a period of 100 seconds.
 - c. Experiment 2 was repeated.
4. Continue experiment 3 by incrementing the cycling amplitude (from v_1 to $v_1+0.05\text{V}$) of step b until the maximum voltage reaches 1V.

Figure 1c shows the first 5 cycles of 0 to 0.8 V cycling, applied to the working electrode and Figure 1b illustrates its corresponding current. The 0.2V square wave of Experiment 2 was reapplied after each cyclic experiment in order to investigate the effect of increase in voltage on the extent of charging. This is done by comparing corresponding charge transfers after each cycling.

Figure 2 shows Polypyrrole charging during the last cycle of each cyclic experiment. We can see from Figure 2a that the amount of charge transferred during the incremental cyclic experiment is increasing with voltage up to 0.8 V; and according to the plot of Figure 2b it decreases dramatically at 0.9V and 1V. During the last cycle the charge amplitude falls by $\sim 70\%$ at 0.9V and by about 90% at 1V. This suggests that polymer charge transfer degradation had occurred at 0.9V. It is known from the literature that overoxidation and degradation of Polypyrrole starts when hydroxyl groups attack the positive charges on the polymer backbone [10]. Oxidation of hydroxylated product yields carbonyl-substituted structures, which have been identified by the use of IR spectroscopy [10-11].

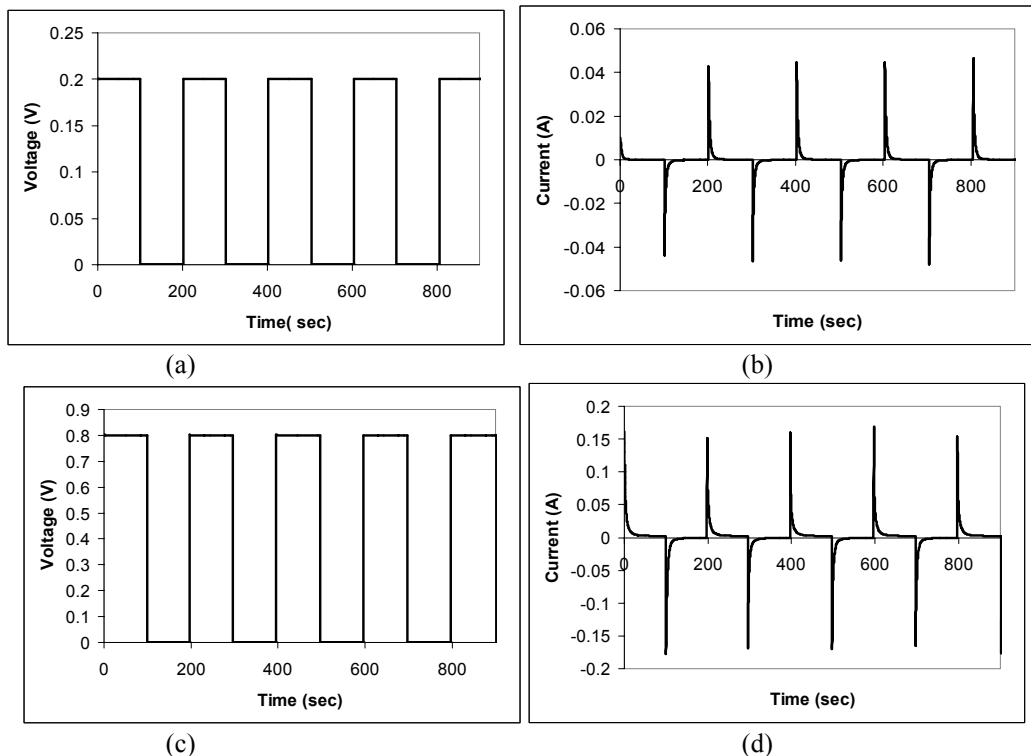


Figure 1: a & c Voltage cycling showing 4.5 of 20 cycles, b & c corresponding currents.

At 0.2V cycling shown in Figure 2a, the amount of charge transferred on the last cycle was ~ 0.1 C. Assuming the polypyrrole in this form acts like a capacitor [12], the expected charge transfer at 0.8 V cycling is ~ 0.4 C. In fact at 0.8 V cycling the measured charge was 0.73 C. This excess charging is due to the parasitic charge which is also increasing with the voltage, as is clear in Figure 3, which shows the total charge during cycling to the higher voltages.

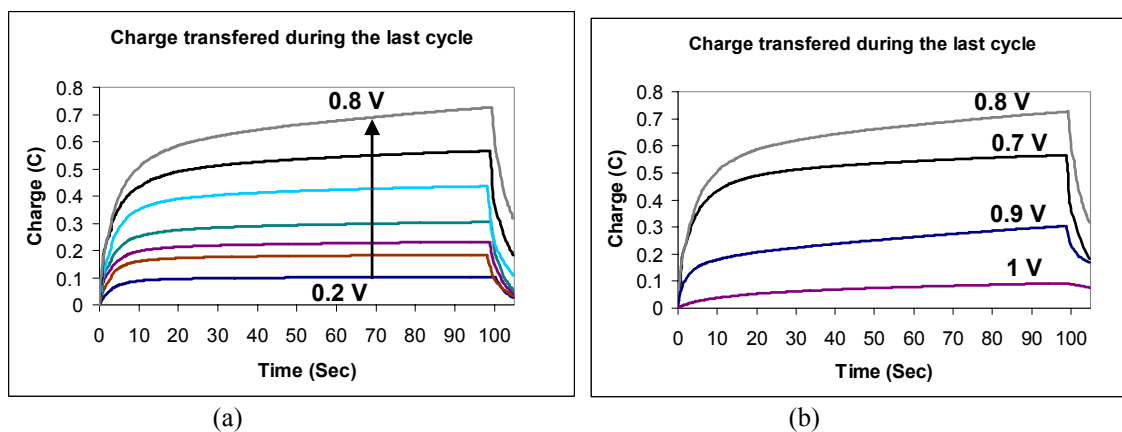


Figure 2: Polypyrrole charging during the last cycle of each cyclic experiment, a) $v_1=0.2\text{V}$ to 0.8V . b) $v_1=0.8\text{V}$ to 1V

The drift observed in charge in Figure 3 is very likely due to kinetics limited reactions that occur at high voltages. At 0.9 V the charge passed through the polymer during the first two cycles is still increasing, however it starts decreasing over cycles and as shown in Figure 2b, it drops significantly during the last cycle. There is an obvious reduction in the amount of charge transfer at 0.95 V and 1 V cycling suggesting the degradation of the polymeric structure.

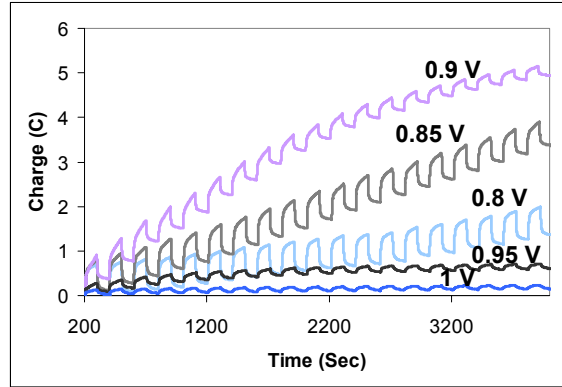


Figure 3: Polypyrrole charging over entire cycles

As was mentioned a sequence of 0 to 0.2 V steps was applied after each incremental cyclic experiment. Comparing the amount of charge transferred after each incremental cycling of this experiment also shows charge reduction at 0.9 V. Figure 4 illustrates charge reduction behavior after charging (i.e. 0.2 V) and discharging (i.e. 0 V). The result presented in Figure 4 shows that cycling the Polypyrrole film at voltages below 0.8 V results in relatively constant charge transfer at 0.2 V cycling. This means that voltages smaller than 0.8 V do not cause noticeable degradation in polypyrrole charge transfer. We can see that the amount of charge transfer decreases by $\sim 30\%$ at 0.85 V and by $\sim 70\%$ at 0.9 V.

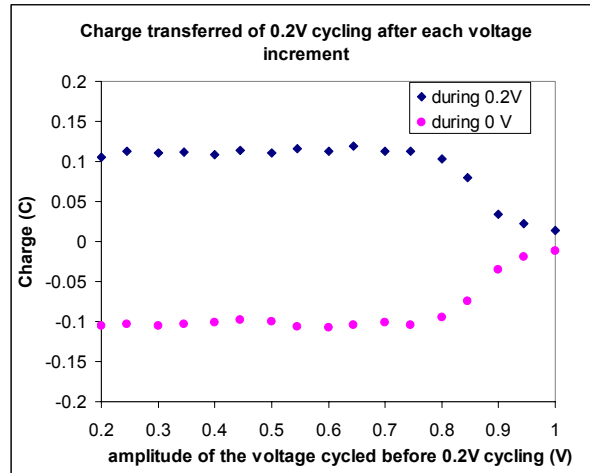


Figure 4: charge transfer at 0-0.2V cycling after each incremental cycling experiment.

The drop in charge transfer at 0.2 V cycling corresponds quite closely with that observed during actuation at higher voltages. This can be seen in Figure 5 where the polymer capacitance in these two cases are plotted using the measured charge of Figures 2 and 4. The parasitic charges have been subtracted from the total charge shown in Figure 2 in the capacitance plot of this figure. The parasitic charges have been estimated using the current versus time plot (see Figure 1c & 1d). It was assumed that the polymer was completely charged during the period of 100 seconds, and the current responsible for charging the polymer capacitor ideally reaches to zero at the end of each cycle. Therefore any excess current (i_p) at the time $t=100$ seconds could represent parasitic charge of $q_p = i_p \times t$.

According to Figure 5, polypyrrole volumetric capacitance is between $3 \times 10^8 \text{ F/m}^3$ to $4 \times 10^8 \text{ F/m}^3$ at low voltages. The capacitance measured from 0.2 V cycling drops steeply beyond 0.9 V cycling. The capacitance measured from incremental cyclic experiment starts from $3.4 \times 10^8 \text{ F/m}^3$ and begins to increase slightly at 0.6 V and shows a peak at 0.85 V. This increase in capacitance may be due to underestimation of parasitic charges at high voltages. More accurate separation of parasitic effects is needed in order to achieve the precise volumetric capacitance at highly oxidized states. However this plot still shows the capacitive degradation behavior of polypyrrole matches that of 0.2 V cycling. Both

plots show that volumetric capacitance starts decreasing at 0.9V and suggest that irreversible degradation of the polymer is occurring.

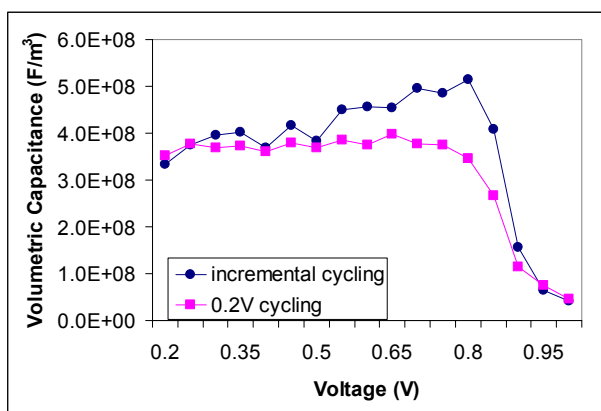


Figure 5: volumetric capacitance of Polypyrrole versus the applied voltage

2.2 Over-reduction

The ionic conductivity across the polypyrrole film depends on the electrolyte concentration but also on the degree of oxidation of the film. Also it is believed that in a strongly reduced state, the ions diffuse more slowly than in an oxidized and relaxed state [13, 14, 15]. In order to investigate this effect another set of experiment was performed where the polypyrrole film was initially cycled between 0 and 0.2 V, and then was cycled at reduced states, following the same steps as before but incrementing the voltage, v_1 , negatively. The film was again cycled between 0 and 0.2 V to see if there is any change in the amount of charge transferred after being reduced.

The resulting charge transfer at different reduced states is shown in Figure 6. We can see from Figure 6a that the amount of charge transferred during 0 to -0.3 V cycling was about -0.15 C. This amount increases to -0.24 C at -0.4 V cycling and seems to stay constant as the cycling amplitude increases. According to Figure 6b the amount of charge transferred is smaller during cycling at more negative voltages. A relatively large charging delay is also observed at reduction potentials (see Figure 6). Since the strain in conducting polymers is approximately proportional to the amount of charge transfer, this delay results in a small strain at short cycling periods (i.e. high frequency).

It is possible that low ionic conductivity of polypyrrole at highly reduced state explains the reduction in charge transfer beyond -0.6 V. So the effect shown in Figure 6 could be due to a change in the polymeric structure which prevents (or at least dramatically slows) subsequent ions from diffusing into the polymer. It could also be due to irreversible degradation. This will be discussed more in the following paragraphs.

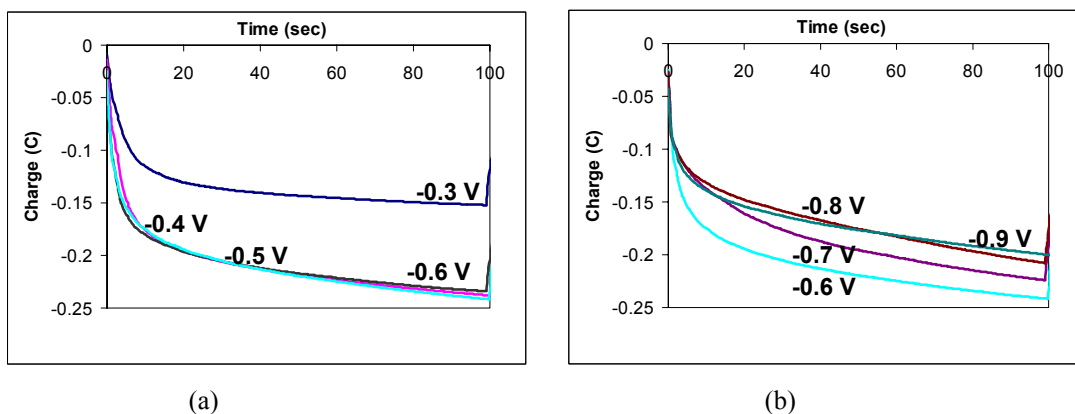


Figure 6: Polypyrrole charging during the last cycle of each cyclic experiment, a) $v_1 = -0.3$ V to -0.6 V. b) $v_1 = -0.6$ V to -0.9 V

Figure 7 shows the amount of charge transfer during 0 to 0.2 V cycling after the polymer had been cycled to various reduced states. This experiment helps determine the effect of cycling at negative voltages on the polymer charging characteristics. The plot in Figure 7 shows relatively fast response for initial polymer charging when applying 0 to 0.2 V cycles. After being cycled between 0 and -0.5 V, the polymer charging rate at 0.2V is less steep and as a result the polymer is not fully charged at the end of cycle. This effect is more obvious after larger negative cycling. Warren and Madden have reported a relatively linear relationship between charge and potential within the voltage range of -0.8 V to 0.4 V and with the cycling period of 700 seconds and more [12]. The effect seen in Figure 7 could be due to the short cycling period during which the polymer is not fully charged. A drift in charge was also observed during the 0.2 V cycling experiments after polymer reduction, which did not stabilize over cycles. This also supports the idea that the charging was not complete after 100 seconds and structural degradation is less likely to happen. Otero *et al.* suggested that higher oxidized potential is required to recover highly reduced polymer [19]. It is likely that the polymer structural change which appears to cause the low ionic conductivity at highly reduced states has not been fully reserved during the 0 to 0.2 V cycling. The polymer is not degraded, but rather transport has slowed, leading to a reduction in charge transfer.

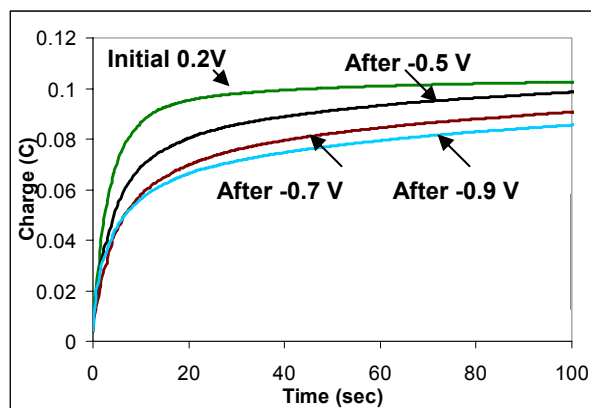


Figure 7: charge transfer at 0-0.2V cycling after each incremental cycling experiment

3. CYCLIC VOLTAMETRY

As was discussed in previous sections, over-oxidation of Polypyrrole inside Aqueous solution of NaPF_6 results in structural degradation at +0.9 V, and its over-reduction seems to reduce the ionic conductivity dramatically at voltage < -0.6 V. In order to confirm these observations cyclic voltammetry was performed on a 10 μm thick polypyrrole film on a glassy carbon versus Ag/AgCl reference electrode. The scan rate was 1mV/s and the voltage range was from -0.8 V to +0.9 V. Figure 8 shows sequential voltagrams generated from this experiment. Polypyrrole acts as a capacitor from -0.2 V to 0.4 V. There is a peak at -0.4 V which drops in amplitude. A similar cathodic peak is observed by others and appears to result from a transient exchange of ions and solvent when the film is first cycled [17-18]. At 0.4 V the current rises steeply, suggesting a kinetics limited parasitic reaction. Presumably this reaction is the same reaction that is degrading the polymer. This current peak is decreasing every cycle, suggesting degradation. In fact the entire CV decreases in amplitude, as would be expected from a reduction in the redox activity. At extreme negative potentials (< -0.4 V) redox activity decreases even more dramatically. This drop is consistent with the results shown in Figure 6 which showed that at higher reduced state the amount of charge transferred is limited. As was discussed in section 2.2 this effect could be due to either reduction in ionic conductivity at highly reduced state or the short cycling period resulting in an incomplete charging, or a combination of both of these effects.

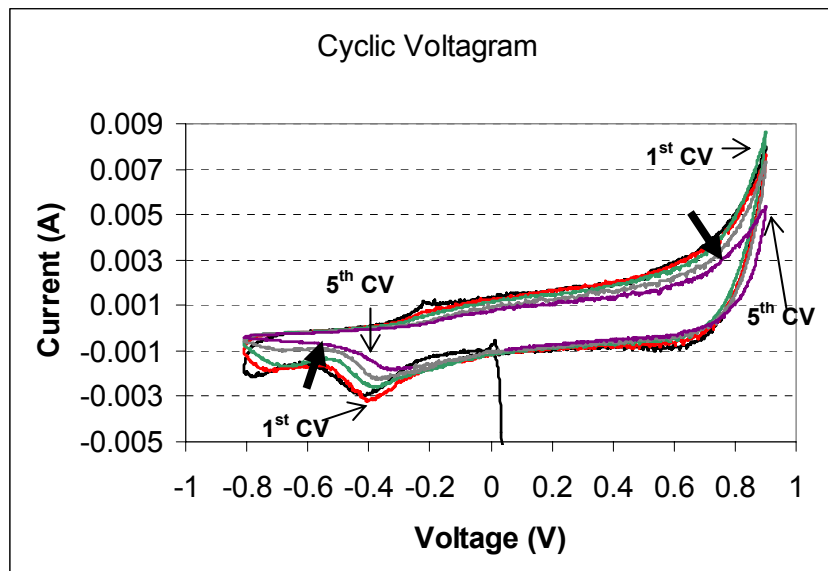


Figure 8: Cyclic Voltammogram of polypyrrole inside 1 M of AQ-NaPF₆. Arrows indicate the time sequence.

DISCUSSION AND CONCLUSIONS

The electrochemical degradation of polypyrrole inside AQ-NaPF₆ as a function of voltage was investigated by stepping the polymer film between fixed voltages and measuring the charge transfer. The dependence of charging on voltage and the rate of reduction in the extent of charging were measured. The result of cycling shows that polypyrrole acts as a capacitor from 0.2 V to 0.8 V. At 0.85 V the amount of charge transferred through the polymer structure decreased by ~ 30% and dropped further to ~ 70% at 0.9 V. According to the charge plots there is not a noticeable increase in the time constant with the voltage at oxidized states. The CV plots also showed a steeply rising current at 0.9 V. These results are consistent with an irreversible degradation of the polymer redox capacity which results from parasitic reactions that are rapid at voltages of > 0.8 V. The mechanisms of degradation at potentials beyond 0.8 V appear to be the substitution of hydroxyl ions in the polymer backbone, as suggested in reports on degradation of polypyrrole in other electrolytes [10-11]. The result of stepping voltage to reduced states suggested a reduction in polypyrrole ionic conductivity at voltages less than -0.4 V. This reduction in activity at low voltages is confirmed by the CV plot where the amount of charge transfer decreases at reduced states. This effect could be due to a change in the polymeric structure which dramatically slows subsequent ions from diffusing into the polymer. Polymeric degradation at reduced states cannot be ruled out. However the 0.2 V amplitude cycling experiments suggest that charge is gradually recovered. Unfortunately we did not wait long enough to see if full recovery is achievable.

The voltage range for effective operation of the device was found to be -0.4 V to 0.8 V versus a Ag/AgCl reference electrode in order to achieve stable performance over at least 30 minutes.

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