Study of overoxidized polypyrrole using X-ray photoelectron spectroscopy

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Overoxidation of polypyrrole was carried out electrochemically and studied by X-ray photoelectron spectroscopy. It is shown that overoxidation starts on the polymer adjacent to the electrode and then advances to the polymer facing solution. During overoxidation, original positive charges on polypyrrole ($-NH^+-$) are mostly replaced by –NH–, accompanied by the loss of counterions. Overoxidation progresses in two steps. Carbons are oxidized into C–OH in the first step and into C=O in the second step. Changing the pH of the media and increasing the potential have no significant effects on the degree of overoxidation in the range studied.

(Keywords: polypyrrole; overoxidation; X.p.s.)

INTRODUCTION

Overoxidation of polypyrrole (PPy) at high potentials has been reported by many researchers[1–3]. In contrast to reversible oxidation of PPy accompanied by doping, overoxidation is an irreversible process. It has been reported that during overoxidation, PPy loses its electroactivity, changes colour and undergoes an increase in film thickness[4]. Overoxidation has often been regarded as an undesirable process[1–3,5,6]; however, it has been used for various purposes. It has been shown that overoxidized PPy can exclude anions[7] to form ion-selective and porous membranes[8]. Preconcentration of chromate using overoxidized PPy membrane has been reported previously[9]. Overoxidized PPy films have been characterized by *FT*i.r.[4], cyclic voltametry[3,7,8] and ellipsometry[4]. However, there have been no detailed mechanistic studies of overoxidation of conducting polymers using X-ray photoelectron spectroscopy (X.p.s.), even though X.p.s. has been used extensively for structural analysis of PPy[10–18]. In this paper, overoxidation of PPy was performed electrochemically using various potentials, times and solution pH values. The overoxidation process was studied by X.p.s.

EXPERIMENTAL

Reagents and materials

All chemicals were of analytical grade unless otherwise stated. Pyrrole (Merck) was distilled before use. An aqueous solution of 0.1 mol l^{-1} pyrrole and 0.1 mol l^{-1} $NaClO_4$ was used for electrochemical polymerization of pyrrole. A 0.1 mol l^{-1} $NaClO_4$ aqueous solution was used for electrochemical overoxidation of PPy. $HClO_4$ and NaOH were employed to adjust the pH of the solution for overoxidation. Gold foil (Aldrich) was cut into 1.0 cm × 0.7 cm pieces, cleaned with chromic acid and then rinsed with distilled water. PPy was electrodeposited on these pieces in an area of 0.7 cm × 0.7 cm.

Instruments

Electropolymerization of pyrrole and electrochemical overoxidation of PPy were carried out using a PS-07 polarization unit (Toho, Japan). All potentials were measured against an Ag/AgCl reference electrode. A stainless steel tube was used as a counter electrode. Chronoamperograms were recorded on a Rikadenki X-Y recorder (Japan). The X.p.s. measurements were made on a Kratos Analytical XSAM800 spectrometer with an MgKα X-ray source (1253.6 eV photons).

Procedures

PPy was electrodeposited galvanostatically on gold films with a current density of 0.5 mA cm^{-2} for 60 s in a 0.1 mol l^{-1} pyrrole and 0.1 mol l^{-1} $NaClO_4$ solution. The polymer film was rinsed with water and then dried in a nitrogen stream. Overoxidation of PPy was performed potentiostatically at 1.3 V for 120 s in 0.1 mol l^{-1} $NaClO_4$, unless otherwise stated.

In order to obtain X.p.s. spectra of PPy on the electrode side, the samples were carefully detached from the gold foil and mounted on standard sample studs by means of double-sided adhesive tape. To avoid possible denaturing of PPy, no sputtering was performed before taking spectra. The X-ray source was run at 12 kV and 15 mA.

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The pressure in the analysis chamber was maintained at or below 2.66×10^{-6} Pa during measurements. All binding energies were referenced to the C1s neutral carbon peak at 284.6 eV to compensate for surface charging effects. Deconvolution of the spectra was carried out by the DS800 software provided with the spectrometer. The full width at half-maximum (*FWHM*) of the Gaussian peak components was kept constant in a particular spectrum.

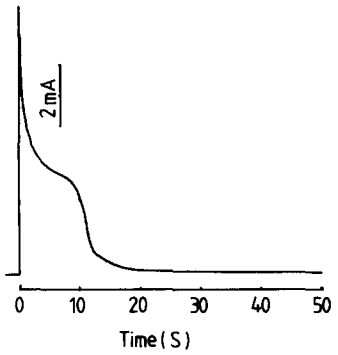


Figure 1 Chronoamperogram during electrochemical overoxidation of polypyrrole perchlorate

RESULTS

Upon application of a potential over +0.9 V to gold foil coated with PPy perchlorate in 0.1 M $NaClO_4$, overoxidation of PPy occurred. A chronoamperogram, as shown in *Figure 1*, indicated that the overoxidation occurred in two steps. The first step started immediately after a sharp decrease of current, possibly due to charging, and ended at about 5 s. The second step began after the first step and terminated at about 12 s, followed by a slow current decay. The charge consumed in the second stage was roughly equal to that in the first stage. The total charge consumption during overoxidation was about 73% of the total polymerization charge consumption.

The X.p.s. wide scans of as-prepared (i.e. before overoxidation) and overoxidized PPy are shown in *Figure 2*. Obviously, the Cl2p core-level signal at about 207 eV due to ClO_4^- was lost during overoxidation.

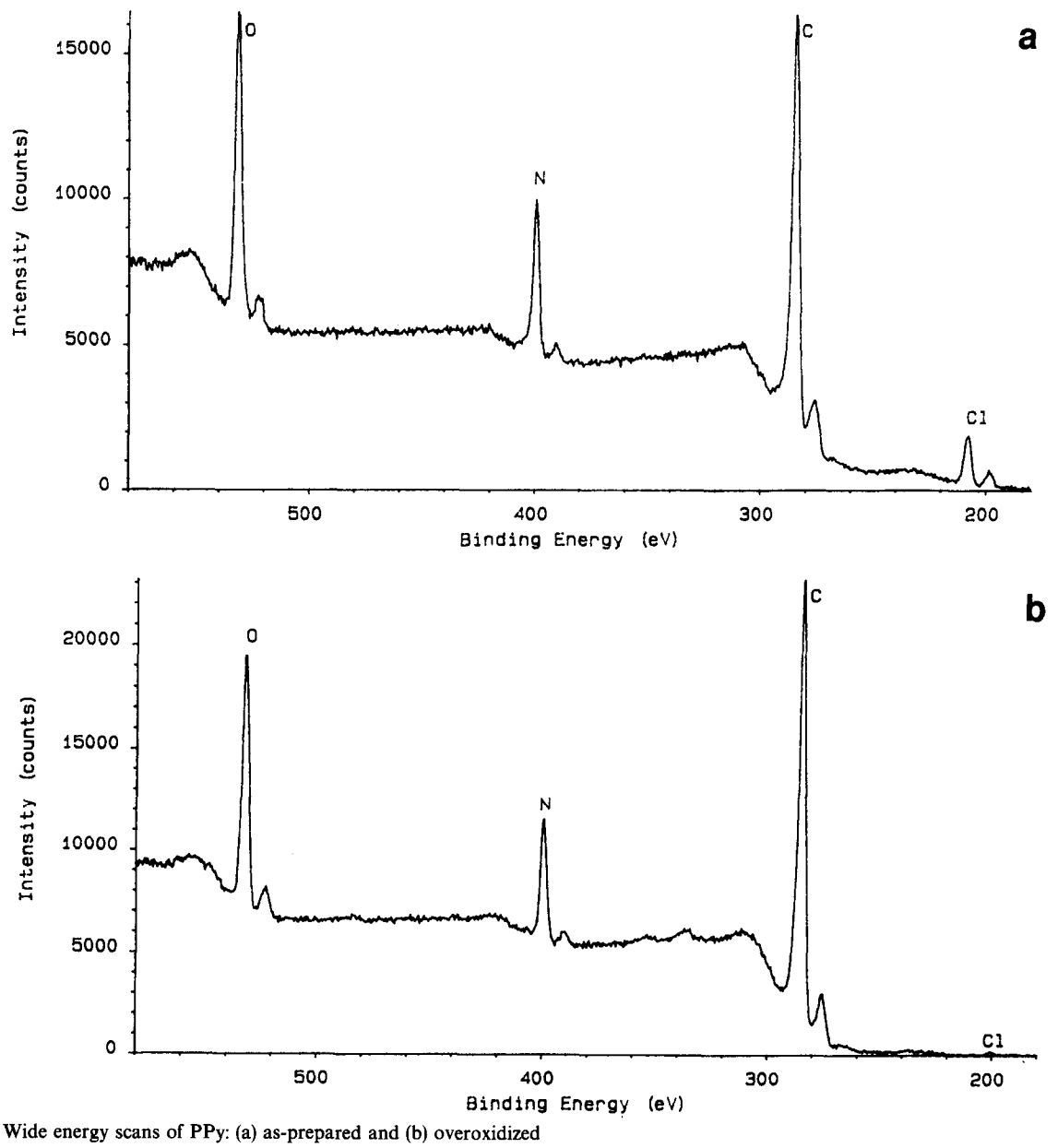
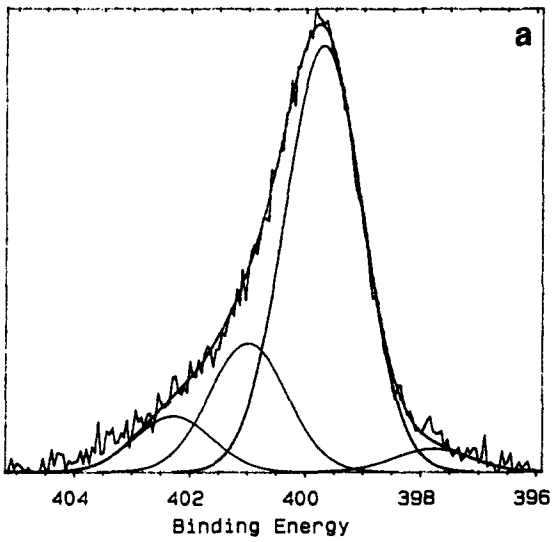


Figure 2 Wide energy scans of PPy: (a) as-prepared and (b) overoxidized

X.p.s. N1s core-level spectra of as-prepared and overoxidized PPy (*Figure 3*) indicated that core-level nitrogen at 399.7 eV was accompanied by a high binding energy (BE) tail over 401 eV, as well as a very small low BE component at 397.7 eV. The amount of high BE nitrogen reduced significantly after overoxidation while the low BE component increased.

X.p.s. C1s core-level spectra of the as-prepared and overoxidized PPy (*Figure 4*) demonstrated that the BE of the C1s electrons at 284.6 eV had a large *FWHM* value of 2.3 eV followed by a high BE tail. After overoxidation, a new peak at about 287.4 eV appeared clearly on the high BE tail.

The results of deconvolution of the N1s and C1s spectra



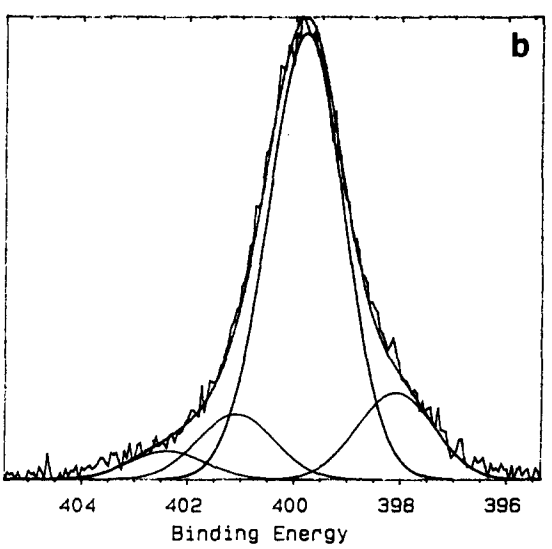
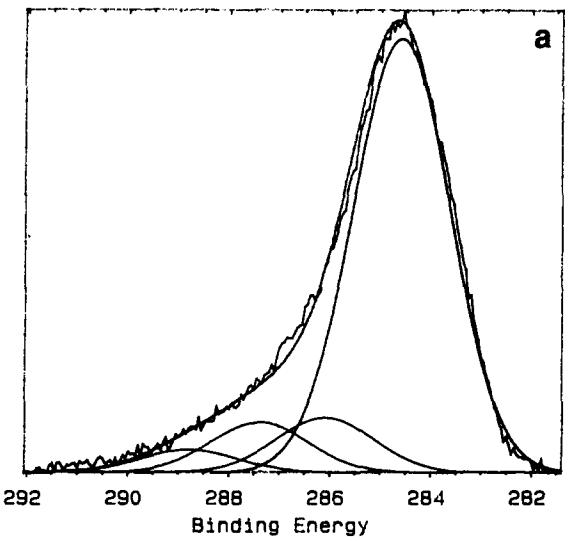


Figure 3 N1s core-level spectra of PPy: (a) as-prepared and (b) overoxidized



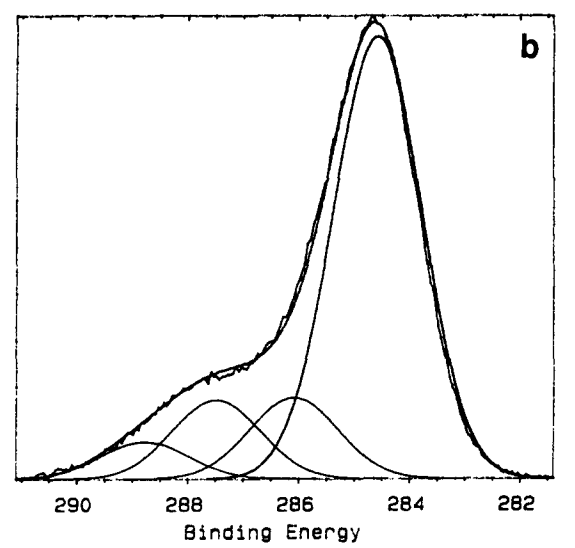


Figure 4 C1s core-level spectra of PPy: (a) as-prepared and (b) overoxidized

Table 1 Comparison of overoxidized PPy with as-prepared PPy

Element state	Element binding energy (eV)	Components in as-prepared PPy (%)		Components in overoxidized PPy (%)	
		Sample 1	Sample 2	Sample 1	Sample 2
C	284.6	77.2	77.3	69.3	72.2
COH	286.1	9.8	9.0	12.7	8.1
CO	287.4	9.0	9.0	12.3	15.6
COOH	288.8	4.0	4.7	5.8	4.0
$C_{oxidized}/C_{neutral}$		0.30	0.29	0.44	0.38
-N=	397.7	3.6	1.4	14.3	8.2
-NH-	399.7	67.5	68.8	73.4	79.2
$-NH^+$	>401	29.9	29.8	12.3	12.6
$-NH^+-/-NH-$		0.43	0.43	0.17	0.16
ClO_4^-/C (%)	207.1	3.9	6.5	0	0.8

are summarized in *Table 1*. The N1s spectrum has been deconvoluted into neutral nitrogen (–NH–) at 399.7 ± 0.1 eV, positively charged nitrogen (–NH^+–) over 401 eV and imine-like nitrogen (–N=) at 397.7 ± 0.1 eV. As-prepared PPy had about 68% –NH– and 29% –NH^+–, but little –N= (3.6%). After overoxidation, –NH– and –N= increased, while –NH^+– decreased. The C1s spectrum has been deconvoluted into neutral carbons at 284.6 eV and oxidized carbon species at 286.1 ± 0.1, 287.4 ± 0.2 and 288.8 ± 0.3 eV, which correspond to –COH, –CO and –COOH, respectively[19]. The as-prepared PPy had about 77% neutral carbon as compared to 70% in overoxidized PPy. Thus, 7% of carbon has been oxidized during overoxidation. The ratios of –NH^+– to –NH– and oxidized C to neutral C indicated that the C band became more positive while the N band became more negative after overoxidation. Oxidation occurred on carbon but nitrogen was also affected. Duplicate experiments showed similar results.

Determination of the overoxidation position was carried out by taking X.p.s. spectra of the same sample from different sides, namely the solution side and the electrode side. The results are shown in *Table 2*. Compared with the as-prepared PPy (*Table 1*), oxidized carbon species increased while –NH^+– and perchlorate anions decreased after overoxidation. However, more –NH^+– and perchlorate anions existed on the solution side than on the electrode side.

There is no significant effect of changes in overoxidation potentials on PPy composition in a range from 0.9 to 1.3 V. A potential effect was not seen from chronoamperograms during electrochemical overoxidation.

The effect of overoxidation time on the degree of overoxidation is demonstrated in *Figure 5*. A progressive increase of oxidized carbon species and a decrease of –NH^+– and perchlorate anions were observed.

No clear changes of $C_{oxidized}/C_{neutral}$ and –NH^+–/–NH– with changes of pH were found. However, an increase of –N=/NH– with increasing pH was demonstrated.

The composition of PPy before and after overoxidation is as follows:

PPy as-prepared: $C_{5.3}N_{1.0}O_{0.37}ClO_{4\,0.24}$

PPy overoxidized: $C_{6.5}N_{1.0}O_{1.58}ClO_{4\,0.05}$

Oxygen from sources other than ClO_4^- was found even before overoxidation. After overoxidation, the contribution of the ClO_4^- to the oxygen content decreased while the contribution from other sources increased.

Table 2 Overoxidation on the electrode side and the solution side

Response	Electrode side	Solution side
$C_{oxidized}/C_{neutral}$	0.38	0.41
–NH^+–/–NH–	0.16	0.28
–N=/–NH–	0.10	0.10
ClO_4^-/C (%)	0.8	2.0

DISCUSSION

The state of nitrogen in PPy was found to be similar to that reported[11–16] (*Figure 3*). Thirty per cent of nitrogen existing as –NH^+– (N1s BE > 401 eV) was balanced by ClO_4^- as a counterion. Little –N= (N1s BE = 397.7 eV) was present, possibly due to hydrolysis of PPy during polymerization or post-polymerization rinsing with water. This hydrolysis may initially introduce some αC–OH, as indicated by other researchers[3]. This has also been evidenced by the existence of oxygen in PPy before overoxidation. A significant increase of –NH– after overoxidation indicated that most –NH^+– turned into –NH– rather than –N=, which was found in hydrolysis by other researchers. However, –N= contents were higher if overoxidation was carried out in electrolyte with higher pH or treated in 0.1 mol l^{-1} NaOH after overoxidation. This indicated that –N= was mainly due to hydrolysis, which is in agreement with other reports[11,14].

The state of carbon is more complicated. It has been reported[6,10,18] that carbon could be divided into α-C and β-C. However, splitting the peak may result in many possibilities unless accurate BE values of α-C and β-C are known. High BE tailing of the C1s peak (*Figure 4*) is due mostly to different states of β-C (C–NH–, C–NH^+–

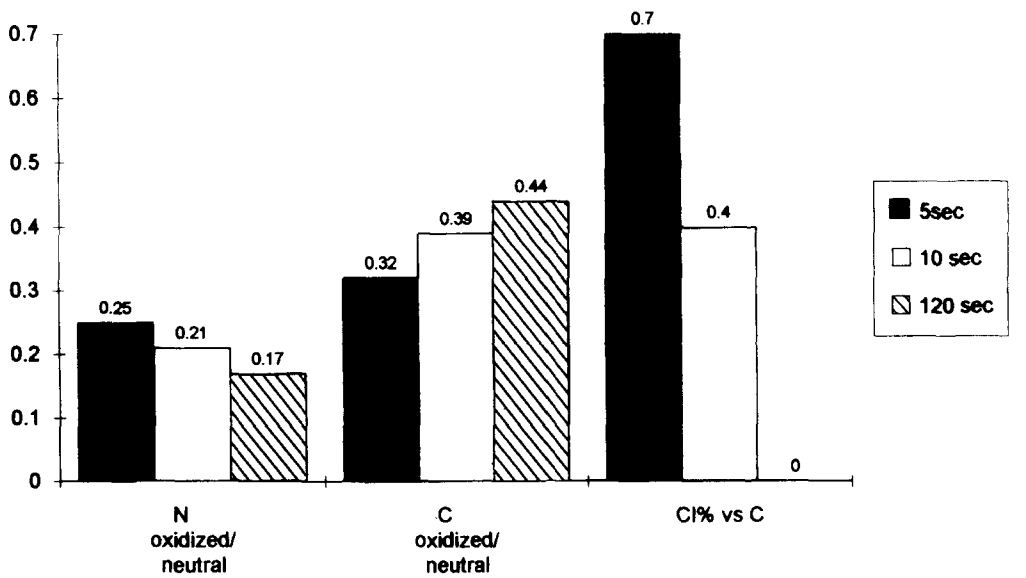
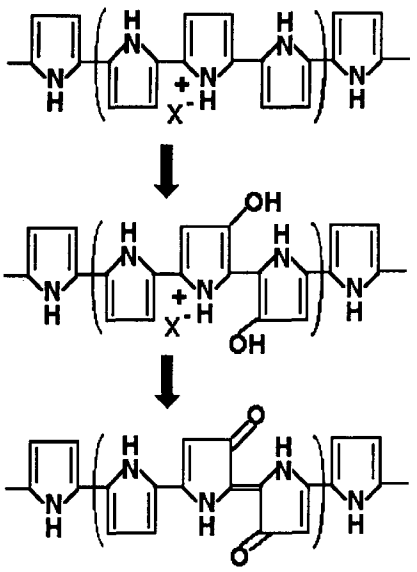


Figure 5 Effect of overoxidation time on the degree of overoxidation



Scheme 1 Overoxidation of polypyrrole

and C–N=). However, most of the β-C may be merged with α-C, resulting in a broadening peak (*FWHM* = 2.3 eV). The high BE tail of each C1s spectrum was curve-fitted with three peaks, corresponding to C–OH, C=O and COOH at 286.1, 287.4 and 288.8 eV, respectively, in order to reveal overoxidation of carbon. After overoxidation, a decrease of neutral carbon and increase of C=O were obvious (*Table 1*). A peak at the position of C=O was observed, as in *Figure 4*. The $C_{oxidized}/C_{neutral}$ increased after overoxidation.

Based on the results obtained, a PPy overoxidation mechanism is suggested, as shown in *Scheme 1*. Overoxidation takes place in two stages (as indicated in *Figure 1*). In the first stage, β-C was oxidized to C–OH. Further oxidation of C–OH into C=O followed accompanied by the loss of positive charge on $-NH^+-$ and the release of ClO_4^-. This was evidenced by two steps in the chronoamperograms (*Figure 1*) and the appearance of a C=O peak (*Figure 4*). Decrease in the $-NH^+-/-NH-$ ratio and amount of ClO_4^- were also observed during overoxidation (*Figure 5*). From the fraction of $-NH^+-$, it was estimated that every three pyrrole units in the polymer shared one positive charge and were balanced by one ClO_4^-, i.e. every three pyrrole units lost seven electrons during polymerization. Overoxidation caused about five electrons to be lost for every three pyrrole units, since charge equivalent to 73% of total polymerization charge was consumed in the overoxidation. This observation indicated that C=O was formed.

Overoxidation started on PPy facing the electrode rather than the solution, probably due to a potential drop formed across the PPy film, especially when it was overoxidized and tended to be resistive. This has been supported by the lower ClO_4^- and $-NH^+-/-NH-$ ratios for the PPy on the solution side (*Table 2*). The solution pH and overoxidation potential had little effect on the degree of overoxidation, at least over the ranges studied. This indicated that PPy was overoxidized as soon as a high potential, reported as 0.7 V (ref. 4) or 1.0 V (ref. 1), was applied.

However, overoxidation time played an important role in the overoxidation process. Progressive overoxidation was shown by the increase of $C_{oxidized}/C_{neutral}$ and decrease of $-NH^+-/-NH-$, as well as ClO_4^- concentration (*Figure 5*). This indicated that overoxidation was controlled by mass transfer rather than electron transfer, since no effect of potential increase on overoxidation was seen. Diffusion of ClO_4^- out of the polymer and oxygen sources into the polymer would be rate limiting.

The composition of the polymer changed after overoxidation. The high carbon mole ratio observed may be partly due to peak integration errors from the atomic sensitivity factors, which has been noted previously[18]. However, the increase of C/N ratio after overoxidation may also be due to ring opening and COOH formation.

Oxygen, other than the part from perchlorate, was present before overoxidation, as reported[18], but increased significantly after overoxidation. The extra oxygen (C–OH and C=O) was added to PPy after oxidation. The ClO_4^- decreased after overoxidation, as expected.

CONCLUSION

Overoxidation of PPy occurred upon application of a positive potential, for example over 0.9 V. The oxidation process progresses in two stages. Carbon is oxidized into –C=O while $-NH^+-$ is rearranged, mostly into –NH–, and this is accompanied by the loss of ClO_4^-. Overoxidation of PPy was more advanced on the electrode side than on the solution side. Mass transfer during overoxidation may be a rate-limiting factor.

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