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XPS Studies on Conducting Polymers: Polypyrrole Films Doped with Perchlorate and Polymeric Anions

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Conducting polypyrrole (PPy) films, doped with perchlorate and polymeric anions, were prepared by electropolymerization and analyzed by XPS in order to clarify the interaction between polymer redox sites and various dopants. The X-ray photoemission data indicate that the electrostatic interaction of ClO_4^- anions with PPy occurs at specific sites. The electric field produced by the anion affects the entire pyrrole ring in its proximity and makes all atoms, carbons and nitrogen, to look more positive. If the electrostatic bonding were with the nitrogen heteroatom alone, this would yield a considerably larger shift than is observed in the N 1s core level spectra. The geometric arrangement of the ring-anion pair consistent with the observed interaction behavior requires that the tetrahedral ClO_4^- anion overlays the planar ring with its triangular oxygen plane parallel to the planar ring. The negative charge of the counterion is localized, and the polymer responds to it by local modification of the chain geometry and the appearance of defined bipolaron entities. However, if the PPy is doped with large anions, uniform electronic charge extraction from the carbon backbone prevails. In this case, a majority of the negative charge carriers are presumably not placed close enough, nor at a favorable disposition with respect to the planar pyrrole ring, to accomplish interaction at specific sites.

Introduction

Conducting polymers have been studied by many workers because of their wide range of useful applications, particularly in electrochromic devices, ion sensors, capacitors, and batteries.[1-6] Of the various means for synthesizing the materials, electropolymerization is one of the most effective to produce good-quality conducting polymer films.

It is generally accepted that the polymerization of PPy is initiated via electrochemical oxidation of an adsorbed pyrrole monomer (Py). The oxidation of the monomer generates pyrrole radical-cation ($Py^{\bullet+}$) intermediates on the electrode substrate which react with neutral monomer species to extend the chain through dimers, trimers, to higher oligomers.[1b,6b] The polypyrrole chain growth occurs in a strongly nucleophilic environment of solvent molecules and anions. To preserve local electrical neutrality, the positive charge is compensated by coexisting anions. The electrostatic interaction traps electrolyte anions in the growing structure.

The radical-cation ($Py^{\bullet+}$) species may also form an intermediate state with one or more nucleophilic anions, as postulated in the polymerization scheme in Figure 1. By a variance in the polymerization conditions, the stability of intermediate radical cation-counterion couples is altered and this results in PPy films of different structure.

The size of the anions and the electrochemical potential have been reported as important parameters of the electropolymerization process which affect the structure and morphology of resulting polymer films as well as their electrochemical properties.[7-9] During film formation, steric factors may become significant for much larger anions, especially in the follow-up chain propagation reaction. For each anion, there appears to be an optimum potential range in which radical-cation intermediates are stabilized. By forming the PPy film at this optimum potential, the chain-propagating reaction, at the cationic sites of the radical-cation intermediates,[6b] becomes dominant. As the reactivity of the radical cation intermediate increases, the chemical selectivity decreases and the intermediate may react with solvent species or anions to yield soluble byproducts.

Nondestructive surface analysis by X-ray photoemission spectroscopy (XPS) is suitable to provide information on the chemical and electronic structure of the PPy films doped with monomeric and polymeric anions. Several studies have recently been performed using XPS and ultraviolet photoemission spectroscopy to determine the chemical state and nature of the polymeric cation and the anion and to examine the valence electronic structure of π-conjugated conductive polymers.[1,10-20] The published

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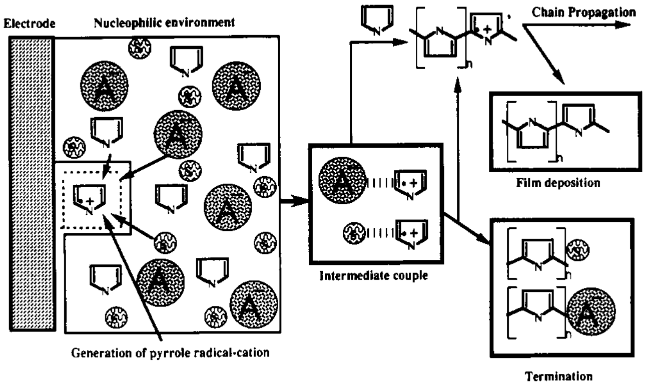

Figure 1. Radical cation formation of pyrrole monomers and their interaction with nucleophiles existing in the vicinity of the electrode surface.

XPS results on polypyrroles performed by different groups are often inconsistent, and, for example, the exact location of the incorporated anions with respect to the polypyrrole chains is not known at present.[12] There is also disagreement concerning the interaction between the anions and polypyrrole matrix. The charge has been assumed to be either withdrawn uniformly from all pyrrole units associated with each anion[11] or at localized sites to yield bipolaron entities of limited spatial extent.[12-14]

In the models which propose that the positive charges induced by anions are localized along the polymeric chains, a detailed picture of the structure of bipolaron defects, the bipolaron width, and the spatial extent between defects is not complete.[18] In previous studies, the N heteroatom was considered to be the specific site for the electrostatic bonding,[15,16] but the nature of the anion should also influence the electrostatic interaction.[15,16]

In the present study, PPy films were prepared by electrooxidative polymerization, and two factors which determine their structure and morphology were varied, viz., anion type and potential of deposition,[7,9,29] and the films were carefully investigated by X-ray photoemission spectroscopy. The spatial arrangements of the dopant anion–pyrrole ring couple is proposed and correlated with the mechanism of conduction.

Experimental Section

All chemicals used in the present study were reagent grade. Acetonitrile (AN) (Burdick & Jackson) and doubly distilled water were used as solvents. Water in AN was removed by adding molecular sieves and letting it stand for a few days before use. AN solutions used for preparation of $PPy^+ClO_4^-$ films contained 0.2 mol dm^{-3} pyrrole and 0.2 mol dm^{-3} $LiClO_4$. For the preparation of polypyrrole with polymeric anions, poly(vinylsulfonate) (PVS) and poly(styrenesulfonate) (PSS), aqueous solutions containing 0.1 mol dm^{-3} pyrrole and 0.01 mol dm^{-3} of KPVS or NaPSS were employed. The solutions was purged with N_2 gas before polymer films were formed. $PPy–ClO_4^-$ films were prepared by using electrooxidative polymerization at several potentials, viz., 0.4, 0.6, 0.8, 0.9, 1.0, and 1.2 V vs $Ag/AgNO_3$ (0.01 mol dm^{-3}).

$PPy–PVS^-$ and $PPy–PSS^-$ films was prepared at 1.0 V vs SCE. Gold (ca. 2000 Å thick) was deposited onto a silicon wafer and was employed as a substrate for polymer deposition. The size of the working Au/Si electrode was 10 × 10 mm. The films were rinsed with the solvents used for their preparation (either acetonitrile or doubly distilled water). A large area electrode was used as a counter electrode. The deposited amount of polymers was controlled by the amount of charge (1 C cm^{-2}) passed during electropolymerization (200–300-Å-thick polypyrrole films were formed).

The XPS studies were performed using a Perkin-Elmer Physical Electronics 555 spectrometer (Mg Kα X-ray source) with a PDP-11 computer for data acquisition and analysis. The energy calibration was checked using the Au $4f_{7/2}$ line of the gold substrate which appears in the survey spectrum of sputtered polypyrrole films. The surface composition of doped polypyrrole samples was calculated from the areas of the C 1s, O 1s, N 1s, and Cl 2p photoelectron peaks corrected by appropriate sensitivity factors.[21] Analysis of the core level spectra included background subtraction and iterative line-shape decomposition based on the summed Gaussian/Lorentzian functions (90/10%). The full width at half-maximum (fwhm) of each decomposed C 1s line was 1.7 ± 0.05 eV. The relative concentration of each observed carbon feature was determined from the area under the corresponding resolved component with respect to the total C 1s photoemission.

Results and Discussion

$PPY^+ClO_4^-$ Films. The C 1s, O 1s, N 1s and Cl 2p core level spectra shown in Figure 2 are typical for the PPy^+-ClO_4^- films formed in the potential range 0.4–1.2 V. The major feature in the C 1s photoemission is centered at about 284.5 eV (Figure 2a). The carbon peak is asymmetric and skewed toward the high binding energy side. According to Pfluger and Street[12] (see also the XPS study of the related thiophene-based conducting polymers[19]), the main carbon feature is complex and does not originate from a single photoemission. It contains the contribution of two superimposed lines characteristic of the α and β carbons of the pyrrole or thiophene ring. In previous studies of conducting polymers,[12,15-19] the asymmetry at higher binding energies of the C 1s peak has been attributed to disorder phenomena, steric effects, cross-linking, or chain termination, since it is known that disorder can lead to inhomogeneous broadening of the core level.[22]

Since the energy-resolution limit of the XPS technique does not permit the contributing photoemissions to be resolved in the C 1s core level spectra of polypyrrole and other conducting polymers, the line-shape analysis has remained uncertain until now. Previous XPS studies (see ref 12 and references therein) of the pyrrole monomer report a binding energy split of 0.9 eV between α and β carbon lines (the α carbon is shifted by 0.9 eV with respect to β carbon). For the line-shape analysis carried out here, we adopted this split, and constrained the relative positions of α to β carbon peaks to 0.9 ± 0.05 eV (Figure 2a). For the deconvolution, we also assumed that the core hole lifetime does not differ for the carbons in different pyrrole ring environments by more than ±5%, so that the fwhm could be fixed within these limits. As seen from Figure 2a, the C 1s spectra can be deconvoluted into four lines (labeled I–IV) by varying only their relative intensities. The ideal pyrrole monomer unit contains two α and two β carbon atoms, so that the difference in intensity between

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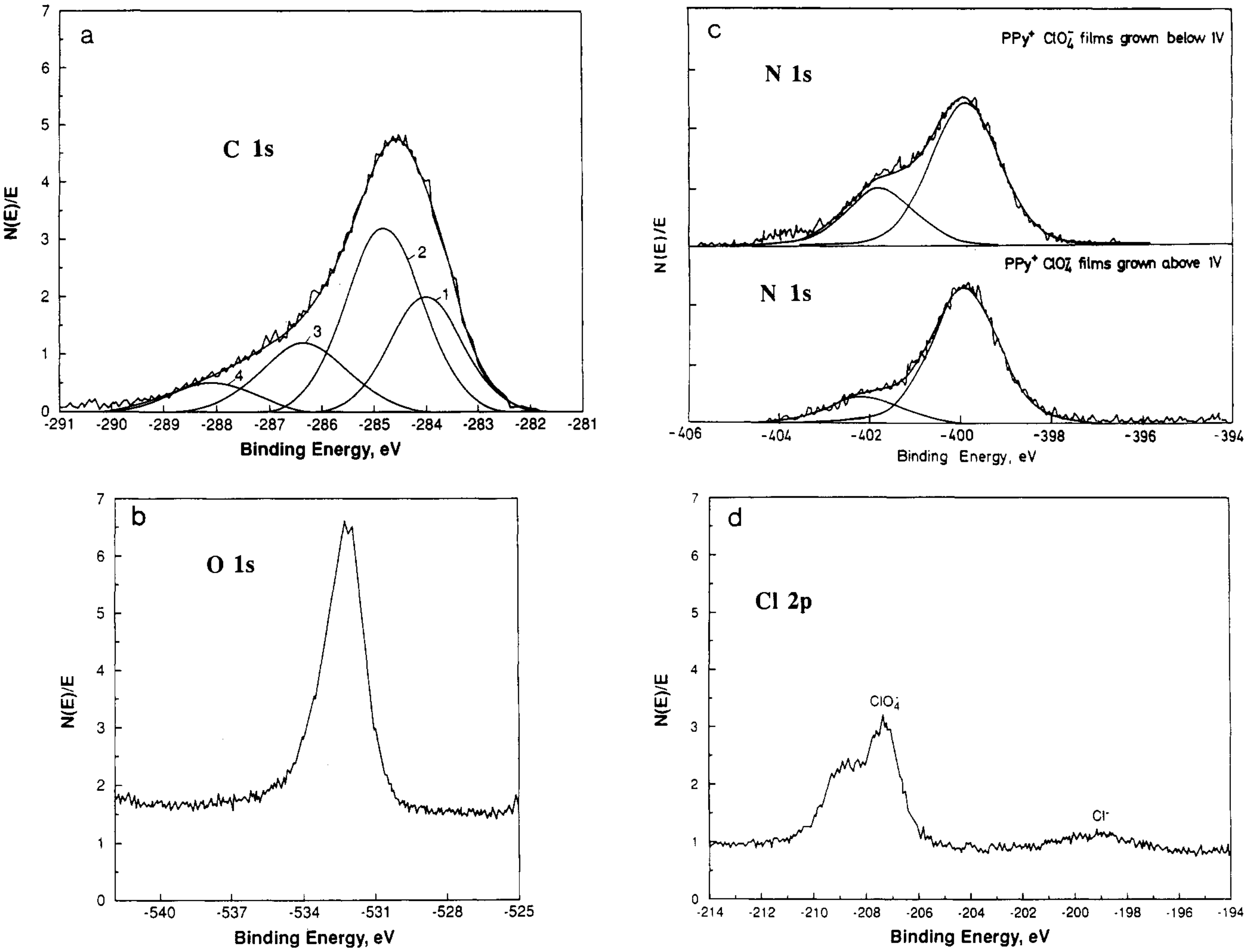

Figure 2. Core level photoelectron peaks for the as received $PPy^+ClO_4^-$ films: (a) C 1s; (b) O 1s; (c) N 1s; (d) Cl 2p.

the α and β carbon lines has been explained by Pfluger and Street[12] to be due to the presence of hydrocarbon contamination. Considering that contamination is a random phenomena, one would expect to find different line shapes of C 1s peaks for polypyrrole samples prepared under different experimental conditions. However, the C 1s data for the potential range 0.4–1 V could always be fitted with approximately the same contribution of the four peaks: C-I 27 ± 3%, C-II 44 ± 2%, C-III 22 ± 2%, and C-IV 9 ± 2%. The α to β carbon peak ratio, found by deconvolution, was 1.6 ± 0.1. The constant value of the ratio implies that the enhanced intensity of the α-carbon peak arises as a consequence of some structural arrangement of doped polypyrrole and not by contamination. In addition, it would be expected that any hydrocarbon contamination would enhance the intensity of the β carbon photoemission which is more hydrocarbon-like than α carbon. Further, when the polymerization potential is increased to 1.2 V, pyrrole ring cleavage occurs and causes an increase in hydrocarbon-like carbon atoms. The relative contributions of I, II, III, and IV types of carbon to the total C 1s photoemission were 35, 37, 22, and 7%, respectively, which indicates an increase in the number of aliphatic, hydrocarbon-like carbon atoms and a decrease of the C-II/C-I ratio from 1.6 to 1.

Our interpretation is that the C 1s line shape originates from inequivalent pyrrole units inside the doped polypyrrole matrix because of interaction with perchlorate anions. Considering the doping level and the structural effect, it is clear that a portion of the polypyrrole is not affected by the presence of the counterions. Regardless of the microscopic picture proposed for the cationic PPy chains (bipolaron defects[12–14] or uniform charge extraction from the polymer backbone[11]) the carbon atoms of the pyrrole rings modified by the interaction with anions become more positive and their photoemission is shifted towards higher binding energies. As a result, the α,β-carbon photoemission doublets of the modified and unmodified pyrrole units will partially overlap. Thus, peak II contains contributions of α carbons from neutral pyrrole units and β carbons from cationic pyrrole units. Also, the C-III peak contains a contribution of α carbons from pyrrole units involved in the electrostatic interactions with anions.

Besides the photoemission from the α carbons in the electrostatically modified pyrrole units, the C-III feature contains the contribution of disorder-type carbons. By considering the binding energy location (286.2 eV) and the chemical shift of the C-III feature,[18,23,24] we conclude that the disorder type carbons have to be assigned to the formation of single C–O bonds. The type of disorder is further defined if we refer to other XPS work on composites of PPy/PEO.[25] The binding energy position of the C–O bonds of poly(ethylene oxide) (PEO) in the C 1s

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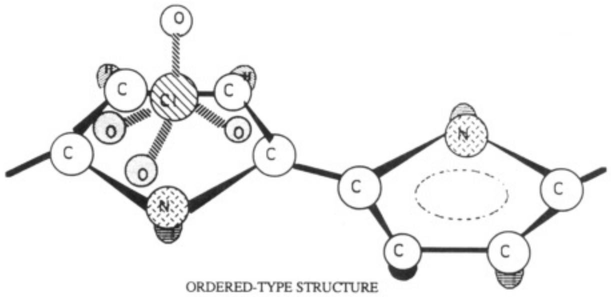
spectra of the composite PPY/PEO is at 286.3 eV.

The disorder type carbon IV feature is shifted by 4 eV with respect to the β carbon peak. Skotheim et al.[15] attributed the feature shifted by 4 eV from the main carbon peak to the formation of the single C–O bonds. However, such large shifts have always been observed for a carbon atom bound to more than one oxygen, such as in carboxyl species.[24] Therefore the C-IV peak may be due to carboxylation at polypyrrole chain terminations or at the points of pyrrole ring cleavage. It can also be due to formation of carbonyl bonds at α-carbon sites because a shift of 4 eV was observed for the structurally related imide carbonyl carbons.[26]

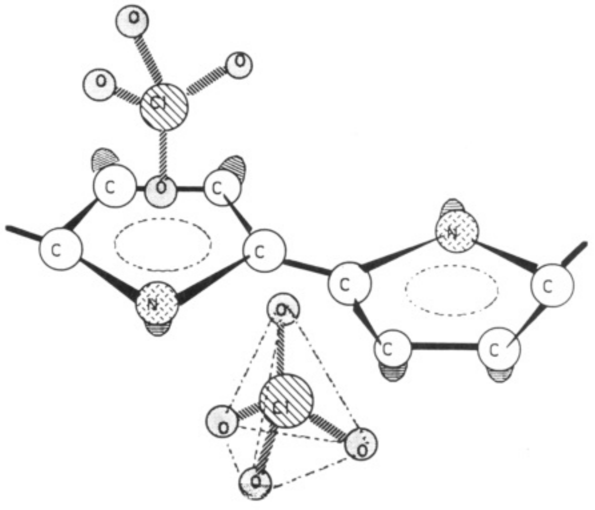
The O 1s core level peak centered at 532.5 eV (Figure 2b) is not very informative. It is not possible to separate the contribution of the oxidized polypyrrole sites from that due to oxygen atoms in perchlorate anions.

The N 1s spectra of the polypyrroles polymerized at different potentials indicate clearly the existence of two inequivalent nitrogen heteroatoms (Figure 2c). The chemical splitting of the N 1s peak indicates specific site electrostatic interaction, i.e., the presence of bipolaron defects (dications spatially localized along the PPy chain).[12-16] The appearance of a single peak in the nitrogen core level photoemission has been interpreted to be due to complete delocalization of positive charges (holes).[10,11] The major peak in Figure 2c appears at 399.9 eV and is attributed to nitrogen that is least influenced by the presence of the anions. The shoulder shifted by 1.8 eV with respect to the main nitrogen feature is attributed to the electrostatic interaction with anions. A similar shift of 1.6 eV was reported previously by other authors.[15,16] The line-shape decomposition of the N 1s region for $PPy^+ClO_4^-$ films grown below 1 V indicates that only about 30% of the polypyrrole is involved in the electrostatic interaction with perchlorate anions (the peak ratio of electrostatically unscreened to screened nitrogen atoms is 2.5 ± 0.1). The polypyrrole films formed above 1 V are damaged and the electrostatically screened nitrogen contributes ~15% to the total N 1s photoemission (Figure 2c). We do not observe the low binding energy shoulder assigned by others to tertiary aza-type nitrogen.[17] The aza-type nitrogen forms as a result of deprotonation and rearrangement of the pyrrole bonds.

The analysis of the observed shift of electrostatically screened nitrogen suggests that the electrostatic interaction does not occur at specific nitrogen sites but involves the whole pyrrole ring unit. The complete transfer of one unit charge to nitrogen by specific electrostatic binding at the heteroatom site should yield a considerably larger shift than that observed in the N 1s region. Using the empirical relation of 5.8-eV BE shift of N 1s core level per unit charge,[12,15,16,27] for the observed 1.8-eV shift one calculates a charge transfer of $^{1}/_{3}$ e (1.8 eV/5.8 eV) per inequivalent nitrogen. It seems that interaction with the singly charged perchlorate anion is not uniformly distributed among four carbon atoms and one nitrogen heteroatom in the pyrrole ring (otherwise the charge transfer per each pyrrole ring atom would be $^{1}/_{5}$ e). The charge of $\sim+^{1}/_{3}$ e is induced on nitrogen and the rest of $\sim+^{2}/_{3}$ e is confined to the four pyrrole carbon atoms. This is in agreement with the results of Skotheim et al.,[16] who reported a charge transfer of $^{1}/_{3.5}$ e per inequivalent nitrogen. Pfluger and Street[12] also did not find complete transfer of one unit charge to nitrogen.



ORDERED-TYPE STRUCTURE



DISORDERED-TYPE STRUCTURE

Figure 3. Proposed models for a doped polypyrrole structure: (a) ordered-type; (b) disordered type.

The Cl 2p region shows that the ClO_4^- ions are incorporated into the polypyrrole films intact. However, traces of Cl^- species are always observed in electropolymerized samples (Figure 2d), presumably as a contaminant residue from the initial electrochemical polymerization. The ratio of the chlorine signals corresponding to perchlorate and chloride for the polypyrroles polymerized in our laboratory was on average 9:1. For polypyrrole films synthesized in PEO electrolytes, Skotheim et al.[15,16] observed two chlorine signals due to ClO_4^- and Cl^- of approximately equal magnitude and a very pronounced shoulder in the N 1s region. The ratio of perchlorate to chloride signal for the polypyrrole synthesized in MeCN-TEAP was reported to be about 7:1.[15,16] Also, the high-energy shoulder in the N 1s spectrum was less pronounced than that of polypyrrole films synthesized in PEO electrolytes. As to which of the two anions is responsible for the electrostatic interaction, Skotheim et al.[15,16] considered that the chloride anion is smaller than the perchlorate anion and would have stronger interaction with the polymer matrix because of the higher charge density. The model of electrostatic interaction with chloride ions was also supported by the XPS data of Salaneck et al.[11] who found no comparable should in BF_4-doped polypyrrole. On the other hand, Nelson et al.[19] found a second chemical state of sulfur exhibited as a shoulder in the S 2p core level photoemission of PF_6-doped poly(3-methylthiophene). The matter appears to be more complex than only the question of ClO_4^- or Cl^- electrostatic interaction.

On the basis of the experimental evidence, a microscopic picture of the ClO_4^--doped polypyrrole formed by electrochemical polymerization is proposed. The presence of electrostatically screened nitrogen atoms demonstrates that the positive charges are localized along the chain. The localized positive charge provokes a local geometric re-

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laxation and the formation of bipolaron defects. The whole pyrrole ring is involved in the electrostatic interaction with the counterion. To accomplish such an interaction, the anion has to approach the ring as close as possible. The perchlorate anion has a tetrahedral structure, and it will be assumed here that the triangular oxygen plane is positioned over the planar pyrrole ring (Figure 3a). It will be also assumed that the ring planarity is not distorted to a great extent (the ring planarity is associated with aromaticity[19] and during the formation of bipolarons the bonding order of the polymer changes from aromatic to quinoidal). This type of the pyrrole ring–counterion pair arrangement will be referred to here as an *ordered type structure*.

For such an ordered type configuration, the Cl atom at the center of the perchlorate tetrahedron will be located approximately above the middle of the pyrrole ring. It should be noted that the size of the triangular face of the ClO_4^- tetrahedron is close to the size of the pyrrole monomer unit.[28] Therefore, the counterion will produce an electric field which is not restricted to the specific nitrogen heteroatom site. The cation hole created and localized within the ring in the proximity of the perchlorate anion will affect all the atoms in the ring, and they will look more positive. However, the XPS data do show that a somewhat greater portion of the localized positive charge ($\sim +^1/_3$ e) is induced on the nitrogen atom which stabilizes the ring by covalent σ-bonding with neighboring carbon atoms.

In the second model it will be assumed that the counterions are randomly oriented along the chain. As shown in Figure 3b, the perchlorate tetrahedrons are supposed to be either oriented with an apex or edge facing the pyrrole ring plane or located between two pyrrole rings. In this so-called *disordered type* of structure, the counterions are not placed as close to the planar pyrrole rings as in the ordered structure. As a result, the negative charge of the counterions is apparently not localized at planar ring sites but it is randomly distributed along the chains. The charge is withdrawn uniformly from the several pyrrole units associated with each counterion. The created hole is delocalized along the π-conjugated carbon path (carbon backbone), which does not include the N heteroatoms. The positive charge in the random anion arrangement does not produce inequivalent nitrogen heteroatom sites and no splitting in the N 1s peak should be observed.

The splitting in the N 1s peak observed for ClO_4^- doped polypyrroles suggests that, during electrochemical polymerization, a large portion of the perchlorate ions tend to incorporate into the polymer matrix in close proximity to the ring sites.

PPy Films Doped with Polymeric Anions. The proposed models for the order and disorder type of doped polymer structures are supported by further experimental evidence. We have electropolymerized polypyrrole films by incorporating two polymeric anions, poly(vinyl sulfonate) (PVS) and poly(4-styrenesulfonate) (PSS). In Figure 4 the N 1s photoemission for the polypyrroles grown with ClO_4^-, poly(vinyl sulfonate), and poly(4-styrenesulfonate) anions are compared. The high binding energy shoulder in the N 1s region is most pronounced for the polymer doped with perchlorate anions. When the polymeric anion of aliphatic structure is incorporated into the polypyrrole matrix, the shoulder in the N 1s region is less pronounced.

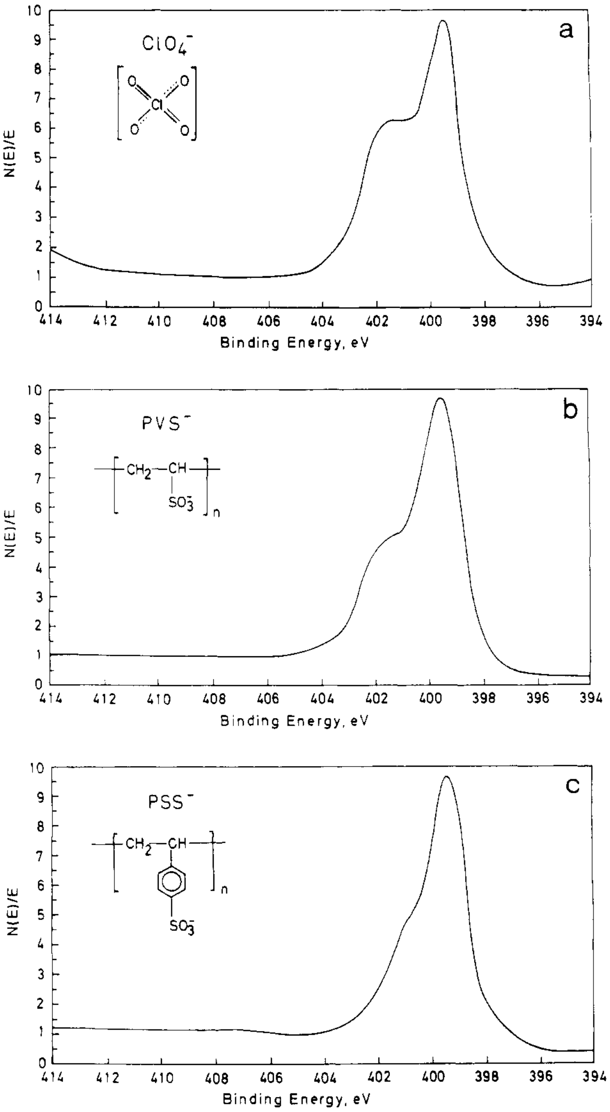

Figure 4. N 1s photoemission for the polypyrrole grown with different size anions: (a) ClO_4^-; (b) poly(vinyl sulfonate); (c) poly(4-styrenesulfonate).

For the polypyrrole–poly(4-styrenesulfonate) combination, the N 1s region exhibits only a slight tailing at the high binding energy side of the peak. The N 1s data in Figure 4 demonstrate that the electrostatic interaction of polypyrrole chains with the polymeric anions (especially anions containing benzene rings) is less specific than that with perchlorate ions. This can be related to the lower charge density of the polymeric anions and the greater restrictions on their motion. Results from scanning tunneling microscopy have shown that helical polypyrrole chains are overcoated by polymeric anions in contrast to the perchlorate anions which are incorporated inside the helical structure.[7] The negatively charged sulfonate groups are not free to approach specific pyrrole rings while attached on the polystyrene chains. As a result, the created holes are delocalized along the π-conjugated carbon path of the polypyrrole chains, and the electrostatic interaction is less specific.

The anion position with respect to the ring is the key feature that determines the mode of charge transfer. The location of an anion in the polymerized structure is determined by its size and the conditions of the polymer preparation and subsequent treatment. The pyrrole ring–anion geometric arrangement determines whether charge is extracted from a specific ring site (favored by an

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Table I. Stoichiometry of Polypyrrole Films Formed at Different Electrochemical Potentials

	polymerization voltage, V			
atomic ratio	0.4	0.6	0.8	1
C:N	4.4	4	5.0	5.3
O:Cl	3.7	4.7	5.1	6.3
N:Cl	1.2	1.3	1.6	1.6
C:Cl	5.2	5.3	7.8	8.5

ordered arrangement) or extracted uniformly from the carbon backbone (favored by a disordered-type arrangement).

$PPy^+ClO_4^-$ Stoichiometry. The atomic ratios of carbon, oxygen, nitrogen, and chlorine derived from the experimental XPS data for the ClO_4^--doped polypyrrole samples prepared at different potentials are given in Table I. The composition of the $PPy^+ClO_4^-$ samples which are electropolymerized at 1.2 V is not included in Table I because a serious degradation of the polymer and the solvent takes place at this potential (the C:N ratio derived from our data for the samples polymerized at 1.2 V is on average 8.5).

Table I shows that the atomic ratio C:N for the samples polymerized at 0.4 and 0.6 V is in reasonable agreement with the ideal polypyrrole stoichiometry of 4:1. This indicates an undamaged polymer structure at low polymerization voltages. The C:N atomic ratio for the samples grown at 0.8–1 V increased by about 30% above the ideal polypyrrole stoichiometry which indicates the presence of polymerization damage. Damage in a polymer structure induced by high electropolymerization potentials is related to pyrrole ring cleavage, aliphatic chain formation, and cross linkage.

The O:Cl atomic ratio is close to the ideal stoichiometry of perchlorate anions for electropolymerization potentials lower than 0.6 V. Increasing the electropolymerization voltage causes the O:Cl ratio to be increased by a factor of 1.5. The increase in oxygen content at higher polymerization potentials is related to polymer chain oxidation. Polypyrrole samples grown with the SO_3-based polymeric anions also appeared to have oxidized polymer chains. The O:S atomic ratio for the latter samples was 4.4, which is larger than the ideal stoichiometric ratio of 3.[9]

The polypyrrole concentration in the $PPY^+ClO_4^-$ samples is close to 85% (perchlorate anion concentration 15%). The number of pyrrole rings per ClO_4^- anion was estimated from the atomic N/Cl and C/Cl ratios. The average $PPY^+ClO_4^-$ repeating segment for polymerization potentials of 0.4 and 0.6 V (Table I) is composed of 1.3 pyrrole rings and 1 anion. For the polymerization potentials 0.8 V and above the XPS compositional analysis shows 1.6 pyrrole rings per 1 perchlorate anion. This is in agreement with the results of Zeller and Hahn,[18] who found a dependence of the anion content (N/Cl) on polymerization conditions. However, it disagrees with previous results of 3 monomer units per 1 anion.[12,19] The XPS data demonstrate that the doping level of polypyrrole is on average 2 anions per 3 pyrrole rings, but the electrostatic interaction involves 1 anion per 3 pyrrole monomer units (30% of modified pyrrole units). Only half of the incorporated anions appears to be located favorably (with respect to the planar rings) for the specific electrostatic interaction (Figure 3a). Approximately half of the anions trapped into polymer matrix are not involved in the specific electrostatic interaction with the polypyrrole. These anions are not removed by careful rinsing of the films with the proper solvents. On the basis of the XPS evidence, it is not possible to determine whether the "excess anions" are involved (i) in nonspecific interaction with the polypyrrole (N 1s photoemission exhibits a single peak for complete delocalization of positive holes), or (ii) in ion pairs with lithium ions. The Li/Cl atomic ratio cannot be determined reliably from the XPS data because the sensitivity factor for Li 1s photoemission is about 37 times smaller than the sensitivity factor for Cl 2p photoemission. Excess perchlorate anions are known to form ion pairs with litihium cations in PPY films under certain conditions.

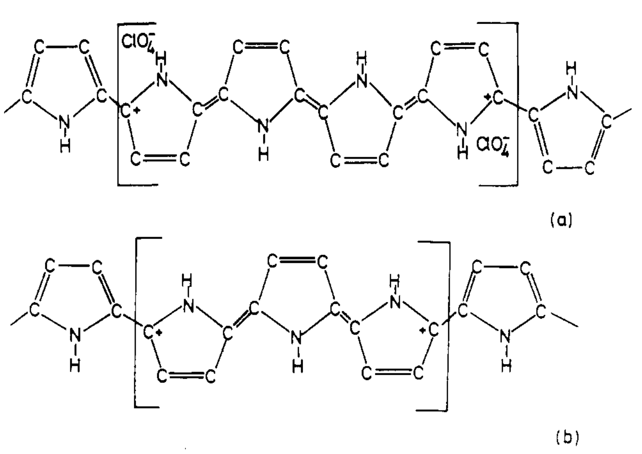

Figure 5. Ideal structure of oxidized (conducting) polypyrrole showing two positively charged defect structures: (a) bipolaron extending over four pyrrole rings; (b) bipolaron extending over three pyrrole rings.

Finally, the spatial extent or the width of bipolarons can be estimated from the calculated number of electrostatically screened nitrogen atoms. Two possible bipolaron structures are shown in Figure 5. The participation of 1 nitrogen heteroatom per 3 pyrrole units in the electrostatic interaction with one perchlorate anion suggests that the geometric defect extends over four rings. The width of the bipolaron compatible with our compositional analysis is given in Figure 5a.

Conclusions

Electrochemically grown, conductive polypyrrole films, doped with perchlorate and polymeric anions, were characterized by means of X-ray photoemission spectroscopy. XPS data show that the pyrrole units are preserved in the polymer up to 1 V. The dopant anions remained intact as ClO_4^-, poly(vinyl sulfonate), and poly(4-styrenesulfonate), respectively. Dopant anion content depends slightly on the polymerization voltage. We find on average 3 pyrrole rings per 2 ClO_4^- counterions. The N 1s lineshape analysis of the polypyrrole films doped with perchlorate anions indicates the formation of localized positive charges along the chain associated with local modification of the chain geometry and the appearance of bipolaron defects. In addition, the entire pyrrole ring unit interacts electrostatically with anions. In the ordered type of polymer–anion arrangement, the center of the tetrahedral perchlorate anion is assumed to be located approximately above the middle of the pyrrole ring with all three oxygen atoms of a triangular face accommodated parallel to the ring plane. As a result, the negatively charged ClO_4^- ion will produce an electric field which affects all four carbons and the nitrogen in the ring by making them more positive. A specific electrostatic binding of ClO_4^- at the nitrogen heteroatom site alone would have resulted in a shift of the shoulder in the N 1s core level that is larger than that observed in the present measurements. The influence of charge transfer on the electronic and geometric structures of polypyrrole is found to be different for the PPy doped with large anions as compared to the ClO_4^--doped films. In the case of polypyrrole doped with polymeric anions, the negative charge carriers (sulfonate groups) cannot easily approach the pyrrole ring site to form ring–anion pairs which are suitable for specific electrostatic interaction. The specific anion–ring electrostatic interaction is replaced by uniform charge extraction from the polymer backbone in the latter case. Our data indicate that when the negative charge carriers are not located in close proximity to the pyrrole ring site, the charge is withdrawn from the π-conjugated carbon path, and the created cation hole is delocalized and does not affect the nitrogen heteroatom.

Registry No. $PPy^+ClO_4^-$, 82200-25-7; PVS, 26101-52-0; PSS, 50851-57-5; PPy, 30604-81-0.

Time-Resolved in Situ X-ray Difffraction Studies of a Lithium Nickel Oxide Catalyst during the Oxidative Coupling of Methane

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A lithium nickel oxide catalyst of composition $Li^+{}_xNi^{2+}{}_{1-2x}Ni^{3+}{}_xO$, $x = 0.45$, active in the oxidative coupling of methane, has been studied in the presence and absence of added gaseous oxygen at 700 °C using simultaneous in situ X-ray powder diffraction with gas chromatography. In the presence of gaseous oxygen the bulk structure remains essentially unchanged for more than 5 h, and during this time the catalyst is selective for C_2 production; following this there is rapid reduction of the catalyst through NiO to Ni metal, with corresponding evolution of CO_2 and finally CO as the dominant gaseous products. By contrast, in the absence of gaseous oxygen the bulk structure immediately starts to decompose, yielding successively a total of four rock salt-type lithium nickel oxide phases. In this case the initial selectivity for C_2 production is 100% and declines as the solid breaks down. The in situ measurements allow direct correlation of the appearance of different solid phases during the experiments with variations in the rate of production of gaseous products, giving important insights into the behavior of this material as catalyst. A reaction scheme is proposed based on the catalytic and structural results. Additional studies of the structure of $Li^+{}_{0.45}Ni^{2+}{}_{0.10}Ni^{3+}{}_{0.45}O$ as a function of temperature in air using Rietveld structure refinements have been carried out to augment the in situ studies, showing that the ordered lithium nickel oxide structure is essentially invariant up to 700 °C in air.

Introduction

There has been much interest in the conversion of methane, an abundant natural resource, to more economically useful products by direct oxidation using heterogeneous catalysis. Although some attention has been given to the oxidation of methane to methanol and formaldehyde,[3] the majority of the research has involved the oxidative coupling of methane to ethane and ethene.[4] The oxide catalysts used have involved a wide variety of cations, including those from the s and p block, especially Li/MgO,[5] the lanthanides, notably Sm_2O_3,[6] transition metals,[7] and complex compounds, including oxychlorides.[8] Lithium-doped solids have received much attention as catalysts for oxidative coupling, particularly Li^+/MgO.[9]

Various alkali-metal-doped first-row transition-metal oxides have been screened by Hatano and Otsuka for their selectivity toward methane coupling,[10] and they concluded that lithium-doped nickel oxide was the most promising catalyst. Ungar et al.[11] have investigated various complex oxides with rock salt structures; the two most promising catalysts included in their study, $LiNiO_2$ and $LiYO_2$, have different structures and apparent mechanisms for oxidation. $LiNiO_2$ appeared to involve a bulk redox mechanism (in agreement with Hatano and Otsuka[10]), whereas $LiYO_2$ apparently catalyzed the oxidation of methane via a surface reaction. In further studies of the lithium nickel oxide catalyst, Hatano and Otsuka have shown[10] that an increase of lithium in the catalyst increases the selectivity for C_2 hydrocarbons, and they have used temperature-programmed desorption measurements to show that oxygen is desorbed in vacuo above 873 K, with a peak at ca. 1100 K. They have additionally investigated[12] the effect of changing pressures of reactants, C_2 selectivity increasing

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