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X-ray photoelectron spectroscopy was used to characterize electropolymerized polypyrrole films doped with monomeric (ClO_4^-) and polymeric, poly(vinylsulfonate) and poly(4-styrensulfonate) anions. Electrostatic interaction between the polymer and the incorporated anions involves the whole pyrrole ring rather than specific nitrogen heteroatom sites only. ClO_4^- counterions have a planar configuration and are incorporated parallel to the planar rings. On the other hand, the large polymeric counterions are more randomly distributed around polymeric chain. After sputtering, counterions were found to be randomly distributed along the polymer chain. The analysis of the XPS data which leads to these conclusions will be discussed. (AW)

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XPS Studies of Doped Polypyrrole Films

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Introduction

Electropolymerized conducting polymers have been studied because of their wide range of useful applications in electronic devices such as batteries, capacitors, ion sensors and electrochromic devices.[1] Electropolymerization has proved to be one of the best means to produce good quality electroactive conducting polymer films with doped anions under in-situ conditions. However, the structure of such conducting polymers has yet not been clarified in spite of the substantial effort at characterization with various surface analysis techniques[2].

In the present paper, the authors will describe the microscopic structure of polypyrrole films which were electrochemically grown with monomeric and/or polymeric anions. The rigorous ex-situ XPS analysis enabled us to interpret the chemical and structural environment within the polymer with interactions by dopant anions which were incorporated into the polymer matrix during electropolymerization.

Results and Discussion

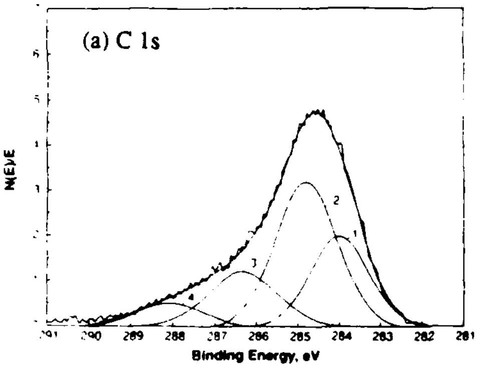
The C 1s, O 1s, N 1s and Cl 2p core level spectra shown in Figs.1a-1d are typical of the $PPY^+ClO_4^-$ films formed in the potential range from 0.4-1.2 V(vs. $Ag/AgNO_3$(acetonitrile)).

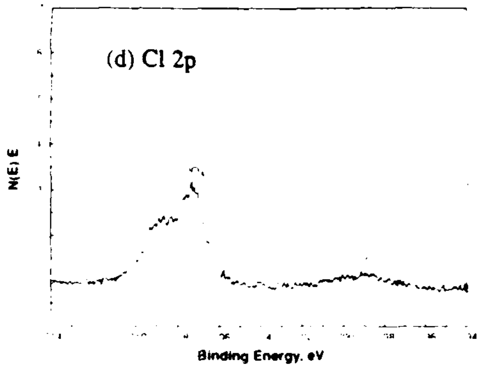
The major feature in the C 1s photoemission is centered at about 284.5 eV(Fig.1a). The carbon peak is asymmetric and skewed towards high binding energies. As seen from Fig.1a, the C 1s spectra can be decomposed into four lines (labeled 1-4) by varying only their relative intensities. Peak 2 is assigned to the α carbons and is always more intense than peak 1 due to β carbons. The ideal pyrrole monomer unit contains two α and two β carbon atoms and the difference in intensity between the α and β carbon lines has been explained by the presence of the hydrocarbon contamination.[3] However, hydrocarbon contamination would add to the intensity of β carbon photoemission which is more hydrocarbon-like than α carbon, and would be a random function of the experimental conditions. The latter is contrary to experimental results. We suggest instead that the C 1s lineshape originates from *inequivalent pyrrole monomer units* in terms of electrostatic interactions with perchlorate anions. The photoemission of the pyrrole rings modified by electrostatic interaction with nearly anions would be shifted towards higher binding energies.

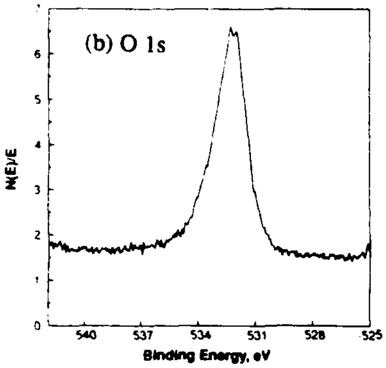
The N 1s spectra of the polypyrroles polymerized at different potentials indicate clearly the existence of two inequivalent nitrogen heteroatoms (Fig.1c). The shoulder shifted by 1.6 eV with respect to the main nitrogen feature is attributed to those nitrogens in pyrrole rings which have strong electrostatic interaction with nearly anions.

The presence of Cl^- species is always observed in the Cl 2p region of as received polymer samples (Fig.1d). After sputtering, the high energy shoulder in the N 1s region disappeared indicating that the N heteroatoms in the sputtered films are not modified the electrostatic interaction. This finding can be explained by a sputter-disturbance of a doped polymer structure. The lineshape of the C 1s photoemission was not changed upon sputtering.

The C 1s and N 1s lineshape analysis indicate that the entire pyrrole ring unit is modified by the electostatic interaction with anion. We propose that an ordered type of doped polypyrrole structure is formed in which the flat ClO_4^- anion is placed parallel to the planar pyrrole ring. The negatively charged ClO_4^- ion is approximately the same size as the monomer unit and produces an electric field at the ring site which affects all 4 carbon and 1 nitrogen atoms in its vicinity by making them more positive. Any specific electrostatic bonding at the nitrogen heteroatom site would result in a considerably larger shift of the shoulder of the N 1s core level than the one observed in our measurements. A disorder-type of doped polypyrrole structure develops upon sputtering or by doping the polypyrrole with the large size anions like poly(4-styrensulfonate). The relative position and angle betwween the ring and the planar anion vary randomly for the sputter-disordered $PPY^+ClO_4^-$ films. The large anions of complex three dimensional configuration can not form closely packed parallel ring-anion pairs which are suitable for the specific ring site electrostatic interaction. The anions are randomly distributed along the polymer chains and the specific anion-ring electrostatic interaction is converted into a uniform charge extraction from the polymer back bone. The C 1s lineshape is preserved in the random type of anion distribution, which indicates that the carbon atoms are affected more strongly than nitrogen hetroatom by such uniform charge extraction.







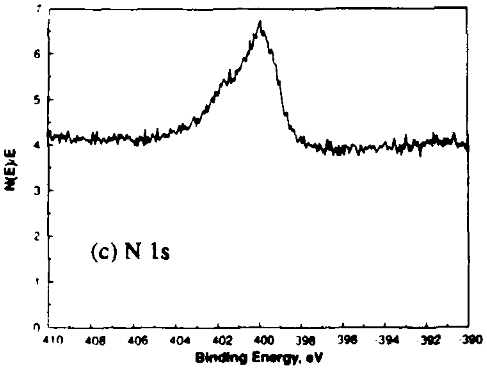


Fig.1 Core level photoelectron peaks for as-grown polypyrrole films(PPYClO$_4^-$): (a) C 1s; (b) O 1s; (c) N 1s; (d) Cl 2p.

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