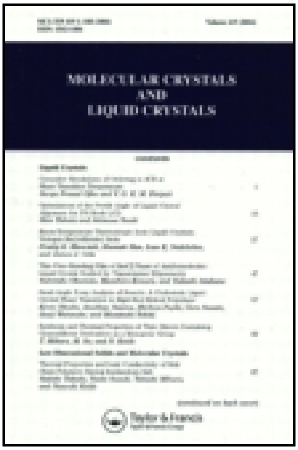

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ULTRA HIGH VACUUM ELECTROCHEMISTRY WITH CONDUCTING POLYMERS

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Abstract

Solvent free polymer solid electrolytes based on high molecular weight poly(ethylene oxide) (PEO) complexed with alkali metal salts are compatible with ultra high vacuum (UHV). This has been taken advantage of in the design of electrochemical cells for electrochemical synthesis as well as reduction/oxidation of polypyrrole in UHV. This allows in situ application of surface spectroscopies (XPS) to study the material as a function of its state of oxidation.

Recent XPS studies of polypyrrole (1,2) have lead to conflicting conclusions about the interactions between the anions and the polypyrrole matrix. Salaneck et al (1) concluded that uniform charge extraction from the polypyrrole backbone occurs whereas the results of Pfluger and Street (2) seemed to indicate that a specific electrostatic interaction occurs between the majority of the anions and the nitrogen heteroatoms.

The purpose of the present study is to attempt to resolve these ambiguities and extend the XPS studies on polypyrrole using a new technique which allows us to perform electrochemical oxidation and reduction of the polymer in situ . The material can then be studied with XPS spectroscopy as a function of its state of oxidation (3).

A key element of the in situ electrochemical technique is the application of thin film polymer solid electrolytes in the construction of electrochemical cells which are compatible with UHV. The polymer solid electrolytes are based on high molecular weight poly(ethylene oxide) (PEO) complexed with alkali metal salts (e.g. $NaClO_4$) (4) and have a sufficiently low vapor pressure to be compatible with UHV (10^{-9} torr).

Fig. 1 shows a schematic of the UHV electrochemical cell. The UHV cells are constructed by solution casting from MeOH a $PEO.NaClO_4$ film (10 um) onto a transparent conducting substrate (indium-tin oxide (ITO) on glass), followed by vacuum evaporation of a thin semitransparent Au film (180-200 Å). The Au film at that thickness still maintains a high density of pinholes and microcracks through which monomers can diffuse and photoelectrons escape (3). During polymerization the sandwich cell $ITO/PEO.NaClO_4/Au$ is kept in a preevacuated chamber into which is released pyrrole vapor. Pyrrole monomers will diffuse through the pinholes of the Au film and into the PEO electrolyte. By the application of a sufficiently positive potential to the Au electrode electrochemical polymerization of a conducting polypyrrole film takes place on the Au. With a transparent substrate the average thickness of the film as it grows can be monitored optically by mounting the chamber in a spectrophotometer. Films of thicknesses 200-300 Å were used. Optical spectra showed that the films could be completely reduced in situ with the PEO electrolyte.

The cells with the as made, oxidized polypyrrole films were subsequently transferred to the UHV chamber for XPS analysis, being exposed to air for less than 5 minutes.

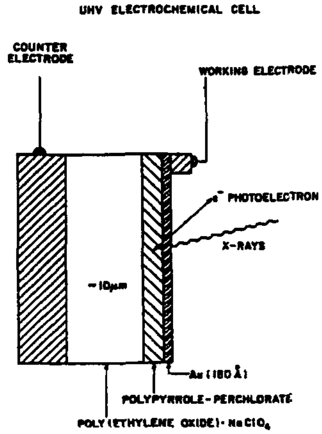

Fig.1 Schematic of UHV electrochemical cell

During the XPS experiments only photoelectrons emitted from the polypyrrole in the pinhole regions could be collected due to the short electron mean free path in Au, of the order of 10 Å.

Nitrogen 1s Spectra

Fig. 2 shows the N(1s) spectra of polypyrrole synthesized and cycled (between oxidized and reduced states) with PEO.$NaClO_4$.
The N(1s) spectrum of as made polypyrrole indicates the existence of three inequivalent nitrogens. The main pyrrole peak at 401.3 eV has a well resolved shoulder on the high energy side at 402.9 eV as well as a shoulder in the 399 eV region. The high energy shoulder is visible only when the polymer is in the oxidized state and is attributed to electrostatic interaction with anions. The structure reappears when the polypyrrole is reoxidized but at a lower energy and less pronounced, indicating a somewhat weaker electrostatic intraction between the nitrogens and the anions and involving a smaller fraction of the nitrogens. This means that the polypyrrole film is not fully reoxidized to its original state.

The low energy shoulder could be due to dehydrogenation of a certain fraction of the nitrogens followed by rearrangement of the pyrrole bonds to satisfy the three nitrogen valences (5).
Alternatively, the low energy shoulder could be the result of

incorporation of Na cations from incompletely dissociate salt. The low energy shoulder vanishes when the polymer is reduced and does not reappear upon reoxidation.

The N(1s) spectra of fig.2 also show satellite (shake up) structures on the high binding energy side. These are usually attributed to π-π^* transitions accompanying core level excitations and can be taken as evidence for the preservation of the pyrrole ring structure (1,3,6).

No high energy shoulders were visible in the carbon 1s spectra (3). The C (1s) spectra are skewed towards the high energy side and are essentially identical for oxidized and reduced polypyrrole. The skewing is therefore attributed to disorder phenomena rather than the excitation of fermi surface electrons (3).

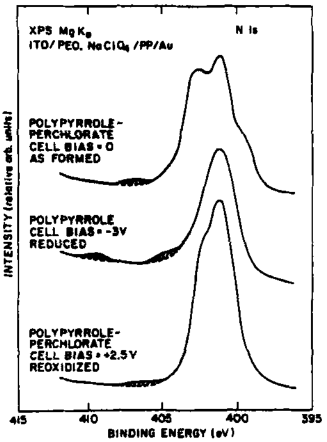

Fig.2 N (1s) spectra of polypyrrole oxidized and reduced *in situ* with PEO electrolyte

Anion Concentration

The anion concentration was measured using the chlorine 2p signal. In fig. 3 the anion concentration in polypyrrole in the oxidized state is plotted as a function of the number of cycles (reduction-reoxidation) of the polymer. In both PEO.$NaClO_4$ and polypyrrole polymerized in PEO.$NaClO_4$ two chlorine signals of approximately equal magnitude are observed, one at 199 eV corresponding to a chloride species and one at 208.9 eV corresponding to perchlorate, whereas in the pure $NaClO_4$ salt (on double stick tape) only the perchlorate species is observed. It appears then that both species are built into the polypyrrole matrix during polymerization with equal probability. The perchlorate anion is known to be thermodynamically unstable and may react with organic materials to generate Cl^- and O_2 in the presence of water (7), trace amounts of which are present during complexation and solution casting, as well as during transfer prior to insertion in the UHV chamber due to the hygroscopic nature of PEO.

As fig. 3 clearly shows, the anion concentration decreases dramatically with the number of switching cycles. This implies a high degree of irreversibility in the electrochemistry of polypyrrole. The difference in the results of polypyrrole films cycled in MeCN and PEO electrolytes is likely due to swelling effects and solvent assisted ion insertion with MeCN electrolytes.

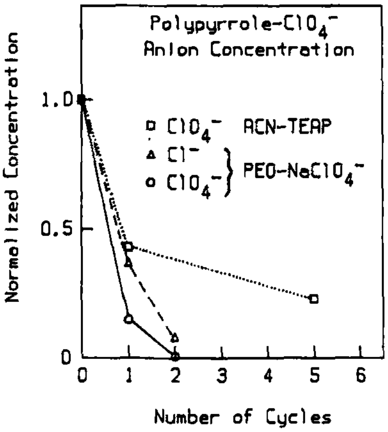

Fig.3 Anion concentration of oxidized polypyrrole

These results are consistent with the evolution of the N(1s) spectra during cycling (fig. 2).

We cannot conclusively determine from the present data which anion species is responsible for the electrostatic binding to the nitrogen heteroatoms as exhibited by the high energy shoulder of the N(1s) spectrum. The chloride anion, being smaller than the perchlorate anion and with a higher charge density, could conceivably have stronger interaction with the polymer matrix.

The high energy shoulder could therefore be due to a chloride, rather than a perchlorate, anion species. In this context one should note that Salaneck et al did not observe a high energy shoulder with BF_4 doped polypyrrole (1).

In summary, we have demonstrated the technique of *in situ* electrochemistry/XPS and its utility for detailed surface spectroscopic studies of conducting polymer films. The advantage of the technique lies in being able to study the polymer throughout its continuum of oxidation states and to perform the electrochemistry with the rigorous exclusion of oxygen that the UHV permits.

The results show a fundamental irreversibility in the electrochemistry of polypyrrole which carry important implications for the use of polypyrrole as electrode material in rechargeable polymer batteries.

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