

Role of Ions in Polypyrrole Films.

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It is well known that during the electrochemical formation of conductive polymers a stoichiometric amount of anions from solutions is incorporated into the polymer to neutralize the positive charge of the polymer chains. But the role of anions is not limited only to guaranteeing of the electroneutrality of the polymer during synthesis and electrochemical treatment.

An essential role of anions appears already during the electropolymerization. It is generally accepted that the electrochemical polymerization of polypyrrole (PPy) proceeds via the formation of oligomers. Semi-empirical quantum-chemical calculations have shown that anions essentially stabilize the charged oligomers formed [1]. More detailed analysis has shown that the interaction between positively charged oligomer and an anion depends essentially on the nature of the anion. It was also established that *syn*-conformation leads to the formation of helical chains of PPy, it is quite probable that such form of polymer chain is common. The helical form of PPy chains was established experimentally by STM studies in the first state of formation of the polymer deposit [2]. It was also established that anions have remarkable influence on the formation of the morphology of the polypyrrole film [3,4].

The electrochemical properties of the PPy film depend considerably on the mobility of anions in the polymer. The mobility of ions in the polymer depends on the properties of the polymer and the ion. We have studied the influence of the properties of ions on the voltammetric behavior of PPy films in close detail.

The PPy films deposited in the presence of different anions [ClO_4^- , NO_3^- , Cl^- , SO_4^{2-} , dodecylsulfate (DDS), naphthalene-2-sulfonate and naphthalene-1,5-disulfonate] were studied by cyclic voltammetry in solutions of various electrolytes. Water, methanol, ethanol and acetonitrile were used as solvents. The changes in the chemical composition of the films during electrochemical treatment were determined by electron probe microanalysis (EPMA). In addition to the common single-layer films some bilayers of PPy films doped with anions of limited (DDS⁻) and good mobility (Cl^-) prepared by consecutive electrodeposition were studied.

It was established, that if the mobility of anions is good as in the case of ClO_4^- or NO_3^- , there is no essential difference between the first, second and the following voltammograms, and there is a good proportionality between the peak current I_p and the potential sweep rate v . Such behavior of conducting polymer films can be described by the model of "free" ions [6,7]. The mobility of halogenide-anions such as Cl^- and Br^- in PPy films is almost as good as ClO_4^- or NO_3^- and the shapes of the voltammograms are similar.

The difference in the mobility of anions can be related to their different interaction strength with the conducting polymer chain. The strength of interaction of the ions with the charged polymer chain was estimated using semi-empirical quantum chemical calculations. The complexation enthalpies of the anions with pyrrole oligomer dications in both *syn*- and *anti*- conformation were calculated. The chloride and bromide anions show relatively similar stabilization energies somewhat higher apart from the nitrate and perchlorate anions. The double

charged sulfate forms a different class with much higher stabilization energies than the single charged anions. The calculated stabilization enthalpies are in good reciprocal correlation with the experimental mobilities of the anions in the polymer.

If the mobility of anions in the polymer is not good as in the case of SO_4^{2-} or DDS^- , the situation is much more complicated: the voltammograms are less reversible, the first and the following voltammograms are remarkably different. It was established that during the reduction of the PPy|DDS or PPy| SO_4 films electroneutrality of the film is established not mainly by anions leaving the film but by the incorporation of cations from the solution into the film [4,8]. The nature of the cations has a remarkable influence on the dependence of the peak current $i_{p,c}$ on the potential scan rate (Fig 1.). The electrochemical properties of PPy|DDS and PPy| SO_4 films can be described by the model of exchangeable "bond" ions [7].

It was found that the shape of cyclic voltammograms for PPy|DDS films depends essentially on the solvent used and in methanolic media the shape of CV curves for PPy|DDS films is more similar to those obtained in aqueous solutions with small inorganic anions. The main reason of this phenomenon is obviously connected with the good swelling ability of PPy in organic solvents.

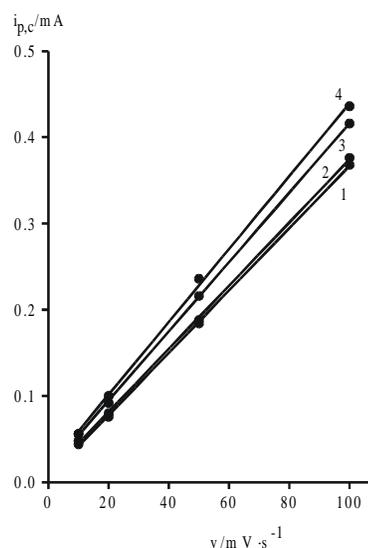


Fig. 1. The dependence of the peak current i_p on sweep rate v for PPy| SO_4 film ($1\mu\text{m}$) in 0.1 M (aqueous) solution of 1) Li_2SO_4 ; 2) Na_2SO_4 ; 3) K_2SO_4 ; 4) Cs_2SO_4

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