

# Polypyrrole Films Formed by Competitive Electrooxidation of Halogenides and Pyrrol

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At the date, there is high interest to prepared polypyrrole (ppy) films for specific applications such as batteries, electrochromic devices and sensors among another. The ppy films properties depends on their surface morphology, which in turn are affected by the electrosynthesis conditions. Relationship of ppy films with the halogenides or halogens are limited to both preparation of ppy films with monomers halogenided [1] and to employ the halogenide anions ( $\text{Br}^-$  or  $\text{Cl}^-$ ) as doping anions in aqueous media using high halogenide concentrations [2].

In this communication, ppy films were prepared on polycrystalline Pt by competitive electrooxidations of pyrrol (py) and halogenide anions ( $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  at  $ca\ 1 \times 10^{-3}\text{ M}$  and equimolar with the py concentration). Here, we were used an inert electrolyte the  $\text{Et}_4\text{NBF}_4$ , 0.1 M and acetonitrile as solvent. Films were studied by *ex situ* AFM (contact mode) at room temperature (*ca.*  $25^\circ\text{C}$ ).

Results indicated that in solution without py, halogenides presented one ( $\text{Cl}^-$ ) and two ( $\text{Br}^-$  y  $\text{I}^-$ ) oxidation peaks at less anodic potentials that py oxidation. In contrast, with py in solution,  $\text{Cl}^-$  oxidation do not change, but oxidation of  $\text{Br}^-$  and  $\text{I}^-$  only is seen as one peak. The two observed oxidation peaks for the last two halogenides is due to formation of tri-bromide and tri-iodine species respectively, which are not detected when py is in solution. This means that the electrogenerated species after the first oxidation peak can react with the py monomer. This electrochemical behavior for the halogenide, in non-aqueous solution, origins specific surface morphologies of the ppy films.

Figures 1, 2 and 3 show representative surface morphologies of ppy films preaped in presense of iodine, bromide and chlorine respectively.

The formed films shown common morphological surfaces: nodules distributed homogeneously and grooves, which seems nano and microtubules placed randomly on the nodules. However, nodules and grooves have different shape and size. While, depending on both halogenide anion and applied cycle number different thickness and conductivities were obtained for the ppy films.

Results indicated that the halogenide electrochemistry in non-aqueous dissolution affects mainly the surface morphology, thickness and conductivity of the formed ppy films

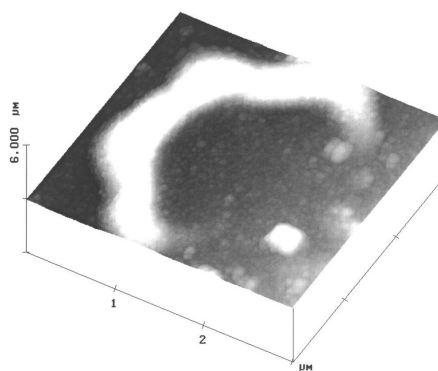


Figure 1. AFM image of ppy film formed in acetonitrile solution containing  $1.4 \times 10^{-3}\text{ M I}^-$  and  $0.1\text{ M Et}_4\text{NBF}_4$ .  $E_{I=0} = -0.2$ ,  $E+ = 1.6\text{ V}$  and  $E- = -1.3\text{ V}$ .  $v = 0.1\text{ V/s}$ .

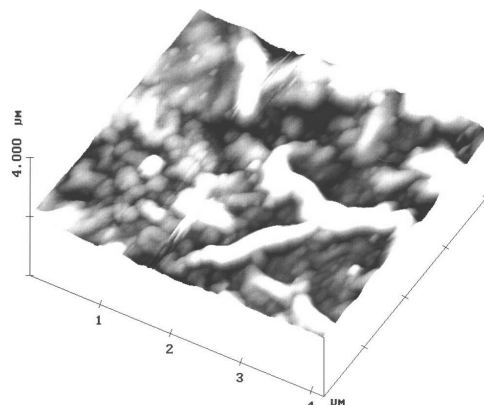


Figure 2. AFM image of ppy film formed in acetonitrile solution containing  $1.5 \times 10^{-3}\text{ M Br}^-$  and  $0.1\text{ M Et}_4\text{NBF}_4$ .  $E_{I=0} = -0.1$ ,  $E+ = 1.9\text{ V}$  and  $E- = -1.4\text{ V}$ .  $v = 0.1\text{ V/s}$ .

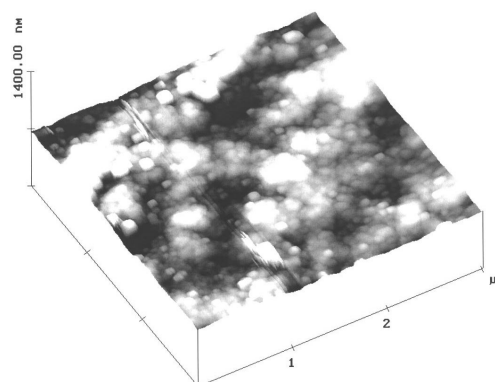


Figure 3. AFM image of ppy film formed in acetonitrile solution containing  $1.7 \times 10^{-3}\text{ M Cl}^-$  and  $0.1\text{ M Et}_4\text{NBF}_4$ .  $E_{I=0} = -0.2$ ,  $E+ = 1.4\text{ V}$  and  $E- = -0.3\text{ V}$ .  $v = 0.1\text{ V/s}$ .

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