Pyrrole electropolymerization in the presence of sulfonated polyelectrolytes of different structure

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Polypyrrole (PPy) films were electrochemically synthesized in the presence of water-soluble polysulfonic acids and their sodium salts: poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA, flexible-chain); poly(styrene-4-sulfonic acid) (PSSA, flexible-chain), poly-(p,p'-(2,2'-disulfonic acid)-diphenylene-iso-phthalamide) (i-PASA, semi-rigid-chain) in aqueous solutions. The pyrrole electropolymerization was performed in potentiostatic (PS), galvanostatic (GS) and cyclic voltammetry (CV) regimes and the results were compared with common synthesis of PPy in aqueous solutions of inorganic electrolytes. It was shown that the use of polyelectrolytes both in acid and salt form in PPy electrosynthesis leads to its acceleration and the possibility of using lower concentrations of reagents compared to electrosynthesis in inorganic acids and salts (Fig. 1).

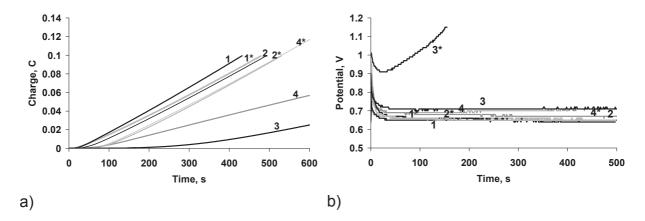


Fig. 1. Time dependences of the charge during PS synthesis (a) and potential during GS synthesis (b) of PPY in aqueous solutions containing PAMPSA - 1, PAMPSNa – 1*, PSSA - 2, PSSNa – 2*, H_2SO_4 - 3, Na_2SO_4 – 3*, i-PASA – 4 and i-PASNa – 4*.

Using Vis-NIR spectroscopy, cyclic voltammetry and spectroelectrichemistry it was shown that the course of synthesis and electronic structure of PPy depends strictly on the structure of polyelectrolyte and the nature of its cation. Shorter induction period of PS electropolymerization and lower potential of GS electropolymerization were observed in the presence of acid forms of flexible-chain polyelectrolytes compared to the syntheses in the presence of their sodium salt forms (Fig. 1). In the presence of acid forms of flexible-chain polyelectrolytes films are formed with higher degree of charge carriers' delocalization (Fig. 2), with rougher surface and spectroelectrochemical properties similar to those of PPy films obtained in inorganic electrolytes. Contrarily, in the presence of acid form of semi-rigid-chain polyelectrolyte PPy films are formed at lower rate; they are characterized by lesser roughness and lesser degree of charge carriers' delocalization (Fig. 2).

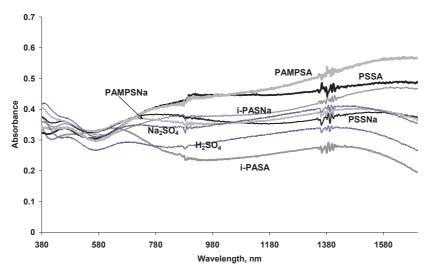


Fig. 2. UV-Vis-NIR spectra of the PPy films, electrodeposited in the presence of sulfonated polyelectrolytes of different structure, H₂SO₄ and Na₂SO₄.

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