Perchlorate Interchange during the Redox Process of PPY/PVS Films in an Acetonitrile Medium.  
A Voltammetric Study.  

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Abstract:

Polypyrrole/poly (vinyl sulfonate) (PPY/PVS) films in acetonitrile containing 0.1M LiClO$_4$ were studied by cyclic voltammetry. Consecutive voltammograms pointed to a continuous increase in charge involved in the process, suggesting a rise in the number of the electro active participants involved in the redox process. However, voltammograms obtained for the PPY/ClO$_4^-$ films in analogous conditions pointed to a steady state behavior from the very early cycles. Theoretical studies based on the Nernst and Butler-Volmer equations indicated that perchlorate ions are involved during the oxidation/reduction process of the PPY/PVS films when the steady state is reached.

Introduction

Since the 1970, a great number of research groups have focused their interest on conducting polymers, such as polycetylene, poly pyrrole (PPY), poly aniline, and so forth, studying them from several points of view, including their synthesis, characterization, and technological application. PPY is one of the most widely studied conducting polymers because pyrrole is easily synthesized .In addition, PPY shows good long term stability of its electric conductivity, together with good redox properties and the possibility of forming polymeric blends with optimal mechanical properties [1-3].

PPY synthesis by electrochemical oxidation of pyrrole monomers is well –known and well controlled method. Anions of different sizes can be used to dope PPY during the Polymerization process. Examples of these anions include ClO$_4^-$, NO$_3^-$, Cl$^-$ [4, 5].
Experimental Section:

Pyrrole monomer (Fluka, > 97%) and Sodium poly (vinyl sulfonate) (PVS-Na; Aldrich), LiClO$_4$ (Merck), LiClO$_4$ (Merck) and AN (Merck, with a water content <0.01%) were used. PPY/PVS and PPY/ClO$_4$ films were generated by electrochemical oxidation on GC electrode at +0.7V (vs Ag/Agcl) in aqueous solutions of 0.1 M pyrrole and 0.05M PVS-Na or 0.01M LiCl04. A three-electrode cell composed of a GC working electrode, an Ag/Agcl reference electrode, and a Pt wire as auxiliary electrode was used. Cyclic voltammetry studies were performed in similar three electrode cell using Solatron SI 1287 potentiostat/galvanostat.

Results and Discussion:

Cyclic Voltammetry of PPY/PVS and PPY/ClO$_4$ Films. Figure (1) shows 5th consecutive voltammograms, from (-1 V), to (+0.8 V), performed on a PPY/ClO$_4$ film in a (0.1 M) LiClO$_4$/AN solution at a scan rate of 0.8 V/S .The first catholoid voltammogram showed an anomalous shoulder at (-0.81V), which is known as the first scan effect. This peak gradually shifted toward lower potentials and stabilized at (+0.45V), on the 5th cycle.

And also the voltammetric behavior of a PPY/PVS film in the same electrolyte and the same potential range was studied. The achieved results revelied that during the five initial cycles, the anodic charge was very small, measuring 1.33mC/cm$^2$ for the 2nd cycle, and increased to 8.02mC/cm$^2$ for the 45th cycle when it reached a voltammetric steady state. Moreover, a shift the anodic potential peak to higher potentials was observed for consecutive cycles.

![Cyclic voltammograms of PPY/ClO$_4$ polymer in a 0.1 M LiClO$_4$/AN solution. Scan rate 80mV/s.](image)
References