Electrochemical Relaxation at Electrically Conducting Polymers

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Abstract. In this study, slow relaxation (SR) associated with the electroreduction of polyaniline (PAn) films during polarization to high cathodic potentials was investigated by cyclic voltammetry technique. Anodic voltammetric currents were used as experimental variable to indicate the relaxation occurring in PAn films deposited electrochemically on the Pt electrode surface.

The dependence of SR on polymer film thickness, waiting potential, and mobility of the doped anion was investigated.

Percolation threshold potential for heteropolyanion doped PAn was estimated to be between 150 and 200 mV depending on polymer thickness on the electrode surface.

A new model of the conducting to insulating conversion is described by the percolation theory and mobility gap changes during the process.

1. Introduction

The slow relaxation of conducting polymers (CPs) is an interesting phenomenon which has been extensively studied theoretically or experimentally by numerous researchers from different field of science [1-8]. In cyclic voltammetry (CV) experiments, when the polymer is exposed to a potential value in the neutral state for time $t_w$, the oxidation peak of the first run differs from the steady-state profile, thereby, called 'first cycle effect', 'memory effect' or 'slow relaxation'. It is well-known that peak potential, $E_p$, peak width at half current, $\Delta E_{1/2}$, current density, $j_p$, and amount of electric charge depend on the logarithmic electrolysis time spent in the insulating state. Several explanations have been proposed to describe the origin of the relaxation effect [1-8].

Change in the degree of order along with the redox process [2], percolation of redox sites [5,9-12], change in the Fermi level during polarization [1], modification of the structure of the double layer during the polarization in the insulating state [3], incomplete reduction of the polymer [8], structural and morphological changes taking place during electrochemical reduction and oxidation of CPs (ESCR model) [4, 13-19], different electrical conductivity of oxidized and reduced forms of CPs [9], and anion movement during redox switching of CPs [2], are some arguments which have been taken into account by several researchers groups for this purpose.

In fact redox switching of CPs, involves a cascade of events including electron exchange between the polymer and electrode, transport of counter ions into or out of the film, solvent exchange between
the polymer and the solution and rearrangement of polymer chains to accommodation the new charge site and mobile species populations. All of the above mentioned models, except ESCR, assume that electrochemical responses of CPs are unable to provide information about structural changes in the film. They consider only a single electrochemical process and do not take into account that CP films behave as three dimensional electrodes and then the validity of three models is restricted to simple electrochemical process such as electron transfer, counter ion diffusion or capacitive effects. Aoki et. al. postulated that conductive domains in the polymer film propagate with the well-defined boundary from the metal/polymer interface to the polymer/solution boundary and that these domains behave as the conducting phase mediating oxidation of the polymer [12]. In contrast, the conducting-to-insulating conversion occurs uniformly without any definite boundary and can be explained by percolation theory. Conducting to insulating conversion, also, is associated with electrochemical slow relaxation which caused by competition between the diffusional retrieval of electric paths from the local conducting domains to the electrode and the electrochemical cut-off of electric paths. It means that relaxation of the polymer occurs during the reduction process.

Otero et. al. presented a model of electrochemically stimulated conformational relaxation. According to this model, the oxidation process can be divided into four steps [14]:
- Electron loss from the polymer chains, with formation of polaron (radical cations) and bipolarons (dication).
- Conformational relaxation of the polymer chains with generation of free volume, being the process initiated from surface nuclei: relaxation-nucleation process. It means relaxation of the polymer occurs during oxidation process and is accompanied with the opening of polymer structure.
- Exchange of counter ions between the polymer chains and solution in order to keep the electroneutrality in the film: counter ion diffusion process.
- Additional exchange of ion pairs (salt-draining) and solvent molecules.

ESCR theory seems to be suitable for the description of the relaxation phenomena and simulation of voltammograms. However, there are some aspects which have to be considered in modeling for better interpretation.
- Gibbs energy should be used instead of enthalpy.
- This model assumes high cathodic potentials or long polarization times lead to a 2D interface between the neutral polymer and the solution. But it seems that presence of remaining solvent molecules and counter ions which have been trapped inside of the polymer matrix even in high cathodic potentials inhibits formation of 2D structure.
- This model assumes subsequent oxidation of polymer involves the opening of 2D closed network from polymer-solution interface toward electrode-polymer interface with formation of channels large enough to allow the penetration of counter ions whereas, it is more reasonable that formation of oxidized phase occurs at the electrode-polymer interface, because it is electrode that injects required charge into the polymer matrix.
- Gradual shrinkage of polymer due to the cathodic polarization can lead to the reduction of subsequent reaction and electrical current which must be considered in current voltage equation.

It is obvious that the existing models are not either consistent with each other or can not describe the process completely.

The present work has been aimed to the study of electrochemical SR in order to better understanding of the mechanism of this phenomenon.

2. Experimental
Aniline (Merck) has been distilled under reduced pressure before use. K₃PW₉O₃₈ heteropolyanion was synthesized according to the procedure cited in the literature and used as heavy dopant anion. Polyaniline films were built up on Pt electrode by electropolymerization of the monomer at room temperature from 0.1 M aniline in 0.5 M sulfuric acid in the presence or absence of heteropolyanion under controlled potential conditions (0.8 V versus Ag/AgCl). Polymer films with different thicknesses were deposited on the surface of the Pt electrode. The charge consumed for
polymerization was used as thickness criterion. For different polymerization time, the charge densities of 4.5, 8.8, 30.4 and 7.8 mC/cm² were obtained. The experimental setup for voltammetric measurements was a three-electrode glass electrochemical cell, with a Pt working electrode, 3 mm diameter, Pt wire counter electrode, and a saturated Ag/AgCl reference electrode.

Quantitative characterization of the relaxation effect was observed in CP by the potential pulse sequence shown in Fig. 1. First, a well-cathodic pulse for a given long time brings the polymer into the relaxed reduced state. Then, the potential is stepped and maintained for a waiting time t_w at a value where the film partially oxidizes. Last, the redox current generated by a triangular potential scan is recorded. This reverse method of relaxation study in comparison with direct method [] is less time consumption and more precise to estimate of percolation potential threshold.

3. Results and Discussion

Fig. 2 shows cyclic voltammograms obtained for PAn films and heavy anion doped PAn with different thicknesses before and after the holding of electrode at 250 mV oxidative potential.

As it can be seen, peak current reduces and anodic peak shifts to less positive potentials by a few tens of millivolts when the polymer is held at an oxidation potential for a definite time (t_w). This behavior represents a slow relaxation phenomenon.

Data of relative peak current versus t_w in the range of 0.0-1.0 s heteropolyanion doped PAn is given in Fig. 3. The relative peak current decreases with increasing waiting time, and reaches a nearly steady value dependence of thickness. The more thickness of the polymer, the more reduction of relative peak current and then the more SR is observed. At a short oxidation time, a part of PAn is converted to oxidized form. Therefore, lower anodic peak currents, passed in the next following anodic potential sweep, are observed. The more oxidation time or potential, the smaller part of PAn remains in its reduced form and then the lower anodic peak current are observed.

The SR behavior, observed for PAn film doped with heavy anion resembles the corresponding behavior for small anion doped PAn with the reduction of the relative peak current of 55-75% depending on thickness. It has been shown that when the anion charge/size ratio decreases, the proton contribution to the charge compensation process of PAn increases and large anion like heteropolyanion remains in the polymer matrix during the repetitive potential cycles. The rate of switching process then should be related to proton entrance into the film and the structural rearrangements of the polymer. Then SR behavior can not be attributed to the movement of anion during the redox switch of CPs. Thus, it could be assumed that the SR effect, observed for heteropolyanion doped PAn is concerned with the amount of repulsive forces between the polymer chains due to the presence of charges on the polymer segments, which determining the distance between polymer chains and causing lower hopping rate of electron from one polymer chain to its neighbor and then is related to its lower conductivity. This conclusion could be supported by the data obtained from self-doped sulfonated polyaniline (SPAn) [20]. The copolymer of aniline and meta-aminobenzene sulfonic acid contains sulfonated group, covalently bonded to a benzenoid ring of polymer backbone. Since the sulfo group is linked to the polymer backbone via a covalent bond, no anion movement should proceed during redox switching. Thus during the reduction step, polymer chains can not come to close to each other. The resulting copolymer showed SR behavior as well as PAn doped with small anions. Similar behavior has been observed for a copolymer of poly(sodium-4-styrene sulfonate) co polyaniline [8].

Fig. 4 (a and b) shows the semi-logarithmic plots of relative anodic peak currents on waiting time for heteropolyanion doped PAn films at different pH and charge densities. At very short time of potential step and after that, two distinct slopes can be determined; indicating two types of relaxation process is involved. It is evident that the behavior observed can not be described by a single logarithmic relaxation. Similar behavior has been observed by Csaak et. al. [7]. It can be seen that with decreasing the pH, slopes of two sections of the plots are approached to each other. Higher concentration of H⁺ increases its share in the relaxation process, with this difference that the volume
change of the polymer reduces. For all waiting potentials, from 0.0 to 250 mV, changing the slope occurs at 0.2 s waiting time and it is independent of the waiting potential.

The results obtained could be interpreted as follows:

When the polymer is poised at low potential value of -200 mV for long time (300 s), the polymer film is reduced and relaxed, however, the relaxation process of the polymer can not be completed because some counter ions and solvent molecules remain inside the polymer matrix since the more reduction of the polymer, egress of the counter ions is more hindered and the removal of the isolated polarons is more difficult. Then the polymer is exposed to the oxidative potential for definite time. At the first steps of oxidation, polarons are formed near the electrode/polymer boundary and distributed uniformly over the film rapidly. However, because of low percolation threshold of PAn, the total volume of the polymer rapidly is oxidized, and density of polarons increases to the percolation level and diffuses from electrode/polymer boundary toward the polymer/solution interface with a well-defined boundary (Fig. 5). Formation of conducting zones take places only when the oxidative potential is greater than percolation potential and if the oxidation potential is smaller, the density of polarons can not reach to the percolation level, due to the increasing of their formation energy [22]. In other words, polarons with the well-defined boundary (conducting zones with different color) propagate after primarily distribution of polarons (due to the repulsive forces between them at low potentials or initial time of oxidation). In this state, despite of oxidation, the color of the polymer dose not change.

Fig. 6 shows variations of relative peak current with oxidative waiting potential for different thicknesses at 10 s waiting time. It can be seen relative peak currents decrease as waiting potential increases to the 150 mV for thin film and to 200 mV versus Ag/AgCl for thick film and then increase. It is expected that relative peak currents achieve to a steady value, however they increase and this can be attributed to the transfer from Tofel to Butler-Volmer state and reverse reaction at this potential range (0.0-250 mV). From these plots it can be determined that percolation threshold potential for heteropolyanion doped aniline lies between 150 to 200 mV dependence of thickness. The percolation threshold potential is defined as the potential at which the conducting zones begin to grow when the conducting polymer was electrochemically switched from the insulating to the conducting state [12]. The percolation threshold potential for SO4^2- doped PAn has been reported by Aoki et. al. [12] and Csaohok et. al [7] 220 mV vs. SCE and 180 mV vs. Ag/AgCl respectively. Conducting to insulating conversion which is associated with SR can be explained by percolation theory, according to which the conversion decelerates at lower percolation threshold of the molar fraction of the conducting species.

The slow relaxation is thought to be caused by:

Elimination of polarons from near the edge of valence and conduction bands, i.e. elimination of shallow traps increases the mobility gap; thereby conduction of polymer reduces dramatically. Conduction in the band gap instead of hopping and tunneling between localized states then would have to be performed by escape of electrons from localized states given sufficient energy and drift to the other localized states under influence of local electric field. However, conduction in the band gap by this method is very slow since carriers spend most of their time in the traps.

Elimination of polarons can causes the polymeric chains lie in closer proximity since repulsive forces reduces during conducting to insulating conversion and it may be possible for electrons to tunnel or hop between sites. The inter-state distance is very critical for the occurrence of this form of conduction. According to this idea retrieval of electric paths occurs via conformational rearrangement. Competition between the conformational retrieval of hopping and tunneling (process 2) and increasing of the mobility gap (process 1) and changing the conduction mechanism to drift of electrons is origin of electrochemical relaxation in polymers.
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Captions for Figures

Fig. 1. Potential sequence applied to the polymer film. The redox current is recorded during the triangular scans for different waiting times.

Fig. 2. Cyclic voltammograms for electrodes, modified with SO$_4$$^{2-}$ doped PAn (a) and heteropolyanion doped PAn with the charge density of 4.5 (b), 8.8 (c), 30.4 (d) and 7.8 (e) mC/cm$^2$ obtained in the first cycle before (1) and after (2) the holding of the electrode for 10 s at 250 mV.

Fig. 3. Dependence of relative anodic peak current of heteropolyanion doped PAn films of different charge densities (as indicated) on the waiting time spent at electrode potential of 250 mV.

Fig. 4. Dependence of relative anodic peak current on waiting time in semi-logarithmic co-ordinates for heteropolyanion doped PAn films at different pH (a) and different charge densities (b).

Fig. 5. Illustration of charge distribution and propagation for (A) highly reduced film, (B) $E_p>E_w$, (C) $E_w>E_p$.

Fig. 6. Dependence of relative anodic peak current of heteropolyanion doped PAn films of different charge densities (as indicated) on the waiting potential.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6

Charge density $= 4.5 \text{ mC/cm}^2$

Charge density $= 78.6 \text{ mC/cm}^2$