

Electrochemical Relaxation At Electrically Conducting Polymers

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Several theoretical models for explaining the electrochemical behavior of conducting polymers are available in literature and some of them seem to be in contradiction with each other [1-4]. Change in electric conductivity [1], change in double layer structure [2], percolation of redox sites [3] and structural and morphological changes taking place during electrochemical reduction and oxidation of conducting polymers (ESCR model) [4] etc. are some basis of presenting models. All of the above mentioned models, except ESCR model, assume that electrochemical responses of conducting polymers 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 conducting polymer films behave as three-dimensional electrodes and then the validity of these models is restricted to simple electrochemical process such as electron transfer, counter ion diffusion or capacitive effects. ESCR theory seems to be suitable for the description of the relaxation phenomena and simulation of voltammograms. However, in this model role of several effects are neglected or not understood yet:

- (1) Gibbs energy should be used instead of enthalpy.
- (2) 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 trapped inside of the polymer matrix even in high cathodic potentials inhibit formation of 2D structure.
- (3) 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.
- (4) 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.

The present work has been aimed to bring the existing models together into one comprehensive theory and better understanding of the mechanism of electrochemical relaxation.

The slow relaxation is thought to be caused by:

- (1) 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 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.
- (2) Elimination of polarons can causes the polymeric chains lie in closer proximity since repulsive forces reduces during C to I 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.
- (3) 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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[4] T. F. Otero, H. J. Grande, J. Rodriguez, *J. Phys. Chem., B*, 3688-3697, 101, 1997, Reinterpretation of Polypyrrole Electrochemistry after Consideration of Conformational Relaxation Processes.