

INFLUENCE OF "OVEROXIDATION" POTENTIAL ON THE ELECTROACTIVITY DEGRADATION OF A PPy/PVS COMPOSITE.

T.F. Otero, V. Olazábal, M. Bengoechea

Univ. del País Vasco, Fac. Química, Dep. Ciencia y Tecnología de Polímeros, Lab. de Electroquímica. P.O. Box 1072, 20080 San Sebastián. Spain.

SUMMARY

Conducting polymer composite, polypyrrole/polyvinylsulphonate film prepared on a Pt electrode was degraded by applying anodic potentials at which the irreversible oxidation occurs. The effect of the "overoxidation" potential and polarization time on the electroactivity degradation was determined through the percentage of loss of stored charge. The degradation kinetic promoted by anodic polarization was obtained.

Keywords: conducting polymer, polyelectrolyte, doping, electroactivity, overoxidation, degradation kinetic.

INTRODUCTION

The electrochemical oxidation of pyrrole (Py) in the presence of a soluble polyanion such as the poly(vinylsulphonate)[NaPVS], leads to the formation of a conductive composite (polypyrrole/polyvinylsulphonate) (PPy/PVS) film adhered to the electrode surface⁽¹⁻⁴⁾. The ultimate properties that molecular composite result from the intrinsic properties of both, conducting polymer and polyelectrolyte.

When an conducting polymer/polyanion is submitted to electrochemical switch between the oxidized (doped or conducting) and the reduced (undoped or semiconducting) states, oxidation and reduction process, occurs involving electron and cation transport, in and out the film respectively^(1,5). The ion-transport properties of conducting polymer/polyanion composites are very different from those of conducting polymer doped with small anion. This fact has been used to develop new applications, such as cation-exchange membranes, systems for water deionization and electrodes for rechargeable batteries without storage of ions in the electrolyte⁽⁶⁻⁷⁾.

One of the most important criteria for many of the applications of conducting polymer is its stability during prolonged redox switching (doping-undoping). The doping process promotes positively charged species on the backbone of the conducting polymer which are susceptible to nucleophilic attacks by solvents, impurities, and/or electrolytes, giving rise to a irreversible oxidation, commonly termed "overoxidation"⁽⁸⁾. This leads to electrical conductivity and charge storage capacity deterioration.

Even though there are studies to determine the most positive potential at which those polymers can be held without irreversible degradation, the influence of the "overoxidation" potential is not clear.

In this work the influence of "overoxidation" potential and polarization times on the electroactivity (ability to store charge) degradation of a polymer composite film such as polypyrrole/polyvinylsulphonate (PPy/PVS) was studied. The degradation kinetic promoted by anodic polarization was obtained

EXPERIMENTAL PART

The monomer (Py) was a commercial product from Aldrich. This product was utilized once distilled at 59°C and 50mmHg under vacuum.

The polyelectrolyte, polyvinylsulphonate of sodium (PVSNa) and lithium perchlorate (LiClO₄) were used without previous purification and were the commercial products from Aldrich.

The PPy/PVS composite films were synthesized at a constant potential of 800mV maintained during 65s. An inert atmosphere was maintained by argon bubbling. A 0.1M pyrrole and 0.1M PVSNa aqueous solution was utilized during electrogeneration. The working electrode and counterelectrode were platinum sheets of 1 and 4 cm² surface area, respectively. A saturated calomel electrode (SCE) was employed as reference electrode.

The composite degradation was promoted by anodic polarization at constant potential during different polarization times, in a 0.1M LiClO₄ aqueous solution. The degradation process was followed at 600, 800, 900, 1000, 1100, 1200mV.

After each polarization times the stored charge was obtained checking the films by cyclic voltammetry between -800mV and 50mV in 0.1M LiClO₄ aqueous solution. The second voltammogram was stored and used to obtain oxidation and reduction charges.

RESULTS AND DISCUSSION

The figure 1 show the evolution of oxidation charge loss along the polarization time. The loss of charge was obtained through the expression $[(Q_0 - Q_t)/Q_0]$ where Q_0 and Q_t are, both, the stored oxidation charge of the composite film when it is in the state no degraded and when the film was submitted to a polarization time t , respectively. Three zones were obtained with the polarization time. A first at the short times where the most of loss of charge is produced, a second zone of transition, and a third zone where the degradation process is less important, at long times. Increasing potentials favour the degradation process and the loss of the polymer electroactivity: initial slopes for the relative change on the stored charge increase at increasing polarization potentials. The beginning of the transition zone is observed at major polarization times for lowers potentials.

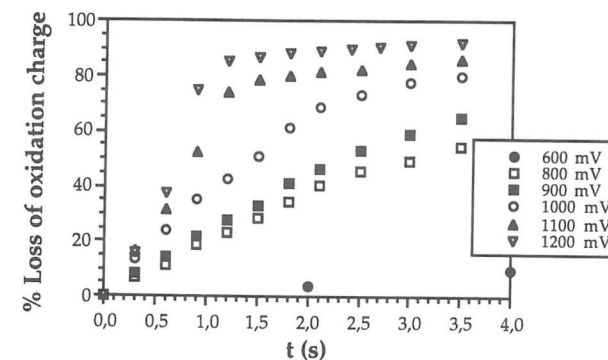


Fig. 1. Evolution of the stored oxidation charge with the polarization times for the different "overoxidation" potentials.

The first zone show a lineal evolution with the polarization time, figure 2 that may be alike to the equation:

$$(Q_0 - Q_t)/Q_0 = A + d[(Q_0 - Q_t)/Q_0]/dt \cdot t \quad (1)$$

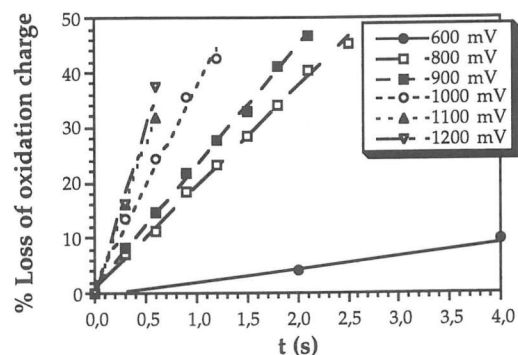


Fig. 2. Evolution of the stored oxidation charge with the polarization times for the different "overoxidation" potentials. for the first zone of polarization times.

Taking account the lineal evolution obtained with the time for the "overoxidation" potentials studied we can obtained the degradation process kinetic through the representation of the slopes of the straight lines from the different polarization potential.

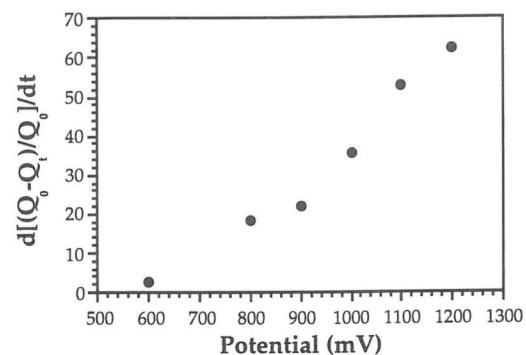


Fig.3. Rate of loss of oxidation charge, $d[(Q_0 - Q_i)/Q_0]/dt$, as a function of polarization potentials .

The figure 3 shows the existence of a lineal dependence between the rate of electroactivity loss and the overoxidation potential applied.

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