

## A THEORETICAL INSIGHT INTO ELECTROCHEMICAL SWELLING IN CONDUCTING POLYMERS.

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### SUMMARY

Swelling process related to electrochemical switching of conducting polymers between their reduced and oxidized states has been modeled, by using a thermodynamic treatment based on polymer gels swelling theories. A free energy function is assigned to both reduced and oxidized states, depending upon chemical and physical features of the polymer. The model is able to explain the changes in polymer volume observed when oxidation charge or electrolyte concentration are varied.

**Keywords:** conducting polymer, doping, electrochemical swelling, free energy, equilibrium

### INTRODUCTION

It is generally accepted that redox processes of conducting polymers taking place in polar solvents are accompanied by reversible molecular movements (i.e. conformational changes) occurring in the solid polymer. When a conducting polymer film is oxidized, positive charges (polarons or bipolarons) are generated along the polymer chains, which are compensated (in a simplified version of redox processes) by the penetration of solvated counterions from the electrolytic solution. Along reduction, electrons are injected into the polymer and counterions and solvent molecules are expelled to the solution. In this situation, Van der Waals attractive forces between polymeric chains prevail. So the polymeric structure is opened during oxidation and closed during reduction. Concomitant changes in the polymeric volume are the origin of some of the most important technological applications of conducting polymers: actuators (1), artificial muscles (2) and electrochemically controlled membranes (3). From this point of view the modelation and control of

volume changes in conducting polymers will allow the optimization and improvement of these devices.

### THEORETICAL

A mathematical treatment was developed in our laboratory, based on theories of swelling equilibria in ionized polyelectrolytes (4-7) and adapted to the specific features concerning to conducting polymers. So the swelling process in the network is accepted to be controlled by a free energy function ( $\Delta G$ ), related to the neutral polymer state in absence of solution (where volume is determined only by polymer-polymer Van der Waals soft interactions). When the neutral polymer is introduced into the electrolytic solution, the free energy changes ( $\Delta G_{red}$ ) due mainly to the new polymer-solvent interactions.

$$\Delta G_{red} = \Delta G_{conformational} + \Delta G_{solvent - polymer} + \Delta G_{elastic} \quad [1]$$

Entropy variations during mixing of the polymer with the solvent are included in  $\Delta G_{conformational}$ . The elastic term  $\Delta G_{elastic}$  takes into account the resistance to swelling caused by chain crosslinking.

During the electrochemical switching to the oxidized state, the free energy changes again according to the opening of the polymeric structure caused by the entrance of solvated (and hence voluminous) counterions. So the free energy in the oxidized state ( $\Delta G_{ox}$ ) will be given by:

$$\begin{aligned} \Delta G_{ox} = & \Delta G_{entropic} + \Delta G_{solvent - polymer} + \Delta G_{elastic} + \Delta G_{ion - ion} + \\ & \Delta G_{solvent - polaron} + \Delta G_{ion - polaron} + \Delta G_{ion - ion} + \\ & \Delta G_{polaron - polaron} + \Delta G_{osmotic} \end{aligned} \quad [2]$$

Polaron-polaron and ion-ion repulsive interactions can be neglected when ion-polaron attractive interactions prevail or when a polar solvent (with high dielectric constant) is used. On the other hand, ion-polaron interactions have been treated by the definition of a solvation number for the oxidation positive charges. The osmotic pressure term is due to the different concentration of counterions in the polymer and in the solution.

The stationary state for free swelling is attained when:

$$\Delta G_{ox} = 0 \quad \text{and} \quad \Delta G_{red} = 0 \quad [3]$$

Both volume and free energy depend on the number and type of penetrating species (being anions or solvent molecules) in the reduced or oxidized state. So a dependence between polymer volume and degree of oxidation, depending on the nature of the polymer (degree of crosslinking, etc.), the solvent (interaction parameter with the polymer, dielectric constant, etc.) and the electrolyte (ionic radius, electric charge, etc.) can be obtained from a numerical solution of eq. [3], as will be shown in the next section.

### RESULTS AND DISCUSSION

A given electrochemical system, consisting of a platinum electrode coated with a conducting polymer film (0.2  $\mu\text{m}$  of thickness  $\times$  1  $\text{cm}^2$  of area), immersed in a 0.1 M  $\text{LiClO}_4$  aqueous solution, was chosen. The interaction parameter between water and the reduced polymer was estimated as 1.5.

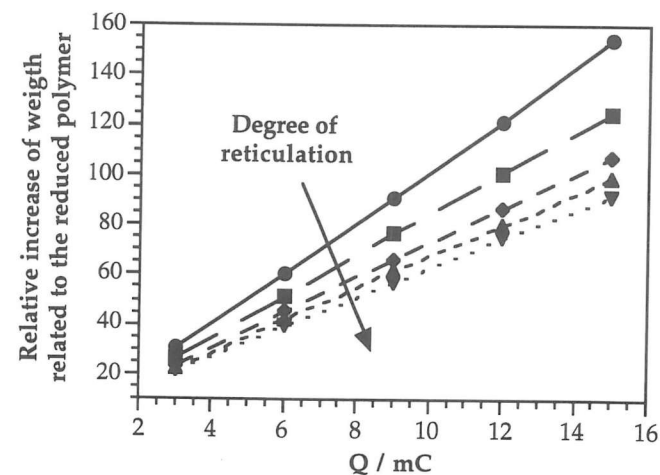


Fig.1.- Relative increase in polymeric weight related to the reduced state, as a function of the stored charge, at different degrees of reticulation.

The relative increase in polymer weight during transition from reduced to oxidized state is represented on fig. 1, as a function of the electrical charge stored, for different degrees of reticulation ranging between 0 (uncrosslinked polymer) and 1 (total reticulation). This linear behaviour is in agreement with experimental observations (2).

Otherwise, the evolution of the relative increase of volume with the concentration of electrolyte in the solution is depicted by fig. 2. From the figure it can be deduced that, whatever the stored charge was, the relative increase of volume is independent on the electrolyte concentration present on the solution, according to experimental data (8).

### CONCLUSIONS

A thermodynamic model based on the definition of a free energy function for both reduced and oxidized states is able to simulate the volume changes occurring in conducting polymers along electrochemical

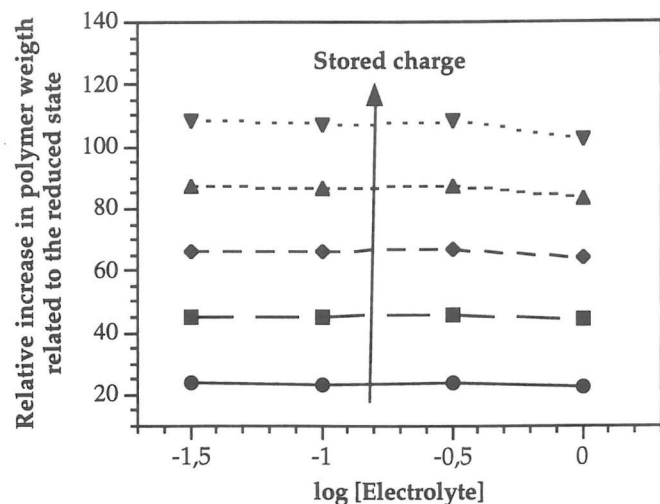


Fig 2.- Relative increase in polymeric weight related to the reduced state, as a function of the electrolyte concentration, at different oxidation charges.

switching. Evolution of relative volume increase with the consumed charge and the electrolyte concentration placed on the solution shows qualitative agreement with experimental results.

### ACKNOWLEDGMENTS

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