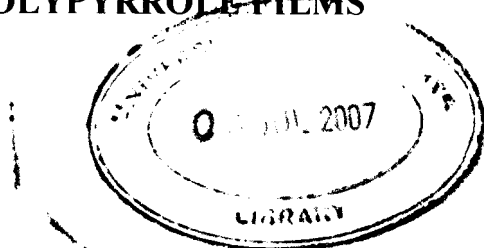


**ELECTROCHEMICAL AND ELECTROMECHANICAL  
BEHAVIOUR  
OF  
POLYPYRROLE FILMS**



A THISIS PRESENTED BY

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**ELECTROCHEMICAL AND ELECTROMECHANICAL  
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In the present study the doping of polypyrrole with large anionic detergent Dodecyl Benzene Sulfonate (DBS) has been investigated by using cyclic voltammetry, optical spectroscopy, and electrochemical quartz crystal microbalance techniques. The study focused on improving the use of PPy / DBS films with respect to the actuation mechanism and on providing an experimental test of the proposed osmotic mechanism for the motion of species between the film and the electrolyte.

The analysis of the results indicated that the kinetics of the electrochemical doping of a conducting polymer films depends on the history of the electrochemical events undergone by the film. The influence of different parameters (Wait-time at the starting potential, number of cycles) on the redox process is described, when doping is achieved by a potential scan.

During the redox process water is also inserted or expelled in two ways: as molecules bound to the moving ions and as a result of the osmotic effect. It was found that while the dominant cation motion does not depend very much on the speed of cycling, the water transport strongly depends on the rate of the potential scan, since the insertion caused by the osmotic mechanism is much slower, and does not follow the cations directly.

Significant changes in the redox properties of the films were observed with the increase of the cycling electrolyte concentration. The effective diffusion coefficient of counterions in 0.1 M, 1 M and 3 M NaCl are nearly  $3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ,  $20 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  and  $55 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  respectively. The diffusion coefficient in 3 M NaCl is approximately 18 times the value in 0.1 M NaCl reflecting that the amount of salt and solvent taken up by the polymer is linked to the electrolyte composition by osmotic balances. These findings have implications for the design of polypyrrole based electrodes and actuators that are required to operate at higher frequencies.

Experiments were carried out for the purpose of elucidating the precise nature of the mobile species during redox cycling, and to seek confirmation for the osmotic mechanism of actuation.

Three testable aspects of the model were confirmed:

- The number of inserted  $\text{H}_2\text{O}$  molecules decreases with electrolyte concentration.
- At the same time the mechanism gradually changes from almost pure cation transport to nearly equal amount of anion transport.
- Exchanging  $\text{Br}^-$  for  $\text{Cl}^-$  ions has only negligible effect at lower concentrations at equal osmotic pressures.

Nearly 4  $\text{H}_2\text{O}$  molecules are tightly bound to each  $\text{Na}^+$  ion at concentrations below 1 M.

The electronic conductivity of the PPy / DBS film has been characterized. The conductivity was measured by van der Pauw measurements on PPy / DBS in the oxidized, dry state as function of temperature. Synthesis at lower temperatures generally leads to higher conductivity.

The force and strain change during redox process of a PPy / DBS actuator was measured by using a potentiostat combined with force measurement set up. The results show that the time constants for the change of length and for the stiffness change are significantly different. The change in stiffness is a faster process than the change in strain. In addition to this the Young's modulus of the PPy / DBS actuator during the redox process was measured using the force measurement set up. The results indicated that the Young's modulus is not a constant and it depends on the oxidation state of the actuator.

To improve the lifetime of the polypyrrole actuators, PPy films were cycled in an ionic liquid composed of 1-butyl-3-methyl imidazolium cations together with anion hexafluorophosphate. The results revealed that the films cycled in ionic liquids have enhanced lifetimes without failure (up to 4700 cycles). Experiments were performed under ambient conditions in four consecutive days, yet the polymer film showed negligible loss in electroactivity

