

**STABILITY, STRAIN AND SPEED OF POLYPYRROLE  
ACTUATORS**

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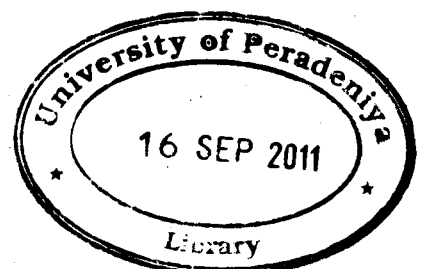
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## Stability, Strain and Speed of Polypyrrole Actuators

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Polypyrrole doped with large immobile dodecyl benzene sulfonate (PPy/DBS) anions operating in aqueous electrolytes is one of the successful and low cost systems suitable for the use as soft actuators. However, considerable improvement in the performance of the PPy/DBS actuators is still required for successful applications of these actuators. The present work aims to get a better understanding of the processes associated with actuation mechanism of PPy/DBS actuators so as to improve their performance. A second aim has been to use the unique physico-chemical environment of polypyrrole to determine hydration numbers of cations. The PPy/DBS films were prepared electrochemically with constant currents and characterized using cyclic voltammetry (CV), electrochemical quartz crystal microbalance (EQCM), optical absorption spectroscopy, and force-displacement measurement techniques.

The electrochemical processes associated with the actuation of the PPy/DBS films in alkali halide and alkali earth halide chloride aqueous electrolytes having varying concentrations were investigated. The redox behaviour of the films in electrolytes having various concentrations shows that the cathodic peak potentials during the cathodic reduction of the films depend on the concentration of the cycling electrolytes used. The results also indicate the necessity of water in the right amount in the cycling electrolytes to ease the reduction process. Cyclic voltammetric studies at different sweep rates show that the mobility (diffusion) of counter ions into the PPy/DBS film is larger in concentrated electrolytes having smaller cations.

In highly concentrated alkali halide aqueous electrolytes, the mass of a PPy/DBS film at the end of each redox cycle is found to drift. The change in mass depends on the concentration of the cycling electrolytes used and the number of cycles. The mass drift during cycling can be controlled by interchanging the cycling electrolytes.

The electrochemical stability of PPy/DBS films in aqueous alkali halide electrolytes depends strongly on the concentration of the electrolyte used. While the cycling capacity in dilute electrolytes decreases significantly after about 50 cycles, the capacity remains the same even at the 300<sup>th</sup> cycle in highly concentrated electrolytes indicating that the

films are more stable in highly concentrated alkali halide electrolytes. This is an important result with respect to the usability of this type of actuator.

Very thin nano-sized (nm thick) PPy/DBS films were also prepared using electrochemical polymerization and characterized using EQCM measurements. The results show that ionic motion in nano-sized thin PPy/DBS films during redox cycling in alkali halide aqueous electrolytes has similar characteristics as those of ionic motion in comparatively thicker PPy/DBS films. The results further indicate that the initial layers of a PPy/DBS film are somewhat different in structure from the layers added later in the film.

The hydration numbers of metal cations in aqueous electrolytes were determined using the novel physico-chemical environment of polypyrrole. The primary hydration numbers obtained for alkali, alkali earth and alkali rare earth metal cations in respective chloride aqueous electrolytes having various concentrations (0.02 M – 1 M) are:

$\text{Li}^+$  : 5.5-5.3;  $\text{Na}^+$  : 4.5-4.3;  $\text{K}^+$  : 2.3-2.5;  $\text{Rb}^+$  : 0.9-0.8 ;  $\text{Cs}^+$  : ~0;  $\text{Mg}^{2+}$  : 10.4-10.6 ;  $\text{Ca}^{2+}$  : 7.9-8.1;  $\text{Sr}^{2+}$  : 5.7-6.1;  $\text{Ba}^{2+}$  : 3.0-3.1;  $\text{Y}^{3+}$  : 13.6 - 13.8 ;  $\text{La}^{3+}$  : 9.0-9.1.

The values of the primary hydration numbers of these metal ions are found to remain constant in the above aqueous electrolytes having concentrations up to 1 M. For all cations the primary hydration numbers show an approximate linear variation with the total charge per surface area of each cation, which is a measure of the surface charge density. The model using the surface charge density may well be the best simple model for primary hydration number of a metal ion. Furthermore the primary hydration numbers of metal cations in highly concentrated aqueous electrolytes are smaller than those in dilute electrolytes and the free water in highly concentrated electrolyte is absolutely a 'different kind of water' containing loosely bound water molecules rather than entirely free molecules.

Electro-chemo-mechanical behaviour of PPy/DBS actuators was investigated using the computer automated Force-Displacement setup. Experiments demonstrated that the electrochemical strain of a PPy/DBS actuator in aqueous electrolytes depends on of the actuation frequency and on the type of cations in the cycling electrolytes. At high actuation frequencies, strains depend solely on the cation plus the hydrated water molecules (i.e. on the hydration number) and At low frequencies, on the other hand, the strain depends on the sum of the hydrated water molecules and those inserted by an osmotic process. Between the two frequency regions the strain decreases significantly. Therefore, the highest speed of response (larger strain at high actuation frequency) for PPy/DBS actuators is achievable in the cycling electrolytes containing cations having larger hydration numbers.