

A Study of Electrochemical Behaviour of Polypyrrole Films in Highly Concentrated Aqueous Electrolytes

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Abstract: Polypyrrole polymer films doped with large surfactant anions, dodecyl benzene sulfonate, (PPy/DBS) can be used as soft actuators and their performance and stability depend on the type of the cycling electrolytes and their concentrations. In an attempt to discover suitable electrolytes for such actuators, the diffusion of counter ion into PPy/DBS films in various aqueous electrolytes has been investigated in this work. The PPy/DBS films were cycled at different scan rates in various alkali halide aqueous electrolytes having concentrations ranging from 0.1-1 M in order to determine the diffusion coefficients of alkali halide ions. The effective diffusion coefficients were found to increase with the concentration of the electrolytes and decrease with the increase in size of cations. Since the effective diffusion coefficient of counter ions is a direct measure of the speed of response when such films are used as electrodes in artificial muscles or in batteries, this finding is especially useful for the design of fast actuators based on PPy/DBS polymers.

Introduction

Polypyrrole (PPy) films have been found to be useful to fabricate soft actuators [1,2]. The mechanism of actuation in such actuators is the insertion/expulsion of counter ions present in aqueous electrolytes as the polymer is redox cycled between the reduced and oxidized states [3]. During the actuation process, a considerable change in volume of PPy actuator occurs as the insertion/expulsion of counter ions is accompanied by water molecules present in the

cycling electrolyte. Even though the electrochemical behavior of PPy films depends on a variety of conditions such as concentration of the cycling electrolyte, type and size of counter ions, type of solvent used, etc. [4], the concentration of the cycling electrolytes mainly determines the actuation behaviour. This is because the amount of water accompanying the counter ions depends not only on the solvating ability of the counter ions but also depends on the osmotic pressure of water inside and outside the film [5-7]. The present work is focused on PPy films doped with large surfactant anions, dodecyl benzene sulfonate (DBS), operating in aqueous electrolytes, since the films have been shown to be a promising system for use in soft actuators [8-10]. One of the advantages of the PPy(DBS) actuator is its low cost.

In PPy/DBS polymer system, the speed of response of the films is one of the severe limitations when such films are used in artificial muscles or as electrodes in batteries and other devices [9, 10]. The diffusion of counter ions into the PPy/DBS films during the redox actuation determines the speed of response of the films and strongly depends on the operating cycling electrolytes [9]. In this study, we have investigated the effect of the concentration of the cycling electrolyte and of the size of counter ions on the diffusion of counter ions in PPy/DBS films in order to identify cycling electrolytes which can provide larger speed of response. In this investigation, the effective diffusion coefficients of counter ions in PPy/DBS films operating in various alkali halide

aqueous electrolytes having different concentrations were determined using cyclic voltammetry measurements and the optimum cycling electrolyte among the alkali halide electrolytes for high speed response is reported.

Experimental

Pyrrole (Aldrich 98%) monomer was distilled under nitrogen and stored in a freezer in a sealed vial prior to use. Other chemicals, sodium dodecyl benzene sulfonate (SDBS) (Aldrich, technical quality), LiCl (Merck, analar grade), MgCl₂, SrCl₂, BaCl₂ (of purity 99.9 %, Aldrich) and CaCl₂ (of purity ≥ 99.5 %, Sigma-Aldrich) were used as received. For all polymerizations, a 0.05 M SDBS aqueous solution containing 0.05 M pyrrole was used and the films were prepared using galvanostatic electropolymerization with a constant current density of 0.1 mA cm⁻². The PPy/DBS films were prepared on the Pt wire to have a thickness of 5 μm corresponding to a synthesis charge of 800 mC [11] and the aqueous electrolytes of MgCl₂, CaCl₂, SrCl₂ and BaCl₂ having concentrations ranging from 0.05 M to 1.5 M were used. All cycling aqueous electrolytes used were thoroughly purged with nitrogen gas for an hour to remove dissolved oxygen. All electrochemical investigations were carried out using a three electrode arrangement with a Pt sheet and a standard Ag/AgCl (3 M KCl) electrode serving as the counter and reference electrodes respectively.

Results and Discussion

In order to investigate the effect of concentration of cycling electrolytes on the diffusion of counter ions into the PPy/DBS polymer matrix, which plays the key role in determining the speed of response of the PPy/DBS soft actuator in aqueous media, the effective diffusion coefficients for PPy/DBS films operating in alkali earth metal cation halide electrolytes were determined using the model as adopted by Careem *et.al.* [12]. Accordingly, in the present context of our system, when it is assumed that transport in PPy/DBS coatings is treated as a planar diffusion and charge insertion is related linearly with potentials in the potential range investigated, then a mathematical

equation for the charge accumulated at the cathode may be written as

$$U = \frac{4}{3} \sqrt{\frac{(E_1 - E_2)}{\pi \tau \alpha}}$$

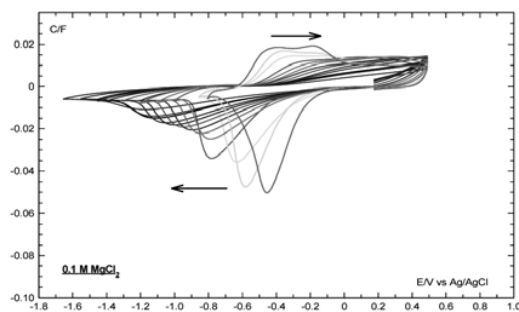
where, U is defined as the ratio of the charge accumulated in the electrode relative to the maximal charge that can be accumulated under equilibrium conditions, $E_1 - E_2$ is the potential window used for the scan and τ is the time constant for diffusion in the electrode and α is the scan rate. Plots of U vs. $1/\sqrt{\alpha}$ for PPy/DBS films cycled in aqueous electrolytes should demonstrate that U is approximately proportional to $1/\sqrt{\alpha}$ down to a critical sweep rate, and at lower sweep rates U becomes independent of α . From this plot, τ can be determined from the critical sweep rate marking the transition between the two linear regimes. Then the effective diffusion coefficient of ion movements in the polymer film can be obtained using the relation

$$D = l^2 / \tau \quad 3.1$$

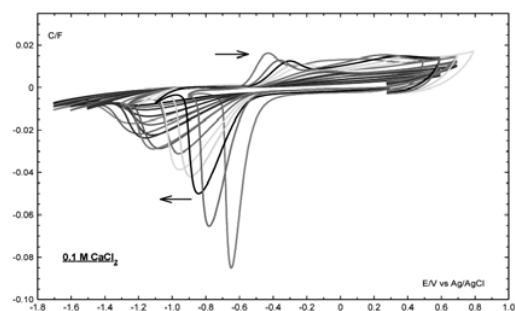
where l is the length of diffusion and τ is time constant. If the diffusion is assumed to occur across the film uniformly, l will correspond to the thickness of the film. For this investigation, the aqueous electrolytes of MgCl₂, CaCl₂, SrCl₂ and BaCl₂ having concentrations ranging from 0.05 M to 0.1 M were used.

Figs. 1 (a-d) show a series of cyclic voltammograms at different sweep rates for a 5 μm thick PPy/DBS film cycled in 0.1 M MgCl₂, CaCl₂, SrCl₂ and BaCl₂ electrolytes respectively. In each case the film was cycled in non sequential order of sweep rates. To avoid the problem caused by 'memory effects' or 'slow relaxation', the sweep rate test was done on each film after 10 initial conditioning cycles. In order to facilitate comparison of all curves the current values were divided by the sweep rates. In the resulting differential capacity versus voltage diagrams, the area under a curve is a direct measure of the charge that is cycled in and out of the film during redox cycling.

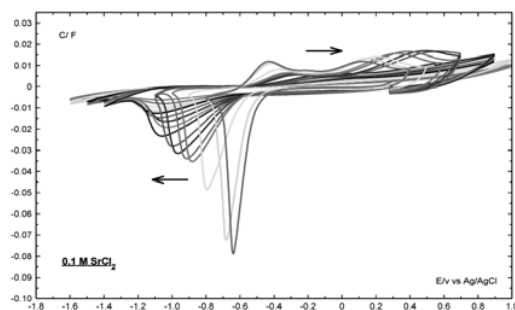
Significant changes are observed in the cyclic voltammograms with the sweep rate. The scan rate significantly affects the positions of nearly all peaks and this fact proves the important role of kinetic factors in the redox process.



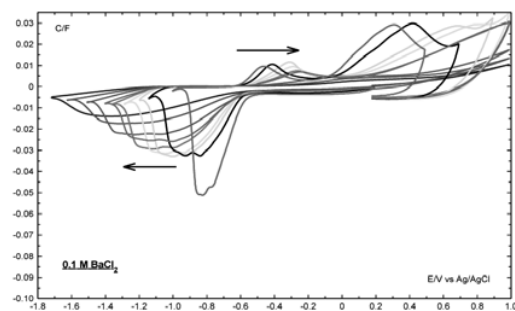
(a)



(b)



(c)



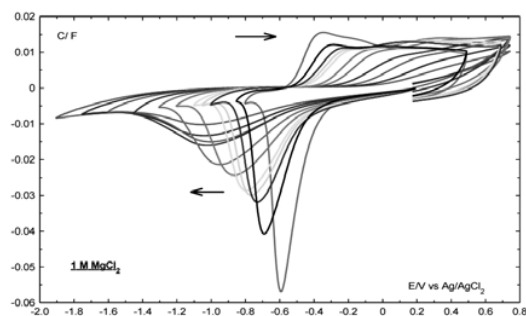
(d)

Fig. 1: A set of cyclic voltammograms obtained for a 5 μm thick PPy/DBS film cycled in 0.1 M electrolytes of (a) MgCl₂ at different sweep rates: 10, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000 and 1150 mV/s; (b) CaCl₂ at different sweep rates: 10, 50, 100, 150, 200, 250, 300, 350, 400, 450, 480, 520, 540, 580, 600, 650, 700 and 750 mV/s; (c) SrCl₂ at different sweep rates: 5, 10, 50, 125, 150, 200, 250, 300, 325, 350, 380, 400, 450, 500, 550 and 600 mV/s and (d) BaCl₂ at different sweep rates: 20, 50, 80, 100, 130, 150, 200, 230, 250 and 280 mV/s.

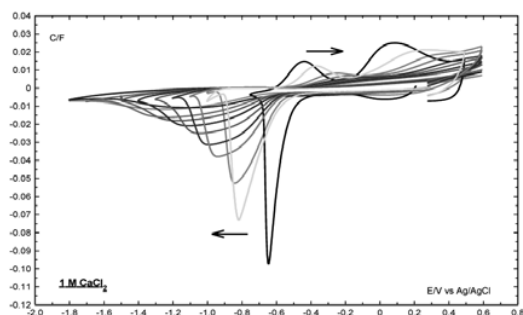
The cyclic voltammograms in alkali earth metal electrolytes have the characteristic feature of a sharp cathodic peak during the reduction of the film (due to insertion of cations) and two oxidation peaks during the oxidation (1st - smaller peak due to expulsion of cations whereas 2nd - broad peak due to insertion of anions). It can be seen from each figure that with increasing scan rate the cathodic peaks become progressively broader and shift to more negative potentials, whereas the 1st anodic peaks become gradually smaller while 2nd anodic peaks become progressively broader, and both anodic peaks shift to more positive potentials. Further, all peaks turn out to be smaller at higher scan rates. This implies that the cations and anions are no longer able to participate fully in the doping/dedoping process at high sweep rates. Interestingly, 1st anodic peak changes more than the 2nd one with increasing scan rate and the first peak overlaps with the second peak and become one peak at higher scan rates. This may be caused because the expulsion of cations is a slower process than the insertion of anions into the polymer matrix.

Figs. 2 (a-d) show a series of cyclic voltammograms at different sweep rates for 5 μm thick PPy/DBS films cycled in 1 M MgCl₂, CaCl₂, SrCl₂ and BaCl₂ electrolytes respectively. As in 0.1 M concentration, the cyclic voltammograms obtained for 1 M MgCl₂, CaCl₂ and SrCl₂ electrolytes have a sharp cathodic peak and two oxidation peaks but the cathodic peak obtained for 1 M BaCl₂ is not well defined (even in the extended potential window) and diminishes with increasing scan rate. This is because the insertion of Ba²⁺ ions into the PPy/DBS film in 1 M BaCl₂ has great difficulty in entering the polymer

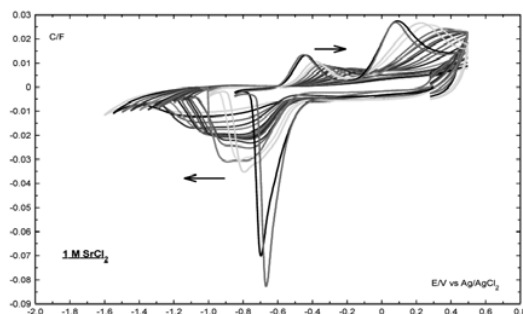
matrix and this becomes a very slow process. This observation indicates that the kinetics of redox process of PPy/DBS film in highly concentrated BaCl_2 electrolyte is a slower process and results in low speed of response.



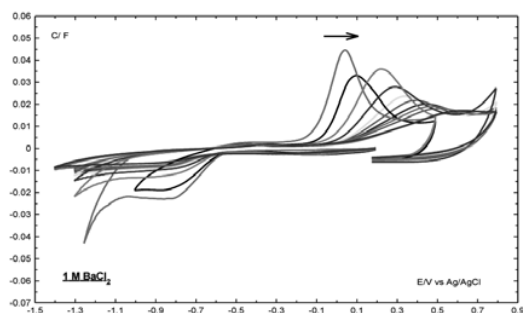
(a)



(b)



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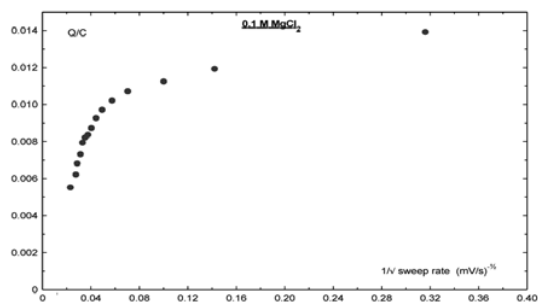
(d)

Fig. 2: A set of cyclic voltammograms obtained for a 5 μm thick PPy/DBS film in 1 M electrolytes of (a) MgCl_2 at different sweep rates : 50, 200, 400, 500, 600, 800, 1000, 1400, 1600, 1900 and 2150 mV/s : (b) CaCl_2 at different sweep rates: 5, 50, 100, 200, 300, 400, 500, 600, 650, 700 and 800 mV/s: (c) SrCl_2 at different sweep rates 5, 10, 50, 75, 150, 200, 250, 275, 300, 325, 350, 400, 450, 500, 550 and 600 mV/s and (d) BaCl_2 at different sweep rates 10, 20, 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV/s.

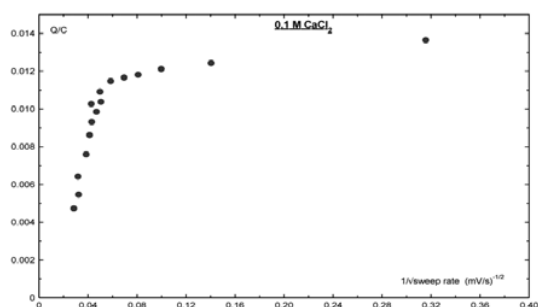
It can be easily seen from each figure except in 1 M BaCl_2 electrolyte that the electrode charge during the cathodic scan decreases with the increasing scan rate. However, in 1 M BaCl_2 electrolyte, even though the cathodic peaks are not well defined, the 2nd anodic peak (due to insertion of Cl^-) is well developed progressively and its position shifts to more positive potentials with increasing scan rates. It is a clear sign to indicate that the system switches to anion mechanism [8]. For the determination of the diffusion coefficient for the PPy/DBS film in 1 M BaCl_2 , the 2nd anodic peak (due to insertion of Cl^-) was used.

In order to find the diffusion coefficient for the PPy/DBS film in each electrolyte used, the cathodic electrode charge vs. inverse square root of the sweep rates was plotted for each electrolyte using the data from Figs. 3.6 (a-d) and Figs. 2 (a-d). Fig. 3 shows the electrode charge during the cathodic scan of the PPy/DBS film in 0.1 M (a) MgCl_2 , (b) CaCl_2 , (c) SrCl_2 and (d) BaCl_2 and in 1 M (e) MgCl_2 , (f) CaCl_2 , (g) SrCl_2 and (h) BaCl_2 as a function of the inverse square root of sweep rates. As predicted in [12], it can be seen from each figure that the electrode charge during the cathodic scan increases linearly with the inverse square root of scan rate at high scan rates, and then reaches an approximately constant maximum value at low scan rates (high values of the inverse square root of scan rate) except in 1 M BaCl_2 . However, a similar relation was obtained for the 2nd anodic peak (due to insertion of Cl^-) using the data in Fig. 2 (d). The intersection of the tangent to the curve through the origin and a linear approximation to the data obtained at low sweep rates is used to get the transition scan rate. Finally, the diffusion coefficients of the PPy/DBS film in 0.1 M and 1 M MgCl_2 , CaCl_2 ,

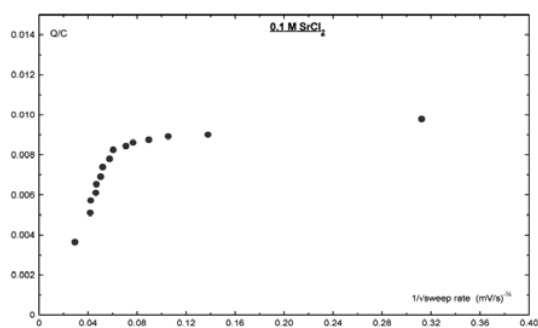
SrCl_2 and BaCl_2 were estimated using the equation 3.1
are given in Table 1.



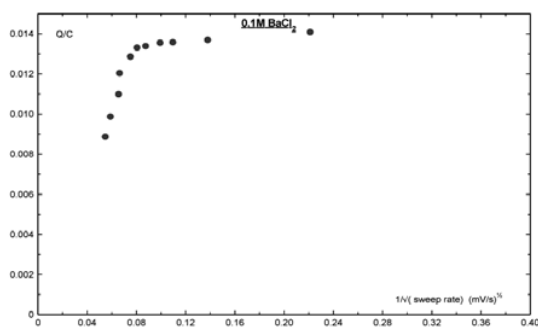
(a)



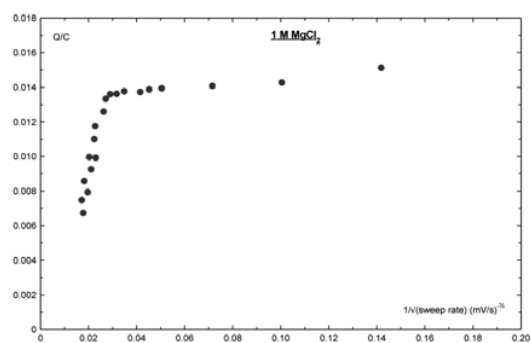
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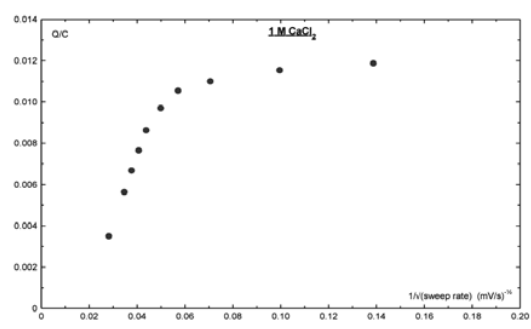
(c)



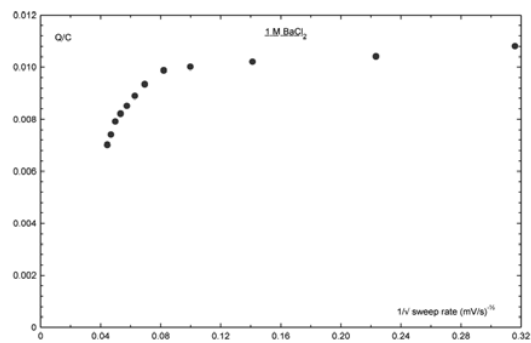
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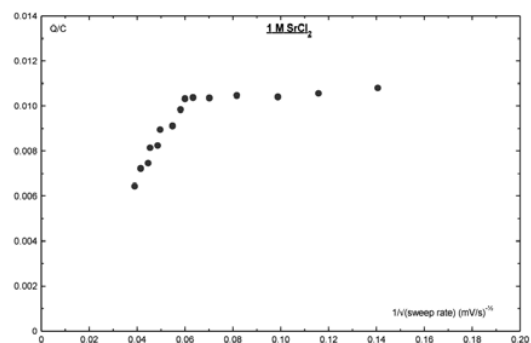
(e)



(f)



(g)



(h)

Fig. 3. The electrode charge vs. inverse square root of the sweep rates for a PPy/DBS film cycled in 0.1 M (a) MgCl₂, (b) CaCl₂, (c) SrCl₂ and (d) BaCl₂ electrolytes and in 1 M (e) MgCl₂, (f) CaCl₂, (g) SrCl₂ and (h) BaCl₂ electrolytes. Film thickness: 5 μm.

The results shown in Table 1 confirm that the effective diffusion coefficient for a PPy/DBS film in alkali earth cation halide cycling electrolyte increases with the concentration of the electrolytes and the coefficients decrease with the increase in size of cations in the electrolyte. The increase of effective diffusion coefficient with concentration is an indication that at 0.1 M, part of the diffusion limitation is in the electrolyte phase. Since the effective diffusion coefficient of counter ions is a direct measure of the speed of response when such films are used as electrodes in artificial muscles or in batteries, this finding is especially useful for the design of fast actuators based on PPy/DBS polymers. As seen in the table, since the diffusion coefficient for the PPy/DBS film in 1 M MgCl₂ electrolyte is larger, it can be concluded that the speed of response of a PPy/DBS film may be enhanced by operating the film in concentrated electrolytes having smaller cations such as Mg²⁺.

Table 1: Effective diffusion coefficients for a PPy/DBS film cycled in MgCl₂, CaCl₂, SrCl₂ and BaCl₂ electrolytes of 0.1 M and 1 M concentrations. The thickness of the film is 5 μm.

| Con. (M) | Effective Diffusion Coefficients <i>D</i> (m ² s ⁻¹) | | | |
|----------|--|--------------------------|--------------------------|-------------------------|
| | MgCl ₂ | CaCl ₂ | SrCl ₂ | BaCl ₂ |
| 0.1 | 11.1 × 10 ⁻¹² | 9.4 × 10 ⁻¹² | 9.1 × 10 ⁻¹² | 4.1 × 10 ⁻¹² |
| 1 | 27.0 × 10 ⁻¹² | 14.7 × 10 ⁻¹² | 11.0 × 10 ⁻¹² | 5.3 × 10 ⁻¹² |

Conclusions

The diffusion of counter ions into PPy/DBS films in alkali earth cation halide cycling electrolyte has been studied. The effective diffusion coefficient for a PPy/DBS film in alkali earth cation halide cycling electrolyte increases with the concentration of the electrolytes and the coefficients decrease with the

increase in size of cations in the electrolyte. The increase of effective diffusion coefficient with concentration is an indication that at low concentrations 0.1 M part of the diffusion limitation is in the electrolyte phase. Since the effective diffusion coefficient of counter ions is a direct measure of the speed of response when such films are used as electrodes in artificial muscles or in batteries, this finding is especially useful for the design of fast actuators based on PPy/DBS polymers. In this study the diffusion coefficient for the PPy/DBS film in 1 M MgCl₂ electrolyte is the largest and therefore it can be concluded that the speed of response of a PPy/DBS film may be enhanced by operating the film in concentrated electrolytes having smaller cations such as Mg²⁺.

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