

## **A cyclic voltammetry study of polypyrrole conducting polymer film in aqueous BaCl<sub>2</sub> and LiCl electrolytes**

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### **Abstract:**

The emergence of electronically conducting polymers having fascinating properties has opened up a novel class of polymers suitable for modern applications, including smart soft actuators or ‘artificial muscles’. The change in volume of these polymers when the redox state is altered in aqueous electrolytes is exploited in these actuators. The actuation property of these polymers highly depends on cycling electrolytes, types and concentrations. The present study aims to explore the possibilities to use Polypyrrole, doped with the immobile anion dodecyl benzene sulfonate (PPy/DBS) films cycled in LiCl and BaCl<sub>2</sub> electrolytes. In this study, PPy (DBS) films of thickness 400 nm were electropolymerized on 6 MHz AT-cut quartz crystal electrodes from a synthesized solution containing 0.05 M pyrrole monomer in 0.05 M NaDBS solution and characterized by simultaneous cyclic voltammetry and Electrochemical Quartz Crystal Microbalance (EQCM) measurements. The films were cycled in 0.1 M BaCl<sub>2</sub> 0.1 M LiCl, 2 M LiCl and 1 M BaCl<sub>2</sub> electrolytes. The actuation mechanism of the film in LiCl electrolytes (up to 2M concentrations) is exclusively based on cations motions while that in BaCl<sub>2</sub> (up to 1M concentrations) is contributed with both cations and anions in electrolytes. It implies that the redox ionic motion resulting from the actuation of PPy (DBS) films is not exclusively based on metallic ion presence in the electrolyte but depends on the type of metallic ions present in the cycling electrolytes used. When comparing with high and low concentrations in LiCl and BaCl<sub>2</sub>, a larger frequency change was obtained in low concentrations rather than in higher concentrations, indicating that the actuation in thin concentrations is larger than higher.

**Keywords:** Polypyrrole, redox process, soft actuators.

### **Introduction**

The emergence of electronically conducting polymer having fascinating properties has opened up a novel class of polymers suitable for modern applications and led to the Nobel Prize in Chemistry to Shirakawa and co-workers, in 2000 [1]. It is often referred to as inherently conjugated polymers. These polymers change their properties greatly when they are electrochemically flipped with low potentials. Polypyrrole (PPy) is one such outstanding polymer system widely tested for numerous applications, including soft actuators or artificial muscles [2]. The potential fruitful polymer suitable for soft actuator applications is PPy doped with large immobile dodecyl benzene sulfonate (DBS) anions; PPy(DBS) polymer cycled in aqueous solutions is the low coast system [3]. The actuation of these conducting polymer actuators is primarily based on the electrochemical redox process and highly varies with the properties of the cycling solution. This study aims to investigate the actuation characteristic of PPy(DBS) films in LiCl and BaCl<sub>2</sub> aqueous electrolytes at various concentrations since the actuation property of PPy(DBS) system solely depends on the insertion/expulsion of cations

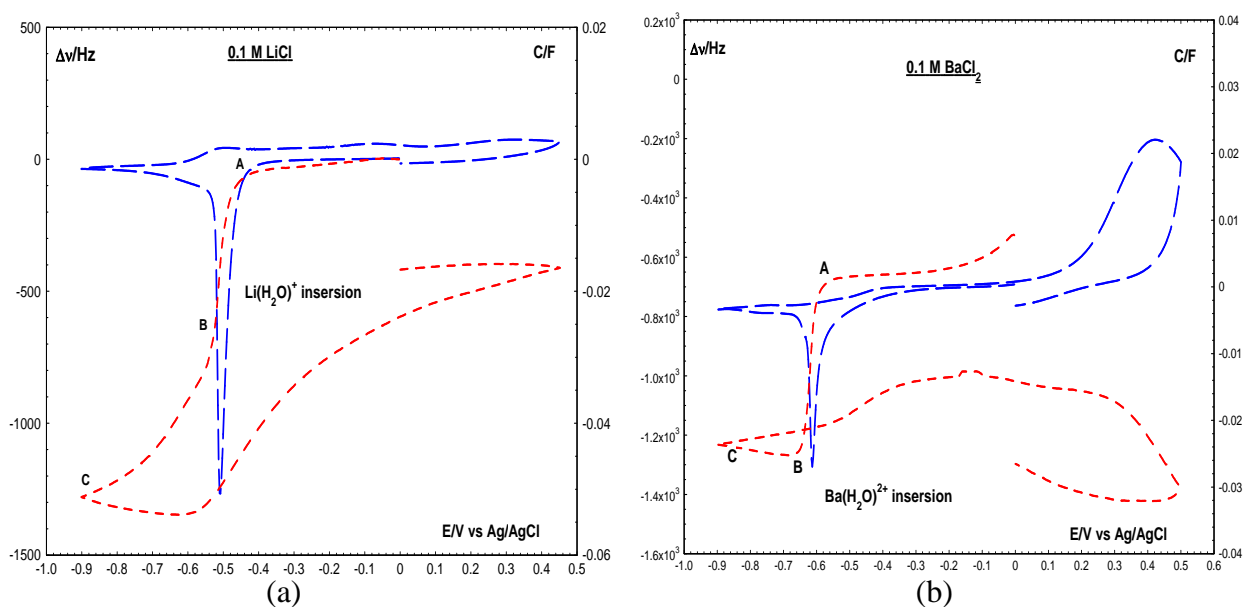
presence in the cycling electrolytes. The prime focus of this investigation is to test the dependence of the actuation mechanism on the type of cations used.

### Experimental

The revelation of insertion /expulsion of ions into/out of PPy(DBS) films was done using in situ Cyclic Voltammetry driven Electrochemical Quartz Crystal Microbalance (EQCM) experiments (Autolab PGSTAT128N with EQCM module with 6 MHz quartz crystals of depositing area of  $0.4 \text{ cm}^2$ ). For each experiment, a 400 nm thick-PPy (DBS) film was uniformly formed on the gold electrodes as assumed in [4] with reference to a standard Ag/AgCl (3 M KCl) electrode. Pyrrole monomer and Sodium dodecyl benzenesulfonate (SDBS) obtained from Aldrich and LiCl and BaCl<sub>2</sub> from Merck were used (with technical quality). The synthesis aqueous solution of 0.05 M SDBS having 0.05 M pyrrole, distilled under nitrogen, was electropolymerized for the film preparation, the current density of  $0.1 \text{ mA cm}^{-2}$  was supplied in galvanostatic mode. To eliminate the dissolved oxygen in the cycling solutions, the nitrogen gas was thoroughly purged into the solution for an hour just before each experiment. A Pt sheet was served as the counter electrode for all experiments.

### Results and Discussion

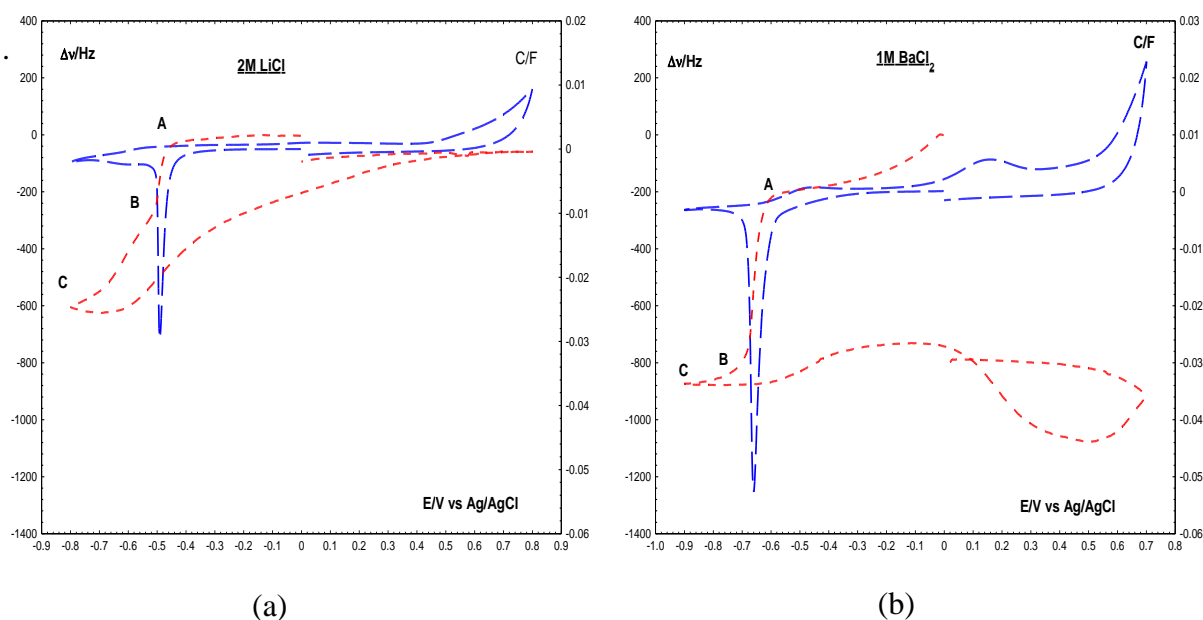
To reveal the redox mechanism, separate experiments with fresh PPy (DBS) films were done in 0.1 M LiCl and 0.1 M BaCl<sub>2</sub> aqueous solutions. The first cyclic voltammograms and the frequency measurements in 0.1 M (a) LiCl and (b) BaCl<sub>2</sub> electrolytes are given in Figure 3.1 respectively. The cycling of the film was started at 0.0 V for all experiments. The potential of the film was gradually decreased to -0.9 V and subsequently increased to up to 0.45 V in order to complete the full cycle.



**Figure 1:** Cyclic voltammograms and simultaneous frequency measurements for identical PPy/DBS films cycled in 0.1 M (a) LiCl and (b) BaCl<sub>2</sub> electrolytes. Scan rate:  $10 \text{ mV s}^{-1}$ . The small dash line (red colour) indicates the frequency changes.

It can easily be seen from the Figure 1 that a sharp peak evolves during the decrease in potential, centered at -0.6 V and -0.5 V respectively. This first cathodic reduction peak appears due to the only insertion of hydrated cations into the film, since there are no moving cations inside the fresh film and the DBS<sup>-</sup> anions are immobile as well. In the subsequent oxidation of the films, there exists a broad anodic peak in each electrolyte centered approximately at 0.4 V, representing a slow expulsion of Li<sup>+</sup> and Ba<sup>2+</sup> respectively from the polymer matrix. Similar features have been reported by Skaarup *et al.* during the first redox cycling of identical PPy (DBS) films in 0.05 M KCl and in 0.1 M NaBr [5] cycling electrolytes. During the further oxidation of the film, another oxidation peak centered at approximately +0.4 V is observed in the 0.1 M BaCl<sub>2</sub> electrolyte. This peak represents the insertion of anions (Cl<sup>-</sup> ions) into the film [5]. Moreover, sharp changes in simultaneous frequency measurements corresponding to these peaks further confirm the motion of ion species into the films. The larger frequency changes would result in 0.1 M LiCl electrolyte due to higher surface charge density of Li<sup>+</sup> than in Mg<sup>2+</sup>.

To further verify this electrochemical characteristic of PPy(DBS) films, similar experiments with pristine films were performed in 2 M LiCl and 1 M BaCl<sub>2</sub> with the same experimental conditions. Figure 3.2 shows that one cathodic peak during cathodic reduction and one anodic peak during anodic oxidation are observed in 2M LiCl electrolyte (as in 0.1 M LiCl) while one cathodic peak during cathodic reduction and two anodic peaks during anodic oxidation are observed in 1 M BaCl<sub>2</sub> electrolyte (as in 0.1 M BaCl<sub>2</sub>). These experimental observations imply the fact that the electrochemical actuation mechanism in LiCl electrolytes solely depends on the cations mechanism. But in the case of BaCl<sub>2</sub>, it is both cation and anion process. For this investigation, the different high concentrations are chosen due to different saturation concentrations of salts used.



**Figure 2:** Cyclic voltammograms and simultaneous frequency measurements for identical PPy/DBS films cycled in (a) 2 M LiCl and (b) 1 M BaCl<sub>2</sub> electrolytes. Scan rate: 10 mV s<sup>-1</sup>. The small dash line (red colour) indicates the frequency changes.

### **Conclusion**

The actuation mechanism of PPy(DBS) films highly depends on the type of electrolytes used. The actuation mechanism of the film in LiCl electrolytes (up to 2M concentrations) is exclusively based on cations motions while that in BaCl<sub>2</sub> (up to 1M concentrations) is contributed with both cations and anions in electrolytes. It implies that the redox ionic motion resulting from the actuation of PPy(DBS) films is not exclusively based on metallic ion presence in the electrolyte but depends on the type of metallic ions present in the cycling electrolytes used.

### **Acknowledgment**

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### **References**

1. A.G. MacDiarmid. (2001): *Rev. Mod. Phys.*, Vol. 73, pp. 701.
2. S. Sadki, P. Scotland, N. Brodie, G. Sabouraud (2000). *Chem. Soc. Rev.* 29, pp. 283.
3. S. Maw, E. Smela, K. Yoshida, and R.B. Stein. (2005) *Synth. Met.* 155, 18.
4. M. Benslimane, P. Gravesen, K. West, L. Bay, S. Skaarup. (2000) *Proc. 7th Int. Conf. New Actuators*, Bremen, Germany, pp. 635.
5. M.J.M. Jafeen, M.A. Careem and S. Skaarup. (2014) *Ionics*, 20, pp. 535.