Dependence of polypyrrole bilayer deflection upon polymerization potential

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\textbf{Abstract}

The nature of polypyrrole (PPy) is largely influenced by the potential used for its polymerization. To investigate this influence, PPy-bilayer actuators were created using different polymerization potentials in order to examine the effect of the polymerization potential on the involvement of anions and cations in the actuation process.

Cyclic voltammetry and chronoamperometry methods were used to record the ion behaviour while simultaneous measurements were made of the PPy-bilayer deflection in order to characterize the PPy-bilayer actuation properties. A polymerization potential close to 0.85 V and 1.1 V produced a PPy-bilayer actuator which managed an optimum deflection in an electrolyte consisting of TBAPF\textsubscript{6} (tetrabutylammonium hexafluorophosphate) in propylene carbonate (PC).

Electrochemical quartz crystal microbalance (EQCM) measurements showed the degree to which solvated cations and anions are involved in the charging and discharging processes during actuation of the PPy-bilayers. The influence of anions and cations during actuation of the PPy-bilayer at reduction and oxidation is described by the model of reversible \(\sigma\)-dimerization.

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1. Introduction

Polypyrrole (PPy) has become one of the most widely studied conducting polymers in recent years. Many potential applications are based on the biocompatible and actuation properties of PPy and involve various biomaterial [1] and micro-fabrication [2] applications (micro-robots, micro-valves [3–5], micro-pump [6] and biosensors [7]).

The deposition of a conducting polymer such as PPy on a non-conductive layer (e.g. a polyethylene terephthalate foil of 12 \(\mu\)m in thickness, covered on one side with 80 nm of Pt) leads to the bending of a bilayer upon charging and discharging. One of the main interests is in controlling and reproducing the bending of the bilayer to make it applicable to industrial products. To guarantee proper functioning of these actuators it is necessary to optimize the properties of such devices, which depend on the conditions of polymerization. Thus, the positional control of PPy bilayers upon charging and discharging has been studied for different concentrations of electrolyte [7], different PPy thicknesses on a gold bilayer [8] and upon changing the pH value during polymerization [9]. To investigate the influence of the polymerization potential on the actual charging and discharging PPy bilayers at polymerization potential between 0.85 and 1.5 V are prepared and the bending beam method (BBM) [10,11] is applied with different electroanalytical methods.

The effect of polymerization potential upon actuation behaviour has already been studied by Smela et al. [12] using a PPy/Au/polymide laminate in aqueous NaClO\textsubscript{4} and Kiefer et al. [13,14] using PEDOT bilayer actuation (PC/TBAPF\textsubscript{6}) and PEDOT free standing films (PC/TBACF\textsubscript{3}SO\textsubscript{3}) which were prepared at different formation potentials.

In order to analyze the ion transport in the polymeric films, ECQM measurements [15,16] were carried out. Cyclic voltammetry experiments correlated with the frequency change were performed and the participation of different ion species upon oxidation and reduction was determined. The different methods were combined with cyclic voltammetric measurements in order to compare the PPy bilayer deflection with mass transport.

In order to understand the charging/discharging of conducting polymers and their influence on actuation relevant models are discussed in the literature. Otero et al. [17–20] have designed the ESCR model (electrochemical stimulated conformational relaxation). They assume that anions are inserted in the film during oxidation and expelled during reduction causing volume changes. During oxidation the polymer structure opens via conformational changes of the chains and ion channels are formed. The polaron/bipararon
model describes the charging of polymer chains [21] with three redox steps starting from neutral to the polaron state, from the polaron to the bipolaron state and from the bipolaron to the metallic state at different potentials.

The model of “reversible σ-dimerization”, which has been developed by Heinze [22,23], is based on the observation that during polymerization “σ-dimers” are formed. These result from the intermolecular coupling of charged conjugated oligomers via the formation of α,α′- or β,β′-bonds between different chains, forming two sp²-centers with localized charges. Normally, during oligomerisation, protons are eliminated and a neutral fully conjugated system is formed.

The goal in this work was to investigate the influence of the polymerization potential of the PPy generation to the actuation properties of the PPy bilayers and to find an explanation for anion and cation participation during the reversible redox process.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade. Pyrrole was obtained from Aldrich. Propylene carbonate (PC, 99%) and tetrabutylammonium hexafluorophosphate (TBAPF₆, 99.9%) were obtained from Fluka and used without further purification.

2.2. Electrochemical polymerization and bending beam measurements

Cantilever strips were prepared by sputtering a 12 μm thick poly(ethylene terephthalate) (PET) foil with a 80 nm thickness platinum layer. The Pt-covered foil was cut into pieces 15 mm long and 5 mm wide. PET/Pt strips as the working electrode were produced with a standard three-electrode configuration under an argon atmosphere using an Ag/AgCl/KCl(sat.) reference electrode and a Pt foil as counter electrode. PPy was generated potentiostatically from a monomer solution of pyrrole (0.1 M) and TBAPF₆ (0.1 M) in propylene carbonate by applying different polymerization potentials (0.85–1.5 V). A HEKA Potentiostat/Galvanostat, PG 28, was used for electrochemical control. All of the experiments were conducted at room temperature. The polymerization of each PPy bilayer was stopped at a constant charge value of 200 mC, which relates to a thickness of PPy in the range of 8 μm. To test for reproducibility, at least three PPy bilayers were produced and tested for polymerization potential. After polymerization the polymer film (the PPy covered an area of 12 mm × 5 mm) was discharged at a potential of 0.0 V. For chronoamperometric and cyclic voltammetric measurements the PPy bilayer was transferred to a monomer free cell with a similar three-electrode set-up. Cyclic voltammograms were obtained using a Jaisle potentiostat Type 1002 PC.T. The movement of the bilayer was recorded with a CCD camera (EHk kam06, EHD Imaging GmbH, Germany) connected to a PC installed frame grabber card (The Imaging Source DFG/LC1) and set to begin recording at the same time as the cyclic voltammetric and chronoamperometric experiments.

2.3. Electrochemical quartz crystal microbalance

AT-cut quartz crystals (5 MHz) of 15 mm diameter were obtained from KVG Quartz Crystal Technology GmbH (Neckarsulm, Germany). Both sides of the quartz crystals were coated with platinum by vacuum deposition. A chromium adhesion layer was used to improve the mechanical stability of the platinum films. The quartz was clamped between two O-rings. One side of the platinum covered quartz crystal was used as a working electrode facing the solution, while the other side faced the air. The oscillating area was 0.28 cm². The counter electrode was a Pt mesh and a silver wire was used as a quasi reference electrode. Potentials versus the Ag quasi reference electrode were then rescaled to Ag/AgCl, which was calibrated using a ferrocene/ferrocenium redox couple (0.35 V vs Ag/AgCl). A Hameg HM 2122 frequency counter connected to an IEEE-488 interface bus and IBM personal computer was used to measure the resonance frequency. The voltammetric experiments were performed using a three-electrode potentiostat (Amel model 533) connected to a computer via an A/D-D/A converter. In house software was used for the data processing. The polymer films were potentiostatically deposited under an argon atmosphere at different potentials (0.9–1.5 V) on the Pt electrode side of the quartz in propylene carbonate containing 0.1 M pyrrole and 0.1 M TBAPF₆. The deposition was stopped when the resonance frequency had decreased by ca. 5 kHz. Subsequently, the polymeric layer was discharged at a potential of 0.0 V. After polymerization the coated electrode was transferred in a monomer-free 0.1 M TBAPF₆/PC electrolyte solution and cycled at room temperature at a scan rate of 10 mV/s, and the change in frequency or mass were followed in situ as a function of the change in potential. The Sauerbrey equation (Eq. (1)) describes the relation between the change of mass (Δm) and the change of frequency (Δf) for every electrochemical process to a good linear approximation:

\[ \Delta m = C_{QMW} \cdot \Delta f \]  

(1)

Additionally the mass change is related to the amount of charge (ΔQ) described by a modified Faraday law (Eq. (2)):

\[ \Delta Q = \frac{nF}{M} \cdot \Delta m \]  

(2)

where \( F \) is the Faraday constant, \( n \) the number of electrons and \( M \) the molecular mass in this reaction. The combination of Eqs. (1) and (2) defines the molecular mass of a charge compensating species \( M_{CSS} \) (Eq. (3)):

\[ \frac{\Delta f}{\Delta Q} = \frac{M}{nF_{QMW}} = C_{EQMW} \cdot M_{CSS} \cdot C_{EQMW} = -1.98 \text{ (mol Hz/g mC)} \]  

(3)

The value of \( M_{CSS} \) in Eq. (3) was determined using linear regression in the frequency (f) versus charge (Q) plots. In this case, \( M_{CSS} \) represents an average value for the corresponding potential range.

3. Results

3.1. BBM measurements

The deflection of the PPy bilayer over a certain potential range was measured using screenshots (Fig. 1a and b) of constant time intervals combined with chronoamperometric (Fig. 1c) measurements. PPy bilayers deflection polymerized at different polymerization potentials are presented in Fig. 1d. To test the reproducibility of the deflection more than three PPy bilayers were produced for each polymerization potential.

The movement of the PPy bilayer was recorded using a CCD camera and individual frames were captured from the recorded video stream. Fig. 1a and b shows two example images of the PPy bilayer (\( E_p = 0.85 \text{ V} \)) at 0.0 V (Fig. 1a) and 1.0 V (Fig. 1b). The deflection \( \Delta \delta \) (\( \delta_p - \delta_n \)) for chronoamperometric experiments was calculated from the bending beam curve (−) and the charge related to the PPy film oxidation was calculated by integration of the current time curve (−) (Fig. 1c).

The deflection and charge per unit area of the PPy bilayers are also presented (Fig. 1b) with an error of 5–10%. The two lowest polymerization potentials (0.85 V and 0.90 V) showed nearly the same deflection \( \Delta \delta \) of 5.1 mm. A charge of 23.1 mC/cm² was recorded for \( E_p = 0.85 \text{ V} \) and this increased to 27.8 mC/cm² for \( E_p = 0.9 \text{ V} \). At a
polymerization potential of 1.0 V the deflection of the PPy bilayers decreased to 4.4 mm, but the charge passed at these polymerization potentials (0.9–1.0 V) remained similar (26.7–27.8 mC/cm²). At the next highest polymerization potential of 1.05 V, the deflection of the PPy bilayer for a potential step to 1.0 V increased to 4.9 mm. While the charge passed for the PPy films formed at the polymerization potential of 1.1 V was higher (35.4 mC/cm²) than for a polymerization potential of 1.05 V (25.7 mC/cm²), a similar deflection $\Delta \delta$ (4.95 mm) was found. For higher polymerization potentials (1.15–1.3 V) the deflection of the PPy bilayers decreased almost linearly ($-82\%$). The charge passed increased for a polymerization potential up to 1.3 V (36.4 mC/cm²) and then decreased at higher polymerization potentials to 1.5 V (29 mC/cm²). The deflection for polymerization potentials between 1.3 and 1.5 V showed almost the same value (1.4–1.5 mm). These results thus displayed a non-linear behaviour for PPy bilayer deflection, based upon the use of different polymerization potentials and the charge passed during the oxidation step. The lowest (0.85 V) and the middle polymerization potential (1.1 V) showed the highest deflection of 5.0 mm.

To investigate the effect of the polymerization potential upon charging and discharging (in the potential range $-1.0$ to 1.0 V), during the bilayer deflection, cyclic voltammetric experiments were carried out (Fig. 2). To avoid errors, through the time dependent delay of the deflection, the cyclic voltammetric measurements were carried out with a constant scan rate of 5 mV/s.

The experiment was started at a potential of $-1.0$ V where the PPy bilayers already showed a deflection. In the potential range between $-1.0$ and 0.0 V the PPy bilayer contracted until the first sharp oxidation peak was reached in the cyclic voltammetric experiment at $-0.02$ V. After a second broad oxidation peak was reached at around 0.4 V the polymer expanded and consequently the strip bent. The reverse scan shows only one reduction peak (at $-0.38$ V) when a polymerization potential of 0.85 V was used. For higher polymerization potentials of 1.0–1.2 V, a new reduction peak occurred at $-0.17$ V. After this reduction peak the PPy film started to expand and the PPy bilayer deflected. After discharging at a potential of $-1.0$ V every PPy bilayer, regardless of polymerization potential (Fig. 2), showed a deflection and returned approximately to the starting position. The two minima in the deflection, using a polymerization potential of 0.85 V, were seen at 0.35 V. Compared with the bending beam curves for polymerization potentials of 1.0–1.2 V, the minima of deflection for the PPy bilayers was located close to 0.1 V. The deflections of the PPy bilayers (the main values with standard regressions), at anodic (1.0 V) and cathodic (−1.0 V) potentials, as a function of polymerization potential (0.85–1.5 V) are presented in Fig. 3.

At a low polymerization potential of 0.85 V, the deflection at $-1.0$ V showed the highest value of 6.8 mm, and this decreased linearly (by 42%) to 4 mm for a polymerization potential of 0.95 V. At polymerization potentials between 0.95 V and 1.05 V, the deflection of the PPy bilayer at a potential of $-1.0$ V was similar (ca. 4 mm). The polymerization potential of 1.1 V (marked by arrow) produced the second largest deflection of 5.5 mm, and with higher polymerization potentials up to 1.3 V the deflection decreased (by 78%). The deflection during oxidation at 1.0 V was of nearly the same extent as the deflection after reduction at $-1.0$ V. The lowest polymerization potential of 0.85 V ($\Delta \delta = 4.3$ mm) and the middle polymerization potential of 1.1 V ($\Delta \delta = 4.8$ mm) produced two deflection maxima. The polymerization potential 1.0 V gave the first deflection minimum ($\Delta \delta = 3.25$ mm). At every polymerization potential the deflection at the negative potential ($-1.0$ V) after reduction, gave a higher value than that at the positive potential (1.0 V) after oxidation. The comparison of the cyclic voltammograms for polymerization potentials of 0.85 up to 1.0 V (Fig. 4a) and from 1.0 to
1.2 V (Fig. 4b) of the PPy bilayers presents a significant change in the current–potential curves. The oxidation peak at −100 mV at the broad oxidation wave between 150 and 500 mV increased with higher polymerization potential (Fig. 4a). Also, the oxidation peak at −100 mV ($E_p > 0.85$ V) shifted to more positive potentials at −50 mV at higher polymerization potential ($E_p = 1.0$ V). The reduction peak at −450 mV decreased with higher polymerization potential. The cyclic voltammogram at the polymerization potential 0.9 V shows a second reduction peak at −120 mV, which increased with higher polymerization potential. Between both reduction peaks an isopotential point at −350 mV was found. The cyclic voltammograms show a decrease of the oxidation peak and of the oxidation wave (shown in Fig. 4a) upon increasing the polymerization potential (Fig. 4b) of the bilayers to 1.2 V. The sharp oxidation peak shifts back to more negative potentials. The reduction peak at −120 mV decreases and the reduction peak at −450 mV grow with higher polymerization potential. Also, an isopotential point at −350 mV was observed between both reduction peaks.

3.2. EQCM study

The electrochemical quartz crystal microbalance (EQCM) can be used to register the mass changes of polymer films during an electrochemical cycle. During charging (oxidation) electrons are withdrawn from the polymer and to maintain electroneutrality counter ions from the electrolyte penetrate the polymer film. These induce a mass change within the deposited polymer which can be measured as a frequency change of an oscillating quartz crystal. The frequency change can be calculated as a mass change (1 Hz corresponds 4.85 ng). On discharging (reduction) the polymer film, counter ions leave the polymer film and the mass decreases. Fig. 5 shows the mass change $\Delta m$ with current $I$ for PPy films polymerized

![Fig. 2. Deflection $\delta_{CV}$ (–) of the PPy bilayers ($E_p$: 0.85, 1.0, 1.1 and 1.2 V) in PC/TBAPF$_6$ (0.1 M) in one operation with voltammetric measurements (...) ($v=5$ mV/s).](image)

![Fig. 3. Deflection $\Delta \delta$ of PPy bilayers after reaching an oxidation potential of 1.0 V (■) and reduction at −1.0 V (△) for different polymerization potentials $E_p$.](image)

![Fig. 4. Cyclic voltammograms (5 mV/s, between potential of 1.0 V and −0.8 V) of PPy bilayers with polymerization potentials $E_p$: (a) 850 mV (–), 900 mV (…), 950 mV (−−) and 1000 mV (−); (b) 1000 mV (−), 1050 mV (−−), 1100 mV (…) and 1000 mV (−).](image)
at different potentials during cyclic voltammetric experiments (v = 10 mV/s).

The EQCM studies of the PPy films produced at polymerization potentials of 0.85, 1.0, 1.1 and 1.2 V are presented at Fig. 5, and show upon oxidation from −1.0 to −0.5 V an overall mass decrease of 1.1 %. At 0.0 V the mass increased, which correlated with the oxidation peak seen in the various experiments. On the reverse scan the polymer film discharged and the mass decreased until the reduction peak was seen at about −0.5 V. For the polymerization potential of 0.85 V the PPy film showed a small mass increase (2.1 %) over the potential range of −0.7 to −1.0 V. The PPy films produced at a polymerization potential of 1.0–1.2 V showed a c. 4 % decrease in mass upon full reduction.

The amount of cations and anions, with or without solvent, incorporated or expelled from the polymer film during charging and discharging can be determined from the ratio of frequency change Δf to the electrical charge passed ΔQ. If the frequency decreases then the mass increases, while it decreases for a shift to higher frequencies. On different parts of the curve (Fig. 5) the slope can be obtained and used to calculate the value of M_{CCS} (Eq. (3)) to indicate the amount and type of ions, with or without solvent (M_{ion} = 102.09 g/mol), which are incorporated or expelled during charging and discharging. A negative value of M_{CCS} shows a loss of mass explained as ions with solvent leaving the polymer, while a positive M_{CCS} indicates ions moving into the polymer film during the redox process. The mass of the anion PF_{6} - amounts to 144.96 g/mol and the cation TBA⁺ 247.47 g/mol. If the values of M_{CCS} are smaller than the molar mass of the anion, then anions and cations with solvent (a mixed process) are involved during charging and discharging (Fig. 6).

Fig. 6 shows that for all polymerization potentials E_P (0.85, 1.0, 1.1 and 1.2 V), upon oxidation and reduction anions and cations are involved due to the lower values for the charge compensating species M_{CCS} compared to the molar mass of the anion PF_{6} - (144.96 g/mol). The polymerization potentials 0.85 and 1.0 V showed upon oxidation (■) at −0.5 V a negative M_{CCS} of −15. This can be explained due to the mixed process of charging where more cations move out than anions move in. For polymerization potentials of 1.1 and 1.2 V, the M_{CCS} showed at −0.5 V a positive value of around 14. In this case the mixed process led to more anions moving inside than cations moving out. Further oxidation to 1.0 V showed an increase of M_{CCS} for all polymerization potentials (Fig. 6). The value of M_{CCS} at a potential of 1.0 V decreased for higher polymerization potentials E_P: 90 (E_P = 0.85 V) > 79 (E_P = 1.0 V) > 68 (E_P = 1.1 V) > 66 (E_P = 1.2 V). On the reverse reduction scan (—), at potentials between 1.0 and 0.0 V, for all polymerization potentials a value for M_{CCS} of −60 was observed, indicating that more anions move out than cations move in. At a potential −0.5 V, near the main reduction peak (see Fig. 5), positive values for M_{CCS} were obtained for the polymerization potentials of 0.85 V (M_{CCS} = 9), 1.1 V (M_{CCS} = 5) and 1.2 V (M_{CCS} = 2). This indicates that upon reduction a mixed process is involved where more cations are incorporated than anions expelled from the conducting polymer. Further reduction to −1.0 V showed, only for the polymerization potential of 0.85 V, a positive value of M_{CCS}, while for higher polymerization potentials a negative values of M_{CCS} were obtained between −21 (E_P = 1.0 V) and −55 (E_P = 1.1 V). The values of M_{CCS} during the redox process showed only for the polymerization potential of 1.1 V a significantly higher discharging at the end of the cyclic voltammetric measurement.

4. Discussion

In the case of conducting polymers, the actuation process is based on the charging and discharging of the electro active material. Both sequences lead to the movement of ions and solvent in and out of the films and consequently volume changes take place which generate the actuation process.

The experiments show that when the applied potential for actuation is outside the range of −0.25 and 0.25 V, deflection occurs for both reduction and oxidation of the PPy film (Fig. 2). They also show that the extent of the deflection depends on the formation potential applied during polymerization (Fig. 3).

Heinze et al. [24–28] put forward that the structural properties of PPy depend on the oxidation potential applied during the polymerization of pyrrole. The PPy structures were divided into three categories based on the chain length and degree of cross-linking of the polymer films. The first category, polymeric I (PPy I), has relatively long chains, between 30 and 60 units and was produced with polymerization potentials close to 1.0 V. PPy II with short chains of the oligomer (8–16 units), occurred at lower potentials in
acetonitrile with some water (1%, w/w) and a low acid concentration. Polymerization potentials above 1.0 V but below 1.5 V produced the PPy III form, which consisted of cross-linked, conjugated chain segments containing 8–16 pyrrole units.

PPy II showed cation movement at low actuation potentials, while anion movement dominated in the PPy I and III. However, our in situ EQCM measurements (Figs. 5 and 6) clearly show that anion and cation movement [15,16,29] during charging and discharging processes take place for all polymerization potentials investigated i.e. for each category.

In the past, cation insertion [30–32] was mainly found when large anions such as DBS− were used for polymerization. In that case, the anions could not move out during reduction and so cations were incorporated to maintain electroneutrality. The size of the cations determined the degree of the actuation. Inganäs et al. [33–35] carried out studies of a PEDOT bilayer by applying a square wave potential and observed actuation for oxidation as well as for reduction. They suggested a polaron/bipolaron model to explain the reduction phenomenon, in which conformational changes lead to the expansion of the polymer during reduction. Skompska et al. [36] suggested that cation and anion insertion takes place during polymerization and that they both effect the final actuation properties during redox processes.

The experimental observation of PPy II presented above, seems to suggest a simpler explanation for the cation movement. PPy II with its short chain lengths between 8 and 16 units “dimerizes” in the initial phase of charging thereby forming σ-dimers between the chains. The σ-dimerisation model [23] proposes that anions are immobilized on localized charges at the polymeric chain during the final step of polymerization and the initial phase of all the successive charging cycles. Consequently, at the “end” of discharging, anions are trapped in the polymer film and anion expulsion is hindered. In order to maintain the electroneutrality during reduction at negative potentials, cations move into the polymer and increase the volume of the layer, leading to the characteristic actuation seen in Fig. 2. Then during charging, cations are expelled from the polymeric layer because the negative charges of the fixed anions are now compensated by the positive charges generated at the PPy chains. This consequently reduces the deflection up to the potential where σ-dimerization is complete and anion movement begins. The anion movement is coupled with the generation of positive mobile charge carriers in the polymeric chain.

We propose that at certain polymerization potentials there are multiple structural forms of the PPy mixed together and that this can explain the differences in actuation behaviour. For the low polymerization potential of 0.85 V the fraction of cation movement upon reduction was greater than that for higher polymerization potentials. We can assume that a mixture of PPy I and II, with a higher proportion of PPy II, can explain the high actuation at both cathodic and anodic potentials.

The magnitude of the actuation has a maximum for films prepared at +0.85 V. The cyclic voltammogram for a polymerization potential of 0.85 V (Fig. 4a) shows one sharp oxidation peak at −0.1 V and one broad one at 0.45 V. The intensity of the first oxidation wave increases for higher polymerization potentials while the broad oxidation wave almost disappears. Only one reduction wave at −0.45 V is found for the lower polymerization potentials and for higher polymerization potentials a new reduction peak appears at −0.1 V.

At potentials higher than 1.05 V, characteristic changes of the voltammetric response can again be observed (Fig. 4b). The sharp oxidation wave at −0.1 V decreased, as to did the reduction wave at −0.12 V, indicating that the redox behaviour of the polymeric film is changing as a function of its formation potential (isopotential point in Fig. 4a and b). There is a direct correlation between the changes in the voltammetric response and the magnitude of actuation. The PPy II form has more localized charges due to reversible σ-dimerization [23], with subsequently more anions immobilized, will therefore require the incorporation of cations upon reduction to maintain electroneutrality [28]. High polymerization potentials up to 1.2 V showed a decrease in actuation behaviour upon oxidation and reduction. The degree of cross-linking for high polymerization potentials leads to a lower conductivity [22] in the mixed forms of PPy III with a low proportion of PPy I. Likewise with the actuation of the PPy bilayers, the best actuation at anodic potentials was found for an intermediate polymerization potential of 1.1 V. From this, it appears that the partly cross-linked
PPy (a combination of PPy I and III) leads to optimal actuation properties. Long-term stability measurements (square wave potentials between 0.0 V (30 s) and 0.8 V (30 s), data not shown) indicated that the stability of PPy bilayers produced in low polymerization potentials was greater (over 3000 cycles) compared to that of PPy bilayers produced at a polymerization potential of 1.1 V (to 1500 cycles).

5. Conclusions

The actuation behaviour of PPy bilayers produced at different polymerization potentials (0.85–1.5 V) was tested using different electrochemical methods (chronoamperometry and cyclic voltammetry), which showed an effect of polymerization potential upon actuation. To ensure that the amount of polymer deposited at different polymerization potentials was the same, the charge, related to the surface area of the polymer. For repeat experiments for each PPy bilayer (at least in triplicate) the reproducibility was found to lie in the range of 10% for each polymerization potential.

Cyclic voltammetric measurements showed that a minimum of deflection occurred at a potential of about 0.0 V. This behaviour is attributed to the generation of different polyppyrole modifications for the different applied potentials used in the electropolymerization. In situ EQCM measurements revealed that anion insertion took place upon oxidation of a film and cation insertion upon reduction pointing to mixed PPy modifications consisting of PPy II with varying fractions of PPy I and PPy III. For the low polymerization potential of 0.85 V mainly PPy II and I were formed, while for higher polymerization potentials an increase in cross-linking is involved (PPy III+I and a small amount of PPy II). We have thus shown that the electropolymerization potential of the polymer plays an important role in possible applications of PPy actuating bilayers.

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