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Viscoelastic Study of Conducting Polymers Using Quartz Crystal Microbalance

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ABSTRACT

Application of conducting polymers has been growing widely in different fields such as batteries, solar cells, capacitors and actuators. Mechanical properties of conducting polymers like flexibility, high power to mass ratio and high active strain make them potentially applicable to robotic and automation industries. Obviously, a dynamic model of the actuation phenomenon in conducting polymers is needed to study its controllability and also to optimize the mechanical performance. De Rossi and colleagues suggest treating the mechanical behaviour of conducting polymers separately from the viscoelastic structural model and electrochemical actuation ^[1]. But it has been observed that the effects of electrochemical actuation and diffusion of ions on the viscoelastic coefficients cannot be neglected in some conducting polymer actuators, as shown in ^[1]. In this paper, we present the effects of cyclic voltammetry actuation on shear modulus of polypyrrole in propylene carbonate and EMI.TSFI as measured by an electrochemical Quartz Crystal Microbalance (eQCM). The QCM consists basically of an AT-cut piezoelectric quartz crystal disc with metallic electrode films deposited on its faces. One face is exposed to the active medium. A driver circuit applies an AC signal to the electrodes, causing the crystal to oscillate in a shear mode, at a given resonance frequency. QCM has been routinely used for the determination of mass changes. Measured resonance frequency shifts are converted into mass changes by the well-known Sauerbrey's equation. In this paper, we correlate the admittance output of QCM to the real shear modulus of polypyrrole. Then the results of the correlation which contains mechanical data are presented during actuation using two different types of electrolyte.

Keywords: conducting polymers, polypyrrole, micro actuator, QCM, shear modulus.

1. INTRODUCTION

The conventional application of QCM device is to detect nano-scale mass change on the working surface as shown in Figure 1. The formulation of the rigid thin deposited layer has been done as the well-known Sauerbrey's equation, which states that the mass change of the layer is proportional to the shift in resonance frequency. Recently, researchers have been trying to use QCM for thick and non rigid surfaces. The formulations done by Hillman^[2, 3] showed that viscoelasticity of the deposited layer on the crystal surface makes deviation from Sauerbrey's equation. This work has shown that the QCM provides the opportunity to detect viscoelastic properties of the deposited layer. Several studies have been conducted by Hillman and co-workers on polythiophene ^[4-13]. Their work had been carried out using a QCM device working with an impedance system.

The QCM device utilised by Lucklum's group is similar to the QCM device used in this research ^[14-21]. It works in resonance frequency of the crystal and has two output signals, which obviously can be interpreted to two variables. These variables in this study are real shear modulus and the thickness of the polymer. The aim of the present study was to determine how shear modulus and polymer thickness change during cyclic voltammetry of polypyrrole in two different electrolytes: tetrabutyl ammonium hexafluorophosphate (TBA-PF₆) in propylene carbonate (PC) and an ionic liquid, 1-ethyl,3-methyl imidazolium trifluoromethane sulfonimide (EMI-TFSI) ^[22-24].

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Figure 1. (Left) Bare Crystal oscillates at its natural frequency. (Right) A deposited layer causes a shift in the natural frequency which is proportional to the mass of the layer.

2. MATERIALS AND METHOD

Propylene carbonate (PC) (Aldrich) and tetrabutylammonium hexafluorophosphate (TBA-PF₆, obtained from Sigma) both of AR grade were used. Pyrrole monomer from Merck was distilled and stored under -18°C before use. The constant current required for polymerisation was supplied using an EG and G Princeton Applied Research Model 363 potentiostat / galvanostat. PPy films were grown galvanostatically with a $0.15\text{ [mA/cm}^2\text{]}$ current density. Polymerisation solution was PC containing 0.5M Pyrrole and 0.25M TBA-PF₆. The polymerization temperature was controlled around -25 to -28°C . The reference electrode was Ag wire in 0.01M AgNO₃ and 0.1M TBA.PF₆ in acetonitrile (ACN) using 0.1M TBA.PF₆ in PC as a salt bridge. All the experimental data was processed and recorded by MacLab/4e AD instruments and computer.

The quartz crystal microbalance device was QCM200 Stanford Research Systems with ability to work in electrochemical bath with liquid electrolyte and equipped with Capacitance Cancellation system. The experimental set up is shown in Figure 2, illustrating the QCM electrode on which a PPy layer has been deposited, and subsequently stimulated by cyclic voltammetry. The output signals of QCM are the change in resonance frequency in Hz and the admittance variation parameter in Ohm. The methodology of the experiment is explained in Figure 3, showing it to be divided into four regions. In the first region, the bare crystal is in air and the resonance frequency signal must be 5 MHz and the frequency variation signal Δf should be adjusted to zero. In the next region, the crystal has been placed in the liquid environment, so that ΔR and Δf can be related to the viscosity and density of the electrolyte. This part of the experiment confirmed that the QCM is a very precise instrument for detecting the density and viscosity of the liquids in the both form of Maxwell's and Newton's liquids. Polymerisation has been carried out in the third step; the frequency signal is varying while admittance signal remains constant. The latter guarantees that the deposited layer fits Sauerbrey's equation criteria and we are able to calculate the layer thickness using the frequency signal. By comparing AFM thickness measurement and QCM output, polymer density has been calculated. Finally, the electrolyte was exchanged and actuation of the PPy was studied using CV.

Figure 2. Experimental set up, QCM crystal coated with PPy was stimulated using cyclic voltammetry at different scan rates. The QCM and electrochemical signals were used to determine viscoelastic variables using a mathematical solver.

Figure 3. Experimental Method: figure shows how QCM device outputs changed during the experiment. The output is divided into four regions: 1) Bare crystal in the air. 2) Crystal in the the polymerisation electrolyte causes a frequency and resistance change which were used to determine viscosity and density of the electrolyte. 3) After polymerisation begins, the primary thickness of the polymer can be calculated from the frequency signal. The constant resistance signal proves the validity of Sauerbrey's equation. Comparing AFM measured thickness and QCM thickness was used to calculate polymer density. 4) The main part of the experiment happens in the fourth region by voltage applying to the polymer after the electrolyte has been exchanged. The analytical solver program described below converts the QCM signals to thickness and shear modulus.

The next step after the experiment was the interpretation of the QCM output signals to produce the desired mechanical data. As shown in Figure 4, the output signals form a complex (containing both real and imaginary part) mechanical impedance parameters which should be equalised with the mechanical impedance. This analysis comes from a mathematical model of viscoelastic layer deposited on a oscillated surface^[2, 3].

The unknown parameters in this calculation are shear modulus of the polymer and its thickness. A solver program has been designed to solve the real part and imaginary part of this equation as simultaneous system of equations in MATLAB software.

Figure 4. Numerical methodology, the measured signals build a complex impedance parameter, which should be equal to the theoretical complex impedance as calculated in the literature [insert reference]. A solver program has been designed to solve the equation and find the variables shear modulus (G) and polymer thickness (h_f).

3. RESULTS

Figure 5 shows the shear modulus and thickness variation of PPy in PC electrolyte taken at 50 mV/s scan rate. The thickness at the beginning point and end point has been confirmed by AFM thickness measurements. Both patterns are reversible with a small hysteresis. Figure 5 compares the thickness and shear modulus change with the current flow during the CV experiment. As shown in Figure 5b) the expansion of the PPy film begins when an oxidation current occurs. The oxidation of the PPy induces anions (and solvent) to enter the film causing swelling. The film continues to expand, however, after the oxidation peak has been reached, perhaps as a result of continuing electro-migration as recently described by Smela^[25]. Swelling continues for a short time during the reverse scan due to kinetic delays and

then the film contracts as a result of the reverse electro-migration and reduction of the polymer film causing the ejection of the counter ions and solvent.

In addition to the change in thickness, the QCM results show that the shear modulus also changes significantly during electrochemical cycling, as has also been observed in previous studies [26, 27]. The modulus changes between 5 and 8 MPa, which is lower than measured in other studies on bulk films and fibres and may reflect a different density of structure formed in the thin films grown for QCM experiments. The change in the modulus value during CV cycling is approximately 25% which is similar to many previous studies, but is smaller than the 500% change reported in one study [26]. These differences may be due to the differences in the mechanical stimulation frequency, which is in the megahertz range for QCM so that only fast strain responses are detected. The change in modulus measured during CV in the QCM is dominated by two processes. From the fully reduced state, the modulus first decreases and then increases as the polymer is oxidised. It is possible that the swelling and the introduction of charged units on the polymer backbone produce competing influences on the modulus. Swelling would reduce the concentration of elastically-active network chains, therefore reducing modulus. However, the charging of the chains would stiffen the molecules therefore increasing modulus. Further studies are being considered to identify the processes occurring.

Figure 6 shows the shear moduli taken during CV at different scan rates using PC electrolyte. A larger change in modulus (especially at cathodic potentials) was observed at lower scan rates. In contrast, only a very slight increase in the thickness change was observed as the scan rate decreased. The larger change in modulus at slower scan rates suggest that the extent of the electrochemical reduction is increased at the slower scan rates, leading to a larger reduction in the charge on the polymer backbone. Interestingly, the change in modulus that occurs at anodic potentials is not very much influenced by the scan rate. The calculated change in thickness is of the order of 30%, which is similar to that reported previously for thickness direction actuation in PPy [28].

Figure 5. The real shear modulus variation and the thickness change are shown vs. voltage beside CV diagram (50mV/s scan rate) and 0.1M TBA.PF₆ in PC electrolyte.

Figure 6. Change in shear modulus obtained at different scan rates and 0.1M TBA.PF₆ in PC electrolyte

Figure 7. Change in thickness of PPy at different scan rates in 0.1M TBA.PF₆ / PC electrolyte

Figure 8, 9 and 10 show the results as obtained in ionic liquid electrolyte. Using this kind of electrolyte can eliminate the effects of solvent molecules diffusion into and out of the polymer. As expected, the maximum thickness change in the

ionic liquid is about the half of that obtained from PC electrolyte (almost 16%) and in the swelling occurs in the reverse direction. The CVs in both electrolytes were similar with oxidation peaks at $\sim 0.1\text{V}$ and reduction peaks occurring near -0.5V (vs. Ag/AgCl reference). The modulus-voltage curves, however, were quite different in the two electrolytes. The differences may be due to the absence of solvent effects in the ionic liquid. Further analysis is needed to fully elucidate the mechanisms for the modulus shift. As with the PC electrolyte, the scan rate strongly influenced the modulus shift but only had a small effect on the change in thickness for PPy operated in the ionic liquid. The shear modulus changed by as much as 45% at a scan rate of 20mV/s but this change was reduced to less than 20% when the scan rate increased to 100mV/s .

Figure 8. The shear modulus variation and thickness change obtained at 50mV/s scan rate in EMI.TSFI Ionic Liquid electrolyte. As expected, the thickness change in IL electrolyte is in the inverse direction compared to PC

Figure 9. Shear modulus change in EMI.TSFI Ionic Liquid electrolyte obtained at different scan rates

Figure 10. Thickness variation at different scan rates in EMI.TSFI Ionic Liquid electrolyte

4. CONCLUSIONS

This study has focused on the effect of electrochemical stimulation on real shear modulus of PPy during electrochemical cycling in both IL and PC electrolytes. Diffusion of ions and / or solvent during oxidation may cause the initial increase and then decrease in real modulus of polypyrrole observed in the PC electrolyte. The modulus variation can be considered almost reversible with a small hysteresis. Since solvent effects are absent in the ionic liquid, a simpler actuation mechanism is expected. Indeed, the shift in modulus was less complicated in the ionic liquid than in the PC electrolyte. Further studies are required to fully elucidate the mechanisms for the modulus shift.

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