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Taking into account of surface roughness for the calculation of elastic moduli of polymer films from acoustic impedance data

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ABSTRACT

The surface roughness of deposits contributes to their acoustic impedance and affects the results of calculation of elastic moduli (G) of thin polymer films from acoustic impedance data. A simple approach was developed in this paper to account for roughness in form of small random corrugations with Gaussian spectrum. The theory used was developed originally for bare crystals and is based on Rayleigh diffraction method. Experimental acoustic impedance data for poly-3,4-ethylendioxythiophene (PEDOT) films deposited from ionic liquids (1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide, [BMP][TFSA], containing 1 mM of EDOT monomer) were analyzed in terms of this new developed approach. The roughness was estimated ex situ by a laser profilometer. The contribution of roughness-corrected liquid impedance changes G values significantly. Further, the film elastic properties in two ionic liquids ([BMP][TFSA] and 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) amide, [EMIm][TFSA]) were compared by using mean-field model.

1. Introduction

The electrochemical Quartz Crystal Microbalance, EQCM, technique allows in situ monitoring of the mass changes on the surface of the working electrode, which usually is an Au electrode deposited on a quartz crystal [1]. The EQCM can determine very accurately small amounts of electrodeposited or adsorbed species [2] (on the order of magnitude of ng/cm^2), as well as viscoelastic properties of the adjacent medium [3–9]. Also one can get information about the roughness of the deposited layer [10–14]. In previous studies, the authors of this present paper have shown that the EQCM can be applied for the study of electropolymerization of conducting polymers. One could extract from the EQCM data information on the viscoelastic properties of these layers and their doping in various electrolytes [15,16].

Acoustic impedance data of thin polymer films can be used for the calculation of complex shear moduli of electrodeposited polymer at EQCM fundamental frequencies and harmonics, normally $\omega/2\pi = 10$, 30, 50 MHz. From acoustic wave equations for a polymer film of thickness h_f deposited on the quartz surface in contact with solvent the following equation for the compound impedance is obtained [17]:

$$Z = i\omega\rho_s + Z_P\left(\frac{Z_L\cosh(\gamma h_f) + Z_P\sinh(\gamma h_f)}{Z_P\cosh(\gamma h_f) + Z_L\sinh(\gamma h_f)}\right) \quad (1)$$

In Eq. (1) the acoustic impedances of the film of density ρ_f and of the liquid (ρ_l) are, respectively, $Z_p = (\rho_f G)^{1/2}$, $Z_L = (i\eta_l\rho_l\omega)^{1/2}$. The term ρ_s describes the areal density of the trapped liquid between the surface features.

The impedance of the film includes complex shear elastic modulus $G = G' + iG''$, while the impedance of liquid depends on its viscosity η_l. The hyperbolic terms contain the complex wavenumber for the shear acoustic wave $\gamma = i\omega(\rho_f/G)^{1/2}$. So far the only appearance of roughness was in the term $i\omega\rho_s$ with $[\rho_s] = \mathrm{g\,cm^{-2}}$, which accounted for roughness of bare crystal in contact with liquid and it was used for calibration purposes before polymer deposition. Usually this term is very small when compared to the second term from Eq. (1).

From ex situ profilometer measurements one can observe that in some cases the deposited polymer film can be rough (Figs. 1 and 2), with non-uniformities in thickness significantly larger than those for quartz substrate. This should contribute to the liquid impedance thus accounting for more significant part of measured impedance and consequently "leaving" less for the film itself.

It is well known that surfaces with an average roughness, R_a, below 0.15*δ, where δ is the penetration depth of the shear

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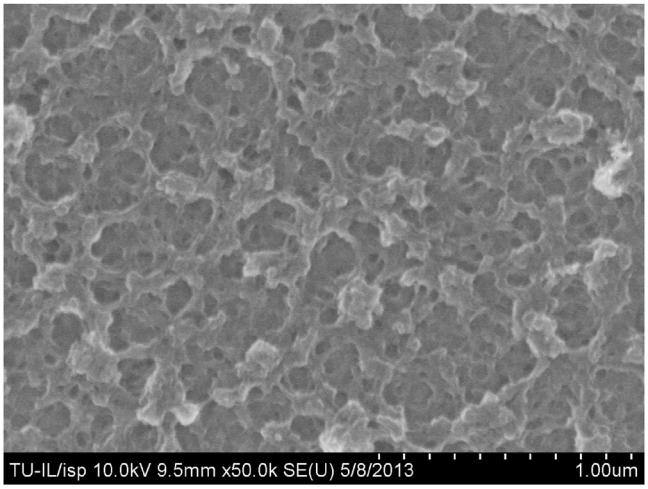

Fig. 1. SEM image of the deposited PEDOT film from 1 mM EDOT in [BMP][TFSA] at 0.8 V vs Pt reference electrode and room temperature, until a shift Δf of 10 kHz was reached.

wave (δ = 180 nm for a quartz oscillating in water at 10 MHz), are expected to behave as hydrodynamically smooth [18–20]. However, when the roughness of the electrodes exceed this roughness, pressure waves occur at even harmonics of the resonance frequency [19,20]. The presence of these compressional waves was proved with the help of a microphone [19,20]. Also, an increase of both imaginary and real parts of the surface shear mechanical impedance was observed with increasing the roughness of the electrodes [18]. The imaginary part increased due to the presence of the trapped liquid, which acts as a rigidly attached mass layer, in the rough microstructures. The asperities present on the surface tend to convert the shear motion of the surface into a surface normal liquid motion, thus generating compressional waves. The real part of the surface shear mechanical impedance increases due to the presence of these compressional waves [18]. However, to the best of authors' knowledge, nobody so far included, when calculating the shear moduli of conducting polymers, the influence of the surface roughness. This study is dedicated to analysing the effect of surface roughness of thin poly-3,4-ethylendioxythiophene (PEDOT) films on the value of the shear modulus. The measurements have been performed with an EQCM system in relatively viscous media, namely in two ionic liquids.

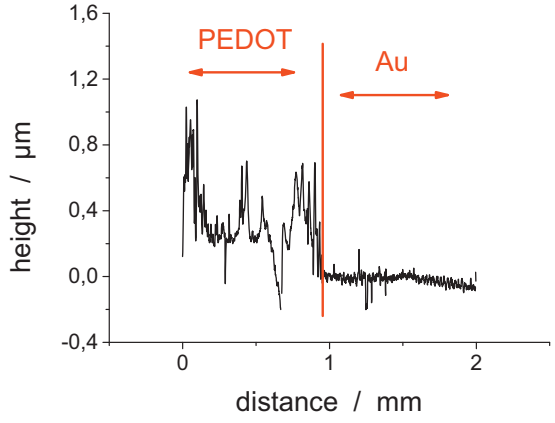

Fig. 2. The profile of a PEDOT layer electrodeposited on an Au electrode of a quartz crystal, along a line-scan. Deposition conditions were: 1 mM EDOT in [BMP][TFSA], E = 0.8 V vs Pt reference electrode until a shift of resonance frequency of 10 kHz was reached, room temperature.

2. Experimental

The experimental procedure was similar to one described in [15]. 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl) amide, [BMP][TFSA] and 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) amide, [EMIm][TFSA] were purchased from Iolitec (Germany). They were dried for more than 6 h at 100 °C prior to use. 3,4-Ethylenedioxythiophene was purchased from Alfa Aesar. The electrode electrochemical set-up included Pt wires as counter and pseudo-reference electrodes. The working electrode was the Au covered surface of a quartz crystal with an active area of 0.22 cm^2.

Polymerization was achieved by potential steps from 0 to 0.8 V vs Pt in 1 mM EDOT in [BMP][TFSA], until a 10 kHz shift of the fundamental mode was obtained. This frequency shift corresponds to a mass increase of ca. 45 $\mu g/cm^2$, as calculated with the Sauerbrey equation. After its synthetizing, the film was transferred into monomer free [BMP][TFSA] and afterwards in [EMIm][TFSA] where acoustic impedance measurements were carried out at a constant potential. Therefore G values are reported for the same film in two ionic liquids at one potential. Different values of the potential were analyzed in different set of experiments, in order to check the effect of the state of the PEDOT (in its reduced or oxidizing form) on the calculated G values. In this study just the results obtained at E = 0 V vs Pt reference electrode will be presented, as no effect of the potential on G values could be noticed.

Experiments were conducted in a glove box in Ar atmosphere at T = 26, 30, 40 and 50 °C and at 10, 30 and 50 MHz. Acoustic admittance spectra over a 200 kHz span centered around the fundamental frequency of 10 MHz were recorded by a network analyzer as described in [21]. For the higher harmonics the used span was 300 kHz and 500 kHz for 30 MHz and 50 MHz, respectively.

Beside the fundamental resonance frequency, just to two overtones (30 and 50 MHz) were considered in this work. With increasing the number of the overtone, one gets beside a better sensitivity to frequencies changes, also an increase in the damping of the quartz crystal. At higher harmonics, the influence of the viscous medium adjacent to the quartz crystal becomes more significant than at the fundamental frequency. This can be easily observed by the broadening of the resonance curves at higher harmonics in the ionic liquids. Starting from the 70 MHz, a huge damping was recorded in both ionic liquids, and the fitting of the resonance curve became more tricky, fact that induced focusing in this paper only on the three resonance frequencies mentioned above.

Film thickness (according to DIN 4762) and roughness (DIN 4768, ISO 4288) were determined by laser profilometry (UBM, USA). The average thickness of the film was 0.2 µm, as indicated by the BMT evaluation software of the profilometer data, according to a Gaussian fitting procedure.

The quartz crystals used were covered with key shaped Au electrodes. Just the central part of the electrodes was used in deposition, as it is well known that here the mass sensitivity is the highest [22]. Therefore, in the profilometer measurements, one could perform a scanning along a line from the rim of the electrode where the polymer film was deposited, over the whole deposit, until the end of the Au electrode (the arm of the key shaped electrode), which was not covered with any polymer film (Fig. 2).

3. Results

3.1. State of the art and developing of the mathematical approach

A detailed treatment of hydrodynamic flow induced by shear-mode oscillations in quartz crystals has been calculated and described in [10]. By using Rayleigh diffraction method Urbakh and