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Short Communication

The measurement of specific capacitances of conducting polymers using the quartz crystal microbalance

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Abstract

Mass specific capacitance (F g^{-1}) of conducting polymers is an important factor in selecting these materials for use in supercapacitors. Presented in this work is a new method for measuring the mass specific capacitance of conducting polymers using the electrochemical quartz crystal microbalance (EQCM). It can be done by one of two ways: (1) using one thin deposit, calculating the capacitance and dividing by the deposition mass, or (2) conversion of the capacitance per deposition charge (for thick deposits) to capacitance per mass using Faraday's Law and the EQCM data (for thin deposits). Using the new method, specific capacitances of polyaniline, polypyrrole and poly[3,4-ethylenedioxythiopene] comparable to those quoted in the literature are found. Such obtained mass specific capacitance should effectively be the theoretical maximum capacitance that can be extracted from a thick film. The standard plots of mass vs. potential were converted to "massograms" by differentiating the mass with respect to time. As the mass variation rate, dM/dt, is proportional to the current, I, the plot is directly comparable to the voltammogram. The onset of polymerisation and nucleation loops are made more apparent using the massogram plot. Using this data, the ideal deposition potentials for the conducting polymers can be determined.

Keywords: Supercapacitor; Mass specific capacitance; Conducting polymers; Electrochemical quartz crystal microbalance; Massogram

1. Introduction

The electrochemical quartz crystal microbalance (EQCM) is a powerful technique for studying solid state reactions [1,2]. This technique involves using quartz crystals with metal discs (typically gold) coated on both sides with one side used as a working electrode. This device utilises the piezoelectric properties of quartz crystals to measure the attached mass (down to nanogram levels) on the electrode surface. A change in the resonant frequency can be related to a change in the mass according to the Sauerbrey equation [3].

The EQCM has been used extensively to study conducting polymers such as polypyrrole [4–12], poly(3,4-ethylenedioxythiopene) [12–17] and polyaniline [18–27]. This technique can be used for three main purposes in studying conducting polymers. Firstly, it can be used to monitor the deposition of the conducting polymer from the monomer solution. Secondly, the EQCM can be used to study the intercalation of ions into the deposited conducting polymer layer. Finally, something that few publications calculate, the EQCM can be used to calculate the mass specific capacitance (C_{spec}, F g^{-1}) of the polymer layer. This can firstly be done by capacitance measurements (C_{thin}) on a single thin deposit (of measured mass, Δm_{thin}):

$$C_{\text{spec}} = \left(\frac{C_{\text{thin}}}{\Delta m_{\text{thin}}}\right) \tag{1}$$

Alternatively, it can be extended to thicker layers by converting the capacitance per deposition charge (F C^{-1})

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for thick deposits to C_{spec} using Faraday's Law. i.e. $Q = nNF = n(M/M_{eq})F$, where F is Faraday's constant, Q the deposition charge, n the number of electrons, N the number of moles reacted, M the mass of the deposited polymer and M_{eq} the equivalent polymer mass per electron transferred during polymerisation:

$$C_{spec} = \frac{C}{M} = \left(\frac{C}{Q}\right)\frac{F}{M_{eq}} \qquad (2)$$

where C/Q is the slope of a plot of capacitance vs. deposition charge for thick deposits. The value of M_{eq} can be calculated from the EQCM data from deposition of a thin layer, again using Faraday's Law:

$$M_{eq} = \frac{F \cdot \Delta m_{thin}}{Q_{thin}} \qquad (3)$$

where Δm_{thin} and Q_{thin} are respectively the deposition mass and charge of the thin layer.

This calculation of capacitance per gram of material is very important when evaluating conducting polymers as possible supercapacitor materials. An accurate calculation of this value allows the usefulness of a variety of conducting polymers as supercapacitor materials to be determined.

None of the reports cited in this paper uses massograms [28] to investigate the conducting polymer systems. Massograms are the plots of differentiated mass vs. potential, which are directly comparable to voltammograms as $\frac{d(\Delta M)}{dt} \propto I$. In this paper, massograms will be used to investigate the deposition of the polymers. Nucleation loops [29] are made more apparent in the massogram plot and confirm that the growth of the polymers is via a nucleation and growth mechanism. This observation has been previously reported for polypyrrole [4]. Also, massograms more clearly show the optimal potential for deposition of the polymers so that over-oxidation is avoided.

2. Experimental

Pyrrole (Py) (98%, Aldrich), aniline (Ani) (98%, Aldrich), 3,4-ethylenedioxythiophene (EDOT) (Bayer), tetrabutylammonium bromide (>99%, Fluka), lithium chloride (99%, May & Bayer) and potassium chloride (>99%, Sigma) were all used as purchased. Distilled water was used for preparation of electrolytic solutions. Polypyrrole (PPy) was deposited from either an aqueous solution of 0.1 M Py and 0.5 M lithium chloride or from an aqueous solution of 0.5 M Py and 0.5 M potassium chloride. Polyaniline (PAni) was deposited from an aqueous solution of 0.25 M Ani and 1.0 M HCl. Poly-(3,4-ethylenedioxythiophene) (PEDOT) was deposited from an acetonitrile solution of 0.2 M EDOT and 0.5 M lithium perchlorate.

Voltammograms and massograms were recorded using the CH Instruments 440 Potentiostat or the EG&G PAR Model 173 Potentiostat coupled with the EG&G PAR Model 175 Universal Programmer (Princeton Applied Research Corp., New Jersey, USA). Data acquisition was assisted by the Elchema EQCN (Elchema, Potsdam, NY) and the Maclab 8s system. All experiments were carried out at ambient temperatures (20.0 ± 2 °C). The reference half cell was Ag/AgCl in 3.0 M KCl(aq). Working electrodes were 13 mm diameter AT-cut α-quartz crystals (CH Instruments). These crystals had gold disks (5 mm diameter) vapour deposited on each side and resonated in air at 8 ± 0.05 MHz. The crystals used for Fig. 2 resonated at 10 ± 0.05 MHz (Bright Star Crystals, Rowville, Victoria, Australia). The auxiliary electrode was a platinum wire. AC impedance of the thicker deposits was recorded using the Autolab PGSTAT30 potentiostat using a 1.6 mm diameter platinum disc as the working electrode for PPy and PEDOT and using a 6.5 mm diameter graphite disc as the working electrode for PAni.

3. Results and discussion

3.1. Mass data for polymer depositions

The EQCM results are presented in Fig. 1 for the deposition of PEDOT from an acetonitrile solution of 0.2 M EDOT and 0.5 M lithium perchlorate. There are significant currents flowing between 0.5 V and 0.8 V (vs. Ag/AgCl). However, no significant mass change occurs in the same potential range, which means these currents are background currents resulting in no deposition of PEDOT onto the electrode surface. Previous work [30] suggests this is the reaction of gold adsorbed EDOT species. The mass plot shows that significant deposition begins to occur at 1.0 V (vs. Ag/AgCl). There is a slight current loop, which is indicative of nucleation and growth [29] of the polymer. The massogram plot of dM/dt vs. potential reveals a more apparent mass loop, that further confirms that polymer growth is via a nucleation and growth mechanism. In addition, it can be seen from the massogram that significant deposition begins to occur at 1.0 V. Hence, the authors recommend a constant deposition potential of 1.0 V to avoid over-oxidation and to deposit a polymer layer of sufficient thickness. Table 1 indicates this as a suitable potential for constant potential deposition of thicker deposits.

Using constant potential deposition data (Q_{thin} and Δm_{thin}), it was found $M_{eq} = 87 \pm 16\ g\ mol^{-1}\ e^{-1}$. A list of values is given in Table 2. According to theory, $M_{eq} = (M_{polymer} + M_{counter-ion})/(2 + \gamma)$, where γ is the molar ratio of dopant ions and monomeric units (i.e. dopant level) in the oxidised polymer and $(2 + \gamma)$ is the number of electrons withdrawn from one monomeric unit during anodic deposition of the polymer [30]. The typical values of γ are given in Table 2 [31]. Given $\gamma \approx 0.3$ for PEDOT, $M_{eq} = 74\ g\ mol^{-1}\ e^{-1}$. Consequently, the QCM data matches closely with theory, taking into account possible solvation of the cation and experimental errors. As long as the deposition is reasonably thin, the equivalent mass per electron calculated should be very accurate. The equivalent mass per electron was also calculated for a thick layer ($30\ C\ cm^{-2}$) which was removed from a platinum electrode and weighed using a mechanical balance. The value