Application of PEDOT layers for the electrogravimetric detection of sulphate and phosphate in aqueous media

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Abstract

Poly(3,4-ethylenedioxythiophene), PEDOT, films were electrochemically prepared from aqueous solutions containing different supporting electrolytes (ClO_4^-, SO_4^{2-} and $H_2PO_4^-$). Characterization of the resulting films was carried out using cyclic voltammetry and potential step experiments combined with the dissipative quartz crystal microbalance technique. The ion incorporation caused an increase of the film mass and below 10^{-2} M depended on the concentration of the solutions. Potential step experiments showed that the pH of the solutions also has an influence on the mass change of the films, which can only be partially attributed to the pH dependence of the charge of the anions. In principle, the ratio of the mass and the passed electric charge (apparent molar mass) during the redox switching of the polymer can be used to identify the ionic species.
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1. Introduction

Conducting polymers are used in various applications like electronic devices, light-emitting diodes, electrochromic displays, energy conversion and storage and sensors. A great deal of attention has been dedicated to poly(3,4-ethylenedioxythiophene) (PEDOT) because of its high electronic conductivity and chemical resistance in the oxidized state. Further advantages are the low oxidation potential of the monomer and the relatively well ordered structure of the polymer layers resulting from polymerization. This is because in the monomer 3,4-ethylenedioxythiophene (EDOT) the 3 and 4 positions of the thiophene ring are blocked, and cross-linking reactions are effectively prevented. As the monomer is sparely soluble in water, organic solvents (e.g. acetonitrile) [1–3] or aqueous surfactant emulsions [4–6] are mainly used as media for the electropolymerization reaction.

Upon oxidation of the polymer electroneutrality inside the film is maintained by the inclusion of anions and/or the ejection of cations. In general all species of the bathing solution can move in or out of the film, including the solvent [7]. Cycling or switching the polymer between the neutral and oxidized state will thus change its composition and mass.

A sophisticated way of monitoring the mass changes of the film is the electrochemical quartz crystal microbalance (EQCM). Using the Sauerbrey equation (Eq. (1)) the shift of the resonance frequency of a piezoelectric quartz crystal, Δf, can be converted to the mass load per unit area, $\Delta m/A$ [8].

$$\Delta f = -\frac{2f_0^2}{\sqrt{\mu_Q \rho_Q}} \frac{\Delta m}{A} \tag{1}$$

where f_0, μ_Q and ρ_Q denote the resonance frequency, the shear modulus and the density of the quartz crystal, respectively.

The relation of the electric charge, Q, and mass change can be used to calculate the apparent molar mass, M_{app}, of the electroactive species (Eq. (2)):

$$M_{app} = \frac{\Delta m}{Q} zF \tag{2}$$

where z is the charge of the ion and F is the Faraday constant.

This apparent molar mass is the sum of all species which move in or out of the polymer during oxidation or reduction. In other words M_{app} is the weighted sum of the molar masses of all involved species, Eq. (3). Upon oxidation, anions (subscript

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A) will enter the film. In parallel solvent molecules (here water, H_2O) and cations (subscript C) may be transferred. The factors x and y (notice that x and y must not be integers and can be positive or negative) denote how many of the respective species are transferred per anion.

$$M_{app} = M_A + xM_{H_2O} + yM_C \qquad (3)$$

At sufficiently high electrolyte concentrations, i.e. when the concentration is comparable to the volume density of the active (charged) sites in the polymer (up to several mol/l), cations can enter the polymer [9]. In lower concentrated electrolytes PEDOT is permselective and cation incorporation can be neglected, i.e. $y = 0$ in Eq. (3) [10].

In this paper we explore the possibility of using Eq. (3) for the recognition of anions in aqueous solutions via their apparent molar mass, M_{app}.

2. Experimental

A sketch of the experimental setup is shown in Fig. 1. A lab made PTFE cell was used to accommodate a three electrode configuration. A quartz crystal ($f_0 = 10$ MHz, Vectron International, Germany) with gold electrodes was placed horizontally at the bottom of the cell, and the electrode facing the solution was used as working electrode ($A = 0.22$ cm^2). A Luggin capillary filled with the bulk electrolyte was positioned 3 mm above the quartz crystal surface to hold an Ag/AgCl (sat. KCl) reference electrode (KSI Meinsberg, Germany). In the following all potential values refer to this reference electrode. It is crucial to prevent chloride ions from leaking into the cell, as this will lead to strong gold dissolution during the anodic electropolymerization. A platinum ring was used as counter electrode.

All chemicals were p.a. grade and used as received except the monomer EDOT (Baytron M, H.C. Starck, Germany) which was distilled under vacuum prior to use. Highly purified water (18 MΩ cm) from a Seralpur PRO 90 CN purification system was used for the preparation of all solutions. For the preparation of the polymer films an aqueous solution of 0.01 M EDOT and 0.1 M supporting electrolyte was used. The latter was either LiClO$_4$ (Fluka), Na$_2$SO$_4$ (J.T. Baker) or NaH$_2$PO$_4$ (Merck). In

the following the anion used for the preparation of a film is given in parentheses, e.g. PEDOT(ClO$_4$) denotes a PEDOT film polymerized in a perchlorate solution. Electropolymerization was carried out by stepping the potential to 1 V after polarization at 0 V for 60 s using a EG&G Versastat II potentiostat/galvanostat. The resonance curve of the quartz crystal was monitored using a Saunders 250B Network Analyzer PCI computer card (Saunders&Associates Inc., USA). The real part of the admittance of the quartz crystal near the resonance frequency was recorded every second. The resonance frequency, f, and the damping, w, of the quartz crystal were extracted from these data by fitting the resonance curve with a Lorentzian [11]. Thus, f is obtained as the frequency value where the real part of the admittance is maximal, and w is the full width at half maximum of the resonance curve. Notice, that in this approach the damping has the same unit (Hz) as the resonance frequency. Polymerization was stopped when the resonance frequency of the quartz crystal had decreased by 10 kHz which corresponds to a layer thickness of ca. 350 nm (assuming a polymer density of 1.3 g/cm^3). The electrolyte was removed, and the cell was rinsed with copious amounts of water. Finally, the film was reduced (-0.4 V, 240 s) in pure water which was purged with nitrogen.

Characterization of the films was carried out by cyclic voltammetry (-0.4 to 0.8 V, 10 mV s^{-1}, 10 cycles) and consecutive potential step experiments ($-0.4/0.6/-0.4$ V, 60/180/180 s, 3 cycles) in different electrolytes purged with nitrogen. Phosphoric acid and NaH$_2$PO$_4$ as well as NaH$_2$PO$_4$ and Na$_2$HPO$_4$ (Merck) were used to prepare solutions of pH 2.7 and 7.0 and Na$_2$HPO$_4$ and Na$_2$HPO$_4$ were used for the pH 4.7 and 9.1 solutions, respectively. Sulphate solutions were prepared from NaHSO$_4$ and Na$_2$SO$_4$ (Merck). The pH of the solutions was checked using a calibrated glass electrode (KSI Meinsberg, Germany) with a pH-meter (Knick, Germany).

Scanning electron microscope (SEM) images were taken with a Zeiss SEM DSM 982 (Oberkochen, Germany).

3. Results and discussion

3.1. Electrolytes of different concentrations

Fig. 2 compares the currents and mass responses of a PEDOT(ClO$_4$) and a PEDOT(H$_2$PO$_4$) film in solutions containing between 10^{-4} and 10^{-1} M H$_2$PO$_4{}^-$. The CVs have a capacitor-like shape displaying no distinct redox peaks which is in agreement with literature [4,12]. The QCM indicates an increase of the polymer mass at potentials above 0 V which is associated with anion incorporation. Below 10^{-2} M the current and the mass change of the polymer films strongly depend on the electrolyte concentration. The maximum ion incorporation for low concentration electrolytes (a and b) is reached in the return sweep while it coincides with the upper potential for electrolytes of concentrations higher than 10^{-2} M (c and d). These results indicate that the kinetics of the ion incorporation depends on the conductivity of the electrolyte. Takashima et al. [13] observed similar effects in electrochemomechanical deformation experiments of poly pyrrole films in sodium chloride solutions. They observed shifts in the redox potentials towards lower potentials
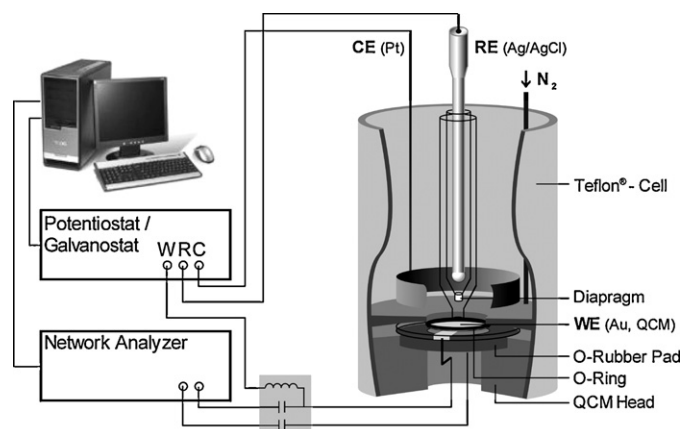

Fig. 1. Schematic sketch of the experimental setup.