



# Electrochemical characterisation of poly(3,4-ethylenedioxythiophene) film modified glassy carbon electrodes prepared in deep eutectic solvents for simultaneous sensing of biomarkers



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## ABSTRACT

Electrodeposition of the conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) in deep eutectic solvents (DES), prepared by the simple mixing and heating of an H-bond acceptor, choline chloride and H-bond donors such as urea, ethylene glycol and glycerol, is described. The PEDOT modified glassy carbon electrodes prepared in different DES and in the presence of conventional aqueous surfactants or HClO<sub>4</sub> media were characterized during and after growth by electrochemical and quartz crystal microbalance studies. PEDOT synthesized in the best performing DES medium, choline chloride – urea (Reline) in the presence of HClO<sub>4</sub>, was used for the sensing of the biologically relevant molecules ascorbic acid, dopamine and uric acid. The sensing characteristics were compared with those of PEDOT-modified electrodes prepared in aqueous media.

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## 1. Introduction

Innovative research on conducting polymers since their discovery by MacDiarmid, Heeger and Shirakawa [1,2] in 1977 has been directed towards development of materials with specific physico-chemical and mechanical characteristics such as high conductivity, higher capacity to accumulate charge, higher elasticity and stability [3,4]. Electrodeposition of  $\pi$ -conjugated polymers to give conducting polymer modified electrodes has led to application in diverse areas such as in supercapacitors, mechanical actuators, sensors, light emitting diodes, solar cells, electrochromic displays and switching materials [4–6]. Among these, poly(3,4-ethylenedioxythiophene) (PEDOT) exhibits good electrochemical stability, a wide potential window, low band gap and distinct spectral absorption for oxidized and reduced states [7]. Interesting properties exhibited by these materials is mainly due to their doping/dedoping as a function of applied potential [8].

The electrochemical synthesis of conducting polymers in the presence of different additives such as surfactants, acids and ionic liquids influences the properties of the electrodeposited material in terms of conductivity, redox behaviour and doping levels [9–12]. Room temperature ionic liquids (RTIL) are alternative solvents

utilized for the electrosynthesis of conducting polymers due to their high conductivity, low volatility and wide potential windows compared to conventional aqueous and organic solvents [12]. Although conventional RTIL possess such advantageous properties, they are costlier, involve tedious synthetic protocols and are non-biodegradable [13].

In the present study, we have carried out the electropolymerisation of 3,4-ethylenedioxythiophene (EDOT) in deep eutectic solvents (DES), which are formed by the interaction between suitable hydrogen bond donors and acceptors [13,14]. These solvents can be easily prepared by mixing a quaternary ammonium salt, which acts as H-bond acceptor, with an H-bond donor (HBD), in specific mole ratios to form a eutectic mixture, with melting point much lower than the two components and which are liquid at room temperature. Commonly used H-bond acceptors are choline chloride, proline, alanine, betaine etc., while a large variety of hydrogen bond donors comes from the family of alcohols, carboxylic acids or amides such as ethylene glycol, glycerol, succinic acid or urea [13–15]. Advantages of deep eutectic solvents include ease of preparation, low cost, easily available components and biodegradability, in addition to the properties exhibited by conventional ionic liquids. Hence, these solvents possess great potential as electrolytic media for the electrodeposition of metals and polymers [16]. The electrochemical synthesis and characterization of conducting polymers such as polyaniline and polypyrrole

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in deep eutectic solvents has been reported elsewhere [11,17]. Hillman et al. conducted studies on the ion transfer mechanism of p-doped PEDOT films prepared in acetonitrile [18]. Recently, we reported the preparation of PEDOT films for highly sensitive electrochemical sensors by electropolymerisation in DES, for the first time [19]. Electrochemical and surface microscopy characterisation of the PEDOT films formed in ethaline, reline and glyceline were carried out.

We now report detailed studies on the electrodeposition of PEDOT in various DES and characterization of the films using quartz crystal microbalance (QCM) gravimetry as well as electrochemical techniques. A gravimetric study using an electrochemical QCM is a powerful tool to detect and quantify the mass change, ion dynamics and polymer film characteristics. Detailed study of the polymerisation parameters, its sequential optimization and comparative evaluation of the sensing characteristics of PEDOT modified electrodes prepared in different DES is carried out using ascorbic acid (AA) as model analyte. Furthermore, the developed modified electrodes were used for the simultaneous detection and quantification of the biomarkers ascorbic acid (AA), dopamine (DA) and uric acid (UA) [20,21]. Techniques often used to detect and quantify these biomolecules are chemiluminescence [22], UV-vis spectroscopy [23] and spectrofluorimetry [24]. However, these techniques are complicated, expensive, time consuming and usually require prior separation of components by chromatography [25] or electrophoresis [26]. For this reason, voltammetric electrochemical methods have been employed exploiting modified electrodes, which are able to separate the potentials for oxidation of these analytes sufficiently well. The voltammetric oxidation peaks of these compounds are in the range 0.2 to 0.7 V at bare glassy carbon electrodes (GCE) within one broad peak [27]. Modifiers which give selective electrocatalysis such as polypyrrole/poly(4-vinyl pyridine) films [28,29], carbon based nanomaterials [30,31], enzymes [23], or semiconductor quantum dots [22] have been employed to obtain well-separated oxidation peaks and high peak currents. Here, we have successfully used PEDOT modified GCE prepared in deep eutectic solvents for the simultaneous detection and quantification of AA, DA and UA.

## 2. Experimental

### 2.1. Reagents and buffer electrolyte solutions

Ethylene glycol, urea, glycerol, choline chloride, 3,4-ethylenedioxythiophene (EDOT), ascorbic acid, dopamine, uric acid, monobasic and dibasic potassium phosphate, sodium chloride and sodium poly(styrene sulfonate) (NaPSS) were from Sigma-Aldrich, Germany. Perchloric acid (70%), potassium chloride and monobasic sodium phosphate were obtained from Fluka, Switzerland. For electrochemical sensing studies, the supporting electrolyte was sodium phosphate buffer saline (NaPBS) (0.1 M phosphate buffer + 0.05 M NaCl, pH = 7.0). Millipore Milli-Q nanopure water (resistivity  $\geq 18 \text{ M}\Omega \text{ cm}$ ) was used for the preparation of all solutions. All experiments were performed at room temperature ( $25 \pm 1^\circ \text{C}$ ).

### 2.2. Instrumentation

Electrochemical experiments were performed in a three-electrode cell, containing a glassy carbon disc electrode (GCE), area  $0.0314 \text{ cm}^2$ , as working electrode, a Pt wire counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode, together with a  $\mu$ -Autolab potentiostat/galvanostat (Metrohm-Autolab, Netherlands). For electropolymerisation in eutectic mixtures, an Ag wire was used as the pseudo-reference electrode (Ag/AgCl vs Ag wire  $\sim +90 \text{ mV}$ ). The electrochemical quartz crystal microbalance

(EQCM) used was an eQCM 10 M from Gamry, with 10 MHz carbon-coated crystals. The pH measurements were carried out with a CRISON 2001 micro pH-meter (Crison Instruments SA, Barcelona, Spain) at room temperature.

### 2.3. Preparation of PEDOT films in deep eutectic solvents

Deep eutectic solvents were prepared by mixing the quaternary ammonium salt, choline chloride, with the HBDs ethylene glycol (to give ethaline), urea (to give reline) or glycerol (to give glyceline) in a 1:2 molar ratio, heating at  $60^\circ \text{C}$  until a homogeneous solution was obtained and then allowing the DES to cool down to room temperature. Thin PEDOT film modified GCEs were prepared potentiodynamically by cycling in a solution of 10 mM EDOT in DES in the presence of 4 M  $\text{HClO}_4$  in the potential range  $-0.6$ – $+1.2 \text{ V}$  at  $50 \text{ mV s}^{-1}$ . A uniform, reproducible film was obtained after 15 potential cycles. In order to compare the efficacy of electropolymerisation in eutectic medium, PEDOT films were also prepared in aqueous media, 0.1 M PSS and 4 M  $\text{HClO}_4$ , in the presence of 10 mM EDOT.

### 2.4. Amperometric sensing

Fixed potential amperometric sensing of ascorbate was conducted in pH 7.0 phosphate buffer saline, PBS (0.1 M phosphate buffer + 0.05 M NaCl) at 0.0 V vs Ag/AgCl. Sensing and quantification of ascorbic acid, dopamine and uric acid was carried out by differential pulse voltammetry in the region  $-0.2$  to  $+0.5 \text{ V}$  with a potential increment of 1 mV, pulse amplitude 25 mV and a scan rate of  $5 \text{ mV s}^{-1}$  in PBS buffer medium.

## 3. Results and discussion

Fig. 1 shows typical cyclic voltammograms of the electrochemical synthesis of PEDOT in the eutectic mixtures ethaline, reline and glyceline in the presence of 10 mM EDOT and 4 M  $\text{HClO}_4$ . In order to compare the voltammetric features of PEDOT prepared in DES and other media, the electrochemical synthesis of PEDOT was also carried out in aqueous surfactant medium, 0.1 M PSS, and in aqueous 4 M  $\text{HClO}_4$ .

Characterisation of these PEDOT-modified GCE by cyclic voltammetry, electrochemical impedance and scanning electron microscopy was reported previously [19]. The voltammograms obtained during the potentiodynamic synthesis of PEDOT in various media were analysed, and characteristic peaks were identified. Briefly, the anodic peaks correspond to oxidation of adsorbed monomeric species on the electrode surface and, at 0.70 V, to diffusion-controlled oxidation of radical monomers, dimers or oligomers formed during polymerisation. On the negative scan, the peaks correspond to diffusion-controlled reduction of dimeric/oligomeric species and to reduction of adsorbed polymer. For ethaline and glyceline only, a small shoulder around 0.80 V probably corresponds to oligomer oxidation (only seen after 4 or 5 cycles). More details may be found in [19].

These studies are now complemented by carrying out quartz crystal microbalance gravimetric studies during electropolymerisation for better understanding of the film characteristics and for discussing the doping/dedoping mechanism. Optimisation of sensing film preparation, using ascorbic acid as model analyte, is reported in Section 3.3 and application to simultaneous sensing of ascorbic acid, dopamine and uric acid in Section 3.4.

### 3.1. Electrochemical QCM studies

An electrochemical quartz crystal microbalance (EQCM) with a carbon-coated quartz crystal, was used to monitor the variation in

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