



# Highly sensitive poly(3,4-ethylenedioxythiophene) modified electrodes by electropolymerisation in deep eutectic solvents



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## ABSTRACT

Deep eutectic solvents are evaluated as media for the electropolymerisation of 3,4-ethylenedioxythiophene (EDOT) for the first time. PEDOT modified glassy carbon electrodes (GCEs) were characterised by cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy. PEDOT modified GCEs prepared from choline chloride–urea (reline) and choline chloride–ethylene glycol (ethaline) exhibited interesting electrocatalytic and morphological characteristics. Fixed potential sensing of ascorbate at 0.0 V showed a greater electrocatalytic effect, significantly higher sensitivity and lower detection limit than at hitherto reported PEDOT modified electrodes.

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## 1. Introduction

Conjugated polymers have attracted widespread attention for application in a variety of electrochemical devices such as fuel cells, batteries, sensors, electrochromic displays, actuators, photovoltaic cells, memory devices, and light emitting diodes [1–3]. Since the first synthesis of poly(3,4-ethylenedioxythiophene) (PEDOT) in 1980 by Bayer [4], this polymer has been widely studied due to its high conductivity, interesting electrical and spectrochemical properties associated with its low band gap, as well as electrochromic and antistatic properties [5–7]. Electrosynthesis of PEDOT is often performed in organic media to overcome drawbacks of aqueous methods [8].

Deep eutectic solvents (DES) are a new generation of ionic liquids (IL), a viable alternative to the conventional metal/imidazolium salt based ionic liquids, of interest because of the growing concern with IL toxicity and poor biodegradability [9,10]. DES are mixtures composed of two or three cheap and safe components that can self-associate through H-bond interactions, to form an eutectic mixture of melting point lower than the individual components. They are generally prepared by the simple mixing of quaternary ammonium salt with a hydrogen bond donor (HBD) in certain molar ratios. A commonly used quaternary ammonium salt is choline chloride whereas hydrogen bond donors are exemplified by ethylene glycol, urea or glycerol. Electropolymerisation, as well as ion transfer dynamics, in DES is interesting, since the presence of large ionic species and HBDs in the medium can influence the polymer properties [11,12].

Electropolymerisation of EDOT was carried out for the first time in the eutectic mixtures ethaline, glyceline and reline, and the PEDOT modified electrodes were characterised by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Further, the applicability of PEDOT prepared in DES as sensing substrate is demonstrated using the model compound ascorbic acid (AA), and the sensing characteristics compared with conventional PEDOT(PSS) polymers.

## 2. Experimental

Ethylene glycol, urea, glycerol, choline chloride, 3,4-ethylenedioxythiophene (EDOT), ascorbic acid, monobasic and dibasic potassium phosphate, sodium chloride and sodium poly(styrene sulfonate) (NaPSS) were from Sigma-Aldrich, Germany. Perchloric acid, potassium chloride and monobasic sodium phosphate were obtained from Fluka, Switzerland. Millipore Milli-Q nanopure water (resistivity  $\geq 18 \text{ M}\Omega \text{ cm}$ ) was used for the preparation of all solutions.

Electrochemical experiments were performed in a three electrode cell, containing a glassy carbon electrode (GCE) ( $0.237 \text{ cm}^2$ ) as working electrode, a Pt wire counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode, with a  $\mu$ -Autolab potentiostat/galvanostat (Metrohm-Autolab, Netherlands). For electropolymerisation in eutectic mixtures, an Ag wire was used as pseudo-reference electrode (Ag/AgCl vs Ag wire  $\sim +90 \text{ mV}$ ). EIS experiments were carried out with a Solartron 1250 Frequency Response Analyser, coupled to a Solartron 1286 Electrochemical Interface (Ametek, UK) controlled by ZPlot software. An rms perturbation of 10 mV was applied over the frequency range of 100 kHz–0.1 Hz, with 10 frequencies per decade and an integration time of 60 s. Microscope images were acquired using a scanning

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electron microscope (SEM) Jeol JSM-5310 (Jeol, Tokyo, Japan). The pH measurements were carried out with a CRISON 2001 micropH-meter (Crison Instruments SA, Barcelona, Spain). All experiments were performed at room temperature ( $25 \pm 1$  °C).

Deep eutectic solvents were prepared by mixing a quaternary ammonium salt, choline chloride, with various HBDs such as ethylene glycol (ethaline), urea (reline) or glycerol (glyceline) in a 1:2 molar ratio and heating up to 60 °C until a homogeneous solution was obtained, the mixtures then being allowed to cool down to room temperature. PEDOT was prepared on the GCE potentiodynamically by cycling in 10 mM EDOT in eutectic solvent in the presence of 4 M HClO<sub>4</sub> in the potential range of  $-0.6$  to  $1.2$  V at  $50$  mV s<sup>-1</sup> for 15 cycles in order to form a uniform, reproducible film. To evaluate the efficacy of electropolymerisation in eutectic media, PEDOT was also prepared in aqueous 0.1 M PSS as well as in aqueous 4 M HClO<sub>4</sub>, both in the presence of 10 mM EDOT. Fixed potential amperometric sensing of ascorbate was done in pH 7, 0.1 M phosphate buffer + 0.05 M NaCl (PBS) at 0.0 V vs Ag/AgCl.

### 3. Results and discussion

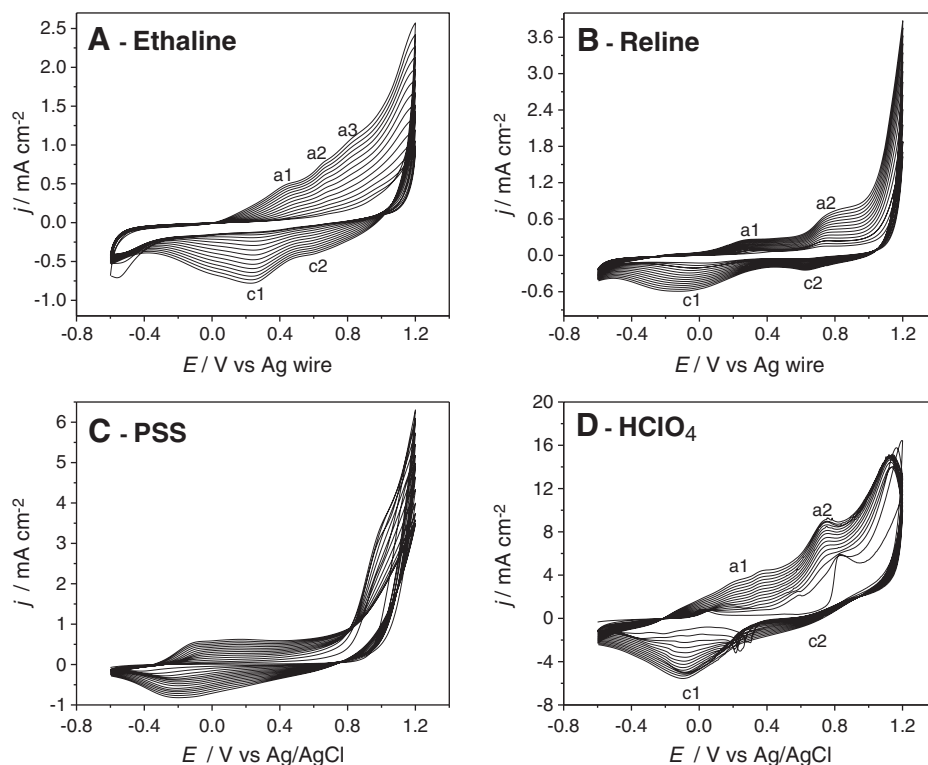
In pure eutectic mixtures, EDOT electropolymerisation was not effective, since after a few cycles the current remained constant between successive cycles or began to decrease, indicating that formation of radicals and propagation was not occurring (not shown). Often, anionic surfactants are added to the aqueous or organic phase for polymerisation, since micellar media enhance the process [8,9]. Hence, different electropolymerisation conditions were tested and it was found that the presence of perchloric acid increases the current during electropolymerisation. Previously, electropolymerisation of thiophene from HClO<sub>4</sub> medium had been reported [13]. The concentration of HClO<sub>4</sub> was varied from 1 to 5 M and the optimum concentration was found to be 4 M for effective polymerisation.

Cyclic voltammograms of electropolymerisation of 10 mM EDOT in ethaline and reline containing 4 M HClO<sub>4</sub> are shown in Fig. 1A and

B respectively. Compared to ethaline, polymerisation in reline shows well defined anodic and cathodic peaks: instead of three badly defined anodic peaks in ethaline, two well-defined anodic peaks a1 and a2 at 0.40 V and 0.72 V were observed. The anodic peak a1 corresponds to oxidation of adsorbed monomeric species on the electrode surface [8], evidence for which is the linear  $I$  vs  $v$  plots (not shown). The 2nd anodic peak at 0.70 V corresponds to diffusion-controlled oxidation of radical monomers as well as of dimers or oligomers formed during polymerisation as deduced from linear  $I$  vs  $v^{0.5}$  plots (not shown). On the cathodic scan, peak c2 corresponds to diffusion-controlled reduction of dimeric/oligomeric species and peak c1 to reduction of adsorbed polymer. For ethaline and glyceline, unlike reline, another small shoulder around 0.80 V probably corresponds to oligomer oxidation as the peak only appears after 4 or 5 cycles. No separate peak was observed in reline as the medium is less viscous than ethaline or glyceline, facilitating easier diffusion of monomers to the electrode surface. The negative shift of the peak potentials after each cycle indicates an autocatalytic effect of the formed polymeric surface. Electropolymerisation in glyceline in the presence of 4 M HClO<sub>4</sub> (not shown) has similar voltammetric characteristics as those in ethaline.

The polymerisation solution, i.e. 10 mM EDOT in eutectic (reline/ethaline/glyceline) in the presence of 4 M HClO<sub>4</sub> leads to some subtle differences in physical properties. In the case of reline, upon addition of EDOT, the solution turned bluish green and remained in the liquid state even after 24 h, whereas ethaline/glyceline in the presence of EDOT changed from yellow to black (see Graphical abstract section) and became gellated. This may be attributed to the formation of EDOT oligomers and their interaction with the DES [13], in reline, due to interactions between amino groups with EDOT monomer/oligomers, unlike hydroxyl moieties in ethaline/glyceline, which is under investigation.

In order to compare with aqueous electropolymerisation in the presence of surfactants as well as in the presence of 4 M HClO<sub>4</sub>, polymerisation of 10 mM EDOT was done in 0.1 M PSS (Fig. 1C) and in 4 M HClO<sub>4</sub> (Fig. 1D). The total charge transferred under the anodic peaks after electropolymerisation in ethaline, reline, PSS and HClO<sub>4</sub> was found to



**Fig. 1.** Potentiodynamic electrodeposition of PEDOT from a solution of 10 mM EDOT in (A) ethaline + 4 M HClO<sub>4</sub>, (B) reline + 4 M HClO<sub>4</sub>, (C) 0.1 M PSS, and (D) 4 M HClO<sub>4</sub> (Ag/AgCl vs Ag wire ~ +90 mV).

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