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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.

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 MΩ 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 cm^2) as working electrode, a Pt wire counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode, with a μ-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 ~ +90 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 ± 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 $HClO_4$ in the potential range of −0.6 to 1.2 V at 50 mV s^{-1} 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 $HClO_4$, 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 $HClO_4$ medium had been reported [13]. The concentration of $HClO_4$ 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 $HClO_4$ 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 ν 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 $\nu^{0.5}$ 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 $HClO_4$ (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 $HClO_4$ 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 $HClO_4$, polymerisation of 10 mM EDOT was done in 0.1 M PSS (Fig. 1C) and in 4 M $HClO_4$ (Fig. 1D). The total charge transferred under the anodic peaks after electropolymerisation in ethaline, reline, PSS and $HClO_4$ was found to

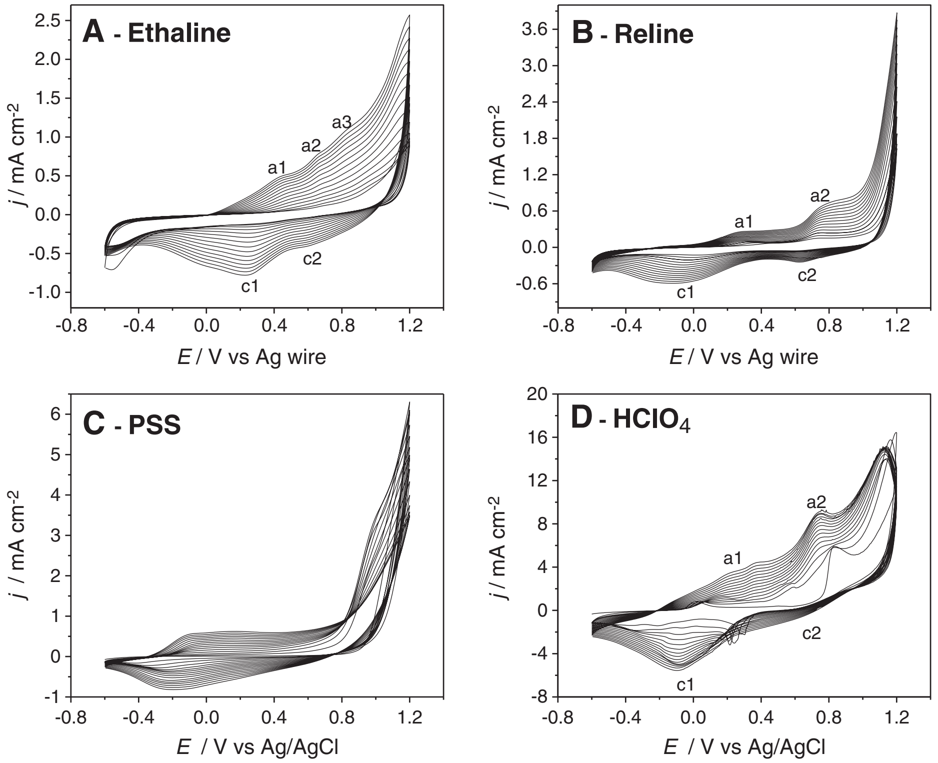

Fig. 1. Potentiodynamic electrodeposition of PEDOT from a solution of 10 mM EDOT in (A) ethaline + 4 M $HClO_4$, (B) reline + 4 M $HClO_4$, (C) 0.1 M PSS, and (D) 4 M $HClO_4$ (Ag/AgCl vs Ag wire ~ +90 mV).

be 22.6, 19.4, 27.9 and 202 mC cm^{-2} respectively. Although the charge values are higher in HClO$_4$, the anodic and cathodic peaks were best defined in reline, probably due to thin film formation in reline allowing easier diffusion of monomers to the electrode surface. This indicates a better mobility of ionic species in reline-based eutectic media than in the other two eutectics during the doping and de-doping processes, a hypothesis supported by SEM micrographs. These show a more compact structure on the surface of the PEDOT(eutectic) micrometric structures e.g. PEDOT(reline) (Fig. 2A) than of PEDOT(PSS) (Fig. 2B) or PEDOT (aqueous 4 M HClO$_4$), which has similar morphology to PEDOT(PSS).

EIS was used to characterise the physical and interfacial properties of the different PEDOT modified electrodes. Fig. 2C shows spectra recorded in 0.1 M KCl. All spectra were dominated by capacitive lines and the polymerisation of EDOT in the presence of surfactant (0.1 M PSS) and the acidic medium (4 M HClO$_4$) shows a decrease of the imaginary part of the impedance, i.e. increase in the capacitance, that could improve the electrochemical response. This was also observed in the cyclic voltammograms where the highest capacitive currents were found for EDOT polymerised in acidic medium alone (Fig. 1C & D). Equivalent circuit modelling was done by a constant phase element (CPE) in series with the cell resistance. The CPE values from fitting the capacitive lines for the films obtained in reline, ethaline, glyceline are 1.7, 1.5, 1.1 mF cm^{-2} s$^{\alpha - 1}$, respectively, with CPE exponent, α values, all close to 0.95. Thus, the PEDOT(reline) modified electrodes showed the highest capacitance values. Films obtained in aqueous HClO$_4$, which were much thicker, had a CPE value of 16 mF cm^{-2} s$^{\alpha - 1}$ with an α value of 0.88, this lower value attributable to the different morphologies.

PEDOT(PSS) spectra showed the qualitative impedance behaviour of a conductive porous structure, in agreement with SEM micrographs, with a high frequency semicircle (*RC* in parallel) and a close to 90° line at lower frequencies [14]. Modelling was done by a CPE in parallel with a resistance, (CPE = 0.37 mF cm^{-2} s$^{\alpha - 1}$; $\alpha = 0.64$, $R_{ct} = 54$ Ω cm^2) in series with a second CPE of 4.4 mF cm^{-2} s$^{\alpha - 1}$, $\alpha = 0.98$.

Fig. 3A and B shows CVs of 1 mM ascorbate in 0.1 M PBS (pH 7.0) at PEDOT modified GCEs prepared in reline, ethaline, glyceline, PSS, and 4 M HClO$_4$. The oxidation of ascorbate occurs at 0.0 V at PEDOT(reline) and PEDOT(ethaline) modified electrodes compared to 0.48 V at bare GCE. Hence, the PEDOT modified GCE in both eutectic mixtures shows an excellent electrocatalytic effect with a ~0.5 V reduction in overpotential. In the case of PEDOT(glyceline) and PEDOT(HClO$_4$) modified electrodes the electrocatalysis is comparatively small. A broad oxidation peak from 0.0 to 0.4 V was observed at PEDOT(glyceline) in the presence of 1 mM ascorbate (Fig. 3A), whereas a relatively small peak, from 0.0 to 0.2 V, was observed at PEDOT(4 M HClO$_4$) modified GCE even in the presence of 2 mM ascorbate (Fig. 3B). Ascorbic acid oxidation at PEDOT modified electrodes was diffusion-controlled as is evident from the linear I vs $\nu^{0.5}$ plots obtained by scan rate variation studies (not shown). The poorer sensing at PEDOT(4 M HClO$_4$)-GCE may be due to the thicker polymer film causing diffusional restrictions for the analyte. In the case of PEDOT(PSS)-GCE, ascorbate oxidation was observed at 0.25 V compared to 0.0 V in PEDOT(reline or ethaline).

Fig. 3C shows calibration curves obtained by fixed potential amperometric sensing of ascorbate at 0.0 V using the various PEDOT modified GCEs of which PEDOT(reline) exhibited the highest sensitivity. This sensor shows an exceptionally good ascorbate response at 0.0 V with a sensitivity of 245 μA cm^{-2} mM^{-1} (RSD = 5.8%, $n = 5$) and an LOD of 0.9 μM which is at least 5 fold lower than previously reported ascorbate sensors, operating at potentials close to or at 0.0 V [15]. Thus, it is evident that formation of PEDOT in eutectic mixture (reline and ethaline) increases the sensing characteristics of the PEDOT film.

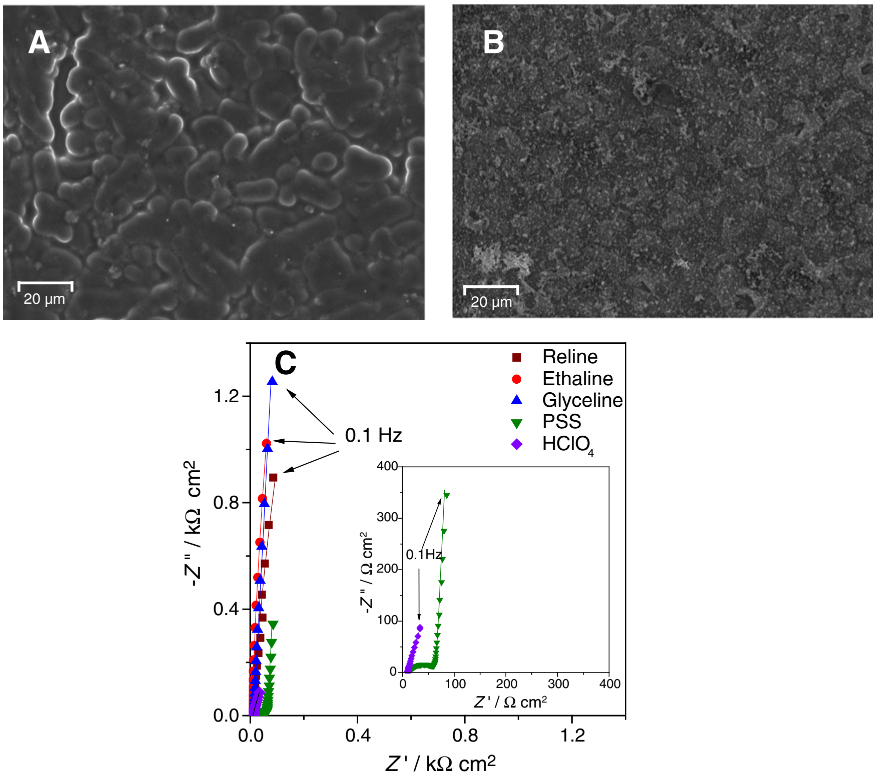

Fig. 2. SEM micrographs of A: PEDOT(reline) and B: PEDOT(PSS) on GCE; C: complex plane impedance spectra of all the PEDOT modified electrodes at open circuit potential (0.1 V vs Ag/AgCl); lines show equivalent circuit fitting.

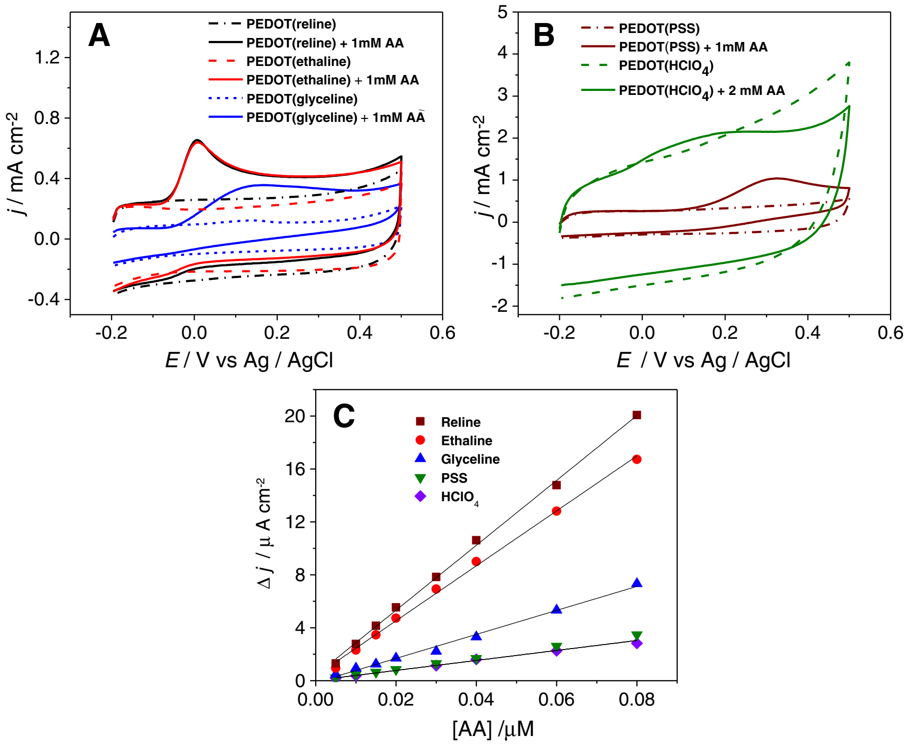

Fig. 3. CVs in presence of 1 mM AA of PEDOT modified GCE prepared from A: reline, ethaline and glyceline; B: 0.1 M PSS, 4 M $HClO_4$; C: calibration curve for ascorbate amperometric sensing in 0.1 M PBS at 0.0 V vs Ag/AgCl.

4. Conclusions

The present study highlights the emergence of DES as alternative “green designer solvents” for electrodeposition of conducting polymers with improved characteristics. EDOT has been electropolymerised in deep eutectic solvents for the first time and electrochemical and surface characterization studies of the polymer films were conducted. The ion exchange properties of the PEDOT film and its electrochemical properties are greatly influenced by the polymerisation conditions. The PEDOT films show excellent electrocatalytic properties and sensing characteristics for the model analyte ascorbic acid. High sensitivity and stability was exhibited by PEDOT(reline) compared to PEDOT(PSS) and PEDOT from other eutectics. The exceptional behaviour in reline needs to be further investigated for a deeper understanding of interactions occurring in the electrolytic media, using gravimetric and spectroscopic techniques.

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