

# Anionic micelles; a new aqueous medium for electropolymerization of poly(3,4-ethylenedioxythiophene) films on Pt electrodes

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For the first time, an aqueous micellar medium (sodium dodecyl sulfate, SDS) is used, at Pt electrodes, to electrosynthesize poly(3,4-ethylenedioxythiophene) (PEDOT) conducting films deposited at lower potential than in acetonitrile and presenting a well organized structure.

Electropolymerization of aromatic and heteroaromatic compounds, leading to anodic deposition of films, has been the subject of a large amount of research in the last fifteen years.<sup>1,2</sup> With the exception of polyaniline and polypyrrole which are sometimes electrosynthesized in aqueous solutions<sup>1,3,4</sup> most polymer films are formed on metallic substrates, using a variety of organic solvent systems. For practical and industrial applications, however, water is the ideal solvent. This is especially true when conducting polymers are considered for organic coatings on metals such as iron and zinc. However, polythiophenes (PT), which have rather positive oxidation potentials are generally obtained in organic solutions.<sup>5</sup> This is due to several obstacles such as the low solubility of monomers in water, the polymerization potential being higher than that of water decomposition, and the relatively strong nucleophilic reactivity of water molecules with the initially formed thienyl radical cations. Acidic solutions of various compositions have also been proposed for the electrosynthesis of PT films,<sup>6-8</sup> but present serious drawbacks for electrodeposition on oxidizable metals, which may be partly dissolved before electropolymerization can take place. A possible way to circumvent these problems is to use surfactant molecules that have the ability of increasing the water solubility of thiophene monomers, producing electrocatalysis and modifying the characteristics of the metal/electrolyte solution interface. Surfactants exist as monomers or micelles, depending on their concentration.<sup>9</sup> Recently, the electrochemistry of surfactant-doped polypyrrole films has been investigated, and an enhanced diffusivity of ions has been reported for polypyrrole prepared in a micellar solution.<sup>10</sup>

Among PT derivatives, poly(3,4-ethylenedioxythiophene) (PEDOT) has recently been described as a remarkably stable, highly conductive material,<sup>11,12</sup> possessing very pronounced electrochromic properties.<sup>13,14</sup> PEDOT has been used to prepare antistatic transparent films,<sup>11,15</sup> polymeric light-emitting diodes,<sup>16</sup> and electroplating for metallization of insulators.<sup>17</sup>

Therefore, in the framework of our studies concerning organic coatings on oxidizable metals in aqueous media,<sup>4,18</sup> we decided to examine the feasibility of the electropolymerization process of 3,4-ethylenedioxythiophene (EDOT) in an aqueous anionic micellar medium, containing sodium dodecyl sulfate (SDS) as surfactant. We investigated the electrochemical activity and the microscopic structure of PEDOT films formed in SDS aqueous solutions above the critical micellar concentration (c.m.c.).

PEDOT films were electrochemically grown on Pt electrodes from 0.05 mol dm<sup>-3</sup> 3,4-ethylenedioxythiophene (EDOT) aqueous solutions, in the presence of 0.07 mol dm<sup>-3</sup> SDS and 0.1 mol dm<sup>-3</sup> lithium perchlorate, using cyclic voltammetry, potentiostatic or potentiostatic methods. Since the c.m.c. value for SDS is 2 × 10<sup>-3</sup> mol dm<sup>-3</sup> in 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>

aqueous solution, all electrochemical measurements were performed above the c.m.c.

Cyclic voltammograms were recorded between -0.5 and 1.2 V vs. SCE in micellar solution (Fig. 1). Under these conditions, the first voltammogram curve presents a rapid growth of the anodic current at 0.76 V vs. SCE, corresponding to the oxidation potential of EDOT; in contrast, in acetonitrile-0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> an  $E_{OX}$  value of 1.04 V was found. This  $E_{OX}$  significant decrease (280 mV) in the micellar medium relative to organic solution can be attributed to the presence of surfactant micelles, which create hydrophobic and hydrophilic regions at the metal/solution interface, inducing an electrocatalytic effect. As can be seen, anodic and cathodic current intensities increase regularly during successive potential scans (Fig. 1); homogeneous, adherent, deep-blue PEDOT films were obtained after a few scans and grew steadily with the number of cycles. A 0.5 μm homogeneous film can also be synthesized by applying a constant current density of 1 mA cm<sup>-2</sup>, over 2 min. The potential rose at about 0.8 V and much more rapidly in the micellar medium than in acetonitrile solution.

To evaluate the degree of reversibility of the PEDOT redox system, we investigated, in a 0.1 mol dm<sup>-3</sup> NBu<sub>4</sub>ClO<sub>4</sub> acetonitrile solution, the evolution of the electroactivity of PEDOT films in the range -1.0 to 0.6 V. The electroactivity loss for films prepared in SDS medium is about 9% after 50 cycles, which indicates good electrochemical reversibility.

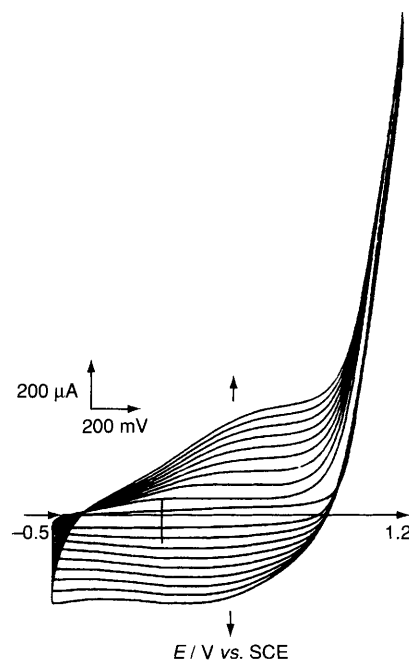


Fig. 1 Cyclic voltammograms for EDOT (0.05 mol dm<sup>-3</sup>) recorded at a Pt electrode in 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> aqueous solution, in the presence of 0.07 mol dm<sup>-3</sup> SDS; scan rate = 100 mV s<sup>-1</sup>

The structure of the PEDOT films was studied using Raman and XPS spectroscopies. The resonance-Raman spectra (Fig. 2) are characterized by better resolved and finer bands than that of unsubstituted polythiophene (PT), suggesting that PEDOT films obtained in a micellar anionic medium, as well as in acetonitrile, are better organized than PT films.<sup>8,19</sup> The most intense band at 1432  $\text{cm}^{-1}$  is assigned to the symmetric stretching mode of the aromatic C=C band, while a less intense band at 1512  $\text{cm}^{-1}$  is attributed to the C=C antisymmetric stretching vibration. Other, weaker bands at 1364 and 1269  $\text{cm}^{-1}$  are assigned, respectively, to the stretching mode of the single C-C bond and the C-C inter-ring bond (Fig. 2).

A comparative XPS study of films obtained in the micellar medium and acetonitrile on Pt was performed. The C 1s region is similar for films prepared in both media, exhibiting four peaks at 285 eV (C-C and C-H bonds), 286.4 eV (C-O-C bonds), 287.5 eV (C-OH or C-Cl groups), and a weaker peak at 289.1 eV (C=O groups). The O 1s signal consists of a small peak at 531.8 (micellar medium) or 532.1 eV (acetonitrile), ascribed respectively to the oxygen of dodecyl sulfate and perchlorate species, and a stronger peak at 533.4 eV, attributed to C-O-C bonds. The sulfur region exhibits two doublets for PEDOT films obtained in the micellar medium; the first doublet [164.2 eV (S 2p<sub>3/2</sub>) and 165.2 eV (S 2p<sub>1/2</sub>)] is ascribed to sulfur atoms of the thiophene ring, whereas the second one [168.1 eV (S 2p<sub>3/2</sub>) and 169.6 eV (S 2p<sub>1/2</sub>)] is typical of sulfur atoms belonging to DS<sup>-</sup> anions, incorporated into the film. By contrast, for films prepared in acetonitrile, the sulfur signal consists of only one doublet at 163.7 eV (S 2p<sub>3/2</sub>) and 166.3 eV (S 2p<sub>1/2</sub>) attributed to sulfur atoms of thiophene ring. For PEDOT films prepared in micellar medium, the Cl 2p signal includes one broad peak made up of two components at about 207.5 eV and 209.5 eV, corresponding to ClO<sub>4</sub><sup>-</sup> species, whereas for films obtained in acetonitrile, the Cl 2p signal consists of two broad peaks, centred at about 207.0 eV (two components, attributed to ClO<sub>4</sub><sup>-</sup>) and 197.3 eV (C-Cl groups). This latter feature seems to show that, during electropolymerization of EDOT in acetonitrile, ClO<sub>4</sub><sup>-</sup> anions are degraded, releasing Cl which become linked to the polymer chains. Similar results, including covalent linkage of Cl atoms to thiophene rings, were obtained recently in the electropolymerization of 3-methylthiophene in acetonitrile.<sup>20</sup>

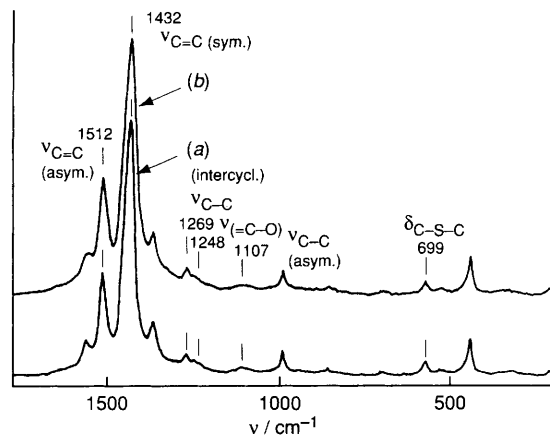


Fig. 2 Resonance-Raman spectra of a PEDOT film (in the doped state) deposited at constant current (1 mA  $\text{cm}^{-2}$ ) during 60 s from (a) aqueous SDS and (b) LiClO<sub>4</sub>-acetonitrile solution

The PEDOT films deposited from SDS aqueous medium and from lithium perchlorate-acetonitrile were morphologically quite distinct. Scanning electron micrographs (SEM) indicate that the films obtained intensively in the SDS micellar medium grow regularly with time and present a smooth homogeneous morphology. In contrast, the polymer electro-synthesized in acetonitrile has a rough, cauliflower-like structure.

In this preliminary work, we have demonstrated that electropolymerization of 3,4-disubstituted thiophene such as EDOT from a self-assembling electrolyte (aqueous SDS) produces a regularly growing and well ordered conductive polymer on a Pt electrode. The use of an anionic micellar solution has the great advantage of increasing the solubility of this thiophene derivative in water and lowering its oxidation potential. Also, spectroscopic and microscopic analyses indicate a good organization of the films deposited from micellar aqueous phases. Studies on the applicability of this novel electropolymerization procedure to organic coating of oxidizable metals in micellar aqueous media are now under way in our laboratory.

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#### Footnote

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