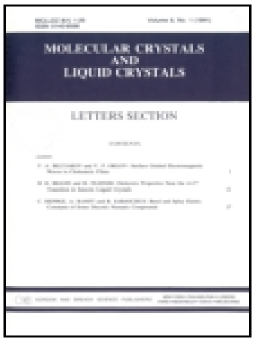

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Comparison of Organic and Aqueous Polymerized PEDOT Sensors

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PEDOT electrodes were prepared in aqueous and organic solutions. A PEDOT-based sensor for the analysis of beverage antioxidants can be effectively prepared in propylene carbonate, and in this study, PEDOT polymerization was also performed in two aqueous solutions, 10% acetonitrile/water and an aqueous solution containing sodium dodecyl sulphate (SDS). The change in the oxidation potential of EDOT due to polymerisation solution was investigated and the film morphology was examined using SEM. The sensitivity of PEDOT sensors was tested by cyclic voltammetry in a gallic acid solution and with a green tea sample. The best sensitivity was obtained with PEDOT polymerized in propylene carbonate.

Keywords PEDOT; sensor; acetonitrile; SDS; aqueous polymerization; cyclic voltammetry

1. Introduction

Conducting polymers are polymers that have high intrinsically conductivity. Polypyrrole, polyaniline and poly(3,4-ethylenedioxythiophene) (PEDOT) are among the most intensively studied conducting polymers due to their good stability, specific properties and wide applicability in technology [1]. Many chemical sensors based on conducting polymers have been developed to detect fire [2], aromatic hydrocarbons [3], microbial and chemical pollutants in water [4, 5], and for the analysis of wines[6, 7] and olive oils[8]. PEDOT-based sensors have been found to be useful in the analysis of beverage antioxidants using the cyclic voltammetry (CV) technique, as reported previously [9, 10]. The advantage of using conducting polymer covered electrodes, over bare electrodes, is that the modified electrodes typically provide a better separation of the oxidation/reduction peaks of different analytes in the obtained voltammograms [11].

Electrochemical polymerization of the monomer, 3,4-ethylenedioxythiophene (EDOT), is an efficient method that allows control of PEDOT thickness as the polymerisation parameters are changed. The properties of PEDOT films are affected by electropolymerization conditions such as the solvent, supporting electrolyte, electrode material, and electrochemical methodology [12, 13]. Most of the PEDOT films have been produced in organic

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solvents. However, the use of water as a solvent is more useful for both economic and ecological reasons. Thiophenes are weakly soluble in water and generally show a higher oxidation potential than that of water itself. Usually, electropolymerization of EDOT is performed in acetonitrile and propylene carbonate. Polymerization of EDOT in micellar medium has been tested with various surfactants such as camphor sulphonic acid (CSA) [14], sodium dodecyl sulphate (SDS) [15], dodecylbenzene sulfonic acid [16], polystyrene sulfontate (PSS) [17], and polyoxyethylene-10-lauryl ether [18]. It has been found that the solubility level of EDOT in water in the presence of 0.1 M SDS was increased to 73 mM from 11 mM in pure water [19].

In previous study, a PEDOT sensor was prepared by polymerization of EDOT in propylene carbonate. In this study, PEDOT polymerization was also performed in aqueous solutions, namely a 10% acetonitrile/water mixture and an SDS water solution. The obtained PEDOT electrodes were compared in terms of sensitivity to antioxidants by performing cyclic voltammetry in a gallic acid solution and with a green tea sample. The morphology difference was also investigated using SEM.

2. Materials and Methods

2.1. Preparation of Aqueous Polymerization Solution

For polymerization in the organic solvent, 0.1 M 3,4-ethylenedioxythiophene (EDOT) and 0.1 M lithium perchlorate ($LiClO_4$) were dissolved in propylene carbonate (PC). Two types of aqueous polymerization solution were prepared and tested. The first one was 10% (*v*/*v*) acetonitrile in water at containing 0.1 M $LiClO_4$ and 0.01 M EDOT. This was prepared by adding EDOT into 1 ml of acetonitrile and diluting with 9 ml of Milli-Q water, before adding lithium perchlorate. The second one was a micellar aqueous solution using SDS as a surfactant. The solution was prepared by adding 0.01 M SDS, 0.1 M $LiClO_4$ and 0.01 M EDOT into Milli-Q water. Then, it was dipped into a sonic bath at 20°C for 15 minutes sonication to obtain a homogenous solution. Before electropolymerization, nitrogen gas was purged into the solutions for 15 min to remove oxygen, but to avoid foaming in the final aqueous solution, the deaeration was conducting before adding SDS.

2.2. Electropolymerization

Electropolymerization of EDOT was carried out with a typical three electrode system. Pt wire (BASi, MW 1032) and Ag/AgCl (BASi, MF 2052) electrodes were used as counter and reference electrodes, respectively, and using a Bioanalytical Systems (BAS) 100A Electrochemical Analyzer. A 1 mm diameter glassy carbon electrode (eDAQ ET-074) was used as the working electrode. The electrode surface was cleaned by polishing with 0.05 μm alumina powder on a cloth pad and rinsed with Milli-Q water before each polymerization. In order to examine the oxidation peaks of EDOT, CV was first performed 1500 mV as the upper potential limit. Electropolymerization in the organic solvent was conducted by cycling for 4 cycles between −300 and 1200 mV (Ag/AgCl) at a scan rate of 100 mV/s. The aqueous polmymerization was performed by cycling for 14 segments between −400 and 1000 mV (Ag/AgCl) at a scan rate of 100 mV/s. In each case the electrode was then rinsed with Milli-Q grade water to remove unpolymerized monomer from the film.

2.3. Testing Samples by PEDOT Electrodes

In order to check sensing properties of PEDOT electrodes, cyclic voltammetry was performed in gallic acid in phosphate buffer at pH 7.4 and green tea sample solution between –200 and 800 mV at a 100 mV/s scan rate. Sodium perchlorate as an electrolyte was added into the samples at a final concentration of 0.1 M. For comparison purposes, a bare glassy carbon electrode was also used.

2.4. SEM Imaging for Surface Morphology

The surface morphology of a PEDOT film polymerized in the organic and aqueous solutions at a 1 mm dia. glassy carbon electrode was examined using SEM. For comparison purposes, a bare 1 mm dia. glassy carbon electrode was also examined. After platinum coating, the morphology of the PEDOT films were observed using a Scanning Electron Microscope (SEM) (Philips XL30S FEG SEM equipped with a SiLi (Lithium drifted) EDS detector with a Super Ultra Thin Window).The electrodes were placed on to stage with an angle to examine the film surface morphology.

3. Result and Discussion

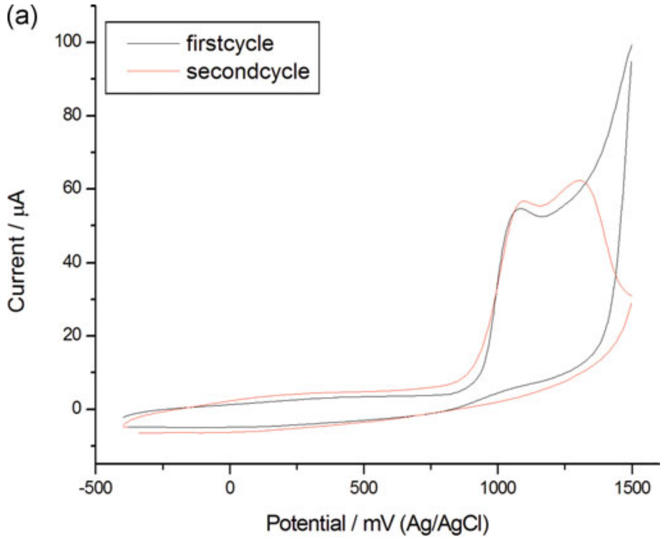
3.1. Oxidation Potentials

Cyclic voltammetry of 0.01 M EDOT to a highest potential value of 1500 mV in the aqueous solutions gave two oxidation peaks. In 10% acetonitrile/water solution, the first peak (P_1) and the second peak (P_2) were observed at around 1090 mV and 1300 mV, respectively (Figure 1A). While P1 can be ascribed to oxidation of the EDOT monomer, and polymerisation of PEDOT, the second P2 is likely due to PEDOT overoxidation, which was not observed on the first cycle because there was not sufficient polymer film on the electrode surface. When the highest potential of the CV was decreased to 1000 mV, PEDOT film grew without overoxidation. A rapid increase at the anodic peak was observed at around 850 mV, and the current intensity increased regularly with each cycle. As a result, cyclic voltammetry between −400 and 1000 mV was found to be suitable to electropolymerize EDOT in 10% acetonitrile/water solution (Figure 2B). When the cyclic voltammetry was performed in SDS solution between −400 and 1500 mV, the voltammogram also showed oxidation peaks at around 1100 and 1400 mV, and again the second (overoxidation) peak was not observed on the first cycle (Figure 1B). The rapid increase in anodic current in the SBS solution was observed at around 850 mV. This result is consistent with previous reports [15, 19], where an anodic peak for a PEDOT film was observed at 760 mV vs. SCE.

On the other hand, polymerization in organic solvent (PC) was different (Figure 2A). A rapid anodic peak current increase started at 1000 mV, which was a higher value than that in aqueous solutions. This result showed that oxidation potential of EDOT was decreased in both aqueous solutions compared to the organic solution. The potential range of from –300 to 1200 mV was found to be suitable for polymerization in PC.

3.2. Testing Gallic Acid and Green Tea

In our previous studies, PEDOT electrodes prepared in PC were found to be suitable for testing antioxidants in beverages [9, 10]. In order to compare the sensitivity of aqueous polymerized PEDOT electrodes with organic polymerized one, CV was performed in



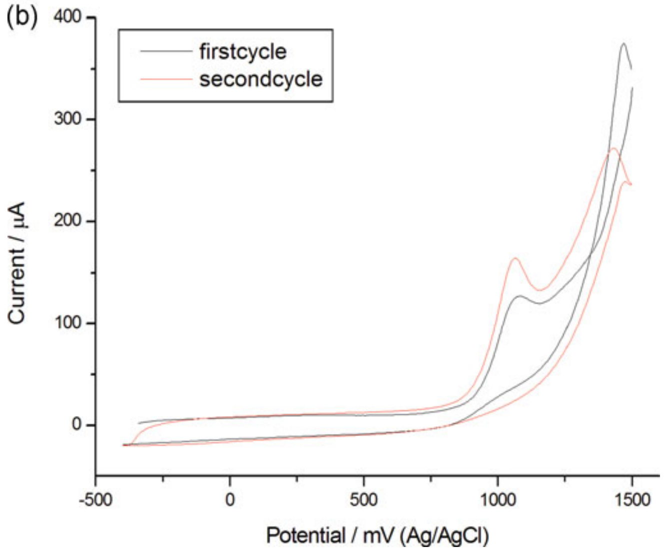


Figure 1. The first and the second cycles of cyclic voltammetry of 0.01 M EDOT between -400 and 1500 mV at a scan rate of 100 mV/s in 10% acetonitrile/water (A), and 0.01 M SDS in water (B), with 0.1 M $LiClO_4$.

gallic acid (1 g/L) in phosphate buffer (pH 7.4) by using PEDOT polymerized in 10% acetonitrile/water solution, 0.01 M SDS solution, PEDOT in PC and a 1 mm dia. glassy carbon electrode (Figure 3). PEDOT/PC showed a well-defined oxidation peak at around 400 mV. On the other hand, the peak current decreased with aqueous polymerized PEDOT electrode, although it was higher compared to the bare electrode. The intensity of the oxidation peak current was found to be 36.3, 24.0, 20.8 and 13.9 μA for PEDOT/PC, PEDOT/SDS, PEDOT/AcetW and bare electrodes, respectively. It can be concluded that PEDOT film prepared in acetonitrile/water and SDS increase sensitivity compared to the

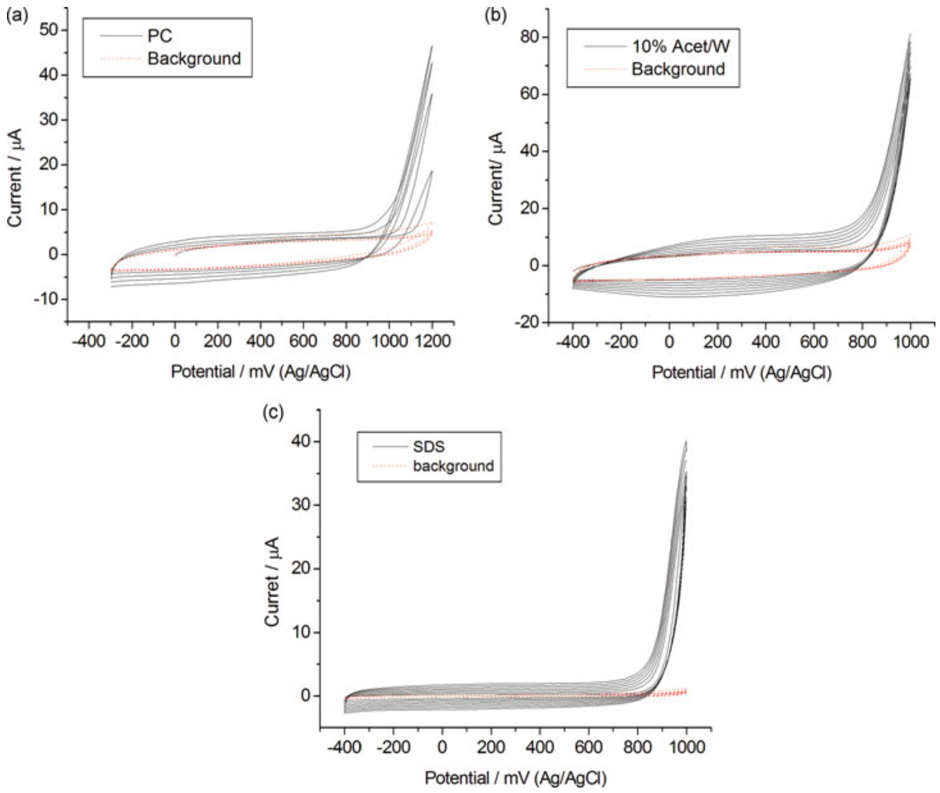


Figure 2. Polymerization voltammograms in PC (A), 10% acetonitrile/water (B) and 0.01 M SDS in water, combined with 0.1 M $LiClO_4$ and 0.01 M EDOT.

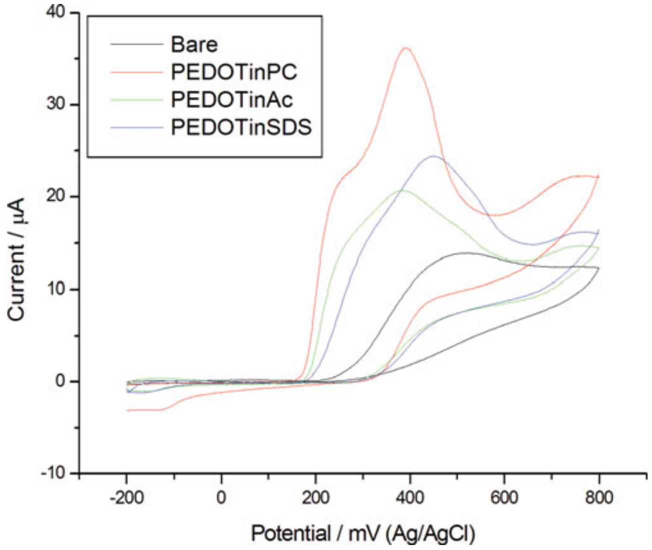


Figure 3. Cyclic voltammetry of gallic acid in phosphate buffer (pH 7.4) at PEDOT/PC, PEDOT/SDS, PEDOT/AcetW electrodes and at a bare glassy carbon electrode.

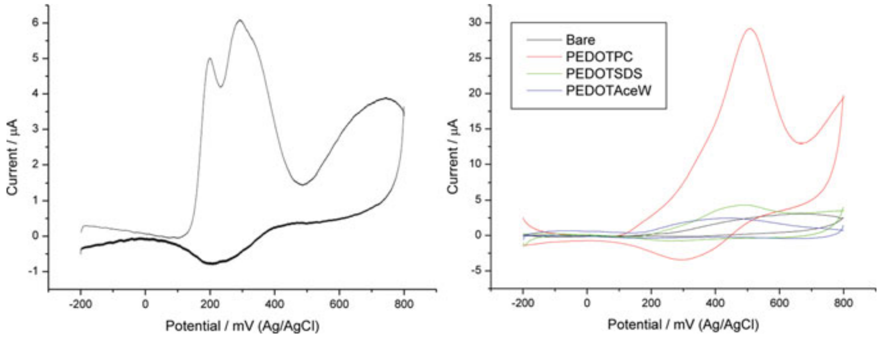


Figure 4. Cyclic voltammetry of 5-fold diluted green tea at the PEDOT/PC electrode (A), and undiluted green tea at PEDOT/PC, PEDOT/SDS, PEDOT/AceW and a bare glassy carbon electrode (B).

bare electrode, however; it was not as sensitive as the PEDOT electrode polymerized in propylene carbonate.

Green tea was tested by the PEDOT electrodes as a real sample. Although 5-fold diluted tea was able to be detected at the PEDOT/PC electrode (Figure 4A), the aqueous polymerized PEDOT electrodes did not give a measurable response. Therefore, undiluted green tea was used for CV at PEDOT/PC, PEDOT/SDS, PEDOT/AcetW and a bare electrode (Figure 4B). While the oxidation peak current of undiluted green tea reached 30 μA by PEDOT/PC, it was less than 5 μA at the other electrodes. In addition, the typical two oxidation peaks of green tea (dominated by epigallocatechin gallate [20]) were not observed.

3.3. SEM

It can be seen from even the lowest magnification SEM images that the film morphology of PEDOT/PC was more rough compared to the aqueous polymerized PEDOT films. Although higher number of segments were used for polymerization in the aqueous solutions, a thinner

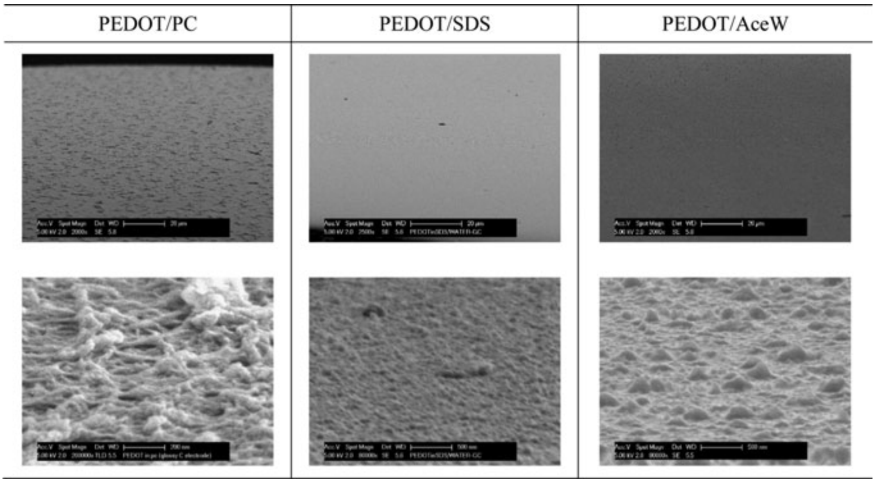


Figure 5. SEM images of PEDOT surfaces prepared by polymerization in PC, SDS and acetonitrile water solutions.

film was obtained. This result is consistent with a previous report [21], were a higher amount of PEDOT was obtained in an organic solvent compared to an aqueous solution.

At a higher magnification, the film was of a globular structure, and cauliflower-like. In addition, PEDOT/PC has some netlike structures as well. When the images at 80000x magnification are compared, it can be concluded that PEDOT/AcetW had larger polymer mounds compared to PEDO/SDS. It has been reported that PEDOT/SDS was of a regular and smooth morphology compared to PEDOT polymerized in pure acetonitrile [15].

4. Conclusions

In addition to polymerization in propylene carbonate, two types of aqueous solution system were used to dissolve and polymerize EDOT. The oxidation potential value decreased in the tested solutions compared to organic solvent and these potential values were found to be less than the oxidation potential of water. The PEDOT film covered electrodes were used in CV of gallic acid and green tea solutions in order to compare sensitivity with the phenolic antioxidants. PEDOT/PC gave better response than PEDOT prepared in aqueous solutions. Among the aqueous polymerizations, PEDOT/SDS gave a higher signal compare to PEDOT/AceW. The film morphology showed differences by SEM, as the film formed in PC was greater than in the aqueous solutions.

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