

Determination of ascorbic acid using differential pulse voltammetry method on aniline-*co-para*-aminophenol modified electrode

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The electro-synthesis of poly(aniline-*co-para*-aminophenol) on graphite electrode was examined using cyclic voltammetry (CV) over the potential window of -0.2 V to 1 V in phosphoric acid medium, which was comprised of potassium chloride and *para*-Toluene sulfonic acid (*p*TSA) as electrolyte support. Fourier transform infrared (FTIR) spectroscopy was employed to identify the electro-synthesized copolymer while impedance techniques were used to determine charge transfer resistance (R_{ct}) in modified and unmodified electrodes. After this, the electro-catalytic effect of the modified electrode on ascorbic acid was examined using differential pulse voltammetry (DPV) and a very strong response was observed. A negative shift of about 0.33 V was found in the peak anodic potentials for ascorbic acid. Measurement using DPV indicated a proper response by the electrode to a wide range of ascorbic acid concentrations, from 0.0001 to 0.0004 M. The peak anodic currents for increased concentrations showed a proper linear range.

Keywords: polyaniline, *para*-aminophenol, ascorbic acid, differential pulse voltammetry.

INTRODUCTION

Polyaniline is one of the oldest synthetic conductive polymers which has gained popularity for its high electrical conductivity^{1–3}. The presence of nitrogen atoms in phenyl rings results in the formation of different redox forms that affect the physical properties of polyaniline^{4,5}. Polyaniline (PAni) can be obtained by chemical or electrochemical oxidative polymerization of aniline (Ani). Electro-polymerization is often carried out in an aqueous acidic medium through three techniques: galvanostatic, potentiostatic and cyclic voltammetry^{6,7}. Electrochemical synthesis of PAni in aqueous solutions depends on different parameters such as the pH of electrolyte⁸, type of doping anion⁹, bed¹⁰, and the techniques used for electrochemical synthesis¹¹. Polyaniline exists in four main configuration states: (i) the fully-reduced leucoemeraldine (LE) form, (ii) the pernigraniline (PN) configuration that is fully-oxidized form, (iii) the half-oxidized emeraldine base (EB) form and the protonation of EB produces the emeraldine salt (ES) form, which contains a stable delocalized poly-semiquinone radical cation^{12,13}. Electrodeposition of the PAni film at the surface of an electrode has been utilized extensively in a field of electrochemistry to modified electrodes for determination of some biological compounds based on electro-catalytic oxidation^{14,15}. These catalytic activities of PAni are generally affected by a variety of solution conditions such as electrolytes, solvents and pH and also its intractable nature, such as insolubility and high brittleness, limits polyaniline's application. To extend its application in solutions, the copolymerization of Ani with ring-substituted Ani derivatives has been studied in order to modify the desired properties of polyanilines^{16,17}. Recently, we synthesized copolymer of poly(aniline-*co-ortho*-phenylenediamine), via the electrochemical copolymerization of Ani with *ortho*-phenylenediamine in aqueous solution¹⁵. The new copolymer had shown excellent electro-catalytic response towards the oxidation of ascorbic acid (AA). Ascorbic acid, commonly known as vitamin C, improves absorption of amino acid and iron in the human body. It also con-

nects tissues, bones, teeth, and the walls of blood vessel. Ascorbic acid is also an antioxidant agent. Therefore, it is essential to have a quick and selective method in the routine analysis of foods and drugs^{18,19}. Many of the analytical methods used for determination of AA such as fluorimetry, chromatography, iodometric titration, enzymatic methods, spectroscopy and electrochemistry^{20–23}. Due to high sensitivity, selectivity, precision, accuracy, wide linear range and low-cost instrumentation and time, electrochemical methods are currently of much interest for AA determination especially; differential pulse voltammetry (DPV) is a practical electrochemical analytical technique that offers quick response, low detection limit and simple use^{24,25}.

This study aims to investigate (i) the electro-synthesis of poly(aniline-*co-para*-aminophenol) on composite graphite electrode, (ii) electro-catalytic oxidation of AA and its measurement on modified electrodes using DPV method and (iii) the charge transfer resistance (R_{ct}) of modified electrode on AA by electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

Material

Aniline (Ani) is distilled in a low-pressure nitrogen atmosphere. The resulting colourless liquid is stored at 5°C . *para*-Aminophenol (*p*AP) was used without purification. Mineral salts like KCl, *para*-Toluene sulfonic acid (*p*TSA), and H_3PO_4 were used without purification. All these substances were chemicals from Merck.

Equipment

CompactStat (manufactured by Ivium Technologies, the Netherlands) was used for the synthesis and identification of Ani-*co-p*AP copolymer. Electrochemical analyses were carried out in a handmade cell that had three common electrodes. Composite 2B pencil graphite (1.8 mm) was used as the working electrode while a platinum electrode

was used as the auxiliary electrode, along with an Ag/AgCl reference electrode.

The structure of the copolymer was determined by fourier transform infrared (FTIR) spectroscopy system 2000 (TENSOR 27, Bruker).

Procedure

Electro-copolymerization of Ani and *p*AP was carried out using cycling voltammetry from -0.2 V to 1 V in a solution comprised of 50 mM of monomers and 10 ml of the supporting electrolytes (KCl 2 M and *p*TSA 0.6 M) in H_3PO_4 medium.

The inductive behaviour of copolymer of Ani with *p*AP was identified in a three-compartment cell with a cell geometry that is similar to what has been described for the copolymerization at a potential of 0.05 V, and a frequency range of 100 kHz to 100 mHz via electrochemical impedance spectroscopy (EIS).

The copolymer film formed on the working electrode was put on crystal (KBr) for FTIR spectroscopy. Using Perkin Elmer 2000, a range of 400 – 2000 cm^{-1} was identified for the FTIR spectra.

DPV was used to measure ascorbic acid content, a modified electrode was selected and put into ascorbic acid solutions (0.0001 , 0.0002 , 0.0003 , and 0.0004 M) and the resulting current vs. voltage was measured at the electroactive potential. CompactStat was again in this part of the analysis as well. The following parameters being employed: potential range of -0.2 V to 1 V; scan rate 0.1 V/s; pulse time 10 ms; pulse amplitude 10 mV and voltage step 10 mV.

RESULTS AND DISCUSSION

Electro-synthesis and characterization

Electro-copolymerization of Ani and *p*AP

Figure 1 depicts the voltammograms for the electro-copolymerization of Ani and *p*AP (0.05 M *p*AP + 0.05 M Ani) in phosphoric acid in the presence of a binary supporting electrolyte from KCl and *p*TSA.

In Figure 1, the first voltammogram reveals two anodic peaks, one corresponding to the oxidation of *p*AP and the other corresponding to the oxidation of Ani. The

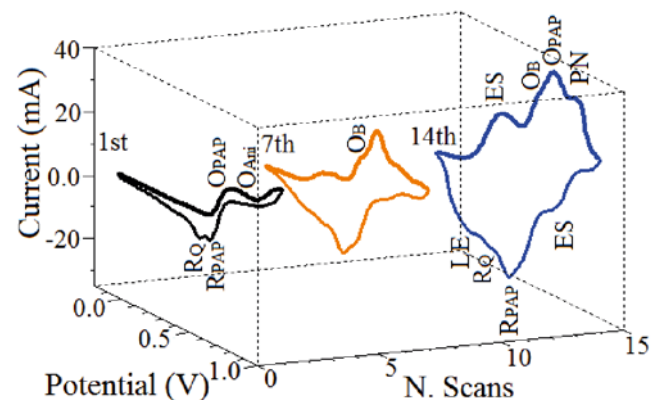


Figure 1. CVs (1^{st} , 7^{th} and 14^{th}) of the electro-copolymerization of 50 mM of monomers (Ani and *p*AP) in phosphoric acid medium in the presence of binary supporting electrolyte (KCl and *p*TSA). The scan rate is 100 mVs^{-1}

anodic peak oxidation of Ani appears at 0.9 V, which can be attributed to the synthesis of polyaniline due to formation of aniline radical cation^{26, 27}. On the reverse scan the cathodic peak is not observed. This is an irreversible electrode process. Two cathodic peaks are observed on the reverse scan indicate that reduction of *p*AP (RpAP) and reduction of Quinoid (Q) rings (RQ) in copolymer chain that is attributed to the degradation of product (quinoid to benzenoid and vice versa)^{5, 12}. In the next scans (Fig. 1: 7^{th} to 20^{th}) redox pairs of PAni configuration and poly *para*-aminophenol (PpAP) appear in copolymer chain²⁸. Given the redox pairs at the oxidation peaks (PN/ES/LE) of polyaniline configuration^{29, 30}, it follows that the synthesis of polyaniline on the electrode occurs more slowly compared to the synthesis of PpAP.

Structural analysis

FTIR spectrum for electro-copolymerization of Ani and *p*AP in phosphoric acid medium in the presence of KCl and *p*TSA is seen in Figure 2. FTIR spectrum resulting from copolymerization of Ani and *p*AP shows properties of both *p*AP and Ani homopolymers. In Figure 2, the absorption bands 1646 cm^{-1} and 1555 cm^{-1} are associated with the quinoid and benzenoid vibration structures³¹ (intensities of quinoid and benzenoid bands are used to measure the level of oxidation in polyaniline films). A zero ratio indicates complete reduction, while a ratio ranging from 0.5 to 1 shows the presence of protoemeraldine. A ratio of 1 indicates relatively low oxidation and ratios greater than 1 imply complete oxidation. The absorption band at 1400 cm^{-1} is related to vibrational transitions³² in C-O-H and the one at 1305 cm^{-1} is related to the vibrational structure of the second aromatic amine that forms the C-N-C structure in the copolymer³³. The band at 1114 cm^{-1} is associated with the modified planar C-H bonds³⁴. The bands at 1149 cm^{-1} and 805 cm^{-1} are related to the in-plane bending vibrations in C-H bond and the out-of-plane bending vibration in aromatic rings respectively³⁵. The presence of the band at 951 cm^{-1} can be attributed to the phosphate group³⁶.

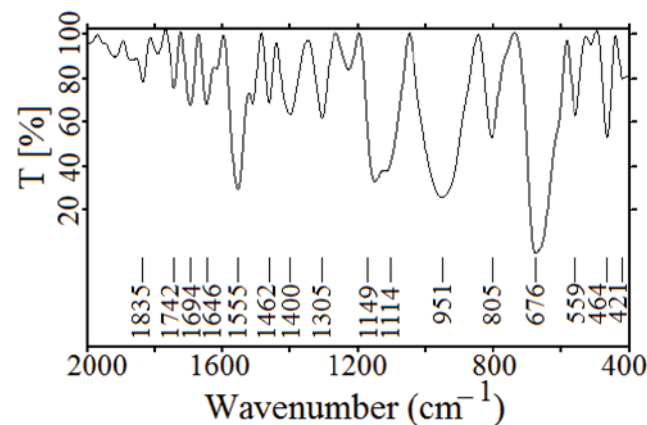


Figure 2. Baseline corrected FTIR spectra (2000 – 400 cm^{-1}) of copolymer of Ani and *p*AP electro-synthesized in 1 M H_3PO_4 containing of binary supporting electrolyte

Measurement of ascorbic acid (AA) using differential pulse voltammetry (DPV)

Figure 3a (black CVs) shows the DPV results for different AA concentrations (0.0001, 0.0002, 0.0003, and 0.0004 M) using graphite electrode. As seen in the figure, peak anodic potential of 0.38 V is observed on the graphite electrode. DPV results for different AA concentrations in phosphoric acid for the potential range of -0.2 V to 1 V on the Ani-*co-p*AP modified electrode can be seen in Figure 3b (blue CVs). As shown in the figure, the use of Ani-*co-p*AP modified electrode shifts anodic peaks to 0.05 V (a 0.33 V shift compared to the case where unmodified electrode is used). In addition, the peak anodic current is directly proportional to AA concentration and the measurement precision is in line with a correlation coefficient of 0.98, which not only indicates the quick and easy oxidation of AA but also confirms the electro-catalytic effects of the Ani-*co-p*AP modified electrode on AA.

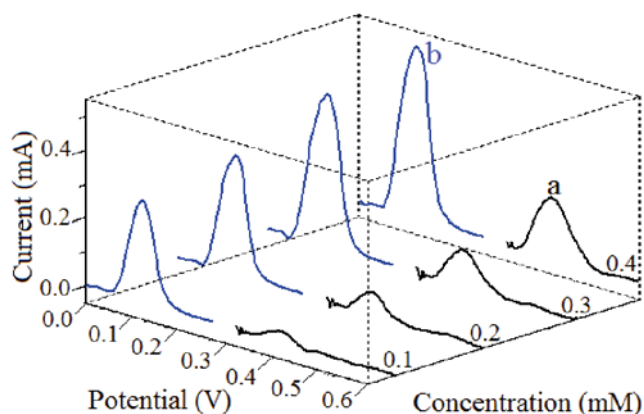


Figure 3. DPV voltammograms obtained from different concentrations (from 0.1 to 0.4 mM) of AA in 1 M H_3PO_4 containing of binary supporting electrolyte (a) on bare graphite electrode and (b) on modified electrode

Electrochemical impedance spectroscopy

Figure 4 depicts the Nyquist plot obtained for Ani-*co-p*AP film in the phosphoric acid medium, which is comprised of supporting electrolytes of KCl and *p*TSA.

The region used for impedance analysis largely falls within 0.05 V in both cathodic and anodic regions. Oxidation structures for Ani and *p*AP depend on the potential and pH of the electrolyte, and these two factors significantly affect the conductivity of the copolymer surface and the electrolyte^{37, 38}. Therefore, the impedance spectra of the Ani-*co-p*AP are expected to be influenced by DC potential. Impedance spectra of higher frequency were obtained for the electric double layer charge-discharge process. No electrochemical reaction occurs at lower potentials, leading to very high transfer resistance. This in turn may indicate a lack of electrical conductivity in Ani-*co-p*AP for the potential

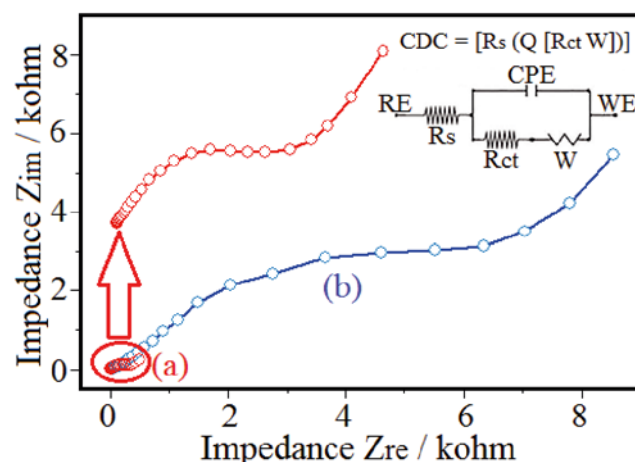


Figure 4. Nyquist plots of AA at the poly(Ani-*co-p*AP) modified electrode (a) and bare graphite electrodes (b) at applied potential of 0.05 V with Randles' equivalent circuit and circuit description code (CDC) (inset). The ac potential amplitude was kept at 10 mV and frequency range used was from 100 kHz to 100 mHz

range examined here. Once monomer oxidization begins at higher potentials, electron transfer takes place and therefore transfer resistance considerably falls³⁹⁻⁴². As seen in Figure 4, spectra have a semi-circular shape indicating transfer resistance of the load. The smaller is the diameter of the semicircle, the easier it will be to transfer the electrons. However, reduced impedance at lower frequencies creates capacitive behaviour in the diffusion process. From Figure 4 it is obvious that the value of charge transfer resistance (R_{ct}) of bare electrode (Fig. 4b) is much higher than poly(Ani-*co-p*AP) modified electrode (Fig. 4a) indicating improved interfacial capacitance. The presence of straight line on modified and unmodified with a slope of 45° at the lower frequency indicates a favourable diffusion-controlled mass transport process. Insert of Figure 4 presents the equivalent circuit for these impedance spectra⁴³⁻⁴⁵ with the following elements: the solution resistance of the bulk electrolyte (R_s), charge transfer resistance (R_{ct}) that corresponds to the kinetic control of the process of electron transfer from solid phase (e.g. electrode) to liquid phase (e.g. solution) and vice versa, double layer capacitance (C_{dl}) and Warburg impedance (Z_w). To get appropriate fitting of the Nyquist plots, C_{dl} is sometimes replaced by constant phase elements (CPE) in the Randles' equivalent circuit. The values of the Randles' equivalent circuit elements obtained by fitting the experimental results from the Nyquist plots at bare electrode and modified electrode at applied potential of 0.05 V are listed in Table 1.

Table 1. The best fitting values of the Randles' equivalent circuit elements in Figure 4 from the simulation of the impedance data for poly(Ani-*co-p*AP) modified electrode and unmodified electrode at applied potential of 0.05 V

Electrodes	Randles' equivalent circuit elements				
	R_s [Ω]	R_{ct} [Ω]	W [$1/(\text{Ohm} \sqrt{\text{Hz}})$]	CPE (F)	N^a
Modified	10	2.6×10^{-2}	$1.9 \times 10^{+2}$	9.0×10^{-6}	8.1×10^{-1}
Unmodified	69	$6.9 \times 10^{+3}$	$1.1 \times 10^{+3}$	1.9×10^{-6}	6.8×10^{-1}

^aDegree of electrode surface roughness or cell geometry.

CONCLUSION

According to the electro-catalytic oxidation, the quantitative determination of ascorbic acid in the pharmaceutical, chemical, cosmetic and food industry was developed by the rapid, reliable, easy to implement, selective and sensitive DPV technique. The electroanalytical techniques advantages include excellent sensitivity, less sensitive toward the matrix effects, simultaneous determination of several analytes and there is no need the derivatization of the samples, extraction, filtration and complex sample preparation. In addition, the developed electroanalytical technique is less expensive than the other techniques.

The electro-copolymerization of Ani and *p*AP was carried out by cyclic voltammetry in a solution comprised of monomers and the supporting electrolytes (KCl and *p*TSA) in H₃PO₄ medium. The poly(Ani-*co-p*AP) modified electrode exhibited electro-catalytic activity towards the oxidation reaction of AA with a higher current density and at lower onset potential. The extension of catalytic reaction depends on charge transfer. The electrochemical impedance spectroscopy was successfully used to interpret the electro-catalytic effect of modified and unmodified electrode on AA. The quantitative determination of ascorbic acid was developed by the quick, easy and sensitive DPV technique.

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