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Development of gallic acid sensors based on polyimide-modified platinum electrode

Aziz Paşahan, Nurcan Ayhan, İmren Özcan, Serap Titretir Duran, and Süleyman Köytepe

Faculty of Arts and Science, Chemistry Department, İnönü University, Malatya, Turkey

ABSTRACT

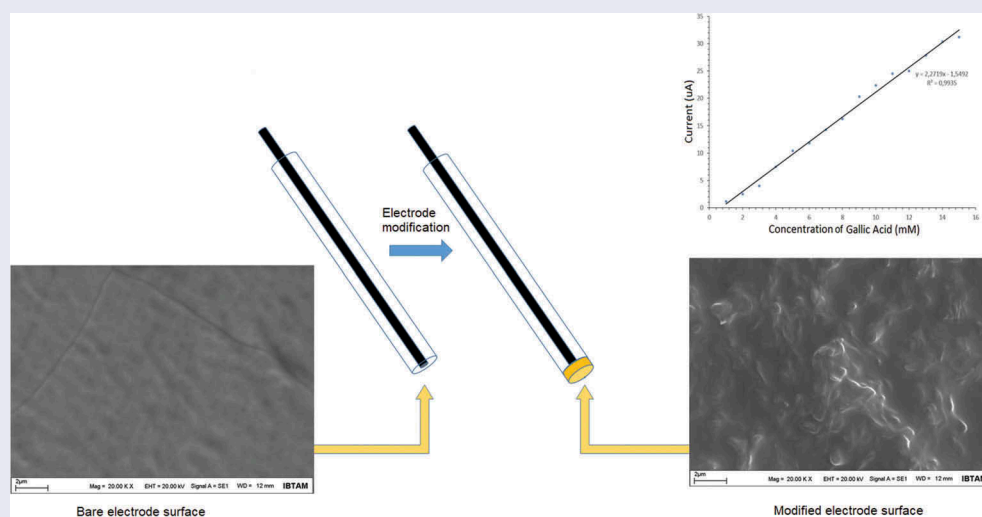
A series aromatic polyimide (PI) membranes in the form of permselective films was synthesised from different dianhydrides with two diamine monomers for gallic acid (GA) measurement. The obtained PI films were examined by Spectroscopic techniques, Scanning Electron Microscopy (SEM) and thermal analysis techniques and then used to fabricate the selective films on the modified electrode. Because of their excellent film properties, as the permselective polymeric membranes were used for determination of GA in the presence of various interferences and real sample. The PI-1-modified Pt electrode showed a very high R-value (0.9935) and reproducibility for GA determination, as well as high selectivity.

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1. Introduction

Gallic acid (GA), an important polyphenol, is produced in plants in the form of catechin derivatives, esters and free acids, and it is found in grapes, blueberries, cantaloupes, bananas and several other fruits.^[1, 2] GA is widely known for its perfect antioxidant and antiradical activity in pharmaceutical properties, anti-inflammatory, anticarcinogenic, antihistaminic, antioxidative and anticancer effects, and protection against cardiovascular diseases.^[3, 4] Therefore, accurate and fast determination of GA is very important for human health. In recent years, many methods such as chemiluminescence spectrophotometry, capillary electrophoresis and chromatography were introduced

to detect phenolic compounds.^[5–7] Especially electrochemical methods are widely used for determination of GA as a polyphenol. These methods have more advantages than those of traditional methods due to very fast response time, low detection limit, lower cost, high sensitivity and simplicity.^[8, 9] However, direct the electrochemical determination of GA on traditional electrodes usually suffers from electroactive interferant compounds and the disadvantages of low sensitivity.^[10–11]

In order to overcome these problems, selective polymeric membranes have been used to eliminate interferant compounds for determination of electroactive molecule in biological samples. These polymeric membranes have

CONTACT Serap Titretir Duran ✉ serap.titretir@inonu.edu.tr Faculty of Arts and Science, Chemistry Department, İnönü University, Malatya 44280, Turkey

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unique properties, ease of manufacture, good adhesive characteristics, suitable porosity, flexibility in design, adjustable pore size and low cost.^[12] More recently, different classes of polymeric materials such as porous polymers, polymer brush, conducting polymers and biopolymeric materials are being widely used as modifiers for electrodes.^[13, 14]

As high performance polymeric materials, polyimides (PI) exhibit excellent properties such as high-temperature stability, physical, chemical and mechanical resistance, electrical properties, low dielectric constant, superior hydrolytic stability, high mechanical strength, low thermal expansion coefficient, and suitable mechanical, tribological and adhesive properties.^[15–19] Polyimide membranes have recently received much attention due to their inert structure, chemical stability and high biocompatibility.^[20, 21] Therefore, polyimides have been widely employed for construction of glucose sensors^[22, 23], gas sensors^[24–29], humidity sensors^[30–32], piezoelectric tactile sensors^[33] and pressure sensors.^[34]

The modification of the bare Pt electrodes surface is important for its stability. However, modification of the bare Pt electrode may extend its practicality to more electrochemical sensor systems. Recent studies show that the Pt electrode yields very reproducible results, fast response, and that it can be used as a convenient reference electrode.^[35–38] Therefore, modified Pt electrodes have been widely employed for electrochemical systems.^[39, 40]

In our previous studies, various polyimide films were prepared as permselective membranes.^[41, 42] Depending on increased molecular weight of polymers, a highly stacked polymer structure was created with the method of thermal imidization. Therefore, in this synthesis, an unsymmetrical diamine monomer was used for preparation of the polyimide films. The PI structures that were prepared with unsymmetrical monomers were more suitable for GA-selective membrane applications because of their high solubility, low stacked structure, high surface roughness and porosity on Pt electrodes. This study synthesised versatile naphthalene-based polyimide films as selective membranes synthesis from 1,5-diaminonaphthalene, 4,4'-Diaminodiphenylmethane and three different dianhydrides. The chemical structure and physical properties of the prepared polyimides were characterized with different instrumental techniques (FT-IR, DTA, DSC, TGA and SEM procedures). The PI-modified Pt electrodes were formed by dropping the polyimide solution on the bare Pt electrode surface. The naphthalene-based polyimide films were used for selective and sensitive determination of GA in the presence of electroactive ((caffeic acid (CA) p-coumaric acid (CoA),

ascorbic acid (AA)) and non-electroactive interferants (lactose (LAC), fructose (FRU) and glucose (GLU)).

2. Experimental

2.1. Materials

All dianhydrides (pyromellitic dianhydride (PMDA), oxydiphthalic anhydride (ODPA) and 3,3',4,4'-benzophenonetetra-carboxylic dianhydride (BPDA)) that were used in the synthesis of polyimides as GA-selective membranes were obtained from Sigma-Aldrich. 4,4'-Diaminodiphenylmethane (MDA) and 1,5-diaminonaphthalene (1,5-DAN) were obtained as unsymmetrical monomers from Acros Organics Company. *N*-methyl-2-pyrrolidone (NMP-99.5%), Methanol (99.8 %), *N,N*-dimethyl formamide (DMF-98%) and tetrahydrofuran (THF-99.9%) were purchased from Merck Chemical, and they were of analytical grade. GA (3-hydroxytyraminium chloride), caffeic acid (CA), p-coumaric acid (CoA), ascorbic acid (AA), lactose (LAC), fructose (FRU), and glucose (GLU) that were used for the voltammetric studies were of analytical grade and supplied either by Sigma-Aldrich Chemical Company or Merck. 0.1 M phosphate buffer saline (PBS) (pH 7) was used as the supporting electrolyte solution.

2.2. Instrumentation

Fourier transform infrared spectroscopy (FT-IR) (Mattson 1000) was used for detecting the polymer film structure and surface modification of the Pt electrode in the range of 400–4000 cm⁻¹ using KBr disks. The thermal behaviours and stability of the synthesised polyimide were determined using TGA-50 (Shimadzu, Japan) and DTA-50 (Shimadzu, Japan) under an air atmosphere and at a heating rate of 10°C/min in a temperature range from 20 to 900°C. The DSC measurements were performed on a DSC-60 (Shimadzu, Japan). All samples (5 mg) were placed in sealed aluminium pans before heating under nitrogen flow (25 mL/min) at a scanning rate of 10 °C/min.

The surface morphologies of the prepared polyimide membranes were examined by using a Leo-Evo 40xVP SEM device at 20 kV. For the SEM measurements, the synthesised polyimides were coated on the glass surface and sputter-coated with a 100-Å-thick layer of gold-palladium in a sputter coater (Bal-Tec SCB 050).

All electrochemical experiments were carried out by using a conventional electrochemical cell with a three-electrode system comprising a platinum electrode (CHI, 2 mm diameter) modified with naphthalene-

based polyimides as the working electrode, a Pt wire coil as the auxiliary electrode and an Ag/AgCl electrode saturated with KCl as the reference electrode. The electrodes mentioned above were dipped into 10 mL glass cells. pH measurements used a Jenway 3010 pH meter. CV and DPV measurements were obtained from a BAS 100W electrochemical analyser (Bioanalytical Systems, Inc.). All electrochemical measurements were performed at room conditions.

2.3. Synthesis of polyimides

For synthesis of PI films, two-steps polycondensation reaction was used. In the first step of the reaction, poly(amic acid)s (PAAs) were prepared from different dianhydrides and a diamine mixture by an addition reaction. Then, a thermal imidization procedure was used on these synthesised soluble PAAs in the second step. MDA (0.75 mmol) and 1,5-DAN (0.75 mmol) were dissolved as a diamine mixture in NMP (20 mL). The dianhydride (1.5 mmol) was slowly added to this solution by stirring under a nitrogen atmosphere. The reaction mixture was stirred at 30°C for 6 h to form a viscous and homogeneous PAA solution. The PAA solution was converted into stable and inert polyimide films by the thermal imidization process. For this process, the PAA solution was spread into a Petri culture dish and baked at 90°C for the removal of the casting solvent. The semi-dried poly(amic acid) film was further dried and converted to polyimide by sequential heating at 120°C for 1 h, 150°C for 1 h, 180°C for 1 h, and 200°C for 3 h. The obtained polyimide was repeatedly washed with methanol and dried at 80 °C in a vacuum for 24 h. The polyimide was dissolved again in 20 mL of NMP. The homogeneous PI solutions were used for modification of electrode surfaces and preparation of gallic acid selective electrodes.

2.4. Preparation of PI-modified Pt electrodes

Before modification of Pt electrodes with polyimide, the surface of a working electrode was carefully cleaned and polished with successively finer grades of diamond polishing compounds and aqueous alumina slurry down to 0.5 mm and finally thoroughly washed with double-distilled water.^[43] For the preparation of naphthalene-based polyimide electrodes, firstly, solutions of naphthalene-based polyimide were made by dissolving about 0.1 g of the obtained dark amber powdery polyimides in 1 mL of NMP. Then, the polyimide solutions (2 µL) covered the surface of bare platinum working electrodes and dried at room temperature for at least 48 h. The schematic representation

diagram of the bare and PI-modified Pt electrodes and their GA sensing mechanism is displayed in Figure 1.

3. Results and discussions

Gallic acid is an important natural polyphenol that is present in fruits, vegetables, tea, wine, fruit juices, some beverages and various medicines.^[44] For detection of GA, voltammetric electrodes were prepared from polyimide membranes. The most important problem in determining gallic acid is the electroactive and non-electroactive interferants in the sample structure. As selective membranes, polyimides have been preferred for elimination of these interferants. Especially AA, CoA and CA are the most important electroactive interferants for voltammetric detection of GA. This is because in a bare Pt electrode, responses of CA, GA and AA are manifested between + 0.25 and + 0.15 V. However, GA is a smaller molecule than CA and AA, and for suppression AA and CA and responses at polymeric electrodes, polyimides are suitable inert materials as permselective membranes. The voltammetric response of CoA is + 0.6V and CoA does not interfere with a measurement made at 0.20 V. Therefore, a polyimide-modified electrode can detect only the gallic acid at 0.20 V. The interference problem was overcome by using polymeric membranes. Polyimide membranes also provide high adhesive properties, good coating characteristics, and chemical, mechanic and thermal stability. Thus, the shelf life and reproducibility of the prepared polyimide modified electrodes would be very high. In this study, we synthesised polyimides from 1,5-diamino naphthalene, 4,4'-diaminodiphenylmethane and dianhydrides. Asymmetric naphthalene groups were chosen for enhancement of solubility and processability of the polymer structure.

3.1. Characterization of PI films

FTIR measurement was also carried out to characterize the chemical and structural properties of the prepared polyimides. As shown in Figure 2, the C = O asymmetrical stretching absorption peaks at about 1791 cm⁻¹, C = O symmetrical stretching peak at 1737 cm⁻¹, C-N stretching peak at 1384 cm⁻¹ and characteristic deformation of imide peak at 720 cm⁻¹ are the basic absorption bands of the aromatic imide group in polyimide structures. After the polymerization reaction, characteristic peaks of poly(amic acid)s around 1660 cm⁻¹ were not detected, which reflected full imidization of poly(amic acid)s. In conclusion, we successfully synthesised a highly rigid structure of PI film. The FTIR result of

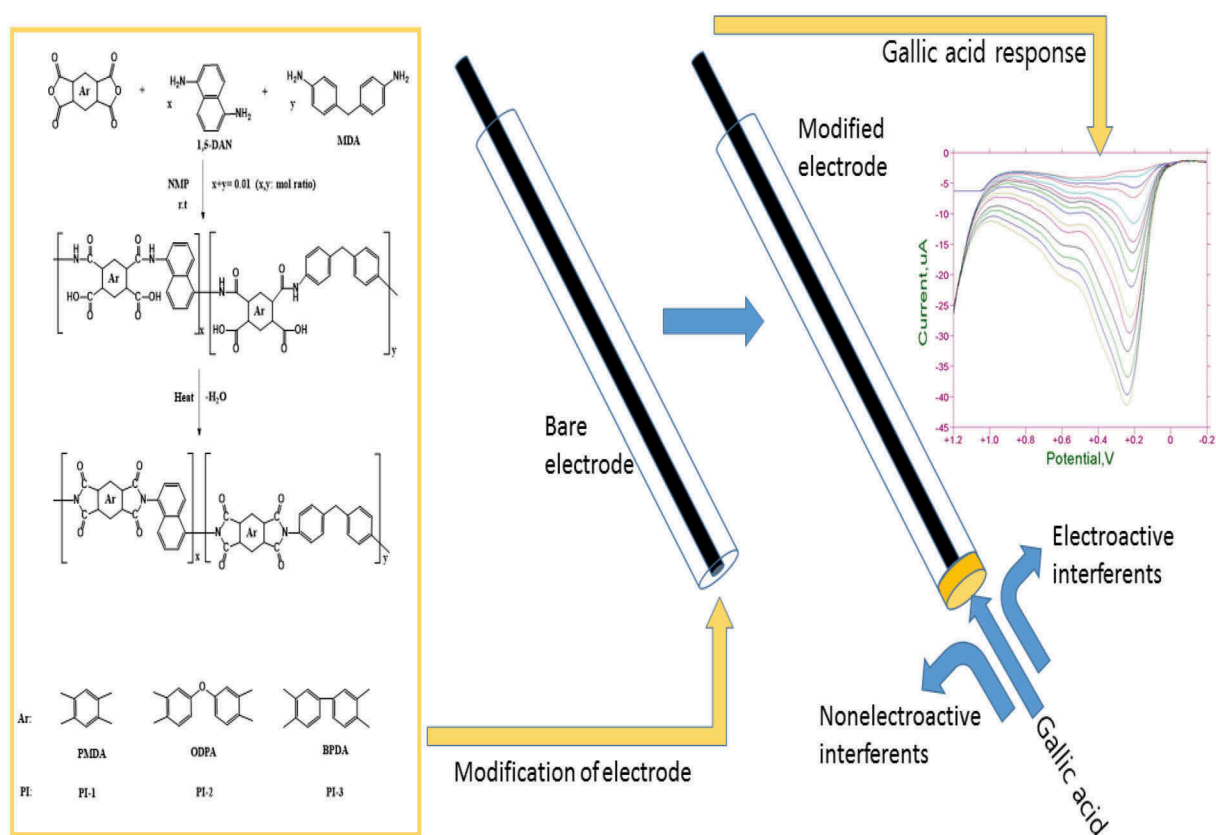


Figure 1. The schematic diagram of the bare and PI-modified Pt electrodes and their GA-sensing ability.

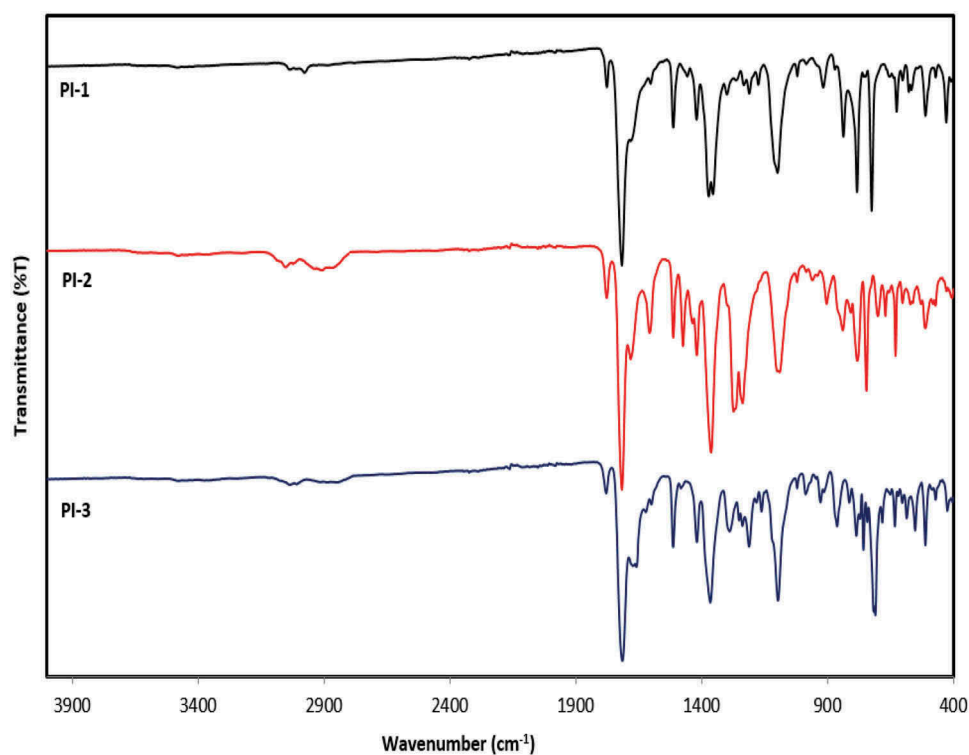


Figure 2. FT-IR spectrum of the naphthalene-based polyimides.

the prepared polyimides provides additional evidence for polyimide formation from monomers.

3.2. Thermal analysis of the PI films

Thermal properties in selective permeable membrane-based sensors and electrodes are an important parameter indicating the stability of the membrane material. In particular, if the thermal stability of the polymeric membrane is high, the electrode can be sterilised, and the shelf life of the electrode is long. The T_g value of the membrane provides us with information about the flexibility, processability, applicability and service temperature range of the polymeric structure. Thermogravimetric analysis was conducted on a thermo-balance (Shimadzu, TGA and DTA system 50) to evaluate the thermal stability of naphthalene-based polyimide films from their 10% weight loss temperatures (T_d^{10}) at a heating rate of $10^\circ \text{C min}^{-1}$ under air atmospheres.

Firstly, the thermal properties and stability of the naphthalene-based polyimides were investigated. The TGA thermograms (Figure 3) of PI membranes showed one thermo-oxidative degradation weight loss. This weight loss was observed in the range of 409–694 $^\circ\text{C}$ because of the thermal degradation of the imide ring in the polymer chain. Aromatic polyimide membranes have high chemical, thermal, mechanical and oxidative resistance due to the presence of heterocyclic imide units in the polymer structure and secondary interaction between polymer chains. These

properties of the prepared naphthalene-based polyimides provide an advantage for sensor applications in various fields.

Figure 4 shows the DTA thermograms of the polyimide membranes. All of the DTA thermograms were suitable for the TGA thermograms in Figure 3. All the polyimide membranes had inherently good thermal stability due to their strong interaction in the polymer chains.

The DSC thermograms and T_g values of the naphthalene-based polyimides were also given in Figure 5. The polyimide structure derived from pyromellitic dianhydride exhibited the highest T_g because of the rigid heterocyclic unit. The T_g value of naphthalene-based PI-1 was observed at 153 $^\circ\text{C}$.

The SEM images of the surfaces of the bare electrodes and polyimide-covered electrodes are presented in Figure 6 with different magnification rates. The polyimide-based electrode surfaces were remarkably different from the surface of the bare Pt electrode. There was an obvious morphology change when the modification of Pt electrodes varied from the bare electrode to the polyimide-based electrode. These results indicate that polyimide modification plays a significant role in electrode surface morphology and surface areas. In Figure 6, the polyimide film on the Pt electrode surface is very homogenous. In addition to porosity, roughness and fractal structure on the surface, large agglomerated particles were also observed on all the SEM pictures. These roughness structures were suitable for selectivity. From these

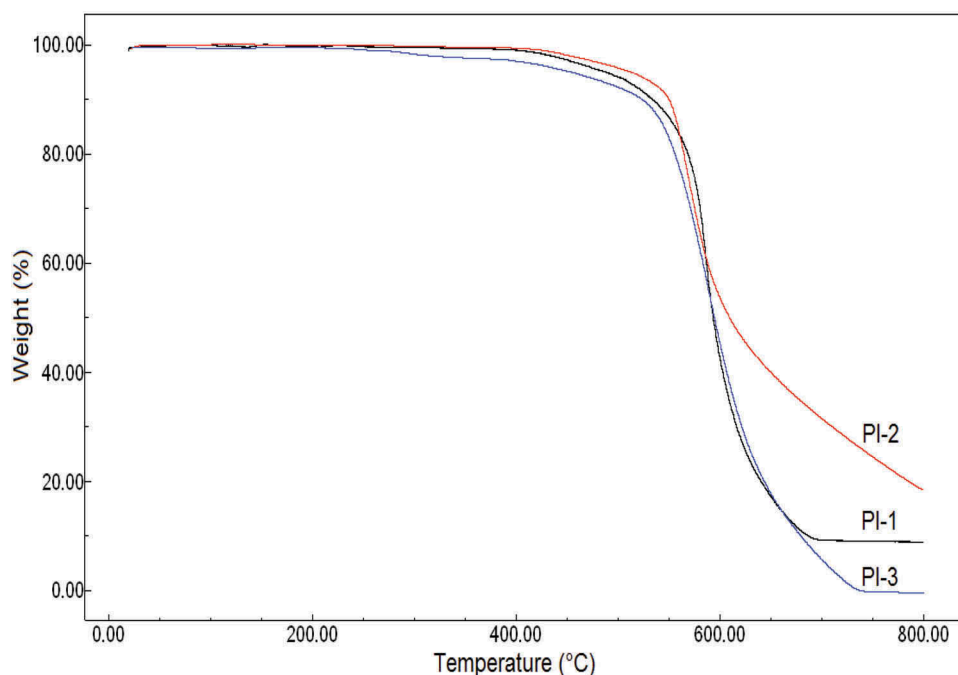


Figure 3. TGA thermograms of the naphthalene-based polyimides.

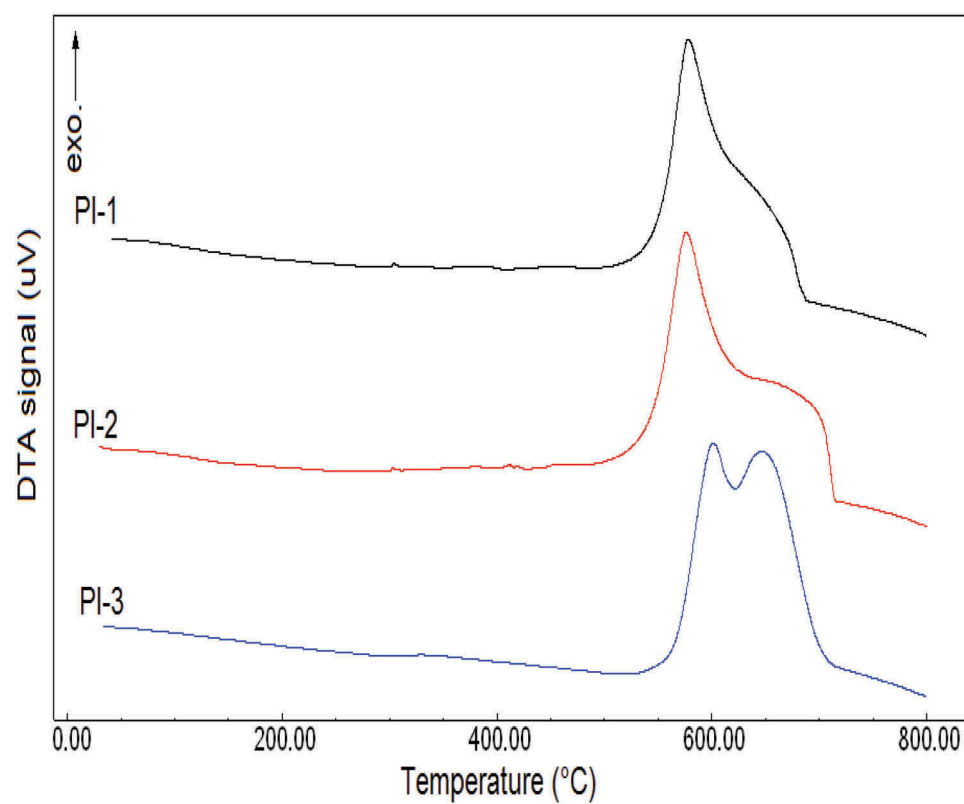


Figure 4. DTA thermograms of the naphthalene-based polyimides.

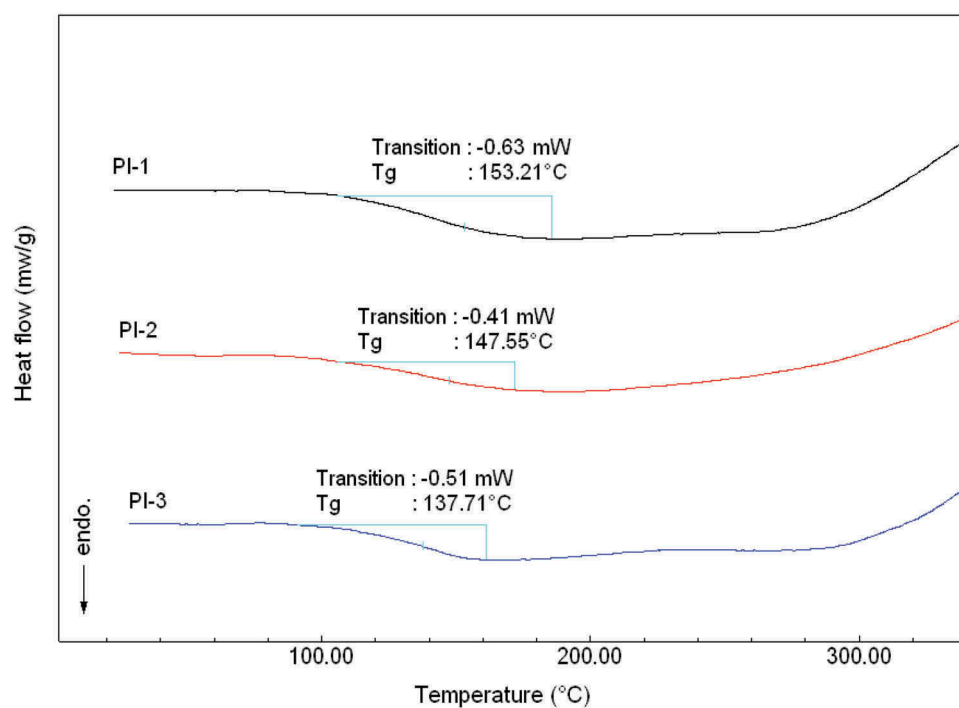


Figure 5. DSC thermograms and T_g values of the naphthalene-based polyimides.

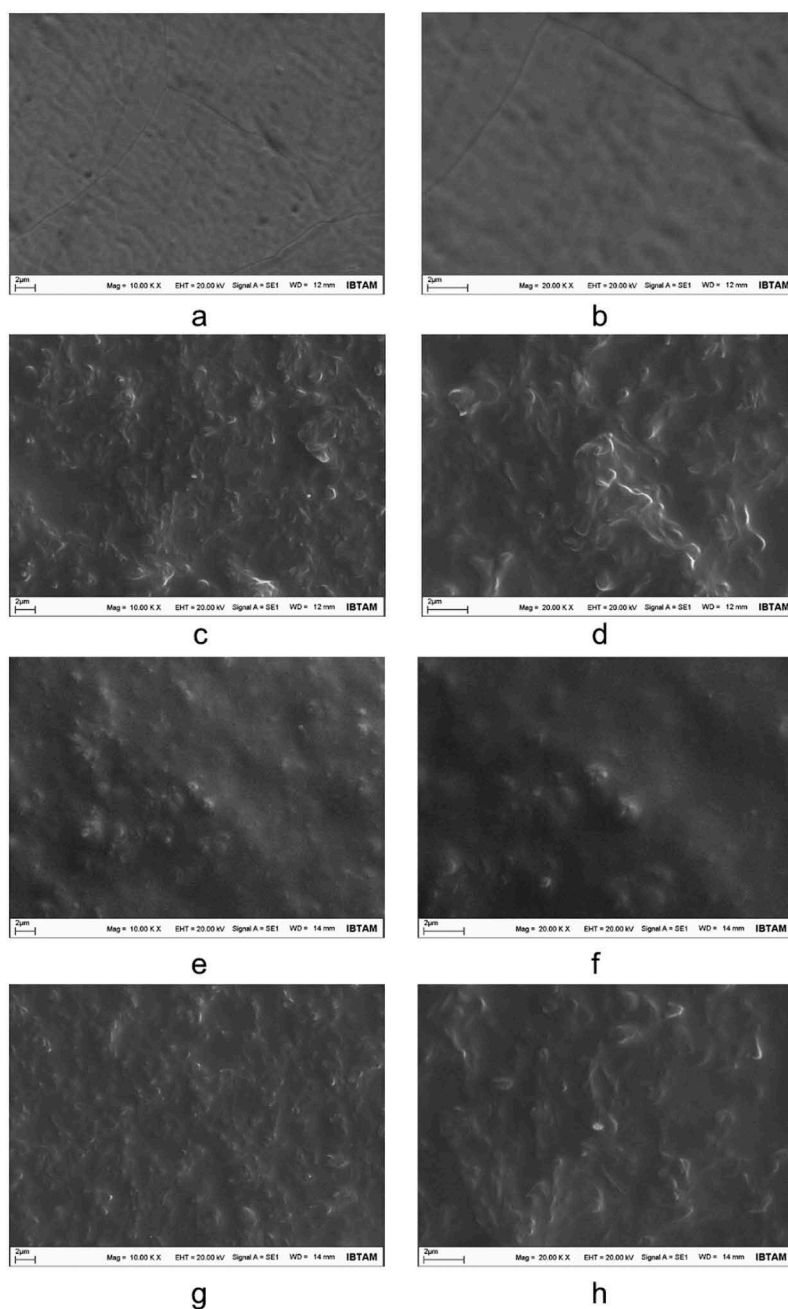


Figure 6. SEM images of the bare electrode (a; low magnification, b; high magnification) and naphthalene-based polyimide films (c; PI-1, e; PI-2, g; PI-3 (low magnification) d; PI-1, f; PI-2, h; PI-3 (high magnification)).

surfaces, the surface of the PI-1 structure was more porous and rougher than those of the polyimide-modified electrodes. For this reason, PI-1 had a higher electrode surface area. Thus, the response of this electrode was higher than those of the other prepared electrodes.

3.3. Voltammetric measurements with the PI-modified Pt electrodes

The various classes of polymeric materials used in electrode modification are selected carefully to improve

sensor selectivity and sensitivity, as well as resistance to fouling in the biological samples. As it is well-known, the major problem that is encountered with detection of GA in phenolic compounds is the coexistence of interfering species such as caffeic acid, p-coumaric acid and ascorbic acid.^[45–47] For this reason, polymer-based films that are going to be used as selective membrane must be only permeable to GA among the interfering compounds.

The DPV technique is more sensitive than the CV technique. Therefore, the DPV technique was used to

investigate the electrochemical behaviour of GA at the PI-modified Pt electrodes. Figure 7 shows the DPV behaviours of CA, CoA, GA and AA at pH 7.0 PBS at

the bare electrodes. Figure 8 shows the DPV behaviours of CA, CoA, GA and AA at pH 7.0 PBS at the PI-1, PI-2 and PI-3 modified Pt electrodes. Figure 8 shows that

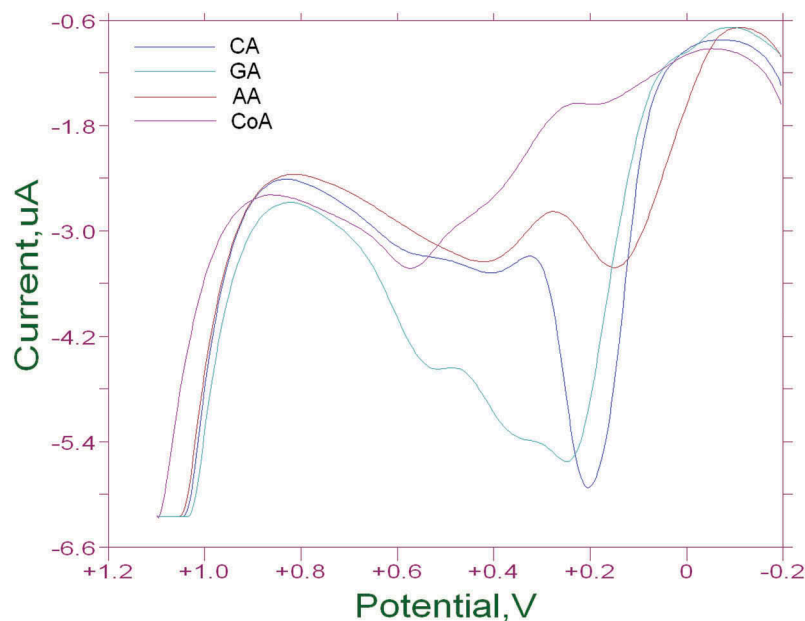


Figure 7. DPV behaviours of CA, CoA, GA and AA in PBS (pH 7.0) at the bare platinum electrode.

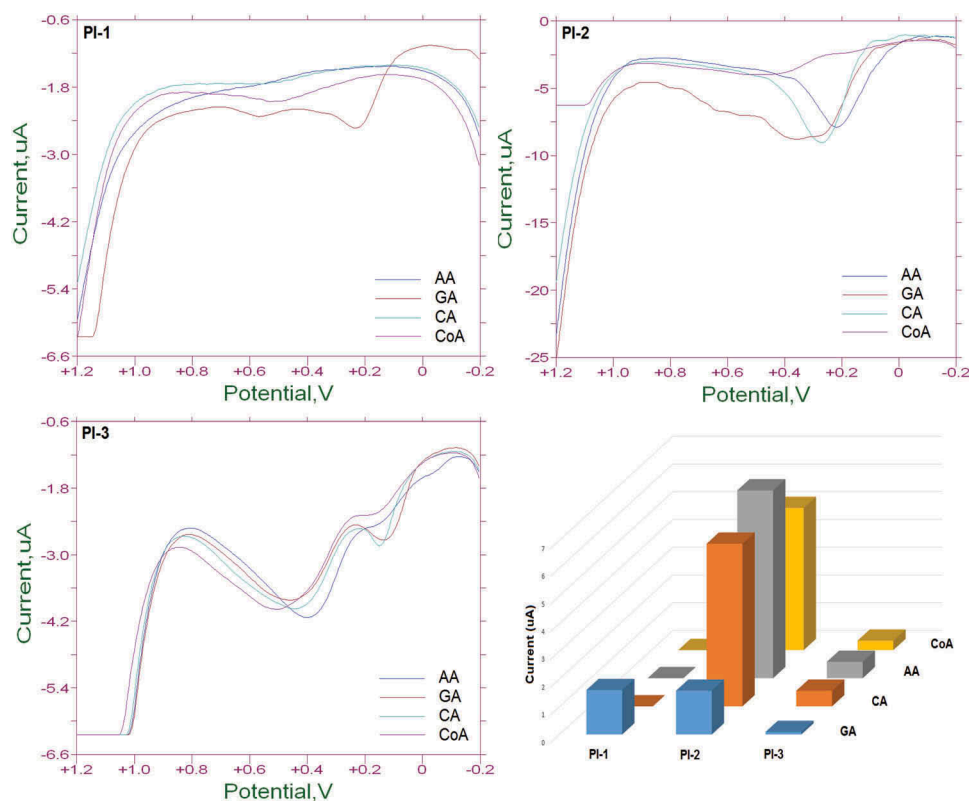


Figure 8. DPV behaviours of 2 mM AA, 2 mM CoA, 2 mM GA and AA and 2 mM CA in PBS (pH 7.0) at naphthalene-based PI-1, PI-2 and PI-3 electrodes.

the PI-1 modified electrode had a good oxidation peak for GA. From these voltammetric results, it is observed that the electrode prepared with 2 μL of PI-1 allowed GA oxidation while blocking unwanted responses from CA, CoA and AA interferences.

To evaluate the influence of film thickness on the performance of the PI-1 modified electrode, we adjusted the amount of the naphthalene-based polyimide solution on the bare Pt electrode. The voltammetric responses to GA of the PI-1 modified electrodes that were prepared with 2, 4, 6, 8 and 10 μL of the PI-1 solution are shown in Figure 9. From Figure 9, it is clearly seen that the voltammetric response towards GA by the PI-1 electrode modified with 6 μL of the PI-1

solution was higher than those of other electrodes. Therefore, the optimal film thickness of the PI-1 modified electrode was chosen as 2 μL for advanced GA biosensor applications.

Electrocatalytic activity of PI-1 modified Pt electrode is studied using cyclic voltammetry (Figure 10). Figure 10 shows that the PI-1 modified electrode had a stable and reversible cyclic voltammetry peaks. The results indicated that this simple modified electrode exhibited good electrocatalytic activity when compared with that at a bare Pt. In Figure 11(a), Cyclic voltammograms 2 mM GA on surface of PI-1 modified electrode at various scan rates (20; 50; 100; 200; 300 mV/s) were showed in PBS of pH 7.0. Dependence of redox peak

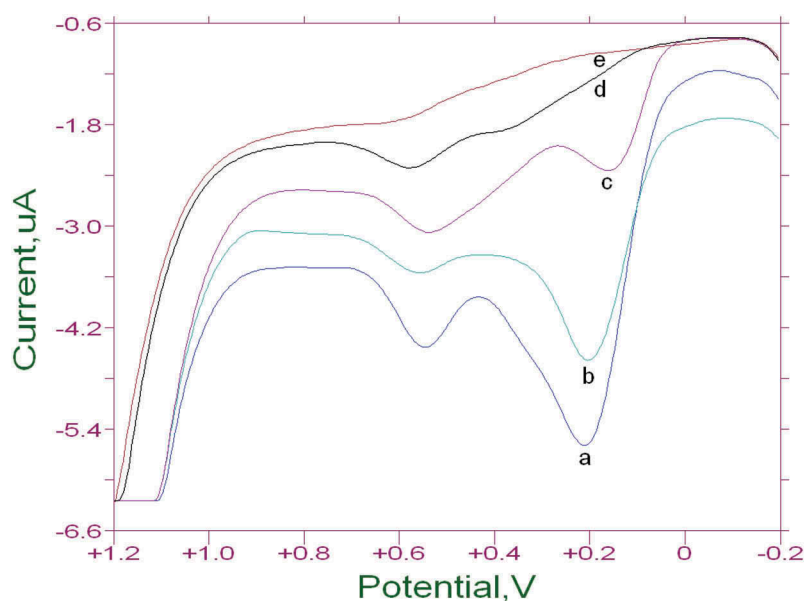


Figure 9. The influence of the film thickness on the GA response (PI-1 electrodes modified with PI-1 solution (a; 2 μL , b; 4 μL , c; 6 μL , d; 8 μL and e; 10 μL)).

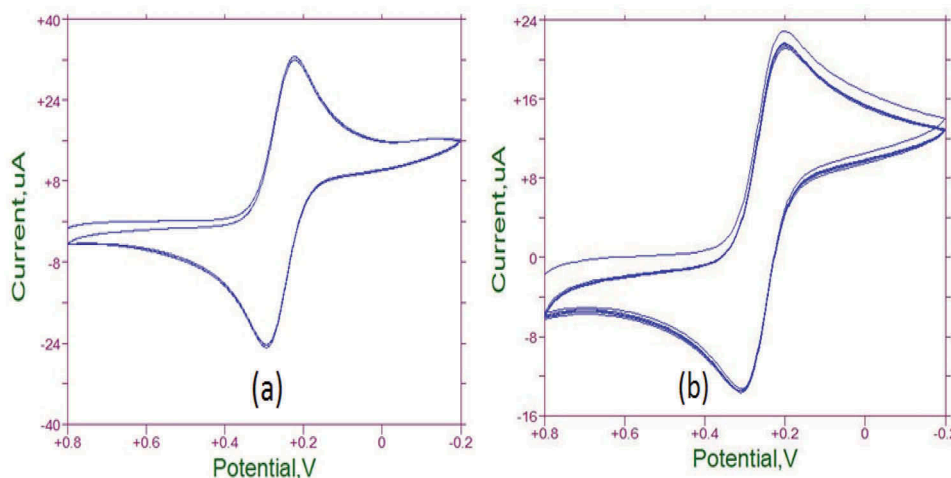


Figure 10. CV of 6mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ in 1.0 M KNO_3 at the bare Pt electrode(a) and PI-1 modified Pt electrode (b).

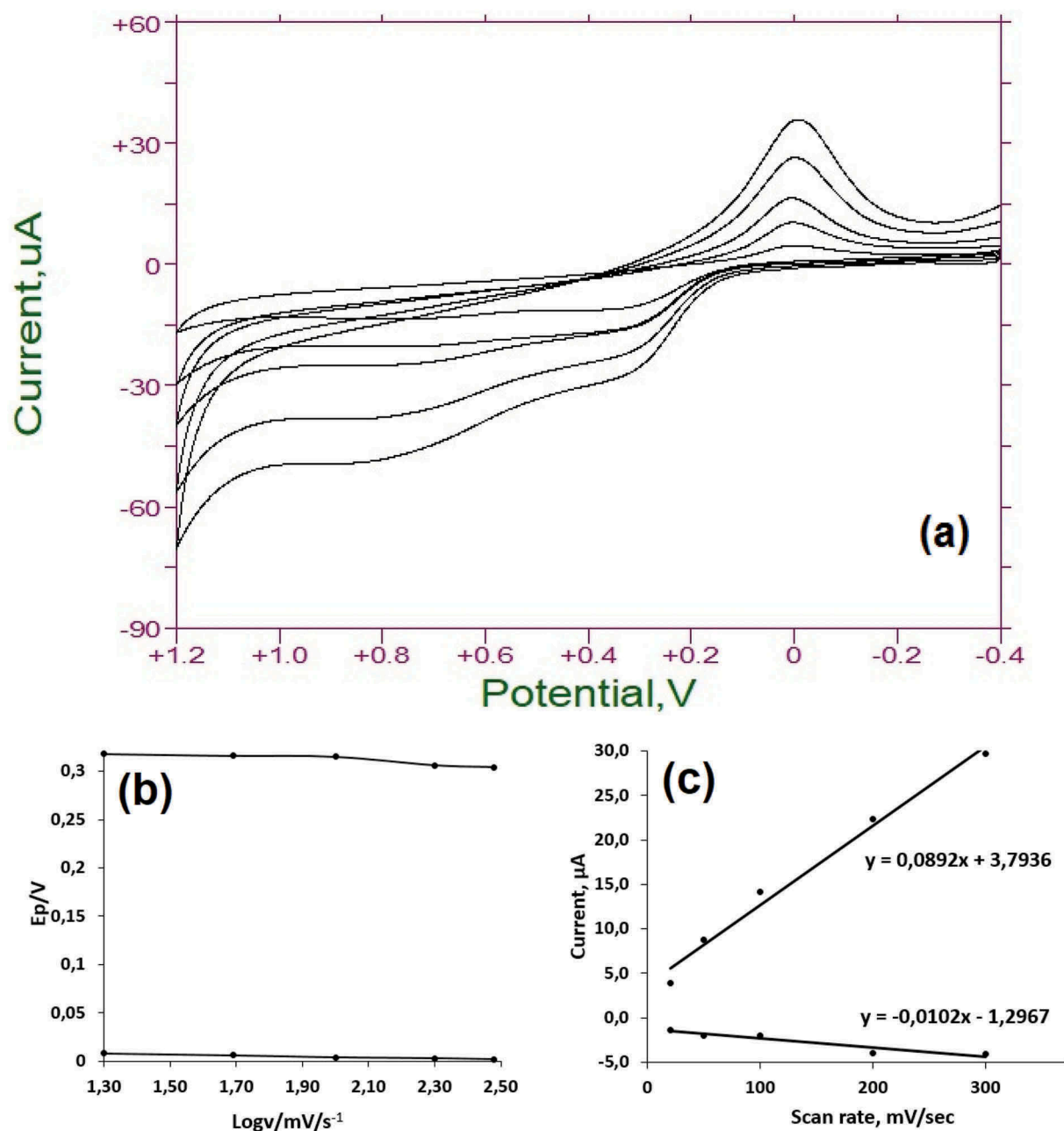


Figure 11. Cyclic voltammograms 2 mM GA on surface of PI-1 modified Pt electrode at various scan rates: 20; 50; 100; 200; 300 mV/s in PBS of pH 7.0 (a). Dependence of redox peak current on scan rate (b). Variation of peak potential vs logarithm of the scan rates from 20 to 300 mV/s (c).

current on scan rate (Figure 11(b)) and variation of peak potential vs logarithm of the scan rates from 20 to 300 mV/s (Figure 11(c)) were investigated.^[48] The results showed that this simple modified electrode exhibited suitable redox peak current.

The DPV curves of the PI-1 electrodes in different GA concentrations were also examined in the presence of various interferences (GA, CA, CoA, AA, LAC, FRU, and GLU) (Figure 12). Consequently, it was found that the oxidation peaks increased linearly with increasing

GA concentration at the PI-1 electrode, even in the presence of general interfering compounds.

From the voltammetric responses observed in Figure 12, a calibration curve was obtained for different GA concentrations (Figure 13). As it could be easily seen from the DPVs of the PI-1 electrode, the oxidation peak currents were linearly dependent on the concentrations of GA in the range of 1–15 mM with a correlation coefficient of 0.9935. The reversibility of the electrochemical measurements for the

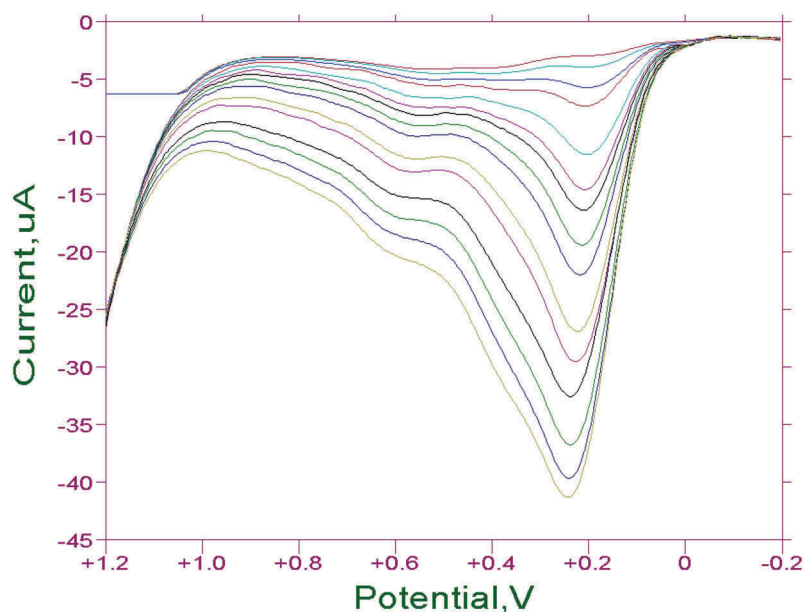


Figure 12. DPVs of the PI-1 electrode to increasing concentration of GA in the presence of interferences. (concentration of GA: 1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15 mM; (interferants: CA, CoA, AA, LAC, FRU, and GLU = 1 mM).

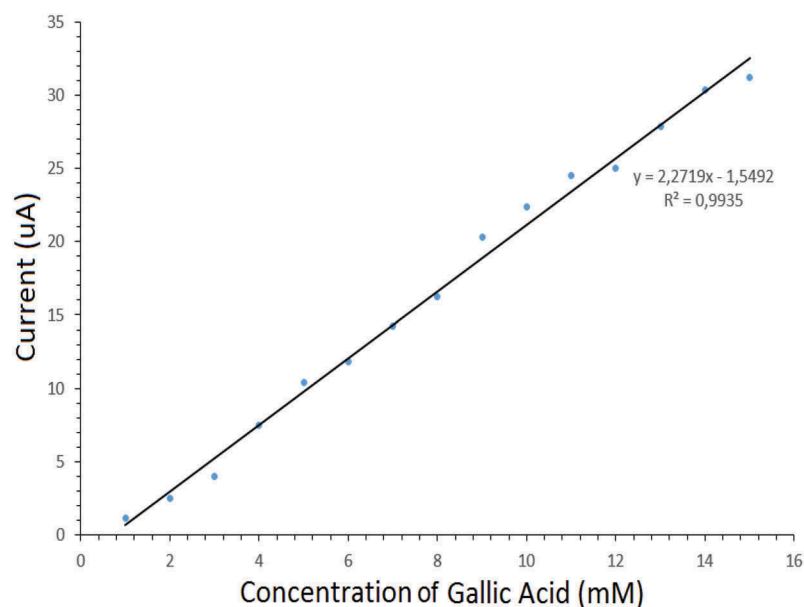


Figure 13. Calibration curves of PI-1 electrode for GA response.

proposed sensor was also investigated for 2 mM GA in the presence of electroactive (GA, CA, CoA and AA) and non-electroactive interferants (LAC, FRU and GLU) (Figure 14). The voltammetric results that were obtained from the successive measurements (8 runs) demonstrated that the PI-1 electrode provided good reproducible responses for the repeated curves.

3.4. Application to real sample analysis of the PI-1 electrode

The PI-1-modified Pt electrode was successfully applied for the determination of GA in real carob powder samples. Firstly, about 2 g three different dried carob sample was dissolved in 100 ml PBS (pH 7.0). Then, 5 mL of this test solution was transferred into the electrochemical cell

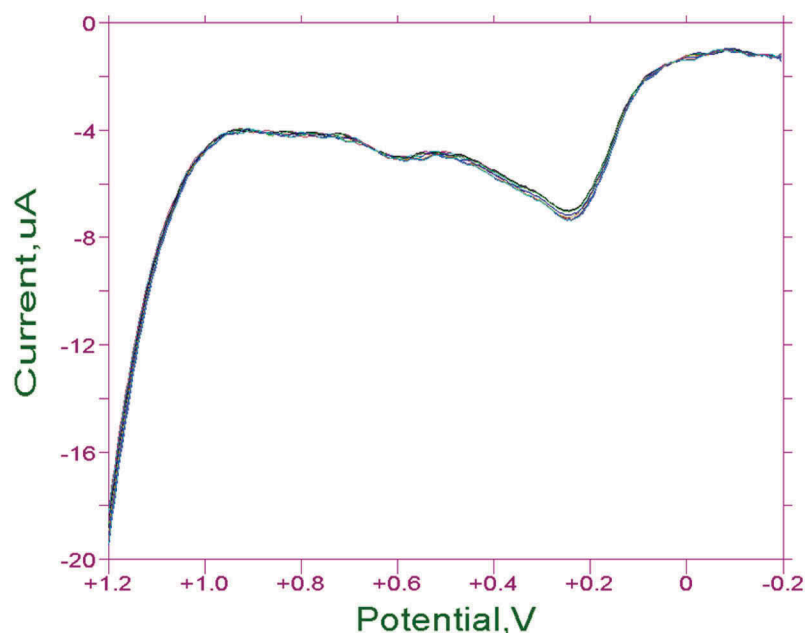


Figure 14. The reversibility of PI-1 electrode for 2 mM GA in the presence of the interfering compounds (interferants: CA, CoA, AA, LAC, FRU, and GLU = 1 mM).

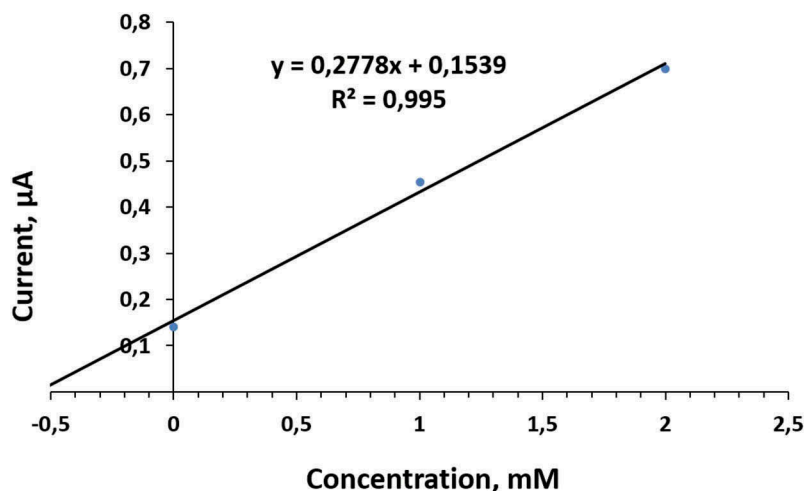


Figure 15. DPV curves of PI-1 modified electrode towards different GA concentrations in real sample.

and the GA contents were determined. Different concentrations from standard solution of GA were injected into the electrochemical cell including 5 mL test solution. In the other word the gallic acid level in the carob was determined by three parallel sample studies with the standard addition method. The standard addition curve was showed in Figure 15.

4. Conclusions

In this paper, a new series of naphthalene-based polyimide films as GA selective membrane was synthesised

from 1,5-diaminonaphthalene and 3,3',4,4'-benzophenonetetra-carboxylic dianhydride. The thermal behaviour, structure and morphology of the naphthalene-based PI films were characterized by FTIR, thermal analysis (DTA/TGA/DSC) and SEM techniques. Furthermore, the study also examined whether these PI films could be used as membranes for accurate and rapid determination of GA in the presence of various interferences. The PI-1 electrode completely eliminated the unwanted responses from CA, CoA and AA. The voltammetric experiment results showed that the PI-1 electrode had easy preparation, selectivity, wide linear

ranges, reproducibility and a very high correlation coefficient (R -value = 0.9935). Consequently, this paper described a selective and sensitive method for rapid and accurate detection of GA by DPV using a platinum electrode modified by naphthalene-based PI-1 film. However, the PI modified electrode can be used without any pretreatment for accurate determination of GA in real samples.

Acknowledgments

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Notes on contributors

Aziz Paşahan received his Ph.D. in Electrochemistry from İnönü University in 2008. He is now working as Assoc Prof. Dr. in Department of Chemistry, İnönü University. His current interest ranges from amperometric biosensors, sensor design and polymeric materials

Nurcan AYHAN obtained her M.Sc. degree from İnönü University. His research interests include amperometric sensor for analytes of biological importance.

İmren ÖZCAN Ph.D. student at İnönü University. She received her master's in 2015 from İnönü University. She is pursuing her Ph.D. degree in the field of polymer polymer synthesis and characterization under the supervision of Prof. Dr. Süleyman Köytepe

Serap Titretir Duran is presently working as a research scholar Department of Chemistry, İnönü University. His current field of interest is Analytical Chemistry. Duran received his Ph.D. in Analytical Chemistry from İnönü University in 2001. He is now working Dr. in Department of Chemistry, İnönü University

Süleyman Köytepe is presently working as a research scholar Department of Chemistry, İnönü University. His current field of interest is Polymer Chemistry. Köytepe received his Ph.D. in Polymer Chemistry from İnönü University in 2007. He is now working as Professor in Department of Chemistry, İnönü University. His current interest ranges from thermal stable polymers, biomaterials, polymeric composite materials and biosensors

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