



Electropolymerization of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (Purpald®)

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(First received 7 April 2019 and in final form 9 May 2019)

(DOI: 10.31590/ejosat.550431)

ATIF/REFERENCE: Soysal, M. (2019). Electropolymerization of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (Purpald®). *European Journal of Science and Technology*, (16), 159-165.

Abstract

In this study electropolymerization of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (Purpald®) on the disposable pencil graphite electrode (PGE) was described and the electroactivity of the polymer film coated and naked PG electrodes were checked against $K_3[Fe(CN)_6]$ / $K_4[Fe(CN)_6]$ in pH 8 Britton-Robinson (BR) buffer solution. The electropolymerization of Purpald® film was performed with cyclic voltammetry (CV). The optimal conditions of Purplad® film coated electrode were performed using electrochemical impedance spectroscopy (EIS). The conductivity of the Purplad® modified electrodes was compared with bare and p-phenylenediamine modified PG electrodes by EIS technique. The results indicated that electrosynthesized poly(Purplad®) film could be used for modification of electrodes to be used in electrochemical analysis and sensor applications.

Keywords: Conducting polymer, electropolymerization, Films, Triazole derivatives, Pencil graphite electrodes.

4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (Purpald®)'un Elektropolimerizasyonu

Öz

Bu çalışmada, tek kullanımlık kalem grafit elektrot (PGE) üzerinde 4-amino-3-hidrazino-5-merkaptto-1,2,4-triazolün (Purpald®) elektropolimerizasyonu tanımlanmış ve polimer film kaplı ve çıplak PG'nin elektroaktivitesi, pH 8 Britton Robinson (BR) tampon çözeltisi içerisinde hazırlanan $K_3 [Fe (CN) 6]$ / $K_4 [Fe (CN) 6]$ çözeltisi ile test edildi. Purpald® filminin elektropolimerizasyonu döngülü voltametri (CV) ile yapıldı. Elektrokimyasal empedans spektroskopisi (EIS) kullanılarak, Purpald® film kaplı elektrotun optimum koşulları belirlenmiştir. Purplad® ile modifiye edilmiş elektrotların iletkenliği, EIS tekniği ile çıplak ve p-fenilendiamin ile modifiye edilmiş PG elektrotları ile karşılaştırıldı. Sonuçlar, elektrosentezlenmiş poli (Purplad®) filmin, elektrokimyasal analizlerde ve sensör uygulamalarında kullanılacak elektrotların modifikasyonu için kullanılabilceğini göstermektedir.

Anahtar Kelimeler: İletken polimer, Elektropolimerizasyon, Filmler, Triazole Türevleri, Kurşun kalem elektrotlar.

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1. Introduction

Polymers are very long chain molecules formed by the recursive addition of relatively small molecules called monomers. Both synthetic and natural polymers are widely used in our daily life because of their wide use in various fields of applied science (Awuzie, 2017; Petersen et al., 2018).

Among the synthetic polymers, conductive polymers have attracted considerable interest as important polymeric materials since the early 1970's of poly(acetylene) and largely was focused on polypyrrole, polyfuran and heterocyclic molecules. Conjugated polymers derived from heterocyclic compounds have cropped out as very rewarding materials for electrochromic devices, electronics, supercapacitor, data storage, photovoltaic cell, biological and chemical sensors (Dispenza et al., 2015; Taşdelen, 2017; Lamiri et al., 2017; Carbas et al., 2017; Belhousse et al., 2017).

Polymer films based on modified electrodes have received extensive interest due to their broad scope of application in the chemical and biological sensor (Mantione et al., 2017; Gu et al., 2017). Modification can be achieved on electrode surfaces either by electropolymerization or by forming a polymer film directly on the electrode surface through a chemical reaction in a suitable medium. Electropolymerization is a facile and effective approach to preparing polymer film based electrodes. Electropolymerization process conditions (concentration, scan rate, the range of potential etc.) can be easily controlled and thus conductive films having different properties, such as thickness, and functions (e.g. impregnation of charge transport agents) can be obtained (Dunst et al., 2017; Kim and Palmore, 2012; Chen et al., 2013; Correa et al., 2016; Mangione et al., 2018; Castaneda et al., 2017; Boursicot et al., 2017; Wolfart et al., 2017; Devasurendra et al., 2017; Si and Song, 2018; Azak et al., 2018; Shamsipur et al., 2018; Rao et al., 2018).

Purplad[®] is a chemical material acting as a pigment and/or a colour exchanger agent used in the detection of aldehyde and aldehyde derivatives. Due to the S, C and N atoms present in the Purplad[®] structure, it shows an ideal ligand effect for metal complexes (Chu et al., 2018; do Carmo et al., 2015; Wondracek et al., 2016; Hill et al., 2009).

The goal of the present research is primarily to expose the similarity and discrepancy in electropolymerization conditions and electroactivities between the Purplad[®] and p-phenylenediamine film coated electrodes. Characterization of these polymer films were performed employing electrochemical impedance spectroscopy and cyclic voltammetry.

2. Material and Methods

2.1. Reagents and Instruments

Purplad[®] ($\geq 99\%$), p-phenylenediamine (98%, HPLC grade), sodium hydroxide ($\geq 98\%$), glacial acetic acid (100%), boric acid ($\geq 99.5\%$), phosphoric acid ($\geq 85\%$), dimethyl sulfoxide ($\geq 99.9\%$) were purchased from Sigma-Aldrich. Britton-Robinson buffer solutions (BR) were prepared with 2.47 g H₃BO₃, 2.29 mL CH₃COOH and 2.69 H₃PO₄ and 5 M NaOH solution of appropriate concentration was added until the desired pH was reached. All the used chemicals were of analytical purity and have not been subjected to any purification process. The chemical solutions used in the experiments were prepared with ultrapure water. All pH buffer solutions were stored at 4 °C. The analyte and monomer solutions were freshly prepared each day. Tombow (HB, 0.5 mm) pencil graphite was purchased from a stationery shop.

An IVIUM Compact Stat Plus Model electrochemical analyzer (The Netherlands) was used for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The three electrode system consisted of a pencil graphite electrode (PGE) as working, an Ag/AgCl electrode (BAS, Model RE-5B, USA) as reference, and a platinum wire as auxiliary. Thermo Scientific Orion 4-Star plus pH/Conductivity Meter was used to identify the pH of buffer solutions. Ultrapure water was provided from a LABCONCO WaterPro Water Purification Systems (USA).

2.2. Preparation of Purplad[®]-PGE

Electropolymerization of Purplad[®] onto the PGE was executed by using CV. Electrosynthesis solution consisted of 1×10^{-4} mol/L Purplad[®] in pH 8 BR buffer solution and the potential of the PGE working electrode was cycled 5 times between from 0.0 to 0.6 V at a scan rate of 25 mVs⁻¹. Then, PGE was removed from the synthesis solution and washed several times with pH 8 BR buffer solution to remove any residual compounds left within the polymer matrix. The p-phenylenediamine-PG electrode was prepared under the same conditions as Purplad[®]-PGE. Other working electrodes used for comparison purposes included bare PGE and p-phenylenediamine-PGE.

2.3. Impedance Measurements

The measurements of EIS were executed in a mixture of a 2.5 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] with 0.1 M KCl as the adjuvant electrolyte. The data of EIS has carried out in the frequency range from 100 kHz to 0.1 Hz by applying an AC voltage with 100 mV wave amplitude and at an electrode potential of 0.222 V, which is the formal potential of K₄[Fe(CN)₆]/K₃[Fe(CN)₆] solution.

3. Results and Discussion

3.1. Electrochemical Behavior of Purplad[®]

The formation of Purplad[®] film on the PG electrode surface is demonstrated in Figure 1. Electropolymerization of Purplad[®] was followed by CV performed in Britton-Robinson (BR) buffer (pH 8). The figure indicates one irreversible oxidation peak, which presumably was responsible for the electrochemical polymerization at 0.280 V vs. Ag/AgCl. As shown in Figure 1, Purplad[®] can easily be polymerized via potentiodynamic polymerization between (0.0) and (+0.6) V. After the first cycle, the oxidation peak current tended to decrease.

After completion of the electropolymerization process, the modified electrode was washed 10 times with 0.1 BR (pH 8) buffer solution and left to dry.

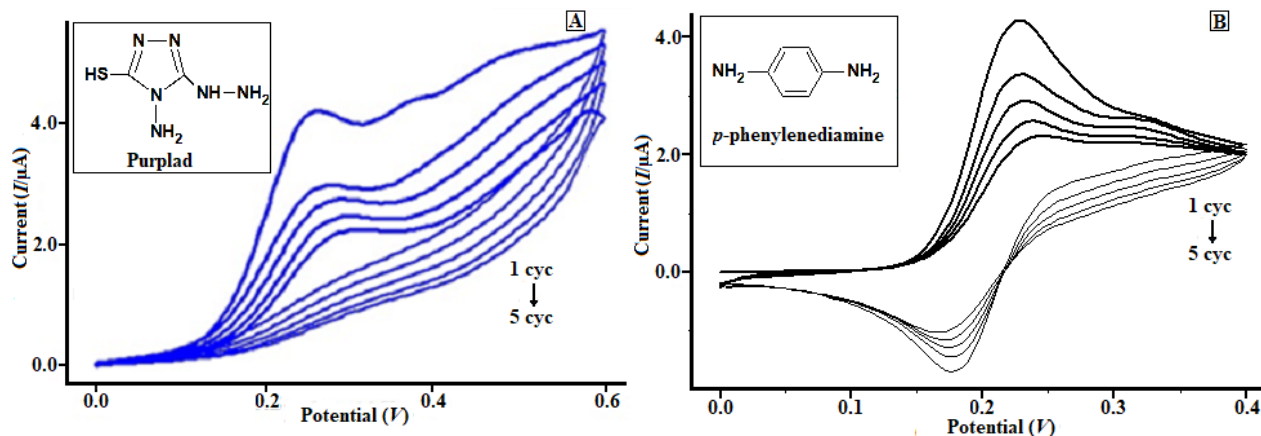


Figure 1. A) Electropolymerization of Purplad[®] on the PGE in pH 8 BR buffer containing 0.1 mM Purplad[®]. The potential sweeps applied between (0.0 V) and (+0.6 V) with the scan rate of 25 mVs⁻¹. B) Electropolymerization of p-phenylenediamine on the PGE in pH 8 BR buffer containing 0.1 mM p-phenylenediamine. The potential sweeps applied between (0.0 V) and (+0.4 V) with the scan rate of 25 mVs⁻¹.

As shown in Figure 1B, in the electropolymerization modification process with the p-phenylenediamine monomer known as conductive monomer, it is seen that the bare electrode surface changes at the end of each cycle and accordingly decrease of peak current values of the monomer obtained in the CV voltammogram. In this study, I claim that the Purplad[®] molecule can be used as a conductive monomer such as p-phenylenediamine. The obtained CV results confirm this argument.

Thereafter, the voltammetric signals of the Purplad[®] in BR buffer solutions at different pH (2, 3, 4, 5, 6, 7 and 8) values were examined by CV as shown in Figure 2. The oxidation peak current of the Purplad[®] shifted cathodically with the increasing pH. This result shows that -NH₂ functional groups in the structure of Purplad[®] molecule are oxidized at lower potential values in acidic media.

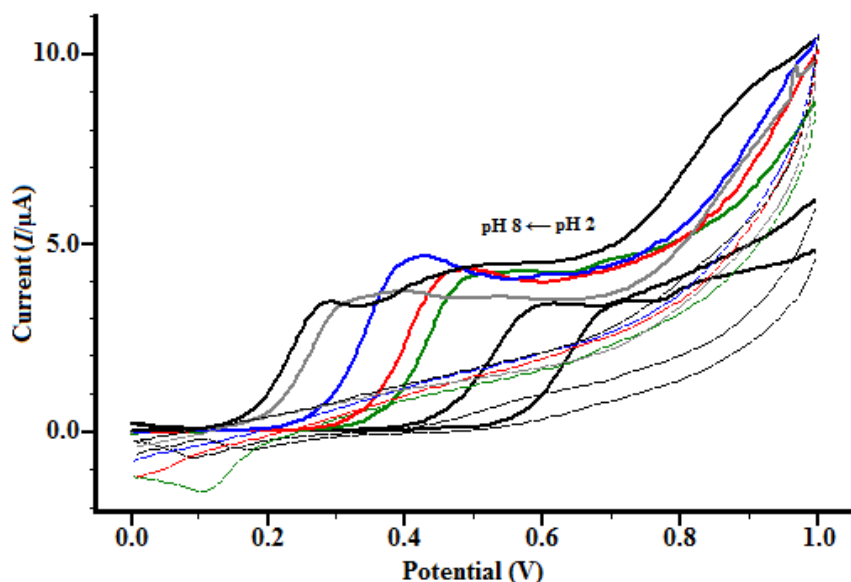


Figure 2. Electropolymerization of Purplad[®] on the PGE in different pH BR buffer containing 0.1 mM Purplad[®]. The potential sweeps applied between (0.0 V) and (+1.0 V) with the scan rate of 25 mVs⁻¹.

3.2. Electrochemical Characterization

The electrochemical behavior of the Purplad[®] film modified PG electrode was studied using [Fe(CN)₆]^{3-/4-} as redox solution by CV as shown in Fig. 3. Figure 3 also depicts the CV obtained by bare PGE. Bare electrode indicated sharp redox peaks at potentials of 0.260 V and 0.180 V; and Purplad[®] film modified PGE indicated wide redox peaks at potentials of 0.292 V and 0.160 V for anodic

and cathodic zones, respectively. When compared with the bare electrode, the modified electrode displayed well defined electrochemical features indicating rapid electron transfer kinetics almost at the same potential and peak current.

There is some decrease in current density compared to the bare electrode. This result suggests that the surface of the bare electrode is coated with Purplad[®] molecule and this case, the coated electrode partially forms an insulator. Although the coated electrode exhibits insulating properties, plenty of NH₂ and HS groups are formed on the electrode surface. These groups will be advantageous in the analysis process with the coated electrodes.

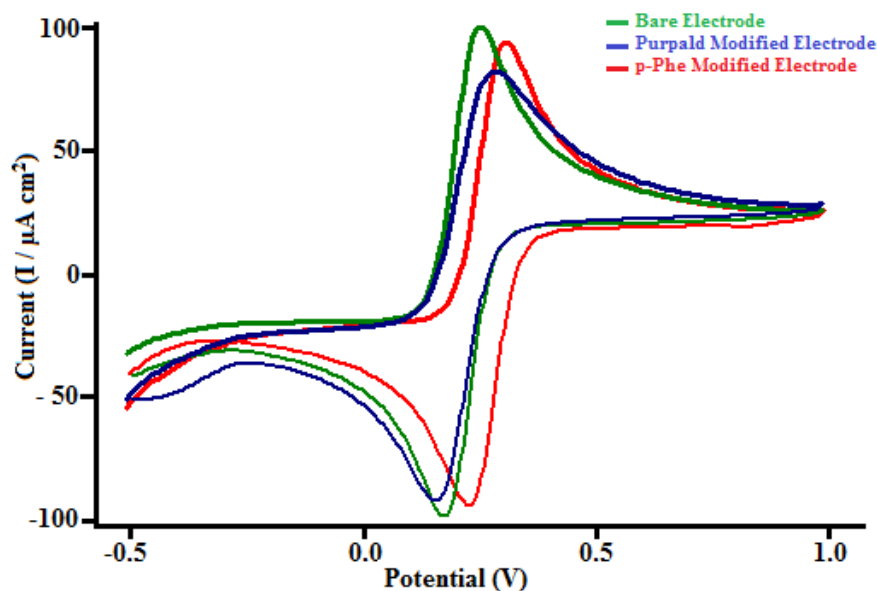


Figure 3. Cyclic voltammograms obtained with Purplad[®] modified and bare PGE using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in BR buffer (pH 8) solution. The potential sweeps applied between (-0.5 V) and (+1.0 V) with the scan rate 25 mVs^{-1}

When CV is used in electrochemical polymerization for the modification of voltammetric electrodes it is well known that the thickness of the resultant polymer film is somehow related to cycle number. Therefore, it may not be wrong to assume that number of the cycles not only has a significant effect on the polymer film thickness and morphology but also on its resistivity and charge transfer characteristics.

On the other hand, electrochemical impedance spectroscopy (EIS) is an efficient and quick method to elucidate physical and electronic properties of electrochemical systems such as diffusion coefficients, electron transfer rate constants, adsorption mechanisms, charge transfer resistances and capacitances.

The EIS is a potent tool for investigating the modified electrode surfaces for their resistivity and charge transfer characteristics. In the Nyquist impedance spectra, the semicircle fragment at higher frequencies corresponds to the charge-transfer limited process and linear fragment at lower frequencies can be attributed to the diffusion process. The diameter of the semicircle symbolizes the charge-transfer resistance (R_{ct}) at the electrode surface.

Figure 4 demonstrates the EIS of the polymer films of varying thickness obtained with various cycles of layers. For the fabrication of electrochemical sensors using polymeric coatings it is generally desirable to obtain reasonably thick films as they may contain large amount of functional groups on the surface and within the matrix. However, with thick films diffusion characteristics of the films are destroyed and conductivity of the electrode surfaces is unfavorably affected. As seen in Figure 4, film thicknesses obtained up to 10 cycles display desirable features in EIS spectra. Namely; semicircle with smaller diameter and linear part with 45° angle. Considering both the conductivity and the amplexness of functional groups film obtained with 10 cycles was chosen as optimum.

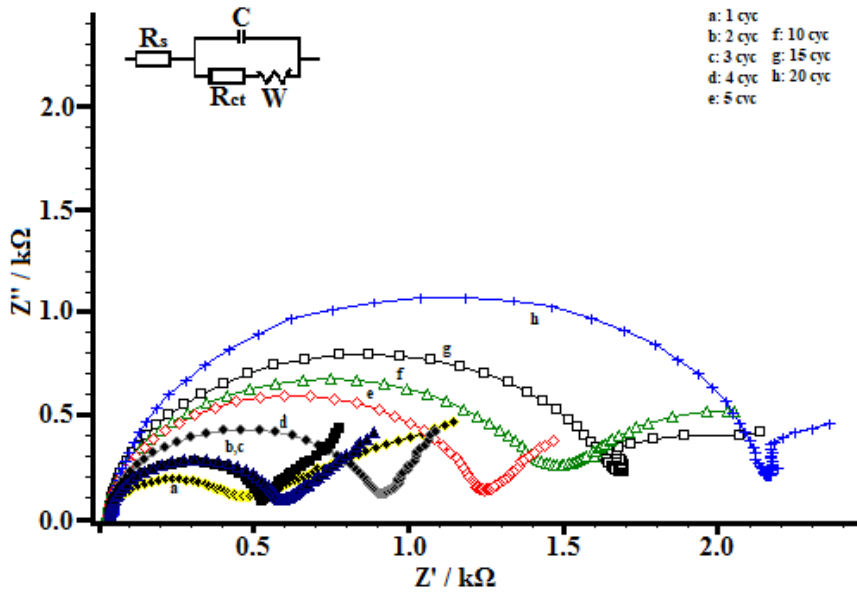


Figure 4. The Nyquist plots of PGE coated by Purplad® in presence of different number of cycle.

The ohmic resistance (R_s) is the resistance of the solution between the electrodes, which, unlike the impedance properties, act as a real resistance to mass transfer in the electrode reaction over a wide range of conditions. The interfacial charge transfer resistance (R_{ct}) is related to interfacial processes of charge/ion transfer through the electrode/electrolyte interface. If the chemical system is kinetically slow-going, it will show a large semicircle (R_{ct}), indicating that mass transfer, which is an important factor, is only effective in a very limited frequency range. The smaller semicircle (R_{ct}) indicates the rapid transfer capability of the charge/ions. This approach suggests that the surface of the electrode is conductive. In order to evaluate the conductivity of the Purplad® modified electrode, a p-phenylenediamine (known as conductive polymer) modified electrode was prepared and R_{ct} values of the bare and the polymer modified (p-Phe-PGE) electrodes were assessed from the EIS measurements (Figure 5).

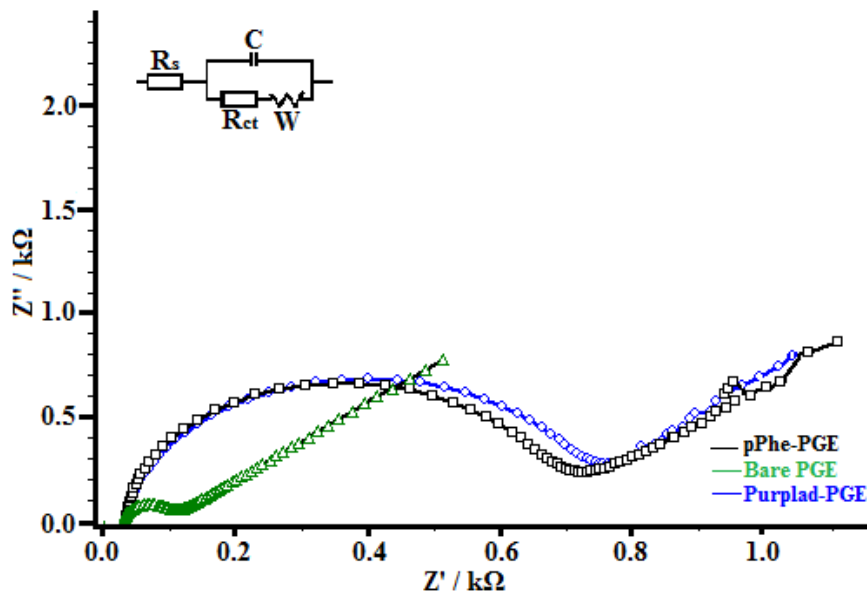


Figure 5. The Nyquist plots of bare PGE, p-Phe-PGE and Purplad®-PGE in the 2.5 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution.

According to Fig. 5, the R_{ct} value of Purplad®-PGE is slightly higher than the value of the p-Phe-PG electrode; yet, this value for both polymer electrodes are much higher than that of the bare electrode. This implies that the charge/ion transfer property on the electrode surface was almost the same for both p-Phe-PGE and Purplad®-PGE electrodes.

Conclusion

The Purplad® modified electrode was prepared by electrochemical polymerization and was successfully characterized by electrochemical techniques. Furthermore, comparison of the electrochemical properties of bare, p-phenylenediamine modified and Purplad® modified electrodes were performed by EIS and CV measurements. As the results implied, Purplad® modified electrodes can be used for further sensor studies.

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