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Research Article/ Araştırma Makalesi

Electrochemical Synthesis of Prussian Blue in Conducting Poly (Vinylferrocene) Film

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Abstract

In this study, preparation of prussion blue (PB) and poly(vinylferrocene) PVF modified disposable pencil graphite electrode (PGE) by formation of PB directly inside the iron-containing PVF is described. The modified electrode has the potential to be used for biosensor studies combining the advantages of PB and PVF mediators. Formation of PB inside the polymer has been confirmed by cyclic voltammetry. Furthermore, experimental studies showed that the modified PGE had electrocatalytic activity towards hydrogen peroxide (H_2O_2) reduction and thus can be used for fabrication of an amperometric H_2O_2 biosensor.

Keywords: Mediator; Prussian blue; Poly(vinylferrocene) ; Hydrogen peroxide reduction ; Pencil graphite electrode

İletken Poli (Vinilferrosen) Filmi İçerisinde Prusya Mavisinin Elektrokimyasal Sentezi

Öz

Bu çalışmada, doğrudan doğruya demir içeren poli (vinilferrosen) (PVF) içerisinde prusya mavisi (PB) oluşturularak PB ve PVF ile modifiye edilmiş tek kullanımlık kalem grafit (KGE) elektrotun hazırlanması anlatılmıştır. Modifiye elektrotun PB ve PVF'in avantajlarını birleştirerek biyosensör çalışmalarında kullanılma potansiyeli bulunmaktadır. PB'nin polimerin içerisinde oluştuğu dönüşümlü voltametri ile gösterilmiştir. Dahası, deneysel çalışmalar modifiye KGE'un hidrojen peroksitin (H_2O_2) indirgenmesine karşı elektrokatalitik aktivite gösterdiğini ve bundan dolayı amperometrik bir H_2O_2 sensörünün geliştirilmesi için kullanılabileceğini ortaya koymuştur.

Anahtar Kelimeler: Medyatör; Prusya mavisi; Poli (vinilferrosen); Hidrojen peroksit indirgenmesi ; Kalem grafit elektrot

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1. Introduction

Electrochemical biosensors are devices which are generally used for monitoring biological analytes. In most cases, the biosensor configuration is composed of an enzyme to ensure selectivity and specificity. Oxidase-type enzymes which act as an oxidizer for a specific substrate produce hydrogen peroxide (H_2O_2) as a side product during the returning of the substrate to its original state (Ricci & Palleschi 2005). Therefore, detection of low amounts of H_2O_2 is of great importance.

Although both enzymatic and non-enzymatic methods are existing in this field, enzymatic approach has the disadvantages of high cost as well as low stability and possibility of denaturation. Thus, non-enzymatic detection of H_2O_2 is gaining more and more interest in biosensor studies. Electrochemical mediators which catalyze either oxidation or reduction of H_2O_2 have been therefore preferred to enable construction of enzymeless H_2O_2 biosensors in the last decade (Zhang et al 2011, Jiang et al 2011).

Prussian Blue (PB) is one of the most well-known electrochemical mediators which efficiently catalyze reduction of H_2O_2. Electrochemical deposition of PB onto a conductive electrode surface can easily be carried out from an aqueous mixture of ferric (Fe^{3+}) and ferricyanide ($[Fe^{III}(CN)_6]^{3-}$) ions either at open circuit or by applying a suitable potential (Karyakin 2001). Electrochemical synthesis of PB using intrinsic iron contained in materials such as clay (Zen et al 2000) and graphite (Vishnu & Kumar 2017) has also been reported.

Poly(vinylferrocene) (PVF) is an iron containing redox type conducting polymer which has long been used as a mediating agent for biosensing purposes (Kuralay et al 2006, Özer et al 2007, Türkmen et al 2014). Due to its hydrophilic properties, the vinyl monomer is compatible with enzymes. Moreover, hydrophilicity of the monomer allows functional groups to relate easily on the surface of the electrode (Saleem et al 2015). A conductive and porous PVF film can simply be deposited onto the working electrode by electrooxidation of methylene chloride solution of the polymer containing tetra-n-butyl ammonium perchlorate (TBAP) as the supporting electrolyte.

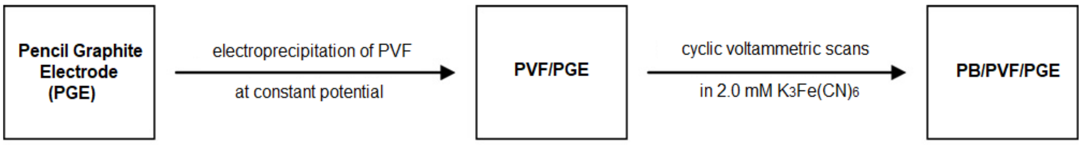
In this study, preparation of PB and PVF modified disposable pencil graphite electrode (PGE) by formation of PB directly inside the iron-containing PVF is described. The most important feature of the modified electrode is lack of an additional Fe precursor together with ease of preparation. The modified electrode has the potential to be used for biosensor studies combining the advantages of PB and PVF mediators. PVF was electrodeposited onto the electrode surface by constant potential electrolysis and PB was generated in the polymer matrix via cyclic voltammetric scans by the interaction of $[Fe(CN)_6]^{3-}$ ions with the iron atoms in the polymer. Formation of PB inside the polymer has been confirmed by cyclic voltammetry. Catalytic activity of PB formed in the polymer matrix was tested for electrochemical reduction of H_2O_2 and the performance of the PB/PVF modified PGE electrode was evaluated by chronoamperometry.

2. Materials and Methods

Poly(vinylferrocene) was obtained from Polysciences and tetra-n-butylammonium perchlorate (TBAP) was obtained from Fluka. $K_3[Fe(CN)_6]$, KCl, NaH_2PO_4, Na_2HPO_4 and methylene chloride were purchased from Sigma-Aldrich and used as received. Hydrogen peroxide solution was diluted from 30% aqueous H_2O_2 stock solution (Sigma-Aldrich). All solutions were deoxygenized with high purity nitrogen gas prior to the experiments.

A three-electrode electrochemical cell was used with a disposable pencil graphite electrode (PGE) ($r = 0.25$ mm) as the working electrode. A saturated calomel electrode (SCE) or a Ag/AgCl was used as the reference electrode and a Pt wire was used as the counter electrode. Cyclic voltammetry, and choronoamperometry studies were carried out with CH Instruments System, Model 600E.

PVF film was electrodeposited onto the working electrode by constant potential electrolysis at +0.7 V vs. Ag/AgCl. Formation of PB inside the polymer film was realized via cyclic voltammetric scans between potentials -0.2 – +1.2 V vs. SCE. Preparation route for PB/PVF modified PGE is given in Scheme 1.



Scheme 1. Preparation route for PB/PVF modified PGE.

3. Results and Discussion

Chemical structure of PVF is given in Figure 1. It is clear from the figure that the polymer film contains one Fe atom per the monomer which is enables synthesis of PB within the polymer matrix.

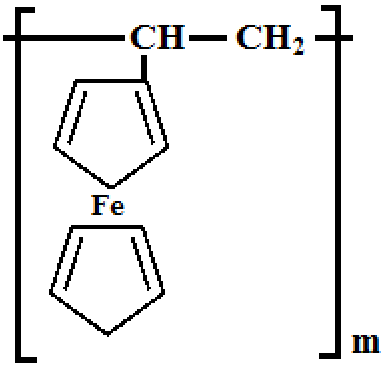


Figure 1. Chemical structure of PVF

PVF was electrodeposited onto the electrode surface by electrooxidation of 1.0 mg mL^{-1} PVF solution in methylene chloride containing 0.1 M TBAP at +0.7 V vs. Ag/AgCl. The charge passed during the electrolysis was 50 mC in order to assure formation of a satisfactory amount of polymer on the electrode surface. Afterwards, the polymer coated electrode was placed in electrochemical cell containing 2.0 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl. PB was generated in the polymer matrix via 20 cyclic voltammetric scans by the interaction of $[Fe(CN)_6]^{3-}$ ions with Fe atoms in the polymer matrix. The polycyclic voltammogram recorded during the formation of PB is given in Figure 2.

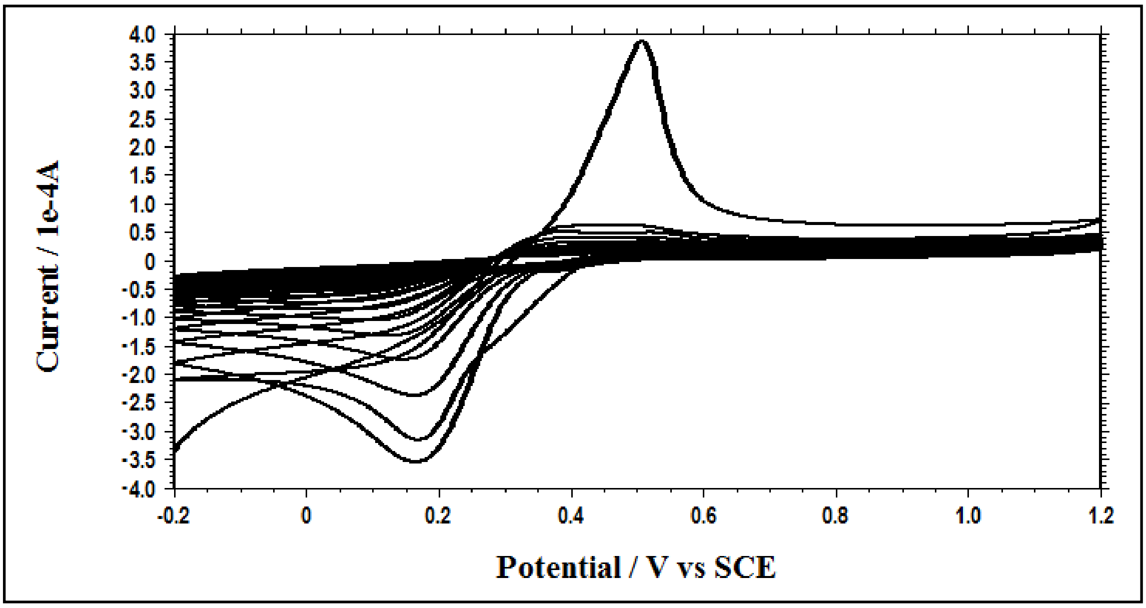


Figure 2. Polycyclic voltammogram of 2.0 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl recorded with PVF coated PGE. (Scan rate: 100 mV s^{-1})

The electron transfer mechanisms occurring at PB modified electrode has been previously reported in the literature (Itaya et al 1982, Abbaspour and Kamyabi 2005). Assuming $Fe_4^{III}[Fe^{II}(CN)_6]_3$ as the formula for PB, the proposed mechanism includes electrochemical reduction and reoxidation steps as given in Equations 1 and 2:

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4e + 4K^+ \rightarrow K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 \qquad (1)$$

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 3A^- \rightarrow Fe_4^{III}[Fe^{III}(CN)_6A^-]_3 + 3e \qquad (2)$$

where A^- represents the anions of the supporting electrolyte used.

Catalytic activity of PB formed in the polymer matrix was tested for electrochemical reduction of H_2O_2. For this purpose, CVs of H_2O_2 solutions from 1.0 mM to 4.0 mM containing 50 mM phosphate buffer solution (PBS) (pH = 7.4) were recorded with PGE containing PB modified PVF film (Figure 3) and compared with the CV of blank PBS solution. As clearly seen from the figure, significant increase in the currents were observed in the negative potential region and this was attributed to the catalytic activity of the formed PB in the polymer film towards reduction of H_2O_2.

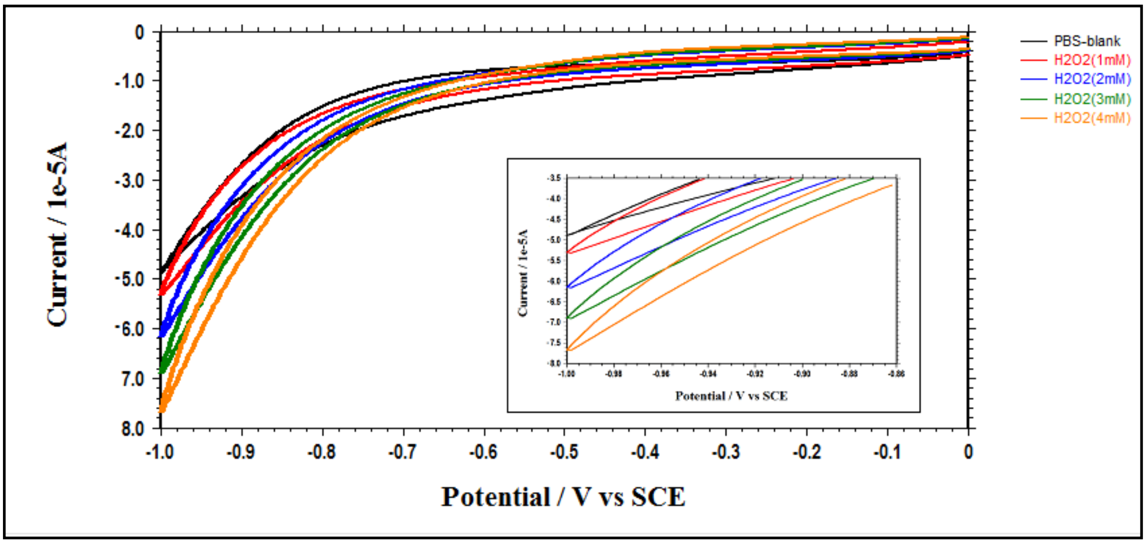


Figure 3. CVs of blank PBS solution and H_2O_2 solutions recorded with PB/PVF modified PGE. (Scan rate: 100 mV s^{-1})

Finally, the potential of the PB/PVF modified PGE as an amperometric H_2O_2 sensor was evaluated with chronoamperometry. Figure 4 shows the typical current-time curve after successive additions of certain concentrations H_2O_2 to a continuously stirred N_2-saturated PBS solution (pH = 7.4). The chronoamperogram indicates that the modified electrode system reveals a significant response to increasing H_2O_2 concentrations.

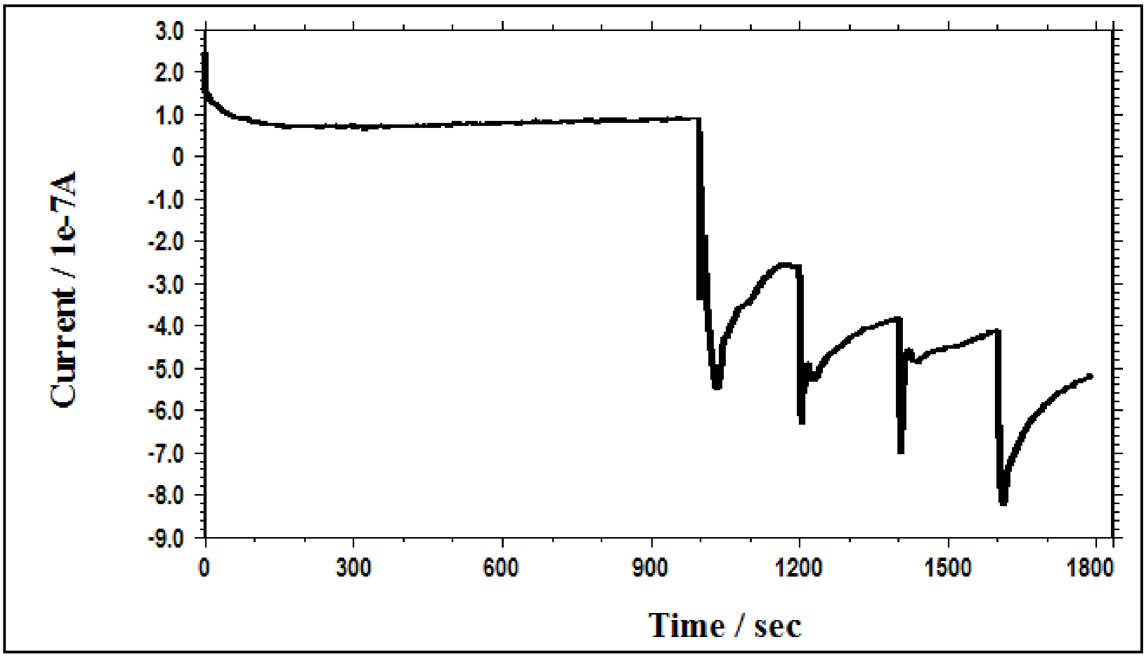


Figure 4. Current-time responses of PB/PVF modified PGE electrode to successive injections of H_2O_2 into 50 mM PBS (pH = 7.4) at 0.1 V vs. SCE

4. Conclusions

In this study, preparation of PB/PVF/PGE was described by formation of PB directly inside the iron-containing PVF. The modified electrode has synergistic effect combining the advantages of PB and PVF mediators. According to the experimental results, PGE has electrocatalytic activity towards H_2O_2 reduction and thus can be further developed as an amperometric H_2O_2 biosensor.

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