



Carbon electrode sensitivity enhancement for lead detection using polypyrrole, ionic liquid, and nafion composite

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Received 6 August 2021; 1st revision 30 May 2022; 2nd revision 1 June 2022; 3rd revision 13 June 2022; Accepted 15 June 2022;
Published online 29 July 2022

Abstract

This paper concerns enhancing a lead detection sensor using a combination of polypyrrole (PPy), Nafion (N), and ionic liquid (IL) with thick-film or screen-printing technology on sensitive material-based carbon electrodes. Electrode characterization using a scanning electron microscope (SEM) was conducted to see the morphology of sensitive materials, showing that the spherical particles were distributed evenly on the electrode surface. Analysis using energy dispersive spectroscopy (EDS) shows that the element's atomic composition is 84.92 %, 8.81 %, 6.26 %, and 0.01 % for carbon, nitrogen, oxygen, and bismuth, respectively. Potentiostat measurement with the ambient temperature of 25 °C on a standard lead solution with concentration ranging from 0.05 to 0.5 mg/l yields an average output voltage ranging from 2.16 to 2.27 V. It can be concluded that the sensor is able to detect lead with a sensitivity of 0.21 V in each addition of solution concentration (mg/l) and give an 84 % concentration contribution to the voltage.

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Keywords: lead detection; thick film; polypyrrole; Nafion; ionic liquid.

I. Introduction

Lead substances can be found in many places, including food and agricultural products such as fruits and vegetables. The lead substance in the body could inhibit the photosynthesis rate, change the shape of cells, reduce the size of cells, hinder the growth rate of children, cause muscle pain, damage the nerves of the brain, weaken liver function, and damage the kidneys until death [1][2][3]. Therefore, it is critical and a source of worry for researchers to identify lead content in environmental, dietary, and bioassays. Lead content assays, such as atomic absorption spectrophotometry [4][5][6], differential

pulse anodic stripping voltammetry (DPASV) [7][8][9], and square wave anodic stripping voltammetry [10][11][12], continue to be effectively developed.

Due to their affordability, ease of use, great stability, high sensitivity, and low detection limits, electrochemical techniques, particularly electropolymerization, have gained widespread acceptance as electrode coatings for heavy metal detection sensors [13][14][15]. The advantages of mercury film-based electrodes (MFE) [16][17], such as their surface cleanliness, repeatability, high sensitivity, and high hydrogen potential, have led to their application in electrode coating processes [18][19]. The issue is that mercury is a harmful substance. The use of bismuth films (BiF), a different technique established in this field, has electrode coating properties that are nearly identical to those

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of mercury electrode coating. Electro polymerization was used to create BiF at electrodes such as glass carbon electrode (GCE) [20][21][22], carbon paste electrode (CPE) [23][24][25], boron-doped diamond electrode (BDDE) [26][27][28], and carbon electrodes with screen printing [29][30]. In this study, the thick film-based SPCE method for producing electrodes was selected after taking process time and production costs into account.

Polypyrrole (PPy) is a conductive polymer with electrical properties that are widely used as sensor materials. PPy can be synthesized to have electrical conductivity up to 1000 S/cm, which is close to metal conductivity [31][32][33]. In addition, PPy can be deposited on a carbon electrode by an electro polymerization method so that the pyrrole precipitates form a sensitive membrane of the sensor. An electrochemical solution and electrode modifier with a high ionic conductivity, ionic liquid (IL) is frequently employed in the production of sensors [34][35][36]. To increase the sensitivity of heavy metal detection, Nafion (N), a material with great anti-pollution capacity, chemical inertia, and high permeability to pertinent cations [37][38], is used.

This study used an electro polymerization approach to modify the SPCE electrode by covering it with PPy on a working electrode. Synergistic effects can be produced in electrochemical applications by combining IL and N composites. A further benefit of adding BiF to the working electrode is that it becomes stronger and more effective in detecting heavy metals. Lastly, utilizing a scanning electron microscope for morphological inspection and potentiostat analysis, this straightforward, inexpensive, and sensitive sensor is used to estimate the Pb (II) level scanning electron microscope (SEM).

II. Materials and Methods

A. Tools and materials

The accu-coat 3230 screen printer uses the carbon (C) paste and silver chloride electrode (Ag|AgCl) printing technique. Following printing, the materials are dried in an oven for 10 minutes at 150 °C before continuing with the sintering procedure on a conveyor furnace machine radiant technology corp (RTC) TF 315 for 30 minutes at 800 °C. Using a potentiostat of the Soliton EM 10/20-APPA 505 type and a digital multimeter linked to a computer via USB cable for the purpose of presenting the measurement's results, the sensor response to Pb (II) concentration is measured.

As the working electrode (positive electrode) and reference electrode (negative electrode), respectively, materials were Ag|AgCl material of the Dupont 5874 type and carbon paste of the Dupont BQ242 type. Aldrich 109-97-7 materials that had

been refined with aluminum oxide were employed in Conductive PPy. Ammonium hydrogen phosphate serves as an anion in this process. 3-Dimethylimidazolium tetrafluoroborate, Nafion D-521, and N-dimethylformamide were combined to create 1-butyl-2, which was employed by ionic liquid (IL) (DMF). In the liquid tester, Pb (II) standard solution in a 1000 mg/l concentration is used.

B. Fabrication of electrodes

Electrodes for lead detection sensor are produced using thick film technology based on the screen-printing technique. This method was applied to create a microelectronics circuit with the benefit of rescaling the sensor's size using tiny conductor lines. In this study, a layer thickness of 100 micrometers is used. While Ag|AgCl paste is used to create working electrodes and counters, printing carbon paste is utilized to create reference electrodes. The production of screen films, printing of paste ingredients, drying, combustion, assembly, and packing are the steps of the electrode fabrication process used in this study. The process flow for fabricating electrodes is shown in Figure 1.

C. Electro polymerization of pyrrole

The amount of 1 M pyrrole (C_4H_5N) was purified using aluminum oxide powder and a 0.1 M concentration of $(NH_4)_2HPO_4$ was prepared. All these substances were dissolved into 17 Ω distilled water and supplied with nitrogen, blown through a tube, for 5 minutes. The electrochemical process was carried out for the polymerization process on carbon electrodes using ammonium hydrogen phosphate. The electropolymerization process was conducted for 10 minutes, powered by a voltage of 1 Volt and at a constant current of 450 - 650 μA . Nitrogen was also simultaneously supplied, which is blown through a tube during the electro polymerization process.

D. Nafion and ionic liquid coating

After electro polymerization, the working electrode was coated with a solution consisting of 0.1 % Nafion and 0.5 % ionic liquid dissolved in 1 mL of DMF. Afterwards, the electrode was dried naturally at room temperature. A reference voltage measurement was performed with the electrode submerged in a 3 M solution of potassium chloride (KCl) to check the electrode's voltage stability.

E. Bismuth film electro polymerization

Electro polymerization is used to create the bismuth film coating on the working electrode. A 0.1 M acetate buffer solution with a pH of 4.5 and 200×10^{-9} g M Bi (III) make up the electro polymerization solution. This solution is combined, agitated, and exposed to a -1.4 V voltage for 2 minutes. The sensor electrode is subjected to an

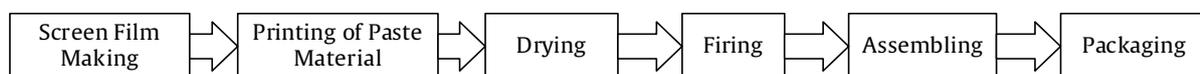


Figure 1. Electrode fabrication process

amperometry measurement in order to assess and characterize the sensor in accordance with several Pb standard solutions. Figure 2 depicts the sensitive membrane doping procedure.

With a 20 k secondary electron microscope (SEM SU3500), morphological properties were examined. Prior to and following the application of the conductive material coating, SPCE was subjected to tests. A potentiostat was used to regulate the electrodes and electroanalytically measure the experiment while testing the sensor electrode's performance. A 700 mV source voltage and a 1 k Ω resistance were employed.

III. Results and Discussions

A. SEM-based electrode characterization

Prior to being coated with conductive material, the morphological properties of SPCE are shown in Figure 3(a), with the carbon layer predominating the SPCE's surface. In Figure 3(b), after electrodeposition, the morphology indicates that the particles are dispersed evenly throughout all of the working electrode's surfaces.

In addition, the testing aims to see the electrode layer's composition includes bismuth, nitrogen, carbon, and oxygen. After testing was carried out using energy dispersive spectroscopy (EDS) to give

the model and make of the spectroscopy, it was discovered that C, nitrogen, oxygen, and bismuth, respectively, have atomic compositions of 84.92 %, 8.81 %, 6.26 %, and 0.01 %. Further information regarding the composition of each element after EDS testing can be seen in Table 1, which shows that carbon elements are more dominant than other elements. This composition gives a good relationship to the specifications of the electrode.

B. Electrochemical characterization of electrodes

1) Stability of reference electrodes

To maintain the voltage stability created by working electrodes and counter electrodes, reference electrode Ag|AgCl is utilized. Figure 4 displays the results of the reference voltage test. A 3 M concentration of KCl electrolyte solution is used for testing. The dispersion of the KCl solution, which is not equally distributed on the electrode surface, causes a drop in voltage in quadrant I. In contrast, the output responses are more consistent in quadrant II. This result demonstrates that the electrode's output voltage has good stability, ranging from 2.02 to 2.5 mV, demonstrating that the electrode is capable of detecting Pb (II) material.

2) Observation of bismuth electro polymerization currents

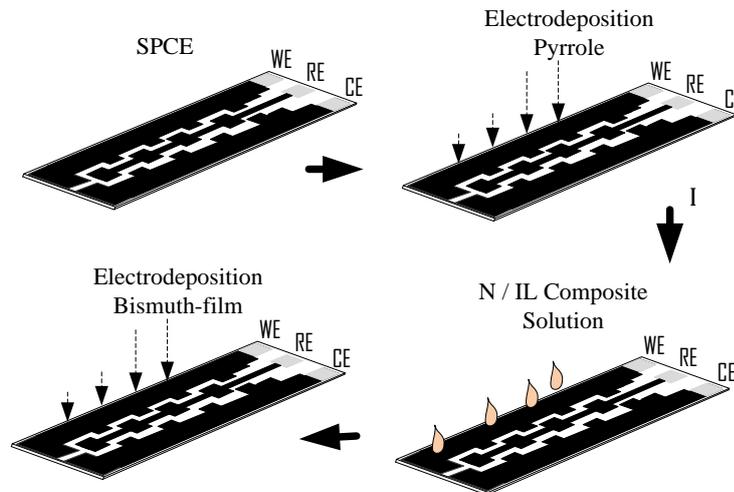


Figure 2. The process of sensitive membranes doping

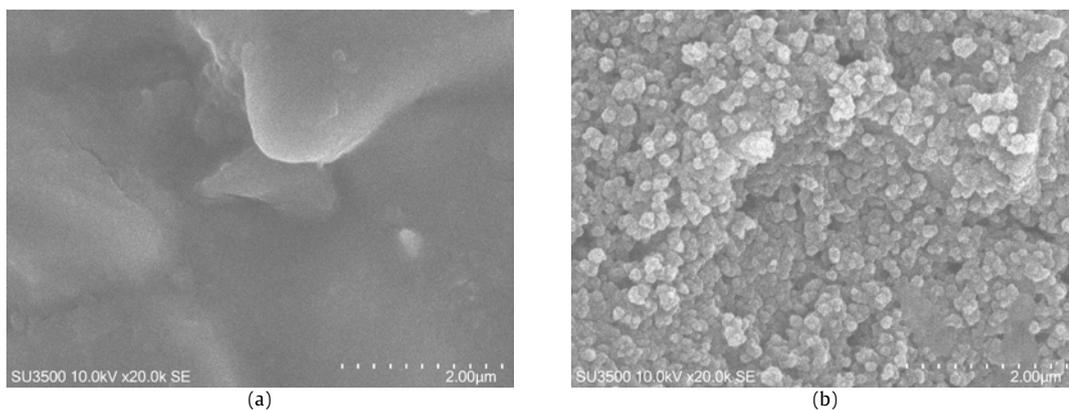


Figure 3. SEM micrograph of electrode carbon: (a) Before electrodeposition; (b) After electrodeposition and added with PPY

Table 1.
Result of energy dispersive spectroscopy (EDS) testing

Element	Weight (%)	Atomic (%)	Error (%)	Net int.	K ratio	Z	A	F
Carbon	81.90	84.92	3.09	2685.16	0.6988	1.0071	0.8473	1
Nitrogen	9.91	8.81	21.95	38.76	0.0062	0.98	0.0643	1
Oxygen	8.05	6.26	17.31	76.07	0.0070	0.9567	0.0912	1
Bismuth	0.14	0.01	27.17	6.47	0.0014	0.5299	1.8243	0.9969

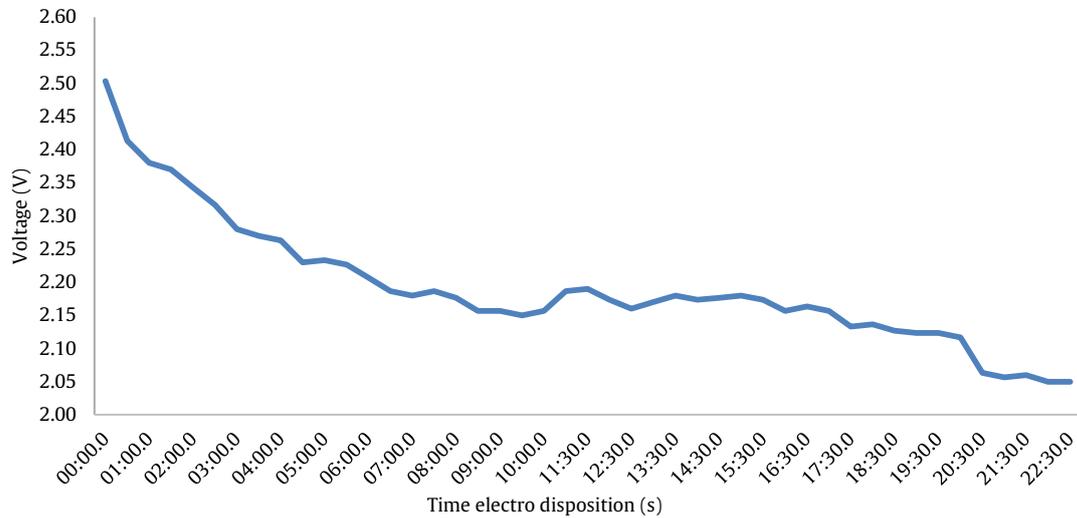


Figure 4. Output response of Ag|AgCl electrode

The Bismuth films are deposited by electrodeposition, which is used to boost the sensor electrode's conductivity. The voltage used in the electrodeposition process is -1.4 V so that bismuth precipitation occurs on the surface of the working electrode. Figure 5 shows the electrodeposition current of the working electrode coated with bismuth film at 0.08 to 0.064 mA during the 2-minute process. The graph shows that the passing current gradually decreased over the period, meaning that the electrical resistance of the electrolyte kept increasing during the period. The

results of the redox reaction in the electrodeposition process work well as the electrode surface can be coated with bismuth film. The amount of bismuth film deposits is directly proportional to the electric current flowing in the electrolyte.

3) Lead electrochemical detection

The Pb substance test output voltage using a typical Pb solution is shown in Figure 6. The 0.05 , 0.1 , 0.25 , and 0.5 mg/l variations made up the produced test concentration. Each sample test solution's average output voltages are 2.16 , 2.21 , 2.23 , and

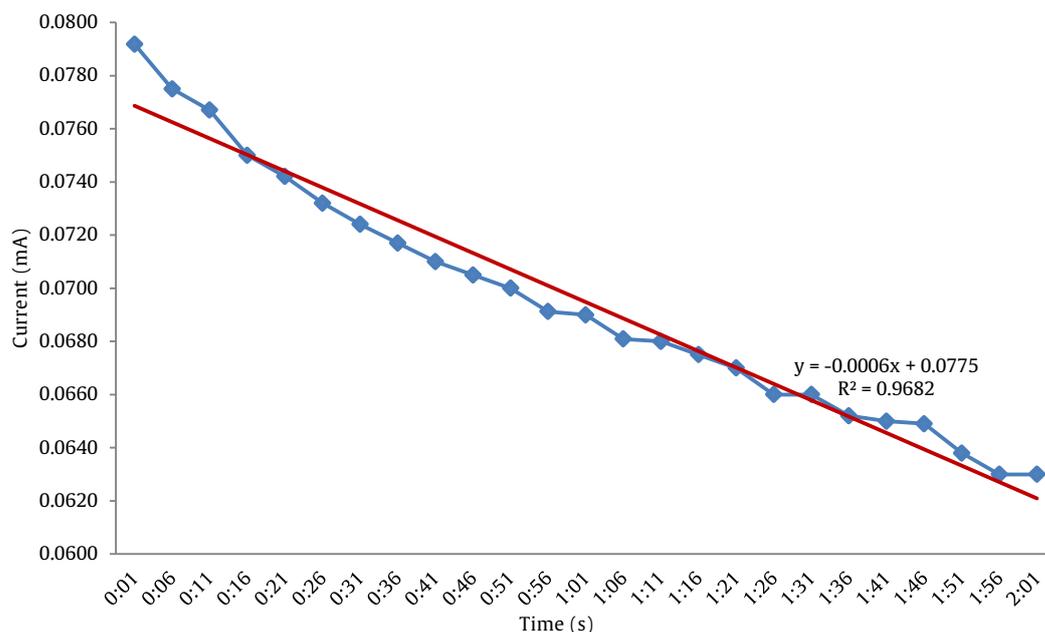


Figure 5. Bismuth electrodeposition time

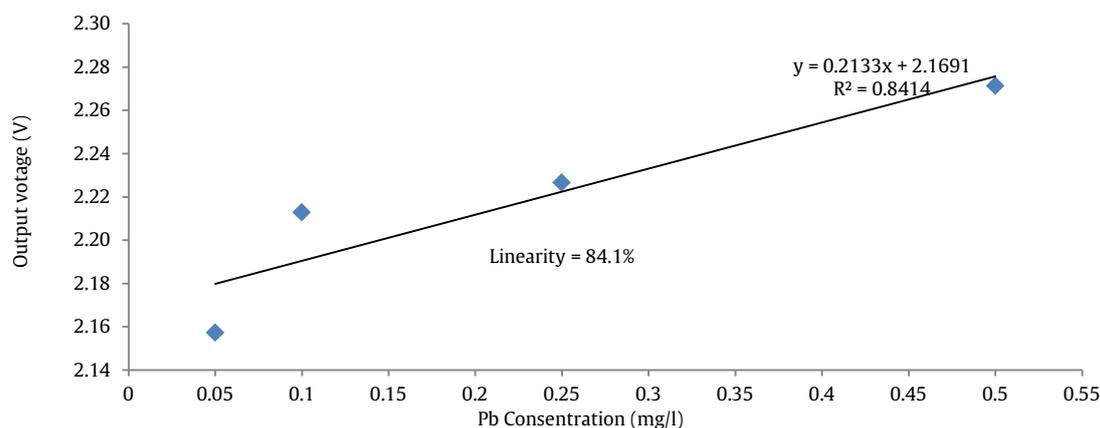


Figure 6. The responses of Pb sensor

2.27 V for 0.05, 0.1, 0.25, and 0.5 mg/l, respectively. The highest voltage difference occurs between 0.05 mg/l test solution and 0.1 mg/l test solution with a difference of 0.06 V. The linearity of these output voltages is 84.1 %, demonstrating that the sensor is able to accurately detect Pb (II) concentration.

IV. Conclusion

According to this research, bismuth films were used to successfully deposit polypyrrole on carbon electrodes and dope it with ionic liquid and Nafion. The morphology of the working electrode's surface as revealed by SEM demonstrates that the particles are dispersed uniformly on all surfaces, indicating that the contributions of carbon and other composite materials have improved the conductivity of Ppy, N, IL, Bi, and SPCE. With a voltage range of 2.02 to 2.5 mV, the reference electrode's voltage stability has produced positive results. After the bismuth film was deposited using electrodeposition for 2 minutes, the sensor electrode's sensitivity was increased. The electrode was subjected to galvanostatic potential, and the results of the measurements revealed that the electrode had an 84.1 % linear response. Averaging between 2.16 and 2.27 V, the measured detection limits range from 0.05 to 0.5 mg/l concentrations. Based on performance, it is apparent that the sensor can effectively detect Pb (II) compounds and that it may be employed as a working electrode for Pb (II) substance sensors.

Acknowledgments

The authors would like to thank the Research Center for Electronics and Telecommunication, Indonesian Institute of Sciences (LIPI), Bandung, and other parties that cannot be mentioned one by one who has shared their expertise and insights regarding details of the research materials, as well as for many helpful discussions.

Declarations

Author contribution

Z. Saputra is the main contributor of this paper. All authors read and approved the final paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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