Measurement 69 (2015) 115–125

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

A novel method for fabricating Fe^{2+} ion selective sensor using polypyrrole and sodium dodecyl sulfate based on carbon screen-printed electrode

Mehdrad Gholami [a,b,*], Majid Rezayi [a], Pooria Moozarm Nia [a], Ismail Yusoff [c], Yatimah Alias [a]

[a] Department of Chemistry, Faculty of Science Building, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Department of Chemistry, Marvdasht Branch, Islamic Azad University, P.O. Box 465, Marvdasht, Iran
[c] Department of Geology, Faculty of Science Building, University of Malaya, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 13 December 2014
Received in revised form 13 February 2015
Accepted 18 March 2015
Available online 26 March 2015

Keywords:
Cationic response
Polypyrrole electropolymerization
Iron II-selective sensor
Differential pulse voltammetry
Sodium dodecyl sulfate

ABSTRACT

In this study, a novel procedure for creating cationic response in polypyrrole is introduced. This method was applied to produce an iron II ion selective sensor based on carbon screen-printed electrode in the presence of pyrrole, iron II sulfate, and Sodium dodecyl sulfate (SDS). The formational mechanism of this procedure is discussed. The composition and morphology of the prepared modified electrode is characterized by the Field Emission Scanning Electron Microscope, X-ray Powder Diffraction, and Fourier Transform Infrared Spectrum. The produced iron II sensor can be used for potentiometric and voltammetric detection. The potentiometric dynamic range was 1×10^{-6} to 1×10^{-1} M with a Nernstian slope of 29.7 ± 0.5 mV per decade and a detection limit of 8.78×10^{-7} M. In addition, the differential pulse voltammetry was applied for the optimized electrode and the dynamic range from 1×10^{-9} to 1×10^{-5} M with a detection limit of 5.8×10^{-10} was obtained. The prepared electrode has good potentiometric selectivity for Iron II with respect to several cations. Electrochemical Impedance spectroscopy showed the charge transfer dramatically decreased with optimized electrode. This sensor was successfully used for the determination of iron II concentration in ferrous fumarate tablet using both potentiometric and differential pulse voltammetry methods.

1. Introduction

The essentiality of both Iron II and Iron III for living organisms is well known. Iron plays an essential role in hemoglobin. It is the most common cause of anemia, on the other hand, high levels of iron may enhance risk of heart disease, cancer and other illnesses such as haemochromatosis [1]. Therefore, reliable, selective, and sensitive methods for detecting and monitoring iron levels not only in biological but also in industrial and environmental samples is very important. There are several approaches for monitoring the concentration of Iron (II) cation, such as colorimetry [2–4] spectrophotometry [5,6], potentiometry [7–9], voltammetry [8] and optode measurements [10,11]. Among these methods potentiometry can be used for the measurement of different cations and anions [12–19].

Owing to imprinting and templating ability of conducting polymers, they have been vastly used in highly selective and sensitive sensors. The ability of introducing chemical recognition elements into conducting polymers during the polymerization step of them makes these kinds of materials very attractive in sensor production [20–26].

---

* Corresponding author at: Department of Chemistry, Faculty of Science Building, University of Malaya, 50603 Kuala Lumpur, Malaysia.

E-mail address: gholami897@gmail.com (M. Gholami).

http://dx.doi.org/10.1016/j.measurement.2015.03.030
0263-2241/

One of the most widely used conducting polymers in chemical sensors is Polypyrrole (PPy). Compared to many other conducting polymers, (Ppy) has a good stability, higher conductivity [25–33]. Furthermore, (PPy) can be coated on various metal substrates or carbon by electropolymerization in both aqueous or organic solvents [34–39]. Due to these characteristics, (PPy) is highly suitable for different electrochemical applications such as potentiometric [25,29,40–42], voltammetric [43–47] amperometric [30,45,48–50] and impedimetric [51,52] techniques for the determination of various anionic, cationic and neutral molecular species [30,50,53–55].

Cationic response of the conducting polymers can be obtained by doping cations with big anions, which can be trapped in the polymer film [25,56,57]. Another way of having cationic response is to dope a bulky organic anion with metal complexing properties toward a selected cation into a conducting polymer [58,59].

In this study, a novel method for creating cationic response in (Ppy) is introduced and the applicability of this method examined for creating the recognition sites for iron II.

To the best of our knowledge, there is no report available in literature regarding the electrochemical sensing of Fe (II) using polypyrrole. In this work, a novel iron II ion selective sensor prepared by electropolymerization of pyrrole on the surface of the carbon screen-printed electrode (SPE) in presence of iron sulfate and sodium dodecyl sulfate SDS. Both the developed potentiometric and voltammetric sensors were successfully applied to detect the Fe (II) ions in ferrous fumarate tablets.

2. Experimental

2.1. Reagents

All chemicals used were of analytical-reagent grade and were purchased from Merck (Germany). All aqueous solutions were prepared using deionized water with resistivity of ∼18 MΩ cm. All glass apparatus was kept in 1.0 mol L^{-1} nitric acid when not in use. Pyrrole was purified by vacuum distillation on the day of use and was shielded from light until the electropolymerization solution was prepared.

2.2. Apparatus and measurements

The electrochemical studies were performed using a Galvanostat-Potentiostat, Autolab 302N with FRA2 impedance module controlled by Nova 1.10 software, Metrohm, Switzerland; A three-electrode system was used for all measurements; a carbon screen printed electrode (Quasense, AI1302-T7, Thailand) as the working electrode a platinum auxiliary electrode. All measurements were carried out with a saturated calomel reference electrode, (SCE) (BAS Inc., Japan). A Thermo Scientific (Orion Versta Star Meter, Indonesia) was employed for pH/potentiometer measurements. Surface evaluation was performed by field emission scanning electron microscopy (FESEM) in a Hitachi SU8000 (Japan) microscope. A bench-top Ultrasonic Cleaner (Powersonic 405, Korea) was used for the sonication process. An X-ray diffraction instrument (Siemens D5000) with Cu Kα radiation was employed to analyze the surface morphologies of the prepared modified electrode. Fourier Transform Infrared (FTIR) spectra of the modified electrode was obtained using a Perkin–Elmer (Frontier FT-IR/FIR Spectrometer) armed with Attenuated Total Reflectance (ATR) sampling tool.

2.3. PPy film electrode preparation

The (PPy) film was prepared by electropolymerization of pyrrole on the surface of carbon screen-printed electrode with 4 mm diameter, using Chrono potentiometry ($\Delta t > 1$ ms) mode at optimized conditions of 480 μA for 200 s. The electropolymerization was carried out from an optimized aqueous solution containing 0.4 M pyrrole, 2.7×10^{-3} M of SDS and 0.05 M $FeSO_4$ that was purged by nitrogen gas for 1 min prior to electropolymerization. The electrodes, after electropolymerization, were washed thoroughly with deionized water. The prepared electrode can be used without any conditioning as an iron II potentiometric sensor. Besides, the prepared electrode was subjected to 30 cycle of cyclic voltammetry between −1 and +1 V with scan rate of 0.1 V/s in 0.1 M acetate buffer solution of pH 4.6. The resulting modified sensor is directly used for differential pulse voltammetry (DPV) measurements.

2.4. Potentiometric measurements

The prepared sensor was used as the indicator electrode in conjunction with a saturated calomel reference electrode. All measurements were performed at ambient temperature (25 ± 1 °C). The calibration curve (potential (mV) vs. −log $[Fe^{2+}]$) of the sensor was plotted using *freshly prepared* standard solutions in the concentration range of 1.0×10^{-6} to 1.0×10^{-1} M by successive dilution of the stock standard 0.1 M solution. The potential readings with an accuracy of ±0.1 mV were recorded when they reached a stable value.

2.5. Differential pulse Voltammetric (DPV) measurements

The differential pulse voltammetry (DPV) was performed in the potential range −0.4 to +0.5 V using pulse amplitude of 25 mV and a scan rate of 10 mV s^{-1}.

2.6. Electrochemical Impedance Spectroscopy (EIS)

The EIS recorded in 1 mM $[Fe(CN)6]^{-3}/[Fe(CN)6]^{-4}$ (1:1) containing 0.1 M KCl solution [60–65] in the frequency range of 0.1 Hz to100 kHz followed by applying a signal amplitude of 5 mV (around the open circuit potential).

3. Results and discussion

3.1. Pyrrole electropolymerization

The polymerization process of pyrrole is followed by producing polyradical cations which attracts sulfate anions