

Full Paper

Electrochemical Preparation of a Copper Ion Selective Electrode based on Polypyrrole Conducting Polymer Doped with Ponceau 4R Azo Dye

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Abstract- A solid state copper electrode is reported based on polypyrrole conducting polymer film doped with Ponceau 4R azo dye. The sensing film was prepared in aqueous solution via electropolymerization of pyrrole (10.0 mM) and Ponceau 4R azo dye (2.0 mM) as ionophore, potentiostatically ($E_{app.}=0.80$ V vs. SCE) using pencil graphite as working electrode. The structural characteristics of the prepared copper electrode were studied by scanning electron microscopy, Fourier transform infrared and energy dispersive spectroscopy. The fabricated electrode showed a linear Nernstian response over the range of 1.0×10^{-5} to 5.0×10^{-2} M with slope of 29.28 ± 0.20 mV per decade over the pH range of 4-6. The sensor shows a fast response time (<15 s), good shelf lifetime and reasonably high selectivity with respect to many cations including alkali, alkaline earth, and transition metal ions. A detection limit of $6.70 \mu\text{M}$ was obtained.

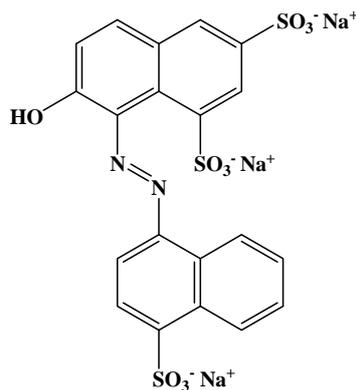
Keywords- Ion selective, Copper (II) ion, Potentiometry, Polypyrrole, Ponceau 4R azo dye

1. INTRODUCTION

During the last decade, there has been an improved renaissance in developing ion selective electrodes (ISEs) as devices for rapid, accurate, low cost, convenient and nondestructive analysis of different samples with small volume specimens. Potentiometric analysis based on ion-selective electrodes, has several advantages such as simplicity of preparation and analysis procedure, simple instrumentation, no contamination and nondestructive, unaffected by color or turbidity, wide dynamic range, and good selectivity. Due to the vital prominence of Cu(II) in multiplexes biological systems, geochemical, environmental, medicinal and industrial samples, the search for new selective and sensitive sensors for its fast determination is still in great importance [1]. Some potentiometric sensors based on liquid membranes or PVC membranes for Cu(II) analysis have been reported previously [2-25]. In spite of availability of a number of Cu(II) sensors, their use for Cu(II) estimation has been limited, because some of them suffer from serious interferences by other cations, complexity of preparation procedure, long response time, non-Nernstian response, limited pH range and cost of the chemicals.

Chemically modified electrodes (CME) with conductive polymers have been found to be much more interesting because of the combination of tunable chemical and electronic properties of conducting polymers [26,27]. The great advantage of conducting polymer based sensors over other available techniques is that the conducting polymers have the potential to exhibit improved response properties and being sensitive to small perturbations. The electrical conductivity and electroactivity or the switching properties of these polymers have been utilized as the basis of their most industrial and analytical applications such as chemical and electrochemical sensors, separation, rechargeable batteries, electrochromic and controlled release devices [28-31]. It has been reported that the electropolymerisation conditions, specifically the size of the counter-ion used, can control the size exclusion selectivity in polypyrrole (PPy) films [32,33]. Some of the most recent applications of conducting polymers as sensor material in fabrication of solid state ion selective electrode has extensively been reviewed by A. Michalska [28].

In the current work, preparation of a solid state copper sensor electrode was performed via electrolymerisation of polypyrrole conducting polymer in the presence of a food colorant azo dye termed as Ponceau 4R as both dopant and ionophore. Ponceau 4R (4-sulpho-1-naphthylazo)-1-hydroxy-2-naphthalene-6,8-disulphonic acid trisodium salt (Scheme 1) is a synthetic organic azo group food colorant which can be found in common food products such as beverages, dry mix and bakery dairy products, candies, sugar confectioneries and has strong affinity to Cu(II) ion to form stable complex [34,35].



Scheme 1. Chemical structure of Ponceau 4R azo dye (P4R)

The original idea developed in the current research is drawn from the unique properties of the polypyrrole conducting polymer in which the anions from the reaction solution can be incorporated into the polymer during polymerization as dopant. The incorporated anions termed as dopants can then induce its property into the polymer product. On the other hand the properties of polypyrrole conducting polymers are generally governed by the incorporated counter-ions or dopants during chemical or electrochemical synthesis. In current work, a different approach the achievement of selective chemical recognition of Cu(II) ions based on electrochemically prepared PPy conducting polymer film is presented. This approach involves electrochemical polymerization of pyrrole monomer under controlled optimized conditions in the presence of Ponceau azo dye as a dopant that allows the generation of selective recognition sites in the formed polymer film during the doping process, which can cause to specific and selective interactions with Cu(II) ions. During electropolymerisation, metal complex dye ions are incorporation of with the polymer matrix (polypyrrole) in order to maintain charge balance. The counterions (ionophore) are not leached out from the polymer under open circuit conditions because of their large size.

2. EXPERIMENTAL

2.1. Chemicals and Instrumentation

All chemicals used were analytical reagent grade (AR) and prepared in double distilled water. Pyrrole was obtained from Merck (Germany, <http://www.merck.com>) and distilled before use. The chemicals used NaOH, HCl, CuSO₄·5H₂O, and nitrate salts of the interfering cations were of analytical reagent grade, purchased from Merck and were used as received. Ponceau 4R is a synthetic organic azo dye which is used as food colorant was prepared from a local industry and used without any further purification. 0.10 M of Cu²⁺ ion (as stock solution) was prepared from CuSO₄·5H₂O in double distilled water. Standard solutions for

calibration graph were then prepared by successive diluting of the accurately prepared stock solution and potential readings started from the least concentrated standard. Electrochemical synthesis of pyrrole was carried out using a Potentiostat/Galvanostat (SAMA 500 potentioscanner, Iran).

A Metrohm pH meter (model 827) (Metrohm, Germany, www.metrohmusa.com) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for pH measurement. The pH of the solutions was adjusted using 0.10 M HCl or 0.10 M NaOH solutions. All potentiometric measurements were carried out at 298 K using a cell of the following type: SCE|Cu²⁺(*a*_A)|PGE/PPy/Cu-P4R. EMF measurements were carried out using an accurate digital electronic voltmeter with high internal impedance to the nearest 0.10 mV. The readings were recorded when the potentials reached a stable and constant value (within 1 mV). The sensing material of the fabricated Cu (II) electrode obtained was characterized using infrared (FT-IR), Energy-dispersive X-ray spectroscopy (EDX) and scanning electron microscopic (SEM) techniques. The surface morphology was examined using of Philips XL30 scanning electron microscope at an accelerating voltage of 25.0 kV with 25000 times magnification. The FTIR spectrum of the electrode was recorded in Bruker (model Vertex 70) at room temperature in the region 500-4000 cm⁻¹.

2.2. Preparation of the copper ion selective electrode

A three electrode system was employed for electropolymerization of pyrrole. Electropolymerization was carried out using potentiostatic method, ($E_{\text{appl.}}=0.80$ V vs. SCE). A pencil graphite electrode (PGE) was used as working electrode and a Pt wire was employed as auxiliary electrode. PGE (0.7 mm diameter) was washed with concentrated HNO₃ (6 M) for removing any possible metal impurities. The developed EMF (E) of the prepared sensor electrode system immersed in a solution of Cu(II) ion can be represented by the following equation:

$$E = K + S \log C \quad (1)$$

Where E is the total potential (mV) developed between the sensing and reference electrodes. K (mV) is a constant which is characteristic of the particular ISE/reference pair. It is the intercept on the y axis of the linear portion of the calibration graph of measured EMF against the logarithm of the target ion concentration and S represents the slope of the electrode. The spectra of the Cu(II) ion, Ponceau 4R dye, and Cu-Ponceau 4R complex were further studied using UV-Vis spectroscopy. The UV-Vis spectra of the Cu(II) ($\lambda_{\text{max}}=800$ nm), Ponceau 4R dye ($\lambda_{\text{max}}=515$ nm), and Cu-P4R complex ($\lambda_{\text{max}}=463$ nm) are shown in Fig. 1. As the spectra show (Fig. 1), complexing of the Cu(II) ions with the Ponceau 4R dye molecules leads to some decrease (blue shift) in the maximum absorption wavelength of the dye (about 52 nm).

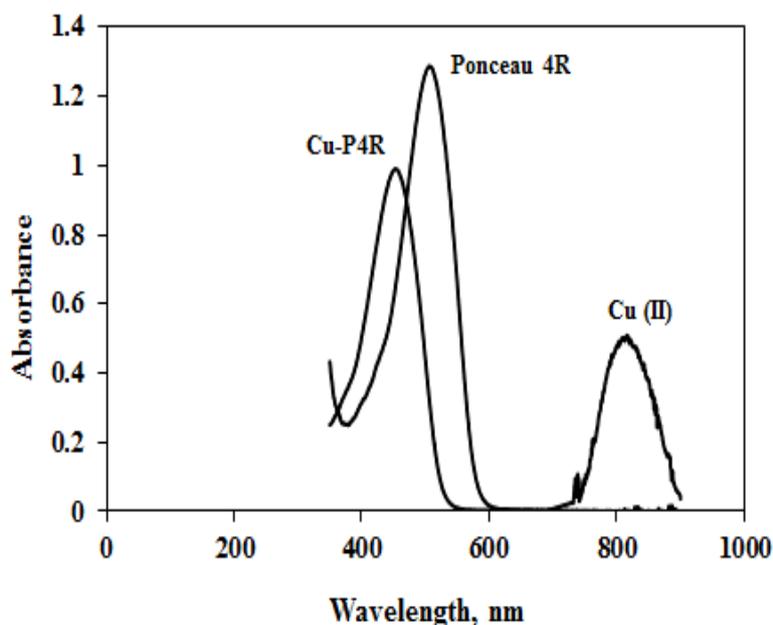


Fig. 1. UV-Vis spectra of the Cu(II), Ponceau 4R dye, and Cu-P4R complex

3. RESULTS AND DISCUSSION

3.1. The electrode composition effect on the potential response of the PGE/PPY/Cu-P4R

We know that, the compositions of membranes have great effect on the characteristics of ISEs such as sensitivity, working concentration range, selectivity and potential stability. Therefore electrodes with different compositions have been prepared and their potentiometric response characteristics were evaluated in order to find out the optimum electropolymerisation conditions.

The influence of CPC technique variables (such as magnitude of applied potential and time) was also studied. The result of some investigated parameters is shown in Table 1.

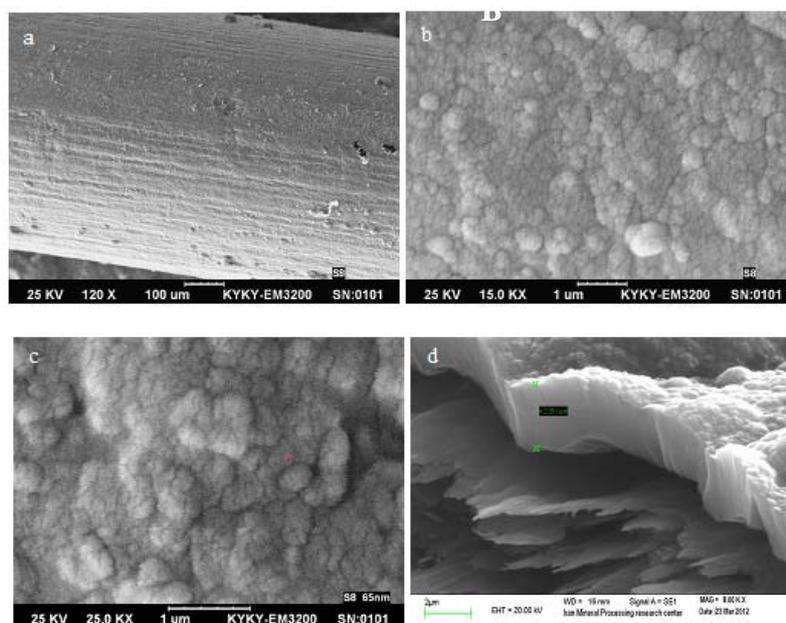
It was found that for observing a Nernstian behaviors for the fabricated copper electrode is resulted when a constant potential of 0.80 V (*vs.* SCE) was applied for duration of 100 s in a cell solution containing 10 mM monomer solution (pyrrole) and 2.0 mM Ponceau 4R dye (No. 10). The polymer coated electrode was conditioned for 30 minutes (optimized) in 1.0×10^{-3} M Cu(II) solution before use in potentiometric measurements.

3.2. Characterization

Scanning electron microscopy (SEM) is a beneficial tool for characterizing of the surface morphology of the polymers. The SEM micrographs of electrodeposited polypyrrole films at the surface pencil graphite electrodes (thickness=2.0-2.5 μ) are shown in Fig. 2. As the SEM micrographs show, the polymer synthesized in the presence of Ponceau 4R dye has smooth, uniform and nonporous cauliflower microstructure.

Table 1. Optimization of the membrane ingredients and technique parameters

Electrode No.	Composition/mM		$E_{\text{appl}}/ \text{time}$	Slope (mV dec ⁻¹)	Linear range/M	R ²
	Monomer (Pyrrole)	Dopant (P4R)				
1	5	1	0.8/V, 100/s	20.40	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.980
2	5	1	0.8/V, 250/s	21.20	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.979
3	5	1	0.8/V, 500/s	24.83	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.984
4	5	2	0.8/V, 100/s	20.10	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.978
5	5	2	0.8/V, 250/s	22.18	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.982
6	5	2	0.8/V, 500/s	23.70	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.985
7	10	1	0.8/V, 100/s	21.15	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.992
8	10	1	0.8/V, 250/s	24.90	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.990
9	10	1	0.8/V, 500/s	26.17	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.986
10*	10	2	0.8/V, 100/s	29.28	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.995
11	10	2	0.8/V, 250/s	30.72	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.993
12	10	2	0.8/V, 500/s	32.65	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.989
13	10	1	0.9/V, 100/s	25.30	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.996
14	10	2	0.9/V, 100/s	31.20	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.988

**Fig. 2.** Surface layer SEM image of PGE/PPy/Cu-P4R (a:×120, b:×15000, c:×25000) and (d) Cross-section SEM image

FTIR spectrum of PPy/Cl is also shown in Fig. 3a. The band at 1570.54 and 1384.60 cm^{-1} may be attributed to typical polypyrrole ring vibration and =C–H band in plane vibration respectively. Fig. 3b shows FTIR spectrum of PPy/P4R, which exhibits absorption peaks at 1101.49 is assigned as S=O stretching band and bands observed at 1638.56 and 3436.56 cm^{-1} may correspond to N=N and O–H stretching band which clearly confirms incorporation of P4R dye within the polymer matrix which has the most important role of sensing the electrode toward Cu(II) ions.

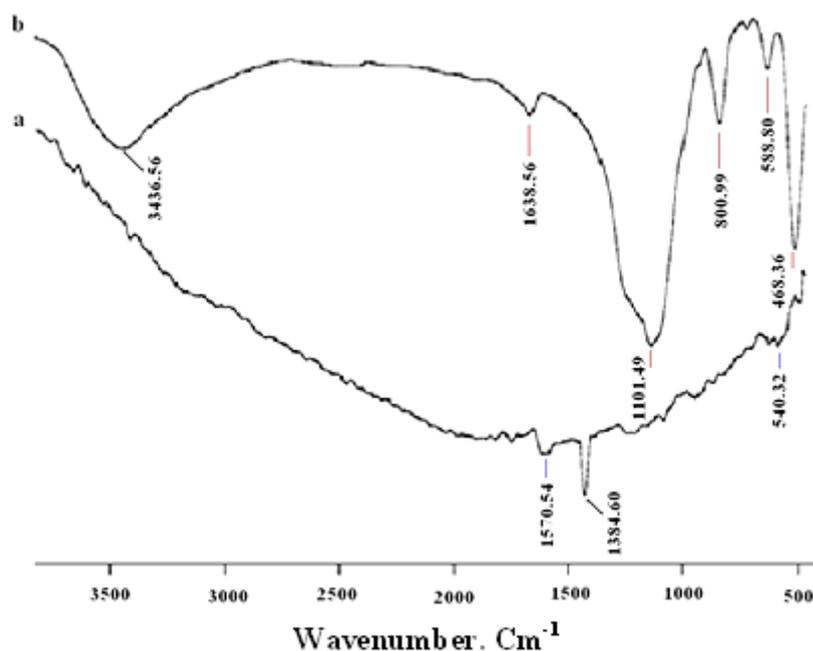


Fig. 3. FTIR spectrum of (a) PPy/Cl and (b) PPy/P4R

Energy-dispersive X-ray spectroscopy (EDS) is another analytical technique which is used for chemical characterization of a sample. Its characterization capabilities are due to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. Comparison of the EDS spectra of the polymer before and after doping with P4R dye is illustrated in Fig. 4a and Fig. 4b respectively. The presence of a sharp and intense peak of sulfur in EDS spectrum appeared at 2.3-2.4 keV (Fig. 4b) is a clear indication of incorporation of Ponceau 4R azo dye (Scheme 1) into the polypyrrole film during electropolymerisation.

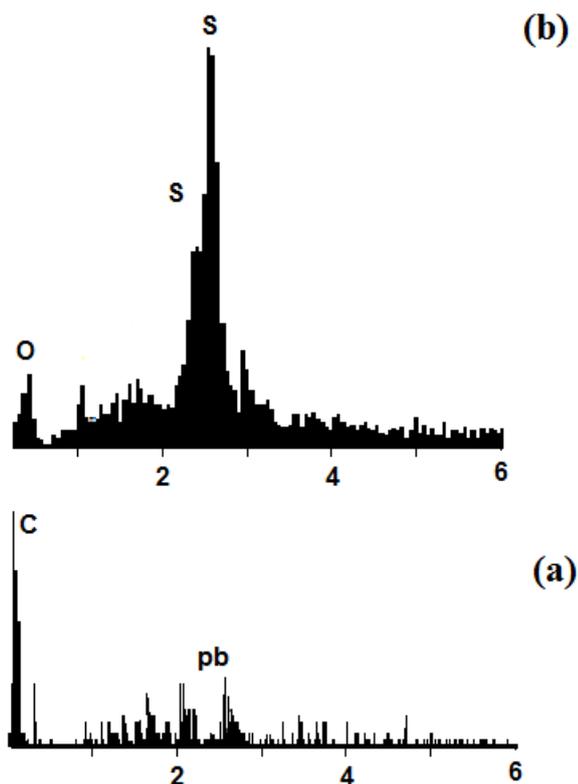


Fig. 4. EDS Spectrum of (a) bare PGE and (b) PGE/PPy/Cu-P4R

3.3. Sensing behavior of the electrode toward other ions

The existence of donating nitrogen atoms, in the dopant structure (dye) was expected to increase both the stability and selectivity of its complexes with transition and heavy metal ions as soft acids, more than other metal ions. The potential response obtained from some cations is depicted in Fig. 5. As can be seen, among of tested cations the resulting electrode showed the most selectivity or sensitivity to Cu(II) ions only and a Nernstian behavior over a desirable concentration range was observed.

3.4. Calibration curve

The concentration range in which a selective electrode produces linear response, is among the key features of these devices, and is usually considered to be the linear part of the calibration graph. The applicable measuring range of the sensor as shown in Fig. 6 is between 1.0×10^{-5} - 5.0×10^{-2} M. Detection limit of the prepared sensor was 6.70×10^{-6} M which was calculated by the extrapolating of the two segments of the calibration curve in Fig. 6. The response characteristics of the prepared copper electrode are also summarized in Table 2.

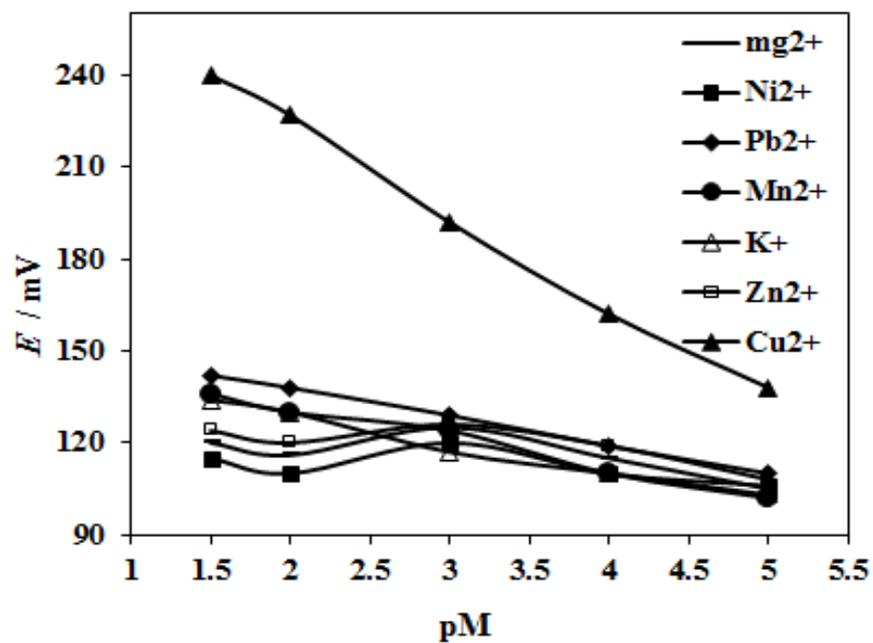


Fig. 5. Potentiometric response curves obtained for some individual metal ions with PGE/PPy/Cu-P4R electrode

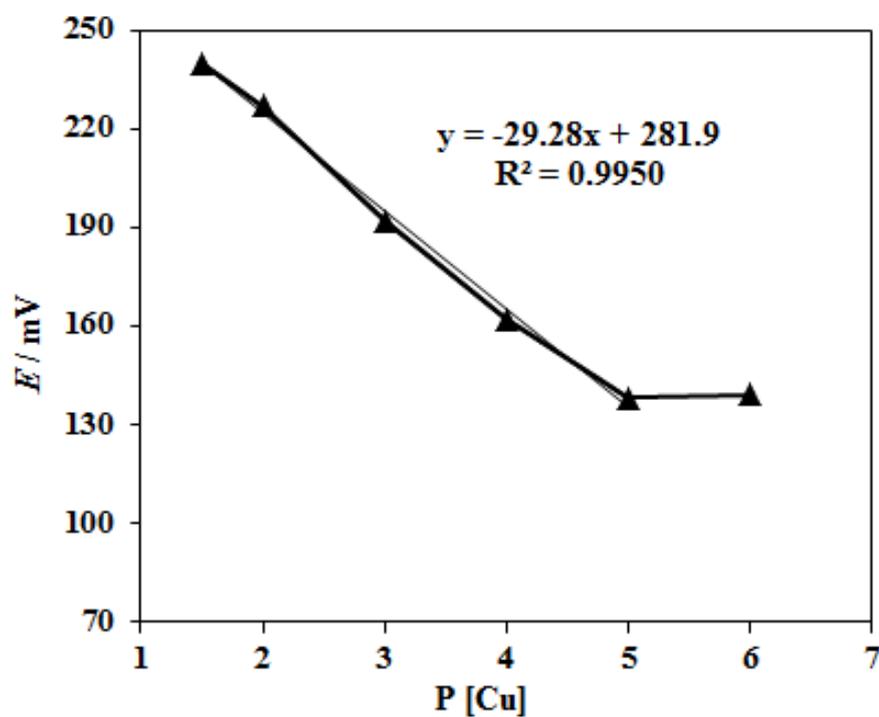


Fig. 6. The calibration curve obtained for Cu(II) ion using PGE/PPy/Cu-P4R electrode

Table 2. General characteristics of PGE/PPy/Cu-P4Relectrode

Properties	Values/range
Preparation technique	Constant potential ($E_{\text{appl}}=0.80/\text{V}$ vs. SCE)
Preparation conditions	PPy 0.010/M, P4R 0.002/M
Electrodeposition time (s)	100
Electrode type	Pencil graphite electrode (PGE)
Best pH range for response	4-6
Conditioning time	30 minute (in $10^{-3}/\text{M}$ Cu^{2+})
Linear range (Cu^{2+} , M)	1.0×10^{-5} to 5.0×10^{-2}
Electrode slope (mV decade ⁻¹)	29.28
Detection limit (M)	6.70×10^{-6}
Static response time (s)	15
Useful shelf lifetime (d)	> 60

3.5. Effect of pH on the electrode response

The pH dependence of response of the electrode has been tested in the range of 2.0 to 7.0 at concentration of 1.0×10^{-4} M of Cu(II) ions. The pH was adjusted with dilute hydrochloric acid and sodium hydroxide solutions. The potential of the sensor was determined as a function of pH and the results are shown in Fig. 7. The potential remains constant over the pH range of 4-6, which may be taken as the working pH range of the sensor assembly. At pH lower than 3.5, the interference of H^+ ions is more which is due to the high rate of diffusion of H^+ ions from sample solution to electrode surface, where they interact with sensing material (protonation of nitrogen atoms in acidic media) and its resulting in decreased selectivity of Cu(II) ions. In this case, the membrane sensor then responds to hydronium ions. At pH higher than 6.5, the deviation in the electrode response (decreasing in potential) is due to the formation of some hydroxyl complexes of Cu(II) ion in solution. Since, the best linearity ($R^2 > 0.99$) and Nernstian slope were observed at pH value of 5.0, therefore, all of the next investigations such as determination of selectivity, life time and response time were carried out at pH 5.0.

3.6. Selectivity of the prepared copper electrode

The selectivity of sensors is one of the most important performance parameters that determine its utility for a potentiometric analysis. In order to investigate the selectivity behavior of the electrode for Cu^{2+} ion with respect to various interfering ions, the potentiometric selectivity coefficient ($K_{\text{Cu}^{2+}, \text{X}^{n+}}^{\text{pot}}$) was evaluated by using both the matched

potential method (MPM) and the separate solution method (SSM), which are recommended by IUPAC [36].

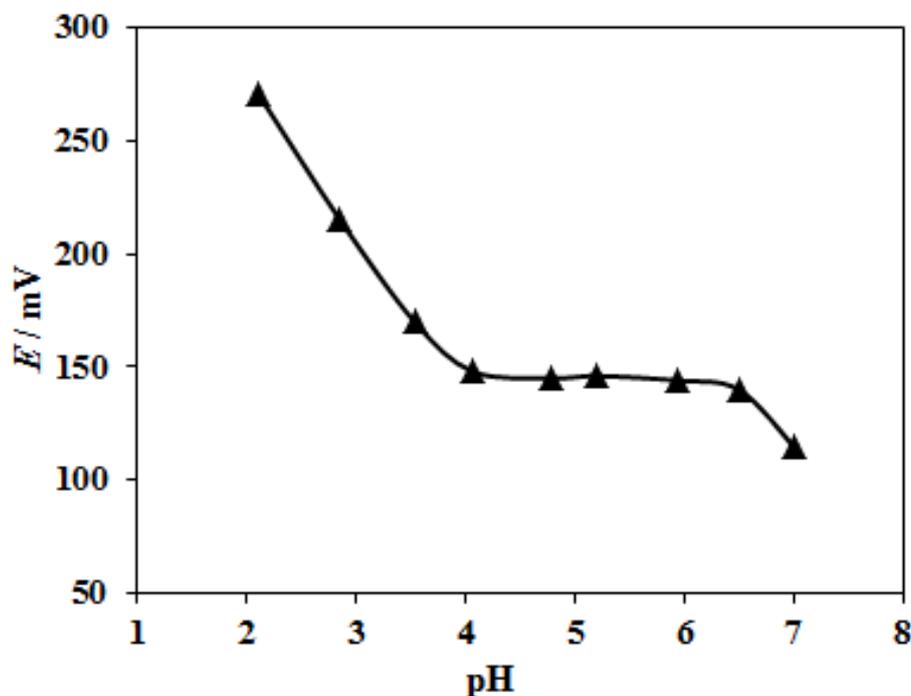


Fig. 7. Effect of pH on the potential response of PGE/PPy/Cu-P4R electrode

According to the MPM method, the specified activity (concentration) of the primary ions is added to a reference solution (1.0×10^{-4} M Cu^{2+} , in this case) and the potential was measured. In another experiment, the interfering ions (B) were successively added to an identical reference solution, until the measured potential matches that obtained after the addition of the primary ions. The MPM selectivity coefficient ($K_{\text{Cu}^{2+}, \text{B}}^{\text{MPM}}$) is then given by the resulting primary ion activity (concentration) to the interfering ion activity ratio:

$$K^{\text{MPM}} = \frac{a_{\text{Cu}}}{a_{\text{B}}} \quad (2)$$

In separate solution method (SSM), the EMF of a cell is measured for each of two separate solutions, one is containing the ion A of the activity a_{A} and charge Z_{A} (but not B), the other is containing the ion B with charge Z_{B} at the same activity $a_{\text{B}}=a_{\text{A}}$ (but not A). If the measured values are E_{A} and E_{B} , respectively, then the value of $\log K^{\text{SSM}}$ may be calculated from the equation (3):

$$\log K_{\text{A,B}}^{\text{SSM}} = \frac{E_{\text{A}} - E_{\text{B}}}{2.303RT/Z_{\text{A}}F} - \left(1 - \frac{Z_{\text{A}}}{Z_{\text{B}}}\right) \log a_{\text{A}} \quad (3)$$

The values of selectivity coefficients calculated by MPM and SSM at the constant pH value of 5.0 are shown in Fig. 8. As the data show (Fig. 8), higher selectivity coefficient was obtained for the prepared copper electrode toward some of the commonly interfering metal ions such as Zn^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} and Fe^{3+} . However, among the tested cations, the interference from silver and zinc ions was more serious than others. Because of the low selectivity of the electrode toward the majority tested interfering ions, it can be concluded that the introduced electrode can be successfully used for measurement or analysis of Cu(II) in real samples.

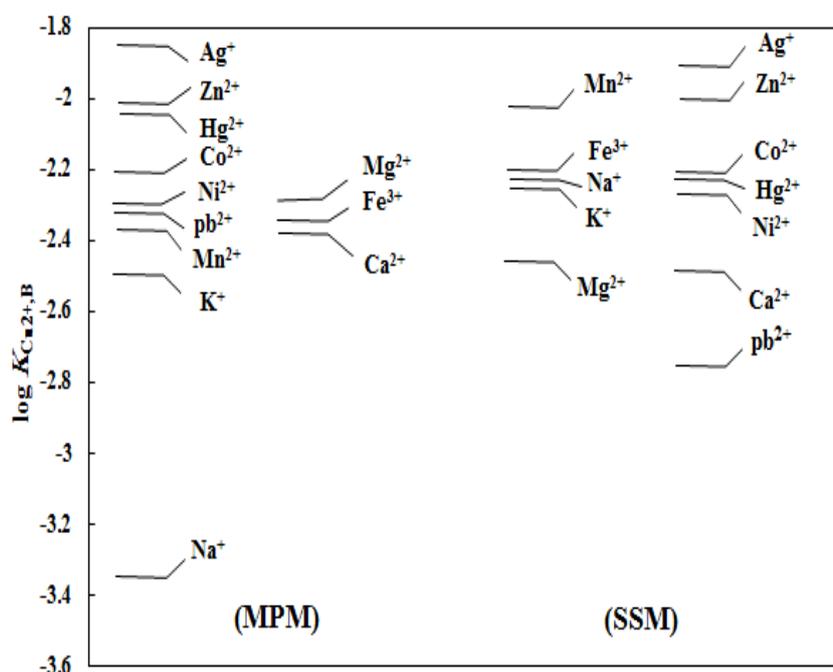


Fig. 8. Potentiometric selectivity coefficient values of PGE/PPy/Cu-P4R electrode

3.7. Response time of the prepared copper electrode

The dynamic response time is an important factor for all of the ion-selective electrodes. The average time required for the Cu(II) ion-selective electrode to reach a potential within ± 1.0 mV of the final equilibrium value after successive immersion of a series of copper ion solutions, each having a ten-fold difference in concentrations, was measured. In this study, the practical response time was recorded by changing the Cu(II) concentration in solution over a concentration range of 1.0×10^{-5} M to 5.0×10^{-2} M. The actual potential versus time traces is shown in Fig. 9.

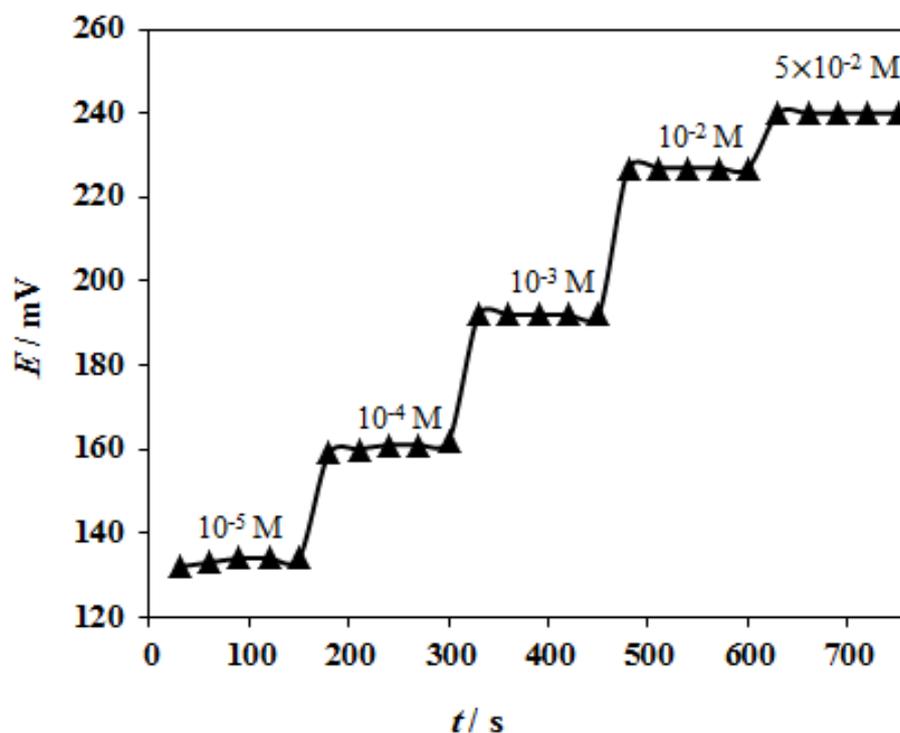


Fig. 9. Dynamic response time of electrode with varying the concentration of Cu^{2+} ion

In order to examine the stability of the potential reading of the electrode, it was also put in a 1.0×10^{-3} M of copper ion. As the result show (Fig. 10), the electrode reaches its equilibrium response in a very short time (~ 15 s) and remained constant for approximately 5 min. The same stability and response time were observed over the whole dynamic concentration range. This can be most probably due to the fast exchange kinetics of complexation/decomplexation of the Cu(II) ion with the ionophore (polymer dopant) at the test solution-membrane interface.

3.8. Reversibility of the electrode response

Reversibility factor is one of the most important parameters in assessing of a sensor performance for its practical application. In order to find out the reversibility of the response, the designed electrode was exposed repetitively in the Cu(II) solutions with two different concentrations (1.0×10^{-4} M and 1.0×10^{-3} M). The consequences observed are shown in Fig. 11. As the data indicates the response of the fabricated electrode toward concentration variation of copper ion is very quick and reversible.

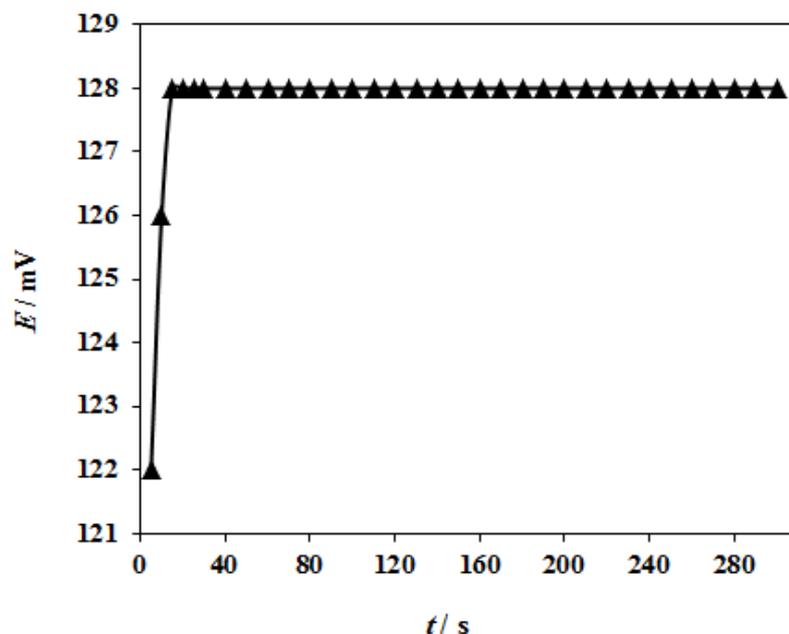


Fig. 10. Static response time of PGE/PPy/Cu-P4R electrode in 1.0×10^{-3} M of Cu^{2+} solution

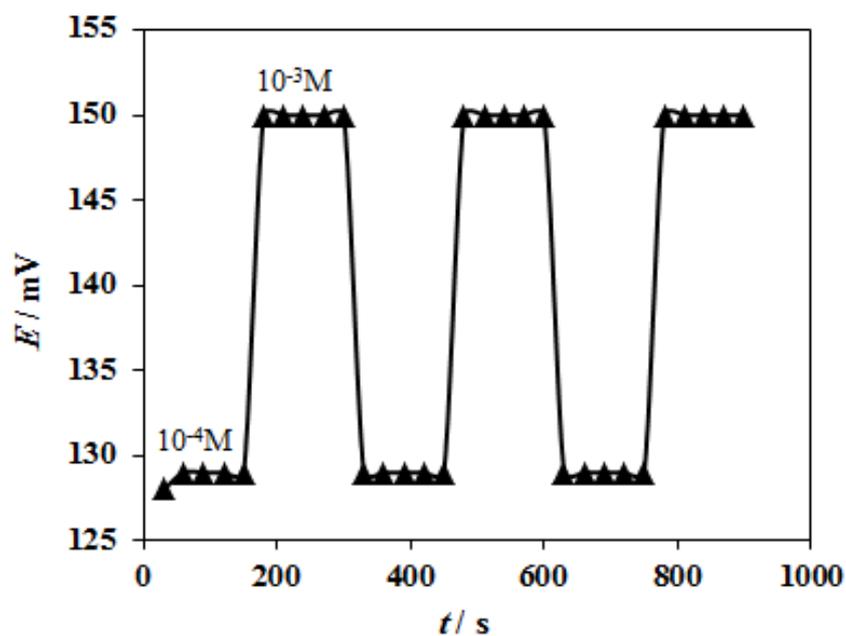


Fig. 11. Reversibility of PGE/PPy/Cu-P4R electrode response to Cu(II) ion

3. 9. Lifetime of the prepared copper electrode (PGE/PPy/Cu-P4R)

The lifetime of the PGE/PPy/Cu-P4R electrode was monitored by periodically recalibrating the potentiometric response to Cu^{2+} ion in standard copper solutions. After the conditioning step, the electrode was repeatedly calibrated three times during a period of two months, and no significant changes in the performance of the electrode were observed (Table

3). Therefore, Cu(II) ion-selective electrode can be used over a several weeks without any considerable change in the value of the slope, working concentration range and detection limit.

Table 3. Lifetime of the prepared Cu(II) ion-selective electrode

Time/day	Linear Range/M	Slope/ mV dec ⁻¹	Detection limit/M
1	1.0×10^{-5} - 5.0×10^{-2}	29.28	6.70×10^{-6}
7	1.0×10^{-5} - 5.0×10^{-2}	29.28	6.70×10^{-6}
21	1.0×10^{-5} - 5.0×10^{-2}	29.15	6.70×10^{-6}
30	1.0×10^{-5} - 5.0×10^{-2}	29.06	7.15×10^{-6}
60	1.0×10^{-5} - 5.0×10^{-2}	28.42	8.29×10^{-6}

3. 10. Effect of temperature on electrode response

The standard cell potentials (E_{cell}°) were determined at different temperatures from the respective calibration plots as the intercepts of these plots at $p[\text{Cu}]=0$, and were used to determine the isothermal temperature coefficient (dE°/dt) of the cell [37]. By Plotting of E_{cell}° vs. $(t-25)$, a straight line is produced (Eq. 4). The slope of this line was taken as the isothermal temperature coefficient of the cell.

$$E_{\text{cell}}^{\circ} = E_{\text{cell}(25^{\circ}\text{C})}^{\circ} + (dE^{\circ}/dt)_{\text{cell}}(t - 25) \quad (4)$$

The standard potentials of the reference (Calomel) and the prepared electrodes were calculated using the equations 5 and 6, respectively.

$$E_{\text{Hg}_2\text{Cl}_2}^{\circ} = 0.241 - 0.00066(t-25) \quad (5)$$

$$E_{\text{reference}}^{\circ} + E_{\text{cell}}^{\circ} = E_{\text{electrode}}^{\circ} \quad (6)$$

A plot of $E_{\text{electrode}}^{\circ}$ vs. $(t-25)$ gives a straight line. The slope of this line was taken as the isothermal temperature coefficient of the prepared copper electrode. Trend of changes of PGE/PPy/Cu-P4R performance at various temperatures (20-60 °C) is depicted in Fig. 12. As the results show, the electrode exhibited good Nernstian behavior at temperature range between 20 and 60 °C. The amount of the isothermal temperature coefficient of the cell and the PGE/PPy/Cu-P4R electrode are obtained 0.96 and 0.95 (mV/°C), respectively.

The small values of $(dE^{\circ}/dt)_{\text{cell}}$ and $(dE^{\circ}/dt)_{\text{electrode}}$ reveal the high thermal stability of the electrode within the investigated temperature range.

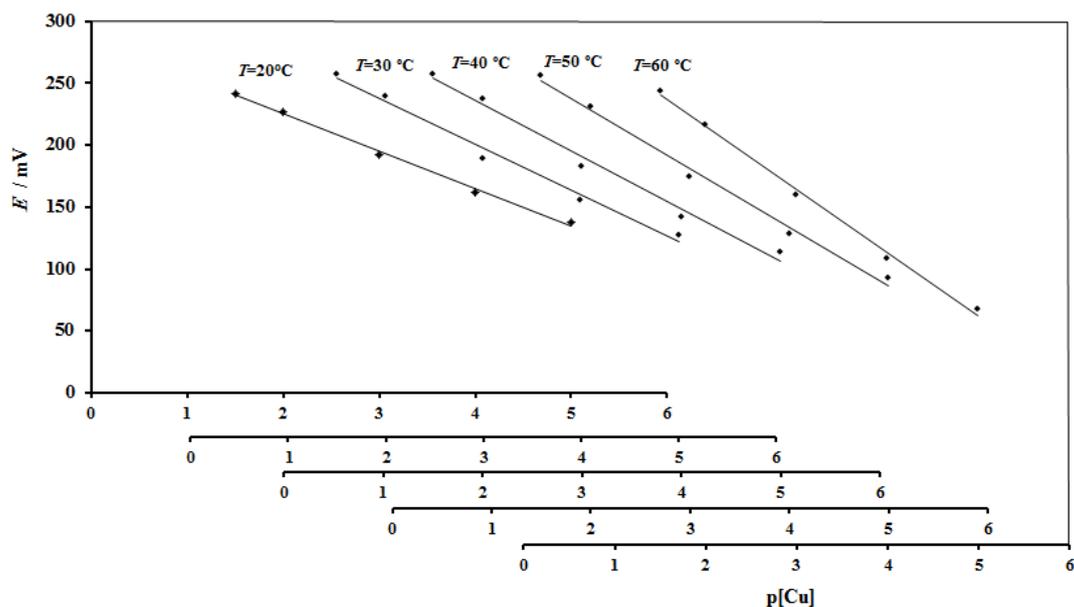


Fig. 12. Calibration graphs of PGE/PPy/Cu-P4R at different temperatures

3. 11. Some practical applications of the prepared copper electrode

The prepared sensor was also used as an indicator electrode in titration of 10 mL of 1.0×10^{-2} M CuSO_4 with 1.0×10^{-2} M EDTA (at pH=5 buffered) and vice versa. The resulting sigmoid titration curve is shown in Figs. 13a and 13b, respectively. As can be seen, the amount of Cu (II) ions in solution could be determined with the fabricated copper electrode. Therefore, the PGE/PPy/Cu-P4R electrode can be used as indicator electrode in potentiometric titration of Cu(II) ions successfully.

Table 4. Determination of Cu(II) recovery by the prepared electrode in the spiked samples

No.	Conc. of added Cu (II) ion/M	Amount found*/M	Recovery (%)
1	5.0×10^{-4}	$5.14 (\pm 0.17) \times 10^{-4}$	102.8
2	1.0×10^{-3}	$0.97 (\pm 0.24) \times 10^{-3}$	97.0
3	5.0×10^{-3}	$5.09 (\pm 0.08) \times 10^{-3}$	101.8

* Average of three determinations \pm S.D

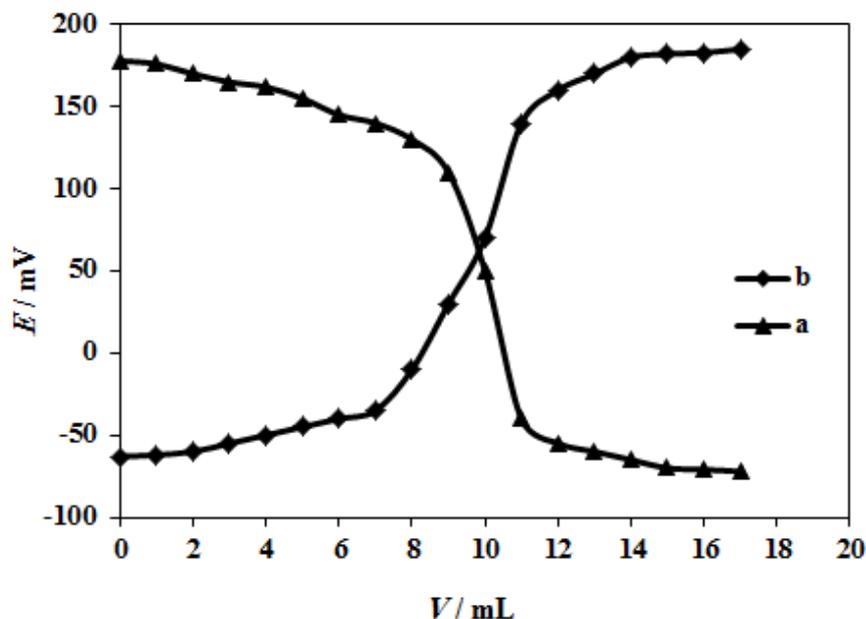


Fig. 13. Potentiometric titration curves of 10.0 mL 1.0×10^{-2} M of Cu^{2+} with 1.0×10^{-2} M EDTA (a), and 10.0 mL 1.0×10^{-2} M of EDTA with 1.0×10^{-2} M of Cu^{2+} (b)

The currently introduced copper electrode was also applied for the determination of Cu(II) ions in tap water samples with satisfactory results. The analysis was performed using standard addition or spike technique [28,29]. The results are summarized in Table 4.

As it is shown, good recoveries were obtained in all of potentiometric analysis of the samples. The electrode was also successfully applied to the direct potentiometric measurement of Cu(II) in a known copper solution prepared from electrical copper (purity > 98%). The experiments were run three times and the results obtained are presented in Table 5. As the data show satisfactory agreement between copper standard solution contents and those measured potentiometry using PGE/PPy/Cu-P4R electrode was observed.

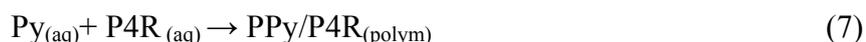
Table 5. Application of fabricated Cu electrode for potentiometric measurement of copper in known solutions prepared from copper electrical wire

No.	Sample known Solution/M	Measured*/M	t-test ^{95%}
1	5.0×10^{-4}	$4.89 (\pm 0.15) \times 10^{-4}$	1.27 (4.30)
2	1.0×10^{-3}	$0.93 (\pm 0.11) \times 10^{-3}$	1.10 (4.30)
3	5.0×10^{-3}	$4.86 (\pm 0.23) \times 10^{-3}$	1.05 (4.30)

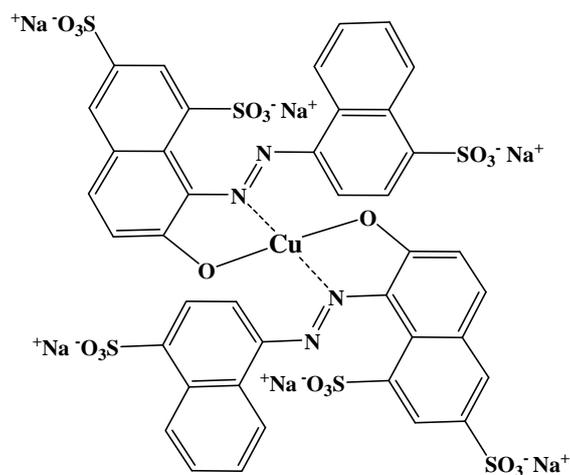
*Mean of three measurements

3. 12. Suggested mechanism

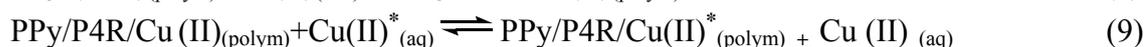
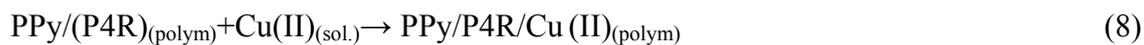
The electropolymerisation reaction of polypyrrole doped with P4R can be shown as Eq. (7). Since just P4R without any other salts was used as the electrolyte during electro polymerization in order to ascertain that only the dye anions (P4R) are permitted to be incorporated into the polymer, in order to maintain charge balance or electro neutrality in the final polymer product. The anodic or oxidative polymerization reaction of PPy conducting polymer in the presence of P4R dye for preparation of copper sensor electrode can be simply shown as the following:



The simultaneous cathodic reaction can be either reduction of water or dissolved O_2 . In the course of conditioning the PGE/PPy/Cu-P4R electrode in a standard solution of copper (II), copper ions may form stable complexes with the P4R counter ions in the polymer matrix due to the high affinity of P4R toward Cu^{2+} ions (Scheme 2 and Eq. 8). It is supposed that the change in potential with the change in Cu^{2+} concentration in the test solution (shown by asterisk) is caused by the shift of equilibrium of complexation reaction and ion exchange process (Eq. 9). It should be noted that the application of the introduced Cu(II) sensor electrode is limited to slightly acidic media (pH~5). In basic solutions, PPy is changed into a nonconducting state; moreover, the cupric ions may also precipitate as $\text{Cu}(\text{OH})_2$. As we have already demonstrated, application of PPy conducting polymers for the preparation of solid-state ion-selective electrodes is most possibly based on the ion exchange properties of the doped polymer [38].



Scheme 2. Complex formation between P4R and Cu(II) ion



4. CONCLUSION

The introduced indicator electrode based on polypyrrole conducting polymer can be easily prepared via simple electrochemical method (potentiostatically at 0.80 V (vs. SCE) for duration of 100 s). The copper sensor electrode fabricated in the current study showed response characteristics with Nernstian behavior over the concentration range 1.0×10^{-5} – 5.0×10^{-2} M of Cu(II) ion. Although, the introduced copper sensor electrode, did not show a very wide linear concentration range, instead, it possess many advantages such as fast response time (<15 s), low detection limit (6.70 μM), low cost and ease of preparation, high shelf lifetime (>60 days), high selectivity, accuracy/precision, and high repeatability/reproducibility. Due to the high toxicity of copper ions to aquatic life, the finding in this study is very important from both analytical and environmental points of views.

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REFERENCES

- [1] D. Stankovic, G. Roglic, M. Jovic, I. Andjelkovic, J. Mutic, and D. Manojlovic, *Anal. Bioanal. Electrochem.* 4 (2012) 238.
- [2] R. Kumar Mahajan, and P. Sood, *J. Electrochem. Soc.* 2 (2007) 832.
- [3] M. B. Gholivand, and N. Nozari, *Talanta* 54 (2001) 59.
- [4] H. A. Zamani, G. Rajabzadeh, M. R. Ganjali, and S. M. Khatami, *Electroanal.* 17 (2005) 2260.
- [5] S. M. Saad Hassan, M. Eman Elnemma, and H. K. Ayman Mohamed, *Talanta* 66 (2005) 1034.
- [6] M. M. Ardakani, S. H. Mirhoseini, and M. Salavati-Niasari, *Acta. Chim. Slov.* 53 (2006) 197.
- [7] M. Mazloun Ardakani, M. Salavati-Niasari, M. Khayat Kashani, and S. M. Ghoreishi, *Anal. Bioanal. Chem.* 37 (2004) 1659.
- [8] M. R. Ganjali, T. Poursaberi, and L. Haj-Agha Babaei, *Anal. Chim. Acta.* 440 (2001) 81.
- [9] M. R. Ganjali, M. Emami, and M. Salavati-Niasari, *Bull Korean. Chem. Soc.* 23(10) (2002) 1394.

- [10] M. R. Ganjali, T. Poursaberi, M. khoobi, A. Shafiee, M. Adibi, M. Pirali-Hamedani, and P. Norouzi, *Int. J. Electrochem. Sci.* 6 (2011) 717.
- [11] V. K. Gupta, A. K. Jain, G. Maheshwari, H. Lang, and Z. Ishtaiwi, *Sens. and Actuators. B* 117 (2006) 99.
- [12] R. Prakash, R. C. Srivastava, and P. C. Pandey, *J. Solid. State. Electrochem.* 6 (2002) 203.
- [13] M. Essi, *Chalcogenide Lett.* 8 (2) (2011) 103.
- [14] M. R. Ganjali, A. Ghafarloo, F. Faridbod, and P. Norouzi, *Int. J. Electrochem. Sci.* 7 (2012) 3706.
- [15] Z. Brzozka, *Anal. Chem.* 35 (1990) 415.
- [16] L. P. Singh, and J. M. Bhatnagar, *Talanta* 64 (2004) 313.
- [17] N. V. Shvedene, N. M. Sheina, and G. V. Silasie, *Anal. Chem.* 46 (1991) 339.
- [18] M. J. Gissera, M. A. Mendiola, J. R. Procopio, and M. T. Sevilla, *Anal. Chim. Acta.* 385 (1999) 143.
- [19] M. J. Gissera, J. R. Procopio, M. T. Sevilla, and L. Hernandez, *Electroanalysis* 15 (2003) 126.
- [20] S. Sadeghi, M. Eslahi, M. A. Naseri, H. Naeimi, H. Sharghi, and A. Sameli, *Electroanal.* 15 (2003) 1327.
- [21] S. Kamata, A. Bhale, Y. Fukunaga, and H. Murata, *Talanta* 36 (1989) 767.
- [22] S. Kamata, H. Murata, Y. Kubo, and A. Bhale, *Analyst* 114 (1989) 1029.
- [23] S. Kamata, Y. Yamasaki, M. Higo, A. Bhale, and Y. Fukunaga, *Analyst* 113 (1988) 45.
- [24] K. Ren, *Talanta* 36 (1989) 767.
- [25] D. Stankovic, G. Roglic, M. Jovic, I. Andjelkovic, J. Mutic, and D. Manojlovic, *Anal. Bioanal. Electrochem.* 4 (2012) 238.
- [26] J. Migdalski, T. Blaz, and A. Lewenstam, *Anal. Chim. Acta.* 322 (1996) 141.
- [27] J. Bobacka, *Electroanal.* 18 (2006) 7.
- [28] A. Michalska, *Electroanalysis* 24 (2012) 1253.
- [29] R. Ansari, A. F. Dellavar, and A. Mohammad-khah, *Microchim. Acta.* 178 (2012) 71.
- [30] R. Ansari, F. Emsakpour, *Anal. Bioanal. Electrochem.* 4(3) (2012) 277.
- [31] R. Ansari, A. Mohammad-Khah, A. Fallah Dellavar, and Z. Mosayebzadeh, *Bull. Korean. Chem. Soc.* 33 (2012) 1247.
- [32] J. Wang, S. P. Chen, and M. A. Lin, *J. Electro. Anal. Chem.* 273 (1989) 231.
- [33] M. Yamaura, T. Hagiwara, and K. Iwata, *Synth. Met.* 26 (1988) 209.
- [34] Q. F. Li, X. G. Chen, H. Y. Zhang, C. X. Xue, S. H. Liu, and Z. D. Hu, *Analyst.* 125 (2000) 1483.
- [35] D. Gautam, R. K. Sinha, and D. B. Milne, *J. Food. Sci. Technol.* 2 (1986) 303.
- [36] E. Bakker, P. Buhlmann, and E. Pretsch, *Chem. Rev.* 97 (1997) 3083.
- [37] M. Arvand, and M. Hashemi, *J. Braz. Chem. Soc.* 23 (2012) 392.

- [38] R. Ansari, A. F. Dellavar, and A. Mohammad-khah, *J. Solid State Electrochem.* 16 (2012) 3315.