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Solid-state ion selective electrode based on polypyrrole conducting polymer nanofilm as a new potentiometric sensor for Zn^{2+} ion

Reza Ansari · Ali Fallah Delavar · Ali Mohammad-khah

Abstract A pencil graphite electrode (PGE) electrodeposited by a polypyrrole conducting polymer doped with tartrazine (termed as PGE/PPy/Tar) was prepared and used as a zinc (II) solid-state ion-selective electrode. For the preparation of the zinc sensor electrode, electrodeposition of a polypyrrole nanofilm was carried out potentiostatically (E_{app}=0.75 V vs SCE) in a solution containing 0.010 M pyrrole and 0.001 M tartrazine trisodium salt. A pencil graphite and Pt wire were used as working and auxiliary electrodes, respectively. The introduced electrode in the current paper can be fabricated simply and was found to possess high selectivity, exhibited wide working concentration range, sufficiently rapid response, potential stability, and very good sensitivity to Zn (II) ion. The sensor electrode showed a linear Nernstian response over the range of 1.0×10^{-5} to 1.0×10^{-1} M with a slope of 28.23 mV per decade change in zinc ion concentration. A detection limit of 8.0×10^{-6} M was obtained. The optimum pH working of the electrode was found to be 5.0.

Keywords Pencil graphite electrode · Polypyrrole/tartrazine · Zn (II) sensor · Direct potentiometry

Introduction

Zinc and its compounds are widely used in various industries such as electroplating, rubber, dye, wood preservatives, ointments, batteries, paint, and pharmaceutical [1]. It is called an "essential trace element" because very small amounts of zinc are necessary for human health. Zinc compounds have biocidal activity because they precipitate and denature the bacterial proteins. For this reason it has been used in dermatology as an antiseptic and disinfectant agent, in ophthalmic solutions, mouthwashes, and mineral–vitamin preparations [2, 3]. It is also present in high-protein foods, and its large doses can cause fever, chills, pulmonary manifestation, gastroenteritis, vomiting, nausea, anemia, and renal failure. Therefore, in view of its toxicity, a selective sensor for the monitoring of zinc is required [1]. A number of electrochemical (none potentiometric) and spectroscopic methods have been used for the determination of zinc ions. These methods are costly and generally involve sample pretreatment therefore they are not very convenient for monitoring of a large number of environmental samples [4–6].

Potentiometric measurements with zinc ion-selective electrode allow to directly determine free ion concentration in aqueous samples. Ion-selective electrodes (ISEs) have been the object of much research efforts since 1950 and have been widely used in the fields of environmental, industrial, agricultural, and pharmaceutical analysis as they offer several advantages over other methods of analysis. Various types of ISEs have been devised based on glass membranes, solid-state homogeneous and heterogeneous membranes, as well as ion-exchange membranes and neutral carrier membranes. The most attractive features of this technique are the speed with which samples can be analyzed, the portability of the device, non-destruction of sample, cost effectiveness, convenience, requiring minimum sample pretreatment, and may also be suitable for online analysis of real samples and large measuring range. Furthermore, solid-state ISEs (without an internal filling solution) can be used at any angle [7–10]. Some zinc sensor electrodes have been reported in literature containing modifiers such as zinc salts

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of bis (4-octylphenyl) hydrogen phosphate in PVC matrix, zinc complex of bis (2-ethylhexyl) phosphate, tetrabutyl thiuram disulfide as the carrier in PVC-based membrane, based on salicylaldoxime-formaldehyde resin, benzo substituted macrocyclic diamides and macrocyclic polyethers [11–16]. However, most of them suffer from the lack of high sensitivity, selectivity, short response time, and long lifetime.

Recently, conducting polymers have attracted more and more attention in materials science due to their interesting and unique electrical conductivity and electroactivity and promising technological applications in rechargeable batteries, light-emitting diodes, super capacitors, solar cells, actuators, separation, sensors and biomedical science [17–22]. Among them, polypyrrole (PPy) stands out because of its high conductivity, structural and good environmental stability biocompatibility, and biodegradation [23]. It can be synthesized both chemically and electrochemically from both aqueous and non-aqueous solvents. Electropolymerization has been shown to have many advantages for deposition of selective layers in fabricating of chemical sensors [24]. PPy is in fact one of the few conducting polymers that can be prepared from neutral or weakly acidic aqueous solutions [25]. By performing the polymerization of PPy in electrolytes containing different counter ions, the functionality and properties of the polymer can readily be changed [26]. Nanostructured PPy can be prepared via electrochemical oxidation of pyrrole. Some recent work indicates that uniform conducting polymer nanofibers can be obtained without the need for any template simply by controlling the electrochemical polymerization kinetics [27]. Although PPy only exists in a neutrally reduced state and a positive oxidized state, it is possible to create both anion and cation sensitive films using small inorganic anions or large organic anions as counter ions during the synthesis. Polymerization reaction of polypyrrole can be simply shown as Fig. 1, where A^- is the counterion or anion of the electrolyte incorporated into the conducting polymer matrix during electropolymerization in order to maintain the electrical charge balance, depending on the type and the charge of the incorporated anion corresponding to one anion for every 3–4 pyrrole units in order to achieve electroneutrality, and this makes up 30–40 % of the final weight of the polymer [28]. Polypyrrole is electroactive and can act as an ion exchanger d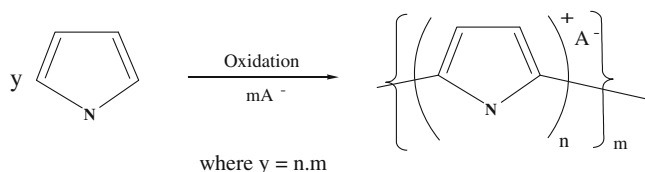uring redox reaction. The charging and discharging (doping–dedoping) processes of polypyrrole are accompanied by the exchange of ions (anions, cations or both) depending on the size of the dopant and potential applied on the membrane [29]. Tartrazine is a synthetic lemon yellow azo dye which is soluble in water. It is extensively used in many fields of technology in soaps, cosmetics, shampoos and other hair products, moisturizers, crayons, leather, textiles industry, lotions, and stamp [30]. The structure of tartrazine is shown in Fig. 2.

Studies of complexation between metals and macrocyclic ligands have yielded valuable information for the construction and design of sensors. Macrocyclic ligands such as crown ethers are novel, cyclic, organic molecules containing O, N, S, etc. capable of forming electron rich interior cavities and possessing the ability to complex through dipole–dipole or ion–dipole interactions with metal ions of compatible dimensions [31, 32].

In this research, a new solid-state electrode was prepared by the electrodeposition of a PPy nanolayer, which was doped with tartrazine (an anionic azo dye). An azo dye host molecule with specific binding properties toward the zinc (II) ions causes the importance of guest–host chemistry in the fabrication of this sensor. The main 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 electropolymerization as dopant or counterion. The incorporated anions termed as dopants can then induce its property into the polymer product. It has been well documented that the polymer dopant anions govern the characteristics and general properties of polypyrrole conducting polymers. In this regard, it has been reported that PPy conducting polymers doped with some dyes possess special nanostructure properties [25, 33]. Among the different heavy metal ions examined, Zn (II) ion showed more affinity to show stable potential readings with polypyrrole-doped tartrazine dye. The polymeric nanofilm (PPy/Tar) used for the preparation of the zinc electrode is an electronically and ionically conducting material based on polypyrrole which allows better defined ion-to-electron transduction compared to the classical coated wire electrodes. The high affinity of Zn (II) ion to the polymer dopant of tartrazine for complex or chelate formation seems to be the basis of the potentials generated in the course of potentiometric analysis.
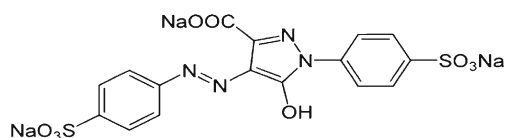

Fig. 1 Polymerization reaction of polypyrrole

Fig. 2 Chemical structure of tartrazine azo dye (Tar)

Experimental

Chemicals and apparatus

All chemicals used were of analytical grade and were prepared in distilled water. Pyrrole was obtained from Merck and was distilled before use. Sodium hydroxide, nitric acid, citric acid, potassium chloride, tartrazine dye (trisodium (4E)-5-oxo-1-(4-sulfonatophenyl)-4-[(4-sulfonatophenyl) hydrazono]-3- pyrazolecarboxylate), $ZnSO_4.7H_2O$ were used for the preparation of standard solutions of zinc ion. Nitrate or chloride salts of interfering cations (Merck) were used for the determination of the selectivity coefficient of the sensor zinc electrode. Standard solutions of Zn (II) ion were prepared from 1.0 M $ZnSO_4.7H_2O$ as stock solution. The working solutions with different concentrations of zinc ions were prepared by successively diluting the stock solution. For the investigation of selectivity, interfering metal ions were prepared as 0.010 M from their pure related salts.

Electropolymerization and cyclic voltammetry analysis (CV) for measuring the electroactivity of the synthesized polymer film was carried out with an electrochemical analyzer (SAMA 500 Iran). A Metrohm pH meter (model 827) 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 with 0.10 M HNO_3 and NaOH. All potentiometric measurements were carried out at 25 °C with a cell of the following type: SCE‖Zn^{2+} (a_A) | PGE/PPy/Tar. A double junction saturated calomel electrode was used as the reference electrode. EMF measurements were carried out using an accurate digital electronic voltmeter with high internal impedance to the nearest 0.1 mV. An HG-AAS Varian (Malgrave, Victoria, Australia) AA220 with a vapor generation accessory VGA-77 was used for the analysis of zinc content in the real samples in order to compare the results obtained with the potentiometric analysis using fabricated electrode (PGE/PPy/Tar). The surface morphology of polypyrrole was examined by scanning electron microscopy (SEM) using the Philips XL30 scanning electron microscope at an accelerating voltage of 17.0 kV and ×30,000 magnification.

Preparation of electrode and procedure

A three-electrode system was employed for the electropolymerization of pyrrole in aqueous solution containing monomer. Electropolymerization was carried out by potentiostatic method ($E_{appl.}$ = 0.75 V vs SCE) using a 0.010-M monomer (pyrrole) and 0.0010 M of tartrazine as electrolyte. A pencil graphite electrode (PGE) was used as the working electrode, and a Pt wire was employed as the auxiliary electrode. PGE (cross area=0.38 mm²) was cleaned with concentrated

HNO_3 (6 M) in order to remove any possible metal impurities from the electrode. Electropolymerization was performed for 300 s, and the charge passed during electropolymerization was 97.2 mC (recorded by an instrument). The thickness of coated PPy film was about 100 nm (estimated from the charge consumed).

The fabricated electrode (PGE/PPy/Tar) was conditioned for 6 h in 1.0×10^{-3} M Zn (II) solution before its use for potentiometric analysis. It is important to emphasize that the electropolymerization conditions have a great effect on the sensing behavior of the electrode. The experimental conditions reported are the optimized conditions that were obtained after preliminary investigations. A PGE was also used for the electrodeposition of polypyrrole from a solution of pyrrole and KCl as electrolyte under the same conditions used for the PGE/PPy/Tar zinc sensor electrode termed as PGE/PPy/Cl. In order to have a good comparison, this electrode (PGE/PPy/Cl) was then used for surface morphological analysis and determination of zinc ions. Since any potential stability, reversibility, and linear response for zinc ion using the PGE/PPy/Cl electrode were not observed, all the potentiometric experiments were shown only for PGE/PPy/Tar electrode. All the potentiometric measurements of zinc ion were carried out using citrate buffer solution (pH=5). The emf (E) of the sensor electrode system dipped in the solution of Zn (II) ion was investigated given by the following equation (Eq. 1):

$$E = k + S \log\left[Zn^{2+}\right], \tag{1}$$

where E (millivolt) is the total potential developed between the sensing and reference electrodes. k (millivolt) is a constant which is characteristic of the particular ISE/reference pair. It can be calculated from the linear plot of E vs log C, and S is the electrode slope. Selectivity coefficient ($K_{A,I}^{Pot}$) values for a range of common interferent cations were calculated by separated solution method (Eq. 2) [34]:

$$\log K_{A,I}^{Pot} = \frac{(E_I - E_A)Z_A F}{RT\ln 10} + \left(1 - \frac{Z_A}{Z_I}\right)\log a_A, \tag{2}$$

where a_A is the activity of Zn (II) ion. E_A and E_I are the potential of target and interfering ions in solutions at the same activity, Z_A and Z_I are the charges of the analyte and interfering ion, respectively. The concentration of interfering and target ions for the determination of the selectivity coefficient of the electrode used in the present study was chosen 1.0×10^{-2} M. For the preparation of the calibration curve, standard solutions of Zn (II) ion were prepared with different concentrations (from 1.0×10^{-1} to 1.0×10^{-7} M), and the potentials were recorded after 50 s or less until the readings were stable. The maximum electrode potential fluctuation was less than 1.0 mV. Potential readings started from the least concentrated solution.

Results and discussion

Working concentration range

The potential of the cell setup with solid-state zinc (II) electrode was determined as a function of Zn (II) concentration. The calibration curve for the analysis of Zn (II) prepared using standard solutions of Zn (II) ion and the electrode (PGE/PPy/Tar) is shown in Fig. 3.

It is seen from Fig. 3 that the fabricated electrode exhibits a linear response over a working concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with a near Nernstian slope of 28.23 mV per decade of activity. The limit of detection was calculated from Fig. 3 as the concentration of zinc ion obtained when extrapolating the linear region of the calibration plot to the baseline potential was 8.0×10^{-6} M. The sensitivity of the introduced electrode toward the zinc ion can be due to the potential developed on the surface of the solid polymeric film containing tartrazine and tartrazine–Zn (II) complex ion and Zn (II) ion in the test solution. The repeatability of the electrode response (readings) was quite high when the concentrations of the zinc ion were changed. In order to find out the repeatability of the potential measurements with the zinc (II) selective electrode, each concentration was analyzed five times. The maximum relative standard deviation (RSD) obtained was less than 1.2 %.

Reversibility of the electrode response

Reversibility factor is one of the most important parameters in evaluating sensor performance for its practical application. In order to find out the reversibility of the response, the fabricated electrode was exposed repetitively in zinc ion solutions at two different concentrations (1.0×10^{-5} and 1.0×10^{-4} M). The results observed are shown in Fig. 4. The potential reported are the mean values of at least three measurements for each concentration. The obtained potentials were 159.0 and 182.0 V for 1.0×10^{-5} M and 1.0×10^{-4} M of Zn (II) ion solutions,

Fig. 4 Reversibility of PGE/PPy/Tar electrode (pH=5.0, response time=50 s, conditioning: 6 h in 1.0×10^{-3} M of Zn (II) ion)

respectively (maximum RSD was ±1.2 %). As the data interestingly indicate, the signal of the fabricated Zn (II) electrode is highly reversible.

Response time and lifetime

The response time of the sensor was determined by measuring the time required to achieve a steady potential for different Zn (II) ion concentrations (1.0×10^{-5} to 1.0×10^{-1} M). The recorded response time of the PGE/PPy/Tar electrode was 50 s for each measurement. Maximum potential fluctuations were ±2.0 mV, at least, for 3 min. The lifetime of PGE/PPy/Tar electrode was further investigated by performing periodic calibration with standard solutions and calculating the response and slope over the range 1.0×10^{-5} to 1.0×10^{-1} M Zn (II). The data obtained are summarized in Table 1. The tests performed in different time intervals (2 months) show that any considerable changes in the slope of the electrode response were not observed, and the observed drift in potential was 4.1 %.
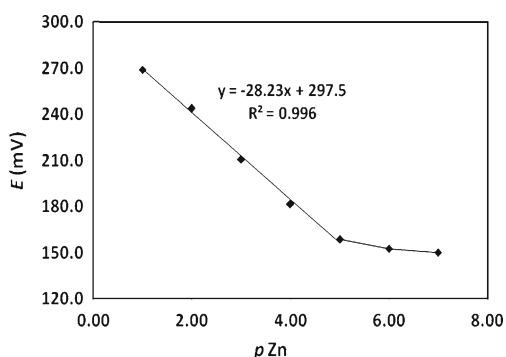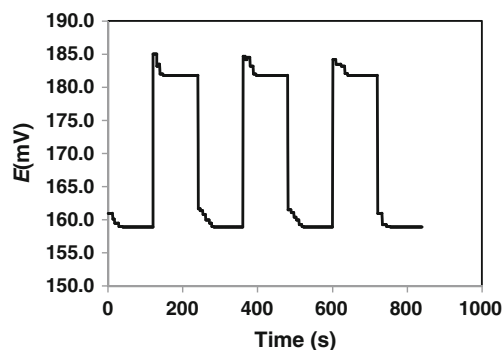

Fig. 3 Calibration curve of Zn (II) using PGE/PPy/Tar electrode (pH= 5.0, response time=50 s, conditioning: 6 h in 1.0×10^{-3} M of Zn (II) ion)

Table 1 Effect of storage time of PGE/PPy/Tar electrode on its Nernstian response

Storage time (day)	Slope (mV per decade)	Intercept (E/mV)
1	28.2	297.5
5	28.2	297.5
15	28.0	292.3
20	27.9	294.5
25	27.5	292.3
30	27.5	315. 8
35	27.5	291.1
40	27.3	289.1
50	27.3	286.9
60	27.1	284.3

Effect of pH

Hydronium is one of the ions that can interfere with potential readings if it exists at high concentrations in a solution. So, it is necessary to find the optimum pH where the electrode is free from the interference of hydrogen ions. In this investigation, pH dependence of the electrode response was tested using 1.0×10^{-4} M of Zn (II) solution over a pH range of 1.0–9.0. The pH of the test solutions were adjusted using diluted solutions of either NaOH or HNO$_3$. The potential of the sensor electrode was determined as a function of pH which is illustrated in Fig. 5. As the results indicate, the potentiometric response for this electrode depends strongly on the pH of the test solution.

The most suitable pH value for potentiometric determination of Zn (II) was 5.0, which was taken as the working pH of the sensor assembly. At acidic conditions (pH <3.0) the electrode response (potential increase) could be related to the interference by hydrogen ions which exists at high concentrations. At higher pH values (pH >9), a dramatic drift in potential (decrease) is also observed which are supposed to be due to the formation of hydroxyl complexes of Zn (II) or changing the polymer (PPy) into a poor conducting material. Therefore, all of our further measurements were performed at pH 5.0.

Cyclic voltammetry analysis

CV is a powerful and the most versatile electroanalytical technique which is widely used for studying the electroactivity of conducting polymers [35]. A great deal of useful information for the characterization of conducting polymers, such as the determination of the potential required for polymerization and the polymer reduction/oxidation potentials, can also be obtained by this technique. The CV experiments were performed using 0.10 M KCl solution as supporting electrolyte after deoxyg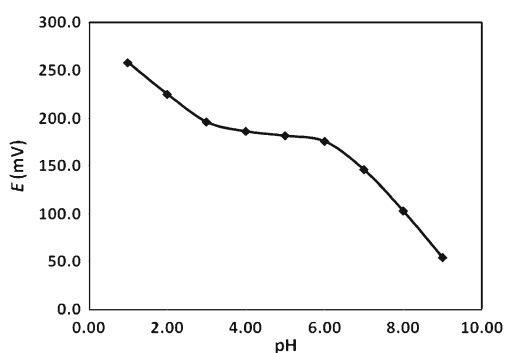enation. The potential scan rate was selected 50 mV S^{-1}. The CV obtained from PPy/Cl shows two well-defined redox peaks related to the polymer matrix which is accompanied by an anion exchange process (Fig. 6).

The CV recorded from PPy/Tar shows some redox properties which is the main characteristic of all conducting electroactive polymers. The CV from PPy/Tar clearly indicates that tartrazine dye has been incorporated with the polymer during synthesis, and the resulted polymer is electroactive. The CV of the bare electrode was also recorded. As it is shown (Fig. 6c), there are no redox peaks in the CV of bare pencil graphite electrode. In the cyclic voltammogram of PPy/Tar, three couples of redox peaks can be distinguished which belong to the redox peaks of the polymer and dopant. The last couple of redox peaks appeared at the more negative potential (−0.53 and −0.40 V) can be due to the cation movements in and out of the polymer which is the characteristic of PPy conducting electroactive polymers doped with large size counterions or dopants [35, 36]. It has also been previously reported that the redox peaks of the electroactive tartrazine dye is strongly dependend on the pH of the supporting electrolyte in which the CV is recorded [37]. The cyclic voltammograms of PPy/Tar and PPy/Cl were further recorded in ZnCl$_2$ (0.10 M) as supporting electrolyte. As the CVs indicate (Fig. 7), the electrochemical behavior of two polymers are different from each other. PPy/Cl showed the same electrochemical behavior as it was observed in KCl solution. So it can be concluded that in the case of PPy/Cl, mostly anion exchange has occurred, and electroactivity of the polymer has not been affected by zinc ions (Fig. 7a). However, in the case of PPy/Tar, because of the presence of larger size of dopant (Tar) as well as its high tendency to zinc ion, electrochemical behavior has been changed and the redox peaks have also been less well defined (Fig. 7b) compared to PPy/Cl and also PPy/Tar in KCl solutions (Fig. 6a, b).
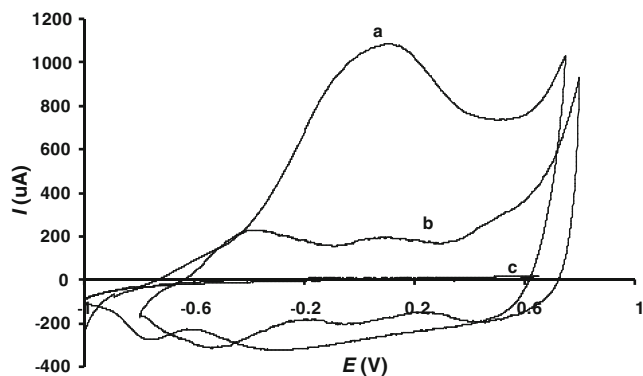

Fig. 5 Effect of pH on the electrode response, the solution contains 1.0×10^{-4} M Zn (II) (pH=5.0, response time=50 s, conditioning: 6 h in 1.0×10^{-3} M of Zn (II) ion)

Fig. 6 The cyclic voltammograms recorded for **a** PPy/Cl, **b** PPy/Tar, and **c** bare PGE. 0.20 M KCl was used as supporting electrolyte, scan rate was 50 mV s^{-1}
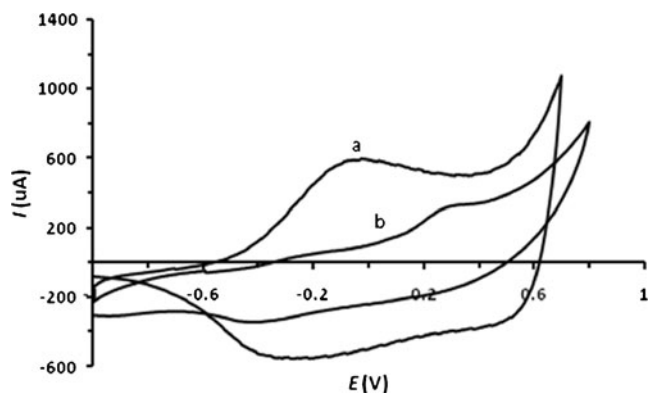
Fig. 7 The cyclic voltammograms recorded for **a** PPy/Cl, **b** PPy/Tar, and **c** bare PGE. 0.10 M ZnCl$_2$ was used as supporting electrolyte, scan rate was 50 mV s^{-1}

Morphology study

Scanning electron microscopy (SEM) is an important tool for the characterization of the surface morphology of the polymers. The micrographs with the same magnification obtained for the polypyrrole used in this investigation are shown in Fig. 8. As the SEM pictures show, the PPy is electrodeposited onto PGE as a nanostructure layer. Based on the SEM images (Fig. 8a, b), PPy shows a mass of clews, which are nonuniformly distributed with a bulk quantity of nanoparticle size.

Selectivity of the prepared zinc electrode

An important performance parameter for an ion-selective electrode is its selectivity towards target ion over other ions. The concentration level of the interfering ion, which an electrode can tolerate, depends on the numerical value of selectivity coefficient. The smaller the value of selectivity coefficient, the higher is the concentration of interfering ion (s), which can be tolerated by the sensor. The selectivity study was carried out using PGE/PPy/Tar electrode, which exhibited the best performance characteristics in terms of working concentration range, slope, response time, shelf life, and storage stability. The selectivity coefficients of the electrode against a series of ions were evaluated under identical conditions using the separate solutions method. In the separate solutions method, the influence of the variation of primary ion and interfering ion concentrations on electrode response was investigated separately. The resulting selectivity coefficients are also presented in Table 2.

As the results present, the electrode is very selective to Zn (II) ions over all the tested interfering ions listed in Table 2. Thus, because of the high selectivity of the electrode toward Zn (II) ions, it could be concluded that the introduced electrode can be successfully employed for measurement of Zn (II) in the real samples. Among the
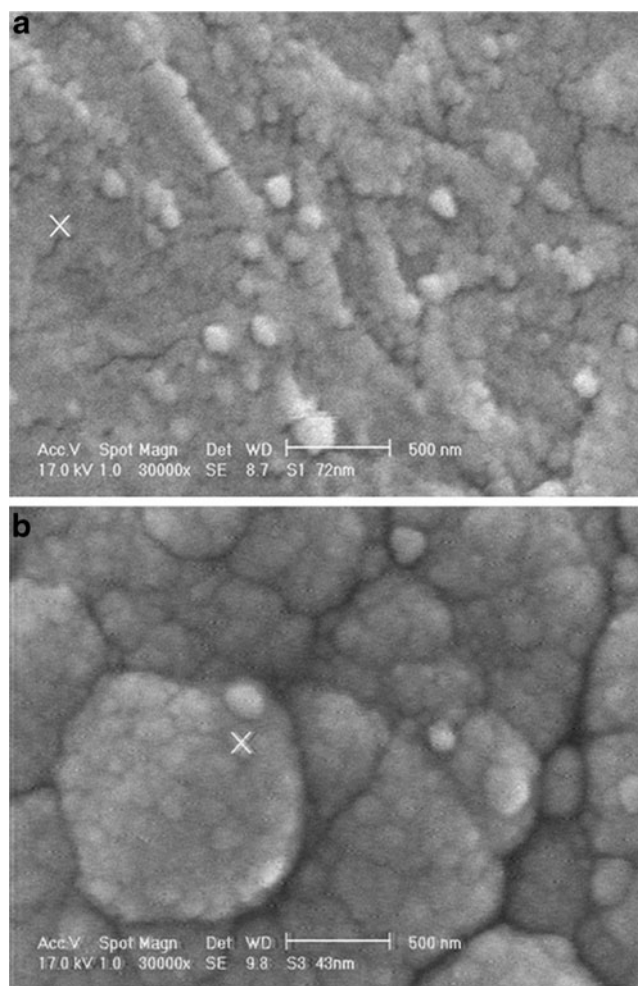

Fig. 8 **a** SEM image of PGE/PPy/Cl (×30,000) and **b** SEM image of PGE/PPy/Tar (×30,000)

Table 2 Selectivity coefficients ($K_{A,I}^{Pot}$) obtained for various interfering ions

Interfering ion	$K_{A,I}^{Pot}$
Na$^+$	3.9×10^{-4}
K$^+$	6.5×10^{-4}
NH$_4^+$	5.7×10^{-4}
Mg^{2+}	8.8×10^{-4}
Ca^{2+}	2.2×10^{-4}
Mn^{2+}	4.6×10^{-4}
Pb^{2+}	1.2×10^{-2}
Co^{2+}	4.8×10^{-4}
Ag$^+$	3.2×10^{-3}
Hg^{2+}	6.3×10^{-4}
Ba^{2+}	3.6×10^{-4}
Ni^{2+}	4.3×10^{-4}
Al^{3+}	5.8×10^{-4}
Fe^{3+}	6.7×10^{-4}
Cd^{2+}	8.5×10^{-4}
Cr^{3+}	1.7×10^{-4}

investigated metal cations as interfering ions, Ag^+ and Pb^{2+} ions showed the most serious interference, if present at higher concentrations.
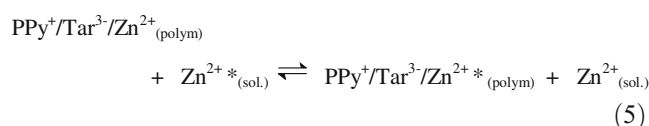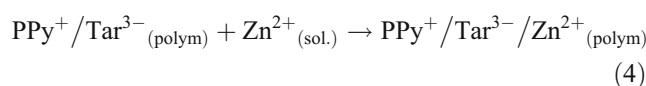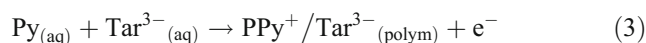
Analytical applications

The analytical applicability of the fabricated zinc electrode was tested using this electrode for measuring the concentration of zinc ion in some real samples. Natural samples such as barley flakes, rice, and dry milk were selected because of possessing zinc ions. The samples were air-dried in porcelain crucibles using an oven (105 °C, 24 h). Known amounts of dried samples were completely burned in the electric furnace (450 °C, 20 min). The ashes obtained from the samples were separately treated with HCl solution (4.0 M) in order to be dissolved before spectroscopic analysis (AAS). The ash solutions were also neutralized before AAS and potentiometric analysis. The results obtained are summarized in Table 3.

As the results interestingly show, there is a close relation between the determined zinc concentration in the tested samples obtained using the AAS technique and those obtained with the application of a zinc sensor electrode fabricated in the current work. The data reported (Table 3) are the mean values of three measurements which were made for each sample.

Suggested mechanism

The oxidation of a pyrrole monomer in the presence of tartrazine dye in aqueous solution is leaded to form a thin conducting electroactive film of PPy/Tar (Eq. 3). A solution of tartrazine dye without any other salts was used as the electrolyte during electropolymerization in order to ascertain that only the dye anions (Tar) are permitted to be incorporated into the polymer (Eq. 3). The PPy/Tar film was readily formed onto the PGE electrode when a constant potential of 0.75 V vs SCE was applied. In the course of conditioning the PPy/Tar electrode in a standard solution of zinc (II), zinc ions may form stable complexes with the Tar counterions in the polymer matrix due to the high affinity of

Tar ions toward zinc (II) ions (Eq. 4). It is supposed that the change in potential with the change in Zn^{2+} concentration in the test solution (as shown by asterisk) is caused by the shift of equilibrium of complexation reaction and ion exchange process (Eq. 5).

$$Py_{(aq)} + Tar^{3-}_{(aq)} \rightarrow PPy^+/Tar^{3-}_{(polym)} + e^- \qquad (3)$$

$$PPy^+/Tar^{3-}_{(polym)} + Zn^{2+}_{(sol.)} \rightarrow PPy^+/Tar^{3-}/Zn^{2+}_{(polym)} \qquad (4)$$

$$\begin{aligned} PPy^+/Tar^{3-}/Zn^{2+}_{(polym)} \\ + Zn^{2+}*_{(sol.)} \rightleftharpoons PPy^+/Tar^{3-}/Zn^{2+}*_{(polym)} + Zn^{2+}_{(sol.)} \end{aligned} \qquad (5)$$

It should be noted that the application of the introduced Zn (II) sensor electrode is limited to slightly acidic media (pH ~5). In basic solutions, PPy is changed into a nonconducting state; moreover, the zinc ions may also precipitate as $Zn (OH)_2$. Application of PPy conducting polymers for the preparation of solid-state ion-selective electrodes is mainly based on the ion exchange properties of the polymer [38–40]. These electrodes are not generally recommended to be used in the presence of strong reductive or oxidative environments too. PPy film is changed into a nonconducting material in the presence of strong reducing agents and loss its electrical conductivity, electroactivity, and chemical integrity (due to overoxidation process) under strong oxidative aqueous media [41].

Conclusions

Zinc sensor or solid-state zinc ion-selective electrode was simply prepared via electrochemical deposition of polypyrrole conducting polymer on the surface of a pencil graphite electrode. The sodium salt of tartrazine dye was employed as a dopant electrolyte during electropolymerization. The prepared electrode (PPy/Tar) showed near Nernstian behavior over the Zn (II) ion concentration in the range of 1.0×10^{-5} to 1.0×10^{-1} M. The response time was also fast enough (50 s). Advantages such as high accuracy and precision, low detection limit, low cost and simplicity of preparation, high repeatability, high shelf time, together with the good selectivity and high sensitivity of the sensor electrode to zinc ions, make this electrode potentially useful for the potentiometric measurement of Zn (II) in real samples. Due to the high toxicity of zinc ions to aquatic life, the finding in this study is very important from both analytical and environmental point of views.

Table 3 Comparison of analysis of samples for Zn (II) ions using two methods

Sample	Conc. of Zn (II) (mg kg^{-1}) using AAS	Conc. of Zn (II) (mg kg^{-1}) using potentiometry (PGE/PPy/Tar)
Barley flakes	16.1±1.1	17.5±0.7
Rice	13.2±0.9	14.5±0.8
Dry milk	41.0±1.8	45.0±1.6

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