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Copper(II) ion sensor based on electropolymerized undoped conducting polymers

Abstract A solid state copper(II) ion sensor is reported based on the application of electropolymerized undoped (neutral) polycarbazole (PCz) and polyindole (PIn) modified electrodes. The new sensor shows high selectivity to Cu^{2+} ions with a detection limit of 10^{-5} M. PCz and PIn are formed respectively by the anodic oxidation of 50 mM carbazole and 5 mM indole monomers in dichloromethane containing 0.1 M tetrabutylammonium perchlorate on a platinum electrode using a single compartment cell. Potentiostatic polymerization of both the monomers are carried out at 1.3 V and 1.0 V vs. Ag/AgCl, respectively. Perchlorate ions were electrochemically removed from the polymer films by applying – 0.2 V vs. Ag/AgCl. Polymer-coated electrodes are incubated in 1 M KCl solution for 8 h followed by incubation in distilled water for 2 h before using as a metal ion sensor. The undoped PCz and PIn electrodes were found to be highly selective and sensitive for Cu^{2+} ions with little selectivity for Pb^{2+} and negligible response towards Ag^{+}, Hg^{2+}, Cu^{+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+} or Zn^{2+}. Potentiometric responses for Cu^{2+} ions are recorded for both the sensor electrodes together with a double-junction Ag/AgCl reference electrode. Calibration curves for Cu^{2+} are reported for both ion sensors. The polymer-modified electrodes were found to be stable for several weeks.

Keywords Conducting polymers · Ion sensor · Ion selective electrodes · Electropolymerization

Introduction

Conducting polymers, particularly polycarbazole and polyindole, have received increasing attention because of

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their potential in developing new technologies of commercial interest, viz. ion sensors, rechargeable batteries and display devices, etc. [1, 2, 3, 4]. One of the major applications of these conducting polymers is their use in designing solid state ion selective electrodes [1, 2, 3, 5]. An all solid state potassium ion selective electrode has been reported on a platinum disk using a bilayer film configuration of polypyrrole/poly(4-styrenesulfonate) (PPy/PSS) composite covered with a plasticized PVC matrix membrane impregnated with valinomycin [6]. The problem associated with the overshoot of the baseline potential of classical-type ion sensing electrodes was reduced because of the electroactivity and cation exchange behaviour of the PPy/PSS composite film. This configuration of the sensing electrodes results in the formation of concentration cells, also referred to as symmetric cells (ions-in, ions-out), at the test solution/PVC and PVC/(PPy/PSS) interfaces. To avoid such a complicated configuration of the ion selective electrodes, we constructed solid state potassium ion selective electrodes based on a bilayer film of polycarbazole (PCz) or polyindole (PIn) and a neutral carrier incorporating a plasticized poly(vinyl chloride) (PVC) membrane impregnated with valinomycin or a crown ether [1, 2]. The contribution of the conducting polymer layer in these sensor electrodes was to maintain a stable potential difference across the conducting polymer/metal interface because of its unique nature of ionic and electronic conductivity in its doped state. The response of the K^{+} selective electrode was based on forming a host-guest linkage of the neutral carriers (valinomycin or crown ether). Later, more simplified single-layer conducting polymer-based ion sensors were developed, where the conducting polymer itself exhibited a new type of host-guest linkage [3, 7].

The conducting polymers, i.e. PCz and PIn, have relatively better stability on the metal electrode surface when it is electrochemically polymerized in non-aqueous solution [1, 4]. The doping-dedoping of the polymers is also very effective in non-aqueous solutions for smaller anions, while in aqueous solution a poor

doping-dedoping is observed. The dedoping of PCz or PIn results in a neutral polymer (with vacant interstices), which may be available for other ions present in the aqueous solution as a result of the formation of a new type of host-guest linkage. This host-guest linkage depends on the size and charge of the ions in the solution as well as on the geometry of the interstices in the polymer matrix. We have earlier reported this type of host-guest linkage in neutral poly(3-cyclohexylthiophene) for H^+ ions [3]. In the present study we have developed a novel solid state Cu^{2+} selective electrode based on the single-layered undoped (neutral) PCz or PIn film without using any ion carrier/exchanger.

Experimental

Materials

Carbazole, indole and tetrabutylammonium perchlorate (TBAP) were obtained from Aldrich (USA). Other chemicals and solvents used were of analytical grade. Platinum electrodes and the double-junction Ag/AgCl reference electrode were constructed in our laboratory with the help of the Instrumentation Division of our Institute.

PCz-modified electrode

Electrochemical polymerization of carbazole was carried out potentiostatically from a non-aqueous electrolyte solution of 0.1 M TBAP and 50 mM carbazole in dichloromethane at a platinum disk electrode. The typical construction of the electrode is described elsewhere [1] and a cell assembly is shown in Fig. 1 along with a reference electrode. All electrochemical experiments were carried out in a three-electrode single-compartment cell comprising a Pt disk/plate, a Pt gauge and Ag/AgCl as working, counter and reference electrodes, respectively, using a Solartron Electrochemical Interface (model 1287, Solartron, UK) connected to a PC through the serial port. A constant potential of 1.3 V vs. Ag/AgCl was applied to the working electrode to obtain a good PCz film over the electrode.

PCz film was electrochemically dedoped (only once, just after formation) in the same monomer-free electrolyte by passing a small current (microamps) at –0.2 V vs. Ag/AgCl (keeping the PCz electrode as cathode). The electrode was washed in dichloromethane and incubated in 1 M KCl solution for 8 h, followed by incubation in distilled water for 2 h for complete removal of perchlorate ions and dopants.

PIn-modified electrode

Electrochemical polymerization of indole was carried out potentiostatically from a non-aqueous electrolyte solution of 0.1 M TBAP and 5 mM indole in dichloromethane as described earlier [1, 4], over a Pt disk/plate electrode. All electrochemical experiments were carried out in a same way as described for PCz.

Potentiometric operation of PCz- and PIn-modified ion sensors

The potentiometric operation of the ion sensors constructed above was carried out in 1 mM tris-HCl buffer (pH ≤ 7) using a double-junction Ag/AgCl reference electrode with the cell assembly Ag/AgCl/3.0 M KCl saturated with AgCl/0.1 M KNO_3/test solution/ion sensor electrode.

The ion sensor electrode together with a double-junction reference electrode were dipped in the stirred electrochemical cell with a working volume of 20 mL (as shown in Fig. 1). The electrode potential was monitored with a pH meter (Orion model 525 A) and an Endress + Hauser Alpha-log x-t recorder. At the steady state potential, varying concentrations of the test solution were injected into the cell and the new steady state potential was recorded.

Results and discussion

First, it is reasonable to discuss the construction and response of the commercially available Cu(II) ion sensor. Such a sensor is a membrane containing sulfides of copper and silver bonded into an epoxy body. When this membrane is in contact with Cu(II) ion solution, a concentration gradient is developed across the membrane, depending upon the level of Cu(II) ions in solution. The electrode shows constant response within the pH range 1–7, beyond which there is a precipitation of copper(II) hydroxide. The Cu(II) sensing electrode can be used in the concentration range 10^{-5} M to 10^{-3} M at temperatures between 0 and 80 °C. A typical calibration curve recorded from this electrode has a slope of 28 mV/decade. Mercury, iron(III) and silver ions poison the electrode sensing element. Therefore, mercury and silver must be absent and iron(III) ion may not exceed one tenth the level of Cu(II) ions present in the sample. Under certain circumstances, chloride and bromide ions interfere with the electrode operation, but only if their concentrations are outside the following limits:

$$[Cu^{2+}][Cl^-] > 1.6 \times 10^{-6} \, M; [Cu^{2+}][Br^-] > 1.3 \times 10^{-2} \, M$$
(1)

In the present study, PCz or PIn were polymerized electrochemically over the Pt metal electrode. The open-circuit potential (OCP) of the PCz and PIn electrodes, in the 1 mM tris-HCl buffer at pH 7 [in the absence of Cu(II) ion], just after making the polymer film was 398 mV and 163 mV vs. Ag/AgCl, respectively. Linear sweep voltammetry experiments were conducted between –0.2 V to 1.4 V and –0.2 V to 1.1 V vs. Ag/AgCl at a scan rate of 0.3 mV/s for the doped PCz and PIn
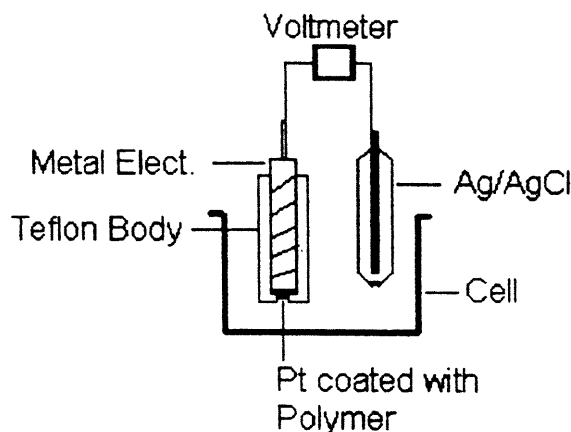
Fig. 1 A cross-sectional view of the sensor electrode along with the reference electrode

modified electrodes respectively in monomer-free electrolyte (dichloromethane containing 0.1 M TBAP) to study the polarizability and kinetics of polymer-coated electrodes. A plot of potential vs. log(I) as shown in Fig. 2 (Tafel plot) was made to identify the values of the equilibrium electrode potential and ion exchange current density. The values of the equilibrium electrode potential were comparable to the OCP of the PCz electrode ($\sim$398 mV) and the PIn electrode ($\sim$163 mV).

In the doped condition, the polymer interstices were occupied by ClO_4^- ions, which also represent the oxidized form of the polymers. When the potentiometric measurements were made using perchlorate ion doped PCz and PIn electrodes, with the addition of chloride ions, a decrease in the equilibrium potential was observed, showing the sensitivity of the oxidized polymer films (both PCz and PIn) towards chloride ions. This result suggested that the addition of chloride ion exchanged the perchlorate ions from the polymer matrix and lead to the formation of chloride-doped PCz and PIn electrodes. Removal of chloride ions (dedoping) from the polymer matrix is easier than for perchlorate ions because of its smaller ionic size and higher hydrophilicity in comparison to perchlorate ions. The dedoping of the polymer electrodes was first carried out by electrochemical reduction of the polymer film and then incubation of the polymer electrode in the 1 M KCl solution for 8 h followed by 2 h incubation in distilled water. The OCP of undoped PCz- and PIn-modified electrodes was also recorded in 1 mM tris-HCl buffer (pH 7) and were 20–25 mV and 80–90 mV vs. Ag/AgCl, respectively. The higher OCP of PIn indicates the presence of some dopants, which depend on the hydrophilicity of the film, the film morphology, the polymer matrix and also the nature of the dopant binding, etc.

The potential responses of the undoped electrodes were measured by adding copper(II) acetate in 1 mM tris-HCl buffer (pH 7). Figures 3 and 4 show the typical responses of the undoped PCz (OCP = 20 mV) and undoped PIn (OCP = 90 mV) on the addition of varying concentrations of copper(II) acetate in the stirred electrochemical cell. The responses were very fast for both the electrodes compared to neutral ion carrier-mediated membrane electrodes, with better linearity. The same experiments were repeated twice and similar responses were observed with a negligible drift in the baseline (5–10 mV) for a 1-week period. Potentiometric responses for both sensors were also taken for the acetate and chloride ions in the 1 mM tris-HCl buffer (pH 7) in the absence of Cu(II) ions. A small decrease in the potential was observed, similar to the typical anionic sensors, as shown in Table 1, which is negligible for the studies of the target cations. The acetate or chloride ion responses were observed because of the doping of the conducting polymers in the Cu(II)-free solution. The chloride ion potential responses were fast and of higher magnitude in comparison to acetate ions because of its strong doping capacity.

The calibration curves for the analysis of Cu(II) ions are shown in Figs. 5 and 6 for PCz and PIn electrodes, respectively. The curves were drawn by plotting each steady state value after subtracting the OCP versus the corresponding log concentration of the Cu(II) ions. The lowest detection limit defined by the calibration curves is 10^{-5} M. The initial slope below 5×10^{-3} M (for PCz) and 5×10^{-4} M (for PIn) sensor electrodes are relatively low, but always greater than the commercially available copper(II) ion electrode (>28 mV/decade). On the other hand, the slope above 10^{-4} M concentration shows a super-Nernstian response for both polymer electrodes. The slope of the sensor to Cu(II) ion analysis is nearly 140 mV/decade under the super-Nernstian behaviour. This shows the novelty of the sensor for Cu(II) ion analysis. The reasons for the super-Nernstian response are not very clear from the mechanistic point of view; however, it may be similar to the super-Nernstian response of the ammonia gas electrode (118 mV/decade) [8].

Fig. 2 Tafel plots of polyindole (*a*) and polycarbazole (*b*) electrodes in dichloromethane containing 0.1 M TBAP at 25 °C
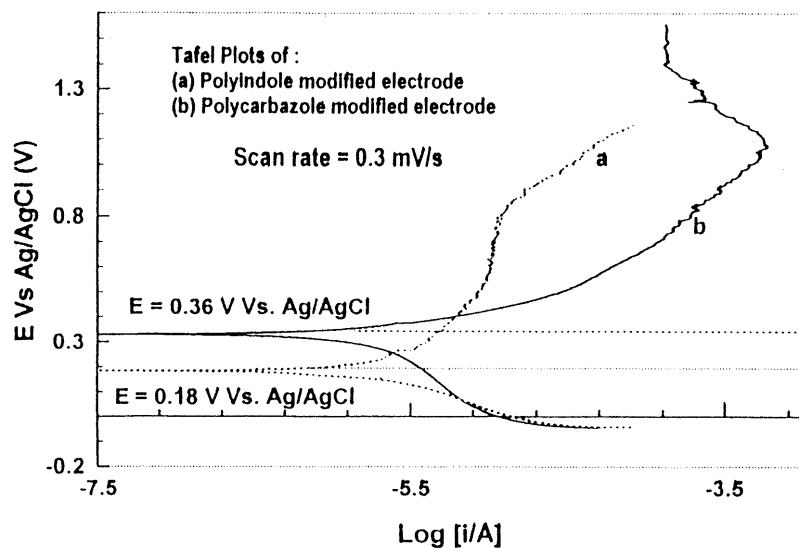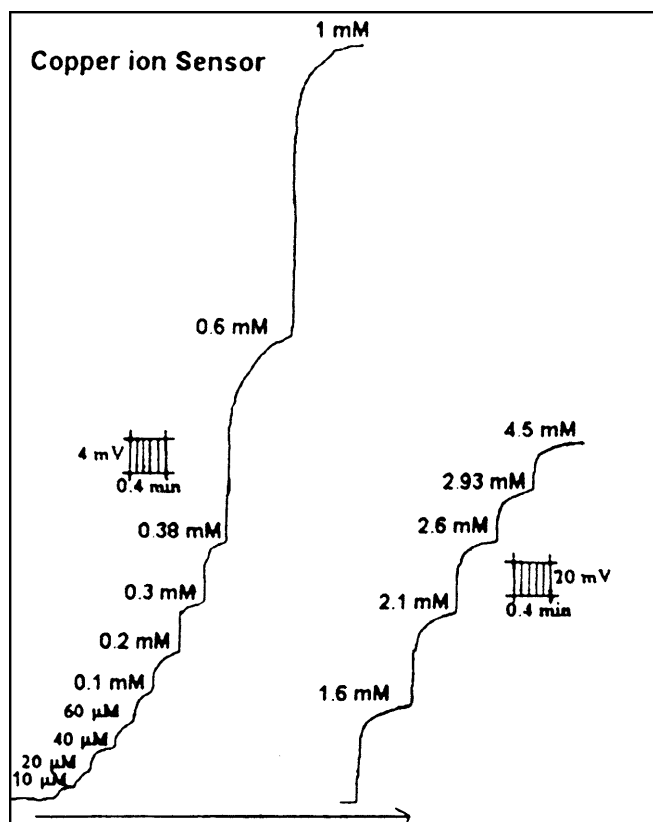
Fig. 3 Typical potentiometric response curve of the undoped polycarbazole (OCP = 20 mV) for varying concentrations of Cu(II) ions in 1 mM tris-HCl buffer (pH 7) at 25 °C

Table 1 Potential response of polycarbazole- and polyindole-modified electrodes for ClO_4^- and Cl^- ions

Concentration of ClO_4^- or Cl^- (mM)	Potential response (mV)			
	Polycarbazole		Polyindole	
	ClO_4^-	Cl^-	ClO_4^-	Cl^-
0.0	80	84	25	24
0.05	79	84	25	21
0.1	78	82	24	19
0.5	76	80	22	16
1.0	73	75	20	12
5.0	71	68	18	6
10.0	68	60	15	0
20.0	64	55	14	−5

The responses of the polymer-modified electrodes (PCz and PIn) towards silver(I), mercury(I), zinc(II), iron(III) and iron(II), cobalt(II), nickel(II), lead(II) and copper(I) ions were studied. Both electrodes were found to be highly selective towards Cu(II) but not for Cu(I), as shown in Table 2. The polymer-modified electrodes show negligible responses towards silver(I), mercury(I), zinc(II), iron(III) and iron(II), cobalt(II) and nickel(II) ions, as for Cu(I) ions as shown in Table 2. A decrease in the potential response may be because of the counter anions (Cl^- or ClO_4^-), as separately shown in Table 1.
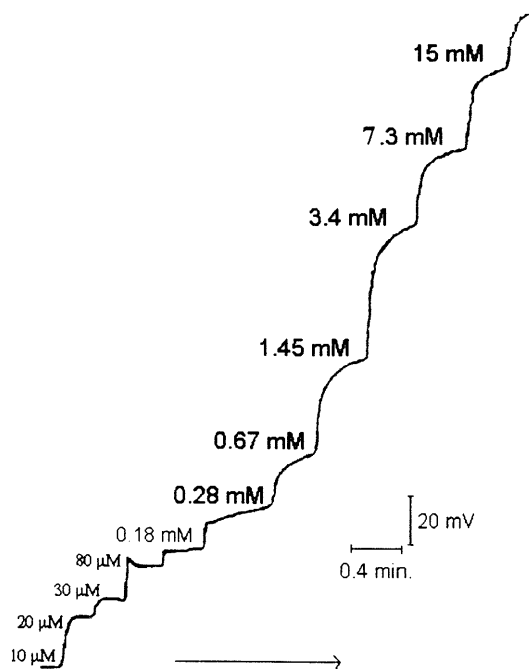

Fig. 4 Typical potentiometric response curve of undoped polyindole (OCP = 93 mV) for varying concentrations of Cu(II) acetate in 1 mM tris-HCl buffer (pH 7) at 25 °C

However, a small response, up to 45 mV for 100 mM lead(II) ion, was observed for both the electrodes, as shown in Table 2.

The response of the neutral polymer to Cu(II) ion is possibly due to the doping of Cu(II) ions within the interstices of the neutral polymer, which can be understood by the secondary doping concept proposed by MacDiarmid and Epstein [9]. The selectivity of Cu(II) ions may be due to those cavities/holes in the polymeric matrix which are surrounded by nitrogen atoms of the monomer units of the chain (i.e. carbazole or indole). Such types of cavities can be compared with Cu phthalocyanine. In the doped form of the polymers, most of the nitrogen atoms of the polymer chains (doping sites) may be positively charged (depending on the doping level) and also surrounded by dopant molecules (anions). In this case, such cavities/holes are either positively charged or occupied by dopant molecules, which do not accept Cu(II) ions, so only undoped PCz or PIn show the response for Cu(II) ions while the doped polymer electrodes show very poor response for Cu(II) ions. The doping-dedoping of Cu(II) ions within the polymer interstices might result in the reversible potential response that tends to establish a dipolar potential at the sensor interface. To a first approximation, such a type of doping and dedoping may be analogous to the host-guest linkage that occurs between well-defined geometrical molecules like crown ethers, valinomycin and nonactin, etc. The size of the Cu(II) ion and the geometry of the interstices possibly contribute to the selective response of the sensor. The host-guest linkage was also supported by testing both the sensor electrodes

Fig. 5 Calibration curve for the polycarbazole-based Cu(II) ion sensor and *inset* showing the enlargement of the same curve between 10 μM to 1 mM concentration of Cu(II) ions

Polycarbazole based Cu(II) Sensor
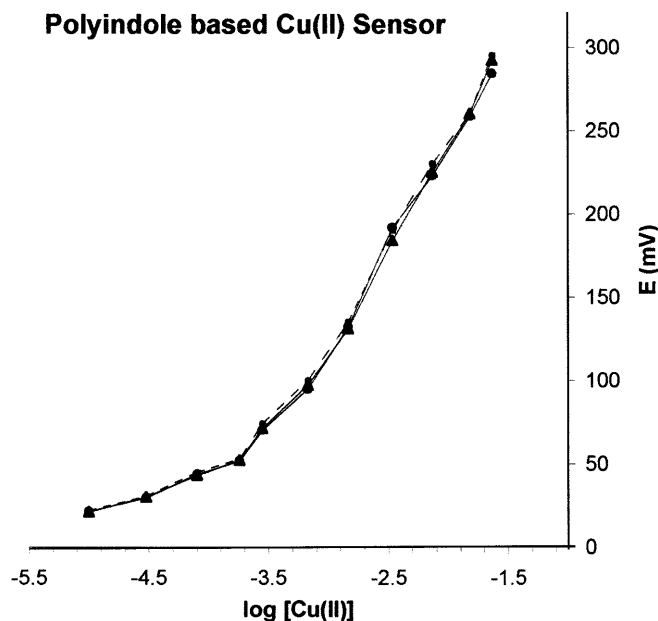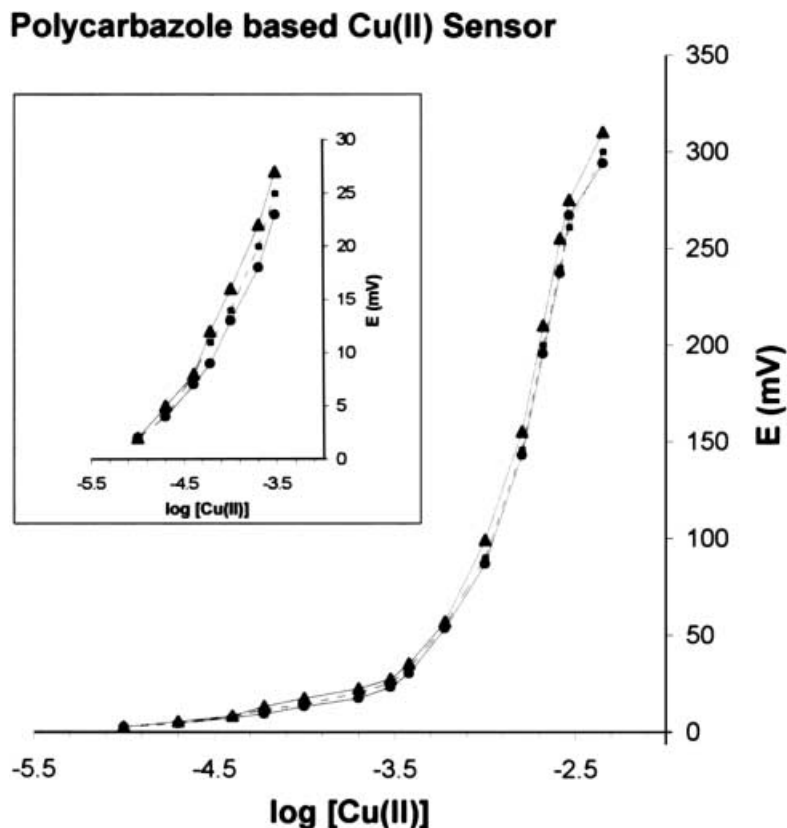
Fig. 6 Calibration curve for the polyindole-based Cu(II) ion sensor

Table 2 Potential response of polycarbazole- and polyindole-modified electrodes for Cu(I) and Pb(II) ions

Concentration of Cu(I) or Pb(II) (mM)	Potential response (mV)			
	Polycarbazole		Polyindole	
	Cu(I)	Pb(II)	Cu(I)	Pb(II)
0.0	85	82	25	23
0.05	82	85	21	25
0.1	84	90	18	30
0.5	79	96	15	35
1.0	74	105	10	43
5.0	68	115	6	55
20.0	62	124	3	62
100.0	58	128	–1	68

indicates the reversible linkage of Cu(II) ions with the polymers, similar to the neutral ion carriers.

Conclusions

A copper(II) ion selective sensor was described using neutral PCz and PIn electrodes. The undoped PCz and PIn in aqueous solution show a highly selective response (potentiometric) for Cu(II) ions. This selectivity is possibly attributed to the formation of analogous host-guest linkages between Cu(II) ions and interstices surrounded by the nitrogen atoms of the polymers, leading to dop-

in increasing and decreasing concentrations of Cu(II) ions. The sensor electrodes showed a reversible response with an error of ±2 mV. The small variation in the response (2 mV) of both the sensor electrodes for increasing and decreasing concentrations of Cu(II) ions

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ing-dedoping of Cu(II) ion within the neutral polymer interstices.

References

1. Pandey PC, Prakash R (1998) Sensors Actuators 46:61–65
2. Pandey PC, Prakash R (1998) J Electrochem Soc 145:4301–4307
3. Pandey PC, Upadhyay S, Singh G, Prakash R, Srivastava RC, Seth PK (2000) Electroanalysis 12:517–521
4. Pandey PC, Prakash R (1998) J Electrochem Soc 145:999–1003
5. Pandey PC (1988) J Chem Soc Faraday Trans 1 84:2259
6. Momma T, Komaba S, Yamamoto M, Osaka T, Yamauchi S (1995) Sensors Actuators B 24–25:724
7. Saxena V, Prakash R (2000) J Solid State Electrochem 4:234–236
8. Yim H, Kibbey CE, Shu-Ching Ma, Meyerhoff ME, et al. (1993) Biosensors Bioelectronics 8:1–38
9. MacDiarmid AG, Epstein AJ (1995) Synth Met 69:85–92