

Evaluation of a carbon paste electrode modified with Ionic liquid and MnO nanoparticles in the Cu(II)determination by Potentiometric Method

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ABSTRACT

A chemically modified carbon paste electrode with ionic liquid and MnO nanoparticles was prepared and used as a sensor for Cu^{2+} ion. The ionic liquid and MnO nanoparticles were used in the composition of the carbon paste to improve conductivity and transduction of chemical signal to electrical signal. Moreover, incorporation of N,N',N''-Tricyclohexyl phosphoric triamid as an ionophore to this composition caused to significantly enhanced selectivity toward Cu (II) ions. The electrode exhibit a super Nernstian slope of 29.9 ± 0.25 mV per decade for Cu^{2+} ion over a wide concentration range from 1.0×10^{-1} to 1.0×10^{-6} M. The lower detection limits are 3.2×10^{-7} M. The electrode has a fast response time (< 6 s), a satisfactory reproducibility and relatively long life time. The proposed sensor shows a fairly good selectivity toward Cu^{2+} ion in comparison to other common cations and the working pH range was 4.0-11. Finally, these electrode have been successfully applied for the determination of Cu^{2+} ions content in various real samples.

Keywords: copper, Carbon paste electrode, Ionic liquid, Potentiometric, Mnonanoparceles

INTRODUCTION

The universal ion selective liquid-state electrode based on carbon was introduced by Ruzicka et al. in 1970 [1-3]. Copper is one of the most widespread elements in the environment of industrialized countries. Due to many applications of copper in industry [4], in many biological systems [5], and in medicinal and environmental samples, also is an essential element and is toxic at high concentration. Researchers have attempted to develop sensors for copper determination with high selectivity and sensitivity [6-10].

The application of chemically modified electrodes (CMEs) in analytical chemistry has attracted considerable attention. A few number of CPEs have been demonstrated as potentiometric sensors [11-13] in 1979 and 1980. In 1980 Heineman et al. [14] described the first use of a polymer film chemically modified electrode as a potentiometric sensor.

Using ion-selective sensor is very convenient for the analysis of samples having difficult matrices, such as industrial, soil and wastewater [1]. Potentiometric electrodes based on ion-selective electrodes are especially suited for such determination because they offer advantages such as selectivity, high sensitivity, good precision, simplicity, and low cost. This research is to introduce a very simple and inexpensive (potentiometric) method in determination of copper(II) in a wide concentration range.

Carbon paste electrodes (CPEs) have attracted attention as ion selective electrodes mainly due to their advantages over membrane electrodes such as chemical inertness, robustness, renewability, stable response, low Ohmic resistance, no need for internal solution and suitability for a variety of sensing and detection applications [15-17].

Moreover, CPEs belong to nontoxic and environmentally friendly electrodes. In their case, problems with passivation are simply eliminated by a simple and quick renewal of their surface[18]. Due to the above mentioned properties, carbon paste electrode seems to be especially promising. To our knowledge, there are some reports on determination of silver ion using a carbon paste electrode [19- 21], that use a few types of modifiers.

In this study, Cu(II) carbon paste electrode based on N,N',N''-Tricyclohexyl phosphoric triamid (NTHPT) asionophore, Fig1, was constructed in order to decide copper ion concentration. Then the electrode was modified by ionic liquid and MnO nanoparticles to achieve the better electrode response. The modified electrode was successfully used as a sensor for potentiometric determination of Cu(II) in aqueous sample.

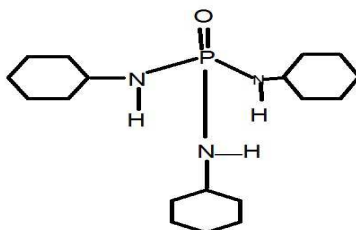


Figure 1. Chemical structure of N,N',N''-Tricyclohexyl phosphoric triamid asionophore

MATERIALS AND METHODS

2.1. Reagents and solutions

All analytical reagent grade chemicals and distilled water were used for preparing all aqueous solutions. The graphite powder with the ionic liquid (1-butyl-3-methyl imidazoliumhexa fluoroborate) was of high purity and was used for the preparation of the carbon pastes. chloride and nitrate salts of the cations used are all purchased from Merck. The synthesis experiments were performed using the following chemicals: MnO (99%, Aldrich), oleic acid, (OA, 90%, Showa). In every case, the chemicals were used in the as received condition without further purification.

2.2.Apparatus

The glass cell in which carbon paste electrode was placed into contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode. The Cu²⁺ CPE was used as an indicator electrode. Both electrodes were connected to a pH/mV meter (Metrohm-691, Switzerland). The following cell was assembled for the conduction of the EMF (electromotive force) measurements:

Carbon paste electrode | sample Cu²⁺ ion solution | Ag/AgCl–KCl (satd.)

2.3 Synthesis of monodisperse MnO nanoparticles

As shown in Table 1, MnO NPs were synthesized with average diameters ranging 42 nm (see fig 2). Taking MnO nano particle for illustration purposes, a mixture of bulk MnO powder (8mmol),oleic acid (38mmol) and ODE (20mL) was loaded into a three-necked round-bottom flask of 500 mL and heated to a temperature of 300 °C at a rate of 15 °C/min under the protection of a flow of N₂. After approximately 35 min, the color of the reactant changed from green to clear yellow; indicating the complete dissolution of the bulk MnO nanopowder. After 80 min, the color of the reactant changed to deep green indicating the formation of MnO NPs. The solution was air-cooled, and the color of reactant changed from deep green (the color similar to bulk MnO) to brown and then to black in 1 day. This may be resulted from the partial oxidation on the NP surfaces.

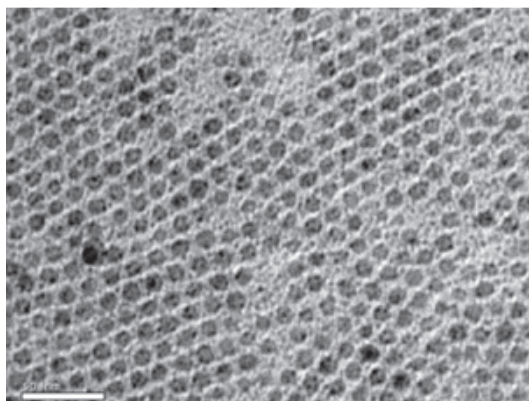


Fig. 2. TEM micrograph of MnO nanoparticle obtained under reaction conditions

2.4. Electrode Preparation

General procedure to prepare the carbon paste electrode was as follows: Different amounts of N,N',N''-Tricyclohexyl phosphoric triamidas an ionophore with an appropriate amount of graphene powder, ionic liquid, Plasticizer (DBP) and MnO nanoparticles were thoroughly mixed. After homogenization of the mixture, the paste was thoroughly packed into the teflon tube and anelectrice wire was inserted into the opposite end of the CPE to set up electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 36 h by soaking it in a $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Cu}(\text{NO}_3)_2$ solution [22-23].

RESULTS AND DISCUSSION

3.1. Carbon paste electrode composition

The sensing element of a potentiometric ion-selective electrode has important role in selectivity behavior of the electrode. The influence of the percent of materials in the carbon paste composition was investigated and the results are summarized in Table 1.

Table 1. The optimization of the carbon paste ingredients

NO	Composition of Carbon Paste (wt.%)					Slope (mV/decade)	Dynamic linear range
	Ionic Liquid	Ionophore	Graphene Powder	MnO nanoparticles	Plasticizer		
1	15	3	68	4	10	24/5	$1/0 \times 10^{-6} - 1/0 \times 10^{-1}$
2	13	4	68	4	11	18/17	$1/0 \times 10^{-6} - 1/0 \times 10^{-1}$
3	12	4	71	3	11	24/8	$1/0 \times 10^{-4} - 1/0 \times 10^{-1}$
4	14	4	70	3	9	21/7	$1/0 \times 10^{-8} - 1/0 \times 10^{-1}$
5	14	5	68	3	10	23/2	$1/0 \times 10^{-6} - 1/0 \times 10^{-1}$
6	11	4	61	4	20	28/8	$1/0 \times 10^{-5} - 1/0 \times 10^{-1}$
7	12	4	60	4	20	28	$1/0 \times 10^{-5} - 1/0 \times 10^{-1}$
8	14	3	64	3	15	29/9	$1/0 \times 10^{-5} - 1/0 \times 10^{-1}$
9	12	4	61	1	20	24/7	$1/0 \times 10^{-6} - 1/0 \times 10^{-1}$
10	8	4	77	1	10	21/1	$1/0 \times 10^{-4} - 1/0 \times 10^{-1}$

The typical CPE with optimized composition (electrode no.8) shows a Nernstian slope of 29.9 mV per decade. The electrode composed of 14% Ionic Liquid, 3% Ionophore, 64% Graphite Powder, 15% Plasticizer and 3% MnO nanoparticle was found to be optimal for Cu^{2+} carbon paste electrode. These results show that the NTHPT is an excellent ionophore for Cu^{2+} ion, also, addition of MnO nanoparticle to the paste improves the linear range and the response time of the electrode. This new carbon paste electrode was selected for further examination.

3.2. Measuring range and detection limit

The response of the optimal modified Cu^{2+} carbon paste electrode (no.8) was tested across Cu^{2+} ion concentration range of $1.0 \times 10^{-6} - 1.0 \times 10^{-1} \text{ mol. L}^{-1}$. The applicable range of the proposed sensor extends from 1.0×10^{-6} to $1.0 \times 10^{-1} \text{ mol L}^{-1}$ as seen in Fig 3.

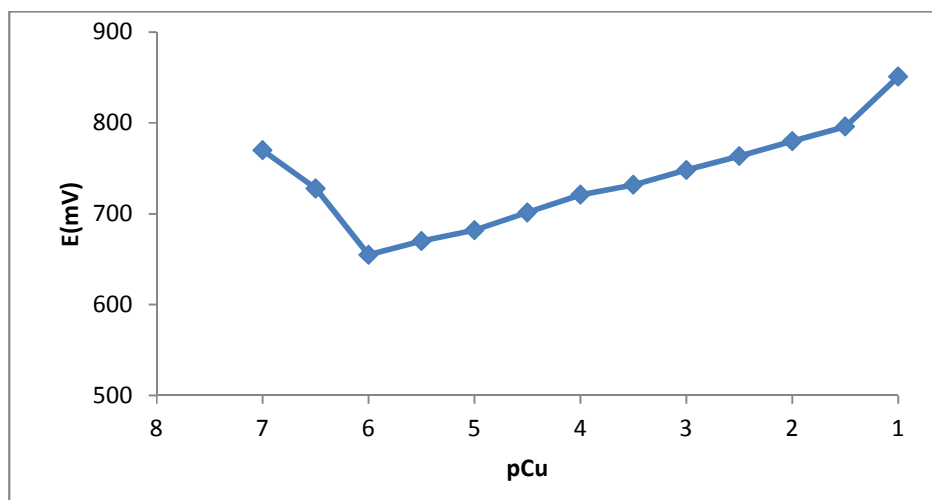


Figure3. Calibration curve of Cu²⁺ carbon paste electrode (Electrode no.8)

3.3. pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified Cu²⁺ sensor (no.8), the potential was measured for a fixed concentration of Cu²⁺ ion solutions at different pH values. The pH was varied from (1-14) by addition of concentrated HNO₃ or NaOH. The change in potential as a function of pH is shown in Fig.4. The potential was constant and quantitative in the pH range of 3.0-12. At pH < 3.0, the electrode response increased rather irregularly with increasing analyte acidity. At such high acidic solutions, the observed increase in potential indicates that the protonated ionophore possesses a poor response to the Cu²⁺ ions and strong response to H₃O⁺ ions in the solution. As can be seen in Fig. 4 the potential decreased sharply at higher pHs (>12) due to the formation of Cu(OH)₂ which not reacts with the ligand.

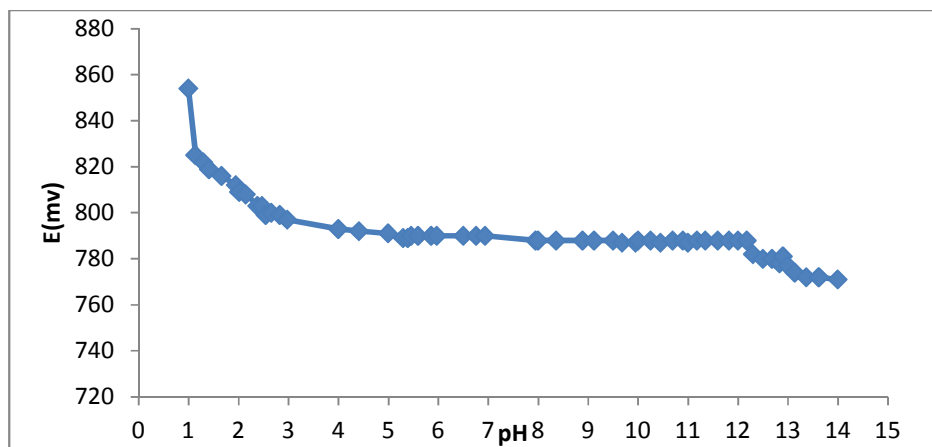


Figure4. Effect of pH on the potential response of the Cu²⁺ carbon paste electrode in the test solution of Cu²⁺ ion (10⁻³ mol L⁻¹)

In addition, Fluctuations at pH greater than 12 might be due to the formation of soluble or insoluble Cu²⁺hydroxy complexes. The fluctuations at a pH value of 3.0 were attributed to the protonation of ligand in the carbon paste.

3.4. Response time

Response time is an important factor for any sensor. For electrochemical sensors, this parameter is evaluated by measuring the average time required to achieve a potential within ± 0.1 mV of the final steady-state potential upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. The measurements of potential versus time were carried out with the Cu(II) nitrate solutions from lower (1.0×10^{-6} M) to

higher (1.0×10^{-3} M) concentrations (Fig.5). For the proposed modified Cu^{2+} sensor, the response time was less than 5s.

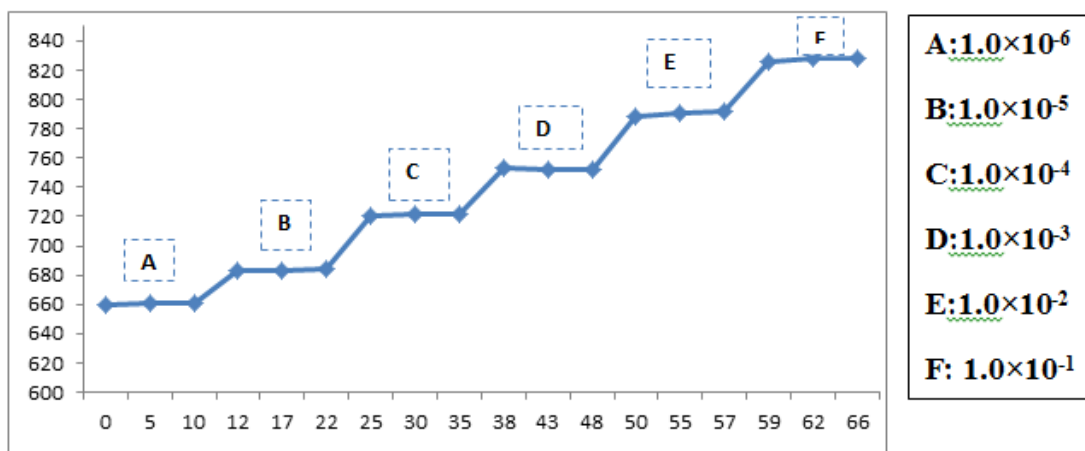


Figure5. Dynamic response time of the proposed carbon paste electrode (no.8)

3.5. Selectivity

Selectivity is the most important characteristic of any sensor, and describes an ion selective electrode’s specificity toward the target ion in the presence of interfering ions, the potentiometric selectivity coefficients of the proposed carbon paste electrode were evaluated by separate solution method (SSM) [8] and the results are depicted in Table 2.

Table2.Selectivity coefficients of various interfering species for proposed sensor (no.8)

Interfering ions	K_{ij}^{pot}	Interfering ions	K_{ij}^{pot}
Cu^{2+}	$7/1 \times 10^{-2}$	Fe^{3+}	$2/7 \times 10^{-3}$
Ni^{2+}	$5/2 \times 10^{-3}$	Na^+	$7/2 \times 10^{-1}$
Co^{2+}	$4/8 \times 10^{-2}$	Ag^+	$1/1 \times 10^{-1}$
Sn^{2+}	$1/7 \times 10^{-4}$	Li^+	$3/3 \times 10^{-2}$
Mg^{+2}	$1/1 \times 10^{-2}$	Zn^{+2}	$1/3 \times 10^{-3}$
Cd^{2+}	$2/2 \times 10^{-2}$	Cr^{3+}	$2/3 \times 10^{-3}$

The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with two separate solutions, one containing the ion (i) at the activity a_i , the other one containing the ion (j) at the same activity $a_i = a_j$. If the measured values are E_i and E_j , respectively, the value of is calculated from the equation:

$$\log K_{ij}^{pot} = \left[\frac{Z_i F (E_j - E_i)}{2.303 RT} \right] + \log \left[\frac{a_i(i)}{a_j(j)^{Z_i/Z_j}} \right]$$

These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

CONCLUSION

In this work, Cu^{2+} carbon paste electrode based on MnO nanoparticle and NTHPT as ionophore is introduced. By incorporating ionophorein composite of this electrode, high selectivity and sensitivity to copper ion were observed. The modified CPEs show better potentiometric response than typical CPEs in terms of sensitivity, Nernstian slope, linear range, and response stability. Since the electrode shows excellent sensitivity, selectivity and stability, it may find application in the analysis of real samples.

The electrode has a great potential to be used in the development of portable analyzers for monitoring Cu(II) ions in very polluted natural waters.

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