



Modified carbon paste electrode with ionic liquid and SiO₂ nanoparticles for potentiometric determination of Copper(II) ions in real samples

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ABSTRACT

1,5 Diphenyl carbazone (DPC) was used as a chemical modifier for design carbon paste electrode of copper ion. A chemically modified carbon paste electrode with ionic liquid and SiO₂ nanoparticles was prepared and used as a sensor for Cu²⁺ ion. The ionic liquid and SiO₂ nanoparticles were used in the composition of the carbon paste to improve conductivity and transduction of chemical signal to electrical signal. The construction, performance, and applications of copper carbon paste electrode are described. The electrode displays a linear log [Cu²⁺] versus EMF response over a wide concentration range of 1.0×10⁻¹ to 1.0×10⁻⁶ M with Nernstian slope of 29.76±0.35 mV/decade with limit of detection 3.2×10⁻⁷ over the pH range 3.8–7.8. The electrode exhibit a Nernstian slope of 29.76 ± 0.25 mV per decade for Cu²⁺ ion over a wide concentration range from 1.0×10⁻¹ to 1.0×10⁻⁶ M. The electrode has a fast response time (<6 s), a satisfactory reproducibility and relatively long life time. The proposed sensor shows a good selectivity toward Cu²⁺ ion in comparison to other common cations and the working pH range was 7.0–11. These electrode have been successfully applied for the determination of Cu²⁺ ions content in various real samples.

Keywords: copper, Carbon paste electrode, Ionic liquid, Potentiometric, SiO₂ nanoparticles

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 electrodes 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.

The present work describes construction, potentiometric characterization, and analytical application of a new modified carbon paste electrode selective for copper ion based on salophen as ionophore (Fig. 1). The results presented in this paper show that the sensor modified by ionic liquid and SiO₂ nanoparticles to achieve the better electrode response for Cu (II) ion. using this electrode has acceptable concentration range, low detection limit and gives reproducible results.

The modified electrode was successfully used as a sensor for potentiometric determination of Cu(II) in aqueous sample.

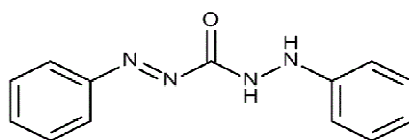


Figure 1. Chemical structure of 1,5 Diphenyl carbazone as ionophore.

MATERIALS AND METHODS

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 imidazolium hexa fluoroborate) was of high purity and was used for the preparation of the carbon past. Tetraethoxysilane (TEOS) were purchased from Sigma. Chloride and nitrate salts of the cations used are all purchased from Merck. In every case, the chemicals were used in the as received condition without further purification.

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.)

Synthesis of monodisperse SiO₂ nanoparticles

As shown in Table 1, SiO₂ NPs were synthesized with average diameters ranging 64 nm (see fig 2). The SiO₂ core was prepared by the sol–gel method proposed through hydrolysis and condensation of TEOS. 42 ml NH₃·H₂O and 88.5 ml ethanol were dissolved into 42 ml deionized water. After preheating 25 min under 55 °C, 33 ml TEOS was added, drop-by-drop, into the solution with a proper agitation to disperse the droplets. Afterward, the mixed solution was stirred for 150 min and aged for 30 h. The resulting dispersions were separated from their mother liquor centrifugation, the precipitates washed several times with deionized water and ethanol before drying at 50 °C for 18 h. Final SiO₂ nanoparticle was obtained by calcining the above powder at 550 °C for 80 min.

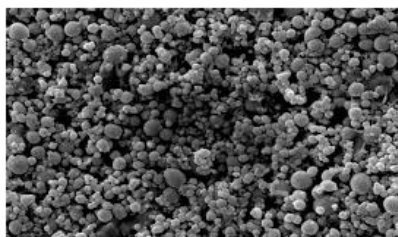


Fig. 2. TEM micrograph of SiO₂ nanoparticle obtained under reaction conditions.

Electrode Preparation

General procedure to prepare the carbon paste electrode was as follows: Different amounts of 1,5 Diphenyl carbazole as an ionophore with an appropriate amount of graphene powder, ionic liquid, Plasticizer(DBP) and SiO₂ nanoparticles were thoroughly mixed. After homogenization of the mixture, the paste was thoroughly packed into the teflon tube and a electric 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 Al₂O₃ powder. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 24 h by soaking it in a 3.0×10⁻³ mol L⁻¹ Cu(NO₃)₂ solution [22-23].

RESULTS AND DISCUSSION

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	Graphite Powder	SiO ₂ nanoparticles	Plasticizer		
1	15	5	68	1	11	24/9	1/0×10 ⁻⁶ -1/0×10 ⁻¹
2	10	3	70	4	13	18/17	1/0×10 ⁻⁶ -1/0×10 ⁻¹
3	14	5	71	3	12	22/4	1/0×10 ⁻⁴ -1/0×10 ⁻¹
4	13	4	71	3	10	23/9	1/0×10 ⁻⁸ -1/0×10 ⁻¹
5	11	5	66	4	14	24/2	1/0×10 ⁻⁶ -1/0×10 ⁻¹
6	10	4	67	4	15	29/76	1/0×10 ⁻⁵ -1/0×10 ⁻¹
7	10	4	67	4	15	26.7	1/0×10 ⁻⁴ -1/0×10 ⁻¹
8	13	5	64	5	13	26/4	1/0×10 ⁻⁵ -1/0×10 ⁻¹
9	14	3	66	2	15	23/8	1/0×10 ⁻⁶ -1/0×10 ⁻¹
10	8	4	72	3	13	23/54	1/0×10 ⁻⁴ -1/0×10 ⁻¹

The typical CPE with optimized composition (electrode no.6) shows a Nernstian slope of 29.76 mVper decade. the electrode composed of 10% Ionic Liquid, 4% Ionophore, 67% Graphite Powder, 15% Plasticizer and 4% SiO₂ nanoparticle was found to be optimal for Cu²⁺ carbon paste electrode. These results show that the DPC is an good ionophore for Cu²⁺ ion, also, addition of SiO₂ 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.

Measuring range and detection limit

The response of the optimal modified Cu²⁺ carbon paste electrode (no.6) was tested across Cu²⁺ ion concentration range of 1.0×10⁻⁵-1.0×10⁻¹ mol. L⁻¹. The applicable range of the proposed sensor extends from 1.0×10⁻⁵ to 1.0×10⁻¹ mol L⁻¹ as seen in Fig 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.6), 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 7.0-11. At pH<7.0, 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 Cu^{2+} ions and strong response to H_3O^+ ions in the solution. As can be seen in Fig. 4 the potential decreased sharply at higher pHs (>11) due to the formation of $\text{Cu}(\text{OH})_2$ which not reacts with the ligand.

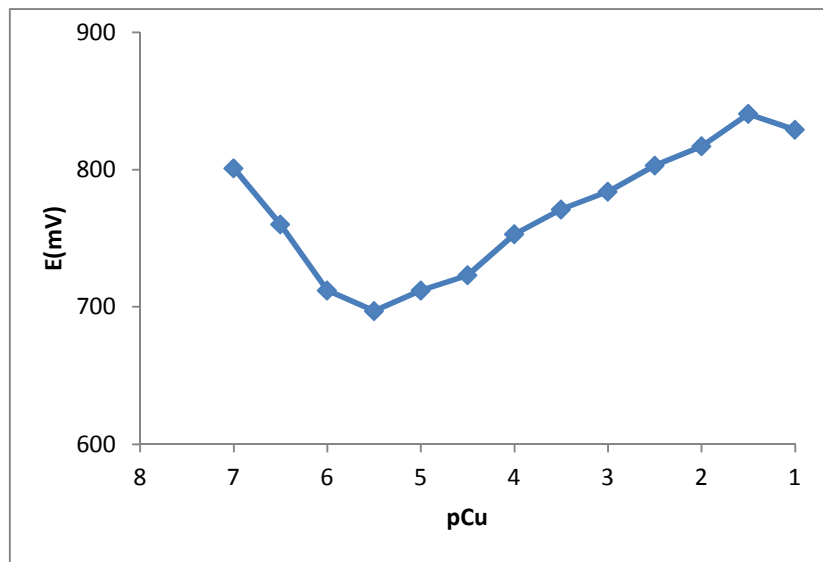


Figure3. Calibration curve of Cu^{2+} carbon paste electrode (Electrode no.6)

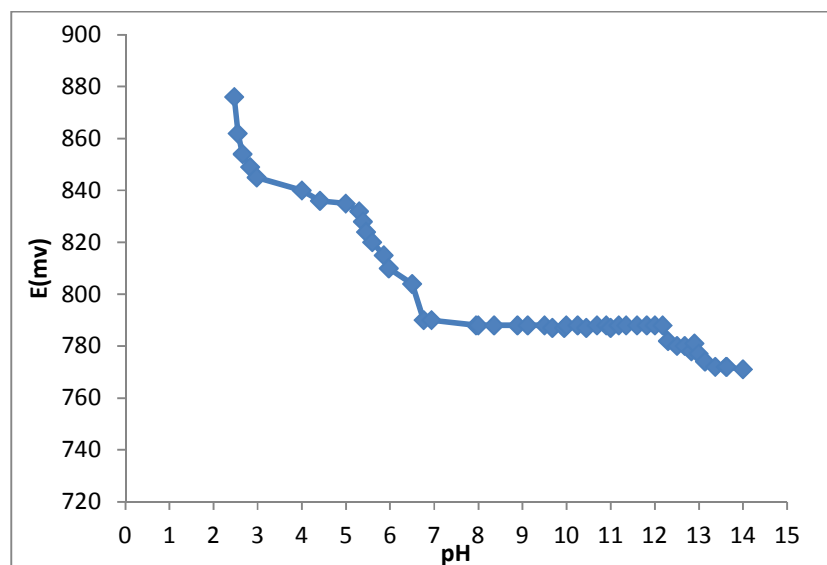


Figure4. Effect of pH on the potential response of the Cu^{2+} carbon paste electrode in the test solution of Cu^{2+} ion ($10^{-3} \text{ mol L}^{-1}$)

In addition, Fluctuations at pH greater than 11 might be due to the formation of soluble or insoluble Cu^{2+} hydroxy complexes. The fluctuations at a pH value of 7.0 were attributed to the protonation of ligand in the carbon paste.

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 $\pm 0.1 \text{ mV}$ 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 $\text{Cu}(\text{II})$ nitrate solutions from lower ($1.0 \times 10^{-6} \text{ M}$) to

higher (1.0×10^{-2} M) concentrations (Fig.5). For the proposed modified Cu^{2+} sensor, the response time was less than 4s.

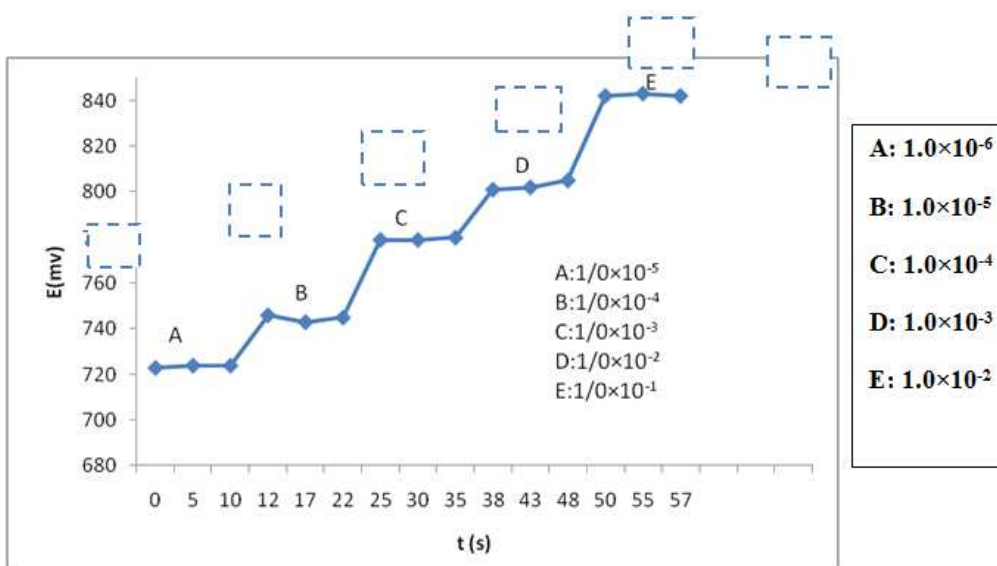


Figure5. Dynamic response time of the proposed carbon paste electrode (no. 6)

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 roposed sensor (no.6)

1.1.1.1	Interfering ions	K_{ij}^{pot}	1.1.1.2	Interfering ions	K_{ij}^{pot}
	Ca ²⁺	$6/9 \times 10^{-2}$		Fe ³⁺	$2/9 \times 10^{-3}$
	Ni ²⁺	$5/2 \times 10^{-3}$		Na ⁺	$6/8 \times 10^{-1}$
	Co ²⁺	$5/9 \times 10^{-2}$		Ag ⁺	$1/3 \times 10^{-2}$
	Sn ²⁺	$5/8 \times 10^{-4}$		Li ⁺	$2/3 \times 10^{-2}$
	Mg ⁺²	$4/1 \times 10^{-3}$		Zn ⁺²	$1/3 \times 10^{-3}$
	Cd ²⁺	$4/5 \times 10^{-3}$		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 SiO_2 nanoparticle and DPC as ionophore is introduced. By incorporating ionophore in 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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