

Improvement of Carbon Paste Ion Selective Electrode Response by Using Room Temperature Ionic Liquids (RTILs) and Multi-Walled Carbon Nanotubes (MWCNTs)

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In this work by using room temperature ionic liquids (RTILs) and multi-walled carbon nanotubes (MWCNTs), response of a cerium carbon paste potentiometric sensor was modified. A room temperature ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF₄, was tested as binder for construction of the carbon paste electrode. The characteristics of these electrodes as potentiometric sensors were evaluated and compared with those of the traditional carbon paste electrode (CPE). The results indicate that potentiometric sensor constructed with ionic liquid shows an increase in performance in terms of Nernstian slope, selectivity, response time, and response stability compared to CPE. This sensor with the membrane composition of 25% [bmim] BF₄, 16% NHMF, 44% graphite powder and 15% MWCNT, exhibits a rapid and good Nernstian response toward Ce(III) ions in the range of 8.0×10^{-7} - 1.0×10^{-1} M with a slope of 19.9 ± 0.2 mV per decade and a detection limit of 3.6×10^{-7} M. The sensor can be used in a pH range from 3.5 to 9.0.

Keywords: ionic liquid; carbon nanotubes; sensor; cerium; potentiometry; ion selective

1. INTRODUCTION

An ionic liquid is a liquid that contains essentially only ions. Nowadays, the term "ionic liquid" is commonly used for salts whose melting point is relatively low (below 100 °C). In particular, the salts that are liquid at room temperature are called room-temperature ionic liquids (RTILs).

Recently RTILs have been used in carbon paste electrodes (CPEs), in which, called carbon ionic liquid electrodes (CILEs) [1-3]. RTILs are a good choice as binder in carbon paste electrodes due

to their interesting properties, such as stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity and good electrochemical and thermal stability [4].

Carbon paste electrodes (CPEs) have attracted attention as ion selective electrodes mainly due to their advantages over membrane electrodes such as renewability, stable response, low ohmic resistance, no need for internal solution [5-10]. Most of CPEs based potentiometric sensors which have been reported up to now are mainly based on incorporation of a selective agent into the carbon paste. The carbon paste usually consists of graphite powder dispersed in a non-conductive mineral oil. Incorporation of mineral oil gives CPEs some disadvantages. Mineral oil is not component-fixed since it is involved in various refining of petroleum and processing of crude oil, and some unaccounted ingredients may engender unpredictable influences on detection and analysis [11]. In addition they have mechanical problem, their mechanical stability is something between membrane electrodes and solid electrodes.

Now a days, carbon nanotubes (CNTs) have also been used in carbon paste electrodes [12-14]. CNTs have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area [15]. The combination of these characteristics make CNTs unique materials with the potential for diverse applications [16-25].

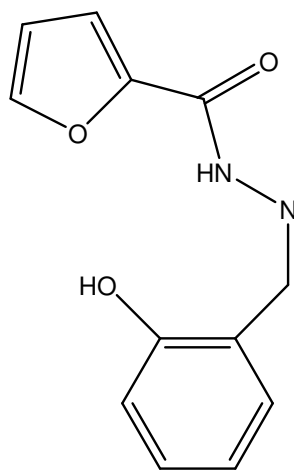


Figure 1. Chemical structure of N-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (NHMF)

In this work, modification of a Ce(III) carbon paste electrode based on N-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (NHMF), Fig. 1, by room temperature ionic liquids (RTILs) and multi-walled carbon nanotubes (MWCNTs) is studied. A RTIL, 1-n-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF₄, are applied as binder for construction of the cerium carbon paste electrode.

The used ionophore, NHMF, was previously applied in construction of Ce(III) PVC membrane sensor [26].

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell, where the Ce(III) carbon paste electrode was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode as a reference electrode. The reference electrode and the carbon paste electrode, as indicator electrode, were connected to a Corning ion analyzer with a 250 pH/mV meter with ± 0.1 mV precision.

2.2. Reagents and materials

The graphite powder with a 1–2 μm particle size (Merck) along with the paraffin oil (Aldrich) was of high purity and was used for the preparation of the carbon pastes. Ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim] BF₄)), chloride and nitrate salts of the cations used are all purchased from Merck. The multi-walled carbon nanotubes (MWCNTs) were purchased from Research Institute of the Petroleum Industry (Iran). The ionophore (NHMF) was synthesized as described elsewhere [26]. Triply distilled deionized water was used throughout.

2.4. Electrode Preparation

The general procedure to prepare the carbon paste electrode was as follow: Different amounts of the ionophore NHMF along with appropriate amount of graphite powder, ionic liquid and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube. The electrode body was fabricated from a glass tube of i.d. 5 mm and a height of 3 cm. After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M Ce(NO₃)₃ solution [6,10].

2.5. Emf Measurements

The following cell was assembled for the conduction of the emf (electromotive force) measurements; Carbon paste electrode | sample solution | Ag–AgCl (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C.

3. RESULTS AND DISCUSSION

The obtained results from some experimental works revealed that the performance of Ce(III) carbon paste potentiometric sensor can be highly improved by using RTIL instead of mineral oil and MWCNTs. For this purpose, the potentiometric responses of the unmodified CPE and modified CPE towards Ce(III) ions were studied in terms of selectivity coefficients, response time, Nernstian slope,

linear range, and response stability which are important characterization of every ion selective electrodes.

3.1. Electrode composition

Selectivity for a certain ion selective sensor is greatly related to the ionophore used [27-30]. The ionophore used in this work was previously applied in a PVC membrane sensor. The selectivity of this ionophore toward Ce(III) ions was well studied in that report [26]. In this study, Ce(III) carbon paste electrode based on the same ionophore was constructed in order to determine Ce(III) ion concentration. For this purpose, different carbon paste compositions, as shown in Table 1, were tested. As it can be seen, two kind of carbon paste electrode was prepared (modified and unmodified CPEs). Unmodified CPE, with optimized composition (electrode No. 4), shows a near Nernstian slope about 15.8 mV per decade. However, the electrode with the composition of 25% [bmim] BF₄, 16% NHMF, 44% graphite powder and 15% MWCNT (no. 9) was the optimum one in the development of this sensor. This membrane composition was selected after many considerations.

Table 1. The optimization of the carbon paste ingredients

Electrode No.	Binder	NHMF	Graphite Powder	MWCNTs	Slope mV/decade	R ²
1	25%-Paraffin	0%	75%	0%	1.5±0.3	0.995
2	25%-Paraffin	5%	70%	0%	6.2±0.5	0.996
3	25%-Paraffin	10%	65%	0%	9.2±0.6	0.992
4	25%-Paraffin	16%	59%	0%	15.8±0.5	0.998
5	25%-Paraffin	20%	55%	0%	14.3±0.3	0.992
6	25%-[bmim] BF ₄	16%	59%	0%	17.7±0.2	0.995
7	25%-[bmim] BF ₄	16%	54%	5%	18.3±0.1	0.991
8	25%-[bmim] BF ₄	16%	49%	10%	19.0±0.5	0.994
9	25%-[bmim] BF ₄	16%	44%	15%	19.9±0.2	0.998
10	25%-[bmim] BF ₄	16%	39%	20%	19.6±0.6	0.991

From Table 1, it was obvious that in the MWCNT absence and the existence of other components (no. 6), the response of the recommended electrode was low (slope of 17.7±0.2 mV per decade).

Using RTIL in the composition of the carbon paste instead of paraffin oil, causes the higher extraction of the Ce(III) which is a high charge density cation, into the CPE. This is due to much higher dielectric constant of the RTIL as the binder than paraffin oil.

Using MWCNT in the composition of the carbon paste improves the conductivity and therefore transduction of the chemical signal to electrical signal. Carbon nanotubes have many properties from

their unique dimensions to an unusual current conduction mechanism that make them ideal components of electrical circuits.

3.2. Measuring range

The measuring range of an ion selective electrode includes the linear part of the calibration graph as shown in Fig. 2. Measurements can be performed in this lower range but it must be noted that more closely spaced calibration points are required for more precise determinations. For many electrodes the measuring range can extend from 1 molar down to 10^{-6} or even 10^{-7} molar concentrations [31-34]. According to another definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits. The applicable measuring range of the proposed sensor is between 8.0×10^{-7} and 1.0×10^{-1} M.

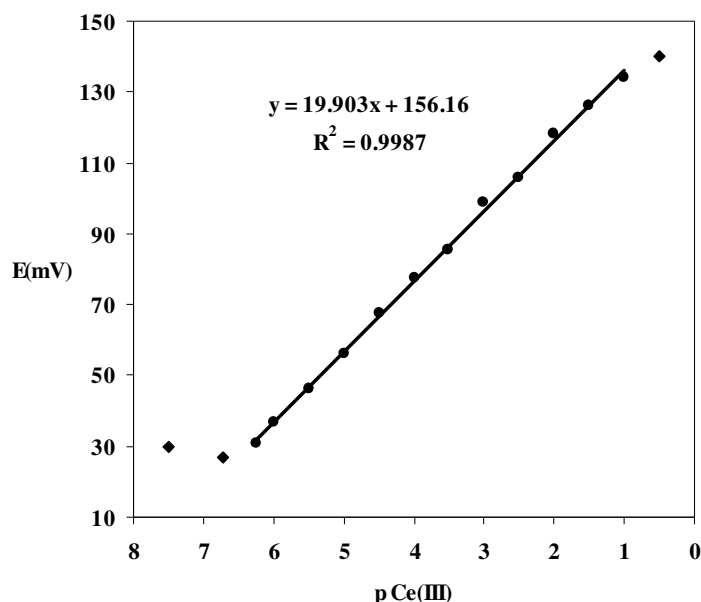


Figure 2. The calibration curve of Ce(III) modified CPE (electrode no. 9).

3.3. Detection limit

By extrapolating the linear parts of the ion selective calibration curve, the detection limit of an ion selective electrode can be calculated.

In this work the detection limit of the proposed membrane sensor was 3.6×10^{-7} M which was calculated by the extrapolating of the two segment of the calibration curve in Fig. 2.

In comparison with Ce(III) PVC membrane sensor with the same ionophore, Table 2 [26], the proposed sensor is superior in terms of linear range, detection limit, selectivity coefficients, response time to the previously reported ones.

Table 2. Characterization of the Ce(III) PVC membrane sensor with Ce(III) modified CPE

Slope (mV per decade)	Linear Range (M)	Detection Limit (M)	Response time (s)	Most Important Interfering ions ($\log K_{\text{sel}} > -2$)	Ref.
19.4	1.0×10^{-5} - 1.0×10^{-1}	7.6×10^{-6}	<15	Ni^{2+} , Pb^{2+} , K^+	26
19.9	8.0×10^{-7} - 1.0×10^{-1}	3.0×10^{-7}	10	-	This work

3.4. pH effect on the electrode response

In order to investigate the pH effect on the potential response of the electrode (no. 9), the potentials were measured for a fixed concentration of Ce(III) solution (1.0×10^{-3} M) having different pH values. The pH varied from (1-14) by addition of HNO_3 or NaOH . The potential variation as a function of pH is plotted in Fig. 3. The composition of the electrode was kept constant during all experiments. The results showed the potential of electrode is constant between pH (3.5-9). Thus the electrode works satisfactorily in the pH range 3.5-9, as no interference from H^+ or OH^- is observed in the range. The fluctuations above the pH value of 9.0 might be justified by the formation of the soluble and insoluble Ce(III) ion hydroxy complexes in the solution, such as $\text{Ce}(\text{OH})^{2+}$, $\text{Ce}(\text{OH})_2^+$ and $\text{Ce}(\text{OH})_3$. And the fluctuations below the pH value of 3.5 were attributed to the partial protonation of the employed ionophore [35-40].

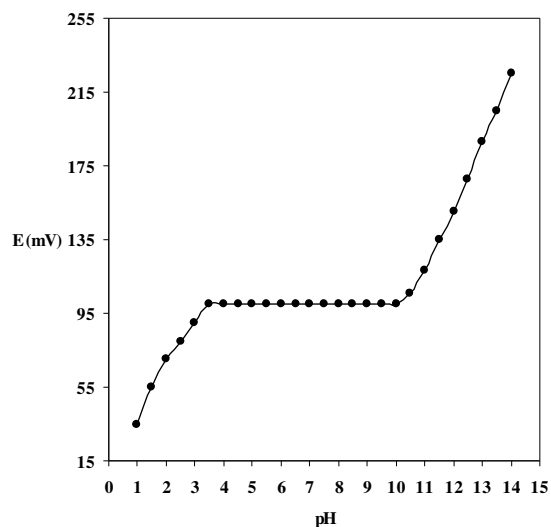


Figure 3. Effect of pH of the test solution (1.0×10^{-3} M) on the potential response of the Ce(III) ion-selective electrode

3.5. Response time

The response time of an electrode, 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. It is notable that the experimental conditions, like the stirring or flow rate, the ionic concentration and composition of the

test solution, the concentration and composition of the solution to which the electrode was exposed before performing the experiment measurement, any previous usages or preconditioning of the electrode, and the testing temperature, are effective on the experimental response time of a sensor [41-45].

In this work, less than 10 s response time was obtained for the proposed electrode when contacting different Ce(III) solutions from 1.0×10^{-4} to 1.0×10^{-1} M, and about 12 s in low concentration solutions which is due to the effect of analyte concentration on the response time of ion selective electrode.

3.6. Selectivity

Selectivity, which describes an ion selective electrodes specificity toward the target ion in the presence of interfering ions, is the most important characteristics of these devices. The potentiometric selectivity coefficients of the Ce(III) sensor were evaluated by the matched potential method (MPM) [46-52].

The resulting values of the selectivity coefficients are given in Table 3. As can be seen from Table 3, for the all mono and bivalent metal ions and trivalent lanthanide ions tested, the selectivity coefficients are about 10^{-3} , which seems to indicate negligible interferences in the performance of the electrode assembly.

Table 3. The selectivity coefficients of various interfering cations for the electrode no. 9

Interference (j)	$K_{Ce,j}$	Interference (j)	$K_{Ce,j}$
Mg ²⁺	4.50×10^{-4}	Cu ³⁺	5.50×10^{-4}
Pb ²⁺	3.40×10^{-4}	Gd ³⁺	2.10×10^{-5}
Co ²⁺	4.30×10^{-4}	Nd ³⁺	6.00×10^{-5}
Ni ²⁺	4.80×10^{-3}	Dy ³⁺	3.50×10^{-5}
Cr ³⁺	6.50×10^{-4}	Eu ³⁺	4.20×10^{-5}
Zn ²⁺	2.90×10^{-3}	Cd ²⁺	1.65×10^{-4}
Fe ³⁺	3.40×10^{-3}	Na ⁺	1.50×10^{-4}
Ba ²⁺	5.50×10^{-4}	K ⁺	1.10×10^{-4}
Mn ²⁺	1.80×10^{-3}	Ag ⁺	1.20×10^{-5}
Sr ²⁺	7.00×10^{-4}	Tl ⁺	2.10×10^{-3}
Al ³⁺	4.00×10^{-5}	Ca ²⁺	4.35×10^{-5}
Sm ³⁺	9.50×10^{-4}	La ³⁺	4.50×10^{-4}

3.7. Lifetime

The average lifetime for most of the reported ion selective sensors is in the range of 4–10 weeks. After this time the slope of the sensor will decrease, and the detection limit will increase. They were tested for a period of 10 weeks, during which the electrodes were used extensively (one hour per

day). The proposed sensors can be used for 8 weeks. Firstly, a slight gradual decrease in the slopes (from 19.9 to 17.6 mV per decade) and, secondly, an increase in the detection limit (from 3.6×10^{-7} M to 7.0×10^{-6} M). It is well established that the loss of plasticizer, carrier, or ionic site from the polymeric film due to leaching into the sample is a primary reason for limited lifetimes of the sensors.

4. CONCLUSIONS

The performance of Ce(III) carbon paste potentiometric sensor can be highly improved by using RTIL instead of mineral oil (paraffin) and also using MWCNTs as a better signal transducers. The potentiometric modified CPE in comparison with unmodified CPE shows better responses in terms of sensitivity, Nernstian slope, linear range, and response stability which are important characterization of every ion selective electrodes.

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