

Praseodymium Selective Carbon Paste Electrode based on Carbon Nanotubes and Ionic Liquids

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Using multi-walled carbon nanotube (MWCNT) and ionic liquid (IL) in the composition of carbon paste electrodes cause improvement in their characterizations. Previous solution studies showed a selective interaction between N,N-bis(a-methylsalicylidene)diethylenetriamine (BMT) and Pr³⁺ ions respect to other lanthanide ions. To have an electrode with enhanced mechanical resistant in analysis, BMT incorporation of MWCNTs and ionic liquid in carbon paste was used in construction of a Pr³⁺ potentiometric electrode. The nano-composite electrode showed better sensitivity, selectivity, response time, response stability and lifetime in comparison with typical carbon paste electrodes. The best performance for nano-composite sensor was obtained with electrode composition of 25% BMT, 25% IL, 45% graphite powder, and 5% MWCNT. The new electrode exhibited a Nernstian response (20.1±0.4 mV per decade) toward Pr³⁺ ions in the range of 1.0×10⁻⁶-1.0×10⁻² mol L⁻¹.

Keywords: Sensor; ion selective electrode; carbon paste; carbon nanotubes; room temperature ionic liquid; praseodymium

1. INTRODUCTION

Ionic Liquids (ILs) are a new class of ionic compounds (salt-like materials) that are unusually liquid at low temperatures. The official definition of ILs uses the boiling point of water as a point of reference and definite them as compounds which are liquid below 100 °C. Recently, because of their

remarkable properties, they widely use in different fields of electrochemistry. Ionic liquids (ILs) can be composed of a large number of cations and anions. Most common ILs which are liquids in room temperature are composed of un-symmetrically substituted nitrogen-containing cations (e.g. imidazolium, pyridinium, pyrrolidinium) with organic or inorganic anions (e.g. Cl^- , PF_6^- , BF_4^-). Ionic liquids based on imidazolium and pyridinium cations have the highest ionic conductivity (~ 1 and 10^{-1} S/m, respectively) [1]. ILs have advantages of good solvating properties, high conductivity, non-volatility, low toxicity and good electrochemical stability [2,3]. Because of the advantages of ILs, they can be used as a suitable binder in carbon paste electrodes (CPEs). They have chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity and good electrochemical and thermal stability [2-5]. The carbon paste usually consists of graphite powder dispersed in a nonconductive mineral oil. Mineral oil gives CPEs some disadvantages. Mineral oil has not fixed component since it is mad of various refining of petroleum and processing of crude oil, and causes some unpredictable effects on analysis [6].

Multi-walled carbon nanotubes (MWCNTs) have been recently used in composition of carbon paste electrodes [3-8]. CNTs have very interesting physicochemical properties, such as an 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 [9]. The combination of these characteristics makes CNTs unique materials with the potential for diverse applications. Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical signal.

Ion selective electrodes are used widely in analysis of a wide variety of ions [10-27] because of some advantages such as portability, simplicity, fast, inexpensive, and reliable response in a wide concentration range in comparison with new electrochemical methods [28]. Carbon paste electrodes are one of the classes of potentiometric sensors which offer renewable surface, stable response, and low ohmic resistance electrodes compared to PVC membrane electrodes [3-5]. CPEs potentiometric sensors generally are composed of a selective agent, graphite powder and a non-conductive mineral oil.

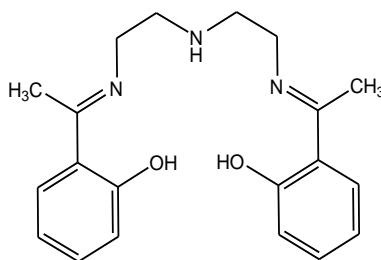


Figure 1. Chemical structure of N,N-bis(a-methylsalicylidene)diethylenetriamine (BMT)

Previous selectivity studies [29] showed a selective interaction between N,N-bis(a-methyl salicylidene)diethylenetriamine (BMT), Fig. 1, and Pr^{3+} ions respect to other common cations. In this work, in order to make a high performance potentiometric electrode with improved mechanical resistant and renewable surface for determination of Pr^{3+} ions in real analysis we used BMT as a

sensing material in new proposed carbon paste composition based on RTIL and multi-wall carbon nanotubes (MWCNTs).

Praseodymium (Pr) is one of the lanthanide members. The main problem in quantitative analysis of this family of elements is the selectivity. Many reagents have been reported for the spectrophotometric determination of lanthanides but they have not been specific and even the most selective requires extractive separation to remove interfering elements. Hence, finding a simple device like an electrode which is able to measure one of these elements selectively is of importance.

2. EXPERIMENTAL PART

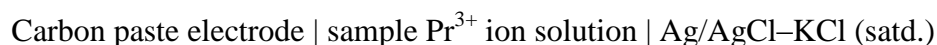
2.1. Reagents and materials

The multi-wall carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length, SBET: 40-600 m^2/g and with 95% purity were purchased from Research Institute of the Petroleum Industry (Iran). Graphite powder with a 1–2 μm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for preparation of the carbon pastes. The ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) and chloride and nitrate salts of the cations were all purchased from Merck Co. The ionophore N,N-bis(a-methylsalicylidene)diethylenetriamine (BMT) was prepared as described elsewhere [30].

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 Pr³⁺ CPE was used as an indicator electrode. Both electrodes were connected to a millivoltmeter.

The following cell was assembled for the conduction of the EMF (electromotive force) measurements:



2.3. Electrode Preparation

General procedure to prepare the carbon paste electrode was as follows: Different amounts of BMT as an ionophore along with an appropriate amount of graphite powder, ionic liquid, and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube (5 mm i.d. and a height of 3 cm). After homogenization of the mixture, the paste was thoroughly packed into the tube tip to avoid possible air gaps, which often enhance the electrode resistance. A copper 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 48 h by soaking it in a 1.0×10^{-3} mol L⁻¹ PrCl₃ solution [3-5].

3. 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 especially in case of lanthanide ions [31-39]. Based on previous selectivity studies [29], BMT shows a selective behavior toward Pr³⁺ ion. Hence, BMT was applied for making both modified and unmodified CPEs with different compositions. Results for these CPEs are shown in Table 1.

Table 1. The optimization of the carbon paste ingredients

Electrode No.	Binder	BMT	Graphite Powder	MWCNTs	Slope mV per decade	R ²
1	25%-Paraffin oil	10%	65%	0%	8.3±0.5	0.752
2	25%-Paraffin oil	15%	60%	0%	12.5±0.3	0.778
3	25%-Paraffin oil	20%	55%	0%	14.8±0.3	0.832
4	25%-Paraffin oil	25%	50%	0%	15.8±0.3	0.912
5	25%- Paraffin oil	30%	45%	0%	15.7±0.4	0.902
6	25%- [bmim]BF ₄	25%	50%	0%	17.6±0.3	0.937
7	20%- [bmim]BF ₄	25%	55%	0%	16.3±0.4	0.913
8	30%- [bmim]BF ₄	25%	45%	0%	17.7±0.3	0.914
9	25%- [bmim]BF ₄	25%	47%	3%	18.6±0.4	0.944
10	25%- [bmim]BF ₄	25%	45%	5%	20.1±0.4	0.998
11	25%- [bmim]BF ₄	25%	43%	7%	19.6±0.3	0.973
12	25%- [bmim]BF ₄	0%	70%	5%	No Response	-

The typical CPE with optimized composition (electrode no. 5) shows a sub-Nernstian slope of ~15.7 mV per decade. Addition of ionic liquid instead of paraffin oil causes a better Nernstian response in electrode No. 6. Using room temperature ionic liquids instead of paraffin oil in the carbon paste electrodes yields more efficient extraction of ions with high charge density into the carbon paste surface. This is due to the much higher dielectric constant of the ionic liquids as binder compared to paraffin oil. As it can be seen from Table 1, using [bmim]BF₄ instead of paraffin oil in the carbon paste composition yields more efficient extraction of Pr³⁺ ion (which is a high charge density cation) from solution into the surface of CPE. Addition of MWCNTs also has a remarkable effect on electrode response. As it is seen in electrode no. 9, 3% MWCNTs in the paste composition affects the electrode response drastically. This is due to the electrical properties of MWCNTs which can improve the transduction and amplification of the signal. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values.

As the result, the electrode composed of 25% [bmim]BF₄, 25% BMT, 45% graphite powder, and 5% MWCNT (no. 10) was found to be optimal for Pr³⁺ carbon paste electrode. This new nano-composite electrode was selected for further examination.

3.2. Measuring range and detection limit

The response of the optimal modified Pr³⁺ carbon paste electrode (no. 10) was tested across Pr³⁺ ion concentration range of 1.0×10^{-7} - 1.0×10^{-1} mol L⁻¹. The applicable range of the proposed sensor extends from 1.0×10^{-6} to 1.0×10^{-2} mol L⁻¹ as seen in Fig. 2.

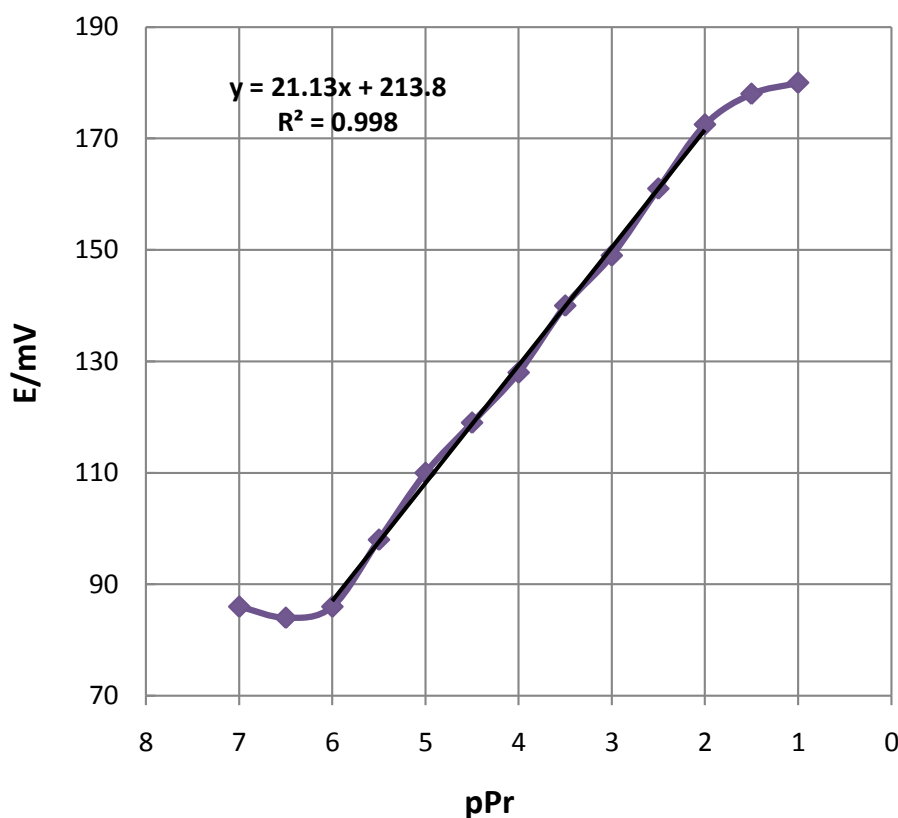


Figure 2. Calibration curve of Pr³⁺ nano-composite carbon paste electrode (Electrode no. 10)

By extrapolating based on the linear portion of the electrode's 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 6.3×10^{-7} mol L⁻¹.

3.3. pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified Pr³⁺ sensor (no. 10), the potential was measured for a fixed concentration of Pr³⁺ ion solutions () at different pH values. The pH was varied from (2-12) by addition of concentrated HNO₃ or NaOH. The change in potential as a

function of pH is shown in Fig. 3. As it can be seen from Fig. 3, the response of the sensor is independent of pH in the range from 3.0-8.0.

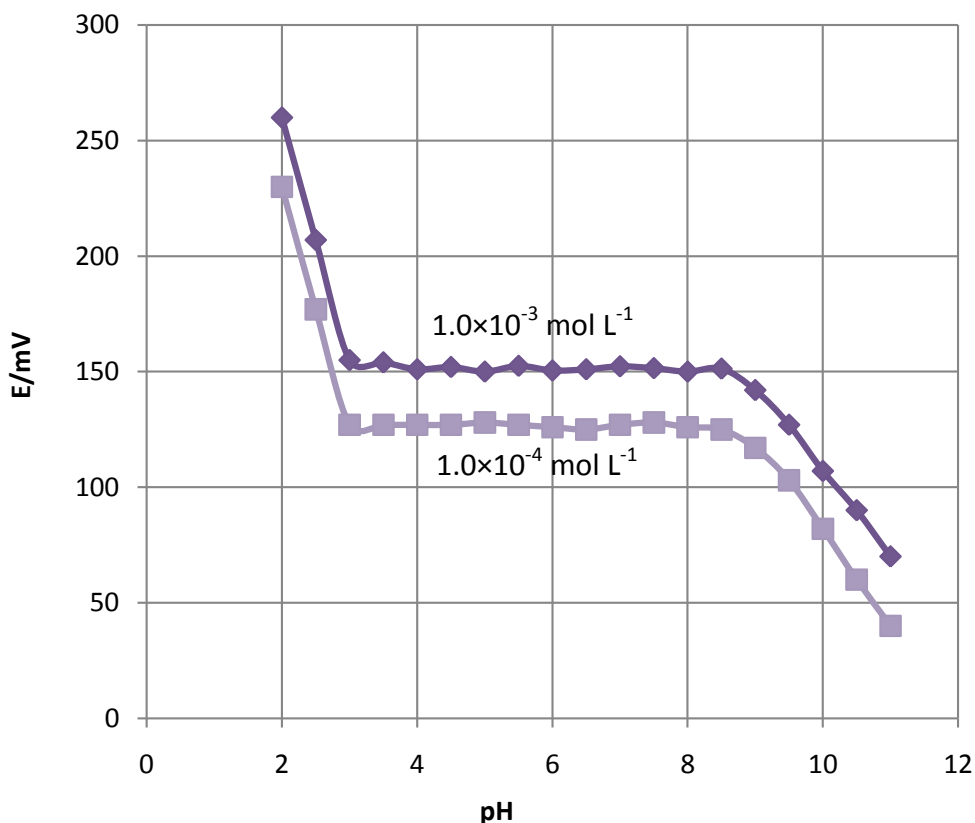


Figure 3. Effect of pH on the potential response of the Pr^{3+} nano-composite carbon paste electrode based on BMT (Electrode no. 10) in the test solution of Pr^{3+} ion (10^{-3} and 10^{-4} mol L^{-1})

In addition, there is no visible interference from H^+ or OH^- in this pH range. Fluctuations at pH greater than 8.5 might be due to the formation of soluble or insoluble Pr^{3+} hydroxy complexes, such as soluble $\text{Pr}(\text{OH})^{2+}$ and $\text{Pr}(\text{OH})_2^+$, or insoluble $\text{Pr}(\text{OH})_3$. The fluctuations at a pH value of 3.5 were attributed to the protonation of BMT 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. Experimental conditions such as stirring or the 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 usage or preconditioning of the electrode, and the testing temperature can all affect the

experimental response time of a sensor [35-43]. For the proposed modified Pr^{3+} sensor, the response time was less than 10s in the concentrated solution (10^{-3} - 10^{-2} M) and about 20s in diluted solutions (10^{-6} - 10^{-4} M).

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 nano-composite carbon paste electrode were evaluated by matched potential method (MPM) [44-49], and the results are depicted in Table 2.

Table 2. The selectivity coefficients of various interfering cations for electrode no. 10; concentration of the reference solution of Pr^{3+} ion was 1.0×10^{-6} mol L⁻¹ and the concentration of interfering ions was between 1×10^{-4} to 1.0×10^{-1} mol L⁻¹

Cation	Selectivity Coefficient	Cation	Selectivity Coefficient
Na^+	1.3×10^{-4}	Gd^{3+}	4.2×10^{-3}
K^+	2.0×10^{-4}	Yb^{3+}	6.6×10^{-3}
Nd^{3+}	3.7×10^{-3}	Tb^{3+}	5.7×10^{-3}
Ho^{3+}	8.6×10^{-4}	La^{3+}	1.3×10^{-3}
Ca^{2+}	7.4×10^{-4}	Sm^{3+}	5.0×10^{-3}
Cu^{2+}	2.2×10^{-4}	Dy^{3+}	4.1×10^{-3}
Pb^{2+}	2.5×10^{-4}	Lu^{3+}	7.0×10^{-4}
Fe^{3+}	1.5×10^{-4}	Eu^{3+}	2.0×10^{-3}
Zn^{2+}	4.2×10^{-4}	Ce^{3+}	4.6×10^{-3}
Tm^{3+}	6.4×10^{-3}	Er^{3+}	5.5×10^{-4}

As it can be seen from Table 2, the selectivity coefficients of our sensor are 6.7×10^{-3} or lower for all tested cations. These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

3.6. Lifetime

The average lifetime for most ion selective sensors ranges from 4–10 weeks. After this time the slope of the sensor decreases, and the detection limit increases. The lifetime of the proposed nano-composite Pr^{3+} sensor was evaluated for a period of 12 weeks, during which the sensor was used two hours per day.

The obtained results showed that the proposed sensors can be used for at least 10 weeks. After this time, a slight gradual decrease in the slope from 20.1 to 15.4 mV per decade is observed, as is an increase in the detection limit from 6.3×10^{-7} mol L⁻¹ to 1.5×10^{-5} mol L⁻¹ (Table 3). It is well understood that the loss of sensing material is the primary reason for limited lifetimes of carbon paste electrode.

Table 3. Lifetime of Pr³⁺ nano-composite carbon paste electrode

Week	Slope (mV decade ⁻¹)	DL (mol L ⁻¹)
1	20.1 ± 0.4	6.3×10^{-7}
2	20.0 ± 0.3	8.5×10^{-7}
3	19.9 ± 0.2	9.6×10^{-7}
4	19.7 ± 0.3	1.0×10^{-6}
5	19.5 ± 0.3	1.2×10^{-6}
6	19.4 ± 0.2	1.5×10^{-6}
7	19.2 ± 0.3	2.7×10^{-6}
8	19.0 ± 0.4	3.2×10^{-6}
9	19.1 ± 0.2	4.5×10^{-6}
10	18.9 ± 0.3	5.5×10^{-6}
11	17.2 ± 0.2	8.5×10^{-6}
12	15.4 ± 0.4	1.5×10^{-5}

4. CONCLUSIONS

In this work, Pr³⁺ nano-composite carbon paste electrode based on MWCNT and ionic liquid is introduced. The performance of Pr³⁺ nano-composite carbon paste sensor can be greatly improved by using RTIL instead of mineral oil (paraffin), and also by using MWCNTs as enhanced signal transducers. The modified CPEs show better potentiometric response than typical CPEs in terms of sensitivity, Nernstian slope, linear range, and response stability. The proposed sensor exhibits a long lifetime.

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