

Er³⁺ Carbon Paste Electrode Based on New Nano-composite

Parviz Norouzi,^{1,2,*} Zahra Rafiei-Sarmazdeh,¹ Farnoush Faridbod,² Mina Adibi³ and

Mohammad Reza Ganjali^{2,1}

¹ Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

² Endocrinology & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran

³ Specialty Chemicals Research Department, Chemical and Petrochemical Division, Research Institute of Petroleum Industry, RIPI, Tehran, Iran

*E-mail: norouzi@khayam.ut.ac.ir

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Our previous studies showed a strong interaction of N¹-(2-hydroxy-1,2-diphenylethylidene) benzohydrazide (HDEBH) with Er³⁺ ions. To have a high performance sensor with enhanced mechanical resistant for determination of Er³⁺ ions in real samples, HDEBH was used as a sensing material in new composite carbon paste electrode. The carbon paste were made based on a new nano-composite including multi-walled carbon nanotube (MWCNT), nanosilica, and room temperature ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄. The constructed nano-composite electrode showed better sensitivity, selectivity, response time, response stability and lifetime in comparison with typical Er³⁺ carbon paste sensor. The best performance for nano-composite sensor was obtained with electrode composition of 20% HDEBH, 20% [bmim]BF₄, 47% graphite powder, 10% MWCNT and 3% nanosilica. The new electrode exhibited a Nernstian response (19.6±0.3 mV decade⁻¹) toward Er³⁺ ions in the range of 7.5×10⁻⁸-1.0×10⁻² mol L⁻¹ with a detection limit of 6.0×10⁻⁸ mol L⁻¹. The proposed modified Er³⁺ sensor can be used over the pH range of 3.0 to 8.0.

Keywords: sensor; ion selective electrode; carbon paste; carbon nanotubes; nanosilica; ionic liquid

1. INTRODUCTION

Potentiometric sensors have shown to be very effective tools for analysis of a wide variety of metal ions [1-10]. They are very simple, fast, inexpensive, and capable of reliable response in wide concentration ranges. PVC membrane electrodes and microelectrodes, coated wires, and carbon paste electrodes are different types of potentiometric sensors. Among them, carbon paste electrodes (CPEs) have attracted interest as a result of their improved renewability, stable response, and low ohmic resistance compared to membrane electrodes [11-13]. In general, CPE-based potentiometric sensors

reported are based on incorporation of a selective agent into the carbon paste. The typical carbon paste 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 derived from refining of petroleum and processing of crude oil. Thus, contaminants or matrix components may unpredictably influence detection. The mechanical stability of CPEs places between membrane electrodes and all solid state electrodes.

Ionic liquids are salts with relatively low melting points (below 100 °C). Salts that are liquids at room temperature are called room temperature ionic liquids (RTILs). Ionic liquids have advantages of good solvating properties, high conductivity, non-volatility, low toxicity and good electrochemical stability [14,15]. Due to the advantages of RTILs, they can be used as a binder in carbon paste electrodes (CPEs) because of their chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity and good electrochemical and thermal stability [16,17].

Carbon nanotubes (CNTs) have recently been used in composition of carbon paste electrodes [18-24]. CNTs have very interesting physicochemical properties, such as an ordered structure with a high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area [25]. The combination of these characteristics makes CNTs unique materials with the potential for diverse applications.

Our previous studies [26,27] showed a strong interaction of N'-(2-hydroxy-1,2-diphenylethylidene) benzohydrazide (HDEBH), Fig. 1, with Er³⁺ ions. In this work, in order to make a high performance potentiometric electrode with improved mechanical resistant and renewable surface for determination of Er³⁺ ions in real samples we used HDEBH as a sensing material in new proposed carbon paste composition based on RTIL, nanosilica and multi-walled carbon nanotubes (MWCNTs).

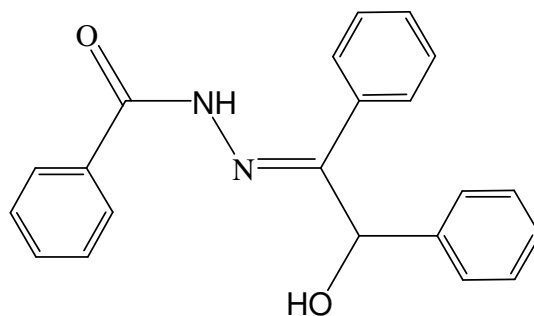


Figure 1. Chemical structure of N'-(2-hydroxy-1,2-diphenylethylidene) benzohydrazide (HDEBH)

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell in which Er³⁺ carbon paste electrode was placed contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode. The Er³⁺ CPE was used as the working electrode. Both electrodes were connected to a mili-voltmeter.

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

2.2. Reagents and materials

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 purchased from Merck. The multi-walled 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). The nanosilica used is Wacker HDK[®] H20 with BET surface of the hydrophilic silica of 170-230 m^2/g . Distilled deionized water was used throughout all experiments.

2.4. Electrode Preparation

The general procedure to prepare the carbon paste electrode was as follows: Different amounts of the ionophore HDEBH along with an appropriate amount of graphite powder, ionic liquid, nanosilica and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube with 5 mm i.d. and a height of 3 cm. After homogenization of the mixture, the paste was carefully 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 establish 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 $1.0 \times 10^{-3} \text{ mol L}^{-1}$ Er(NO₃)₃ solution [21-24].

3. RESULTS AND DISCUSSION

3.1. Carbon paste electrode composition

It is well known that selectivity of any ion-selective sensor (especially in case of lanthanide ions) is closely related to the ionophore used as sensing material [28-32]. Based on the results from the solution studies, HDEBH was used to fabricate both modified and unmodified CPEs with a variety of compositions. Results for these CPEs are given in Table 1. The typical CPE with optimized composition (electrode no. 4) shows a sub-Nernstian slope of ~ 15.7 mV per decade. However, the electrode composed of 20% [bmim] BF₄, 20% HDEBH, 45% graphite powder, 15% MWCNT, 3% nanosilica (no. 10) was found to be optimal for the Er³⁺ electrode. This new nano-composition was selected for further examination.

As it can be seen from Table 1, using RTILs instead of paraffin oil in the carbon paste yields more efficient extraction of Er³⁺ (which is a cation with high charge density) into the CPE. This is probably due to the much higher dielectric constant, low vapor pressure, low toxicity, low melting

temperature, high ionic conductivity and good electrochemical and thermal stability of RTIL, they may be a better binder compare to paraffin oil.

Table 1. The optimization of the carbon paste ingredients

| Electrode No. | Binder | HDEBH | Graphite Powder | MWCNTs | Nanosilica | Slope mV per decade |
|---------------|----------------------------|-------|-----------------|--------|------------|---------------------|
| 1 | 20%-Paraffin | 10% | 70% | 0% | 0% | 10.5±0.4 |
| 2 | 20%-Paraffin | 15% | 65% | 0% | 0% | 12.3±0.3 |
| 3 | 20%-Paraffin | 20% | 60% | 0% | 0% | 15.8±0.3 |
| 4 | 20%-Paraffin | 25% | 55% | 0% | 0% | 15.7±0.2 |
| 5 | 20%-[bmim] BF ₄ | 20% | 60% | 0% | 0% | 17.3±0.3 |
| 6 | 20%-[bmim] BF ₄ | 20% | 55% | 5% | 0% | 17.9±0.3 |
| 7 | 20%-[bmim] BF ₄ | 20% | 50% | 10% | 0% | 18.8±0.4 |
| 8 | 20%-[bmim] BF ₄ | 20% | 50% | 15% | 0% | 17.7±0.3 |
| 9 | 20%-[bmim] BF ₄ | 20% | 49% | 10% | 1% | 19.3±0.2 |
| 10 | 20%-[bmim] BF ₄ | 20% | 47% | 10% | 3% | 19.6±0.3 |
| 11 | 20%-[bmim] BF ₄ | 20% | 45% | 10% | 5% | 18.0±0.2 |

Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical one. Carbon nanotubes have many properties that make them ideal as components in electrical circuits, including their unique dimensions and their unusual current conduction mechanism. 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.

Using nanosilica in the composition of the carbon paste can also improve the response of the electrode. Nanosilica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the CPE. Also, it enhances the mechanical resistant of the electrode.

3.2. Measuring range and detection limit

The response of the optimal modified Er³⁺ carbon paste sensor (no. 10) was tested across Er³⁺ ion concentration range of 1.0×10^{-8} - 1.0×10^{-1} mol L⁻¹. The range of an ion selective electrode is defined as the activity range between the upper and lower detection limits. The applicable range of the proposed sensor extends from 7.5×10^{-8} to 1.0×10^{-2} mol L⁻¹ (Fig. 2). 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 6.0×10^{-8} mol L⁻¹.

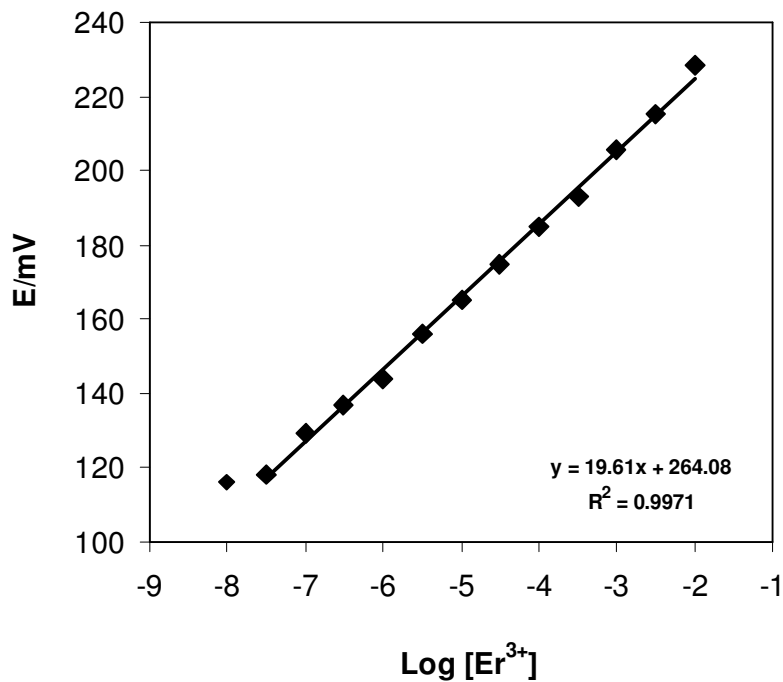


Figure 2. The calibration curve of the Er³⁺ nano-composite carbon paste electrode based on HDEBH (Electrode no. 10)

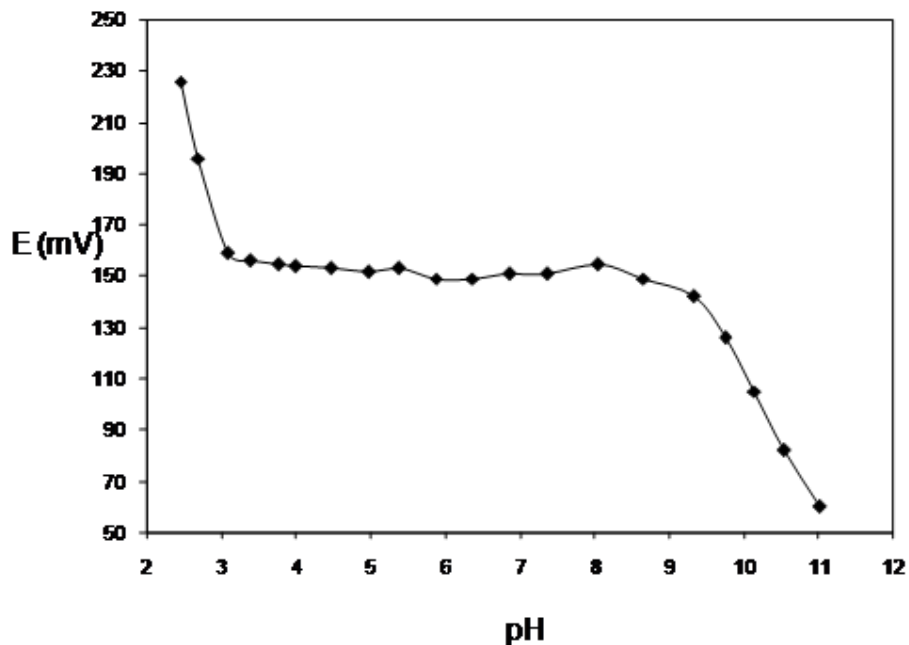


Figure 3. Effect of pH on the potential response of the Er³⁺ nano-composite carbon paste electrode based on HDEBH (Electrode no. 10) in the test solution of Er³⁺ ion (10⁻⁵ mol L⁻¹)

3.3. pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified Er^{3+} sensor (no. 10), the potential was measured for a fixed concentration of Er^{3+} ion solution ($1.0 \times 10^{-5} \text{ mol L}^{-1}$) at different pH values. The pH was varied from (2-12) by addition of concentrated HNO_3 or NaOH . The change in potential as a function of pH is shown in Fig. 3. As can be seen from Fig. 3, the response of the sensor is independent of pH in the range from 3.0-8.0. In addition, there is no visible interference from H^+ or OH^- in this pH range. Fluctuations at pH greater than 8.0 might be due to the formation of soluble or insoluble Er^{3+} hydroxy complexes, such as soluble $\text{Er}(\text{OH})^{2+}$ and $\text{Er}(\text{OH})_2^+$, or insoluble $\text{Er}(\text{OH})_3$. The fluctuations at a pH value of 3.0 were attributed to partial protonation of the HDEBH in the sensor [33-36].

Table 2. The selectivity coefficients of various interfering cations for electrode no. 10; concentration of the reference solution of Er^{3+} ion was $1.0 \times 10^{-7} \text{ mol L}^{-1}$ and the concentration of interfering ions was between 1×10^{-6} to $1.0 \times 10^{-1} \text{ mol L}^{-1}$

| Ion | Log K(I,J) | Ion | Log K(I,J) |
|------------------|------------|------------------|------------|
| Dy^{3+} | -4.03 | Eu^{3+} | -4.11 |
| Nd^{3+} | -4.32 | Yb^{3+} | -4.21 |
| Gd^{3+} | -4.45 | Mg^{2+} | -4.73 |
| Tm^{3+} | -4.12 | Co^{2+} | -4.59 |
| Sm^{3+} | -4.51 | Na^+ | -4.76 |
| Ce^{3+} | -3.10 | Pb^{2+} | -4.64 |
| Pr^{3+} | -4.24 | K^+ | -4.78 |
| Ho^{3+} | -3.13 | Cu^{2+} | -4.35 |
| Lu^{3+} | -4.23 | Ca^{2+} | -4.43 |
| La^{3+} | -4.34 | Fe^{3+} | -4.81 |
| Zn^{2+} | -4.56 | Ni^{2+} | -4.45 |
| Cr^{3+} | -4.78 | Mn^{2+} | -4.33 |

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 $\pm 0.1 \text{ mV}$ of the final steady-state potential upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. 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 [37-41]. For the proposed modified Er^{3+} sensor, the response time over the whole concentration range was less than 16 s.

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 Er^{3+} nano-composite carbon paste electrode were evaluated by matched potential method (MPM) [42-46], and the results are depicted in Table 2. As it can be seen from Table 2, the selectivity coefficients of our sensor are 6.5×10^{-4} or lower for all tested cations. These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

Table 3. Lifetime of Er^{3+} nano-composite carbon paste electrode

| Week | Slope (mVdecade ⁻¹) | Detection limit (M) |
|------|------------------------------------|------------------------|
| 1 | 19.6±0.3 | 6.0×10^{-8} |
| 2 | 19.5±0.2 | 6.0×10^{-8} |
| 3 | 19.5±0.3 | 6.5×10^{-8} |
| 4 | 19.4±0.3 | 7.9×10^{-8} |
| 5 | 19.6±0.4 | 8.3×10^{-8} |
| 6 | 19.4±0.5 | 8.6×10^{-8} |
| 7 | 19.5±0.3 | 8.9×10^{-8} |
| 8 | 19.3±0.4 | 9.2×10^{-8} |
| 9 | 19.1±0.3 | 9.8×10^{-8} |
| 10 | 19.2±0.3 | 1.5×10^{-7} |
| 11 | 18.8±0.2 | 3.8×10^{-7} |
| 12 | 17.2±0.3 | 2.0×10^{-6} |
| 13 | 16.7±0.2 | 5.5×10^{-6} |
| 14 | 15.8±0.3 | 9.4×10^{-6} |
| 15 | 13.2±0.4 | 4.0×10^{-5} |

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 Er^{3+} sensor was evaluated for a period of 15 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 12 weeks. After this time, a slight gradual decrease in the slope from 19.6 to 17.2 mV per decade is observed, as is an increase in the detection limit from $6.0 \times 10^{-8} \text{ mol L}^{-1}$ to $2.0 \times 10^{-6} \text{ mol L}^{-1}$ (Table 3). It is well understood that the loss of plasticizer and ion carrier is the primary reason for limited lifetimes of many electrochemical sensors.

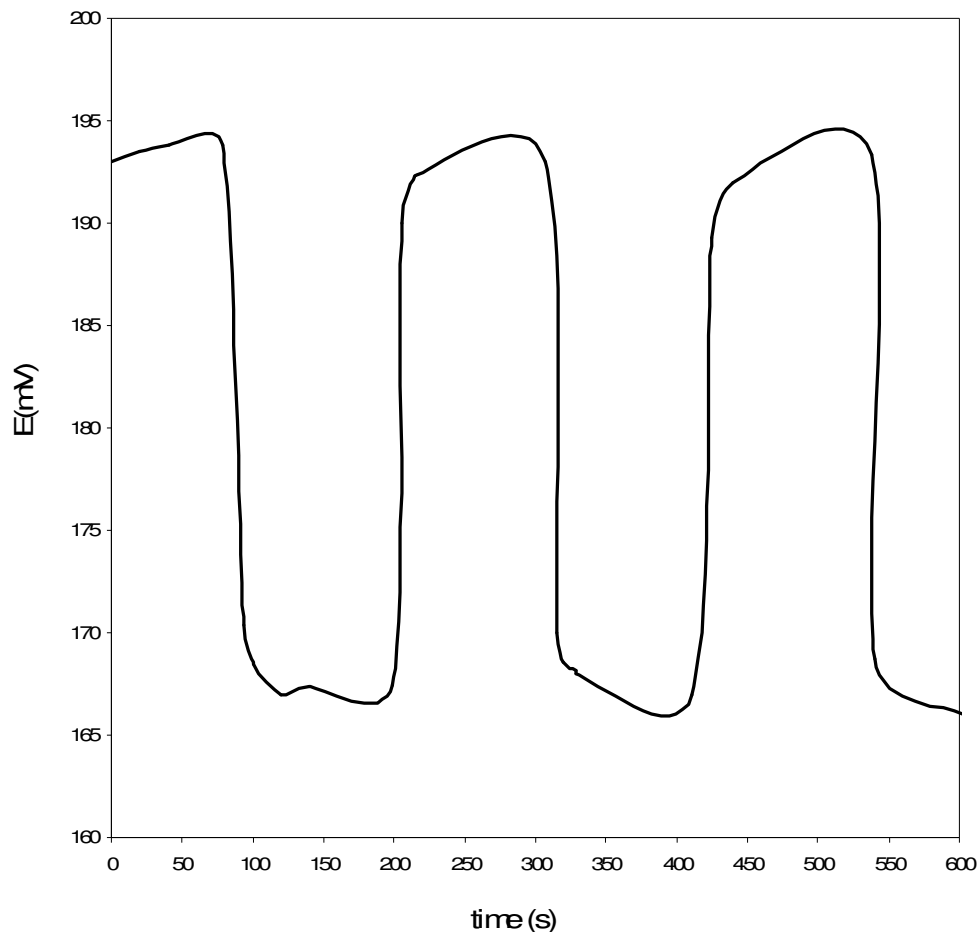


Figure 4. Dynamic response characteristics of the Er^{3+} nano-composite electrode for several high-to-low sample cycles

3.7. Reversibility of the electrode response

To evaluate the reversibility of the electrode, the practical potential response of the modified electrode was recorded by changing solutions with different Er^{3+} concentrations from 1.0×10^{-4} to $1.0 \times 10^{-5} \text{ mol L}^{-1}$. The measurements were performed from the highest concentration to the lowest, and the results are shown in Fig. 4. The potentiometric response of the sensor was reversible and had no memory effect, although the time needed to reach equilibrium was longer than that when the solution sequence was reversed. This finding is consistent with that for other electrochemical sensors reported in the literature.

4. CONCLUSIONS

In this work, Er^{3+} nano-composite carbon paste electrode based on nanosilica, MWCNT and ionic liquid is introduced. The performance of Er^{3+} 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 (about three months).

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