Int. J. Electrochem. Sci., 5 (**2010**) 1103 - 1112

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

MWCNTs-Ionic Liquids-Ionophore-Graphite Nanocomposite Based Sensor for Selective Determination of Ytterbium(III) Ion

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Received: 20 June 2010 / *Accepted:* 15 July 2010 / *Published:* 10 August 2010

Fluorescence studies in acetonitrile solution proved a strong interaction between N'-(1-oxoacenaphthylen-2(1H)-ylidene) furan-2-carbohydrazide (**L**) with Yb^{3+} ions in comparison with other lanthanide ions. Thus, **L** can be used as a suitable ionophore in construction of the Yb^{3+} potentiometric sensor. To have an electrode with enhanced mechanical resistant in real samples, **L** 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-wall carbon nanotube (MWCNT), and room temperature ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4. 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% L, 25% [bmim]BF_4, 45% graphite powder, and 5% MWCNT. The new electrode exhibited a Nernstian response (19.6±0.3 mV per decade) toward Yb^{3+} ions in the range of 1.0×10^{-8}-1.0×10^{-2} mol L^{-1}

Keywords: sensor; ytterbium; ion selective electrode; carbon paste; room temperature ionic liquid; carbon nanotubes

1. INTRODUCTION

Our fluorescence studies [1] showed a strong interaction of N'-(1-oxoacenaphthylen-2(1H)-ylidene) furan-2-carbohydrazide (L), Fig. 1, with Yb^{3+} ions among the other lanthanide ions. In this work, in order to make a high performance potentiometric electrode with improved mechanical resistant and renewable surface for determination of Yb^{3+} ions in real samples we used **L** as a sensing material in new proposed carbon paste composition based on RTIL and multi-wall carbon nanotubes (MWCNTs).

Ion selective electrodes are used widely in analysis of a wide variety of metal ions. They offer some advantages such as portability, simplicity, fast, inexpensive, and reliable response in a wide concentration range [2-13]. Carbon paste electrodes are one of the classes of potentiometric sensors. CPEs offer renewable surface, stable response, and low ohmic resistance electrodes compared to PVC membrane electrodes [14,15]. CPEs potentiometric sensors generally are composed of a selective agent, graphite powder and a non-conductive mineral oil. However during the recent years for improvement of these kinds of electrode responses, new composition was used [14-18]. Mineral oil gives CPEs some disadvantages. It is derived from refining of petroleum and processing of crude oil. Thus, its matrix components may unpredictably influence the sensor response. The mechanical stability of CPEs places between membrane electrodes and all solid state electrodes. Thus, they can be easily replaced with ionic liquids.

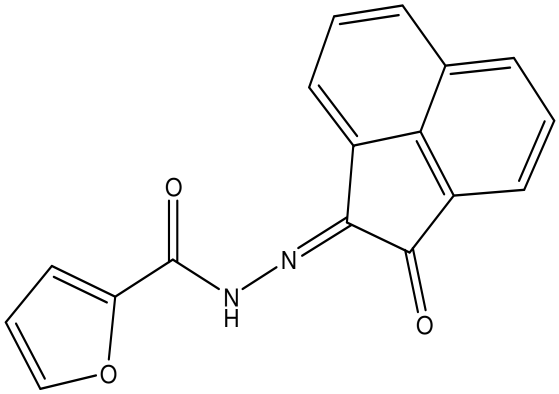

Figure 1. Chemical structure of N'-(1-oxoacenaphthylen-2(1H)-ylidene) furan-2-carbohydrazide (**L**)

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 [19,20]. 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 [18-20].

Carbon nanotubes (CNTs) have been recently used in composition of carbon paste electrodes [21-25]. 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 [26]. The combination of these characteristics makes CNTs unique materials with the potential for diverse applications.

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 ($[bmim]BF_4$) and chloride and nitrate salts of the cations were purchased from Merck.

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 Yb^{3+} CPE was used as the working electrode. Both electrodes were connected to a milivoltmeter.

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

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

2.3. Electrode Preparation

The general procedure to prepare the carbon paste electrode was as follows: Different amounts of L as a sensing material along with an appropriate amount of graphite powder, ionic liquid, 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 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} $Yb(NO_3)_3$ solution [23-25].

3. RESULTS AND DISCUSSION

3.1. Carbon paste electrode composition

The sensing material of a potentiometric sensor has important role in selectivity behavior of the electrode especially in case of lanthanide ions [27-31]. Based on the results from the fluorescence studies [1], **L** shows a selective behavior toward Yb^{3+} ion. The formation constant of **L** with some metal ions are listed in Table 1.

Therefore, **L** was used to make both modified and unmodified CPEs with different compositions. Results for these CPEs are shown in Table 2. The typical CPE with optimized composition (electrode no. 6) shows a sub-Nernstian slope of ~17.9 mV per decade. However, the electrode composed of 25% [bmim] BF_4, 25% **L**, 45% graphite powder, and 5% MWCNT (no. 10) was found to be optimal for the Yb^{3+} carbon paste electrode. This new nano-composition was selected for further examination.

An ionic liquid is a salt in the liquid state which is largely made of ions and short-lived ion pairs. 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 2, using RTILs instead of paraffin oil in the carbon paste yields more efficient extraction of Yb^{3+} ion (which is a high charge density cation) 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. Formation constant of L with Yb^{3+} ion

Cation	K_f	Cation	K_f
Na^+	<2	**Ce^{3+}**	2.47±0.09
Li^+	<2	**Pr^{3+}**	<2.0
K^+	<2	**Nd^{3+}**	<2.0
Mg^{2+}	<2	**Sm^{3+}**	2.88±0.07
Ca^{2+}	<2	**Eu^{3+}**	2.93±0.05
Cu^{2+}	2.15±0.10	**Gd^{3+}**	2.67±0.07
Zn^{2+}	3.25±0.11	**Tb^{3+}**	<2.0
Co^{2+}	<2.0	**Dy^{3+}**	2.77±0.14
Cd^{2+}	2.47±0.12	**Ho^{3+}**	<2.0
Ni^{2+}	<2.0	**Er^{3+}**	<2.0
Fe^{3+}	2.49±0.09	**Tm^{3+}**	2.15±0.10
Pb^{2+}	2.27±0.07	**Yb^{3+}**	<6.0
Hg^{2+}	2.91±0.13	**Lu^{3+}**	<2.0
La^{3+}	2.89±0.07	**Ag^+**	<2.0

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

Table 2. The optimization of the carbon paste ingredients

Electrode No.	Binder	L	Graphite Powder	MWCNTs	Slope mV per decade	R^2
1	25%-Paraffin	10%	65%	0%	9.7±0.3	0.779
2	25%-Paraffin	15%	60%	0%	13.7±0.3	0.825
3	25%-Paraffin	20%	55%	0%	15.5±0.4	0.889
4	25%-Paraffin	25%	50%	0%	16.5±0.2	0.901
5	25%- Paraffin	30%	45%	0%	15.8±0.3	0.897
6	25%- RTIL	25%	50%	0%	17.9±0.2	0.923
7	20%- RTIL	25%	55%	0%	17.6±0.3	0.963
8	30%- RTIL	25%	45%	0%	18.0±0.2	0.955
9	25%- RTIL	25%	47%	3%	18.8±0.4	0.944
10	25%- RTIL	25%	45%	5%	19.8±0.3	0.998
11	25%- RTIL	25%	43%	7%	19.3±0.2	0.995

3.2. Measuring range and detection limit

The response of the optimal modified Yb^{3+} carbon paste electrode (no. 10) was tested across Yb^{3+} ion concentration range of 1.0×10^{-9}-1.0×10^{-1} mol L^{-1}. The applicable range of the proposed sensor extends from 1.0×10^{-8} to 1.0×10^{-2} mol L^{-1} as seen in 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 1.0×10^{-8} 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 Yb^{3+} sensor (no. 10), the potential was measured for a fixed concentration of Yb^{3+} ion solutions (1.0×10^{-5} and 10^{-4} 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 it can be seen from Fig. 3, the response of the sensor is independent of pH in the range from 3.5-8.5. 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 Yb^{3+} hydroxy complexes, such as soluble $Yb(OH)^{2+}$and $Yb(OH)_2^+$, or insoluble $Yb(OH)_3$. The fluctuations at a pH value of 3.5 were attributed to the protonation of the **L** in the carbon paste [29,30].

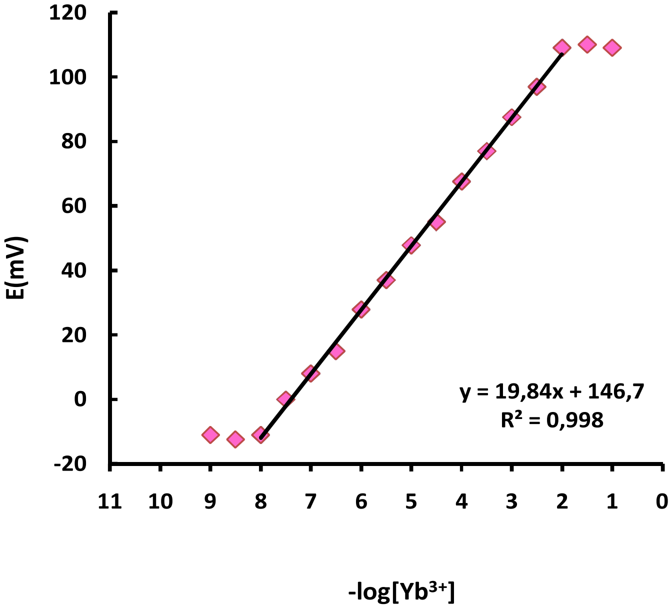

Figure 2. Calibration curve of Yb^{3+} nano-composite carbon paste electrode (Electrode no. 10)

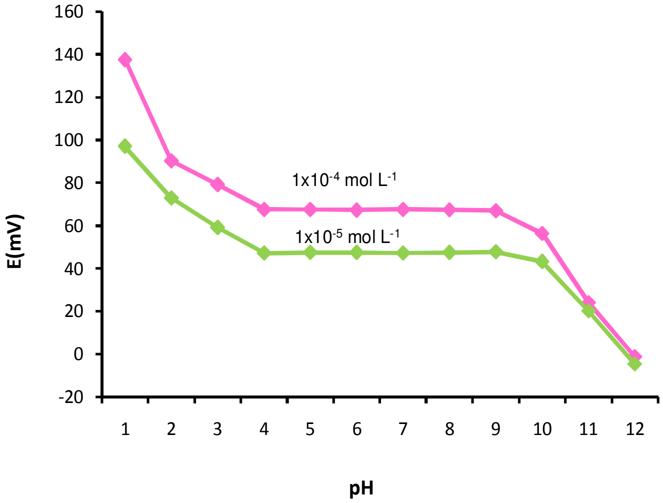

Figure 3. Effect of pH on the potential response of the Yb^{3+} nano-composite carbon paste electrode based on **L** (Electrode no. 10) in the test solution of Yb^{3+} ion (10^{-5} and 10^{-4} mol L^{-1})

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 [31-46]. For the proposed modified Yb^{3+} sensor, the response time over the whole concentration range was less than 20 s.

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

Cation	K_{MPM}	Cation	K_{MPM}
Na^+	2.3×10^{-5}	La^{3+}	8.9×10^{-4}
Li^+	1.5×10^{-5}	Ce^{3+}	5.8×10^{-4}
K^+	2.4×10^{-5}	Pr^{3+}	4.1×10^{-5}
Mg^{2+}	4.4×10^{-5}	Nd^{3+}	4.2×10^{-5}
Ca^{2+}	5.7×10^{-5}	Sm^{3+}	6.5×10^{-4}
Cu^{2+}	1.4×10^{-4}	Eu^{3+}	7.6×10^{-4}
Zn^{2+}	1.8×10^{-3}	Gd^{3+}	3.5×10^{-4}
Co^{2+}	7.5×10^{-5}	Tb^{3+}	3.5×10^{-5}
Cd^{2+}	3.7×10^{-4}	Dy^{3+}	4.1×10^{-4}
Ni^{2+}	8.1×10^{-5}	Ho^{3+}	4.3×10^{-5}
Fe^{3+}	4.8×10^{-4}	Er^{3+}	4.7×10^{-5}
Pb^{2+}	3.5×10^{-4}	Tm^{3+}	2.1×10^{-4}
Hg^{2+}	8.5×10^{-4}	Lu^{3+}	3.5×10^{-5}

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) [37-40], and the results are depicted in Table 3. As it can be seen from Table 2, the selectivity coefficients of our sensor are 1.8×10^{-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 Yb^{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 8 weeks. After this time, a slight gradual decrease in the slope from 19.8 to 17.7 mV per decade is observed, as is an increase in the detection limit from 1.0×10^{-8} mol L^{-1} to 2.4×10^{-7} mol L^{-1} (Table 4). It is well understood that the loss of sensing material is the primary reason for limited lifetimes of carbon paste electrode.

Table 4. Lifetime of Yb^{3+} nano-composite carbon paste electrode

Week	Slope	DL (mol L^{-1})
1	19.9±0.2	8×10^{-10}
2	19.8±0.3	8×10^{-10}
3	19.9±0.1	9×10^{-10}
4	19.7±0.2	1×10^{-9}
5	19.8±0.2	1×10^{-9}
6	19.7±0.3	1×10^{-9}
7	19.8±0.4	1×10^{-9}
8	19.6±0.2	7.6×10^{-8}
9	19.7±0.3	2.4×10^{-7}
10	19.6±0.3	7.8×10^{-7}
11	19.5±0.1	1.3×10^{-6}
12	0.4±17.7	7.0×10^{-6}

4. CONCLUSIONS

In this work, Yb^{3+} nano-composite carbon paste electrode based on MWCNT and ionic liquid is introduced. The performance of Yb^{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.

ACKNOWLEDGEMENTS
The authors wish to express their appreciation to the Research Council of the University of Tehran for financial support of these investigations.

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