

Permanganate Selective Nano-composite Electrode

Farnoush Faridbod^{1,*}, Mohammad Reza Ganjali¹, Morteza Hosseini², Parviz Norouzi¹

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

² Faculty of New Science and Technology, University of Tehran, Tehran, Iran

*E-mail: faridbodf@gmail.com

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Fluorescence spectroscopic studies showed a selective interaction between a new modified SBA-15 and permanganate ion respects to a number of inorganic anions. Aluminum complex of 8-hydroxyquinoline was used for modification of the channels of SBA-15. Hence, modified SBA-15 was used as a selective sensing element in construction of a nano-composite carbon paste electrode for measurement of permanganate ions. The nano-composite paste was composed of 5% Multi-walled Carbon Nanotube (MWCNT), 55% graphite powder, 20% room temperature ionic liquid (RTIL) and 20% of sensing element. Carbon paste electrode based on MWCNTs and RTILs show superior performance over traditional carbon paste electrodes. Addition of MWCNT to the composition of the carbon paste, owing to its high conductivity, improve the dynamic working range, detection limit, response time, lifetime, and stability of the nano-composite sensor. Replacement of paraffin oil with RTIL improved the sensitivity of the sensor from a near-Nernstian slope to Nernstian one. The sensor worked well with a Nernstian response of -58.7 ± 0.5 mV decade⁻¹ of MnO_4^- anion in a wide dynamic concentration range of 1.0×10^{-6} - 1.0×10^{-1} mol L⁻¹. The electrode had relatively short response time (25 s), and it was found to produce stable responses for more than 8 weeks.

Keywords: Permanganate anion, Sensor, Ion selective electrode, Potentiometry, Multi-walled Carbon Nanotube, Room temperature ionic liquid

1. INTRODUCTION

Potassium permanganate, KMnO_4 , is a purplish-black crystalline solid in which manganese has a valence of plus 7. It is an exceptionally strong oxidizer. It is used primarily to control taste and odors, remove color, control biological growth in treatment plants, and remove iron and manganese [1-3].

There are some analytical methods for measurement of permanganate ion such as colorimetric methods [4]. An alternative method for measurement of this anion is potentiometry using an ion selective electrode. Such methods are simple, low cost, accurate and rapid, which is the reason behind

the increasing interest in them [5-17]. Carbon paste electrodes are a class of ion selective electrodes with a high physical stability, long lifetime, the versatility of chemical modification, miniaturization, and rapid renewal of the electrode surface [18-27].

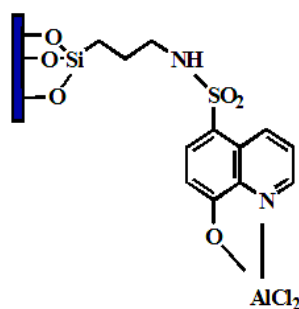
In recent years, large-scale nano-structured materials such as SBA-15 and MCM-41 have attracted significant interest in development of the chemical sensors [28-30]. SBA-15, Among the mesoporous silica compounds, possessing hexagonal arrays of uniform pores with ultra large pore diameters, large surface area, high pore volume and thicker pore walls, excellent homogeneity and chemical/mechanical stability is a potential candidate for interacting with guest species on its surface [31,32].

Multi-walled carbon nanotubes (MWCNTs) have been also used in the compositions of carbon paste electrodes [20-27] due to their surprising physicochemical properties, such as ordered structures with high aspect ratios, ultra-light weight, high thermal conductivity, metallic or semi-metallic behavior, high surface area, high electrical conductivity and remarkable mechanical strength [33, 34].

Ionic liquids are as well a good choice as a binder in the composition of carbon paste electrodes due to their interesting properties, including stability, low vapor pressure, low toxicity, low melting temperature, ion-exchange properties, extraction and catalytic activity, high ionic conductivity and good electrochemical and thermal stability [20,21].

Carbon paste electrode based on MWCNTs and RTILs types of electrodes show superior performance over traditional carbon paste electrodes.

Previous fluorescent studies [35] shows a selective interaction between the modified SBA-15 (Scheme 1) and permanganate anion respect to a number of anions tested, thus, the compound was used as sensing material in construction of a MnO_4^- nano-composite carbon paste sensor based on MWCNTs and RTILs.



Scheme 1. Chemical structure of modified SBA-15

2. EXPERIMENTAL SECTION

2.1. Equipments

A glass cell where the carbon paste electrode was used consisting of an R684 model Analion Ag/AgCl double junction electrode as a reference electrode. A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C.

2.2. Reagents

Graphite powder with a $<50\ \mu\text{m}$ particle size (Merck), and $2.2\ \text{g/cm}^3$ density; along with the paraffin oil (Aldrich) of the highest purity, and 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄, were used for the preparation of the carbon pastes. The multi-walled carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length, core diameter: 5-10 nm, SBET: 40-600 m^2/g , V_{total} : $0.9\ \text{cm}^3/\text{g}$, bulk density $0.1\ \text{g/cm}^3$, true density $2.1\ \text{g/cm}^3$ and with 95% purity were purchased from a local company (Iran). The sensing element, modified SBA-15, was synthesized as described elsewhere [35].

2.3. Fabrication of nano-composite based permanganate sensor

Various amounts of modified SBA-15, graphite powder, paraffin (in case of traditional carbon paste) or 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄, and MWCNTs (in case of nano-composite sensor) were thoroughly mixed. The resulting mixtures were transferred into a glass tube. The electrode body was fabricated from a glass tube of 5 mm i.d. and a height of 3 cm. After the mixture was homogenized, the paste was carefully packed 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 [20-27]. The external electrode surface was smoothed with soft abrasive paper to produce a new surface and replacing the carbon paste. The electrode was finally conditioned for 48 h by soaking in a $1.0 \times 10^{-3}\ \text{M}$ KMnO₄ solution.

2.4. Emf measurements

The electrochemical cell can be represented as follow:

Ag, AgCl(s), KCl (3 M) || sample solution | nano-composite carbon paste surface | copper wire

Calibration graph was drawn by plotting the potential, E, versus the logarithm of MnO₄⁻ ion concentration.

3. RESULTS AND DISCUSSIONS

The selectivity behavior of a certain ion selective sensor is greatly dependant on the sensing materials used [36-46]. Due to the affinity of the sensing element toward permanganate ion according to the previous fluorescence studies [35], the compound was taken to be a suitable sensing element in construction of a number of potentiometric electrodes with different composition and modification. Also, it was found that a stable complex having a certain stoichiometric ratio between the receptor (modified SBA-15) and MnO₄⁻ was formed.

3.1. Electrode composition and modification

To find the performance of the electrode, different compositions were made according to Table 1. As it can be seen, paste composition no. 2 revealed that the optimum amount of modified SBA-15 should be 20%. In this case the traditional carbon paste electrode showed a near Nernstian slope of about $-48.7 \text{ mV decade}^{-1}$ in the absence of any modifier.

Replacement of paraffin oil, which is an organic binder, with RTIL, improved the sensitivity of the sensor to a near-Nernstian slope (no. 7). Enhancement of the electrochemical behavior of RTIL based electrodes can be related to its enhanced conductivity. Because of the good solubility and high viscosity, the IL can form a layer on the carbon particles and can fill in the empty spaces between carbon particles, so the conductivity of the IL-based electrodes was greatly enhanced compared to the traditional CPE. Also, RTIL can be a better solvent and extract the analyte from the solution to the electrode surface. High conductivity of MWCNT increases the dynamic working range and response time of the sensor. Addition of 5% of MWCNT to the composition was found to increase the response to a Nernstian slope of about $-58.7 \text{ mV decade}^{-1}$ (no. 10).

Table 1. The optimization of the carbon paste ingredients

CPE No.	Binder	Sensing Material	Graphite Powder	MWCNTs	Slope (mV decade^{-1})	Linear Range (M)	R ²	Response time (s)
1	Paraffin oil-20%	15%	65%	-	-39.3 ± 0.6	$5.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.904	68 ± 4
2	Paraffin oil-20%	20%	60%	-	-48.7 ± 0.4	$1.0 \times 10^{-5} - 5.0 \times 10^{-2}$	0.945	40 ± 2
3	Paraffin oil-20%	25%	55%	-	-47.4 ± 0.5	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.933	44 ± 2
4	Paraffin oil-15%	20%	65%	-	-39.6 ± 0.4	$5.0 \times 10^{-4} - 1.0 \times 10^{-2}$	0.892	76 ± 5
5	Paraffin oil-25%	20%	55%	-	-26.0 ± 0.5	$4.0 \times 10^{-5} - 5.0 \times 10^{-3}$	0.764	49 ± 6
6	RTIL-15%	20%	65%	-	-49.8 ± 0.3	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	0.971	34 ± 4
7	RTIL-20%	20%	60%	-	-54.6 ± 0.4	$5.0 \times 10^{-6} - 5.0 \times 10^{-2}$	0.954	31 ± 3
8	RTIL-25%	20%	55%	-	-53.8 ± 0.3	$5.0 \times 10^{-6} - 5.0 \times 10^{-2}$	0.922	31 ± 4
9	RTIL-20%	20%	57%	3%	-56.5 ± 0.6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.978	27 ± 3
10	RTIL-20%	20%	55%	5%	-58.7 ± 0.5	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.997	25 ± 2
11	RTIL-20%	20%	53%	7%	-57.7 ± 0.5	$2.0 \times 10^{-6} - 1.0 \times 10^{-1}$	0.983	26 ± 3
12	RTIL-20%	-	75%	5%	-6.9 ± 0.7	$8.0 \times 10^{-4} - 5.0 \times 10^{-3}$	0.633	84 ± 8

Consequently, the composition containing 20% modified SBA-15, 5% MWCNT, 20% RTIL and 55% graphite showed the best performance with a Nernstian slope of $-58.7 \text{ mV decade}^{-1}$ (no. 10). According to Table 1, the electrode having the best composition but absent the sensing element (no.12) showed too low potential response.

3.2. Calibration curve

The measuring range of ion selective electrodes refers to the linear part of the calibration graph. According to IUPAC definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits [44-51]. The applicable measuring range of the modified electrode as shown in Fig. 1 was found to be between 1.0×10^{-6} - 1.0×10^{-1} M. 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 sensor is 8.3×10^{-7} M which was calculated by the extrapolating of the two segment of the calibration curve in Fig. 1.

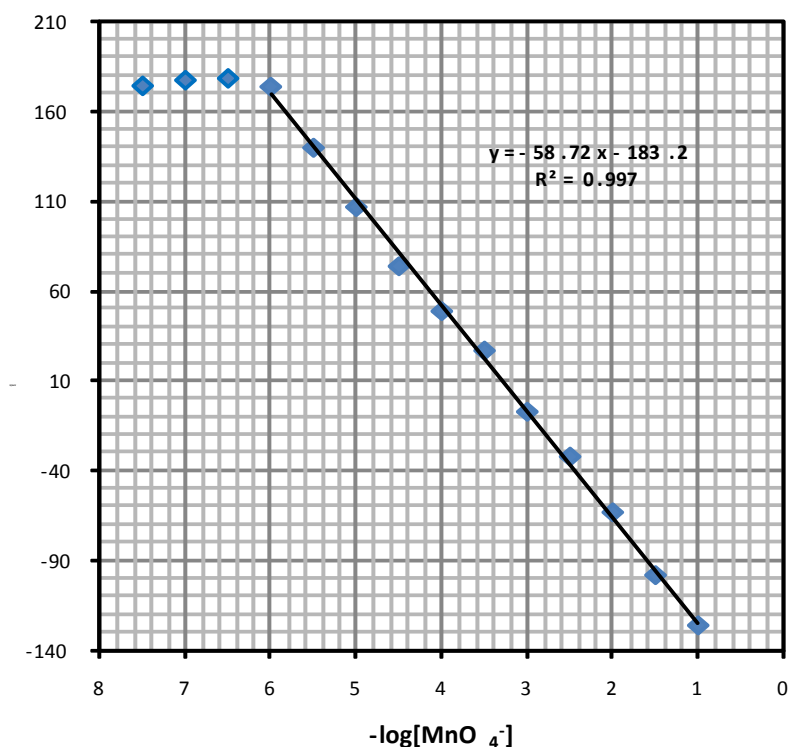


Figure 1. The calibration curve of the MnO_4^- nano composite based sensor with the sensor no. 10

3.3. pH effect on the electrode response

In order to investigate the effect pH on the potential response of the sensor, the potentials were measured at a fixed concentration of MnO_4^- ion (1.0×10^{-4} M) having different pH values. The pH was altered from 4-10 by adding HNO_3 or NaOH . The variations of the potential response of the best sensor as a function of pH showed the potential of electrode is constant between pH values of 6.8-7.8. Thus, the electrode works satisfactorily in this pH range, and no interference from H^+ or OH^- is observed in the range. In this pH the permanganate ion species is dominant to the other form of manganese. The fluctuations above pH value of 7.8 might be due to the sensor response to OH^- ions in

the solution. And the fluctuations below the pH value of 6.8, is most probably due to the formation of other form of manganese. The best performance of the electrode was achieved in pH of 7.

3.4. Response time

The response time of an ion-selective electrode is also an important factor for any analytical application. The average response time of the electrodes, defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference [35-40] was found to be 25 ± 2 seconds. The resulting potential–time responses for the mentioned electrode were obtained by changing MnO_4^- concentration from 0.000001 to 0.1 M (by fast injection of μL -amounts of a concentrated solution of KMnO_4). Results in Fig. 2 showed that the potentiometric response time of the electrode was about 20 s in whole concentration range.

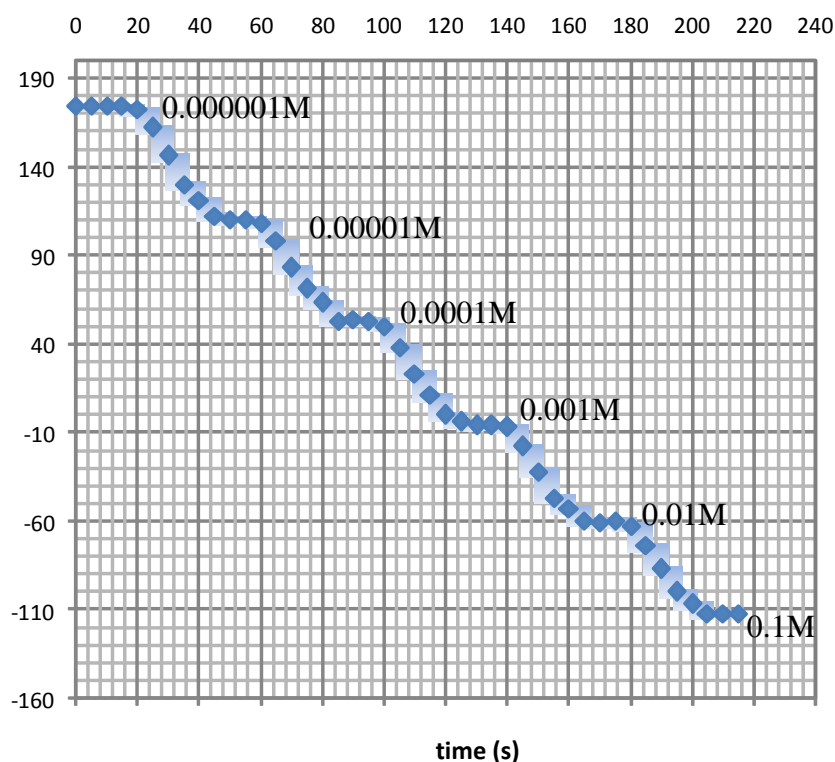


Figure 2. Dynamic response time of the MnO_4^- nano composite based sensor with the sensor no. 10

3.5. Interference studies

The selectivity behavior, expressed as the relative response of the sensor to the primary ion over the other ions present in the solution. It is obviously one of the most important characteristics of a

selective sensor. Potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, X, with reference to MnO_4^- , were determined by the matched potential method (MPM) [47-51]. The MPM is recommended by IUPAC to overcome the difficulties associated with the methods based on the Nicolsky–Eisenman equation.

According to this method, the specified activity (concentration) of the primary ion is added to a reference solution (0.000001 M MnO_4^- ion, in this case) and the potential is measured.

In a separate experiment, interfering ions (X) are successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficient, $k_{A,X}^{MPM}$ is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $k_{A,X}^{MPM} = \Delta a_{\text{MnO}_4^-} / a_X$.

The resulting values for MnO_4^- sensor are listed in Table 2. As it can be seen from Table 2, anions tested have not significance interfere in the monitoring of permanganate ion. Since the interaction between the modified SBA-15 with MnO_4^- is a kind of anion coordination to the metal center of the modifier (Aluminum complex of 8-hydroxyquinoline), it is not according to Hofmeister series (i.e. hydrophobicities of the anions).

Table 2. Selectivity coefficients of various interfering anions for the electrode no. 10

Interference (x)	$\log k_{A,X}^{MPM}$
Cl^-	-4.0
Br^-	-3.8
I^-	-4.2
NO_3^-	-3.4
SO_4^{2-}	-3.5
ClO_4^-	-3.0
ClO_3^-	-2.9
CH_3COO^-	-3.1
$\text{C}_2\text{O}_4^{2-}$	-3.0
SCN^-	-3.5
HPO_4^{2-}	-2.8
CrO_4^{2-}	-3.6
S^{2-}	-3.2
CN^-	-3.9
HCO_3^-	-3.6
$\text{Cr}_2\text{O}_7^{2-}$	-2.5

3.6. Lifetime

Lifetime of the nano-composite electrode was studied by periodically recalibrating and using the electrode to measure its potentiometric response to MnO_4^- ion in the standard solutions in a period

of time. After the conditioning step the electrodes were repeatedly calibrated three times a day during a period of two months (the electrode worked one hour a day). Before eight weeks no significant change in the performance of the electrode was observed. This shows that the lifetime of the proposed electrode was about 8 weeks. After 8 weeks, the slope of the sensor decreases from -58.7 to -34.6 mV per decade and the detection limit reduces from 8.3×10^{-7} M to 4.7×10^{-5} M.

4. CONCLUSION

A new MnO_4^- nano-composite carbon paste electrode was introduced. Aluminum complex of 8-hydroxyquinoline was used for modification of the channels of SBA-15. Then, modified SBA-15 was used as a selective sensing element in construction of a nano-composite carbon paste electrode for measurement of permanganate ions. Carbon paste electrode based on MWCNTs and RTILs show superior performance over traditional carbon paste electrodes. Addition of MWCNT to the composition of the carbon paste, having high conductivity, improve the dynamic working range, detection limit, response time, lifetime, and stability of the nano-composite sensor. Replacement of paraffin oil with RTIL improved the sensitivity of the sensor from a near-Nernstian slope to Nernstian one. The electrode based on modified SBA-15, MWCNT and RTIL exhibits linear response over a wide concentration range with a Nernstian slope, and a short response time of about 25 ± 2 s.

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