Novel Chromate Sensor Based on MWCNTs/Nanosilica/Ionic Liouid/Eu Complex/Graphite as a New Nano-Composite and Its Application for Determination of Chromate Ion Concentration in Waste Water of Chromium Electroplating

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Received: 20 December 2010 / Accepted: 1 February 2011 / Published: 1 March 2011

Fluorescence studies of interaction between europium ß-diketone complex (EDC) and a number of inorganic anions proved EDC to be a promising ionophore for construction of a chromate ion sensor. Accordingly, a nano-composite electrode containing 5% multi-walled carbon nanotube (MWCNT), 67% graphite, 3% nano-silica and 15% room temperature ionic liquid (RTIL), 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄ and 10% of EDC as a sensing material was prepared and it exhibited the best performance with a Nernstian response (-29.6±0.2 mV decade⁻¹) toward CrO_4^{2-} ions in a dynamic concentration range of 1.0×10^{-7} - 1.0×10^{-2} mol L⁻¹ and detection limit of 7.0×10^{-8} mol L⁻¹. The sensor response was found to be invariable in pH range from 6.5 to 10.5. The electrode had relatively short response time (20 s), and it was found to produce stable responses for more than two months. It was also used for monitoring of chromate ion concentration in waste water samples of chromium electroplating samples.

Keywords: Multi-walled Carbon Nanotube, Nano-silica, Ionic liquid, Chromate Ions, Sensor, Ion selective electrode, Potentiometry

1. INTRODUCTION

Chromium compounds are extensively used in corrosion control, oxidation processes, leather industry, electroplating and so forth. It is reported that chromium concentration in discharged waste is up to several thousand parts per million causing serious threat to microorganisms of aquatic systems and human life in nearby areas. Cr(III) and Cr(VI) are the predominant oxidation states of the element, among which Cr(VI) is a well known carcinogen [1].

Some analytical methods including atomic absorption, UV–Vis spectrometry and inductively coupled plasma (ICP) are utilized for determination of chromate ion at low concentrations. The methods are however either time consuming, involve multiple sample manipulations, or are rather expensive.

An alternative method for determination of chromate ion is potentiometry using an indicating selective electrode. Such methods are simple, low cost, accurate and rapid, which is the reason behind the increasing interest in them [2-14]. The design of any new selective sensor, including those of CrO_4^{2-} , has hence been a challenging as well as inviting field of research.

Our team has recently reported a number of electrochemical sensors for anions and cations. In this work we wish to introduce a highly selective and sensitive chromate sensor based on europium β -diketone complex (EDC).

On the other hand, carbon paste electrodes (CPEs) have obtained noticeable attention as useful materials for the fabrication of sensors and biosensors [15-24]. The factors promoting the use of CPEs include ease of preparation, the versatility of chemical modification, and rapid renewal of the electrode surface.

Nano-silica based materials are robust inorganic solids displaying both high specific surface area (200-1500 m² g⁻¹) and a three-dimensional structure made of highly open spaces interconnected to each other. This would impart high diffusion rates of selected target analytes to a large number of accessible binding sites, which constitutes definite key factor in designing sensor devices with high sensitivity [25].

Multi-walled carbon nanotubes (MWCNTs) have recently also been used in compositions of carbon paste electrodes [26-34] due to their extraordinary physicochemical properties, such as ordered structures with high aspect ratios, ultra-light weight, high thermal conductivity, metallic or semimetallic behavior, high surface area, high electrical conductivity and remarkable mechanical strength [31, 32].

Ionic liquids 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 [32].

Since fluorescence study of interactions between EDC and a number of anions carried out in this work had showed that among all anions tested, EDC had a selective tendency toward CrO_4^{2-} ion comparison with other tested anions, the complex was used as sensing material in construction of a CrO_4^{2-} nano-composite sensor comprising nano-silica, MWCNTs and RTILs.

2. EXPERIMENTAL SECTION

2.1. Apparatus

A glass cell where CrO_4^{2-} 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 μ m particle size (Merck), and 2.2 g/cm³ 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 μ m length, core diameter: 5-10 nm, SBET: 40-600 m²/g, V_{total}: 0.9 cm³/g, bulk density 0.1 g/cm³, true density 2.1 g/cm³ and with 95% purity were purchased from a local company (Iran). Nano-silica used is Wacker HDK[®] H20 with BET surface of the hydrophilic silica of 170-230 m²/g, V_{total}: 0.81 cm³/g and tamped density 40 g/lit. The sensing material, europium β-diketone complex (EDC), Eu(CH₃COCH₂COCH₃)₃, was purchased from Sigma.

2.3. Fabrication of nano-composite based chromate sensor

Various amounts of EDC, graphite powder, nano-silica, 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄ or paraffin, and MWCNTs 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 [31,32]. 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 36 h by soaking in a 1.0×10^{-3} M K₂CrO₄ solution.

2.4. Emf measurements

The electrochemical cell can be represented as follows:

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

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

3. RESULTS AND DISCUSSIONS

The selectivity behavior of a certain ion selective sensor is greatly dependant on the ionophore used [35-40]. Due to the affinity of EBC for chromate ion according to the solution study, the compound was taken to be a promising ionophore for the construction of a number of chromate sensors with different composition and modification.

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3.1. Electrode composition and modification

To evaluate the behavior of the sensor, compositions according to Table 1 were prepared. As can be inferred composition no. 2 revealed the optimum amount of EDC to be 10%. In this case the sensor showed a near Nernstian slope of about 21.7 mV decade⁻¹ in the absence of any modifier.

CPE No.	binder	L	Graphite Powder	MWCNTs	Nano-silica	Slope (mVdecade ⁻¹)	Linear Range (M)
1	P-15%	5%	80%	0%	0%	-17.8±0.1	1.0×10 ⁻⁵ -1.0×10 ⁻²
2	P-15%	7%	78%	0%	0%	-19.9±0.3	1.0×10 ⁻⁵ -5.0×10 ⁻²
3	P-15%	10%	75%	0%	0%	-21.7±0.2	5.0×10 ⁻⁶ -1.0×10 ⁻²
4	P-15%	12%	73%	0%	0%	-21.7±0.3	5.0×10 ⁻⁶ -1.0×10 ⁻²
5	P-15%	10%	72%	3%	0%	-26.0±0.4	2.0×10 ⁻⁶ -1.0×10 ⁻²
6	P-15%	10%	70%	5%	0%	-27.1±0.2	8.0×10 ⁻⁷ -1.0×10 ⁻²
7	P-15%	10%	68%	7%	0%	-27.0±0.3	7.0×10 ⁻⁷ -1.0×10 ⁻²
8	P-15%	10%	68%	5%	2%	-28.1±0.4	6.0×10 ⁻⁷ -1.0×10 ⁻²
9	P-15%	10%	67%	5%	3%	-28.3±0.2	5.0×10 ⁻⁷ -1.0×10 ⁻²
10	P-15%	10%	66%	5%	4%	-28.2±0.3	5.0×10 ⁻⁷ -1.0×10 ⁻²
11	IL-15%	10%	67%	5%	3%	-29.1±0.2	2.0×10 ⁻⁷ -2.0×10 ⁻²
12	IL-15%	0%	77%	5%	3%	-4.7±0.5	1.0×10 ⁻⁴ -1.0×10 ⁻²

Table 1. The optimization of the carbon paste ingredients

Due to the conductivity of MWCNT, addition of MWCNT to the composition of the carbon paste was expected to increase 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 near-Nernstian slope of about 27.1 mV decade⁻¹ (No. 6).

Addition of nano-silica to the composition of the modified carbon paste chromate sensor was also found to improve the sensitivity of the sensor. This can be attributed to the increase the extraction of the ions into the surface of the carbon paste sensor due to the high specific surface area of nano-silica. As can be seen from Table 1, addition of 3% wt of nano-silica to the modified carbon paste chromate sensor increased the slope of the sensor from 27.1 to 28.3 mV decade⁻¹ (No. 9).

Replacement of paraffin with RTIL, that has a higher conductivity and better electrical properties, improved the sensitivity of the sensor to a Nernstian slope (no. 11). However, the composition containing 10% EDC, 5% MWCNT, 3% nano-silica, 15% RTIL and 67% graphite showed the best performance with a Nernstian slope of 29.1 mV decade⁻¹ (No. 11). According to Table

1, the sensor with best composition (no.12) but lacking the ionophore showed a very low potential response.

3.2. Calibration curve

The measuring range of any analytical method, including ion selective electrodes, refers to the linear part of the calibration graph. According to one accepted definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits [41-46].



Figure 1. The calibration curve of the CrO_4^{2-} nano composite based sensor with the sensor no. 11

The applicable measuring range of the modified sensor as shown in Fig. 1 was found to be between 1.0×10^{-7} - 1.0×10^{-2} 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 7.0×10^{-8} M which was calculated by the extrapolating of the two segment of the calibration curve in Fig. 1.

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 CrO_4^{2-} (1.0×10⁻⁴ M) having different pH values. The pH was altered from 2-12 by adding HNO₃ or NaOH. The variations of the potential response of the best sensor as a function of pH are plotted in Fig. 2. The results showed the potential of electrode is

constant between pH values of 6.5-10.5. Thus, the electrode works satisfactorily in this pH range, and no interference from H^+ or OH^- is observed in the range.



Figure 2. pH effect on the potential response of the CrO_4^{2-} nano composite based sensor with the sensor no. 11



Figure 3. Dynamic response time of the CrO_4^{2-} nano composite based sensor with the sensor no. 11

The fluctuations above pH value of 10 might be due to the sensor response to OH^- ions in the solution. And the fluctuations below the pH value of 6.5, is most probably due to the formation of $HCrO_4^-$ ions and response of the sensor to $HCrO_4^-$ and H_3O^+ .

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 [47-50] was found to be 20 seconds The resulting potential–time responses for the mentioned electrode were obtained by changing the CrO_4^{2-} concentration from 0.000001 to 0.01 M (by fast injection of μ L-amounts of a concentrated solution of CrO_4^{2-}). Results in Fig. 3 showed that the potentiometric response time of the electrode was about 20 s in whole concentration range.

3.5. Interference studies

Potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, X, with reference to the chromate ion, $\text{CrO}_4^{2^-}$, were determined by the matched potential method (MPM) [51-53]. The MPM is recommended by IUPAC to overcome the difficulties associated with the methods based on the Nicolsky–Eisenman equation.

Interference (x)	$k_{Cu,X}^{MPM}$
	,
Cl	4.7×10 ⁻⁵
Br	4.5×10^{-4}
I	2.5×10^{-4}
NO_2^-	5.1×10 ⁻⁵
NO_3^-	1.5×10^{-5}
SO4 ²⁻	7.2×10^{-4}
ClO ₄	1.1×10^{-5}
CH ₃ COO ⁻	2.0×10^{-4}
$C_2O_4^{2-}$	1.1×10 ⁻⁵
SCN	3.5×10 ⁻⁵
$H_2PO_4^-$	3.0×10 ⁻⁵

Table 2. Selectivity coefficients of various interfering anions for the electrode no. 11

According to this method, the specified activity (concentration) of the primary ion is added to a reference solution (0.000001 M cromate ion, in this case) and the potential is measured. In a separation 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, $k_{Cu,X}^{MPM}$ is then given by the resulting primary ion to the

interfering ion activity (concentration) ratio, $k_{Cu,X}^{MPM} = \Delta a_{CrO4}^{2^2}/a_X$. The resulting values for $CrO_4^{2^2}$ sensor are listed in Table 2. As can be seen from Table 2, anions tested have not significance interfere in the monitoring of chromate monitoring.

3.6. Lifetime

Lifetime of the modified electrode was studied by periodically recalibrating and using the electrode to measure its potentiometric response to CrO_4^{2-} ion in standard chromate ion solutions over time. After the conditioning step the electrodes were repeatedly calibrated three times a day during a period of two month. 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.

3.7. Chromate ion analysis in waste water sample of chromium electroplating

The proposed nano-composite based chromate sensor was applied for monitoring of chromate ion concentration in waste water chromium electroplating as a real sample and waste water samples. Before the monitoring studies, the pH of the waste water should be adjusted at about 7.0 with sodium hydroxide.

Table 3. Determin	nation of CrO ₄ ²⁻	ion in waste	water of	chromium	electroplating	samples;	the results
are based o	n triplicates me	asurements.					

Sample	CrO ₄ ²⁻ ion concentration	
	CPE	ICP-OES
1	$6.1\pm0.3\times10^{-4}\mathrm{M}$	$6.2\pm0.2\times10^{-4}\mathrm{M}$
2	$7.7\pm0.3\times10^{-4}\mathrm{M}$	$7.5\pm0.2\times10^{-4}M$
3	$3.5\pm0.2\times10^{-4}\mathrm{M}$	$3.7\pm0.2\times10^{-4}M$
4	$1.6\pm0.2\times10^{-4}\mathrm{M}$	$1.5\pm0.1{ imes}10^{-4}M$

The analyses were performed using direct potentiometry using calibration curve method. The results as given in Table 3 were compared with those obtained by inductively coupled plasma optical emission spectrometry (ICP-OES) method. The results demonstrated the applicability of the sensor with the employment of the nano-silica and carbon nanotubes for interference-free determination of chromate traces in the analyzed environmental samples.

4. CONCLUSION

A new CrO_4^{2-} nano-composite carbon paste electrode was introduced. The electrode based on europium β -diketon complex, MWCNT, nano-silica and RTIL exhibits linear response over a wide concentration range with a Nernstian slope, and short response time of about 20 s. The present sensor can be used over the pH range of 6.5-10.5. Also it was successfully employed to chromate ion analysis in waste water chromium electroplating samples.

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