Anal. Bioanal. Electrochem., Vol. 15, No. 9, 2023, 767-777
https://www.doi.org/10.22034/abec.2023.708106

Analytical &
Bioanalytical
Electrochemistry

2023 by CEE
www.abechem.com

Full Paper

Monitoring Cerium Concentration in Waste Water Samples using a Novel All-Solid-State Electrode

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Received: 12 June 2023 / Received in revised form: 27 August 2023 /
Accepted: 6 September 2023 / Published online: 30 September 2023

Abstract- A Ce^{3+} all-solid-state ion selective electrode (ASS-ISE) was developed and applied in the analysis of this ion in samples with complex matrices. The electrode includes conductive multi-walled carbon nanotubes (MWCNTs) -epoxy resin substrate on a copper wire, which was later coated with a Ce^{3+}-selective PVC membrane film, optimally composed of 25% wt. of PVC, 65% wt. of nitrobenzene (NB), 2% wt. of sodium tetraphenyl borate (NaTPB)), and 8% wt. of N'-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (L) as a Ce^{3+}-selective ion carrier. The optimal ASS-ISE showed a Nernstian behavior with a calibration curve slope of 19.3±0.4 mV/decade in the concentration window of 1.0×10^{-7} M to 1.0×10^{-4} M, and its limit of detection (LOD) reached 5.0×10^{-8} M. The electrode had outstanding selectivity for the target ion in the presence of varied commonly occurring interfering ions and could be satisfactorily used in the determination of cerium ion concentration in wastewater samples.

Keywords- Sensor; All-solid-state; Potentiometry; Cerium; Wastewater

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1. INTRODUCTION

Cerium has a wide range of applications in catalysis, fuel additives, glass and enamel doping agents, screens and lamps, and polishing formulations. Ce_2O_3 is used in the catalytic converters of automobile exhaust [1], or as an additive for enhancing the efficiency of diesel [2]. Similar to other widely used compounds, the safety of these materials is under debate, especially when they are present in the exhaust gases of automobiles [3,4]. Ce_2O_3 has been further used in self-cleaning ovens and petroleum cracking catalysts [5].

Cerium compounds have various applications as additives or dying agents in producing and treatment of glass. For instance, Ce^{4+} and Ti^{4+} oxides have been reportedly used to produce glass samples with gold yellow color, with enhanced UV absorption. CeO_2 has also been reported to act as a fine polishing compound for use in treating glass elements used in optics. Cerium oxide is further used in enamel formulations to create opaque materials [5]. Together with oxides of La, Yb, Th, Mg, CeO_2 is present in mixtures used in the Welsbach mantle [6]. CeO_2 has additionally been used in solid electrolyte formulations for use in mid-temperature solid oxide fuel cells [7]. The large lifetime of Ce phosphors in television screens, lowering the chances of gradual darkening over time has led to their widespread applications [5].

The element is further used in preparing Misch Metal [8], as well as in different aluminum and iron alloy compositions, in order to enhance the corrosion resistance thereof. Moreover, the considerable affinity of the Ce compounds to sulfur and oxygen leads to the presence of lower amounts of sulfides and oxides in steel., as well as its hardness. The latter effect has been associated with the prevention of the graphitization phenomenon. Furthermore, traces of Ce and Zr in magnesium alloys has been reported to modify the enhance the casting and heat resistance of the alloys [5,9]. Permanent magnets, and wolfram arc welding electrodes.are based on La and Ce alloys.

Cerium oxalate is used in nausea treatment formulations, and sulfate of the ion and ammonium nitrate are known as oxidizing agents used in analytical routines. Other applications of the ce compounds are their application in zinc-cerium redox flow batteries [10], which work based on the generation of electricity in the presence of Ce^{4+} in the charge phase, or oxidation of zinc (2.43 V) [11]. The key element of the batteries is their electrolyte (i.e. methane sulfonic acid), which readily dissolves Ce salts [12], and Ce^{4+} is formed through electrical forces applied in the course of electro-synthesis of naphthoquinone [13].

There is no need to mention that design and construction of sensitive, and accurate analytical tools for the analysis of various samples are always in demand. Because of widely usage of cerium, it is increasingly getting into the environment, accumulating in organisms, and finally entering in the food chains. Therefore, the development of monitoring techniques for cerium is of most importance. The spectrophotometric determination [14] is a general method for the measurement of Ce(III). Other instrumental techniques including inductively coupled plasma atomic emission spectrometry (ICPAES) [15] chemiluminescence [16], fluorimetry [17], ion-selective electrodes [18, 19] and neutron activation analysis (NAA) [20] have been applied to the cerium determination.

On the other hand, figures of merit associated with ion selective electrodes (ISEs) range from accuracy, portability, sensitivity and selectivity, low cost, have made them powerful candidates for various applications the mentioned techniques, and hence the development and application of ISEs based on various natural and synthetic ionophores has been an interesting area of research on the analysis of different analytes including Ce^{3+} ion [21-26].

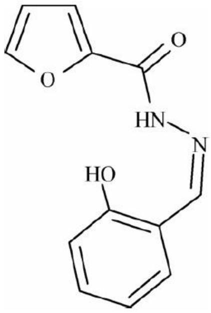
More specifically, ASS-ISE offers various advantages including the elimination of the internal filling solutions and the resulting shortcomings of symmetrical devices such as higher detection limits, and shorter life times. These instruments have hence attracted a great deal of interest and attention among researchers [27-35].

In this light and given the wealth of knowledge on the ionophores used in the construction of polymeric Ce^{3+} ISEs this work was focused on the design and construction of a novel Ce^{3+} selective ASS-ISE, based on the application of a conductive polymeric composite (CPC) as the all-solid-state element. A layer of comprised MWCNTs and an epoxy resin was covered on a copper wire to prepare the all-solid-state element, which was later coated using a thin film of a Ce^{3+}-selective PVC membrane.

2. EXPERIMENTAL SECTION

2.1. Reagents

Tetrahydrofuran (THF), dibutyl phthalate (DBP), benzyl acetate (BA), *o*-nitrophenyloctylether (*o*-NPOE), nitrobenzene (NB), potassium tetrakis (p-chlorophenyl) borate (KpClTPB) and sodium tetrapenyl borate (NaTPB), graphite powder (1–2 μm particle size), the MWCNTs and all nitrate or chloride salts of the cations, and high molecular-weight polyvinylchloride (PVC), were all of analytical regent grade (Merck Co.). The materials were used as received. The ionophore (L) i.e. N'-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (Scheme 1), was synthesized as described before [36]. Macroplast Su 2227 epoxy and the desmodur RFE hardener were from Henkel Co. and Bayer Ag.



Scheme 1. Structure of N'-[(2-hydroxyphenyl)methylidene]-2-furohydrazide (L)

2.2. Preparation of the ASS-ISEs

The conductive polymeric composite was prepared through admixing different amounts of the graphite powder, MWCNTs, epoxy, and hardener in THF. The resulting mixtures were aged for around 20-30 minutes in the air to reach proper viscosity, at which point a part of a copper wire (0.5 mm diameter and 15 cm length) was first polished and then dipped into the mixtures. The wires coated with the CPC compositions were allowed to dry for 12 hours to yield the ASS element. These elements were next dipped into a mixture of PVC membrane solutions three or four times, to be covered by the ion selective membranes. These electrodes were then allowed to dry in the air for 24 hours prior to conditioning and use [37-40].

Studies revealed the best response when a membrane composition of 8% wt. of L, 65% wt. of the NB, 25% wt. of PVC, and 2% wt. of NaTPB were used to prepare the membrane compositions. All membranes were prepared through admixing different quantities of L, PVC powder, the membrane solvent (plasticizer) and the ionic additive in THF to form a homogenous liquid, which was next transferred into a 2 cm (i.d.) glass dish, where its THF content was allowed to evaporate to yield a viscose liquid. The resulting mixtures were then coated on the ASS elements, as mentioned before. After coating with the selective membrane compositions and drying for 24 hours, the ASS-ISEs were dipped in a 10^{-3} M solution of Ce^{3+} ion and rested therein for conditioning.

The response of the electrodes was recorded by using the ASS-ISEs as indicator electrodes, in potentiometric setups including an Ag/AgCl double junction reference electrodes (Azar-Elelectrode Co., Iran) as reference electrodes:

Cu wire/ASS layer/ion selective PVC membrane | cerium ion solution || Ag-AgCl, KC1(satd.)

The cell potential readings were determined via externally linking the reference and indicator electrodes to an ion analyzer 250 pH/mV meter (±0.1 mV).

3. RESULTS AND DISCUSSION

Studying the existing reports on ion-selective electrodes indicate that the majority of these sensors have been symmetrical electrodes, which means the selective electrodes are located between an internal standard and the external sample solution [41].

Asymmetrical ISEs (e.g. ASS-ISEs), on the other hand do not required using internal solutions. So, in the course of performing the analyses only their exterior surfaces come in contact with the analyte solution, while the inner contact is established between the selective membrane and the solid-state element. It is known that in the case of the symmetrical ISEs, the presence of the inner solution is key to the electrode function. This mechanism, however, suffers disadvantages and limitations, decreasing the robustness and miniaturization ability of the electrodes. It is hence clear that the absence of the inner solution in asymmetric electrodes, can help overcome these properties, which makes asymmetric electrodes interesting choices for various medical, biological, and in-vivo experiments. The fact that ASS-ISEs are based on conductive epoxy support composites and ion selective membranes (ISMs) with adaptable compositions, makes these instruments very powerful analytical tools. Knowing that the composition of the ion-selective membranes is key in the response of an ASS-ISE, various polymeric membrane compositions based on the L, were prepared and tested to evaluate the optimal electrode composition. An overview of the key information used and obtained during the optimization process is given in Table 1.

Various studies have revealed that the optimal response of electrodes is observed at plasticizer/PVC ratios in the range of 2.0 to 3. Hence, this value was kept in the range in all compositions in Table 1. For the sake of simplicity, the quantity of PVC powder was kept at 25% wt. in all compositions.

Table 1. Various membrane compositions evaluated

No	Composition of the membrane			Characterization of AAS-PME		
	Plasticizer	Ionophore	Ionic Additive	Slope mV/decade	DL (M)	Response time
1	NB,71	4	-	8.7±0.7*	1.0×10^{-6}	50 s
2	NB,69	6	-	13.3±0.4	8.0×10^{-7}	47 s
3	NB,67	8	-	17.9±0.4	5.0×10^{-7}	32 s
4	NB,65	10	-	16.9±0.5	7.0×10^{-7}	33 s
5	NB,66	8	1 NaTPB	15.3±0.3	1.0×10^{-7}	27 s
6	NB,65	8	2 NaTPB	19.3±0.4	5.0×10^{-8}	12 s
7	NB,64	8	3 NaTPB	19.2±0.7	5.0×10^{-8}	12 s
8	NB,65	8	2 KpClTPB	19.2±0.6	5.0×10^{-8}	14 s
9	NPOE,65	8	2 NaTPB	18.9±0.6	8.0×10^{-8}	15 s
10	DBP,65	8	2 NaTPB	15.7±0.7	1.0×10^{-7}	21 s
11	BA,65	8	2 NaTPB	16.6±0.3	1.0×10^{-7}	24 s
12	NB,673	-	2 NaTPB	4.2±0.5	5.0×10^{-5}	56 s

*standard deviation of five repeated measurements

Another important membrane ingredient is the plasticizer or membrane solvent. This component facilitates mobility and complexation of the ion-carriers throughout the membrane. Generally, non-volatile liquids which can physically dissolve PVC and other membrane components are used as the membrane solvents. The membrane solvent should not compete with the ion-carrier in complexation of the target species and its polarity also influences the response if the ISE and should match the properties of the ingredients and the analyte.

Dibutyl phthalate (DBP), *o*-nitrophenyloctylether (NPOE), nitrobenzene (NB) and benzylacetate (BA), that are common membrane solvents used in various ISEs were evaluated and the results (compositions 9-12, Table 1) proved NB to produce better results. This behavior was attributed to the rather high charge density of Ce^{3+} ion which is expected to prefer highly polar media like NB.

Another key membrane component is the ionic additive, which can improve the membrane polarity to reach acceptable levels of analyte extraction and exchange by the membrane. It has been observed that incorporating small quantities of ionic additives leads to such effects, and also lowers the Ohmic resistance of ISMs. In this work, KpClTPB and NaTPB were evaluated as ionic additives and the best response was observed with 2% wt. of NaTPB (membrane no. 6).

The effect of the quantity of the ion carrier can be the key variable in optimizing membrane compositions. According to Table 1, the presence of 8% wt. of L (membrane no. 3) led to the best response behavior, even when other ingredients were not present in their optimal amounts. To illustrate the key influence of the presence of L on the function of the membrane, a blank membrane composition was also constructed using no ligand (membrane no. 12). As anticipated the ASS-ISE based on the blank membrane yielded poor results.

A review of the data in Table 1, makes it clear that the optimal Nernstian slope of 19.3±0.4 mV/decade, was produced by membrane no. 6. Hence this composition was used for all other evaluations.

To determine the linear response window of the electrodes, their responses were recorded in solutions containing different Ce^{3+} concentrations in the range of 1.0×10^{-9} to 1.0×10^{-1} M, and potential *vs.* –log [Ce^{3+}] plots were drawn (Figure 1), which indicated the linear behavior of the optimal sensor occurred 1.0×10^{-7}-1.0×10^{-4} M, which is reported as the linear response range of the electrode.

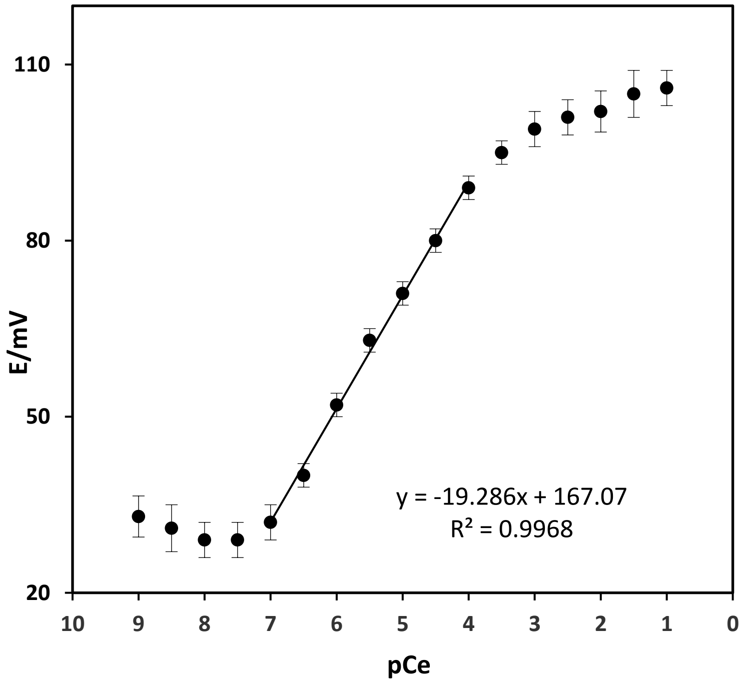


Figure 1. Calibration curve of the Ce^{3+}-ASS-ISE

It has been established that conventional symmetric PVC membrane sensors have responses ranging from 0.1 to 10^{-5} to 10^{-6} M. Asymmetric devices, however, are known to offer lower detection limits in sub 10^{-8} M range [27-35], which is also the case, in this case, offering a lower detection limit of 5.0×10^{-8} M. This value was approximated through extrapolating the linear parts of the calibration plot at low concentrations. The upper detection limit of the electrode was 10^{-3} M. This is ascribed to the saturation of the active sites of the ISM at this and higher concentrations. This is expected in the case of asymmetric tools, which possess smaller surface areas in comparison to larger symmetrical electrodes.

Furthermore, the dynamic response time (DRT) of the electrode was evaluated. DRT is the time required for reaching responses within ±1 mV of the equilibrium potential of the electrode, upon a 10-fold concentration change [27-35]. DRT is determined by successively immersing an ISE in solutions of the target ion, each having 10-fold concentration differences and determining the time required for reaching equilibrium. Here, the study was performed using solutions in the concentration range of 1.0×10^{-7} to 1.0×10^{-4} M. Based on the observations, the time required by the sensor to reach its equilibrium was about 12s, in the whole concentration range.

The effect of the test solution pH, on the electrode response is usually studied through monitoring the response in a fixed concentration of the target ion (here 1.0×10^{-5} M of Ce^{3+}) at varying pH values. Changes in the pH are induced by adding small volumes of concentrated acid or base solutions (NaOH or HCl solutions, in this case), in order to change the pH while not influencing the concentration of the test solution. Here, the study was conducted in the pH window of 2.0 to 10.0, and the plot of the recorded results is given in Figure 2. Based on these results the response of the ASS-ISE was pH-independent in the range of 4.0 to 8.0.

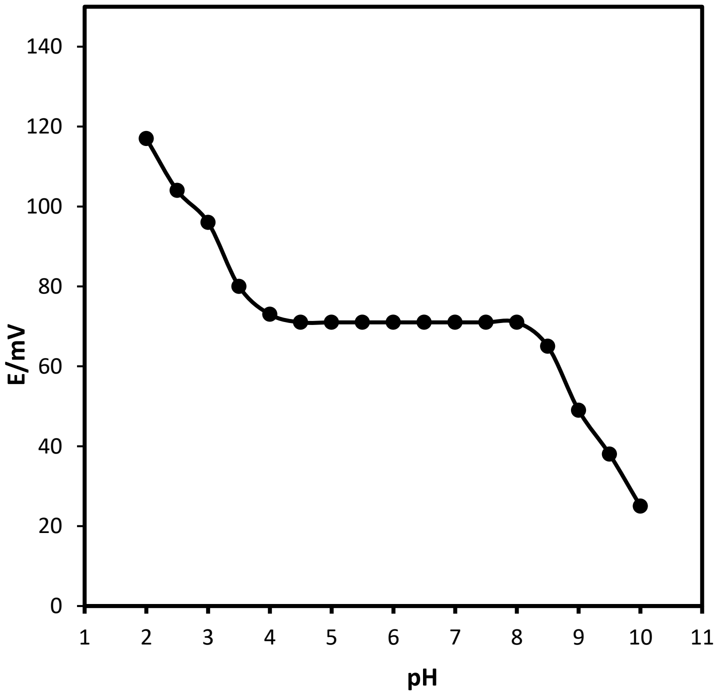


Figure 2. Effect of solution pH on the response of the Ce^{3+}-ASS-ISE in a 1.0×10^{-5} M solution of Ce^{3+}

The changes in the potential below and above this range has different mechanisms. Below 4.0, the response changes, most probably due to the protonation of the donor nitrogen atoms of L, while above 8.0 soluble $Ce(OH)^{2+}$, $Ce(OH)_2^+$ or $Ce(OH)_3$ can form, which lower the concentration of the free Ce^{3+} ion, and may also compete with the target species.

Table 2. Data on the evaluation of the lifetime of Ce^{3+}-ASS-ISE

Week	**ASS-ISE Performance**	
	Slope (mV per decade)	DL (M)
First	19.3±0.4	5.0×10^{-8}
Second	19.2±0.4	4.5×10^{-8}
Third	19.0±0.2	5.5×10^{-8}
Fourth	19.1±0.3	5.0×10^{-8}
Fifth	19.2±0.3	6.0×10^{-8}
Sixth	19.1±0.4	6.0×10^{-8}
Seventh	19.0±0.3	6.5×10^{-8}
Eighth	15.7±0.4	3.5×10^{-7}
Ninth	12.1±0.3	7.5×10^{-7}
Tenth	10.4±0.2	1.0×10^{-6}
Eleventh	8.9±0.6	2.0×10^{-6}
Twelfth	5.7±0.8	3.0×10^{-6}

Evaluation of the lifetime of the developed ASS-ISE was performed by using it for 1 hour a day, during a three-month period, and monitoring the sensor behavior (Table 2). It was found that lifetime of the device is 7 weeks. The data in Table 2 indicates that after 7 weeks of use under the mentioned conditions the slope of the calibration plot of the sensor considerably drops, and its detection limit is increased. This is attributed to the leakage and loss of the plasticizer, L and NaTPB from the membrane [27-35].

The selectivity profile of the ASS-ISEs was also studied through measuring its response to Ce^{3+} in samples also containing other (interfering) ions and calculating the so-called matched potential method (MPM) [30-35]. The results are illustrated in Table 3. Based on these results none of the tested interfering ions, leave considerable effects on the ASS-ISE. response

Eventually the applicability of the electrode to the analysis of real samples was evaluated using industrial wastewater samples. Prior to each analysis, the samples were acidified using HNO_3 solutions to reach a pH of 5. The analyses were performed using the calibration curve technique. The results were opposed to inductively coupled plasma optical emission spectrometry (ICP-OES) results for the same samples. Both results were in good agreement (Table 4), reflecting the success of the analyses using the developed ASS-ISE.

Table 3. Selectivity coefficients obtained for the sensor

Interfering species	**Log (K_{MPM})**
Na^+	-4.5
K^+	-3.3
NH_4^+	-4.1
Ca^{2+}	-2.9
Mg^{2+}	-3.7
Co^{2+}	-4.5
Ni^{2+}	-4.6
Zn^{2+}	-4.1
Cd^{2+}	-4.8
La^{3+}	-2.8
Dy^{3+}	-3.1
Nd^{3+}	-4.5
Eu^{3+}	-2.8
Sm^{3+}	-3.1
Gd^{3+}	-3.4

Table 4. Results of the cerium content analysis of wastewater samples

Sample	**Found by Ce^{3+}-ASS-ISE (ppm)**	**Found by ICP-OES (ppm)**
1	4.6±0.5	4.4±0.3
2	4.7±0.6	4.9±0.3
3	5.3±0.7	15.0±0.4

4. CONCLUSIONS

An all-solid-state ion selective electrode (ASS-ISE) for Ce^{3+} was prepared and optimized and also tested for the analysis of the target ion in wastewater samples. The ASS element wa prepared using a CPC, composed of graphite powder, MWCNTs, and an epoxy resin, which was coated on a polished copper wire. Next the ASS element was coated with a liquid membrane (optimally composed of 25% wt. of PVC, 65% wt. of NB, 2% wt. of an ionic additive, and 8% of L). The optimal ASS-ISE had a linear response in the range of 1.0×10^{-7} to 1.0×10^{-4} M of Ce^{3+} ad a lower detection limit of 5.0×10^{-8} M. Comparing the results of the analysis of Ce^{3+} ion concentration in waste water samples using the developed electrode and ICP-OES indicated its applicability to the analysis of real samples with complex matrices.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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