

Lead selective electrode based on chalcogenide bulk glass for multi-sensor applications

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The sensing properties of two chalcogenide materials were investigated. It is shown that membranes based on the $\text{PbI}_2\text{-Ag}_2\text{S-As}_2\text{S}_3$ and $\text{PbS-Ag}_2\text{S-As}_2\text{S}_3$ materials show sensitivity to the presence of Pb^{2+} species in solution. In both cases they exhibit near-Nernstian response. We mainly focused on the best matrix. The basic physicochemical parameters were then measured. The developed ISE exhibits a near-Nernstian slope of 27 mV/decade versus Pb^{2+} in the range of $10^{-5.5}$ - 10^{-3} M. Moreover the proposed Pb-SE shows excellent out-put signal in the presence of foreign ions. The analytical properties such as reproducibility, response time, and stability were studied. We report a multi-sensor process that we developed for in-situ real-time monitoring of waste water. The very first results of prototype measurements are presented.

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1. Introduction

Heavy metals can be emitted by both natural and anthropogenic sources. In particular, heavy metal ions are apt to combine with the body's biomolecules, thus interfering with the normal metabolic processes of human beings [1, 2]. The monitoring of toxic species and including metal ions in aquatic systems is crucial. Commonly used analytical procedures to detect heavy metals are highly complex and require experienced operators. Measurements to be taken directly on-site are not possible by means of these methods [3, 4]. A substantially more cost-effective alternative delivers the use of Ion Selective Electrodes (ISE) that allow continuous measurements in liquids [4-6]. Different options can be adopted for this latter purpose [7]. On the whole, not all analytical techniques offer appropriate characteristics for field work implementation and an excellent alternative is the use of potentiometric ions selective electrodes (ISEs) for in situ analysis. Potentiometric sensors have the advantage of being small and portable devices, with low costs and low energy consumption compared to other analytical techniques [8-10]. Potentiometric sensors for heavy metal ions represent a wide class of sensors with sensitive membranes based on organic ion-exchangers and ionophores [11], chalcogenide glass and crystalline ionic conductors [12]. Chalcogenide glasses are semiconductor materials with several important properties that make them suitable for their technological applications [9, 13]. One of these applications is the successful use as chemical sensors for the detection of metals ions concentration in solutions [9]. Consequently there exists a large variety of ISEs based on chalcogenide glasses device [9]. The first effort trying to detect lead ion with chalcogenide glass was with the $\text{Pb-Cu-As}_2\text{Se}_3$ glass composition. Adding silver to the glass composition improve the ionic conductivity [14]. Glasses with silver in its composition (i.e. AgAsS_2 and $\text{PbS-Ag}_2\text{S-As}_2\text{S}_3$) showed reliable out-put signal to lead ion [15, 16]. The glass of composition $\text{PbS-As}_2\text{S}_3$ exhibited sensitivity versus Pb^{2+} ion. However out-put signal was less reproducible [16]. Another sensor with the $\text{GeSe}_2\text{-PbSe-PbTe}$ glass system showed good lead sensitivity [17]. PLD technique was used to make suitable micro sensors with a thin layer of chalcogenide Pb-Ag-I-As-S glass [18]. Sensors with a thin film of Pb-Ag-As-S were also developed [19]. These sensors showed a great sensitivity. The aim of this paper is to investigate the sensing properties of bulk chalcogenide membrane to be used in multi-sensor

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array. The basic electrochemical characteristics of the Pb-ISE in the presence of Pb^{2+} ions are reported.

2. Experimental

$25\text{PbI}_2\text{-}40\text{Ag}_2\text{S-}35\text{As}_2\text{S}_3$ and $20\text{PbS-}40\text{Ag}_2\text{S-}40\text{As}_2\text{S}_3$ chalcogenide bulk glasses were prepared from high-purity (4N) elements. Stoichiometric proportions are weighted, mixed and sealed in an evacuated quartz ampoule. The ampoule is then heated to 1200 K for 24 h and is quenched in water. The tubes containing the melt were continuously rotated to ensure complete mixing and reaction. A thermal treatment process follows at a temperature below the glass-transition temperature for 2 h to remove the stresses of the sample.

All solid state ISEs were constructed by cutting the glasses into rectangular plates. The two faces were polished initially using Struers silicon carbide paper of various grit size. Then all membranes were thoroughly polished with diamond spray of decreasing sizes to obtain plane-parallel plates. A silver contact was sputtered on one side as inner reference and a metallic wire was attached to it with silver paste. The non-working surface (i.e. the inner reference and the electrical contact) was insulated from the aqueous media by encapsulating them in epoxy resin.

Ion-selective electrodes are chemical sensors that convert the ionic signal into a measurable electronic signal. As one type of potentiometric sensing, ISE typically requires the use of a reference electrode to determine the concentration of primary ions. The external reference electrode was a commercial Ag/AgCl electrode used with a double junction. Electrochemical measurements were taken at room temperature with a high impedance millivoltmeter. KNO_3 10^{-1} M was used as supporting electrolyte in order to insure a constant ionic strength under stationary conditions at constant stirring. Test solutions in concentrations from 10^{-2} to 10^{-5} M were prepared by successive 10-fold dilutions of a 10^{-1} M solution of the $\text{Pb}(\text{NO}_3)_2$.

3. Results

Structural characteristics and the homogeneity of the prepared alloys were verified by an X-ray analysis. The XRD measurements were performed on powder samples at 40kV and 25 mA using Cu $\text{K}\alpha$ radiation. The result from the X-ray diffraction (Fig. 1 (a)) shows that studied composition is typical glass without peaks on the diffractogram. The morphology of the sensing bulk membrane was characterized by scanning electron microscopy (Hitachi, S-4800). Fig. 1 (b) shows a panoramic picture of the obtained material. The SEM observation shows a smooth and homogeneous surface of the sample.

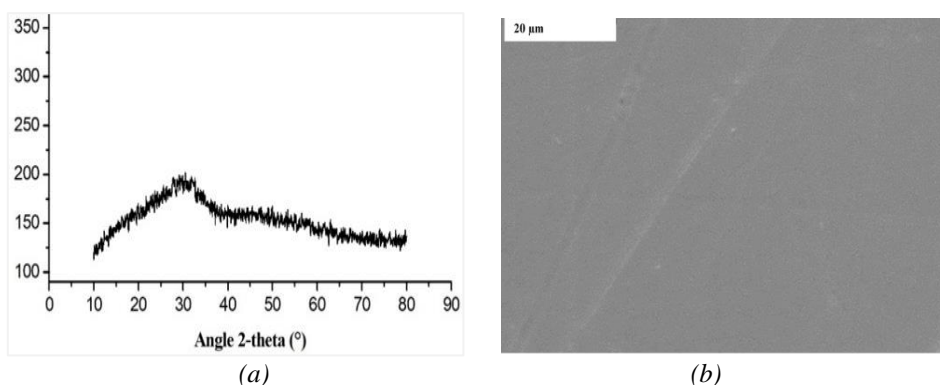


Fig. 1. XRD pattern (a) and SEM image (b) of bulk $25\text{PbI}_2\text{-}40\text{Ag}_2\text{S-}35\text{As}_2\text{S}_3$ sensing device.

The thermal properties of chalcogenide matrix are specified by certain characteristic temperatures like glass transition temperature (i. e. T_g) which is related to the magnitude of

cohesive forces within the network. The investigated glass transition temperature determined by thermal analysis was found to reach a low value (i. e. 152° C). This is in agreement with DRX study. It is known that chalcogenide glass with very low conductivity cannot be used successfully as sensitive membranes for chemical sensors. Indeed it induces very long response times and unstable electrochemical out-put signal. The total electrical conductivity of the synthesized membrane of composition 25PbI₂-40Ag₂S-35As₂S₃ was studied by the method of impedance spectroscopy (GenRad 1693 RLC Digibridge™) at room temperature in a frequency range of 200 kHz–12 Hz. Platinum thin layer contact was deposited on the parallel sample sides polished to form contact electrodes. The impedance spectra were analyzed using self-made cell. The room temperature conductivity for studied sample (i. e. 1.5×10⁻⁵ S.cm⁻¹) should be large enough to allow in situ experiments. Moreover a large part of ionic conduction in the sample should be noted.

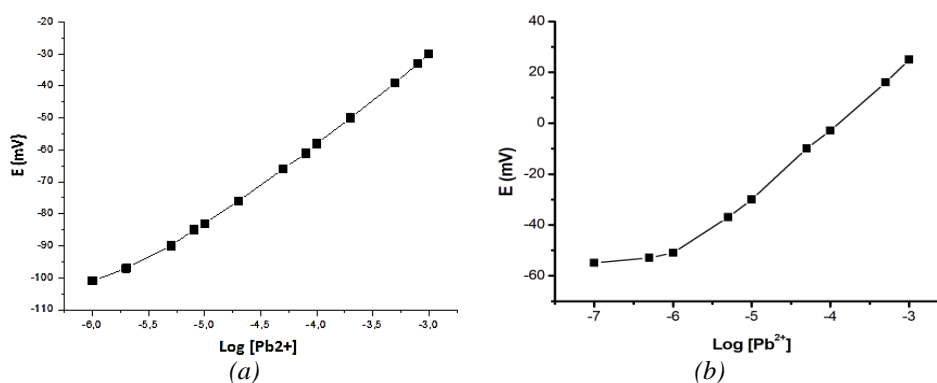


Fig. 2. Calibration curves of 25PbI₂-40Ag₂S-35As₂S₃ (a) and 20PbS-40Ag₂S-40As₂S₃ (b) chalcogenide bulk membranes.

To calibrate a new ISE, some parameters must be determined. The first one is the sensitivity which is the linear coefficient for the linear part of the calibration curve. Typical calibration curves are shown in Fig. 2. Both sensing membranes (i. e. PbI₂-Ag₂S-As₂S₃ and PbS-Ag₂S-As₂S₃) exhibited satisfying responses to Pb (+II) species. As describe elsewhere [6] we confirm that the first calibration previous to conditioning differed from the subsequent ones by lower sensitivity. After few measurements the sensors parameters became more stable. As shown in Fig. 2 (a) 25PbI₂-40Ag₂S-35As₂S₃ chalcogenide sensor exhibits a great out-put signal. The slope (i. e. 27 mV) of the measuring chain in the linear measurement range from 10^{-5.5} M to 10⁻³ M Pb²⁺ was in good agreement with the Nernst equation for bivalent ions. The calibration curve of 20PbS-40Ag₂S-40As₂S₃ chalcogenide electrode is shown in Fig. 2 (b). The lead selective electrode shows a near Nernstian sensitivity with 24 mV/pPb²⁺. The second important parameter to determine is the limit of detection, which is the lowest concentration the sensor could measure. For both sensing materials, the limit of detection was close to 10⁻⁶ M Pb²⁺. Unfortunately, the studied PbS sensor had a short lifetime. This worst result might be due to PbO or other lead oxygen compound formation which did not display reliable out-put signal against primary ions [20]. ISE based upon the PbI₂ matrix alone was then investigated more thoroughly since we were looking more specifically for a reliable system to be used in a multi-sensor array in the future. The main challenge when working with chalcogenide glass sensors is the cross sensitivity. Selectivity of the lead-ISE to interfering ions is vital for ensuring a reliable detection and quantification of the primary ion concentration. The International Union of Pure and Applied Chemistry (IUPAC) recommended a fixed interference method or a separate solution method to determine selectivity coefficients [21]. We selected the first one to obtain the true or unbiased selectivity coefficient. As can be seen in Fig. 3 (a), Pb-SE was slightly sensitive to Cd²⁺ and Cu²⁺ and practically non-sensitive to Cr³⁺ and Ca²⁺. The ability of the sensor to distinguish the interfering ions from the primary ion can be expressed as the selectivity coefficient. The selectivity coefficient is determined as follows.

$$K_{M-S} = \frac{a_M}{a_S^{z_M/z_S}}$$

where a_M is the measured ion activity, a_S is the interfering ion activity, z_M is the ion valence of the measured ion, z_S is the ion valence of the interfering ion. The determined selectivity coefficients are presented in Table 1. It is indicated that Cd and Cu interfere slightly with the response of the ISE to the primary ion. We observed no interference by the other studied ions since the lower the coefficient, the smaller is the influence of the interfering ion. Cu^{2+} main interference is perhaps due to the strong competition of copper with lead in the deposition at the electrode [2]. However, it is possible to use KCN masking reagent, to avoid the interfering effects of copper as KCN forms a complex with Cu^{2+} while it does not interact with Pb^{2+} .

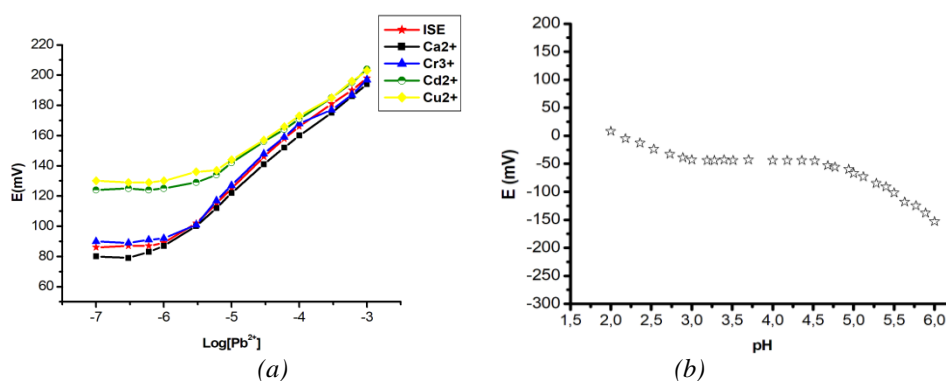


Fig. 3. Determination of the selectivity coefficient (a) and Potential as a function of pH (b) of the bulk $25\text{PbI}_2\text{-}40\text{Ag}_2\text{S-}35\text{As}_2\text{S}_3$ chalcogenide glass matrix.

Table 1. Selectivity coefficients against the interfering ion species.

Interfering ion	K_{M-S}
Ca^{2+}	10^{-6}
Cr^{3+}	10^{-6}
Cd^{2+}	10^{-4}
Cu^{2+}	10^{-4}

The applicable pH range is another important parameter. We measured the potential of the electrode in primary ion solution, whereby the ionic strength was kept constant with KNO_3 supporting solution. Fig. 3 (b) shows that the out-put signal of sensitive electrode remain stable in the range of $\text{pH} = 3 - 5$ independent on pH changes in the measuring solution. The PbSE response decreased in the range $\text{pH} > 5$ due to precipitation of hydroxide. The decrease became more pronounced at higher pH values. Moreover the sensor is sensitive to H^+ species in the range $\text{pH} < 3$. To obtain the dynamic response of Pb-SE, the potential was registered as a function of time as the concentration of primary ions in the KNO_3 solution was changed. The typical time-dependent EMF response is shown in Fig. 4 (a). Clearly, the potentiometric response of the developed sensor is fast and stable, even for lower concentrations, which is due to the high interfacial potential stability. First of all, selective membrane exhibits a positive potential drift upon changing from low (step 1) to high primary ion concentrations. During this time the potential increased until it reached a steady value (step 2 and step 3). The changes in the potential at low concentrations were the usual ones, as measured for other all-solid state ion selective electrodes based on chalcogenide matrix [22]. KOH was added to the measured solution to allow the formation of $\text{Pb}(\text{OH})_2$. A different phenomenon was then observed. Immediately after the step, the potential started to decrease rapidly and reached a steady value (step 4 and step 5). The electrode potential was found

to return reversibly to the original lower potential. This asymmetry enables simple in situ monitoring. Another parameter to establish is the response time of an electrode. Response time is the time required for the electrode to reach more than 95% of its final value. As can be seen in Fig. 4 (b), it should be noted that the membrane showed a fast response time (less than 30s). The ion exchange on the electrode surface is controlled by the ions transport times. Thus it could be considered that high diffusion driving force of the diffusion layer from which the electrode surface is separated involve high ion transport.

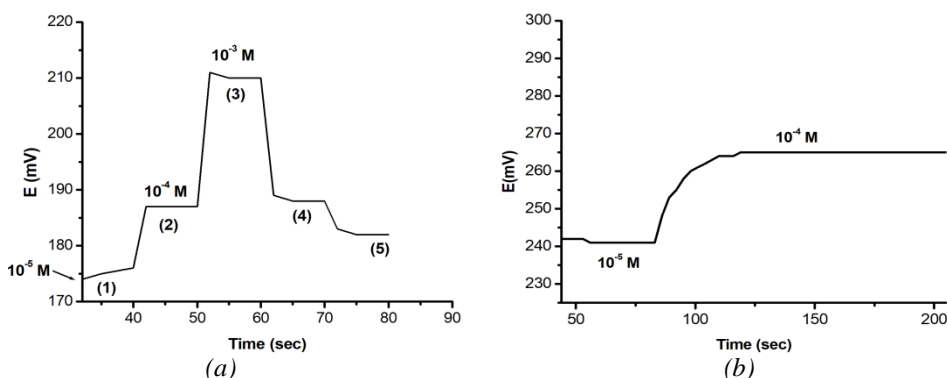


Fig. 4. Dynamic potentiometric out-put signal depending on the time and the varying primary ion concentration (a) and Response time (b) of 25PbI₂-40Ag₂S-35As₂S₃ ISE.

The electrode response gradually changes over a period of time. Once the extent of drift is known, then it should be possible to find the optimum time of use. The PbI₂-Ag₂S-As₂S₃ electrode showed good long term stability as shown in Fig. 5 (a). However a slight drift in absolute potential with time, i. e. a change of about 10 mV per day, was observed. Moreover, the investigation of potential stability within a period of one month indicated a slight response drift in the region of higher concentrations. The response drift near the detection limit was more significant. The primary cause of the drift of the potential is the ion flux leakage across the sensing membrane. The rate and extent of drift may vary depending ageing and degree of contamination of the sensor. On the whole, the present studied sensor is easily restored by simply polishing while retaining high reproducibility and stability. ICP-MS analysis was carried out after drift study. The experience revealed the appearance of lead and silver species in the solution. Multi-sensor system was suggested for environmental monitoring of various contaminants. The system was installed in waste water in a populated region and was designed for simultaneous detection of heavy metals such as copper, lead, and cadmium. The device comprised three analytical detection systems based on bulk chalcogenide membranes (i. e. Cu-As₂S₃, PbI₂-Ag₂S-As₂S₃ and CdS-AgI-Ag₂S-As₂S₃ respectively) and commercial Ag/AgCl reference electrode. The submersible prototype was also equipped with recorder and transmission apparatus. Fig. 5 (b) presents reversible out-put responses of multi-sensor prototype in waste water. In agreement with significant concentrations of metal species (2000 ppb) the fluctuations in potential of lead selective electrode follow the anthropogenic pumping system. This result is in agreement with electrochemical characterisation and indicates good sensitivity of the prototype. The multi-sensor system was tested just for a few hours. Obviously further in situ experiments are then needed to conclude that prototype is reliable.

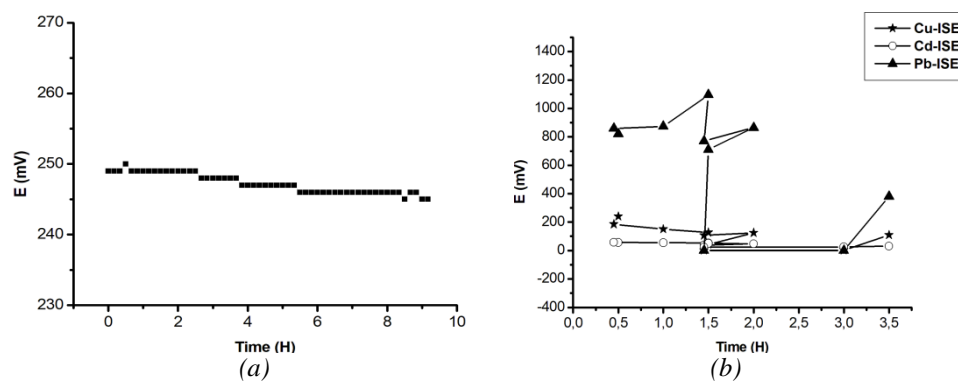


Fig. 5. Change in time in the response of the $25\text{PbI}_2\text{-}40\text{Ag}_2\text{S-}35\text{As}_2\text{S}_3$ chalcogenide electrode (a) and Profiles of multi-sensor system versus various species in waste water (b).

4. Conclusions

A simple procedure was used to make all solid state ISE based on chalcogenide glass for the detection of lead in solution. Two membranes were studied for their ion sensing properties. Even though they are different electrodes both proved to be sensitive to lead (+II) ion. The experimental data indicate that the PbI_2 electrode has a great response versus primary ion. At the laboratory or in situ scale electrochemical characterization exhibits fast reliable response, good stability and a reasonable reproducibility. We conclude that studied membrane is a good component of the multi-electrode prototype which also includes our well-known electrodes. After further in situ experiments we believe that the prototype may serve as a promising tool for ecological monitoring in aquatic media.

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