Journal of Physics and Chemistry of Solids 89 (2016) 115–119

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Multi-ion and pH sensitivity of AgGeSe ion selective electrodes

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ARTICLE INFO

Article history:
Received 14 August 2015
Received in revised form
2 October 2015
Accepted 30 October 2015
Available online 3 November 2015

Keywords:
ISE
Chalcogenide glass
Thin film
Selectivity
Electronic tongue

ABSTRACT

Many chalcogenide glasses have been found to combine benefits such as good chemical durability, selectivity, and reproducibility for applications as solid-state sensitive membranes of ion selective electrodes (ISEs). In previous works, we have shown that ISEs with ionic conductive AgGeSe membranes have good sensitivity to Ag^+ ions. In the present work, we explore the $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$, $10 \le x \le 30$ (at%) system as candidate for ISEs applications detecting several other ions (K^+, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}). We evaluated ISEs fabricated with bulk as well as with thin film membranes. We found no dependence of the sensing properties on the Ag content of the ionic conductive membranes. Thin films exhibited the same properties than bulk membranes, indicating that these chalcogenide glasses have great potential for miniaturization. The ISEs showed a high response (Nernstian or super-Nernstian) to the presence of Hg^{2+}, Pb^{2+}, and Fe^{3+}, a low response (sub-Nernstian) to the presence of Cr^{3+}, and a total lack of response to the presence of Cd^{2+}, Ni^{2+}, Mg^{2+}, and K^+. We also tested how the pH of the solution affected the response of the ISEs. The potentials of the ISEs were practically constant in neutral or acidic solutions, while decreased drastically in basic solutions when the primary ion was not present. The latter phenomenon was caused by the slow dissolution of the membrane into the solution, meaning that long-term basic environments should be avoided for these ISEs. We concluded that ISEs with ionic conductive AgGeSe membranes are good candidates to integrate multi-electrode systems.

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1. Introduction

Chalcogenide glasses are being widely studied for membranes of ion selective electrodes (ISEs) because they usually exhibit better chemical durability, selectivity, reproducibility, and lifetime than polycrystalline chalcogenides [1]. The development of all-solid-state electrodes (i.e. with internal metal contact) and thin film deposition techniques (e.g. pulsed laser deposition, sputtering) have facilitated ISEs miniaturization [2,3]. This, in turn, has enabled the fabrication of electrode arrays by silicon-processing techniques leading to miniaturized electronic tongues [4–8]. ISEs used in arrays must exhibit: cross-sensitivity (i.e. different levels of sensitivity to different ions), stable and reproducible parameters, and good chemical durability [5,9].

$Ag_x(Ge_ySe_{1-y})_{100-x}$ (at%) glasses have a large miscibility gap with two separated phases: a Ag-rich and a Ag-poor amorphous phase [10]. When $x \le 8$ at%, the AgGeSe system is a semiconductor. In previous works, we measured no response of electrodes with these membranes [11]. When $x \ge 8$ at%, the Ag-rich phase percolates, increasing the conductivity by seven orders of magnitude, and the material becomes a fast ionic conductor [12]. Previously, we reported that ISEs with ionic conductive AgGeSe membranes are highly sensitive to Ag^+ and Cu^{2+} in aqueous solutions (with detection limits $\sim 10^{-7}$ M for both ions, and slopes $\sim$65 mV/pAg and $\sim$50 mV/PCu) [13,14]. We also found that AgGeSe-based bulk ISEs are sensitive to Fe^{3+}, and not sensitive to Mg^{2+} and Cd^{2+} [13].

In this work, we explored whether ISEs with ionic conductive $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ ($10 \le x \le 30$) membranes possess the characteristics required for electrode arrays used in electronic tongues. To this end, we measured the sensitivities to a relatively broad set of interfering ions, including alkali, alkaline and transition metals: K^+, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. With the goal of fabricating miniaturized devices in a future work, we compared the response of thin film membranes to response of larger bulk membranes. Finally, we tested how the pH of the solution may affect the response of these ISEs.

2. Experimental

Chalcogenide bulk glasses with compositions $Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ (x=10, 15, 20, 25, and 30) were prepared by melt-quenching [15]. The high purity elements in the desired

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http://dx.doi.org/10.1016/j.jpcs.2015.10.015
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stoichiometry were sealed in quartz ampoules, evacuated to 10^{-6} mbar, heated to 950 °C and then kept in liquid state at that temperature for about 10 h. After this time, the liquid samples were rapidly quenched in an ice–water mixture.

Thin film chalcogenide membranes (300 ± 50 nm thick) were prepared by pulsed laser deposition (PLD) in an on-axis geometry [16]. A Nd:YAG pulsed laser ($\lambda = 355$ nm, 5 ns, 10 Hz) with a fluence of 5–8 J/cm^2 was used and bulk chalcogenide glasses were employed as targets.

Two types of all-solid-state ISEs were fabricated: using either bulk or thin film membranes. Bulk membrane ISEs were constructed by cutting the glasses into rectangular plates. Two opposing faces were polished until achieving mirror finish and a metal contact (either Au or Cr) was sputtered on one of the faces. The thin film ISEs were made first by sputtering the metal contact on a substrate (microscope slides) and then, depositing the chalcogenide film on top of the metal contact and the substrate (leaving part of the metal contact exposed). Cables were attached to the metal contacts with silver paint and then the electrical connections were insulated from the aqueous media by encapsulating in epoxy resin [14]. The response of the ISEs was studied by direct potentiometry [14] in aqueous solutions containing the ions: K^+, Mg^{2+}, Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, or Pb^{2+}, in the concentration range 10^{-8}–10^{-3} M. A double junction Ag/AgCl(sat.) reference electrode was used with KCl (4 M) in the inner container and KNO_3 (0.1 M) in the outer container. Nitrate salts were used as sources of all cations. Potential measurements were taken at room temperature (25 °C) with a high impedance millivoltmeter with 0.1 mV accuracy. KNO_3 (0.1 M) was used as supporting electrolyte in order to insure a constant ionic strength. All measurements in solutions of Hg^{2+} and Fe^{3+} were performed at pH=2 to prevent the formation of hydroxides [17–19].

Calibration curves were obtained by plotting the potential of the electrode vs the logarithm of the concentration. Values of the slope (S) and the detection limit (DL) were extracted from the calibration curves. Nernst's law should be expected under thermodynamic equilibrium and considering ion exchange between the solution and the membrane as the sensing mechanism. Accordingly, the Nernstian slopes observed for the calibration curves at room temperature are: 59.2 mV/decade for monovalent ions, 29.6 mV/decade for divalent ions, and 19.7 mV/decade for trivalent ions.

Selectivity coefficients were calculated by the "fixed interference method", according to the procedure recommended by IUPAC [20]. We used a constant concentration of each interfering ion (10^{-3} M) and changed the concentration of the primary ion (Ag^+) from 10^{-8} to 10^{-3} M.

The pH sensitivity was studied with a Hanna pH 211 pH-meter in the range 2–10 (with a 2-point calibration before each measurement). Two solutions were studied: (i) KNO_3 (0.1 M), and (ii) KNO_3 (0.1 M)+$AgNO_3$ (10^{-4} M). The pH of the solutions was changed by adding nitric acid or potassium hydroxide.

Surface images were obtained with a Field Emission-Scanning Electron Microscope (FE-SEM) Zeiss SUPRA 40 equipped with an in-lens detector of secondary electrons. The samples observed by FE-SEM of composition $Ag_{10}(Ge_{0.25}Se_{0.75})_{90}$ were purposely fractured before introducing them into the FE-SEM chamber and the images were taken in the fractured zones. The fractured samples were observed as-fractured and after being submerged for 10 h in three different solutions: (i) potassium hydroxide at pH=10, (ii) potassium hydroxide+$Ag(NO_3)$ (10^{-4} M) at pH=10, and (iii) $Ag(NO_3)$ (10^{-4} M).

3. Results

We found that the studied electrodes exhibited stable and reproducible responses but these were very different in the presence of different ions. For each of the ions, all electrodes presented similar calibration curves, regardless of the membrane's composition or geometry.

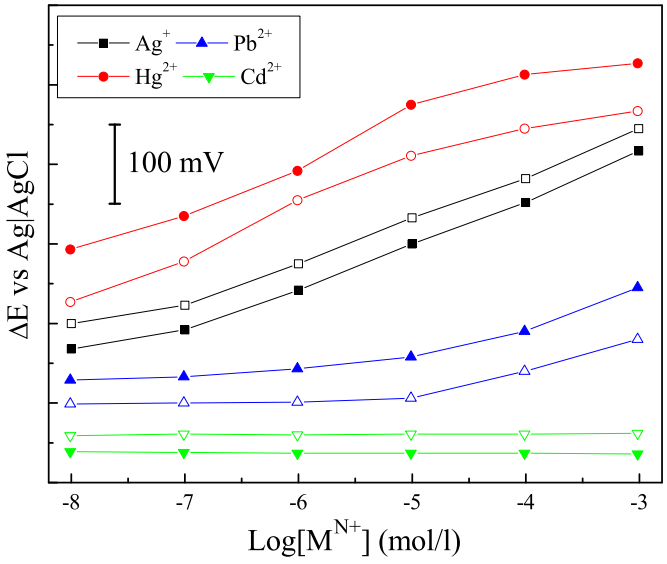

Fig. 1. Calibration curves of bulk (solid) and thin film (hollow) ISEs for each of the ions. Hg^{2+} solutions were prepared at pH=2.

Figs. 1 and 2 show the calibration curves for the studied ions. Since all the studied membranes ($Ag_x(Ge_{0.25}Se_{0.75})_{100-x}$ with $10 \le x \le 30$) exhibited approximately the same slope and detection limit (within experimental error), their compositions are not reported in Figs. 1 and 2.

Table 1 presents the mean values and confidence intervals of the slope, detection limit and the logarithm of the selectivity coefficient of the ISEs for each of the studied ions. The mean values were calculated over electrodes of all membrane's compositions and geometries.

The electrodes showed a high response (Nernstian and super-Nernstian) to the presence of Hg^{2+}. Both bulk and thin film ISEs presented S-shaped calibration curves (Fig. 1). In the middle concentration range, 10^{-7}–10^{-5} M, a super-Nernstian slope of 70 mV/pHg was reached, while at higher concentrations ($> 10^{-5}$ M) the

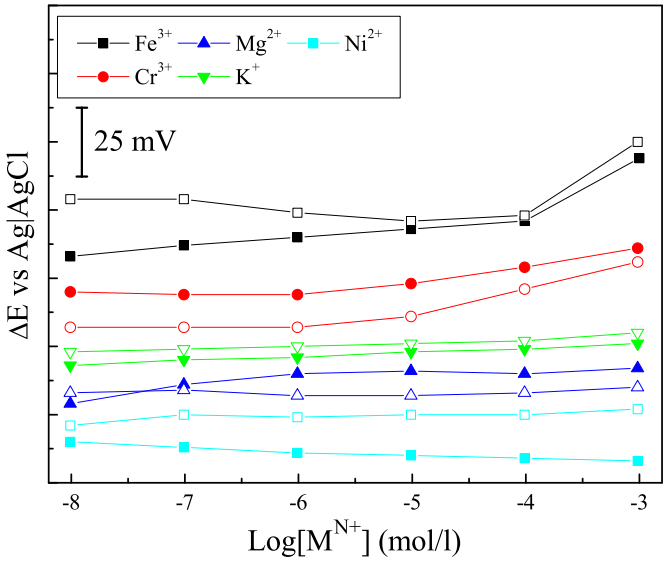

Fig. 2. Calibration curves of bulk (solid) and thin film (hollow) ISEs for each of the ions. Fe^{3+} solutions were prepared at pH=2.

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