



Ion selective electrodes based on chalcogenide glasses

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ARTICLE INFO

Article history:

Received 16 September 2008

Received in revised form 15 July 2009

Accepted 20 August 2009

Available online 27 August 2009

Keywords:

Amorphous materials

Ionic conduction

Liquid quenching

ABSTRACT

The properties of chalcogenide glasses as sensitive membranes in ion selective electrodes (ISEs) have been investigated. It is shown that ISEs based on the AgGeSe system show sensitivity to the presence of Ag^+ and Cu^{2+} ions in aqueous solutions and in both cases they exhibit super-nernstian responses.

The analytical properties such as reproducibility, linear range, sensitivity and detection limit were studied.

The response of the electrodes is apparently conditioned by the amount of Ag in the membrane. The addition of Cu to the membrane composition does not improve the sensitivity of the electrodes.

The sensitivity to Cu^{2+} ions of thin film ISEs of composition (AgCu)GeSe was found to be smaller than the one of bulk ISEs, but still super-nernstian.

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1. Introduction

Chalcogenide glasses (ChGs) are semiconductor materials with several important properties that make them interesting for their technological applications [1]. One of these applications is the use of ChGs as membranes in ion selective electrodes (ISEs) for the detection of heavy metals in aqueous solutions (Ag^+ , Cu^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , etc) [2–6].

ISEs based on chalcogenide glasses have many advantages over those commercially available, based on crystalline materials. Some of these advantages include their ability to be built as all-solid-state electrodes (without liquid inner reference), their greater sensitivity, more stable potential, higher selectivity and excellent chemical durability in acidic media due to their high chemical stability [7].

In the present, micro-fabrication of sensors and multi-sensor arrays and their use in integrated circuits by means of micro-electronics technology are the main objective of research in the chemical sensors field. By these methods different transducing devices can be fabricated, such as μ ISE, ISFET (Ion sensitive field effect transistor) and LAP (Light-addressable potentiometric sensor) [8–10]. An important step in the fabrication of these devices is the deposition of a thin film of sensing material. ChGs turn out to be ideal for this instance since they can be easily deposited as thin films by several techniques, such as RF sputtering, chemical deposition from vapor and pulsed laser deposition (PLD). PLD is one of the simplest, quickest and more versatile techniques and allows the deposition of thin films with complex stoichiometry [11,12].

When ChGs are doped with Ag above a certain threshold concentration, they change from semiconductors to fast ionic conductors and enhance their conductivity from 10^{-13} to 10^{-5} – 10^{-3} S cm^{-1} [13].

The aim of this work is to investigate the sensing properties of the ChG system AgGeSe as membranes of ion selective electrodes in the presence of Ag^+ and Cu^{2+} ions. The basic analytical characteristics of AgGeSe and (AgCu)GeSe systems are reported.

2. Experimental

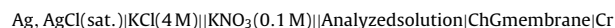
The chalcogenide bulk glasses were prepared from high-purity (4N) elements in compositions: $(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}\text{Ag}_x$ with $x = 10, 15, 20$ and 25 at.% (samples Ag $_x$) and $(\text{Ge}_{0.25}\text{Se}_{0.75})_{75}(\text{Ag}_{1-y}\text{Cu}_y)_{25}$ with $y = 0.05, 0.10, 0.20$ at. (samples Cu $_y$) and were synthesized by conventional melt-quenching technique as described in Ref. [14].

X-ray diffractometry and scanning electron microscopy (SEM) techniques were used to determine the glassy nature and the uniformity of the glasses.

Thin film ChG membranes of composition Cu0.20 (called Cu0.20f throughout this paper) were deposited by PLD. A Nd:YAG (Spectra-Physics Quanta Ray model Lab-170-10) pulsed laser in an on-axis geometry was used ($\lambda = 266$ nm, 5 ns, 10 Hz). A bulk sample of Cu0.20 was used as target.

All solid state ISEs were constructed by cutting the glasses into rectangular plates. The two faces were then polished with alumina water suspension (0.3 μm). Chromium metal contact was sputtered on one side as inner reference and a wire was attached to it with silver paint. The inner reference and the electrical contact were insulated from the aqueous media by encapsulating them in epoxy resin.

The potential measurements were taken by direct potentiometry against a double junction Ag/AgCl(sat.) reference electrode. The electrochemical cell used was of the following type:



Potential measurements were taken at room temperature 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. 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 appropriate nitrates (AgNO_3 and CuNO_3). Calibrations were carried out at constant stirring in the concentration range 10^{-8} – 10^{-3} M by

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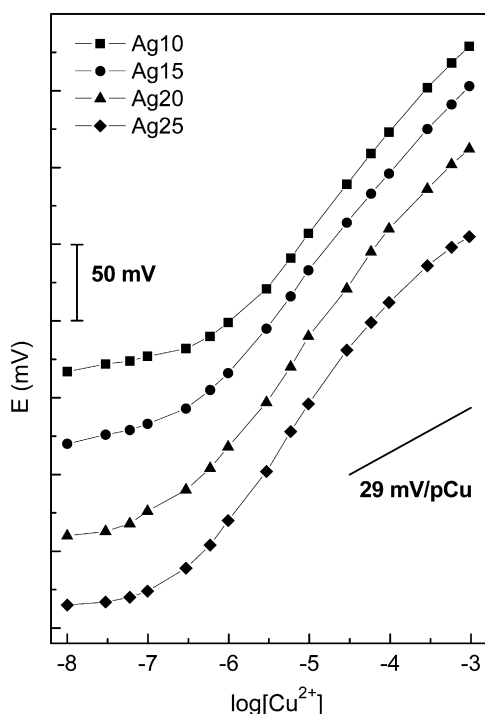


Fig. 1. Calibration curves of Ag_x electrodes in the presence of Cu^{2+} ions.

addition of known volumes of test solutions to 100 ml of supporting electrolyte. After the addition of test solutions 2–5 min were allowed to pass before measuring the potential so that it could reach a stable value.

After each calibration the electrodes were washed in distilled water, allowed to dry and then kept in clean boxes until the next calibration.

Due to the well known sensitivity to light of Ag^+ solutions, potentiometric experiments were performed in darkness.

3. Results and discussion

3.1. Characterization of the membrane materials

The XRD patterns of both the quenched alloys and deposited films show the structure typical of amorphous alloys.

Scanning electron microscopy studies revealed that the glasses $(Ge_{0.25}Se_{0.75})_{100-x}Ag_x$ ($x = 10, 15, 20$ and 25 at.%) are non-homogeneous. Their morphology depends on the composition and consists of bright Ag rich zones and dark Ag depleted zones that can be attributed to a widespread liquid miscibility gap near the Se rich corner of the equilibrium phase diagram [15].

3.2. Analytical characteristics of Ag_x and Cu_y electrodes

The response of the electrodes in the presence of Ag^+ and Cu^{2+} ions was studied and the basic analytical characteristics of the calibration curves: linear range, detection limit and slope are reported.

3.2.1. Response to Cu^{2+} ions

All Ag_x electrodes respond similarly to the presence of Cu^{2+} ions, with detection limits around 3×10^{-7} M, super-nernstian slopes between 60 and 70 mV/pCu and linear ranges 6×10^{-7} – 10^{-4} M (Fig. 1). As the silver content in the membrane composition increases, the slope increases, the detection limit is shifted towards lower concentrations and the linear range is shortened.

The response of the Cu_y bulk electrodes to the presence of Cu^{2+} ions is characterized by detection limits around 10^{-7} M, super-nernstian slopes between 45 and 60 mV/pCu and linear ranges between 10^{-6} and 10^{-4} M (Fig. 2). Samples with lower copper con-

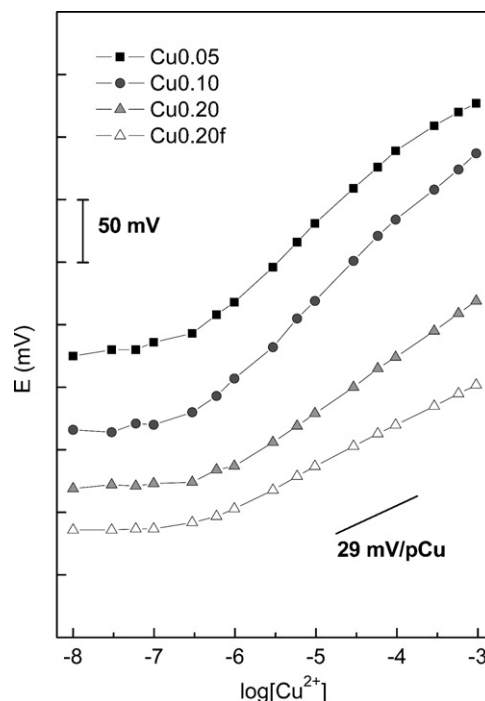


Fig. 2. Calibration curves of Cu_y electrodes in the presence of Cu^{2+} ions.

centration, $Cu0.05$ (23.75 at.% of Ag and 1.25 at.% of Cu) and $Cu0.10$ (22.5 at.% of Ag and 2.5 at.% of Cu), exhibit a behavior similar to that of $Ag25$ electrodes but with lower slope values (60 mV/pCu), lower detection limits and slightly longer linear ranges. Samples with higher copper concentration, $Cu0.20$ (20 at.% of Ag and 5 at.% of Cu), exhibit a behavior similar to that of $Ag10$, $Ag15$ and $Ag20$ electrodes but with lower slope values (45 mV/pCu). The calibration curves of $Cu0.20f$ (thin films) are similar to those of bulk $Cu0.20$ but with lower slopes (35 mV/pCu).

Therefore, the study of the response of the electrodes to the presence of Cu^{2+} ions shows that this response is strongly conditioned by the amount of silver present in the membrane composition. In order to investigate the effect of silver in the sensing mechanism a study of the response of the electrodes to the presence of Ag^+ ions was performed.

3.2.2. Response to Ag^+ ions

The calibration curves of Ag_x electrodes against Ag^+ ions exhibit an interesting dependence with time. The evolution of the calibration curves can be observed in Figs. 3 and 4.

The electrodes which had been previously calibrated against both Cu^{2+} and Ag^+ ions (named c-(Ag,Cu) in Figs. 3 and 4) are characterized by reversible and repetitive calibration curves with super-nernstian slopes between 63 and 67 mV/pAg.

Two electrodes had been previously calibrated against Cu^{2+} ions (named c-(Cu) in Figs. 3 and 4). When these electrodes are calibrated against Ag^+ ions for the first time (Fig. 3) a steep increase in the potential is registered in the medium concentration range and then the slope decreases in the high concentration range. From the second calibration on, the electrodes exhibit the same reversible calibration curves as those which have been calibrated many times both in Cu^{2+} and Ag^+ solutions, as shown in Fig. 4.

The “as prepared” electrodes (which had not been previously calibrated or conditioned, named nc in Figs. 3 and 4) initially exhibit the usual irregular behavior (Fig. 3). According to Vlasov and co-workers [16,17] the reason is that the modified surface layer (MSL) has not been formed yet. During the following calibrations, the exposition of the membrane to Ag^+ solutions causes the formation

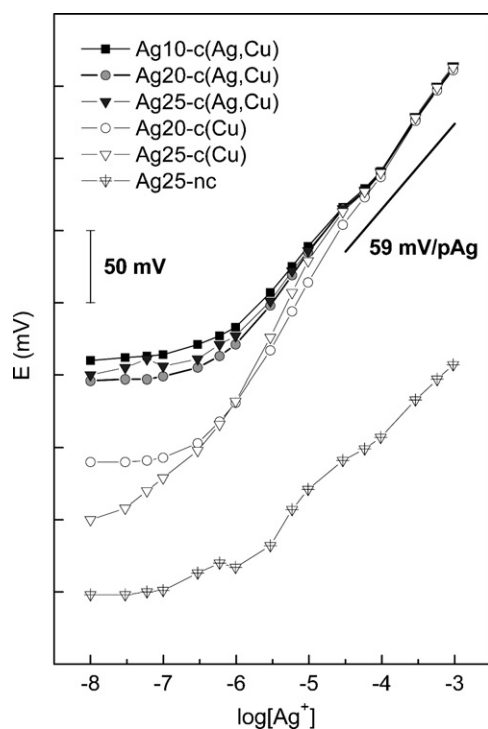


Fig. 3. Calibration curves of Ag_x electrodes in the presence of Ag^+ ions.

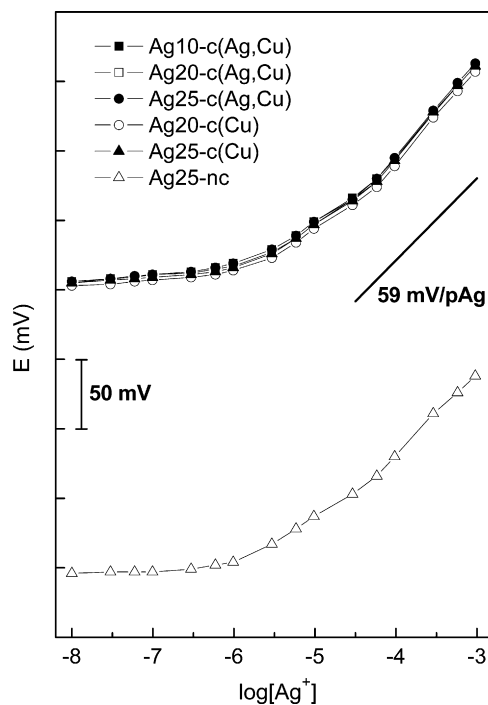


Fig. 4. Calibration curves of Ag_x electrodes in the presence of Ag^+ ions, following calibrations.

of the MSL and therefore the expected reversible calibration curves are obtained (Fig. 4).

In the concentration range 3×10^{-5} – 10^{-4} M a reduction of the potential can be observed (Figs. 3 and 4). In order to investigate this phenomenon one of the electrodes with repetitive calibration curves was chosen and its potential was registered as a function of time as the concentration of Ag^+ in the analyzed solutions was changed. The result of this experiment for an Ag_{25} electrode is pre-

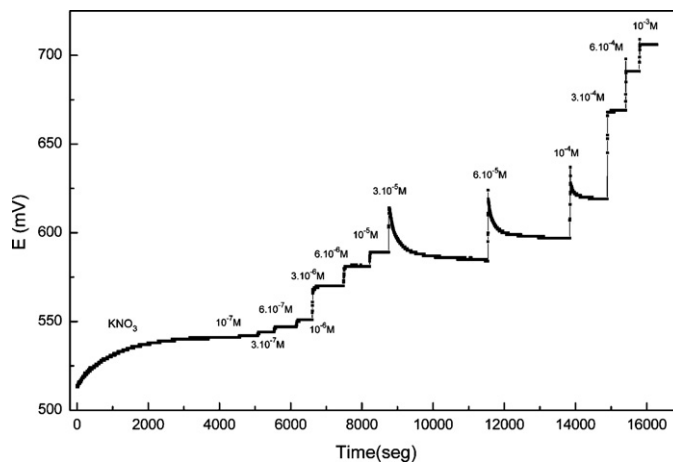


Fig. 5. Potential vs. Time of an Ag_{25} electrode as Ag^+ concentration in the solution was changed.

sented in Fig. 5, the rest of the studied compositions present the same response.

The electrode was left in a KNO_3 (0.1 M) solution for 50 min. During this time the potential increased until it reached a steady value. The changes in the potential at low concentrations (first observed at 10^{-7} M) were the usual ones, as measured for other all-solid state ion selective electrodes [18]. When the concentration of the solution was changed to 3×10^{-5} M a different phenomenon was observed. Immediately after the step, the potential started to decrease rapidly until, after 30 min, it reached a steady value. The same behavior was observed when the concentration of the analyzed solution was changed to 6×10^{-5} M and to 10^{-4} M. For higher concentrations, the behavior was once again the usual one.

Several papers have been published investigating this type of transient response. But to our knowledge in all these cases the transient response was measured in the presence of two kinds of ions (primary and interfering ions) [19–22] whereas in our investigation, the transient signal was obtained in the presence of only the primary ion.

The response of Cu_y electrodes to the presence of Ag^+ is similar to the response of Ag_x electrodes, but with poorer sensitivity and a more notorious potential decrease in the concentration range 3×10^{-5} – 10^{-4} M.

4. Conclusions

Ag_x and Cu_y membranes are sensitive to Ag^+ and Cu^{2+} ions with super-nerstian slopes. The sensitivity was not improved by the addition of metal to the glass formulation but the detection limits were lowered and the linear ranges were slightly extended.

The observations made in Section 3.2 concerning the response to Cu^{2+} can be summarized by stating that an increase of the copper concentration in the membrane composition only affects the response of the electrode by lowering the slope and that an increase of the silver concentration in the membrane composition (above 20 at.%) shortens the linear range.

It appears that Ag in the membranes plays an important role in the sensing mechanism, which results in a significant increase of the slope of the electrode's calibration curve.

These facts suggest that the potential generation comes from multiple simultaneous sources, i.e. ionic exchange plus adsorption/desorption and even surface reactions [21,23,24].

With regard to the results obtained of the potential as a function of time when the concentration of Ag^+ in the analyzed solutions is changed, further investigations need to be performed to accu-

rately assert the mechanism that causes the observed behavior in the medium concentration range.

Acknowledgements

The authors greatly acknowledge the support of ANPCyT, Universidad de Buenos Aires and CONICET from Argentine.

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