Journal of Non-Crystalline Solids 355 (2009) 1566–1570

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Sn(II)-ion-selective electrodes based on chalcogenide glasses for water media analyzes

V. Vassilev [a], K. Tomova [a], S. Boycheva [b,*], V. Parvanova [c]

[a] *Department of Metallurgy of Non-Ferrous Metals and Semiconductor Technologies, University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky Blvd., 1756 Sofia, Bulgaria*
[b] *Technical University of Sofia, Department of Thermal and Nuclear Power Engineering, 8 Kl. Ohridsky Blvd., 1000 Sofia, Bulgaria*
[c] *Department of Inorganic Chemistry, University of Chemical Technology and Metallurgy, 8 Kl. Ohridsky Blvd., 1756 Sofia, Bulgaria*

ARTICLE INFO

Article history:
Received 24 July 2008
Received in revised form 10 June 2009
Available online 13 July 2009

PACS:
07.07.Df
81.05.Gc
82.45.Fk

Keywords:
Glasses
Ion-selective electrodes
Alloys
Sensors
Chalcogenides

ABSTRACT

Sn(II)-ion-selective electrodes (Sn(II)-ISEs) based on chalcogenide glasses (ChGs) from the $GeSe_2$–Sb_2Se_3–SnSe system were created. All-solid-state Sn(II)-ISEs of “coated-wire” type were designed, which consist of inner Ag/AgCl reference electrodes uniformly coated with composite mixtures of binding polymer and $GeSe_2$–Sb_2Se_3–SnSe glassy powder. Sn(II)-ISEs were tested in aqua solutions of the potential-determining ions with respect to their basic analytical characteristics: stability, linear range (L, mol l^{-1}) and slope (S, mV dec^{-1}) of the electrode function, working pH-range, limits of detection (LD, mol l^{-1}), response time (τ_{95}, s) and selectivity coefficients ($K_{i,j}^{pot}$) in the presence of ions, which commonly accompany Sn^{2+}-ions in the analytical media. Potential-generation mechanism, taking place on the membrane/analyzed solution interface, was suggested to explain the peculiarities in the analytical performance of the Sn(II)-ISEs.

1. Introduction

The chemical sensors and microsensors with chalcogenide and chalcohalide glassy membranes are promising devices in environmental pollution control, in-situ management of industrial processes, electronic tongues systems for food and beverages testing, and municipal, industrial and natural water analyzes [1–3]. The recent achievements in the application of chalcogenide glasses (ChGs) as membrane materials in potentiometric sensors have been summarized by Vassilev and Boycheva [4]. In principal, ion-selective electrodes (ISEs) based on ChGs superior their polycrystalline analogs with stronger chemical resistance in acidic and redox solutions [5–7]. Their analytical characteristics are comparable or even better then those of the polycrystalline membranes [8]. Variety of chalcogenide glassy sensors and microsensors reversible to Ag^{+}- [8,9], Cu^{2+}- [8,10], Pb^{2+}-[8,11], Cd^{2+}- [12,13], Fe^{3+}- [14,15], Zn^{2+}-ions [16,17], etc., have been investigated.

Superficial information concerning the development of selective to Sn^{2+}-ions sensors has been found. Sn(II)-ISEs with organic liquid dibenzo-18-crown-6 (DB18C6) membranes have been suggested [18].

Results on the investigation of Sn(II)-ISEs with ChG membranes from the As_2Se_3–As_4SSe–SnTe and As_2Se_3–As_2Te_3–SnTe systems have been reported previously [19,20].

The aim of the present work is to develop all-solid state potentiometric electrodes selective to Sn^{2+}-ions on the base of $GeSe_2$–Sb_2Se_3–SnSe ChGs and to investigate their basic analytical properties. This study is a part of a wide research program directed to the creation of chemical sensors with ChG membranes selective to heavy metal ions with excellent analytical performance.

2. Experimental

Bulk ChGs from the $(GeSe_2)_x(Sb_2Se_3)_y(SnSe)_z$ system, where $x + y + z = 100$ mol%, were used as active components in the Sn(II)-ion-selective membranes. ChG alloys were synthesized by a standard melt-quenching technique described in details in Ref. [21]. ChG compositions selected as membrane materials in the Sn(II)-ISEs are given in Table 1. The all-solid-state Sn(II)-ISEs of the “coated-wire” type were designed as the well-homogenized composite mixtures of binding polymer and 2 mass% ChG powder (with a particle size $\leqslant$63 μm) were uniformly coated onto Ag/AgCl

---

* Corresponding author. Tel./fax: +359 29652537.
E-mail address: sboycheva@tu-sofia.bg (S. Boycheva).

0022-3093/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2009.06.007

Table 1
Compositions of the ChG membrane materials used for Sn(II)-ISEs.

No.	$(GeSe_2)_x(Sb_2Se_3)_y(SnSe)_z$ (mol%)			ISE labels
	x	y	z	
1	81	9	10	ISE(1)
2	54	36	10	ISE(2)
3	36	54	10	ISE(3)
4	36	24	40	ISE(4)

reference electrodes. Pure epoxy resin, which is an electrical isolator, was used as an inert polymeric matrix.

This constructional design has several substantial advantages over the ISEs with liquid junctions and monolithic membranes: (i) ensures an reliable ohmic electrical contact between the membrane and the inner reference electrode; (ii) overcomes the technological difficulties resulted from the insufficient mechanical durability of the ChGs; (iii) economy of the raw materials; (iv) multiple utilization of the inner Ag/AgCl electrode; (v) simple storage; (vi) hermetic constructions.

The preparation of the inner reference Ag/AgCl electrodes have been described in details [22].

The reproducibility of the analytical characteristics of the Sn(II)-ISEs was studied on three different samples from the each selected ChG composition.

The Sn(II)-ISEs were tested in the following standard electrochemical cell:

Hg, Hg_2Cl_2	KCl (saturated)	‖	Investigated solution	‖	Ion-selective composite membrane	Ag, AgCl

The ISEs calibration was performed under conventional working regime in standard solutions prepared from 1 mol l^{-1} $SnCl_2$ by consecutive dilution with bidistillated water.

The potential of the electrochemical cell was measured by the help of a digital mV-meter (HANNA Instruments, Germany) with ±0.2 mV in accuracy. The ISEs were calibrated in sequence of progressively increasing concentrations of the potential-determining ions under constant magnetic stirring (250 rev min^{-1}). Calomel standard electrode (HANNA Instruments, HI 5412) was used as a comparative semielement for the measurements.

Before each series of measurements, conditioning of Sn(II)-ISEs was performed in 10^{-3} mol l^{-1} Sn^{2+}-ions standard solution.

The pH influence on the electrode functions was investigated under constant content of the potential-determining ions varying the concentration of the hydrogen ions, as the pH-values were adjusted adding drops of strong HNO_3 or NH_3.

The response time (τ_{95}) was measured in the concentration range 10^{-3}–10^{-1} mol l^{-1} Sn^{2+}-ions.

The value of the limits of detection (LD) is the concentration of the determining ions at which the measured signal is two times higher than the background. In a case of ISEs, this concentration corresponds to deviation in the Nernstian equilibrium potential with 18/z mV, where z is the valence of the potential-determining ions, according to the IUPAC recommendations [23]. LD for Sn(II)-ISEs were determined by extrapolation of the linear part of the calibration functions at deviation in the equilibrium potential with 9 mV from the Nernstian equation.

Selectivity coefficients ($K_{i,j}^{pot}$) were determined by the method of the mixed solutions under a constant content of the interfering ions and a variable concentration of the Sn^{2+}-ions in the linear concentration range of the electrode functions.

3. Results

3.1. Glass-formation in the $GeSe_2$–Sb_2Se_3–SnSe system

Glass-formation in the pseudo-ternary $GeSe_2$–Sb_2Se_3–SnSe system and the basic physicochemical, thermal and mechanical characteristics of the obtained glasses have been previously studied [21]. Glass-formation has been observed in the binary $GeSe_2$–Sb_2Se_3 system in the concentration range from 0 to 70 mol% Sb_2Se_3, as can be seen from the Gibbs' diagram presented in Fig. 1. No glasses have been obtained in the binary $GeSe_2$–SnSe system. The maximal solubility of SnSe in the glassy alloys has been found up to 57 mol% on the compositional tie-line $(GeSe_2)_3Sb_2Se_3$–SnSe – Fig. 1.

3.2. Analytical characteristics of Sn(II)-ISEs

The analytical reliability of the Sn(II)-ISEs was estimated at the parameters of the calibration functions: slope (S, mV dec^{-1}), linear range (L, mol l^{-1}), limits of detection (LD, mol l^{-1}), and response time (τ_{95}, s) and working pH-range.

The results obtained for the Sn(II)-ISEs characteristics are summarized in Table 2.

The electrode functions were measured on non-conditioned and conditioned Sn(II)-ISEs for 15 min in 10^{-3} mol l^{-1} Sn^{2+}-ions solution. The analytical parameters for the all investigated ISEs were stabilized and improved after the conditioning. The calibration curves of the Sn(II)-ISEs are characterized with a slope closed to the theoretical Nernstian value for one-valence anions (S_{theor} ~59 mV dec^{-1}).

Typical calibration functions for non-conditioned and conditioned Sn(II)-ISE(2) are plotted in Fig. 2. The non-conditioned Sn(II)-ISE(2) is characterized with an electrode function with a linear range $L = 10^{-5}$–10^{-1} mol l^{-1} Sn^{2+} and a slope S = 50.5 mV dec^{-1}. After the conditioning, L preserves in the same range, while the slope increases slightly (S = 56.5 mV dec^{-1}). The LD value for the Sn(II)-ISE(2) was measured of 4.56×10^{-6} mol l^{-1} for non-conditioned and 6.34×10^{-6} mol l^{-1} for conditioned ISEs, respectively (Fig. 2). It can be concluded that the conditioning process improves and stabilizes the functioning of the Sn(II)-ISE membranes, comparing the analytical characteristics of non-conditioned and conditioned ISEs (Table 2). It was also observed that the electrode characteristics were not improved further by longer conditioning (e.g. for 30 min), therefore the next measurements were performed after conditioning for 15 min in 10^{-3} mol l^{-1} $SnCl_2$ solution.

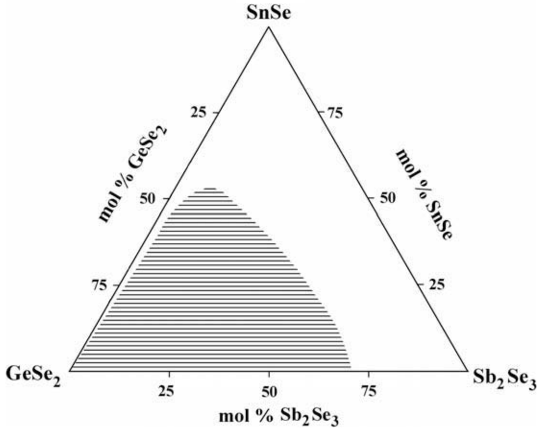

Fig. 1. Glass-forming region in the $GeSe_2$–Sb_2Se_3–SnSe system [21].