

## Ag(I)-ION-SELECTIVE ELECTRODE BASED ON CHALCOGENIDE GLASSES

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*Ag(I)-ion-selective-electrodes (Ag(I)-ISE) were created on the base of new chalcogenide glasses from the  $As_2Se_3-GeSe_2-Ag_4SSe$  and  $As_2Se_3-GeSe_2-Ag_4SSe$  systems. Ag(I)-ISE include construction from the coated wire-type. The basic analytical characteristics of ISE: linear range, slope of the electrode function, limits of detection, results reproduction and response time were studied. The influence of some mono-charged and double-charged interfering ions on the response of Ag(I)-ISE is investigated.*

**Keywords:** ion-selective electrode, chalcogenide glasses, glassy electrode

### 1. INTRODUCTION

One of the possible applications of the chalcogenide glasses (ChG) is their use as ion-selective membranes distinguished with: a high sensitivity of the electrode function, good selectivity, stability in acids, short response time, etc.

Trachtenberg et al. [1-5] are the first who use the ChG as membranes of ion-selective electrodes (ISE). Recently, many chalcogenide glassy sensors for detection of  $H^+$  [6,7],  $Cu^{2+}$  [8,9],  $Pb^{2+}$  [10],  $Cd^{2+}$  [11,12],  $Fe^{3+}$  [13,14],  $Zn^{2+}$  [15,16] and others ions have been developed. ChG are widely spread in application as membrane material of ISE [17].

Ag(I)-ions are often met in different analytical objects. The potentiometrical method is one of the most perspectives for their determination. For the production of the Ag(I)-ISE's membranes are used polycrystalline chalcogenides with addition of different components ( $Ag_2J$ ,  $Ag_2S$ ,  $CuS$ ,  $CuSe$  and others), which increase the level of the ionic conductivity [18,19].

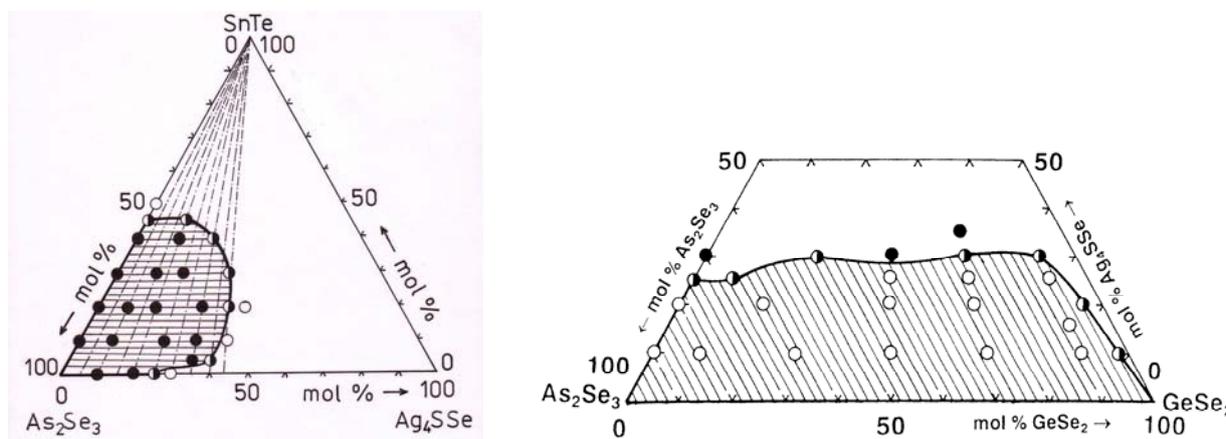
The ISE with crystal membranes are characterized with instability of the electrode function due to the change of the properties on the sensor's surface during its work, as well as to the relatively long time for equilibrium determination. Because of this reason the scientific investigations are turned on the use of ChG as a membrane material.

The aims of this paper are creation of solid-state Ag(I)-ISE on the base of ChG of the  $As_2Se_3-Ag_4SSe-SnTe$  and  $As_2Se_3-GeSe_2-Ag_4SSe$  systems and investigation of their analytical characteristics.

### 2. PROBLEM STATEMENT

A coated wire-type ISE were constructed. For this purpose the active component (ChG) was introduced to an inert polymeric matrix (epoxy resin) at a concentration of

2 mass %. The compositions of the used ChG were from the glass-forming region of the  $\text{As}_2\text{Se}_3\text{-Ag}_4\text{SSe-SnTe}$  and  $\text{As}_2\text{Se}_3\text{-GeSe}_2\text{-Ag}_4\text{Sse}$  systems (Fig. 1). The inner comparative electrode was made the following way: a Ag-wire ( $\varnothing=1$  mm) was cleaned with a 10 %  $\text{HNO}_3$  solution, then it was immersed in a 0,5 M  $\text{FeCl}_3$  solution for 24 hours (the surface got covered with a thick AgCl layer). The composite (ChG+epoxy resin) is laid as a thick layer on the Ag/AgCl-electrode surface.



**Fig. 1.** Glass-forming regions in the  $\text{As}_2\text{Se}_3\text{-Ag}_4\text{SSe-SnTe}$  (system A) [20] and  $\text{As}_2\text{Se}_3\text{-GeSe}_2\text{-Ag}_4\text{Sse}$  (system B) [21]

The following marks are used depending to the composition of ChG in the composite matrix:

#### ISE-from system A



#### ISE-from system B



Potentiometrical measurements are carried out with a cell of the following type:

<b>Hg, <math>\text{Hg}_2\text{Cl}_2</math></b>	<b>KCl</b> <b>(нас.)</b>	<b>Investigated solution</b>	<b>Ion-selective membrane</b>	<b>Ag - AgCl</b>
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The standard calibration solutions were obtained from an initial solution (1 M  $\text{AgNO}_3$ ). The electrode potential was measured during a constant dilution of the solutions with velocity  $300 \text{ rev min}^{-1}$ . The ISE's conditioning was made in a  $10^{-3}$  M solution of the potential-determining ion. The response time and the limits of detection were determined in solutions with concentration of Ag(I)-ions from  $10^{-6}$  to  $10^{-1}$  M.

### 3. RESULTS

As an evaluation criterion for the ISE's function, the following analytical characteristics were used: slope (S) and length (L) of the linear range of the calibration function, limits of detection (LD), response time ( $\tau$ ) and selectivity coefficient ( $K_{i,j}^{\text{pot}}$ ).

### 3.1. Calibration function of the ISE

The electrode functions are made for unconditioned and conditioned (30 min in a  $10^{-3}$  solution of the potential-determining ion) Ag(I)-ISE. The electrode function of all Ag(I)-ISE are characterized by slope close to the theoretical one; the time required for setting of equilibrium electrode potential is of the order of 1-2 min. For the low concentrations of Ag(I)-ions ( $10^{-6}$ - $10^{-4}$  mol/l) equilibrium potential value is set with difficulty. Conditioning of duration 30 min stabilizes and improves the parameters of the electrode function of the electrodes.

Fig. 2 represents the calibration functions of conditioned and unconditioned electrode. The unconditioned electrode type A.1. is characterized by linearity of the function in the limits L -  $10^{-3}$ - $10^{-1}$  mol/l Ag(I) and with a slope of the linear range  $S=112,5$  mV/dec. The calibration function of the conditioned electrode (Fig. 2) is linear in the limits L -  $10^{-4}$ - $10^{-1}$  mol/l Ag(I) with a slope  $S=58$  mV/dec. The limits of detection of the A.1. electrode are  $LD=3,2 \cdot 10^{-5}$  mol/l. The conditioning of the electrode makes its work better.

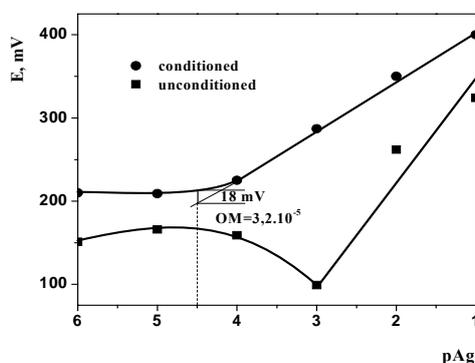


Fig. 2. Calibration functions of coated wire-type A.1. electrode ( $18/z = 18$ ,  $z = 1$ ).

The results of measuring S, L and LD after the initial measurements of the conditioned electrodes are summarized in Table 1.

Table 1. Results of the measurements of the ISE 180 days after their production

Electrode type	A.1-ISE		A.2-ISE		B.2-ISE	
	1 <sup>st</sup> day	180 <sup>th</sup> day	1 <sup>st</sup> day	180 <sup>th</sup> day	1 <sup>st</sup> day	180 <sup>th</sup> day
L, mol/l	$10^{-4}$ - $10^{-1}$	$10^{-5}$ - $10^{-2}$	$10^{-4}$ - $10^{-1}$	$10^{-5}$ - $10^{-1}$	$10^{-4}$ - $10^{-1}$	$10^{-5}$ - $10^{-1}$
S, mV/dec	58	47	68	55	64	40
LD, mol/l	$3,2 \cdot 10^{-5}$	$2,7 \cdot 10^{-6}$	$7,5 \cdot 10^{-5}$	$5,5 \cdot 10^{-6}$	$6,8 \cdot 10^{-5}$	$5,6 \cdot 10^{-6}$

The slope of the electrode function S is near to the theoretical value for mono-valent ion in accordance of the Nernst equation - 59,16 mV/dec. S changes within the limits 53-67 mV/dec, which indicates that the potential-generating process is exchange of mono-valent ions between the ion-selective membrane and the solution. The higher values of S are indication of the presence of a potential-generating processes passing in parallel (such as redoxy, exchange of other type of ions, etc.), which lead to formation of mixed potential on the membrane/solution frontier and to registration of higher values of the slope of the electrode function, the so-called

super-nernst response.

The super-nernst slope might also be a result of the "memory effect" of the electrode from a previous measurement, which in that case is obviously avoided.

After 180 days measurements of the same ISE are taken (Table 1).

For ISE types A.1., A.2. and B.1. a stable response is obtained (Table 1). The calibration function of the B.1.-ISE in the first measurements is linear in the limits  $L - 10^{-4}$ - $10^{-1}$  mol/l Ag(I) with a slope  $S=53,3$  mV/dec (LD is  $6,8 \cdot 10^{-5}$  mol/l). After 180 days the calibration function of the same electrode is unstable and the study on it is discontinued.

After 180 days the electrodes show auspicious results. The slope of the linear function is not smaller than 30 % of the theoretical one and the length of the linear range is at least 4 decades. These data show that ChG of the  $As_2Se_3$ - $Ag_4SSe$ - $SnTe$  and  $As_2Se_3$ - $GeSe_2$ - $Ag_4SSe$  systems, on the basis of which Ag(I)-ISE were developed, are an appropriate membrane material, since in the experimental time taken they did not show any indication of "ageing" (oxidation, crystallization, etc.).

### 3.2. Limits of detection

The "limits of detection" concept at the ISE is defined as the relevant concentration of the determined ion, at which the measured signal is twice higher than the background one. In the current case this is the concentration, at which the deviation of the Nernst straight line equals to  $(59/z) \cdot \lg 2 = 18/z$  at 25 °C and the slope of the linear function is 30 % of the theoretical one. The determination of the LD for the investigated ISE is shown on Fig. 2.

### 3.3. Response time ( $\tau_{95}$ )

The ISE were measured in solutions within the concentration range from  $10^{-1}$  to  $10^{-6}$  mol/l  $AgNO_3$  with a constant value of pH ( $pH < 1$ ). When sinking consecutively the ISE in all solutions on the range of increment of the concentration the time needed for establishing a constant value of the potential is determined.

The response time  $\tau_{95}$  is in the range 20-40 s and increases when decreasing the concentration of the investigated solutions. The composition of the ChG does not have influence on that characteristic, i.e. the exchange reaction of Ag(I)-ions between the membrane and the analyzed solution in the electrodes of the three investigated groups passes with a constant velocity.

Regarding to this analytical characteristic the electrodes show a good results, commensurate with those referred about the electrodes with homogenous membranes. In the common way the diffusion velocity of the potential-determining ions in the heterogenous (composite) membranes is smaller than that in the homogenous ones, formed by a monolyte glass with analogical composition. The response time  $\tau_{95}$  is tightly related to another important characteristic of the electrodes so-called "mean lifetime" and is particularly important in the cases when measurements in aggressive media are led. The investigated Ag(I)-ISE have showed a comparatively quick response for concentrations of the potential-determining ion solutions where the electrode function is linear.

### 3.4. Memory effect in the ISE

The weak reproducibility of the results and the over-nernst response in many ways are result of the memory effect in the ISE, which is conservation of the potential from previous measurement.

To avoid the memory effect, after each measurement series, the electrochemical cell is leaved to work about 2 min in distilled water. According to E. Pungor the over-nernst response does not exist, it contradicts to the rules of the thermodynamics and is a result of incorrect interpretation of the results. The over-nernst response might be also a result of the memory effect, as well as of additional potential-generating process passing simultaneously with the basic one. The passing of these two phenomena is not established at the formation of the potential of the investigated sensors.

### 3.5. Selectivity ( $K_{i,j}^{pot}$ )

The impeding effect of bi-charged ( $Zn^{2+}$ ,  $Cd^{2+}$  и  $Pb^{2+}$ ) and tri-charged ( $Al^{3+}$ ) ions on the response of the ISE types A.1., A.2. and B.2. in a presence of Ag(I)-ions (Table 2).

**Table 2.** Values of  $K_{Ag,Me}^{Pot}$ .

	Concentration of the impeding ion, mol/l	$K_{Ag,Al}^{Pot}$	$K_{Ag,Zn}^{Pot}$	$K_{Ag,Cd}^{Pot}$	$K_{Ag,Pb}^{Pot}$
A.1.-ISE	$10^{-3}$	$3,2 \cdot 10^{-3}$	$2,6 \cdot 10^{-3}$	$2,5 \cdot 10^{-3}$	$2,5 \cdot 10^{-3}$
A.1.-ISE	$10^{-2}$	$1,0 \cdot 10^{-3}$	$8,6 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$
A.2.-ISE	$10^{-3}$	$3,2 \cdot 10^{-3}$	$3,0 \cdot 10^{-2}$	$2,8 \cdot 10^{-3}$	$3,2 \cdot 10^{-3}$
A.2.-ISE	$10^{-2}$	$1,0 \cdot 10^{-3}$	$8,7 \cdot 10^{-4}$	$7,7 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$
B.2.-ISE	$10^{-3}$	$3,2 \cdot 10^{-3}$	$2,4 \cdot 10^{-3}$	$2,5 \cdot 10^{-3}$	$3,2 \cdot 10^{-3}$
B.2.-ISE	$10^{-2}$	$1,0 \cdot 10^{-3}$	$1,0 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$	$1,0 \cdot 10^{-4}$

From the analysis of the electrode functions of the Ag(I)-ISE in addition of the impeding ions in concentrations  $10^{-2}$  and  $10^{-3}$  M is established that concentrations of  $10^{-2}$  and  $10^{-3}$  Cd(II)- and Al(III)-ions impede the determination of Ag(I)-ions if they are in concentration lower than  $10^{-3}$  M  $AgNO_3$ ; the Pb(II)- and Zn(II)-ions in concentrations  $10^{-2}$  M  $Pb(NO_3)_2$  and  $10^{-3}$  M  $Zn(NO_3)_2$ , respectively, start to impede if the concentration of the Ag(I)-ions is  $< 10^{-4}$  M  $AgNO_3$ . The solutions with concentration  $10^{-3}$  M  $Pb(NO_3)_2$   $10^{-2}$  M  $Zn(NO_3)_2$  impede the determination of Ag(I)-ions if their concentration is lower than  $10^{-4}$  M  $AgNO_3$  and  $10^{-3}$  M  $AgNO_3$ , respectively.

From the electrode functions of the Ag(I)-ISE the selectivity coefficients  $K_{i,j}^{pot}$  are calculated for Al(III)-, Zn(II)-, Cd(II)- and Pb(II)-ions with concentrations  $10^{-2}$  и  $10^{-3}$  M - Table 2. These coefficients have much smaller values from one, i.e. in the the given concentration intervals they do not impede the determination of Ag(I)-ions.

## 4. CONCLUSIONS

On the basis of new ChG from the  $As_2Se_3$ - $Ag_4SSe$ - $SnTe$  and  $As_2Se_3$ - $GeSe_2$ - $Ag_4SSe$  systems coated wire-type ISE were constructed.

The suggested construction and technology of the Ag(I)-ISE guarantees a high reproducibility of the analytical characteristics, as well as a very good selectivity about the  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Al^{3-}$ -ions.

The Ag(I) ion-selective membrane does not exhibit any indications of ageing or destruction of the active layer connected to the undesired processes passing (crystallization, polymer destruction, oxidation/reduction of the ChG, etc.).

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#### 4. REFERENCES

- [1]. Baker C.T., I. Trachtenberg, *J. Electrochem. Soc.* **118** (1971) 571-576
- [2]. Jasinski K., I. Trachtenberg, *Anal. Chem.* **44** (1972) 2373-2376
- [3]. Jasinski K., I. Trachtenberg, *J. Electrochem Soc.* **120** (1973) 1169-1174
- [4]. Jasinski K., I. Trachtenberg, *Anal. Chem.* **45** (1973) 1277-1279
- [5]. Jasinski K., I. Trachtenberg, G. Rice, *J. Electrochem Soc.* **121** (1974) 363-368
- [6]. Vlassov Yu.G., E.A. Bychkov, B.L. Seleznev, *Sens. Actuators B* **2** (1990) 23
- [7]. Hadjinicolova St., L. Ilcheva, I. Stojaniva, V. Vassilev, A. Atanasova, *Analyt.. Labor.*, **4**, № 2 (1995) 105-107
- [8]. Vlassov Yu. G., E.A. Bychkov, A.M. Medvedev, *Anal. Chim.* **185** (1986) 137 (in Russian)
- [9]. Hadjinicolova S., S.Boycheva, V. Vassilev, L. Ilcheva, L. Nikolova, 13<sup>th</sup> Conf. "Glass and Ceramics", 29.IX- 1.X.'99, Publ. House "Sci. Invest", Proceedings, v. **1** (1999) 304-309
- [10]. Vlasov Iu.G., E.A. Bychkov, A.V. Legin, *J. Anal. Himii* **40**, № 10 (1985) 1839-1844 (in Russian)
- [11]. Jukov A.F., A.V. Vishniakov, Ia.L. Harif, Iu.I.Urusov, F.K. Bolinec, E.I. Rijkov, A.V. Gordievskii, *J. Anal. Himii* **30**, № 9 (1975) 1761-1766
- [12]. Vassilev V., V. Parvanova, L. Aljihmani, B. Pejova, St. Hadjinicolova, P. Petkov, XVIII Congress of Chemists and Technologists of Macedonia, September 23-25, 2004, Ohrid, R. Macedonia, Extended Abstracts, ICT-19 (2004) 58-60
- [13]. Koenig C.E., E.W. Grabner, *Electroanalysis* **7**, № 11 (1995) 1090-1096
- [14]. Hadjinicolova St., S. Boycheva, V. Vassilev, L. Ilcheva, *God. HTMU-Sofia*, **34** (1999) 45-51 (in Bulgarian)
- [15]. Boycheva S. V., V. S. Vassilev, Z. G. Ivanova, *J. Appl. Electrochem.*, **32** (2002) 281-285
- [16]. Vassilev V.S., S.H. Hadjinicolova, S.V. Boycheva, *Sensors and Actuators B* **106** (2005) 401-406
- [17]. Vassilev V.S., S.V. Boycheva, *Talanta*, **67**, № 1 (2005), 20-27
- [18]. Hirata H., Higashiyama K. *Talanta*, **19** (1972) 39-44
- [19]. Jukov A.F., A.V. Vishniakov, Ia.L. Harif, Iu.I. Urusov, F.K. Bolinec, E.I. Rijkov, A.V. Gordievskii, *J. Anal. Himii*, **30**, № 9 (1975) 1761
- [20]. Aljihmani L., V. Vassilev, P. Petkov, *J. Optoelectr. and Adv. Materials*, **5**, № 5 (2003) 1187
- [21] Vassilev V.S., Z.G. Ivanova, L. Aljihmani, E. Cernoskova, Z. Cernosek, *Materials Letters* **59** (2005) 85-87