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Review

Chemical sensors with chalcogenide glassy membranes

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Abstract

The present review is emphasized on the recent achievements in the application of chalcogenide glasses (ChG) as membrane materials in chemical sensors, microsensors and multisensor systems. The questions concerning material synthesis, sensor designs and the concepts for the potential-generating mechanisms have briefly discussed. Most of the chalcogenide glass-forming systems and compositions investigated as membrane active materials have been summarized, and their analytical characteristics have been considered. The efficiency of chalcogenide-based chemical sensors in the real system analyses, as well as the advantages and disadvantages in their analytical performance have been evaluated and compared with the corresponding polycrystalline analogous.

Keywords: Chalcogenide glasses; Ion-selective electrodes; Membrane materials; Chemical microsensors; Multisensor systems

Contents

1. Introduction

During the last three decades, considerable scientific interest has been paid to the ion-selective electrodes (ISE) with functional membranes based on chalcogenide glasses (ChG). In the period 1971–1974, some initial data on the creation and the investigation of the electrochemical performance of such a type sensor elements have been reported in the literature [1–5]. ChG exhibit better chemical durability in acidic and redox media [6–9], and in many cases, possess better selectivity and reproducibility of the analytical characteristics, and longer time of life [10] as compared with the polycrystalline chalcogenides, which are broadly used as membrane materials, e.g. insoluble pressed sulphides and selenides [11,12]. These sensors are simple in construction, and special conditions are not required; neither for their storage, nor for the surface recovering even after continuous measurements. Due

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to these advantages, ChG became preferred membrane materials in ISEs for Ag^{+}-, Cd^{2+}-, Pb^{2+}- and Cu^{2+}-ions determination [7,13] instead of their crystalline analogous. Moreover, chemical sensors based on ChG are recently widely used for practical purposes, e.g. for waste, industrial and sea water analyses, in doping control in ultrapure metal production, in multisensor “electronic tongue” systems [14–16], etc.

2. Construction of chemical sensors with chalcogenide glassy membranes

2.1. ChG synthesis

Generally, ChG are obtained from the starting pure components (5N) by direct monotemperature synthesis in evacuated (up to 0.10–0.01 Pa) quartz ampoules. The thermal regimes are selected depending on the physicochemical peculiarities of the initial components, the intermediate compounds and the final products; they are determined in such a way to ensure completed interaction between the starting components and constant vapour pressure under a critical value in order to prevent the quartz ampoule destruction. Therefore, during the heating process a few thermal holdings are performed at temperatures about 40–50 °C above the melting points of each initial, intermediate and final component; the maximum temperature of the synthesis depends on the glassy alloy composition and for ChG materials reaches values between 600 and 1100 °C [17]. Finally, vibration stirring is applied to homogenise the melt; then the latter is rapidly quenched to room temperature in air, ice water or in liquid nitrogen. The glassy state is verified by X-ray and electron microscope analyses; the material homogeneity on the surface and in depth is controlled by Auger electron spectroscopy, X-ray microprobe analysis and infrared spectroscopy. Of great importance is the preliminary study of ChG with respect to their basic physicochemical parameters such as density, microhardness, temperatures of glass transition, crystallization and melting, as well as their thermomechanical properties (module of elasticity, compactness and minimal volume of microvoids) [18,19].

2.2. Types of ChG membranes

The most common are so called “homogenous” ISE membranes which are disks either cut from the bulk ChG specimens, and subsequently, polished [20,21] or prepared from ChG powder with average grain size of about 50–63 μm by pressing [22]. The disks are hermetically attached to the end of glassy, polyethylene or quartz tubes by the help of epoxy glue. The inner membrane side contacts with the standard solution in which a reference electrode is immersed. This semielement together with an external reference electrode contacts with the analysed solution. The electrochemical measuring cell can be schematically present as following:

Inner reference electrode |Standard solution| Ion-selective
membrane |Analysed solution| External
reference electrode

In this cell, an electrolytic contact is realized between the inner reference electrode and the membrane. For better reliability, the electrolytic contact is replaced by ohmic one which is created by soldering of a metal wire (e.g. Cu, Ag) on the inner membrane surface preliminary coated with metal film or attached directly with silver epoxy [21,23]. The obtained contact is covered with insolating material and protected with epoxy resin against signal disturbances.

ChG ISEs allow long time of exploitation, and after continuous work they could be easily restored after membrane surface polishing followed by conditioning in 10^{-3} to 10^{-2} mol/l solution of the corresponding potential-determining ion [23]. A drawback of these sensors is potential value diversion with 3–4 mV/h which requires cell recalibration after each 60 min [23].

Composite type membranes are developed in order to overcome the problems originating from the insufficient hardness of the chalcogenide glasses. They consist of ChG powder homogeneously dispersed in an inert matrix [24]. In the general case, the composite membranes possess worse analytical characteristics compared to the bulk analogous: longer response time and lower slope of the electrode function [24]. Better analytical performance is insured by the design of all-solid-state electrodes, so called “coated wire” type electrodes. By them a homogenous mixture of polymer and small amount of ChG powder (1%) is coated on the reference Ag/AgCl electrodes [25].

Recently, considerable interest is attracted by the chemical microsensors which is closely connected with the trends of device miniaturization, ecology of the production and natural raw materials economy [26–28]. The thin films possess significantly lower potential compared to the corresponding bulk materials, which is required for glasses with low conductivity (10^{-9} to 10^{-7} S/cm) to be applied in the microsensors. This requirement is met by a wide range of chalcogenide glassy alloys; in addition, their electrical properties can be adjusted by doping control.

A general microsensor scheme is shown in Fig. 1. The sensitive thin film is deposited by standard microelectronics techniques, e.g. thermal vacuum evaporation, laser ablation or cathode sputtering, onto different substrates (Si/Si_3N_4, Si/SiO_2, Pyrex) covered with contact metal films (Cr, Ag, Cr/Au, Ti/Pt).

The most important point in the microsensor construction is to ensure a stable on the metal/functional film interface, which is connected with the coating adhesion. The density of the exchange current on the membrane/analyzed solution interface depends on the charge transport mechanism across

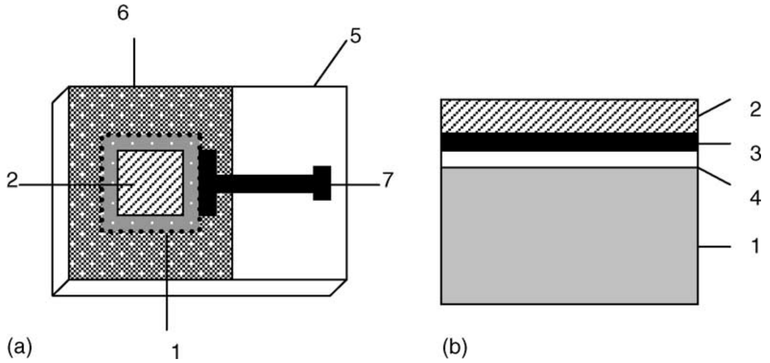


Fig. 1. Thin film microsensor: (a) top-view; (b) cross-section, 1, Si wafer; 2, chalcogenide glassy film; 3, contact metal film; 4, insolating film (SiO_2, Si_3N_4); 5, chip carrier; 6, hermetic film; 7, metal film.

the glass. It is necessary, the ionic part of the conductance to exceed significantly that of the electronic transport.

3. Chalcogenide glass-forming systems as membrane active materials

The most spread chalcogenide and chalco-halide (with chalcogenide as a glass-former) glass-forming systems investigated as membrane materials for chemical sensors, microsensors and multisensor systems have been summarized in Table 1.

Most of the investigated ChG ISEs are characterized with linear electrode functions in the concentration range 10^{-6} to 10^{-1} mol/l of the determined ion [7,30,32,39]. Low detection limits are reached for Fe(III)-ISEs after calibration in appropriate buffer solutions; the analytical useful linear range is from 10^{-25} to 10^{-10} mol/l Fe^{3+} with almost Nernstian slope of 26.3 mV/dec [54]. The ChG sensors are chemically resistant in acidic solutions in contrast to their polycrystalline analogous, e.g. the Ag(I)-ISEs preserve stable work function in 6 mol/l HNO_3 [29], and the Cu(II)-ISEs are 10–30 times more sensitive in strong acidic solutions than the polycrystalline $Cu_{18}Se$ and CuS + Ag_2S membranes [7,39]. In the common case, such sensors are applicable at pH < 8 and also in strong redox electrolytes, but ChG are not stable and dissolve in alkaline media. Fe(III)-ISEs [21] and Cr(VI)-ISEs [61] possess excellent electrochemical performance at very low pH values (pH < 2). Generally, ChG sensors exhibit stable electrode function only after conditioning in the concentrated solutions (10^{-3} mol/l) of the potential-determining ion [38], which is probably connected with the formation of an active modified surface layer (MSL). The response time varies drastically with the membrane composition from few seconds to about a minute and it is determined by the diffusion coefficients of the potential-determining ions from the solution to the active centers in the MSL. A stable potential at heterogeneous membranes is established much slower [24].

As a rule, ChG ISEs are reversible to the metal ions which are included in the composition of the glassy alloy (see Table 1). The problem with the perfect selectivity is not solved up to now at most of the suggested ChG ISEs, which provokes new glasses to be investigated as membrane materials. Ag(I)-ISEs [30,32] exhibit good selectivity in the presence of Na^+-, Ca^{2+}-, Mn^{2+}-, Mg^{2+}-, Cu^{2+}-, Ni^{2+}-, Hg^{2+}- and Fe^{3+}-ions. Fe^{3+}- and Fe^{2+}-ions disturb the electrode function of the Cu(II)-ISEs [20]. Pb(II)-ISEs exceed the selectivity of polycrystalline PbS and Ag_2S ISEs with respect to Cd^{2+}- and Fe^{3+}-ions [46–48]. Number of membrane sensors with ChG as active components behave simultaneously reversibility to a set of ions in mixed solutions. This wide-cross sensitivity combined with good chemical durability make them suitable components in multisensor systems, so called “electronic tongue”. The selectivity of thin film membranes obtained from As_2S_3 and As_2Se_3 glasses can be controlled through compositional changes after light exposition of respective multilayer systems [59]. The doping of ChG films of As_2S_3/Ag, As_2S_3(As_2Se_3)/Ag + Cu and As_2Se_3/PbS/Ag layered structures after light irradiation manage their sensitivity to Ag^+-, Cu^{2+}- and Pb^{2+}-ions, respectively. A set of such microsensors with controlled composition can be arranged in a multisensor system.

ChG sensors and multisensor systems based on arrays of non-specific ChG sensors with the following processing of their complex signals using pattern recognition methods are successfully applied for determination of inorganic pollutants in river [62], ground [63], sea [50,71] and waste waters [64], for corrosion process monitoring of technological equipment [64], technological electrolyses process control [64,65], beverages [66–69] and foodstuffs control [68].

4. Potential generation mechanisms in the ChG chemical sensors

The potential generation concepts for the ChG ISEs are developed according to the generally accepted theory, according to which, only the active groups localized on the working membrane surface participate in the exchange processes [70]. The mechanisms of ionic sensitivity on the membrane/analyzed solution interface could be clarified to a great extent by the investigation of: (i) the direct and alternative

Table 1
ChG systems investigated as active membrane materials

Determined ion	Glass composition, at.% (mol.%)	Reference
Ag^+	Ag–As–S	[29]
	Ag–As–Se	[30]
	$Ag_{1.5–50.1}S_{24.0–33.5}Fe_{0.3–1.9}$ + As	[31]
	$Ag_{15}As_{42.5}Se_{42.5-x}Te_x$, $x = 0–40$	[30,32]
Na^+	$(GeSe)_{20–85}(Ga_3N_2)_{5–35}(NaCl)_{5–30}$ + GeS	[76]
	$GeS_2–Ga_2S_3–NaCl$	[33]
Zn^{2+}	$(GeSe_2)_{72–54}(Sb_2Se_3)_{36–16}(ZnSe)_{10,20}$	[24]
	$(As_2Se_3)_{90–63}(Sb_2Se_3)_{0–27}(ZnSe)_{5,10}$	[24]
	$(GeSe_2)_{94}(ZnSe)_4(ZnTe)_2$	[35]
Cu^{2+}	$Se_{60}Ge_{28}Sb_{12}$ + 2% Fe	[1]
	$Cu_x(As_2S_3)_{100-x}$, $x = 5–25$	[5]
	$Cu_x(As_2Se_3)_{100-x}$, $x = 0–25$; $Cu_{25}(As_2Se_3)_{75}$	[36–38]
	Cu–As–Se, [Cu] = 40–90	[34]
	Cu–As–Se–Te; $Cu_{25}(As_2(Se_{0.5}Te_{0.5})_3)_{75}$	[36–38]
	$Cu_xAg_{25-x}As_{37.5}$, $x = 0–25$	[7,39,40]
	$Cu_xAg_{25-x}As_{37.5}Se_{37.5}$, $x = 0–25$	[7,39,40]
	$Cu_{23}Ag_2As_{37.5}Se_{37.5}$; $Cu_{23}Ag_2Se_{38}As_{17}S_{20}$	[41]
	$Cu_2Se–As_2Se_3$	[37]
	$Se_{60}Ge_{28}Sb_{12}$ + 20.8 % Cu	[20]
Cu^{2+} microsensors	Cu–Ag–As–Se–Te	[26,42]
	$Cu_xAg_y(As_2S_3)_{100-(x+y)}$, $x = 15–30$, $y = 10–20$	[43]
	$Cu_xAg_y(As_2Se_3)_{100-(x+y)}$, $x = 15–30$, $y = 10–20$	[43]
Cd^{2+}	$(Ge_{20}Te_{30}Se_{50})_{100-x}(CdS)_x$, $x \leq 0.5$	[37]
	$CdS–Ag_2S–As_2S_3$; $CdI_2–Ag_2S–As_2S_3$	[9]
Cd^{2+} microsensors	$(CdS)_x(AgI–Sb_2S_3)_{1-x}$, $x = 0–5$	[44]
Pb^{2+}	$(AgAsS_2)_{60}(PbI_2)_{40}$	[45]
	$Pb_{20}(As_2Se_3)_{80}$; $Pb_{30}(As_2Se_3)_{70}$	[36]
	$Pb_{20}Cu_5(As_2Se_3)_{75}$	[36]
	$PbS–Ag_2S–As_2S_3$; $PbI_2–Ag_2S–As_2S_3$	[8,10,46–48]
	Ag–As–S	[26]
Pb^{2+} microsensors	Pb–Ag–I–As–S	[49]
Hg^{2+}	$Ge_{20}Te_{30}Se_{50}–HgS$	[37]
	The composition is not given	[31,50]
	$AgBr–Ag_2S–As_2S_3–HgI_2$	[71,72]
Hg^{2+} microsensors	$As_2S_3–Ag_2S–AgBr$	[51,52]
Fe^{3+}	Ge–Se–Sb+Fe; $Fe_x(Se_{60}Ge_{28}Sb_{12})_{98-x}$, $x = 1–10$	[1,3,22,53,54]
	$Se_{80}As_{10}S_5Fe_5$	[21]
	$(GeSe_3)_x(FeSe_2)_y(Ag_2Se)_z$, $x = 76–85$; $y = 9–14$; $z = 5–15$	[24]
Cr^{6+}	As-based ChG, the composition is not given	[27,31,55]
Br^-	$(AgBr)_{55–65}(Ag_2S)_{15–30}(As_2S_3)_{10–30}$	[56,57]
Multisensor systems	Ag–As–S	[42]
	$(AgI)_x(Sb_2S_3)_{1-x}$, $x = 30, 40, 50, 60$	[58]
	doped As_2S_3 and As_2Se_3 films	[59]
	Pb–Ag–As–I–S, Cd–Ag–As–I–S, Cu–Ag–As–Se	[60]

conductivity of the membrane material; (ii) the diffusion coefficients of the ions with the help of radioactive traces; (iii) the changes in the valence of the elements composing the ChG applying electronic paramagnetic resonance and Mössbauer spectroscopy; (iv) the rearrangements in the near and middle range order in the structural network by X-ray diffraction and EXAFS; (v) the compositional changes on the membrane surface by Auger electron, secondary ion mass and X-ray photoelectron spectroscopy (XPS), etc.

Some authors [50] have considered that the potential-generating mechanism in Cu(II)-, Fe(III)- and Hg(II)-ISEs is due to redox processes taking place on the membrane/analyzed solution interface, e.g. according to reaction (1):

$$\mathrm{Hg}^{2+}_{\mathrm{solution}} + \mathrm{Hg}^{2+}_{2\,\mathrm{membrane}} \leftrightarrow \mathrm{Hg}^{2+}_{\mathrm{membrane}} + \mathrm{Hg}^{2+}_{2\,\mathrm{solution}} \qquad (1)$$

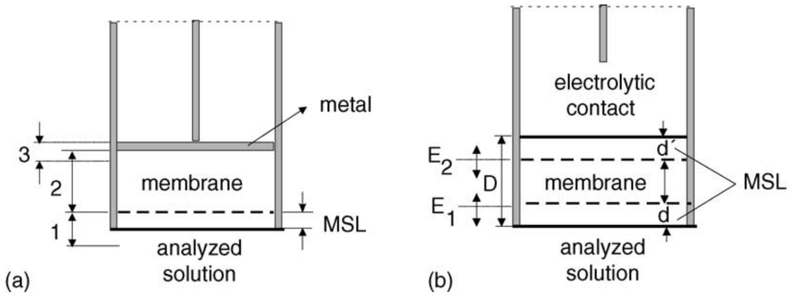


Fig. 2. Modified surface layer (MSL) formation at: (a) solid-state ISE; 1, region of surface ionic exchange; 2, region of bulk membrane transport; 3, region of ionic and electronic exchange equilibrium; (b) ISE with liquid inner connection; *D*, membrane thickness; *d*, *d*′, effective MSL thickness on the interfaces with analyzed and inner solutions, respectively; E_1 and E_2 potential differences across the two MSL.

Detailed surface study of Hg(II)-ISEs with $AgBr–Ag_2S–As_2S_3–HgI_2$ membranes by X-ray photoelectron spectroscopy, secondary ion mass spectrometry, electrochemical impedance spectroscopy and synchrotron radiation-grazing incidence X-ray diffraction reveals that the sensors response is stipulated by surface electron transfer at low Hg^{2+}-ions concentrations, whereas at elevated Hg^{2+}-levels, redox/oxidation reactions become more favorable [71,72].

Vlasov [13] has proposed a model to explain the sensitivity mechanism of ISEs with ChG membranes accepting the existence of a modified surface layer (MSL), which appears on the membrane surface after the contact with the analyzed electrolyte. MSL results from the interaction taking place between the solution of the potential-determining ion and the partially destroyed glassy network, which is accompanied by the creation of active exchange centers. In this case, the direct ionic exchange between the electrolyte and the induced centers on the chalcogenide glassy membrane surface is most probably the main generating process. Fig. 2 presents schematically the MSL formation in ISEs with electrolytic and ohmic contacts.

It has been established that the atomic density of the MSL is more than twice lower than that in the ChG bulk due to vacancies, which appear as a result of structural network distortion. Consequently, the lower density of the surface layer ensures higher diffusion coefficients of the exchanged ions. The concepts for the MSL generation and the ion exchange process between the analyzed solution and the active structural defect centres on the ChG membrane surface are applicable in the interpretation of the sensitivity mechanism of many chalcogenide glassy electrodes [44].

A number of investigations have been devoted to the potential-generating mechanism at Cu(II)-ISEs with ChG membranes because of the unclarities, originating from the variable valence of the copper ions. Jasinski, Trachtenberg [5] and Owen [36] have explained the sensitivity of GhG ISEs against Cu^{2+}-ions by multistage absorption performing after membrane conditioning in concentrated solutions of the potential-generating ions, which is accompanied by surface oxidation. According to Tohge and Tanaka [37], Cu(II)-ISEs based on As–Se–Cu glasses behave as redox electrodes and the potential-determining exchange is expressed by the reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \qquad (2)$$

Vlasov et al. [39] have applied the MSL model to explain Cu(II)-ISEs working mechanism, according to which stipulating is the direct Cu^{2+}-ion exchange between the analyzed solution and the MSL, i.e.

$$Cu^{2+}_{solution} \leftrightarrow Cu^{2+}_{MSL} \qquad (3)$$

The response from the MSL to the bulk of the membrane transmits by the process:

$$Cu^{2+}_{MSL} \leftrightarrow Cu^{2+}_{bulk} + h^+ \qquad (4)$$

The authors have established that in the ChG alloy the copper ions are one-valence, while two-valence ions are generated in the MSL in two ways: diffusion of Cu^{2+}-ions from the solution into MSL or interactions by the scheme:

$$2Cu^+ \rightarrow Cu^{2+} + Cu^0 \qquad (5)$$

followed by oxidation of the metallic copper. The first process is most probable for ChG with low copper content.

Great number of ChG ISEs exhibit superNernstian response, which has been explained by Pungor [73] as a memory effect or as a superposition of two or more potential-generating processes. It is also considered that the superNernstian behavior could be a consequence of insufficient current density through the MSL because of low diffusion of the potential-determining ions or low content of the active component in the membrane composition [39]. In the last cases, a non-equilibrium potential is measured.

In all the Refs. [13,53,74] concerning the Fe(III)-ISEs, the development a superNernstian slope ($S \geq 50$ mV/dec) in the electrode function is reported, i.e. the potential-generating process is not a direct exchange of Fe^{3+}-ions between the investigated solution and the chalcogenide membrane, which corresponds to Nernstian slope of about 19 mV/dec. The first suggestions are for a redox potential-generating mechanism in the Fe(III)-ISEs [1]. According to Vlasov and Bychkov [74], the electrode response is due to the selective exchange of electrons between the deep localized donor Fe^{2+}-centers in

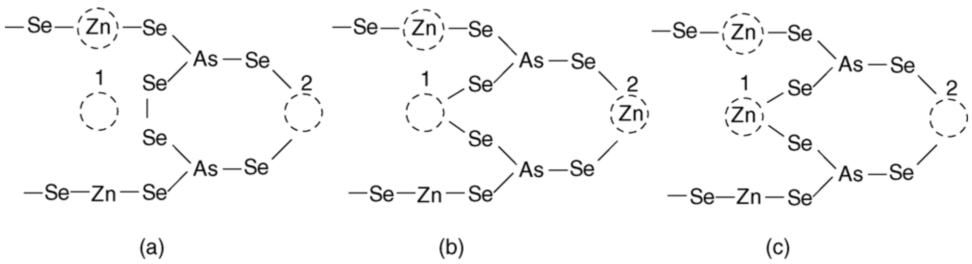


Fig. 3. Structure of the negative charged defect centers in the ChG membranes from the system As_2Se_3–Sb_2Se_3–ZnSe: a, before conditioning; b, after conditioning and in working regime; c, next measurement.

the ChG and the Fe^{3+}-acceptors in the analyzed solution. This exchange is reversible when p-carriers also take part in the current transport, which is determined by the energetic state of the redox couple Fe^{3+}/Fe^{2+} with respect to the Fermi-level in the bang gap of the ChG semiconductors [37].

Koenig and Grabner [23] have supported the concept for the MSL formation on the Fe(III)-ISE membrane surfaces after conditioning and selective exchange of Fe^{3+}-ions on the MSL/analyzed solution interface. The active centers placed in the MSL inject p-carriers in the band gap of the bulk glass and cause displacement of the Fermi-level in the p-type semiconductors. Each Fe^{3+}-ion crossed into the MSL from the solution injects only one p-carrier in the glass volume. Simultaneously, slow oxidizing corrosion takes place on the membrane surface caused by the strong oxidizing ability of the Fe^{3+}-ions. The superposition of these two processes generates a mixed potential, corresponding to superNernstian response. The simultaneous presence of Fe^{2+}- and Fe^{3+}-ions is proved by cyclic voltamperometry, and the enhanced ferrous content in the surface membrane layer by XPS.

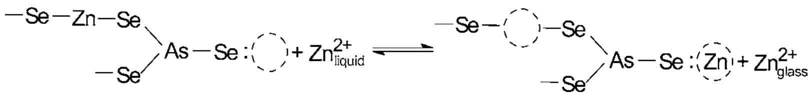
The mixed potential-generation is also confirmed for $Fe_{2.5}(Se_{60}Ge_{28}Sb_{12})_{97.5}$, membranes by electrochemical impedance spectroscopy and XPS [61].

Hadjinikolova et al. [22] have studied the Fe^{3+}-ion sensitivity of $GeSe_3$–$FeSe_2$–Ag_2Se membranes, and have supposed that the ion exchange between the induced centers in the MSL and the solution, i.e.:

$$\mathrm{Fe}^{3+}_{\mathrm{solution}} + (\mathrm{Fe}^{3+}_{\mathrm{MSL}})' \leftrightarrow \mathrm{Fe}^{3+}_{\mathrm{MSL}} + (\mathrm{Fe}^{3+}_{\mathrm{solution}})' \qquad (6)$$

is affected by the inclusion of Ag_2Se in the membrane composition above 5 mol.%. Ag^+-active centers are also apparent in the MSL at relatively high Ag_2Se contents, and they participate in the ion exchange. Ag^+-ion mobility is considerably higher compared with Fe^{3+}-ions and the selective function of the Fe(III)-ISEs is disturbed.

Boycheva et al. [24,25,35] have proposed a model to explain the potential-generation and the changes in the analytical characteristics of the Zn(II)-sensors based on the formation of positive and negative charged defect centers in the glassy network as a result of heterolytical distortions. At the beginning of the measurements, Zn^{2+}-ions from the negative charged defect centers, e.g. $[Se(GeSe_{3/2}R_1R_2)]^-$ for the ISEs with $GeSe_2$–Sb_2Se_3–ZnSe membranes and $R_1AsSe_{2/2}Se^-$ for those based on As_2Se_3–Sb_2Se_3–ZnSe ChG, participate in the $Zn_{liquid}{}^{2+} \leftrightarrow Zn_{glass}{}^{2+}$ exchange, e.g. following the scheme:



Probably for this reason, the initial electrode function has a slope typical for univalent anion (∼59 mV/dec). After continuous measurements, the defects might be extracted from the basic glassy matrix and diffuse in its volume. Meanwhile, they can interact with each other or with fragments from the destructed positive charged defects, creating new defect centers, which take part in the further ion exchange. The structural changes of the negative charged defect centers of As_2Se_3–Sb_2Se_3–ZnSe ISEs in working regime are illustrated in Fig. 3.

Before conditioning, two free positions (1) and (2) exist in the defect center (Fig. 3a). After conditioning, Zn^{2+}-ions coming from the solution occupy position (2), which is accompanied by bond breaking between the two bridged Se atoms (Fig. 3b). This results in the creation of two new bonds. During the measurement cycle, the Zn^{2+}-ions occupy positions (1), while Zn^{2+}-ions in position (2) pass into the solution (Fig. 3c). Again, two free bonds are formed. This consecutive process of occupation and delivery of the active positions (1) and (2) in the defect center repeats continuously, ensuring a permanent working regime of the ISE.

In the literature, data on the study of chemical sensors based on chalco-halide glasses are also published [9,33,58]. The introduction of halogen atoms in the chalcogenide glass-former network enhances the defectiveness and flexibility of the structure [75], which facilitates the ion mobility and the exchange between the membrane surface layer and the investigated solution. The sensitivity mechanism of AgI–Sb_2S_3 membranes against heavy metal ions is connected with the formation of insoluble sulfides at the surface active centers [58]. The selectivity of ISEs based on the AgI–Sb_2S_3 and other sulfide glasses is closely connected with the solubility of the corresponding crystalline sulfides, i.e. the decrease of the selectivity against metal ions in the order $Cu^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+}$ corresponds to the increase of the solubility of their sulfides.

5. Conclusions

The general concepts for the potential-generating mechanisms at the ion-selective electrodes with chalcogenide glassy membranes are based on the model for the formation of modified active layer on the membrane surfaces. This model explains to a great extent the peculiarities in the performance of this kind of sensors, i.e. why membranes with different compositions of the chalcogenide glass and different types of conductivity exhibit similar electrochemical behavior; the changes in the analytical characteristics after continuous exploitation; the selectivity against metal ions included in the membrane composition and the cross-selectivity of the chalcogenide glasses with “opened” structural network. The dynamics of the MSL formation and the exchange ion current density on the MSL/analyzed solution interface determine the sensor response time.

The recent trends in the development of chemical chalcogenide glassy sensors are directed to: device miniaturization, and that is why the thin film microsensors are predominantly under investigation; study of new multicomponent chalcogenide and chalco-halide glasses as membrane materials; control of the electrochemical behavior of chalcogenide glassy membranes through the composition (photodoping with metal atoms, addition of metals or metal-containing compounds during the synthesis); creation of multisensor systems for integrated analyses of complex liquid media and the application of mathematical methods for multiparametric signal diversion, i.e. neuron networks.

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