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Potentiometric sensors with chalcogenide glasses as sensitive membranes: A short review

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ABSTRACT

Nowadays there exists a large variety of Ion Selective Electrodes with chalcogenide glasses as sensitive membrane. This short review paper will discuss the development of these sensors for the last almost fifty years. The glass compositions, response modelling, construction methods, parameters evaluation and applications are reviewed. Research breakthroughs and remaining problems on chalcogenide glass Ion Selective Electrodes are discussed.

1. Introduction

Potentiometric sensors are widely used in many areas, such as environmental monitoring [1-4], industrial factories [5], clinical and biomedical analysis [6-8], wearable sensors [9-11], etc. They are stable and easy to use, and the interpretation of their signals is straightforward. The sensing signal of this type of sensor is, basically, a potential generated at a membrane in contact with a solution in which a specific ion of interest is dissolved. Thereafter, the membrane plays a crucial role in the sensors. In fact, changing the membrane composition will change the sensor characteristics thus making these sensors interesting for many areas of scientific research and industrial applications.

The largest group of potentiometric sensors is the Ion Selective Electrodes (ISEs). The first developed and most widely used ISE is the pH-sensitive glass electrode, which was proposed by Haber and Klemensiewicz in 1909 [12]. Since then a large number of membrane materials were developed for ISE applications. These include oxide and chalcogenide glasses, crystalline membranes, liquid and plasticized organic polymeric compositions containing ion exchangers or neutral carriers [13]. With the advance of thin film and microfabrication technologies, the possibility of making miniaturized sensors becomes a reality. The traditional ISEs could be miniaturized to a few microns by the use of thin films techniques to make the sensitive membranes. These sensors are called μISE. Other class of potentiometric sensors is the Ion Selective Field Effect Transistors (ISFETs) which is a traditional Metal Oxide Semiconductor Field Effect Transistor (MOSFET) with the gate terminal replaced by an ion sensitive membrane. Like the μISE, the ISFET can be easily fabricated by microelectronic technology. However, the main problem associated with ISFET is its stability and short lifetime [14]. After years of research and development, there is a variety of commercial ISEs available for determining concentrations of different ions in liquid samples of different natures [15]. In fact, over the past half-century ISEs have evolved to well-established routine analytical tool [16].

All these sensors have in common the same detection mechanism employed by measuring a potential over a membrane in contact with the test solution. Membranes play an important role in the sensor characteristics, as different material compositions provide the sensitivity to different ions in the solution. One important class of membranes is based on chalcogenide glasses.

Chalcogenide glass-based ISEs were introduced by Baker and Trachtenberg in the 1970s [17, 18]. Since then these glasses have been studied as membranes for potentiometric detection of metal cations like Fe^{3+}, Cd^{2+}, Pb^{2+} and others. The chalcogenide glasses have a number of advantages:

- The possibility of being synthesized with continuously variable compositions provides a wide spectrum of material properties [19, 20]. Since the chalcogenide glasses possess considerable glass-forming ability with several elements, it is possible to make minor changes in the glass compositions to adjust their physical, chemical and electrochemical properties.
- The glasses can be used for fabricating solid-contact sensors.
- They have high chemical stability, which leads to chemical

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durability.

- It is possible to make the glasses into thin films, constructing miniaturized sensors [21]. Furthermore, the low impedance of a thin film compared to that of the corresponding bulk material enables the use of poor conducting glass [22].

These features make chalcogenide glasses attractive for potentiometric sensor membranes for the applications in harsh environments and possible to use microfabrication techniques for mass production. Consequently, ISEs with chalcogenide glasses as sensitive membranes are widely used for determination of heavy metal ions concentration in solutions [23, 24].

However, the main challenge when working with chalcogenide glass sensors is the cross sensitivity, which can induce incorrect interpretations of the measurements. One way to overcome this problem is to construct a sensing system called Electronic Tongue (ET). The ET system is an array of several chemical sensors that uses advanced mathematical algorithm for signal processing. ETs were developed in an attempt to mimic the human gustatory system. There are some important reviews about ET systems in the literature [25-28], therefore ET system is not covered in this particular review.

Although the research on chalcogenide glass ISEs has decreased over the past few years, recently, Li et al. [29] have developed an Ag^+ sensitive chalcogenide glass ISE with nanomolar detection limit and almost no cross sensitivity, showing the current research interest in the development and improvement of chalcogenide membrane sensors. This review will discuss the progress in the development of the ISEs and ISFETs sensors based on chalcogenide glassy membranes and the theory foundation of the sensor response. The paper starts with a brief overview of techniques for chalcogenide glass synthesis, followed by a review on the theory and response modelling and discussions on sensors' construction and development for different ions detection. At the end of this paper, a conclusion of the progress and future perspectives and challenges will be presented.

2. Chalcogenide glass synthesis

The typical high temperature synthesis process is applied depending on the type of glass. According to desired composition - pure elemental or salt components are used as precursors for making the glasses. They are proportional weighted, mixed and sealed in an evacuated quartz ampoule. The ampoule is then heated to 600–1200 K for hours and is quenched in water or air to form the desired glasses. A thermal treatment process follows at a temperature below the glass-transition temperature (T_g) for a few hours up to several days to remove the stresses of the sample. Because of the different physicochemical properties of the initial components, intermediated compounds and a final glass, the temperature range should be carefully selected to ensure a complete interaction between the elements and keep the vapor pressure under a critical value to avoid the quartz ampoule explosion [23].

The glass state can be verified by XRD and/or electron microscopy analysis. X-ray microprobe, Auger Electron Spectroscopy (AES) and Infrared Spectroscopy are used to study the material homogeneity on the surface and within the bulk. Physicochemical parameters such as glass transition, crystallization and melting temperatures, density, microhardness, module of elasticity and so on are of great importance and should be determined [23, 30, 31]. From the electrochemical point of view, doping a chalcogenide glass with Ag above a certain threshold concentration can change it from semiconductor to fast ionic conductor, increasing its conductivity up to 8-10 orders of magnitude. High ionic conductivity and ion transport are necessary characteristics for achieving ion sensitivity of the sensor membranes [32, 33].

3. Theory for electrochemical sensor response

Electrochemical sensor response is a time-dependent phenomenon that depends on the membrane material and the solution under investigation. The electrical signal is produced by a sensing membrane when contacting a solution. The thermodynamic and kinetic properties of the membrane-solution interface play important roles in the signal generation. Modelling the sensor response serves two roles. The first one, centered on basic principles and simple mathematical equations, supports sensor users in applications and quantitative measurements. The second is to model the sensor response with advanced mathematical equations based on electrochemical theory to provide a fundamental understanding of the response [34] and to map electric potential and ion concentration changes in space and time, which could be helpful for the development of sensor membranes.

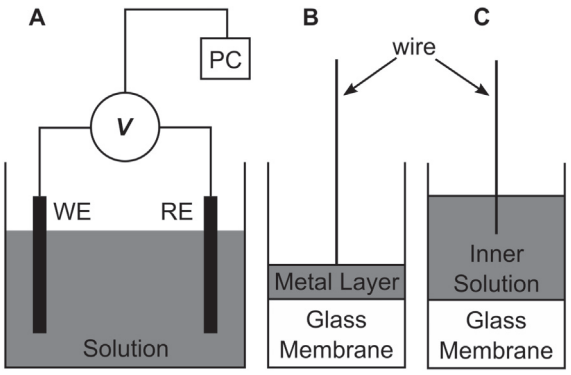

Fig. 1. (A) Scheme of an ISE operation, (B) solid-contact ISE and (C) ISE with inner liquid contact. RE = Reference Electrode, WE = Working Electrode.

In the next subsections, some principles and mathematical models will be discussed in different levels of details and complexity. The models assume that: (i) the sensors are under open-circuit conditions in an electrochemical cell that is consisted of two electrodes, an ISE and a reference electrode (RE), separated by an electrolyte, the solution under investigation; (ii) The electrodes are connected to a high impedance voltmeter as shown in Fig. 1A; (iii) The sensor scheme is sample/ion-sensitive membrane/internal contact (e.g. solution, gel, solid contact) represented by the schemes in Fig. 1B and C. As a start, the Nernst equation is presented. It describes oxidation-reduction processes and serves as a basic model for the sensor response. Moreover, it is a background for the classical models, which avoid mathematical, numerical and computational difficulties stemmed from solving nonlinear equations inherent to advanced models. Classical models are easier to comprehend. However, the use of advanced models is the only way to achieve a fundamental understanding of a sensor response [34].

3.1. The Nernst equation

The Nernst equation indicates that the reduction potential of an electrochemical reaction depends on the standard electrode potential, temperature, and activities of the chemical species undergoing reduction and oxidation. In a reversible electrochemical cell, the Gibbs energy change under non-standard conditions can be related to the standard Gibbs energy change by

$$\Delta G = \Delta G^{\circ} + RT \ln\left(\frac{a_p}{a_r}\right). \quad (1)$$

Here ΔG is the Gibbs free energy or the chemical potential variation of the solution, ΔG° the Gibbs free energy under standard condition, R is the universal gas constant, T the absolute temperature, a_p is the activity of the products, and a_r is the activity of the reagents. The relationship between free energy and cell potential is defined by

$$-\Delta G = zFE, \quad (2)$$

where z is the ions charge, F is the Faraday constant, and E is the electric potential. Substituting Eq. (1) into Eq. (2), we have