



Rational design of all-solid-state ion-selective electrodes and reference electrodes



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ABSTRACT

Potentiometric sensing, which requires the use of ion-selective electrodes (ISEs) and reference electrodes, is used to determine electrochemically the concentration of target ions in a variety of chemical environments. In view of the need for more affordable and portable analytical devices with small sample volumes, all-solid-state ISEs and reference electrodes, in which a solid contact is used as ion-to-electron transducer, are highly desirable. This review describes how all-solid-state ISEs and reference electrodes function and presents important aspects that should be considered when designing such sensors for specific applications. Approaches to improving reproducibility, the stability of the emf response, lowering detection limits, and novel sensor designs are discussed along with specific examples from the recent literature. Emphasis is placed on the ion-to-electron transduction mechanism and the development of new solid contact materials, with a particular view to miniaturized ion-sensing devices with low cost and calibration-free sensing.

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1. Introduction

Ion-selective electrodes (ISEs) are electrochemical ion sensors that convert the activity of a target ion into an electrical potential as the measurable signal. In potentiometry, they are coupled with reference electrodes and used under near-zero current conditions. Over the past half-century, ISEs have evolved into well-established, routine analytical tools, with sensors for more than 60 analytes, and

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they are widely used in various fields, including clinical analysis, environmental analysis, physiology, and process control [1–6].

Conventional ISEs have several limitations that need to be overcome to meet the demand for portable analytical devices with small sample volumes, easy maintenance, simple operation, and low cost. These ISEs contain liquid contacts (typically referred to as inner filling solutions) that separate the sensing membrane from the inner reference element. As a result, they are sensitive to evaporation of these inner filling solutions and changes in the sample temperature and pressure. Moreover, osmotic pressure originating from differences in the ionic strength of samples and the inner filling solution result in net water transport into or out of the inner filling solution, which can lead to large volume changes and delamination of the sensing membrane [7]. Therefore, conventional ISEs have to be well maintained and used with care. Moreover, it is difficult to reduce the volume of the liquid contact to a value much lower than the milliliter level, which poses challenges for sensor miniaturization. Although micropipette-based microelectrodes with sensing areas less than 100 nm have been used for a long time [8], their fabrication requires a delicate process, and they are fragile, which limits their application. Next-generation devices require robust, miniaturized ion-sensing systems that can be integrated with electronic control, measuring, and data acquisition units for acquiring complex biological and chemical information. Thus, it is highly desirable to eliminate the cumbersome liquid contacts by replacing conventional electrodes with all-solid-state potentiometric sensors. In all-solid-state ISEs and reference electrodes, a solid contact is formed between the sensing membrane and an electron-conducting substrate to replace the liquid contact, serving as an ion-to-electron transducer. Note that all-solid-state ISEs are not to be confused with ISEs that comprise a solid-state ion-selective membrane, an expression that has historically been reserved for ion-selective membranes prepared from inorganic materials such as LaF_3 or Ag_2S [9]. It has been more than four decades since the first all-solid-state electrode was proposed, and all-solid-state ISEs and reference electrodes are generally considered to be the future of potentiometric sensors. However, major challenges still remain [10–12]. In this review, we limit our discussions to all-solid-state electrodes with polymeric sensing membranes.

In 1970, Hirata and Date proposed an all-solid-state Cu^{2+} ISE that contained a Pt wire coated with a Cu_2S -impregnated silicone rubber sensing membrane [13]. This was followed by work from Cattrall et al., who used a Pt wire coated with a Ca^{2+} ionophore-doped polymeric membrane, thereby constructing the first coated-wire electrode comprising an ionophore [14]. The resulting Ca^{2+} -ISE is generally considered to be the ancestor of present-day ionophore-based all-solid-state ISEs. As Nikolskii and Materova summarized three decades ago, three conditions need to be fulfilled for stable and reliable response of all-solid-state ISEs: (1) reversible transitions from ionic to electronic conduction and vice versa, (2) ideally nonpolarizable interfaces with high exchange current densities, and (3) absence of side reactions [15].

Although the design of the coated-wire electrode was simple, it was not reliable due to the interrupted ion-to-electron transduction at the 'blocked' solid contact/membrane interface [14]. No charged species could transfer between the membrane and the metal contact, resulting in a purely capacitive interface to the metal wire. Because of the small interfacial contact area, coated-wire electrodes easily pick up noise. They also exhibit large signal drifts, which may be due to both residual currents passing through the membrane but also the formation of an aqueous layer. It was hypothesized based on the observation of O_2 interference that an $\text{O}_2/\text{H}_2\text{O}$ half-cell can form at the metal/membrane interface [16,17], but it is very likely that this $\text{O}_2/\text{H}_2\text{O}$ half-cell is not reversible. Various solid-contact sensors with improved designs were proposed in the literature but many of them still do not match the performance of

conventional electrodes, and quality control criteria for all-solid-state ISEs were not critically discussed until recently [7,18]. Yet, through persistent efforts made by the community, the performance of all-solid-state electrodes has been dramatically improved, with significant advances brought about by the introduction of novel solid-contact materials, the understanding of the transport and accumulation of water in membranes, the control of transmembrane ion fluxes, and the development of novel ion-sensing platforms. Also, complementary to zero-current potentiometry, a new family of all-solid-state ion sensors has emerged that takes advantage of dynamic electrochemical instrumental control techniques [19], such as ion transfer voltammetry [20,21] and chronopotentiometry [22,23]. Regardless of the mode in which these all-solid-state sensors are operated, their electrochemical performance is highly dependent on the solid contact that is employed. Among all the solid contacts, conducting polymers and high-surface-area nanostructured materials are the most studied candidates for commercial all-solid-state potentiometric sensors and have been reviewed previously [24,25].

This review provides an overview of how potentiometric all-solid-state ISEs and reference electrodes function and gives guidance on how to improve their performance. Section 2 describes the ion-to-electron transduction mechanism of all-solid-state ISEs and reference electrodes, with an emphasis on the interface between the solid contact and the sensing membrane. Section 3 discusses the design of high-performance, all-solid-state potentiometric sensors for specific applications, with a focus on improving the reproducibility in order to achieve calibration-free sensors (Section 3.1), enhancing potential stability for accurate measurements (Section 3.2), and lowering detection limits for trace-level analysis (Section 3.3). Section 4 presents recent research on the design of simple and miniaturized potentiometric ion-sensing devices, highlighting disposable and paper-based ion sensors. This review ends with our own perspective of the field. The review focuses primarily on the design of the solid contact and its impact on the performance of all-solid-state ISEs and reference electrodes, and it is aimed mainly at readers who have some basic knowledge of potentiometry. For those readers new to the field, reviews on potentiometric ion sensors [1–6] can serve as introductory reading material. Those interested in non-potentiometric, dynamic control techniques are referred to another recent review [19].

2. Transduction mechanism

Figure 1 represents a typical all-solid-state potentiometric cell that comprises an all-solid-state ISE, an all-solid-state reference electrode, and a high impedance voltmeter to ensure near-zero current conditions. The measured electromotive force (emf) is the difference in electrical potential between the connecting leads (e.g., Cu wires) of the ISE and of the reference electrode. As illustrated by the electrical potential profile in Fig. 1, the measured emf is equal to the sum of all the interfacial potentials within the cell. In an ideally currentless system, there are no potential drops through bulk phases since there is no Ohmic drop, and the only sample-dependent potential is the interfacial potential at the sample/ion-selective membrane interface.

2.1. Transduction mechanism of all-solid-state ISEs

For any ISE, the input signal is the activity of a specific ion and the output is an electrical potential. This part of the overall signal transduction occurs at the interface of the sample and the ion-selective electrode membrane [1,26,27]. Behind that interface, i.e., within the ion-selective membrane, the charge carriers that are free to move are still ions. However, at some point between this membrane and the connecting lead occurs the second half of the overall

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