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Review

A review of screen-printed silver/silver chloride (Ag/AgCl) reference electrodes potentially suitable for environmental potentiometric sensors

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ABSTRACT

The screen-printed (SP), reference electrode (RE) has been shown to be a crucial element of potentiometric sensors but it is also the stumbling block for reliable and accurate SP sensors. The easiest, most common and most environmentally friendly, type of RE is the Silver/Silver Chloride (Ag/AgCl) RE. Unfortunately, until now the only reliable RE of this kind is the conventional, liquid or gel-filled type. However, for most environmental and soil applications the use of the conventional RE is not an option, which raises the demand for a robust, rugged and low-cost version to replace the conventional RE. This paper presents a review of the various attempts to produce reliable, SP, Ag/AgCl REs, and explain why almost all of them never reach the commercialisation stage. The paper provides an overview of the main challenges that need to be overcome, details of the electrode's construction, an analytical comparison of their performance in terms of chloride susceptibility, cross-sensitivity and lifetime, and their suitability in different applications depending on their performance characteristics.

Contents

1. Introduction

The continuous increase in legislation concerning health and safety, food and soil quality, climate change and environmental protection in the last two decades has raised the need for the development of new low-cost, chemical sensors suitable for use in online quality monitoring [1–5]. The scientific community has reacted dynamically to this challenge, as is evident from the increased num-

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ber of publications and allocation of time in sensor conferences and chemical sensor research [6–9]. In particular, electrochemical, ion-selective electrodes (ISE) have received major interest featuring novel sensing structures for various chemical parameters, which have been developed using widely disparate technologies ranging from fibre optics to micromachining [10–12]. Mostly electrodes of the second kind are used as Reference Electrodes (REs). Ag/AgCl REs are widely used due to their environmental compatibility. The Mercury/Mercury Chloride (Hg/Hg_2Cl_2), calomel electrode, has advantages with regard to potential stability and light inertness, but has an upper temperature restriction of approx. 80 °C. Furthermore, mercury presents several environmental hazards and its use is generally restricted to laboratory based tests. The calomel electrode is still commercially available, in comparison to the Thallium(Mercury)/Thallium Chloride (Tl(Hg)/TlCl), the Thalamid^{TM} electrode, which has been banned because of its toxicity [11]. An overview of the classical RE was given by Ives and Janz [13] while Kaden and Vonau [14] reported on electrochemical reference electrodes specifically for pH measurements and discussed advantages and drawbacks of single reference electrodes.

The tendency to develop miniaturised electrochemical systems such as lab-on-chip and to make use of mass production, directs towards REs in a planar embodiment. Although a number of scientific approaches have been reported, with none of them proving successful for all the requirements, the traditional rod-shaped RE is still commercially dominant [11]. Several attempts have however been reported on the development of reference electrodes for ISFETs and silicon based substrates [15–20]. This paper provides a brief description of the construction and operation of the conventional Ag/AgCl RE and a comprehensive review on the advancements of screen-printed Ag/AgCl REs, not necessarily used for potentiometric sensors but that are suitable for implementation in potentiometric sensors. A combination of Thick-Film (TF) technology and electrochemical methods embraces the requirements of these devices by providing cost competitive solutions for the fabrication of compact, rugged and robust systems. TF technology offers several alternative solutions and allows flexible design with a wide range of materials, mass production and cost reduction through economies of scale [5–8,21–26]. Other approaches such as ink-jet printing, thin-film technology, spraying, heat sealing, conducting polymers, semi-permeable membranes and microfabrication have been reported but have yet to achieve the same level of reliability as the conventional silver/silver chloride (Ag/AgCl) RE [27–34]. Several reviews have been published on general techniques with all-solid-state REs with satisfactory results but elevated cost [35,36]. It is our belief that TF technology may be able to overcome some problems of the conventional REs. There are many standard types of REs which most commonly include some 'wet chemistry' in the form of an electrolyte solution that is required for their operation. Implementing such electrolyte regions within new sensor designs as an in-line manufacturing step has been proven to be a stumbling block for more than a decade [15,37–41].

Generally, ISEs are used in potentiometric sensors which are made up of an ISE and a reference electrode (RE) pair. Usually, the potential difference between the two electrodes is proportional to the parameter to be measured [21,42–44]. Publications are mostly focused on improving the performance of the ISE or inventing new and improved ISEs but it is recognised that the real challenge of a solid state potentiometric sensor is the RE [4]. This is the most essential element in any potentiometric measurement system since the response of any other type of ISE is meaningless without a reference to compare against [11,45,46]. From the point of electrochemistry, the thermodynamically defined, classical reference electrode is a special electrode (also called half-cell) featuring a reversible electrode reaction and a stable electrolytic contact to the analyte. That reversible reaction results in a distinct and stable electrode potential [47–49]. Although scientific interest is primarily dedicated to ISEs, improvements to the reference electrode have also been reported [11,50–53].

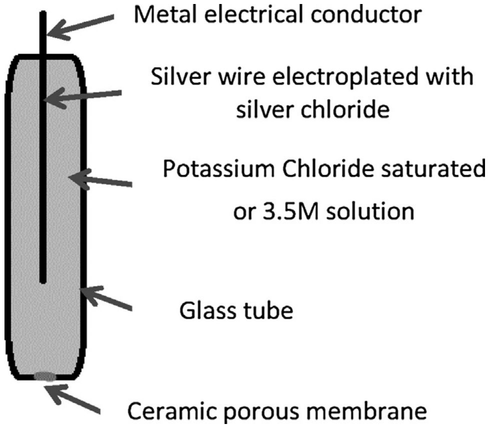

Fig. 1. Typical construction of a silver-silver chloride reference electrode [1].

2. Conventional Ag/AgCl reference electrode

2.1. Construction of the conventional Ag/AgCl reference electrode

The most common type of silver-silver halide electrode is the Ag/AgCl due to the availability of silver chloride and the use of potassium chloride as the electrolyte. The electrode is constructed using a silver wire, electroplated with silver chloride and then immersed into a 3.5 M or saturated potassium chloride (KCl) solution. The electrolyte is generally contained in a glass tube having a porous glass frit at the tip to allow ion exchange at the liquid-liquid junction. The conventional silver/silver chloride reference electrode has a relatively simple construction. A typical construction of such an electrode is shown in Fig. 1.

Potassium chloride is generally chosen as the electrolyte because both chloride and potassium ions have high ion mobilities of approximately equal value. This ensures a low-impedance path for ionic current between the internal and external test solution. The high ion mobilities improve the transient response characteristics of the whole reference electrode. The ratio between Ag and AgCl is an important parameter and according to [1] should ideally be approximately 4:1.

2.2. Operating principle of conventional Ag/AgCl reference electrode

The operating principle of the reference electrode is based on two simultaneous, reversible reactions on the surface of the electrode which is in contact with the solution [13]:

$$Ag^{+}_{(aq)} + e^{-} \rightleftharpoons Ag_{(s)} \quad (1)$$

$$Ag^{+}_{(aq)} + Cl^{-}(aq) \rightleftharpoons AgCl_{(s)} \quad (2)$$

The electrode potential is defined by the Nernst equation, which is modified for this specific electrode for moderate chloride concentrations as [13]:

$$E = E^{o} - 2.303\frac{RT}{nF}\log\left(\left[Cl^{-}\right]\right) \quad (3)$$

where E^0 is the electrode standard potential (a constant) (V), n is the number of electrons involved in the electrochemical reaction, R is the molar gas constant ($J\,K^{-1}\,mol^{-1}$), T is the absolute temperature (K), F is the Faraday constant ($C\,mol^{-1}$), $[Cl^{-}]$ represents the