



A reference electrode based on polyvinyl butyral (PVB) polymer for decentralized chemical measurements



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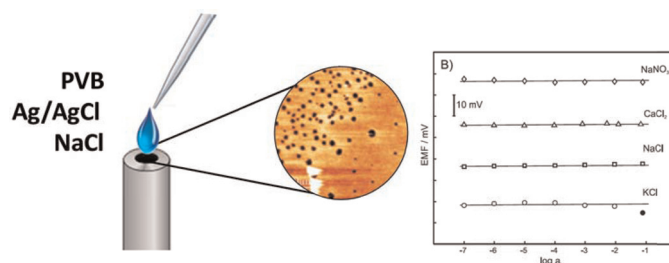
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HIGHLIGHTS

- A disposable solid-contact reference electrode for potentiometry is presented.
- The device shows unsensitivity to most ions, redox potential and light.
- Low-cost and good stability, ideal to build disposable potentiometric sensors.
- Nanopores formed in the membrane control the flux of ions with the solution.

GRAPHICAL ABSTRACT



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ABSTRACT

A new solid-state reference electrode using a polymeric membrane of polyvinyl butyral (PVB), Ag/AgCl and NaCl to be used in decentralized chemical measurements is presented. The electrode is made by drop-casting the membrane cocktail onto a glassy carbon (GC) substrate. A stable potential (less than 1 mV dec^{-1}) over a wide range of concentrations for the several chemical species tested is obtained. No significant influence to changes in redox potential, light and pH are observed. The response of this novel electrode shows good correlation when compared with a conventional double-junction reference electrode. Also good long-term stability ($90 \pm 33 \mu\text{V/h}$) and a lifetime of approximately 4 months are obtained. Aspects related to the working mechanisms are discussed. Atomic Force Microscopy (AFM) studies reveal the presence of nanopores and channels on the surface, and electrochemical impedance spectroscopy (EIS) of optimized electrodes show low bulk resistances, usually in the $\text{k}\Omega$ range, suggesting that a nanoporous polymeric structure is formed in the interface with the solution. Future applications of this electrode as a disposable device for decentralized measurements are discussed. Examples of the utilization on wearable substrates (tattoos, fabrics, etc) are provided.

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1. Introduction

Because of the crucial role that the reference electrode (RE) plays in any electroanalytical technique, its performance is subject to very stringent conditions, which include the insensitivity to

changes in ionic concentration, stability and reproducibility [1] of the response. Since the Ag/AgCl RE fulfills these requirements, it has become almost a universal approach. Typical arrangements of this RE require a liquid reservoir with a positive hydrostatic pressure of the inner electrolyte, which provides a uni-directional flow of an inner solution through a liquid junction in order to keep a high and constant concentration of electrolyte at the solution interface. While extremely effective to provide a stable potential, this arrangement is not free from practical limitations in terms of

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electrode miniaturization, position, maintenance, form factors, etc. In summary, the traditional Ag/AgCl RE is a powerful but delicate device that requires a careful control of the working conditions. This is a serious limitation in an increasingly growing number of situations where chemical measurements need to conduct outside an analytical lab. This is the case, for example, of mobile health devices for point-of-care or telehealth. Also, in the development of emerging technologies such as wearable and embedded electrochemical sensors, the lack of suitable RE is a serious roadblock.

Finding suitable solutions requires a trade-off between performance and practical parameters. For example, the long-term stability of the RE, very important in the lab-base approach, becomes less relevant when developing disposable sensors. In this case, a good short or medium-term performance is tolerable, providing that the cost is minimized. Similarly, versatile and adaptable approaches become paramount when building wearable and embedded sensors. For that reason, several approaches to minimize the hurdles of the inner solution, such as the use of solid polymers [2], solid KCl melt with a ceramic diaphragm [3], micro-fabricated liquid junctions [4], agarose gels containing KCl [5] and different types of heterogeneous membranes separating a KCl reservoir [6] reported during the last years do not fully manage to solve simultaneously the problems of performance, versatility and cost required.

These limitations have become evident in the development of compact and cost-effective potentiometric tools for decentralized chemical monitoring. Potentiometry, traditionally unbeatable in terms of robustness, simplicity, cost, and power consumption, has been further improved through the incorporation of solid-state technology [7–9] and more recently nanotechnology. Miniaturization of the sensors [10,11] and versatile screen-printed [12] and even paper-based [13] potentiometric sensors are now possible. The mass-production of chemical sensors, a traditional barrier for building chemical sensing networks [14], is now becoming possible. Evidently, none of these advantages can be fully exploited without a suitable reference system that can match similar benefits. For this reason, during the last years, significant efforts have been devoted to the development of solid-state technology for building miniaturized and cost-effective RE for potentiometric cells in decentralized settings.

Solid-state pseudo-reference electrodes using metal alloys and composite materials [15], and reference systems using aromatic polyurethane-based membranes [16], nanoporous platinum electrode in combination with a layer-by-layer polyelectrolyte junction [17] and the use of solid-state junctions based on carbon-fiber nanocomposite membranes by incorporating poly(methyl methacrylate) and carbon graphene stacked nanofibers [18] have been proposed. In general, the most promising approaches reported up to date make use the Ag/AgCl couple combined with some type of membrane that creates a high and constant chloride concentration. A solid-state RE using a vinyl ester resin doped with KCl [19] and the use of a layer-by-layer polymer coating have been reported [20]. Mamińska et al. [21] used a combination of a PVC membrane and an ionic liquid and Tymecki et al. [22] used a screen-printed insulator paste. These approaches show good performance, although they are not free from potential interferences caused either by lipophilic species or, in some case, by Ag⁺ ions in solution. A planar RE using a PVC membrane containing dispersed metallic Ag, AgCl and KCl and using a layer of a conducting polymer has been also reported [6]. Other polymers such as polyacrylate microspheres and polypyrrole microcapsules were also used to improve the stability of potential [6,23]. Despite of their benefits, issues such as the light sensitivity and the potential stability problems due to the formation of a water layer could not be fully addressed. Rius-Ruiz et al. took advantage of the use of single-wall carbon nanotubes as potentiometric transducers [24,25] in order to incorporate them into reference system and using polyacrylate

membrane to encapsulate the Ag/AgCl/Cl⁻ system [26,27]. The planar RE electrodes developed with this approach show good stability, response time and light and redox insensitivity. The main drawbacks of this approach are the need for extensive conditioning of the membrane – which can be partly due to the use of acrylate membranes – and the irreproducibility of the deposition process. Very recently a new analytical-quality all-solid-state reference membrane was developed by using polyvinyl acetate with KCl, leading to develop a reference electrode with reduced salt leakage [28]. All these works reflect the strong interest and growing need to search for alternative solutions.

Solid polymer electrolytes (SPE) using polyvinyl butyral (PVB) polymeric membranes have become an attractive topic of research in the field of energy generation and storage [29,30]. PVB is a low-cost and rugged polymeric material with a wide range of industrial applications. Microporous structures of PVB are useful in ultrafiltration membranes [31], whose morphology can be controlled to yield from nanofibers [32] (with pores ranging from 50 to 200 nm) to honeycomb structures [33]. PVB is soluble in polar solvents, which favors the incorporation of polar substances and ionic salts that increase the ionic conductivity of the polymer [34]. Last, but not least, the higher polarity of PVB (when compared to, for example, PVC) makes it less prone to fouling caused by non-polar substances [35].

PVB has been used during the last decade for the development of immunosensors [36–40], but its use for potentiometric solid-state sensors has not been yet explored. In this work, a solid-state RE using a PVB membrane is presented. A PVB solution in methanol where Ag, AgCl and NaCl are dispersed is used as a membrane cocktail that is drop-casted on a glassy carbon substrate. This electrode shows a stable potential and insensitivity to some common ions over a wide range of concentrations. Very good short and medium-term stability is obtained, which is ideal for disposable sensors. The experimental evidence suggests that the mechanism is linked to the formation of nanopores on the surface of the PVB membrane, which control the flow of NaCl. Practical considerations regarding future applications of this electrode are discussed.

2. Experimental

2.1. Reagents

Analytical grade salts and reagents were purchased from Sigma–Aldrich (Germany). AgNO₃ (99.5% purity) was purchased from Riedel-de Haën (Honeywell International Inc., Germany). Polyvinyl butyral (PVB) B-98 from Quimidroga S.A. (Barcelona, Spain). Analytical grade anhydrous methanol was purchased from Fluka AG (Buchs, Switzerland). Doubly distilled deionized water (18.1 MΩ cm⁻¹ resistance) was produced by a Milli-Q water system (Millipore Corporation, Bedford, MA) and was used for all the experiments.

2.2. Materials

Glassy Carbon (GC) (Sigradur-G, Germany) rods (length: 4 cm, diameter: 0.3 cm) were introduced into a Teflon body (length: 2 cm, diameter: 0.6 cm). One end of the GC was first polished with an abrasive paper (Carbimet 600/P1200, Buehler, USA) and afterwards with alumina of different grain-size (1 and 0.03 μm, Buehler, USA).

2.3. Instrumentation and characterization of the electrodes

Electromotive forces (EMF) were measured at room temperature (24 ± 4 °C) using a 16-channel Lawson Laboratories, Inc. (Malvern, USA) high-impedance potentiometer. Measurements were recorded against a double-junction Ag/AgCl/KCl (3 M)

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