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Research paper

Ready-to-use single-strip paper based sensor for multiplex ion detection

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ABSTRACT

Ion-selective electrodes (ISEs) are an efficient and versatile tool for ion detection. However, portability and applicability for field applications are often limited by the need of a conditioning step, and high cost of the needed bulky reference electrode. Herein, the traditional conditioning protocol of ISEs has been eliminated and a paper-based solid-contact ISE (PBSC-ISE) has been integrated with a paper-based solid-contact reference electrode (PBSC-RE) in a single strip format for on-site analysis. The PBSC-RE is based on the copolymer methyl methacrylate-co-decyl methacrylate (MMA-DMA) (support matrix), combined with ionic liquids (ILs) to create and maintain a stable potential that is un-affected by a change in ionic activity. This single-strip ready-to-use sensor yields a Nernstian response towards Na^+ , K^+ , and I^- ions with submicromolar limits of detection, and is able to be used for multiplex analysis.

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1. Introduction

With increasing demand for portable devices, paper-based sensors have become highly attractive due to their thin, lightweight, low-cost and flexible nature [1]. Since paper is made up of cellulose fibers and various pore sizes are largely available, a wide array of applications are accessible [1]. The versatility of paper-based sensors can be augmented by integrating them with ion-selective electrodes (ISEs), specifically polymer-based ISEs, as an analytical platform for ion detection. ISEs have gained momentum as an analysis tool, due to their versatility, high sensitivity and selectivity for ion detection *in situ* [2,3]. Therefore, paper-based solid-contact ISEs (PBSC-ISEs) are the ideal candidate for fieldwork applications, including environmental [2], biological [4] and food analysis [5]. A polymer-based ISE is composed of an ionophore, to render selectivity to the membrane by forming a stable complex with the analyte of interest; an ion-exchanger, to provide electroneutrality and ensure permselectivity; and a polymer matrix to provide the support and mechanical functionality to the membrane. The ISEs response is dictated by the phase boundary potential (E_{PB}) (Eq. (1)) wherein $a_1(aq)$ and $a_1(org)$ are the activities of the primary ion (I^{z+}) of charge z in aqueous and organic phases, respectively. Furthermore, E^0 , R , T , and F are the standard potential, universal gas

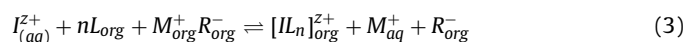
constant, absolute temperature and Faraday constant, respectively [6].

$$E_{PB} = E^0 + \frac{RT}{z_1 F} \ln \frac{a_{I(aq)}}{a_{I(org)}} \quad (1)$$

In order to exhibit a Nernstian response, the activity of the primary ions in the bulk of the organic phase must remain constant and independent of the sample. Therefore, the E_{PB} can be reduced to the well-established Nernst Equation (Eq. (2))

$$E_{PB} = E^0 + \frac{RT}{z_1 F} \ln a_{I(aq)} \quad (2)$$

Furthermore, the ISE must be exposed to the primary ion of interest, to allow the ionophore to chelate the primary ion. This process has been regarded as the conditioning protocols of ISEs. For decades, traditional conditioning protocols have involved exposing the ISE to a high concentration of the ion of interest, a process that can take between 12–72 h [7]. For a cation-selective membrane, the established equilibrium process can be represented by the equation below:

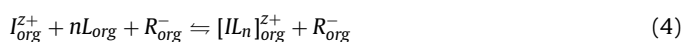


Where, L is the ligand that forms the ion-ionophore complex with primary ion I^{z+} , with stoichiometry n . $M_{org}^+ R_{org}^-$ is the ion-exchanger, composed of a lipophilic anion R^- and a cation M^+ . The cation will partition to the aqueous phase and exchange with the primary ion I^{z+} . The lipophilic anion will remain in the membrane to retain

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electroneutrality and allow permselectivity [6]. This lengthy protocol prevents practical and efficient applications of these sensors. Therefore, new efforts in creating a condition-free ISE are required. Recently, the Buhlmann group used non-conditioned ISEs in a paper substrate. However, a liquid-junction platform was used for both the ISE and RE, and a new sensor must be used for each point of a calibration curve [8]. Herein, to circumvent the conditioning step, addition of the ion of interest directly into the membrane cocktail was done as described in Rich et al. [6] and was optimized for its integration to a PBSC platform. Consequently, the primary ion, I^{z+} is already present in the membrane and is able to form the ion-ionophore complex according to the equilibrium below:



In order to conduct potentiometric measurements, the PBSC-ISE must work in conjunction with a reference electrode. Commonly used reference electrodes are bulky and fragile, preventing their use for in-field applications. In order to overcome this limitation, recent research has proposed various methods to develop an alternative reference electrode that are insensitive to changes in electrolyte concentration [9]. Some approaches include references electrodes based on polyurethanes, silicon rubber, polyvinyl chloride and acrylate membrane, yet all of these approaches require soaking the reference electrode in electrolytes solutions prior to use [10–13]. In addition, various lipophilic additives such as ETH 500 [14] and ionic liquids (ILs) [15–17] were proposed. From these methods, employing ILs, appeared to be the most promising option as the phase boundary potential of the reference electrode is defined by slow partitioning of the IL to the aqueous phase [16,18]. Therefore, ILs are excellent candidates towards a stable reference electrode. It is crucial to assure equipartition of the IL to the aqueous phase in order to avoid ion exchange effects. If an ion of the IL exchanges with an ion of the bulk solution of equal charge, the membrane will render a response to that ion and thus will be unable to function as a reference electrode [15]. Previous research showed that 1-Ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)amide $[C_2mim]^+ [NTF_2]^-$ was the most suitable IL to be used for the development of a reference electrode [15]. Its response in a PVC/IL membrane exhibited a potential change of less than 10 mV for a variety of ions, including, Li^+ , Na^+ , K^+ , Pb^{2+} , over a wide concentration range after conditioning in 1×10^{-3} M KCl solution. Lastly, $[C_2mim]^+ [NTF_2]^-$ based reference electrodes exhibit a great working pH range of 2.7–11.4. The effectiveness of $[C_2mim]^+ [NTF_2]^-$ is likely due to similar mobility of the anion with respect to the cation based on Hildebrand's solubility parameters [19]. Therefore, we propose to develop a sensor that incorporates a PBSC-ISE and a paper-based solid-contact reference electrode (PBSC-RE), integrated in a single-strip style for multiplex analysis, and which does not require a conditioning step, see Fig. S1. In this work, the PBSC-RE will incorporate the copolymer methyl methacrylate-co-decyl methacrylate (MMA-DMA) (support matrix), combined with the $[C_2mim]^+ [NTF_2]^-$ IL to create and maintain a stable potential that is unaffected by an increase in ionic activity and will not require a conditioning step. The chosen matrix (MMA-DMA) does not require the use of a plasticizer, resulting in an extended lifetime. The proposed system could potentially be used to monitor Na^+ , K^+ and I^- levels *in vitro*. In turn, aiding in early prognosis of hyponatremia, hypokalemia and iodine deficiency which can lead to goiter, prior to reaching a critical state. A ready-to-use PBSC-ISE sensing platform would not need highly trained personnel to implement traditional conditioning protocols. The PBSC-ISE platform would also enable cost-effective *on-site* analysis, and its intrinsic flexibility due to a paper-based substrate, would increase durability and lower risk of damage to the sensor due to mishandling.

2. Experimental section

Reagents and Materials. 4-tertbutylcalix[4]arene-tetracetic acid tetraethyl ester (sodium ionophore X, NaIX), sodium tetrakis [3,5-bis-(trifluoromethyl)phenyl]borate (NaTFPB), valinomycin (potassium ionophore I), potassium tetrakis [3,5-bis-(trifluoromethyl)phenyl]borate (KTFPB), bis-(2-ethylhexylsebacate) (DOS), tridodecylmethylammonium nitrate (TDMANO₃), all Selectophore grade, were obtained from Sigma-Aldrich (Milwaukee, WI). [9]-Mercuracarborand-3 (MC3) was synthesized in-house [20] as previously described. Potassium chloride (KCl), sodium chloride (NaCl), calcium chloride dihydrate (CaCl₂·2H₂O), lithium chloride (LiCl), potassium iodide (KI), sodium iodide (NaI) and sodium nitrate (NaNO₃) ACS reagent, ≥99.0%, poly-(3-octylthiophene-2,5-diyl) (POT) and 2, 2' azo-bis(isobutyronitrile) (AIBN, 98% purity), high molecular weight polyvinyl chloride (PVC) and tetrahydrofuran were all obtained from Sigma-Aldrich (Milwaukee, WI). Methyl methacrylate (99.5% purity) and *n*-decyl methacrylate (99% purity) were obtained from Polysciences (Warrington, PA). Single-walled carbon nanotubes (SWCNTs) of 99% purity were obtained from Cheap Tubes Inc (Grafton, VT). The methyl methacrylate-co-decyl methacrylate (MMA:DMA; 42:58) copolymer was synthesized in house following procedure in Qin et al. [21] and characterized as in Mensah, et al. [22] Methylene chloride, chloroform, ethyl acetate, 1,4-dioxane, and qualitative filter paper (Whatman catalog no. 1001090) were obtained from Fisher (FairLawn, NJ). 1-Ethyl-3-methylimidazolium $[C_2mim]^+$ Bis(trifluoromethane sulfonyl)amide $[NTF_2]^-$ IL was acquired from Strem Chemicals Inc (Newburyport, MA). All solutions were prepared using deionized water purified by a Millipore Milli-Q (Billerica, MA).

2.1. Preparation of the paper-based substrate

The paper-based substrates were developed as described in Mensah et al. [20] Briefly, a 3.0 mg/mL SWCNT suspension was prepared and coated onto a 6.5 cm × 5.5 cm qualitative filter paper with a conventional paintbrush. Six coats were applied and allowed to dry at room temperature for 10 min, followed by 20 min in an oven at 60 °C, after each coating. The conductivity was measured using a source measurement unit (Keithley Source-Meter model 2400, Cleveland, OH). At the bottom of each filter paper sheet, a 0.5 cm diameter orifice was exposed and sputtered with gold (Denton Vacuum LLC Desk IV, Moorestown, NJ). At the gold sputtered point, 60 μL of a 25 mM (with respect to the monomer) solution of POT dissolved in methylene chloride (DCM) was drop-casted, 10 μL at a time, at 5 min intervals. The POT was allowed to dry overnight. The filter paper SWCNT substrate was then cut into 1.0 cm × 5.5 cm strips and each sensor were partially covered in a mask of non-permeable D-Wrap Blue Polyester Tape.

2.2. Preparation of Condition-Free PBSC

Na^+ , K^+ , and I^- ISEs. The Na^+ cocktail was prepared by adding 5 mmol/kg of NaTFPB, 10 mmol/kg of NaIX, (66.6 w%) DOS and (33.3 w%) PVC, dissolved in 1 mL of THF and vortexed for 1 h. The K^+ cocktail was composed of 5 mmol/kg of KTFPB, 10 mmol/kg of potassium ionophore I, (66.6 w%) DOS and (33.3 w%) PVC. The I^- cocktail contained 1.0 mmol/kg of MC3, 0.75 mmol/kg of TDMANO₃ and 1.8 μL of 0.1 M NaI aqueous solution to circumvent the conditioning step in a total mass of 240 mg. Control membranes were also prepared following the composition as described in Rich et al. Briefly, sodium and potassium control membranes replaced the ion exchanger to KTFPB and NaTFPB, respectively. In the case of the iodide control membrane, no NaI solution was added. However, the effect of hydration of the membrane upon addition of an aqueous solution

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