

A Solid Contact And An Ion-Selective Electrode

References to Related Application

- 5 This application claims priority to Singapore application number 10202250871E filed with the Intellectual Property Office of Singapore on 31 August 2022, the contents of which are hereby incorporated by reference.

Technical Field

- 10 The present invention generally relates to a method of treating a solid contact and the solid contact obtained from the method. The present invention further relates to a method of preparing an ion-selective electrode and the ion-selective electrode prepared by the method. The present invention further relates to a method of sensing an ion using the ion-selective electrode.

Background Art

- 15 Solid-contact ion-selective electrodes (sc-ISEs) have been widely studied in recent years and have seen applications in medicine, wearables, environmental monitoring, and food production due to their portability, low cost, and quick analysis time. Typically, the sc-ISEs consist of three main layers: electrode, solid-contact (also known as ion-to-electron transduction layer), and ion-selective membrane (ISM).
- 20 In particular, the solid-contact has been a frequent target for modifications to improve the performance of the sc-ISEs. Several materials have been experimented as the solid-contact, such as molecular redox couples, conductive polymers (CPs), carbon nanotubes, graphene and other conductive nanomaterials. CPs are the most commonly used material as they are inexpensive, possess good electrical and optical
- 25 properties, and their conductivity can be readily tuned via structural modifications or doping with ions. Of these, poly(3,4-ethylenedioxythiophene) (PEDOT) has been the foundation of numerous promising sc-ISEs: it is preferred over other CPs such as poly(3-octylthiophene), polypyrrole or polyaniline due to their sensitivity to light, oxidation and pH respectively.
- 30 Conventionally, PEDOT is predominantly used as a solid-contact in sc-ISEs in the form of PEDOT:PSS, a polymer blend with cationic PEDOT and anionic polystyrene sulfonate (PSS), due to its high stability, transparency, conductivity, flexibility and solution-processability from aqueous dispersions. However, while PEDOT:PSS has been widely demonstrated in cation-selective electrodes such as potassium and
- 35 calcium, it is ineffective for sensing anions. While the excess of bulky, immobile PSS dopant aids in cationic potentiometric response, it prohibits the movement of analyte anions, thus acting as an impediment to anion sensing. Additionally, the hydrophilic nature of PSS promotes the formation of a water layer, which may cause sensor drift.

There have been a few reports of electropolymerised PEDOT as CP for other conventional potentiometric anion-selective sc-ISEs: In one report, PEDOT-*Cl* was used as the solid-contact for chloride and acetate sc-ISEs, while in another report, hydrophobic PEDOT-C₁₄ was doped with tetrakis(penta-fluorophenyl)borate (TFPB) for nitrate sensing. In these examples, while the sc-ISEs showed near-Nernstian sensitivity, selectivity and lifespan performances were not ideal. Moreover, electropolymerisation is a tedious fabrication process.

PEDOT-polyethylene glycol (PEDOT:PEG) and its hybrids are flexible, conductive materials that have been utilised in bioelectronics due to their biocompatibility and stability. It is typically doped with small, mobile anions such as perchlorate (ClO_4^-), which makes it suitable for anion sensing. However, the ion selectivity of typical ion-selective electrodes based on PEDOT:PEG is not sufficiently high.

Accordingly, there is a need for a method of treating a solid contact and a method of preparing an ion-selective electrode that ameliorate one or more disadvantages mentioned above.

Summary

In one aspect, there is provided a method of treating a solid contact for sensing an ion, comprising the step of immersing the solid contact in an aqueous medium that is free from perchlorate, wherein the solid contact is a conducting polymer.

In another aspect, there is provided a solid contact obtained from the method as described herein.

In another aspect, there is provided a method of preparing an ion-selective electrode for sensing an ion, comprising the steps of:

(a) forming a layer of solid contact on an electrode, wherein the solid contact is derived from poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(ethyleneglycol) (PEG);

(b) immersing the layer of solid contact and the electrode in an aqueous medium that is free from perchlorate; and

(c) depositing an ion-selective membrane on the layer of solid contact.

Advantageously, the method is a streamlined approach that can be used to prepare both cation solid contact ion-selective electrodes and anion solid contact ion-selective electrodes.

Further advantageously, the method may be regarded as solution processing and the ion-selective electrode prepared by the method may be regarded as a solution-processable ion-selective electrode. Solution processing is simple to operate and readily scalable compared to conventional methods such as those that require electropolymerisation.

Still further advantageously, the method does not require expensive materials or facilities and is simple to perform, thus being capable of mass production of the ion-selective electrode for sensing the ion.

5 Still further advantageously, the method is highly adaptable to different types of substrates ranging from rigid substrates to flexible/stretchable substrates.

Still further advantageously, where a flexible/stretchable substrate is used, the method allows for production of flexible solid contact ion-selective electrodes using a solution processing, which enables customisation to cater for specificity.

10 Still further advantageously, the solid contact derived from PEDOT:PEG has a better hydrophobicity compared with conventional solid contacts (such as solid contacts derived from PEDOT and polystyrene sulfonate). The improved hydrophobicity may reduce sensor drifts due to water layers formed in the ion-selective electrode.

In another aspect, there is provided an ion-selective electrode prepared by the method as described herein.

15 In another aspect, there is provided a method of sensing an ion in a sample, comprising the step of immersing the ion-selective electrode as described herein in the sample.

Definitions

The following words and terms used herein shall have the meaning indicated:

20 The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

25 Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

30 The term "about" as used herein typically means +/- 5 % of the stated value, more typically +/- 4 % of the stated value, more typically +/- 3 % of the stated value, more typically, +/- 2 % of the stated value, even more typically +/- 1 % of the stated value, and even more typically +/- 0.5 % of the stated value.

35 Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3,

from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

- 5 Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

10 Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a method of treating a solid contact for sensing an ion will now be disclosed.

The method comprises the step of immersing the solid contact in an aqueous medium that is free from perchlorate, wherein the solid contact is a conducting polymer.

- 15 The conducting polymer may be polypyrrole (PPy), propylenedioxythiophene (ProDOT) or a copolymer derived from poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(ethyleneglycol) (PEG). Therefore, the solid contact may be regarded or termed as PEDOT:PEG or PEDOT-PEG.

- 20 The conducting polymer may not comprise an anionic polymer chain, such as polystyrene sulfonate (PSS). This is because the conducting polymer comprises an ionic dopant, the ionic dopant in or bound to the anionic polymer chain may not be easily exchanged or removed.

The ion to be sensed may also be regarded as a primary ion or an analyte.

- 25 The solid contact may form an integral part of an ion-selective electrode. Advantageously, the present method improves the selectivity of the ion-selective electrode towards the ion. This is because the solid contact may be substantially free from perchlorate ions after the method. The ion-selective electrode has a lower resistance and a higher selectivity with a lower amount of perchlorate ions.

- 30 The method may remove at least about 2 atomic percentage (at%), 2.1 at%, 2.2 at%, 2.3 at%, 2.4 at% or 2.5 at% of perchlorate from the solid contact as measured by X-ray photoelectron spectroscopy (XPS). Where the solid contact before being treated by the present method has more than about 2 at% of perchlorate, the solid contact after being treated by the present method may have less than or equal to about 1 at%, about 0.5 at% or about 0.1 at% of perchlorate. The solid contact may have an undetectable amount of perchlorate after being treated by the method.
- 35

In the method, the aqueous medium may be an aqueous solution of the ion.

Advantageously, the ion will become a dopant for the solid contact after the method. This will further improve the selectivity of the solid contact towards the ion.

The aqueous solution of the ion may have a concentration in the range of about 0.05 M to about 0.5 M, about 0.1 M to about 0.5 M or about 0.05 M to about 0.1 M. The
5 aqueous solution of the ion may have a concentration of about 0.1 M.

Alternatively, the aqueous medium may be substantially free of any ions. The aqueous medium may be deionised water.

Advantageously, the solid contact will be free from ion dopants after the method. This will further improve the selectivity of the ion-selective electrode towards the
10 ion. The selectivity of the ion-selective electrode may be improved by about 3-fold to about 600-fold via the method.

The ion may be any cation or anion except perchlorate and is not particularly limited otherwise. Non-limiting examples of the ion include nitrate, chloride, nitrite and potassium.

The immersing step may be undertaken for a duration in the range of about 0.2 day to about 10 days, about 1 day to about 3 days or about 3 days to about 10 days. The immersing step may be undertaken for a duration of about 1 day. Advantageously, the immersing step requires a short duration to improve the selectivity of the ion-selective electrode. Therefore, the present method may be regarded as an efficient
15 means to improve the selectivity of the ion-selective electrode.
20

Exemplary, non-limiting embodiments of a solid contact will now be disclosed. The solid contact is obtained from the method as described herein.

The solid contact may form an integral part of an ion-selective electrode. Advantageously, the ion-selective electrode has an improved ion selectivity
25 compared with ion-selective electrodes in the art as the solid contact is substantially free from perchlorate ions after being treated by the method as described herein.

Exemplary, non-limiting embodiments of a method of preparing an ion-selective electrode for sensing an ion will now be disclosed.

The method comprises the steps of:

30 (a) forming a layer of solid contact on an electrode, wherein the solid contact is derived from poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(ethyleneglycol) (PEG);

(b) immersing the layer of solid contact and the electrode in an aqueous medium that is free from perchlorate; and

35 (c) depositing an ion-selective membrane on the layer of solid contact.

The forming step (a) may comprise a step of drop-casting a composition of PEDOT and PEG onto the electrode.

The composition of PEDOT and PEG may be a dispersion of PEDOT:PEG at a concentration of about 0.8 weight%.

5 As PEDOT and PEG are polymers and the layer of solid contact is conductive, the layer of solid contact may also be regarded as a conducting polymer. Therefore, the method may be regarded as a method for producing an electrode for an ion sensor supporting faradaic current and a conducting polymer facilitating ion-to-electron transduction.

10 As there are no aqueous layers in the ion-selective electrode prepared by the method, the method may also be regarded as a method for producing an electrode for an ion sensor supporting faradaic current and a conducting polymer facilitating ion-to-electron transduction and ion-selective membrane contact.

The immersing step (b) may be undertaken as described herein to ensure that the ion-selective electrode is substantially free from perchlorate. As the ion may become a dopant for the layer of solid contact after the immersing step (b), the method may also be regarded as a method for producing an electrode for an ion sensor supporting faradaic current, and an enhanced conducting polymer facilitating ion-to-electron transduction, ion-selective membrane contact, and selectivity to the ion, wherein the
20 conducting polymer is doped by the ion for enhanced stability and selectivity.

The depositing step (c) may comprise a step of drop-casting a precursor composition of the ion-selective membrane onto the layer of solid contact.

Therefore, the method may be regarded as solution processing and the ion-selective electrode prepared by the method may be regarded as a solution-processable ion-selective electrode. Advantageously, the solution-printing process is simple to
25 operate and readily scalable compared to conventional methods such as those that require electropolymerisation.

The precursor composition of the ion-selective membrane may comprise an ionophore, a lipophilic salt, a plasticiser, a polymer matrix and a solvent. The
30 precursor composition may comprise tetradodecylammonium nitrate, 1-(2-nitrophenoxy)octane and poly(vinyl chloride). The precursor composition may alternatively comprise 4,5-bis-[N'-(butyl)thioureido]-2,7-di-*tert*-butyl-9,9-dimethylxanthene, tridodecylmethylammonium chloride, 1-(2-nitrophenoxy)octane and poly(vinyl chloride). The precursor composition may alternatively comprise
35 *N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-benzenediaminocobalt(II), tridodecylmethylammonium chloride, dioctyl sebacate and poly(vinyl chloride). The precursor composition may alternatively comprise valinomycin, potassium tetrakis-4-chlorophenyl borate, dioctyl sebacate and poly(vinyl chloride).

The method may further comprise a step of preparing the precursor composition of the ion-selective membrane before the depositing step (c).

The method may further comprise a step of conditioning the ion-selective electrode in an aqueous solution of the ion after the depositing step (c).

- 5 Advantageously, the conditioning step may make the ion-selective electrode more sensitive and selective towards the ion.

The conditioning step may be circumvented if the ion is in both the solid-contact and the ion-selective membrane. Advantageously, the ion-selective electrode may be regarded as ready-to-use sensors, and the present method could save time and
10 increase the user-friendliness for untrained users.

The aqueous solution of the ion may have a concentration in the range of about 0.01 M to about 1 M, about 0.1 M to about 1 M or about 0.01 M to about 0.1 M. The aqueous solution of the ion may have a concentration of about 0.1 M.

- 15 The conditioning step may be undertaken for a duration in the range of about 8 hours to about 24 hours, about 16 hours to about 24 hours or about 8 hours to about 16 hours. The conditioning step may be undertaken for a duration of about 16 hours.

The electrode may be a screen-printed electrode made of carbon, gold, or carbonaceous materials e.g., carbon fiber, carbon nanotubes on a rigid substrate e.g., ceramic.

- 20 Alternatively, the electrode may comprise, consist essentially or consist of a flexible material. As the layer of solid contact and the ion-selective membrane are both flexible, the entire ion-selective electrode may be regarded as being flexible where the electrode comprises, consists essentially or consists of a flexible material.

- 25 The electrode may comprise, consist essentially or consist of a substrate selected from the group consisting of polyimide, poly(methyl methacrylate (PMMA), polyethylene terephthalate (PET), polyethylene terephthalate glycol (PETG), polypropylene (PP), fluorinated ethylene propylene (FEP), polyethylene (PE), polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS) and poly(ethylene-co-vinyl acetate).

The electrode may comprise, consist essentially or consist of a polyimide substrate.

- 30 Exemplary, non-limiting embodiments of an ion-selective electrode will now be disclosed. The ion-selective electrode is prepared by the method as described herein.

As the ion-selective electrode may be flexible, the ion-selective electrode may substantially keep its sensitivity and/or selectivity performances after bending or compressing.

- 35 The sensitivity and/or the selectivity of the ion-selective electrode may independently be at least 97% after 50 cycles of bending based on the sensitivity and/or the

selectivity of initial ion-selective electrode (that is, before being subjected to the 50 cycles of bending).

Exemplary, non-limiting embodiments of a method of sensing an ion in a sample will now be disclosed. The method comprises the step of immersing the ion-selective
5 electrode as described herein in the sample.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the
10 limits of the invention.

FIG. 1A

[FIG. 1A] is a schematic illustration on how a solid contact ion-selective electrode is prepared according to the present disclosure.

FIG. 1B

15 [FIG. 1B] is a schematic illustration on cross-sectional layers of a solid contact ion-selective electrode according to the present disclosure.

FIG. 2A

20 [FIG. 2A] shows potentiometric responses of a NO_3^- solid contact ion-selective electrode without performing the ion exchange step disclosed in present disclosure towards NO_3^- anions in pure and mixed solutions containing fixed amounts of interfering ions.

FIG. 2B

25 [FIG. 2B] shows potentiometric responses of an optimised NO_3^- solid contact ion-selective electrode according to the present disclosure towards NO_3^- anions in pure and mixed solutions containing fixed amounts of interfering ions.

FIG. 2C

[FIG. 2D] is an X-ray photoelectron wide scan spectrum of a PEDOT-PEG solid contact according to the present disclosure.

FIG. 2D

30 [FIG. 2D] is an X-ray photoelectron fine scan spectrum of a chlorine ($\text{Cl } 2p$) scan of PEDOT-PEG solid contacts according to the present disclosure.

FIG. 2E

[FIG. 2E] is an X-ray photoelectron fine scan spectrum of a nitrogen ($\text{N } 1s$) scan of PEDOT-PEG solid contacts according to the present disclosure.

FIG. 3A

[FIG. 3A] is a dynamic response plot of a solid contact ion-selective electrode according to the present disclosure towards changes in NO_3^- anion concentration and environmental interferences.

5 FIG. 3B

[FIG. 3B] shows effects of pH on the response of the solid contact ion-selective electrode as shown in FIG. 3A.

FIG. 4A

10 [FIG. 4A] shows reversal chronopotentiograms of solid contact ion-selective electrodes according to the present disclosure and a conventional coated-wire electrode.

FIG. 4B

[FIG. 4B] shows Nyquist plots of impedance and subsequent fits of the coated-wire electrode as shown in FIG. 4A.

15 FIG. 4C

[FIG. 4C] shows Nyquist plots of a solid contact ion-selective electrode without performing the ion exchange step as shown in FIG. 4A.

FIG. 4D

20 [FIG. 4D] shows Nyquist plots of an optimised solid contact ion-selective electrode as shown in FIG. 4A.

FIG. 5A

[FIG. 5A] shows sensitivity responses of 8 solid contact ion-selective electrodes according to the present disclosure towards the NO_3^- anion, plotting the average and error bars of three individual measurements ($n = 3$).

25 FIG. 5B

[FIG. 5B] shows a comparison of the potentiometric selectivity coefficients ($\log_{10}K$) of the solid contact ion-selective electrodes shown in FIG. 5A, against various interfering ions determined by a fixed interference method.

FIG. 6A

30 [FIG. 6A] shows results of an aqueous layer test of a solid contact ion-selective electrode according to the present disclosure.

FIG. 6B

[FIG. 6B] shows results of an aqueous layer test of the solid contact ion-selective electrode as shown in FIG. 6A, after immersing in 1mM KNO_3 solution for 17 days.

FIG. 7A

[FIG. 7A] shows X-ray photoelectron wide scan spectra of 8 PEDOT:PEG solid contacts.

FIG. 7B

- 5 [FIG. 7B] shows chloride 2p X-ray photoelectron fine scan spectra of the 8 PEDOT:PEG solid contacts shown in FIG. 7A.

FIG. 7C

[FIG. 7C] shows carbon 1s X-ray photoelectron fine scan spectra of the 8 PEDOT:PEG solid contacts shown in FIG. 7A.

- 10 **FIG. 7D**

[FIG. 7D] shows sulfur 2p X-ray photoelectron fine scan spectra of the 8 PEDOT:PEG solid contacts shown in FIG. 7A.

FIG. 7E

- 15 [FIG. 7E] shows bromine 3d X-ray photoelectron fine scan spectra of 2 PEDOT:PEG solid contacts P1 and P4 shown in FIG. 7A.

FIG. 7F

[FIG. 7F] shows iodine 3d X-ray photoelectron fine scan spectra of 2 PEDOT:PEG solid contacts P1 and P5 shown in FIG. 7A.

FIG. 8

- 20 [FIG. 8] shows Raman spectra of the 8 PEDOT:PEG solid contacts shown in FIG. 7A on carbon screen-printed electrodes.

FIG. 9A

- 25 [FIG. 9A] is a dynamic response plot of a solid contact ion-selective electrode according to the present disclosure for KNO_3 concentration change from 10^{-2} to $10^{-1.3}$ M.

FIG. 9B

[FIG. 9B] is a differential response plot for the KNO_3 concentration change as shown in FIG. 9A.

FIG. 10A

- 30 [FIG. 10A] shows sensitivity and selectivity response of a solid contact ion-selective electrode NP3 according to the present disclosure towards the nitrate anion in the presence of various anions using the fixed interference method, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 10B

5 [FIG. 10B] shows sensitivity and selectivity response of another solid contact ion-selective electrode NP4 according to the present disclosure towards the nitrate anion in the presence of various anions using the fixed interference method, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 10C

10 [FIG. 10C] shows sensitivity and selectivity response of another solid contact ion-selective electrode NP5 according to the present disclosure towards the nitrate anion in the presence of various anions using the fixed interference method, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 10D

15 [FIG. 10D] shows sensitivity and selectivity response of another solid contact ion-selective electrode NP6 according to the present disclosure towards the nitrate anion in the presence of various anions using the fixed interference method, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 10E

20 [FIG. 10E] shows sensitivity and selectivity response of another solid contact ion-selective electrode NP7 according to the present disclosure towards the nitrate anion in the presence of various anions using the fixed interference method, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 10F

25 [FIG. 10F] shows sensitivity and selectivity response of another solid contact ion-selective electrode NP8 according to the present disclosure towards the nitrate anion in the presence of various anions using the fixed interference method, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 11

[FIG. 11] shows reproducibility and reversibility of replicates of a solid contact ion-selective electrode according to the present disclosure. The replicates are shifted up and down for clarity.

30 FIG. 12A

[FIG. 12A] shows performance of the solid contact ion-selective electrode shown in FIG. 11 after storing in 1mM KNO_3 for 12 days, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 12B

35 [FIG. 12B] shows performance of the solid contact ion-selective electrode shown in FIG. 11 after storing in 1mM KNO_3 for 17 days, plotting the average and error bars of three individual measurements ($n = 3$).

FIG. 12C

[FIG. 12C] shows performance of the solid contact ion-selective electrode shown in FIG. 11 after storing in 1mM KNO₃ for 72 days, plotting the average and error bars of three individual measurements (n = 3).

5 FIG. 12D

[FIG. 12D] shows a comparison of the potentiometric selectivity coefficients (log K) of the solid contact ion-selective electrode after immersing in 1 mM KNO₃ as described in FIGS. 12A to 12C.

FIG. 13A

- 10 [FIG. 13A] shows sensitivity and selectivity performances of a flexible chloride solid contact ion-selective electrode with KCl-exchanged PEDOT-PEG as the solid contact (n = 3).

FIG. 13B

- 15 [FIG. 13B] shows sensitivity and selectivity performances of a flexible chloride solid contact ion-selective electrode with an original untreated PEDOT-PEG as the solid contact (n = 3).

FIG. 13C

- 20 [FIG. 13C] shows sensitivity and selectivity performances of a rigid chloride solid contact ion-selective electrode with KCl-exchanged PEDOT-PEG as the solid contact without solution conditioning (n = 3).

FIG. 13D

[FIG. 13D] shows sensitivity and selectivity performances of a rigid chloride solid contact ion-selective electrode with an original untreated PEDOT-PEG as the solid contact without solution conditioning (n = 3).

25 FIG. 14

[FIG. 14] shows shows sensitivity and selectivity performances of a rigid nitrite solid contact ion selective electrode with NaNO₂-exchanged PEDOT-PEG as the solid contact (n = 3).

FIG. 15

- 30 [FIG. 15] shows a schematic diagram on the preparation of flexible solid contact ion-selective electrodes.

FIG. 16A

[FIG. 16A] shows cyclic voltammograms of a PEDOT-PEG/CIO₄⁻ solid contact according to the present disclosure.

FIG. 16B

- 5 [FIG. 16B] shows cyclic voltammograms of a conventional PEDOT:PSS solid contact.

FIG. 17A

- 10 [FIG. 17A] shows sensitivity and selectivity performances of a flexible potassium solid contact ion-selective electrode with PEDOT-PEG/CIO₄⁻ as the solid contact (n = 2).

FIG. 17B

[FIG. 17B] shows sensitivity and selectivity performances of a flexible potassium solid contact ion-selective electrode with PEDOT:PSS as the solid contact (n = 2).

FIG. 18A

- 15 [FIG. 18A] shows results of an aqueous layer test for a solid contact potassium ion-selective electrode with PEDOT-PEG as the solid contact.

FIG. 18B

[FIG. 18B] shows results of an aqueous layer test for a solid contact potassium ion-selective electrode with PEDOT-PSS as the solid contact.

- 20 **FIG. 19A**

[FIG. 19A] shows sensitivity and selectivity performances of a flexible nitrate solid contact ion-selective electrode with KNO₃-exchanged PEDOT-PEG as the solid contact (n = 2).

FIG. 19B

- 25 [FIG. 19B] shows sensitivity and selectivity performances of a flexible nitrate solid contact ion-selective electrode with original PEDOT-PEG/CIO₄⁻ as the solid contact (n = 2).

FIG. 19C

- 30 [FIG. 19C] shows sensitivity and selectivity performances of a flexible nitrate solid contact ion-selective electrode with PEDOT:PSS as the solid contact (n = 2).

FIG. 20A

[FIG. 20A] shows results of an aqueous layer test for a solid contact nitrate ion-selective electrode with ion-exchanged PEDOT-PEG as the solid contact.

FIG. 20B

[FIG. 20B] shows results of an aqueous layer test for a solid contact nitrate ion-selective electrode with PEDOT-PSS as the solid contact.

FIG. 21

- 5 [FIG. 21] shows mechanical bending test results of a flexible nitrate solid contact ion-selective electrode according to the present disclosure.

Examples

- Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting
10 the scope of the invention.

Example 1 – Preparation of Solid Contact Ion-Selective Electrodes*Drop-casting of PEDOT:PEG*

- PEDOT:PEG (0.8 weight% dispersion in propylene carbonate, containing ClO_4^- as dopant, purchased from Sigma Aldrich, Singapore) was subjected to 30 minutes of
15 agitation followed by 30 minutes of sonication. 3 μL of PEDOT:PEG was drop-casted onto the working electrode of carbon (C110) screen-printed electrodes (SPEs, purchased from Metrohm Dropsens, Spain) and dried at 60 °C for 30 minutes.

Ion Exchange of PEDOT:PEG

- PEDOT:PEG-coated SPEs were immersed in 0.1 M solutions of either potassium
20 nitrate (KNO_3 , purchased from Avantor-VWR, Singapore), potassium chloride (KCl , purchased from Avantor-VWR, Singapore), potassium bromide (KBr , purchased from Tokyo Chemical Industry, Singapore), potassium iodide (KI , purchased from Avantor-VWR, Singapore), or lithium perchlorate (LiClO_4 , purchased from Alfa Aesar, Singapore) for 3 days for ion exchange unless otherwise stated. For the
25 control, the PEDOT: PEG-coated SPEs were immersed in deionized (DI) water (or ultrapure water (18.2 M Ω), obtained from a PURELAB Option-Q water system) for 3 days. All ion-exchanged SPEs were rinsed with DI water and dried under vacuum at 60 °C for 4 hours.

Preparation of NO_3^- Solid Contact Ion-Selective Electrodes

- 30 To prepare the solid contact ion-selective electrodes (sc-ISEs), an ion-selective membrane (ISM) cocktail was prepared by dissolving tetradodecylammonium nitrate (TDDANO_3 , 10 mg, purchased from Sigma Aldrich, Singapore), poly(vinyl chloride) (PVC, 47.6 mg, purchased from Sigma Aldrich, Singapore) and 1-(2-nitrophenoxy)octane (NPOE, 42.4 mg, purchased from Sigma Aldrich, Singapore) in
35 tetrahydrofuran (THF, 1 mL, purchased from Sigma Aldrich, Singapore). 10 μL of the ISM cocktail was drop-casted onto the PEDOT:PEG SPEs and dried overnight at ambient temperature, followed by drying under vacuum for 4 hours. The sc-ISEs were then conditioned in 1 mM KNO_3 solution for 16 hour. A schematic of the fabrication process is shown in FIG. 1A.

Example 2 – Characterisation of Solid Contact Ion-Selective Electrodes

X-ray Photoelectron Spectroscopy of sc-ISEs

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific Theta Probe XPS system with monochromatic Al K α X-ray source ($h\nu = 1486.7$ eV) at 400 μm spot size. Photoelectrons were collected at a take-off angle of 50° with respect to surface normal. Wide scan spectra were acquired with pass energy of 200 eV and step size of 1 eV. Fine scans of C 1s, N 1s, S 2p and Cl 2p were acquired with pass energy of 40 eV at 0.1 eV step size. Combined electron/ion flooding was used for charge compensation and further charge shift correction was done based on the C-C peak of C 1s at 284.8 eV.

Raman Spectroscopy of sc-ISEs

Raman spectroscopy was performed using Renishaw inVia confocal Raman microscope with laser wavelength 532 nm at 50 $\times$ magnification and 2400 g/mm grating. The spectra were acquired at 10 s acquisition time for 1 accumulation.

Open Circuit Potentiometry

Measurements were performed at room temperature using a Dropsens Potentiostat (DRP-STAT8000, Metrohm Dropsens) in a 2-electrode setup with a Ag|AgCl|3M KCl|1M LiOAc reference electrode. Three replicates of each sc-ISE were tested. The sensitivity and limit of detection of the electrode were evaluated by measuring the open circuit potential in KNO₃ solutions with concentration ranging from 1 nM to 0.1 M. Selectivity coefficients were evaluated using the fixed interference method (FIM).

Current Reversal Chronopotentiometry

Chronopotentiometry was performed using a 3-electrode setup in 1 mM aqueous KNO₃. A current (± 10 nA) was applied to the working electrode, first positive current for 60 seconds, followed by negative current for 60 seconds, while the electrode potential was continuously recorded.

Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) measurements were performed at room temperature using an Autolab Potentiostat (PGSTAT30, Metrohm Autolab). Nyquist plots were collected in the frequency range of 100 kHz to 1 mHz with a sinusoidal voltage signal of 100 mV. A 3-electrode setup in 1 mM aqueous KNO₃ was used. All impedance spectra were fitted to equivalent circuits using the EIS Spectrum Analyser.

Real Sample Testing

Bold's basal medium (purchased from PhytoTechnology Laboratories, USA) and Power-Gro hydroponics nutrients (purchased from SingCrop, Singapore) were prepared following manufacturers' directions prior to nitrate concentration determination. Bold's basal medium was tested both pre- (clean) and post-use (inoculated with microalgae *chlorella sorokiniana*). For sc-ISE testing, no sample treatment was required. For the comparative method of anion chromatography (IC),

samples were diluted and syringe-filtered to prepare solutions with nitrate concentration between 1 to 10 ppm; 10× dilution was required for microalgae-inoculated basal medium and 100× for hydroponics medium. IC was performed on a 930 Compact IC Flex 1 (Metrohm, USA) system equipped with anion-exchange column of 150×4.0 mm and 5 µm particle size (Metrosep A Supp 5 150/4.0, Metrohm), with Metrosep A Supp 5 Eluent (3.2 mM Na₂CO₃ 0.678g/ 2L and 1.0 mM NaHCO₃ 0.168g/ 2L, Metrohm) as mobile phase. The chromatogram was run at 30 °C at the flow rate of 0.7 mL/minute and the stop time was 19 minute.

Example 3 – Nitrate Doping of PEDOT:PEG Solid-contact

To begin the investigation, PEDOT:PEG solid-contact **P1** was prepared from commercially available solution-based PEDOT:PEG with ClO₄[−] anion as dopant. Drop-casting of NO₃[−]-ISM atop **P1** afforded NO₃[−] sc-ISE **NP1** (see FIG. 1A). Open circuit potential measurements performed in KNO₃ solutions from 1 nM to 0.1 M showed that **NP1** had near-Nernstian sensitivity (−54.3 mV/decade) towards the NO₃[−] anion. Selectivity coefficients for dihydrogen phosphate (H₂PO₄[−]), hydrogen carbonate (HCO₃[−]), chloride (Cl[−]), nitrite (NO₂[−]), bromide (Br[−]) and iodide (I[−]) ions were then determined using the fixed interference method (FIM) as it resembles actual samples containing both the primary and interfering ions. Unfortunately, **NP1** exhibited poor selectivity for the NO₃[−] anion against less chaotropic interfering ions (see FIG. 2A).

Previous studies have shown that the counterion used during PEDOT electropolymerisation can tune the properties of the solid-contact and affect sc-ISE performance. Thus, it was hypothesised that the selectivity of the sc-ISE could be improved by exchanging the dopant anion. To this end, the PEDOT:PEG solid-contact was immersed in 0.1 M KNO₃ for 3 days to form NO₃[−]-doped **P2**.

XPS analysis was performed to assess the effectiveness of the ion exchange protocol in replacing the original ClO₄[−] ions in **P1** with NO₃[−]. The XPS wide scan of **P1** (see FIG. 2C) indicated the presence of C, O, Cl and S elements as expected from the commercially sourced ClO₄[−]-doped PEDOT:PEG (see FIGS. 7A to 7F). The characteristic doublet at *ca.* 207.5 eV (2p_{3/2}) and 209 eV (2p_{1/2}) in the Cl 2p XPS spectrum of **P1** (see FIG. 2D) indicated the presence of the ClO₄[−] dopant. After ion exchange, the ClO₄[−] dopant was diminished in **P2** (see FIG. 2D). Meanwhile, detection of a new peak at *ca.* 406 eV (1s) in the N1s XPS spectrum indicated that doping of **P2** with the NO₃[−] anion was successful (see FIG. 2E). However, XPS estimates of dopant concentrations (Table 1) indicate that the doping level of **P2** (with NO₃[−]) was lower than **P1** (with ClO₄[−]), which can be attributed to the stronger doping ability of ClO₄[−].

Table 1. Ion exchange conditions for the PEDOT:PEG solid-contacts and their estimated XPS dopant concentrations.

PEDOT:P EG	Ion Exchange ^a	Dopant	Dopant At % ^d	S At % ^d	Dopant:S Ratio
P1	NA ^b	ClO ₄ [−]	2.1	10.0	0.211
P2	KNO ₃	NO ₃ [−]	0.5	8.6	0.063

P3	KCl	Cl ⁻	0.8	10.3	0.078
P4	KBr	Br ⁻	1.0	9.8	0.106
P5	KI	I ⁻	0.2	9.9	0.017
P6	DI water	NA	0.5	10.3	0.048
P7	LiClO ₄	ClO ₄ ⁻	2.0	9.5	0.207
P8	KNO ₃ ^c	NO ₃ ⁻	0.5	9.7	0.046

^aIon exchange was performed for 3 days in 0.1 M aqueous salt solution unless otherwise stated. ^bNo ion exchange was performed. ^cIon exchange was performed for 1 day. ^dAtomic percentage (at%) of dopant and S are estimated using the Thermo Scientific Advantage software with Scofield sensitivity factors applied.

Having evidenced the successful ion exchange, NO₃⁻-ISM was drop-casted to fabricate NO₃⁻ sc-ISE **NP2**. Like **NP1**, **NP2** exhibited near-Nernstian sensitivity (−54.9 mV/decade) towards the NO₃⁻ anion, with a micromolar limit of detection (LOD) of 1.58 μM. The selectivity of both sc-ISEs followed the Hofmeister series: H₂PO₄⁻ < HCO₃⁻ < Cl⁻ < NO₂⁻ < Br⁻ < NO₃⁻ < I⁻. However, **NP2** (see FIG. 2B) exhibited markedly improved selectivity for NO₃⁻ against all interfering ions (except I⁻) compared to **NP1**.

Sc-ISE **NP2** was further evaluated for its dynamic response and sensitivity towards environmental interferences such as light, gases, and pH (see FIGS. 3A and 3B). No significant change was observed in the electrode potential when **NP2** was kept in the dark or exposed to ultraviolet (365 nm) or infra-red (800 nm) light (see FIG. 3A), indicating that **NP2** does not exhibit light sensitivity unlike some other solid-contacts. For gas sensitivity, **NP2** was insensitive to O₂ but displayed a small potential drop (*ca.* 3 mV) upon the introduction of N₂ purged solution which was recoverable within 10 minutes. The response time of a sensor is an essential property in determining the analytical applications of the sensor. For **NP2**, stable potential response was rapidly achieved within 15 seconds (see FIGS. 3A (inset), 9A and 9B). Finally, the effect of the pH on the electrode potential was studied over the pH range of 1 – 13 (see FIG. 3B). The operational pH range, in which potential change of **NP2** did not exceed ± 5 mV, was *ca.* 4 – 10.

Current reversal chronopotentiometry was performed to evaluate the electrical properties and short-term potential stability of the sc-ISEs **NP1** and **NP2**, as well as a “coated-wire” electrode (CWE, **N**) where the NO₃⁻-ISM was drop-casted directly onto the carbon SPE (see FIG. 4A). The frequency-independent total resistance (*R*_{tot}) of the ISEs were estimated from the potential drop after current polarity change using the equation $R_{tot} = E/2I$, where *I* was the applied current (10 nA). Both sc-ISEs **NP1** and **NP2** had lower resistance compared to the CWE **N** (see Table 2), indicating that the PEDOT- PEG solid-contact reduced the contact resistance between the ISM and the carbon electrode. The chronopotentiograms were also used to determine the short-term potential drift and estimate the low frequency capacitance (*C*_{LF}) of the solid-contact using the equation $\Delta E/\Delta t = i/C_{LF}$ (Table 2). Sc-ISE **NP2** exhibited

significantly lower drift ($90.9 \mu\text{V s}^{-1}$) and thus the highest capacitance ($110 \mu\text{F}$) compared to **N** and **NP1**, indicating that **P2** is the best solid-contact.

Table 2. Electrical parameters of CWE **N** and sc-ISEs **NP1** and **NP2** determined by current reversal chronopotentiometry.

ISE	R_{tot} ($\text{k}\Omega$)	$\Delta E / \Delta t$ (mV s^{-1})	C_{LF} (μF)
N	14.1	0.436	32.4
NP1	10.9	0.327	30.6
NP2	9.8	0.0909	110

5

To investigate the origin of the difference in selectivity performances, EIS was also performed on these ISEs (see FIGS. 4B to 4D, the equivalent circuits used for fitting impedance data are shown in each spectrum; frequency range: 100 kHz to 1 mHz; amplitude potential: 100 mV; solution: 1 mM KNO_3). Unlike current reversal chronopotentiometry, the frequency sweep offered by EIS enabled us to fully characterize the impedance response of the electrodes. For all Nyquist plots, the high frequency semicircle is attributed to the bulk resistance of membrane (R_1). This was reasonably concluded from a series of experiments where the thickness of the membrane layer was modified. Additionally, the value of capacitance ($\approx 10^{-10}$ F) extracted from the equivalent circuit fit parallel to R_1 corresponds to a geometric bulk capacitance (Table 3).

Table 3. Equivalent circuit values for the impedance data of CWE **N** and sc-ISEs **NP1** and **NP2** doped with ClO_4^- and NO_3^- , respectively.

ISE	R_1 (Ω)	$\text{CPE}(\text{T})^a$	$\text{CPE}(\text{n})^a$	R_2 (Ω)	$\text{CPE}(\text{T})$	$\text{CPE}(\text{n})$	R_3 (Ω) ^b	$\text{CPE}(\text{T})^b$	$\text{CPE}(\text{n})^b$
N	26623	4.18×10^{-10}	0.98	1.0×10^6	8.7×10^{-7}	0.57	-	8.0×10^{-5}	0.79
NP1	11609	4.12×10^{-10}	0.98	2.3×10^5	2.0×10^{-6}	0.51	2.0×10^6	9.5×10^{-6}	0.57
NP2	7257	9.50×10^{-10}	1	6.4×10^5	2.0×10^{-6}	0.61	-	1.5×10^{-5}	0.41

^a CPE (T) and CPE (n) refer to constant phase element (CPE) magnitude and exponent components, respectively. ^b The Warburg element (Z_w) is fitted as (RCPE) for **NP1** and CPE for **NP2**.

The semicircle observed in the middle frequency range is described as the interface resistance (R_2) between the carbon electrode and PEDOT:PEG solid-contact for sc-ISEs **NP1** and **NP2**, and between the carbon electrode and the NO_3^- -ISM for CWE **N**. The insertion of PEDOT:PEG resulted in a decrease in charge transfer resistance at the interface, indicating that PEDOT:PEG serves as an effective ion-to-electron transducer. This effect is more pronounced for **NP1** with the ClO_4^- ion as dopant (Table 3). At low frequency range, the Nyquist plot features a Warburg impedance for both **NP1** and **NP2**, characterizing the diffusion transport. While **NP2** exhibits a

standard Warburg impedance (Z_w , see FIG. 4D), for **NP1** a finite-length Warburg impedance with a limiting diffusion resistance is observed (Z_{w_s} , see FIG. 4C). This indicates that for **NP1** the transduction process is limited by diffusion, which likely arises due to high concentration of ClO_4^- in solid-contact, as observed by XPS (Table 1) and Raman spectroscopy (see FIG. 8). The overall resistance of the cell is hence significantly larger for **NP1** compared to **NP2**. The presence of different anion species, NO_3^- and ClO_4^- , in the ISM and PEDOT:PEG layers respectively could hinder the transport of the primary NO_3^- ion and result in the poorer NO_3^- selectivity of **NP1** as well.

10 **Example 4 – Doping of PEDOT:PEG Solid-contact with Other Anions**

Having shown that doping the PEDOT:PEG solid-contact with NO_3^- significantly improved the performance of sc-ISE **NP2**, the effect of doping the solid-contact with other anions on the NO_3^- selectivity of the sc-ISE was subsequently investigated. Thus, ion exchange was performed by immersing the PEDOT:PEG solid-contact in 0.1 M solutions of various salts (Table 4).

Table 4. Ion-exchange conditions for PEDOT:PEG -solid-contacts and performance of their NO_3^- sc-ISEs

PEDOT	Ion exchange ^a	Dopant	Sc-ISE	Sensitivity /mV dec ⁻¹	LOD / log ₁₀ ($a_{\text{NO}_3^-}$ / M)
P1	NA ^b	ClO_4^-	NP1	-54.3 ± 0.4	-5.50
P2	KNO_3	NO_3^-	NP2	-54.9 ± 0.8	-5.80
P3	KCl	Cl^-	NP3	-53.1 ± 0.7	-5.90
P4	KBr	Br^-	NP4	-54.8 ± 0.1	-5.90
P5	KI	I^-	NP5	-54.0 ± 2.0	-5.80
P6	DI water	NA	NP6	-53.7 ± 2.1	-5.70
P7	LiClO_4	ClO_4^-	NP7	-56.0 ± 5.1	-5.70
P8	KNO_3^c	NO_3^-	NP8	-55.8 ± 0.7	-5.95

^a Ion exchange was performed for 3 days in 0.1 M aqueous salt solution unless otherwise stated. ^b No ion exchange was performed. ^c Ion exchange was performed for 1 day.

XPS analysis of the solid-contacts **P3** to **P5** revealed that the ClO_4^- dopant was successfully exchanged with their respective anions (see FIGS. 7A to 7F). As a control, PEDOT:PEG solid-contact **P6** was prepared and immersed in deionised water, which was also able to remove most of the ClO_4^- ions (see FIG. 7B). In contrast, this peak was hardly changed upon soaking with LiClO_4 (**P7**). XPS estimates of dopant concentrations indicate that the ClO_4^- dopant was present in higher atomic percentage in **P1** and **P7** as compared with the other anions in their

corresponding PEDOT:PEG solid-contacts (Table 1), as is expected from this strong dopant.

Raman analysis was performed to ascertain the doping levels of the different PEDOT:PEG solid-contacts by comparing the ratio of quinoid to benzoid forms of the PEDOT chains (see FIG. 8). As the dopant species and doping levels do not alter the structure and the number of oxyethylene rings of PEDOT, the spectra were normalized to the peak at 990 cm^{-1} which corresponds to the oxyethylene ring deformation. This allowed the comparison of the peak intensities at 1368 cm^{-1} and 1437 cm^{-1} , which are indicative of the stretching of the neutral benzoid form of PEDOT. These peaks decrease in intensity as PEDOT is doped. The Raman spectra show that the PEDOT:PEG solid-contacts doped with ClO_4^- anions (**P1** and **P7**) have the lowest intensity of benzoid peaks centred between 1300 to 1500 cm^{-1} . Upon immersion of the PEDOT:PEG solid-contact in DI water (**P6**), de-doping of the ClO_4^- anions significantly increased the intensities of the benzoid peaks, indicating decreased PEDOT conjugation. Similar increases in benzoid peak intensities were observed upon ion exchange with other anions (**P2** to **P5**, **P8**), even though these ion exchanges were performed at the same concentration as **P7**, which was immersed in 0.1 M LiClO_4 solution. These results indicate that the level of doping was significantly lower for the ion-exchanged solid-contacts, which are in line with estimates of dopant concentration from XPS analysis.

After the NO_3^- -ISM was drop-casted on these solid-contacts, open circuit potentiometry measurements showed that all the sc-ISEs displayed near-Nernstian slopes (see FIG. 5A) and limits of detection (LOD) between 3.16 and $1.12\text{ }\mu\text{M}$ (Table 4). The selectivity of all the ISEs (except **NP7**) followed the Hofmeister series. However, the selectivity coefficients of the sc-ISEs towards NO_3^- varied significantly (see FIG. 5B and Table 5).

Table 5. Ion exchange conditions for the PEDOT:PEG solid-contacts and the performance of their corresponding nitrate sc-ISEs

sc-ISE	Ion Exchange ^a	Sensitivity (mV/decade)	$\log_{10} K_{\text{NO}_3, \text{H}_2\text{PO}_4}$	$\log_{10} K_{\text{NO}_3, \text{HCO}_3}$	$\log_{10} K_{\text{NO}_3, \text{Cl}}$	$\log_{10} K_{\text{NO}_3, \text{Br}}$	$\log_{10} K_{\text{NO}_3, \text{I}}$	LOD ($\log_{10} a_{\text{NO}_3}/\text{M}$) ^d
NP1	NA ^b	-54.3 ± 0.4	-2.15	-1.45	-1.00	-0.45	+0.95	-5.50
NP2	KNO_3	-54.9 ± 0.8	-4.60	-4.00	-2.30	-0.75	+1.65	-5.80
NP3	KCl	-53.1 ± 0.7	-4.75	-3.85	-2.55	-1.15	+1.60	-5.90
NP4	KBr	-54.8 ± 0.1	-4.00	-3.65	-2.20	-1.00	+1.55	-5.90
NP5	KI	-54.0 ± 2.0	-4.40	-3.50	-2.15	-0.75	+1.80	-5.80
NP6	DI water	-53.7 ± 2.1	-4.80	-3.85	-2.40	-1.05	+1.65	-5.70
NP7	LiClO_4	-56.0 ± 5.1	-1.80	-0.80	-0.40	+0.05	+0.80	-5.70
NP8	KNO_3 ^c	-55.8 ± 0.7	-4.85	-4.10	-2.60	-1.25	+1.30	-5.95

^aIon exchange was performed for 3 days in 0.1 M aqueous salt solution unless otherwise stated. ^bNo ion exchange was performed. ^cIon exchange was performed for 1 day. ^dLOD = Limit of detection

Interestingly, the sc-ISEs with other dopants, i.e., Cl^- , Br^- and I^- (**NP3** to **NP5**, see FIGS. 10A to 10C) gave improved selectivity performance similar to **NP2** without any detriment to sensitivity. This can be attributed to the subsequent exchange of the less lipophilic dopants (i.e. Cl^- , Br^- and I^-) with NO_3^- primary ions during conditioning of the ISM in 1 mM KNO_3 solution. Unexpectedly, the control sc-ISE **NP6** (FIG. 10D) also demonstrated sensitivity (-53.7 mV/decade) and selectivity comparable to **NP2** despite the lack of incorporation of other mobile dopants. This result suggests that the high concentration of ClO_4^- dopant in **NP1** is the probable cause of poor selectivity. Notably, **NP7**, where the solid-contact was immersed in LiClO_4 , exhibited similar results to **NP1**, with good sensitivity but poor selectivity towards NO_3^- (FIG. 10E). Indeed, this demonstrates the adverse impact of excess ClO_4^- dopant in PEDOT:PEG solid-contact on the selectivity performance of NO_3^- sc-ISEs. Finally, to evaluate the possibility of reducing ion-exchange duration, **P8** was immersed in KNO_3 for 1 day only. Gratifyingly, the sensitivity (-55.8 ± 0.4 mV/decade) and selectivity performance of **NP8** (see FIGS. 10F and 11) was the best of all the sc-ISEs tested.

Example 5 – Lifespan of Nitrate sc-ISEs

The best-performing sc-ISE, **NP8**, was used for lifespan evaluation. First, an aqueous layer test was performed to evaluate the long-term potential stability of the sc-ISE (see FIG. 6A). The low drift (0.28 mV h^{-1}) observed upon changing the solution from 0.1 M KNO_3 to 0.1 M KCl and back indicated good potential stability and the lack of aqueous layer formation. Next, **NP8** was continuously immersed in 1 mM KNO_3 solution for 17 days, after which a repeat of the aqueous layer test again showed good solid-contact behaviour. This indicated that the sc-ISE could be used for prolonged periods without the build-up of water layer (see FIG. 6B). Furthermore, the sensitivity (-55.1 mV/decade), detection limit (1.12 μM), as well as selectivity (see FIGS. 12A to 12D) of sc-ISE **NP8** after 17 days was comparable to its initial performance. Thereafter, **NP8** was stored dry for 24 weeks and further stored in 1 mM KNO_3 for 55 days, with an overall soaking period of 72 days. Even after the prolonged period of storage and simulated continuous use, there was less than 5% decrease in the sensitivity (-53.3 mV/decade) of the sc-ISE **NP8** and its loss in selectivity was minimal (see FIGS. 12A to 12D and Table 6). Overall, its long-term performance was still significantly superior to the sc-ISE **NP1** with the unmodified solid-contact **P1**.

Table 6. Lifespan testing of the nitrate sc-ISEs **NP8**

No. of Days ^a	Sensitivity (mV/decade)	$\log_{10} K_{\text{NO}_3, \text{H}_2\text{PO}_4}$	$\log_{10} K_{\text{NO}_3, \text{HCO}_3}$	$\log_{10} K_{\text{NO}_3, \text{Cl}}$	$\log_{10} K_{\text{NO}_3, \text{Br}}$	$\log_{10} K_{\text{NO}_3, \text{I}}$	LOD ($\log_{10} a_{\text{NO}_3}/\text{M}$) ^b
1	-55.8 ± 0.7	-4.85	-4.10	-2.60	-1.25	+1.30	-5.95
12	-53.7 ± 3.7	-4.55	-3.85	-2.15	-0.75	+1.30	-5.75
17	-55.1 ± 0.3	-4.80	-4.10	-2.60	-1.20	+1.40	-5.70
72	-53.3 ± 1.9	-4.45	-3.8	-2.15	-0.80	+1.65	-5.70

^aAll sc-ISEs were stored in 1mM KNO₃ to mimic continuous usage. ^bLOD = Limit of detection.

Example 6 – Determination of Nitrate in Agricultural Growth Medium

The foremost important evaluation of every newly developed sensor is its applicability to real sample analysis. Nitrate is an essential plant nutrient and is often applied in a complex matrix with other micronutrients as a solution-based “plant food”. Here, the feasibility of the developed sensor for the determination of nitrate concentration in hydroponics and microalgae culture was investigated. The determination of nitrate concentrations was performed in triplicates using three separate **NP2** ISEs. For each replicate, a standard calibration of ISE **NP2** was first performed from 0.1 M to 1 μM KNO₃, followed by direct immersion of the ISE into the sample without any preparation. The results obtained by this method were compared to the laboratory standard method of anion chromatography (IC), in which the samples had to be pre-treated by dilution and filtration (Table 7).

Table 7. Measured nitrate concentrations of agricultural medium samples using NP2 (n=3)

Sample	Stock [NO ₃ ⁻] / mM	
	NP2 ^a	Expected
Basal medium (clean)	3.10 ± 0.15	2.94 ^b
Basal medium (inoculated with <i>chlorella sorokiniana</i> microalgae)	1.40 ± 0.10	1.37 ^c
Hydroponics medium	8.06 ± 0.76	8.55 ^c

^a Sample activity measured as-is with sc-ISE NP2 (no sample preparation); ^b Expected concentration based on Bold’s basal medium specifications; ^c Samples diluted, then filtered and concentration measured by anion chromatography.

Gratifyingly, **NP2** was able to determine the nitrate activity of the agricultural samples without any pre-treatment in good agreement to IC results (less than ± 2% deviation on the logarithmic scale). Even turbid samples such as the basal medium inoculated with microalgae *chlorella sorokiniana* could be measured as-is. These results demonstrate that the solution-printed PEDOT-PEG based nitrate sc-ISE is a viable method for rapid in-field measurement of nitrate concentration without any pre-treatment.

Example 7 – Performance of sc-ISE

Open Circuit Potentiometry

Open circuit potential measurements were performed at room temperature using a Dropsens Potentiostat (DRP-STAT8000, Metrohm Dropsens) in a 2-electrode setup with a Ag|AgCl|3M KCl|1M LiOAc reference electrode. Aqueous solutions with

different concentrations of KNO₃ and interferences were tested. Three replicates of each sc-ISE were tested.

Sensitivity

5 The sensitivity and limit of detection of the electrode were evaluated by measuring the open circuit potential in KNO₃ solutions with concentration ranging from 1 nM to 0.1 M. The measured potentials (EMF) obtained are plotted against the logarithm in base 10 of primary ion activity. The sensitivity corresponds to the change in potential per decade change in concentration and the limit of detection corresponds to the lowest concentration at which there is observable change in potential, which is defined as the point of the intersection between a linear extrapolation of the Nernstian slope, and the horizontal part of the upper curve where the EMF is a constant value.⁴⁵

Selectivity

Based on IUPAC recommendations, the selectivity of the electrode against other anions was evaluated using the fixed interference method (FIM). The open circuit potential of a cell comprising an ion-selective electrode and a reference electrode is measured with potassium salt solutions of fixed interfering ion, a_B , and varying activity of the primary ion, a_{NO3} . The concentration of NO₃⁻ ions were varied from 10 nM to 0.1 M. The concentrations of dihydrogen phosphate (H₂PO₄⁻) and bicarbonate (HCO₃⁻) ions were 0.1 M, chloride (Cl⁻), bromide (Br⁻) and nitrite (NO₂⁻) ions were 0.01 M, and iodide (I⁻) ions was 0.1 mM; less interfering ions could be measured at higher fixed concentration, while more interfering ions were measured at lower fixed concentration. The EMF obtained are plotted against the logarithm in base 10 of primary ion activity. The intersection of the extrapolation of the linear regions of the plot will indicate the value of a_{NO3} which gives the same EMF value as a_B , which is used to calculate selectivity coefficient, $K_{NO3,B}^{pot}$ from the following equation:

$$\log_{10} K_{NO3,B}^{pot} = \log_{10} a_{NO3} - \frac{z_{NO3}}{z_B} \log_{10} a_B$$

Sensitivity towards Other Interferences

30 The sensitivity of **NP2** towards environmental interferences was investigated in 0.1 M KNO₃. For the light sensitivity test, electrode potentials were first recorded in ambient light condition, followed by a dark condition. The whole electrochemical cell was subsequently exposed to ultraviolet (UV, 365 nm), then infra-red (IR, 800 nm) light while in the dark before returning to ambient light condition, each time with a return to the dark before the next lighting condition. The gas sensitivity of **NP2** was then studied for O₂ and N₂ using 0.1 M KNO₃ solutions purged with each gas respectively.

pH Effect

Measurements were performed in 0.1 M KNO₃ (25 mL), with increasing aliquots (0.20 – 4.5 mL) of concentrated HCl or KOH added to achieve a pH range of 1 to 13, as determined by a Metrohm 913 pH meter with Solitrode (with Pt1000) pH probe.

Response Time

- Potentiometric data were processed on Microsoft Excel using ExceLab 7.0. The DERIVXY(x, y, p, [options]) function was used to calculate the derivative of electrode potential with respect to measurement time (dE/dt). The derivative is then plotted against measurement time to obtain the differential response plot which allows the differential response time to be approximated (see FIGS. 9A and 9B). The dynamic response time was determined as the time between the change in NO₃⁻ concentration and the time when dE/dt (derivative of electrode potential with respect to time) reaches ≤ 0.1 mV/s.

10 Example 8 – Rationale for Improvements in Selectivity from Ion Exchange

Based on the phase boundary theory, if ion exchange is thermodynamically reversible, then the electrochemical potential of the primary ion should be equal to each other in both the aqueous and the membrane phase.

$$\bar{\mu}_I^{aq} = \bar{\mu}_I^m \quad 1.1$$

- 15 where $\bar{\mu}_I^{aq}$ is the electrochemical potential of primary ion I in the aqueous phase, and $\bar{\mu}_I^m$ is the electrochemical potential of primary ion I in the membrane phase.

$$\mu_I^{0,aq} + RT \ln a_I^{aq} + z_I F \varphi^{aq} = \mu_I^{0,m} + RT \ln a_I^m + z_I F \varphi^m \quad 1.2$$

- 20 where $\mu_I^{0,aq}$ and $\mu_I^{0,m}$ are the standard chemical potential of I in aqueous and membrane phases respectively; φ^{aq} and φ^m are the electrical potential for aqueous and membrane interface; a_I^{aq} and a_I^m is the activity of I in the aqueous and membrane phases respectively; z_I is the charge of ion I; R is the gas constant, T temperature, and F faraday constant.

This can be arranged to the phase boundary potential equation

$$E = \Delta_a^m \varphi_I = \varphi^m - \varphi^{aq} = \frac{\mu_I^{0,aq} - \mu_I^{0,m}}{z_I F} + \frac{RT}{z_I F} \ln \frac{a_I^{aq}}{a_I^m} \quad 1.3$$

- 25 Typically, primary ion activity in the membrane phase is assumed to be constant due to the fixed amount of oppositely charged lipophilic sites (R_T), so eqn 1.3 reduces to the well-known Nernst equation:

$$E_I = E_I^0 + \frac{RT}{z_I F} \ln a_I^{aq} \quad 1.4$$

$$\text{where } E_I^0 = \frac{\mu_I^{0,aq} - \mu_I^{0,m}}{z_I F} + \frac{RT}{z_I F} \ln \frac{1}{a_I^m} \quad 1.5$$

In more complex solutions containing both primary and interference ions, the Nikolsky-Eisenman equation is applied,

$$E_I = E_I^0 + \frac{RT}{z_I F} \ln (a_I^{aq} + \sum_J K_{IJ}^{pot} (a_J^{aq})^{z_I/z_J}) \quad 1.6$$

where K_{IJ}^{pot} is the selectivity coefficient of ion I to J, and a_J^{aq} is the activity of interfering ion J.

The selectivity coefficient K_{IJ}^{pot} is defined as

$$\log_{10} K_{IJ}^{pot} = \frac{z_I (E_J^0 - E_I^0)}{s} \quad 1.7$$

Where $s = 2.303RT/F$

5 By substituting in the above equation 1.5,

$$\log_{10} K_{IJ}^{pot} = \frac{z_I}{s} (\Delta_a^m \varphi_J^0 - \Delta_a^m \varphi_I^0) + \log_{10} \frac{a_I^m}{(a_J^m)^{z_I/z_J}} \quad 1.8$$

where $\Delta_a^m \varphi_I^0$ and $\Delta_a^m \varphi_J^0$ are the standard electrode potentials of ions I and J.

Thus, it can now be seen that the selectivity coefficient is determined by two factors. The first term relates to the standard potential difference for the primary and interfering ion, which is governed by solvation energy differences of ions I and J in the respective phases. This typically follows the Hofmeister selectivity sequence. The second term indicates that membrane selectivity can be adjusted by tuning the ion activities in the membrane.

For electrodes **P2** and **P8**, since the dopant ion is the primary ion NO_3^- , its activity in the membrane is approximately equal to the concentration of lipophilic additive:

$$15 \quad a_{\text{NO}_3}^m \approx R_T$$

As such, both the sensitivity and selectivity curves are predictable by the Nernst equation and Hofmeister selectivity respectively. For electrodes **P3** to **P6**, since the amount of dopant ions is small and these ions can exchange to the primary ion NO_3^- , the above still holds true.

20 However, in the case of electrodes **P1** and **P7**, there is excess ClO_4^- dopant ions which are highly lipophilic and thus preferentially partition in the membrane phase.

$$a_{\text{NO}_3}^m + a_{\text{ClO}_4}^m \approx R_T, \text{ where } a_{\text{ClO}_4}^m \gg a_{\text{NO}_3}^m$$

Thus, equation 1.2 is modified to equation 1.9:

$$\begin{aligned} & \mu_I^{0,aq} + RT \ln a_I^{aq} + z_I F \varphi^{aq} \\ &= \mu_I^{0,m} + RT \ln a_I^m + z_I F \varphi^m + \mu_{\text{ClO}_4}^{0,m} \\ &+ RT \ln a_{\text{ClO}_4}^m + z_{\text{ClO}_4} F \varphi^m \end{aligned} \quad 1.9$$

25

Correspondingly, equation 1.8 will be modified to equation 1.10,

$$\log_{10} K_{IJ}^{pot} = \frac{z_I}{s} (\Delta_a^m \varphi_J^0 - \Delta_a^m \varphi_I^0) + \log_{10} \frac{a_I^m + a_{ClO_4}^m}{(a_J^m + a_{ClO_4}^m)^{z_I/z_J}} \quad 1.10$$

- By comparing the equation 1.8 where the primary ion is the dopant, and equation 1.10 where there is excess ClO_4^- dopant ions, we can see that since $a_{ClO_4}^m \gg a_{NO_3}^m$, the selectivity for primary ion over interfering ion will decrease in the presence of these dopants. Thus, removal of the excess lipophilic dopant ions by ion exchange with the primary ion can drastically improve the selectivity.

Summary of Examples 1 to 8

- In summary, nitrate sc-ISEs were developed with solution-printable PEDOT:PEG as a solid-contact. Selectivity of the sc-ISE was drastically improved by anion exchange, as evidenced by XPS and potentiometric sensing. EIS demonstrated that excess ClO_4^- ions in the original PEDOT:PEG solid-contact (**P1**) led to an additional resistance, which hindered the selectivity performance of sc-ISE **NP1**. The removal of ClO_4^- ions through ion exchange reduced the overall resistance for the sc-ISE, thus enhancing NO_3^- selectivity.

- The best-performing sc-ISE, **NP8**, exhibited near-Nernstian response (-55.8 ± 0.5 mV/decade) with a wide dynamic range (down to $1.12 \mu M$) and excellent selectivity against interfering ions over at least 72 days of continuous usage and 24 weeks of dry storage. In comparison to other recently reported nitrate sc-ISEs (Table 8), the disclosed sensor demonstrated good detection range, better selectivity, and extended lifespan with a relatively simple fabrication method. The solution-processability of the biocompatible and flexible PEDOT:PEG, in conjunction with the simple drop-cast and ion-exchange protocol, would enable the scalable preparation of flexible anion sc-ISEs.

Table 8. Comparison of recently reported nitrate all-solid-state electrodes with quaternary ammonium anion exchangers.

Solid-contact	Solid-Contact Fabrication	Anion Exchanger	Sensitivity /mV dec ⁻¹	Linear range / log ₁₀ (<i>a</i> _{NO₃} / M)	LOD ^a / log ₁₀ (<i>a</i> _{NO₃} / M)	log ₁₀ <i>K</i> _{NO₃,Cl}	Lifespan ⁱ	Ref
functionalised-MWCNT ^b	Synthesis + Dropcast	TDDANO ₃	-57.7	-5.1 to -1.0	-5.6	< -1.7 ^h	NA	prior art
Laser-induced graphene	UV laser graphitisation	TDMANO ₃ ^f	-54.8 ± 2.5	-4.7 to -1.0	-5.3	NA	NA	prior art
Graphene-TTF/TTF ^{++c}	Dropcast + Electrochemical oxidation	TDMACl ^f	-59.1 ± 0.3	-6.0 to -1.0	-6.2 ± 0.1	NA	NA	prior art
Reduced graphene oxide	Synthesis + Slurry	TDMANO ₃ ^f	-57.9	-4.3 to -1.0	-4.5	-1.9 ± 0.1	NA	prior art
PtNPs-CB ^d	Dropcast	TDMANO ₃ ^f	-58.6 ± 0.2	-4.4 to -1.0	-6.3	-2.2 ± 0.2	>30 d in aq	prior art
POT/MoS ₂ ^e	Dropcast	TDMANO ₃ ^f + MTPPB ^g	-64	-3.2 to -1.0	-4.0	NA	>25 d in soil	prior art
PEDOT-C ₁₄ /TFPB	Electropolymerisation	TDMANO ₃ ^f	-54.0	-5.5 to -1.0	-7.0	NA	>10 d in aq	prior art
PEDOT:PEG/NO ₃	Dropcast + Ion-exchange	TDDANO ₃	-55.8 ± 0.7	-5.0 to -1.0	-6.0 ± 0.1	-2.6 ± 0.2	>72 d in aq + 168 d dry	This work

^aLOD = Limit of detection; ^bMWCNT = multi-walled carbon nanotube; ^cTTF = tetrathiafulvalene; ^dPt-NPs-CB = carbon black supporting platinum nanoparticles; ^ePOT/MoS₂ = poly(3-octylthiophene)/ molybdenum disulfide; ^fTDMA = tridodecylmethylammonium; ^gMTPPB = methyltriphenylphosphonium bromide; ^hNot tested beyond this point; ⁱd= days, aq = aqueous.

Example 9 – Rigid Chloride Anion (Cl^-) sc-ISEs

Preparation of Chloride Anion (Cl^-) sc-ISEs from PEDOT-PEG coated SPEs

Ion exchange of PEDOT-PEG dopant. The working electrodes of SPEs coated with PEDOT-PEG were submerged in primary salt solution (0.1 M of KCl for chloride sc-ISEs) for three days to perform ion-exchange between the ClO_4^- dopant and the anion in the solution.

Preparation and casting of chloride ISM cocktail. The chloride selective membrane cocktail was prepared as a mixture as well containing 1.0% wt of ionophore (chloride ionophore IV, purchased from Sigma Aldrich, Singapore), 0.5% wt of lipophilic salt (TDMA-Cl, purchased from Sigma Aldrich, Singapore), 65.7% wt of plasticizer (NPOE, purchased from Sigma Aldrich, Singapore) and 32.8% wt PVC dissolved in 2.45mL of THF. 10 μL of the ISM cocktail was drop-casted onto the PEDOT-PEG SPEs and dried overnight at ambient temperature, followed by drying under vacuum for 4 hours. The sc-ISEs were then conditioned in 1 mM KCl solution for 16 hours. The fabrication process followed the protocol in Example 1 and in FIG. 1A.

Performance of Chloride Anion (Cl^-) sc-ISEs with Ion Exchange

Performance after conditioning. Chloride sc-ISEs with KCl-exchanged PEDOT-PEG showed near-Nernstian sensitivity towards the Cl^- anion and good selectivity against HCO_3^- , NO_3^- and Br^- (see FIG. 13A). In comparison, the performance of the sc-ISE with the original untreated PEDOT-PEG/ ClO_4^- as solid-contact was less optimal with poorer slope linearity and sensitivity (see FIG. 13B).

Performance without conditioning. An additional advantage of the present ion-exchange protocol is the ability to function as out-of-box ready-to-use sensors without the need to perform any solution conditioning prior to usage. When chloride sc-ISEs with KCl-exchanged PEDOT-PEG were used before conditioning, their performance was comparable to that after conditioning, achieving near-Nernstian sensitivity towards the Cl^- anion and good selectivity against HCO_3^- , NO_3^- and Br^- (see FIG. 13C), indicating that the conditioning step could be eliminated. In contrast, the performance of the sc-ISE with the original untreated PEDOT-PEG/ ClO_4^- as solid-contact was significantly poorer without conditioning, with sub-Nernstian sensitivity and poor selectivity performances (see FIG. 13D). This example highlights the importance of the present method in preparing readily useable anion sc-ISEs for non-trained users with simple operational procedure.

A comparison of the sensitivity and selectivity performance of both sc-ISEs before and after conditioning is shown in Table 9.

Table 9. Comparison of performance of rigid chloride sc-ISEs with different solid-contacts before and after conditioning

KCl exchanged PEDOT- PEG before conditioning	KCl exchanged PEDOT-PEG after conditioning	PEDOT- PEG/ ClO_4^- before conditioning	PEDOT-PEG/ ClO_4^- after conditioning
--	--	---	--

Sensitivity (mV/decade)	-53.0	-57.1	-27.7	-54.2
Selectivity against HCO_3^- ($\log K_{\text{Cl,HCO}_3}$)	-1.38	-1.50	NA	-1.61
Selectivity against NO_3^- ($\log K_{\text{Cl,NO}_3}$)	0.32	0.48	NA	0.48
Selectivity against Br^- ($\log K_{\text{Cl,Br}}$)	0.45	0.51	NA	0.45

Example 10 – Rigid Nitrite Anion (NO_2^-) sc-ISEs

Preparation of Nitrite Anion (NO_2^-) sc-ISEs from PEDOT-PEG coated SPEs

5 *Ion exchange of PEDOT-PEG dopant.* The working electrodes of SPEs coated with PEDOT-PEG were submerged in primary salt solution (0.1 M NaNO_2 for nitrite sc-ISEs) for three days to perform ion-exchange between the ClO_4^- dopant and the anion in the solution.

10 *Preparation and casting of nitrite ISM cocktail.* The nitrite selective membrane cocktail was prepared as a mixture as well containing 2.0% wt of ionophore (nitrite ionophore VI, purchased from Sigma Aldrich, Singapore), 0.4% wt of lipophilic salt (TDMA-Cl, purchased from Sigma Aldrich, Singapore), 65.1% wt of plasticizer (DOS, purchased from Sigma Aldrich, Singapore) and 32.5% wt PVC dissolved in 0.93mL of THF. 10 μL of the ISM cocktail was drop-casted onto the PEDOT-PEG SPEs and dried overnight at ambient temperature, followed by drying under vacuum
15 for 4 hours. The sc-ISEs were then conditioned in 1 mM NaNO_2 solution for 16 hours. The fabrication process followed the protocol in Example 1 and in FIG. 1A.

Performance of Nitrite Anion (NO_2^-) sc-ISEs with Ion Exchange

20 The nitrite sc-ISE prepared as described above showed near-Nernstian sensitivity (-53.9 mV/decade) towards the NO_2^- anion and good selectivity against Cl^- ($\log K_{\text{NO}_2,\text{Cl}} = -3.74$), NO_3^- ($\log K_{\text{NO}_2,\text{NO}_3} = -1.85$) and ClO_4^- ($= 0.17$) (see FIG. 14). In addition, contrary to past literature, the present nitrite sc-ISE using the same ionophore also demonstrated the ability to perform without the use of buffer. Thus, the present nitrite sc-ISE would simplify the user experience with the elimination of sophisticated pre sample preparation procedure.

25 Example 11 – Preparation of Flexible sc-ISEs

Step 1: Fabrication of Flexible Electrodes

Polyimide (purchased from LIREN®) was used as the substrate for the fabrication of flexible SPEs. The polyimide sheet was cleaned with isopropanol (generic brand) and a sticker stencil consisting of the working electrode shape was applied onto the sheet
30 (FIG. 15, step (i)). Sunchemical Carbon paste was spread onto the stencil using a

- squeegee to make the working electrode (FIG. 15, step (ii)). The carbon working electrode was dried at 100°C for 20 minutes before removing the sticker (FIG. 15, step (iii)). Following that, the carbon was hard annealed by heating at 140°C for 10 minutes. The silver connector was added to the carbon working electrode by
- 5 dispensing silver ink (Dycotec DM-SIP-3061S) using an ink dispenser and dried at 140°C for 20 minutes (FIG. 15, step (iv)). Lastly, a dielectric layer (DuPont 5036) was applied using the squeegee to cover the top half of the silver connector (up until the working electrode) (FIG. 15, step (v)).

Step 2: Preparation of Solid Contact

- 10 Prior to drop-casting, PEDOT-PEG was subjected to 30 minutes of agitation followed by another 30 minutes of sonication. 1 μ L of PEDOT-PEG was drop-casted onto the flexible SPEs (FIG. 15, step (vii)) and dried at 60 °C for 30 minutes, followed by drying in vacuum oven for 4 hours.

- Cyclic voltammetry (CV) was used to investigate the electrochemical characteristics of the PEDOT-PEG/ ClO_4^- solid contact (see FIG. 16A). This solid-contact showed a significantly higher capacitance compared to PEDOT:PSS (see FIG. 16B), which is commonly used in flexible cation sc-ISEs.
- 15

Step 3: Ion Exchange of PEDOT-PEG Dopant

This step is only required for anion sc-ISEs. It can be skipped for cation sc-ISEs.

- 20 The working electrodes of SPEs coated with PEDOT-PEG were submerged in primary salt solution (either 0.1 M of KNO_3 for nitrate sc-ISEs or 0.1 M of KCl for chloride sc-ISEs or 0.1 M NaNO_2 for nitrite sc-ISEs) for three days to perform ion-exchange between the ClO_4^- dopant and the anion in the solution. (FIG. 15, step (viii)). The ion-exchanged electrodes were rinsed with DI water and dried at 60°C for
- 25 four hours. Following that, they were vacuum dried for three hours.

Step 4: Preparation and Casting of ISM

As examples, a potassium ISE was prepared as cation ISE, and nitrate and chloride ISEs were prepared as anion ISEs.

- Preparation of potassium ISM cocktail.** The potassium selective membrane cocktail was prepared as a mixture containing 2% weight of ionophore (valinomycin, purchased from Sigma Aldrich, Singapore), 0.5% wt of lipophilic salt (KTpCIPB, purchased from Sigma Aldrich, Singapore), 64.7% wt of plasticizer (DOS, purchased from Tokyo Chemical Industry, Singapore) and 32.8% wt PVC dissolved in 2mL of THF.
- 30

- Preparation of nitrate ISM cocktail.** The nitrate selective membrane cocktail was prepared as a mixture as well containing 15% wt of lipophilic salt (TDDANO₃
- 35

purchased from Sigma Aldrich, Singapore), 40% wt of plasticizer (NPOE, purchased from Sigma Aldrich, Singapore) and 45% wt of PVC dissolved in 2mL of THF.

Casting of ISM. Similar to the conductive polymer layer (i.e., the solid contact), drop-casting was used to deposit the membrane on the electrode. The dried ion-exchanged electrodes were drop-casted with 5 μ L of membrane cocktail and left to air-dry at room temperature overnight (FIG. 15, step (ix)). Subsequently, the membranes on the electrodes were vacuum dried for four hours. Finally, the electrodes were conditioned by covering the membrane with a drop of 1 mM KNO₃ solution for potassium and nitrate sc-ISEs, and with 1 drop of 1 mM KCl solution for chloride sc-ISEs, or by soaking the membrane in the same solutions.

Example 12 – Performance of Potassium (Cation) Flexible sc-ISEs

A flexible potassium sc-ISE was prepared, which showed near-Nernstian sensitivity towards the K⁺ cation and good selectivity against Na⁺ and NH₄⁺ (see FIG. 17A). In comparison with a similar sc-ISE with PEDOT:PSS as transduction layer (see FIG. 17B), the present sc-ISE showed a larger linear range.

Table 10. Comparison of performance of flexible potassium sc-ISEs with different solid-contacts

	PEDOT- PEG/CIO ₄ ⁻ sc-ISE	PEDOT:PSS sc-ISE	Conventional ISE
Sensitivity (mV/decade)	+55.8	+55.0	+59.2
Selectivity against Na ⁺ ($\log K_{K,Na}$)	-3.2	-3.5	-3.7
Selectivity against NH ₄ ⁺ ($\log K_{K,NH_4}$)	-1.3	-1.2	-1.9
Linear range (log a _K)	-5.2	-4.2	-5.0

In addition, an aqueous layer test was performed on the potassium sc-ISEs based on PEDOT-PEG and PEDOT:PSS to determine the long-term potential stability of the sc-ISE. The test involved changing from 0.1 M KNO₃ to 0.1 M NaNO₃ interfering solution before changing back to 0.1 M KNO₃. Build-up of an aqueous layer between the ISM and the transduction layer can be identified by a large drift after the expected instantaneous response following each solution change.

The present potassium sc-ISEs based on PEDOT-PEG exhibited a relatively stable EMF reading with a drift of less than 2.0 mV/h (see FIG. 18A). Furthermore, the response after each solution change was relatively quick and the EMF values in 0.1 M KNO₃ before and after exposure to NaNO₃ were similar, indicating that the solid-contact was sufficiently hydrophobic to prevent build-up of aqueous layer. In

contrast, the potassium ISEs based on PEDOT:PSS drifted significantly throughout the duration of testing and the EMF values 0.1 M KNO₃ before and after exposure to NaNO₃ were very different (see FIG. 18B).

Example 13 – Performance of Nitrate (Anion) Flexible sc-ISEs

- 5 A flexible nitrate sc-ISE was prepared, which showed near-Nernstian sensitivity towards the NO₃[−] anion and good selectivity against Cl[−] and H₂PO₄[−] (see FIG. 19A). In comparison (see Table 11), a similar sc-ISE with original PEDOT-PEG/CIO₄[−] as solid-contact showed significantly poorer selectivity against the interfering anions (see FIG. 19B). The performance of the sc-ISE with PEDOT:PSS was even poorer, with sub-Nernstian sensitivity and poor potential stability (see FIG. 19C). Thus, the use of PEDOT-PEG and the present ion exchange protocol are essential for the significantly improved performance of our flexible nitrate sc-ISE.

Table 11. Comparison of performance of flexible nitrate sc-ISEs with different solid-contacts

	KNO ₃ exchanged PEDOT-PEG	PEDOT-PEG/ CIO ₄ [−]	PEDOT:PSS
Sensitivity (mV/decade)	−51.2	−54.8	−41.8
Selectivity against Cl [−] (<i>logK_{NO₃,Cl}</i>)	−2.7	−0.9	NA
Selectivity against H ₂ PO ₄ [−] (<i>logK_{NO₃,H₂PO₄}</i>)	−4.5	−2.1	NA

15

In addition, an aqueous layer test was performed on the nitrate sc-ISEs based on KNO₃ exchanged PEDOT-PEG and PEDOT:PSS to determine the long-term potential stability of the sc-ISE. The test involved changing from 0.1 M KNO₃ to 0.1 M KCl interfering solution before changing back to 0.1 M KNO₃. Build-up of an aqueous layer between the ISM and the transduction layer can be identified by a large drift after the expected instantaneous response following each solution change.

20

- The present nitrate sc-ISEs based on KNO₃ exchanged PEDOT-PEG exhibited a relatively stable EMF reading with a drift of less than 2.0 mV/h (see FIG. 20A). Furthermore, the response after each solution change was relatively quick and the EMF values in 0.1 M KNO₃ before and after exposure to KCl were similar, indicating that the solid-contact was sufficiently hydrophobic to prevent build-up of aqueous layer. In contrast, the nitrate ISEs based on PEDOT:PSS drifted significantly throughout the duration of testing and the EMF values 0.1 M KNO₃ before and after

25

exposure to KCl were very different (see FIG. 20B). This further demonstrates the importance of our protocol in preparing high-performance solid-contact anion sc-ISEs.

Example 14 – Flexibility of sc-ISEs

5 To investigate the flexibility of the flexible nitrate ISEs as described in Examples 10 and 11, a durability study was performed after repeated mechanical bending. A flexible nitrate ISE 2102 with a length of 2.5cm was bent 2104 through a distance of 1.2cm for a total of 50 cycles (see FIG. 21) and the performance of the membrane was compared against the initial performance (see Table 12). Gratifyingly, the electrode remains stable after 50 bending cycles, with an average reduction of 2.7% in the sensitivity slope across 2 replicates. Moreover, the selectivity of NO₃⁻ against Cl⁻ and Br⁻ are remains relatively similar after 50 cycles of bending, and hence, demonstrates good mechanical stability.

Table 12. Comparison of performance of flexible nitrate sc-ISEs before and after 50 bending cycles. (n=2)

ISE	0 cycles			50 cycles			Sensi- tivity change
	Sensitivity (mV/dec)	Selectivity Cl ⁻ (logK _{NO₃,Cl})	Selectivity Br ⁻ (logK _{NO₃,Br})	Sensitivity (mV/dec)	Selectivity Cl ⁻ (logK _{NO₃,Cl})	Selectivity Br ⁻ (logK _{NO₃,Br})	
1	-51.6	-2.85	-1.30	-52.70	-2.65	-1.20	-2.1%
1	-53.1	-2.70	-1.15	-54.90	-2.40	-1.05	-3.3%
Av.	-52.4	-2.78	-1.23	-53.8	-2.53	-1.13	-2.7%

Industrial Applicability

The solid contact and the ion-selective electrode of the disclosure may be used in a variety of applications such as medicine, healthcare (e.g., wearables), environmental applications, culture (e.g., cell or algae) monitoring and agricultural sensing (demonstrated by direct measurement of real hydroponics and microalgae culture media, showing the advantages of using the present sensor for rapid in-field monitoring of nitrates). The solid contact and the ion-selective electrode of the disclosure may also be used in aquaculture and food safety/production applications due to their portability, low cost and quick analysis time.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A method of treating a solid contact for sensing an ion, comprising the step of immersing the solid contact in an aqueous medium that is free from perchlorate, wherein the solid contact is a conducting polymer.
- 5
2. The method of claim 1, wherein the aqueous medium is an aqueous solution of the ion.
3. The method of claim 2, wherein the aqueous solution of the ion has a concentration of about 0.1 M.
- 10
4. The method of claim 1, wherein the aqueous medium is deionized water.
5. The method of any one of claims 1 to 4, wherein the ion is selected from the group consisting of nitrate, chloride, nitrite and potassium.
- 15
6. The method of any one of claims 1 to 5, wherein the immersing step is undertaken for a duration in the range of 0.2 to 5 days.
- 20
7. The method of claim 6, wherein the duration is about 1 day.
8. A solid contact obtained from the method of any one of claims 1 to 7.
9. A method of preparing an ion-selective electrode for sensing an ion, comprising the steps of:
- 25
- (a) forming a layer of solid contact on an electrode, wherein the solid contact is derived from poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(ethyleneglycol) (PEG);
- (b) immersing the layer of solid contact and the electrode in an aqueous medium that is free from perchlorate; and
- 30
- (c) depositing an ion-selective membrane on the layer of solid contact.
10. The method of claim 9, wherein the forming step (a) comprises a step of drop-casting a composition of PEDOT and PEG onto the electrode.
- 35
11. The method of claim 9 or 10, wherein the depositing step (c) comprises a step of drop-casting a precursor composition of the ion-selective membrane onto the layer of solid contact.
- 40
12. The method of claim 11, further comprising a step of preparing the precursor composition of the ion-selective membrane before the depositing step (c).
13. The method of any one of claims 9 to 12, further comprising a step of conditioning the ion-selective electrode in an aqueous solution of the ion after the depositing step (c).
- 45
14. The method of claim 13, wherein the aqueous solution of the ion has a concentration of 1 mM.

15. The method of claim 13 or 14, wherein the conditioning step is undertaken for a duration in the range of 8 hours to 24 hours.
- 5 16. The method of any one of claims 9 to 15, wherein the electrode comprises a substrate selected from the group consisting of polyimide, poly(methyl methacrylate (PMMA), polyethylene terephthalate (PET), polyethylene terephthalate glycol (PETG), polypropylene (PP), fluorinated ethylene propylene (FEP), polyethylene (PE), polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS) and poly(ethylene-*co*-vinyl acetate).
- 10 17. The method of any one of claims 9 to 15, wherein the electrode is a screen-printed electrode.
- 15 18. An ion-selective electrode prepared by the method of any one of claims 9 to 17.
19. The ion-selective electrode of claim 18, which has a sensitivity and a selectivity that are independently at least 97% after 50 cycles of bending.
- 20 20. A method of sensing an ion in a sample, comprising the step of immersing the ion-selective electrode of claim 18 or 19 in the sample.