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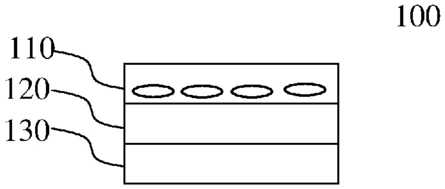

FIG. 2A

(57) Abstract: Aspects concern a layer structure for an ion selective electrode sensor, the layer structure comprising: a porous ion selective membrane; a solid contact layer; an electrical conductor disposed on an electrode, which is connectable to an electronic circuit; wherein the solid contact layer is disposed between the porous ion selective membrane and the electrical conductor.

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SOLID CONTACT ION SELECTIVE ELECTRODE

Technical field

[0001] Various aspects of this disclosure relate to a layer structure for an ion selective electrode sensor. Various aspects of this disclosure also relate to a method of fabricating the layer structure for an ion selective electrode sensor and an ion selective electrode sensor.

Background

[0002] Ion selective electrodes (ISEs) are convenient devices, which are used to make ion determination measurements, of which solid contact ISEs (SC-ISEs) offer convenience in their storage and use. However, SC-ISEs with an ion selective membrane (ISM) have potential reproducibility and/or reliability issues in the determination measurements, due to water induced degradation.

[0003] Therefore, there is a need to provide for improved SC-ISEs.

Summary

[0004] Various embodiments concern a layer structure for an ion selective electrode sensor, the layer structure including: a porous ISM; an SC layer; an electrical conductor disposed on an electrode, which is connectable to an electronic circuit; wherein the SC layer is disposed between the porous ISM and the electrical conductor.

[0005] Various embodiments concern an ion selective electrode sensor including a substrate; the layer structure as defined above disposed on a first portion of the substrate; and a reference electrode disposed on a second portion of the substrate.

[0006] Various embodiments concern a method of fabricating the layer structure for an ion selective electrode sensor as defined above, the method including: providing an electrical conductor disposed on an electrode, which is connectable to an electronic circuit; disposing an SC layer on the electrical conductor; heating the disposed SC layer; and disposing an ISM from a solution including a solvent and a membrane precursor on the disposed SC layer to form the layer structure.

Brief description of the drawings

[0007] The invention will be better understood with reference to the detailed description when considered in conjunction with the non-limiting examples and the accompanying drawings, in which:

- FIG. 1 is an illustration showing in A: the ingress of water from the sample when a SC-ISE is brought into contact with solution; and B: saturation of water, with droplets in the ISM and a water layer between the ISM and SC;
- FIG. 2A is a side view of the SC-ISE architecture according to some embodiments;
- FIG. 2B is a side view of SC-ISE architecture according to some embodiments with water ingress and showing the pathway of primary ions migration;
- FIG. 3 is a schematic drawing of a screen printed electrode;
- FIG. 4 is an optical microscope images of ISMs when the cocktails were deposited at (a) room temperature; (b)40 °C (c) 50 °C and (d) 60 °C accompanied by (e) a cross section view of a 1 mm-wide ISM segment;
- FIG. 5 is a graph showing the electrochemical impedance spectroscopy of K^+ SC-ISEs with ISM cocktails deposited at room temperature, and at elevated temperatures of 40 °C to 60 °C;
- FIG. 6 is a graph showing calibration curves of K^+ SC-ISEs deposited at room temperature, with thicker membranes and with bubbles in the membrane; each curve has been offset by 50 mV from the preceding one for clarity;
- FIG. 7 is a graph showing the electrochemical impedance spectroscopy of electropolymerized PEDOT:PSS in 0.1 M KCl; each spectra has been separated by 20 kΩ for clarity; the inset shows the overlapping spectra;
- FIG. 8 is a graph showing the potential across time for 3 identical SC-ISEs each of DRP-110-60 and DRP-110-RT-Thick in 2 solutions of KCl and NaCl; KCl was alternated between a concentration of 10^{-3} and 10^{-5} M, while NaCl was kept constant at 10^{-1} M;
- FIG. 9 is a flow chart illustrating the method of fabricating the layer structure for an ion selective electrode sensor; and
- FIG. 10 shows a profilometry of the membranes of both DRP-110-RT and DRP-110-Thick, the introduction of bubbles in the membrane doubles the membrane thickness,

as the volume of the solid membrane for both electrodes is the same, the porosity of the membrane is estimated to reach 50% at the maximum.

Detailed description

[0008] The disclosure refers to a layer structure 100 for an ion selective electrode sensor 200. The layer structure 100 includes a porous ISM 110. The layer structure 100 includes an SC layer 120. The layer structure 100 includes an electrical conductor 130 disposed on an electrode 140. The electrical conductor 130 disposed on an electrode 140 is connectable to an electronic circuit 150. The SC layer 120 is disposed between the porous ISM 110 and the electrical conductor.

[0009] During conventional operation of an SC-ISE, water ingress into the SC-ISE may occur, resulting in before mentioned reliability issues of the conventions SC-ISE. It was recognized that while immersed in solution, water enters into the SC-ISE from the sample through diffusion. A schematic of the dry and water saturated ISE is shown in FIG. 1. In FIG. 1, (1) refers to the ISM, (2) refers to the solid contact (SC) layer and (3) refers to the electrical conductor. The arrow shows the water ingress from the sample. As a result, a layer of water may form between the SC layer and the ISM. The volume of the bulk water that develops over time in the ISE is very low. As it is water, the composition of dissolved ions is subject to large changes in the composition even at low rates of absolute ion exchange. In comparison, a small volume of SC is not an issue if the SC does not have ions dissolved inside it.

[0010] Hence, small fluxes of ions between the sample and water layer can cause relatively large changes to the composition of this layer, resulting in correspondingly large shifts in potential. When the SC-ISE is exposed to solutions exceeding the selectivity coefficients of the ISM, primary ions are lost to the solution and exchanged for interfering ions, leading to an accompanying loss of potential stability of the saturated SC-ISEs. The shift in potential over time, even with a constant sample concentration, is indicative of an ongoing change within the SC-ISE. More generally, an ongoing parallel process results in the failure of the stability and reproducibility for an SC-ISE measurement.

[0011] The layer structure 100 for an ion selective electrode sensor as described herein mitigates the perturbation of the chemical composition at the ISM | SC interface that is encountered in conventional SC-ISEs, and which results in an instability of the electrode potential, due to the development of a water layer between the SC layer 120 and the ISM. The mitigation of the perturbation is believed to be the result of the porous ISM 110 that is employed in the present disclosure.

[0012] The “porous ion selective membrane (ISM)”, as used herein, refers to an ISM with intentionally created cavities. These cavities (e.g. pores) may be the result of bubbles formed during the manufacturing process. For example, the pores may be the result of a solvent displacing the membrane material during expansion into the gaseous state. The pores may therefore have a shape of expanded gas within a viscous liquid. The shape of the pores may be ellipsoid, wherein the greatest expansion of the pores may be in a plane that is parallel to a surface of the SC layer 120 (see, FIG. 2). This ellipsoid shape may be the result of the manufacturing process, wherein the heat is emitted to the membrane precursor through the SC layer 120 to a surface thereof. The advantage of the ellipsoid shape is that it further increases the pathway of ions from the sample to the SC layer 120, thereby slowing down the composition change of the water layer to become negligible within the sensing window (see, FIG. 2A and FIG. 2B). In some embodiments, the pores may be in contact with the surface of the SC layer 120 and the shape of the pore may be half an ellipsoid. The shape of the pores as detailed herein is contrasted to a shape that results from, for example, a porosity created by a template.

[0013] The pores (e.g. bubbles) may have a diameter of between 0.1 mm and about 1.0 mm, or between 0.1 mm and about 0.5 mm, in its largest expansion.

[0014] The pores (e.g. bubbles) may be introduced into the SC-ISE by a heating step during the deposition of a membrane precursor. The membrane precursor may include a volatile solvent (e.g. THF), in which the membrane components are dissolved. The membrane precursor may be drop cast onto the SC layer 120 on a SC-ISE and the solvent is left to evaporate.

[0015] By adjusting the heat to be near the boiling point of the solvent, pores (e.g. bubbles) can be formed at the interface of the SC layer 120 and membrane solution. These pores (e.g. bubbles) grow over time, and their growth competes with the increasing viscosity of the cocktail, as more solvent is lost. The bubbles that remain in the cocktail are eventually trapped in the ISM when it solidifies to form the pores of the porous ISM 110.

[0016] Depending on the applied temperature, the number of pores (e.g. bubbles) and the coverage of the pores (e.g. bubbles) on the SC layer 120 can be controlled. As the method is simple and requires no additional chemical components to be added except the membrane precursors, it is highly versatile and can be applied for many different designs of SC-ISE.

[0017] By using such a method, the porous ISM may have a content of pores of at least 10vol% of the total volume of the porous ISM, or at least 20vol%, and up to 50vol%. This content is shown, for example, in FIG. 10, wherein the introduction of bubbles into the porous ISM (110) doubles the membrane thickness.

[0018] Advantageously, the pores may increase the tortuosity of the pathway between the sample solution and the ISM | SC interface. The pores (e.g., bubbles) can hence perform a tailoring role of the ion fluxes between ions entering the membrane from the solution, and can mitigate the composition change of the water layer. Even with this mitigation, the transduction of the signal from an ion current to an electronic current at the ISM | SC interface does not deteriorate compared to a similar SC-ISE without bubbles in the ISM.

[0019] It is also expected that this may also apply to other phenomena where fluxes across the ISM | SC interface are not desired. In addition to fluxes between the ISM | SC interface and the ISM from the sample, fluxes between the ISM | SC interface from the SC layer 120 can also occur. As this also constitutes a parallel process during the use of the SC-ISE, this can also result in loss of potential stability due to changes in SC-ISE composition over time. A tortuous path between the SC layer 120 and porous ISM 110 would hence help to slow the rate of such changes.

[0020] The layer structure 100 may include 3 functional layers, as shown in FIG. 2A. According to some embodiments, the 3 layers may be disposed on (e.g. supported) on a substrate 210, as shown in FIG. 2C. In those embodiments, the porous ISM 110 and the substrate 210 may be the only parts of the sensor in contact with the sample solution. The electrical contact between the electrical conductor 130 and the electronic circuit 150 may be insulated and the electronic circuit 150 may be an external potentiometer for measurements against a standard reference electrode.

[0021] The pores in the porous ISM 110 and the role they play in increasing the tortuosity of the pathway from the solution to the ISM | SC interface are schematically shown in FIG. 2B.

[0022] As schematically shown in FIG. 2B, the pores may be positioned close to the ISM | SC interface. Accordingly, the porosity of the ISM may be higher in a first region than in a second region, wherein the first region is closer to the SC layer 120 than the second region. By having a lower porosity in the second region, that is facing the sample solution, invasion of the sample solution into the porous ISM 110 is impeded. Ideally, the outermost surface of the porous ISM 110 may be non-porous, and advantageously no, or substantially no sample solution invades the pores. Additionally and advantageously, the pores may comprise gas even when the sensor is in liquid. The porosity of the porous ISM 110 may additionally gradually decrease with a distance from the SC layer 120 along a thickness of the porous ISM 110.

[0023] The porous ISM 110 may provide sensitivity and selectivity towards a target ion. The porous ISM 110 may include polyvinyl chloride, optionally in a weight percentage of about 1 wt% to about 50 wt% (relative to the total weight of the porous ISM 110), optionally in a weight percentage of about 10 wt% to about 40 wt%, optionally in a weight percentage of about 20 wt% to about 35 wt%, optionally of about 32.5 wt%. The porous ISM 110 may include a plasticizer, optionally in a weight percentage of about 50 wt% to about 90 wt%, optionally in a weight percentage of about 60 wt% to about 80 wt%, optionally in a weight percentage of about 65 wt% to about 70 wt%, optionally of about 65 wt%. Non-limiting examples of the plasticizer may be any suitable plasticizer compatible with polyvinyl chloride, such as dioctyl sebacate (DOS). The plasticizer may increase diffusivity and hence the ionic conductivity of the ISM.

[0024] The porous ISM 110 may include an ionophore. The ionophore may facilitate selective diffusion of a target ion in the sample into and/or out of the porous ISM 110, or an ionophore disposed in the porous ISM 110, wherein the ionophore may facilitate selective diffusion of the target ion in the sample into and/or out of the porous ISM 110. The ionophore may include, for example, valinomycin. The ionophore, e.g. valinomycin, may have a loading rate of approximately 1 wt% in the porous ISM 110. An ionophore may selectively bind with the target ion and may help to transport it across the membrane to the SC layer 120.

[0025] The porous ISM 110 may include a lipophilic electrolyte, which may be used as an anionic additive. The lipophilic electrolyte may include, for example, tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500). The lipophilic electrolyte, e.g. ETH 500, may have a loading rate of approximately 1 wt% in the porous ISM 110.

[0026] The SC layer 120 may operate at near zero-current ($\sim 10^{-12}$ A) conditions, and the ion current through the porous ISM 110 may be transduced into an electron current that may be measured by standard potentiometers. The SC layer 120 may include polyaniline (PANI), poly-3-4-ethylenedioxythiophene polystyrene sulfonate (PEDOT:PSS), carbon particles, poly(octyl thiophene), polypyrrole, or a combination thereof. In one example, the SC layer comprises PEDOT:PSS.

[0027] As used herein, the term “solid” when used in the phrase “solid contact (SC) layer” takes its normal meaning, and therefore includes references to compositions or substances demonstrating (significant) structural rigidity and resistance to changes of shape or volume (e.g. substances which exhibit no flow). In particular, the term "solid" may refer to substances characterised by their resistance to penetration. The term "solid" is understood not to include a hydrogel.

[0028] The SC layer 120 may have a first main side and a second main side, wherein the second main side is opposite to the first main side. The first main side and the second main side of the SC layer 120 refer to the two largest surfaces of the layer. In particular, a layer typically extends into two directions (perpendicular to each other), while having a thickness in a direction which is perpendicular to the two directions in which the layer extends. The two surfaces that extend into the two directions are referred to herein as the first main side and a second main side. The distance between the two surfaces of the first main side and a second main side may refer to the thickness of the SC layer 120.

[0029] The layer structure according to the disclosure may be arranged in such a configuration that the SC layer 120 is facing (e.g., being in contact with) the porous ISM 110 with a first main side thereof. The ISM | SC interface as used herein may therefore be positioned on the first main side of the SC layer 120. The SC layer 120 may be facing, with a second main side thereof, the electrical conductor.

[0030] The SC layer 120 may have a thickness of about 0.1 μm (micrometer) to about 10 μm, or about 0.5 μm to about 5 μm, or about 0.8 μm to about 2 μm, or about 1 μm. In embodiments wherein the SC layer comprises PEDOT:PSS, a thickness of about 1 μm to about 5 μm of the SC layer 120 advantageously maximizes redox capacitance of the interface between the SC layer 120 and the porous ISM 110.

[0031] The electrical conductor 130 may form an ohmic electrical contact between the SC layer 120 and the wire to the potentiometer. The electrical conductor may include silver.

[0032] According to various embodiments, there is provided an ion selective electrode sensor. The ion selective electrode sensor includes a substrate 210. The ion selective electrode sensor includes the layer structure 100 as described herein disposed on a first portion of the substrate 210. The ion selective electrode sensor includes a reference electrode 220 disposed on a second portion of the substrate 210. The ion selective electrode sensor 200 may be free of a counter electrode. Advantageously, the counter electrode is not necessary for such an ion selective electrode sensor, as it operates under an effectively zero current (10^{-12} A) regime. Only the working and reference electrodes would be used.

[0033] A material for each of the electrodes may be independently selected from, but not limited to, metals, such as gold, silver, nickel, titanium, platinum. Alternatively, a material for each of the electrodes may be independently selected from polymers including poly(3,4-ethylenedioxythiophene), poly(thiophene)s, polyaniline, polypyrrole. The polymers may also be termed “conducting polymers”. When using conducting polymers as the direct contact to an ion selective membrane electrode material, there are advantages due to their redox capacitance. In particular, the additional redox capacitance provided by the conducting polymer may resist polarization of the interface and hence improves the stability of the electrode response. For metals to perform a similar role approaching the robustness of conducting polymers, depositing a lipophilic monolayer before contact with a membrane may be beneficial, as this may reduce interference by water and gas.

[0034] According to various embodiments, there is provided a method of fabricating the layer structure for an ion selective electrode sensor 300 as described herein. The method 300 includes a step 310 of providing an electrical conductor disposed on an electrode. The electrical conductor disposed on an electrode is connectable to an electronic circuit 150. The method 300 includes a step 320 of disposing an SC layer on the electrical conductor. The method 300 includes a step 330 of heating the disposed SC layer. The method 300 includes a step 340 of disposing an ISM from a solution comprising a solvent and a membrane precursor on the disposed SC layer to form the layer structure 100. The method 300 includes a step 350 of allowing a porous ion selective membrane 110 to be formed, wherein a porosity of the porous ion selective membrane 110 is higher in a first region than in a second region, and wherein the first region is closer to the solid contact layer 120 than the second region. In other words, by disposing the solution comprising a solvent and a membrane precursor on a heated SC layer, the solvent evaporates and the pores are created within the membrane precursor such that a porous ISM 110 is formed.

[0035] The electrode 140 may advantageously have a planar form, such that the electrical conductor, the SC layer and the ISM can be easily disposed on the electrode 140 by drop-casting or screen-printing. Additionally, the electrode 140 may be placed on a heating element for the subsequent heating step.

[0036] Disposing the SC layer on the electrical conductor may involve a polymerization of the 3,4-ethylenedioxythiophene and the sodium poly(4-styrenesulfonate) to form the SC layer 120.

[0037] By “heating” is meant that the temperature of the solution containing a solvent and a membrane precursor is deliberately raised such that the solvent may at least partially evaporate. Heating may thus involve to raise the temperature above room temperature. In various embodiments, the heat is emitted from the substrate 210. Hence the electrical conductor and the SC layer 120 are heated and may form a heated surface for the solution containing the solvent and the membrane precursor. The heating may involve heating the disposed SC layer 120 to a temperature of at least 40 °C. The heating may involve heating the disposed solid contact layer to a temperature of at least 40 °C, or to the boiling point of the solvent. Heating the disposed SC layer 120 to a temperature of the boiling point of the solvent used in the membrane precursor may advantageously result in maximizing the formation of pores (bubbles).

[0038] “Room temperature”, as used herein, refers to a temperature greater than 4° C, preferably being in the range from 15 °C to 40 °C, or in the range from 15 °C to 30 °C, or in the range from 20 °C to 30 °C, or in the range from 15 °C to 24 °C, or in the range from 16 °C to 21 °C, or around 25 °C. Such temperatures may include, 14 °C, 15 °C, 16 °C, 17 °C, 18 °C, 19 °C, 20 °C, 21 °C, and 25 °C, each of these values including ± 0.5 °C.

[0039] The membrane precursor may have the same composition as described previously in context with the porous ISM 110.

[0040] The solvent may be a volatile solvent, optionally an organic solvent. The solvent may be capable to dissolve the membrane precursor, e.g. polyvinyl chloride (PVC). The solvent may have a boiling point close to the heating temperature during deposition of the ion selective membrane. The solvent may have a boiling point that is below 120 °C, optionally below 100 °C, optionally below 80 °C, optionally below 70 °C. The solvent may be selected from the group consisting of tetrahydrofuran, cyclohexanone, cyclopentanone, or a combination thereof.

[0041] The step 340 of disposing the ion selective membrane from a solution may be repeated about 1 to 10 times, or repeated 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 times. The process may further comprise a final step of disposing the ion selective membrane from the solution. The final step may be the last step of disposing the ion selective membrane in the process. This step may be carried out at room temperature. Advantageously, when the final step of disposing the ion selective membrane from the solution is carried out at room temperature, the porous ISM 110 thus formed has an outermost layer (facing the sample solution) that is substantially non-porous. This is because no bubbles are formed during deposition, since the solvent may not evaporate.

[0042] Embodiments described in the context of the layer structure 100, or the ion selective electrode sensor 200 are analogously valid for the method of fabricating the layer structure for an ion selective electrode sensor 300. Similarly, embodiments described in the context of the method of fabricating the layer structure for an ion selective electrode sensor 300 are analogously valid for the layer structure 100, or the ion selective electrode sensor 200, and vice-versa.

[0043] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0044] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0045] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

Examples

[0046] **Example 1 - Choice of electrodes:**

[0047] Screen printed carbon connected to silver was chosen as the substrate electrode.

[0048] Electrodes were purchased from a commercial source with the layout as shown in FIG. 3. Working and pseudo reference electrodes are all situated on the same electrode. The model for the working electrode chosen was DRP-110, made from screen printed carbon.

[0049] The electrode has a planar form factor, making it amenable to modification by drop casting or screen printing. The form factor also allows for the electrode to be placed on a hot plate, which is required for the modification of the original ISM cocktail deposition step. The working electrode has a diameter of 4 mm, and only the working electrode was used for measurements.

[0050] **Example 2 - Choice of ISM:**

[0051] The choice of ISM material was approximately 33 wt% PVC, and 66 wt% per membrane weight composition. More particular, the ISM composition was chosen to be for a K_+ membrane: 32.5 wt% PVC, 1 wt% valinomycin, 65 wt% DOS, 1 wt% tetradodecylamonium tetrakis(4-chlorophenyl)borate (ETH 500), 0.5 wt% potassium tetrakis(4-chlorophenyl)borate, 1 wt% valinomycin. The K+ selective SC-ISE system has been used as a model to study the impact of water layers on the SC-ISE performance due to the highly discriminating valinomycin ionophore. To produce bubbles in the ISM, each electrode with a bare SC layer was placed on a hot plate during the first 4 ISM depositions, with the fifth deposition conducted at room temperature, and the details of each type of SC-ISE and deposition are shown in Table 1.

DRP-110-	**Hotplate temperature (°C)**	**ISM Cocktail Concentration (mg ml^{-1})**	**Depositions (µL)**
RT	-	100	4 x 15, 1 x 20
40*	40	100	4 x 15, 1 x 20
50*	50	100	4 x 15, 1 x 20
60*	60	100	4 x 15, 1 x 20
RT-Thick	-	200	3 x 20

Table 1: Deposition conditions of ISMs on SPEs with electropolymerized PEDOT:PSS. SC-ISEs DRP-110-RT and DRP-110-RT-Thick had ISM cocktail deposited on them at room temperature.

[0052] Due to the volume of bubbles present in the ISM, DRP-110-60 had a significantly thicker ISM than DRP-110-RT, even though the volume of cocktail deposited was the same. Hence, DRP-110-RT-Thick with a solid ISM of the thickness of DRP-110-60 was used for comparison. Among the SC-ISEs with ISM cocktail deposited with heat, DRP-110-60 as highlighted in Table 1 showed the greatest impact of the bubbles generated, and is the most optimized.

[0053] **Example 3 - Choice of SC layer:**

[0054] Similar to the use of the K+ selective SC-ISE, the PEDOT:PSS SC was chosen as it has been used as a model system to study the impact of a water layer on potential stability.

[0055] Following an earlier, established procedure, briefly, 0.01 M 3,4-ethylenedioxythiophene and 0.1 M sodium poly(4-styrenesulfonate) supporting electrolyte were dissolved in ultrapure water. DRP-110 with electrode area 0.13 cm^2 were rinsed with ultrapure water, and a constant current density of 0.2 mA cm^{-2} was applied to obtain a total of 18 mC polymerization charge across 716 s of polymerization time, corresponding to a

PEDOT:PSS film with thickness of about 1 μm. During electropolymerization, a platinum wire was used as the counter electrode. After polymerization, the electrodes were rinsed with ultrapure water, dried gently with nitrogen and left to dry for at least 24 hours. Carbon was chosen for the eletropolymerization target as it is an inert, abundant and cheap conductive material that can be made into screen printed electrodes.

[0056] **Example 4: Choice of electrical contact:**

[0057] Silver is a proven electrical conductor ink suited to screen printing, and is stable at the electrical potentials and temperatures experienced during measurements.

[0058] **Example 5:** Impact of temperature on the coverage of bubbles and ISM charge transfer resistance

[0059] FIG. 4 shows the impact of deposition temperature on the coverage of bubbles formed within the ISM in the proposed SC-ISEs.

[0060] The impact of the bubbles on the charge transfer resistance is shown in FIG. 5, as shown by electro-chemical impedance spectroscopy. This was performed at the open circuit potential (OCP) detected immediately before the measurements, in the frequency range of 100 kHz (kilo Hertz) to 10 mHz (milli Hertz) with an alternating current sinusoidal amplitude of 10 mV_{RMS}.

[0061] **Observations**

[0062] As the deposition temperature approaches the THF boiling point of 66°C, the number of bubbles in FIG. 4 increased and their coverage of the SC becomes nearly complete. From the cross section of the membrane seen in FIG. 4, inset (e), it can also be seen that the bubbles retained as voids are near the ISM | SC interface. The hemisphere in FIG. 5 increases in size with increasing temperature of cocktail deposition.

[0063] **Discussion/Conclusion**

[0064] The first hemisphere in the electrochemical impedance spectroscopy may be attributed to the charge transfer resistance of the ISM. By fitting of the hemisphere to a Randles circuit, the charge transfer resistance of the SC-ISEs showed a minimum with DRP-110-RT at 0.72 ± 0.02 to a maximum with DRP-110-60 at 7.72 ± 0.45 MΩ. As only low temperatures of a maximum of 60 °C are used on the SC-ISEs, the components of the ISM or SC do not degrade due to the temperature. The chemical composition of either the ISM or the SC is also hence not expected to change across this range of temperatures. The increased charge transfer resistance is hence expected to occur due to the bubbles introduced to the ISM. The introduction of inert phases into the ISM has been explored before. However, these were introduced at the ISM |

sample interface and were used for liquid contact ISEs, compared to those used for SC-ISEs listed here. However, like the bubbles in this work, the inert phases similar serve to physically constrain the charge transfer across inter-faces.

[0065] **Preservation of ion selective electrode function with bubbles**

[0066] SC-ISE calibration curves: FIG. 6 shows the calibration curves of K^+ SC-ISEs for DRP-110-RT, DRP-110-RT-Thick and DRP-110-60 in KCl solutions, and the properties of 3 identical SC-ISEs for each design are shown in Table 2. As can be seen in Table 2, the slope of the improved electrodes DRP-110-60 approaches the theoretical 59.2 mV dec^{-1}. Both the slope and detection limits of DRP-11-60 are also comparable to the SC-ISEs that were formed at room temperature. Comparing the difference of the y-intercept when calibrating from concentrated to dilute solutions and vice versa, the potential was reproducible generally between all electrodes.

	$Slope_{Desc}$ (mV dec^{-1})	**$Slope_{Asc}$ (mV dec^{-1})**	**$E^0_{Asc-Desc}$ (mV)**	**Detection $limit_{Desc}$ (log a_{K+})**
DRP-110-RT	58.9 ± 0.2	57.6 ± 0.8	-2.8 ± 2.6	-5.49 ± 0.11
DRP-110-RT-Thick	58.9 ± 0.2	57.6 ± 1.2	-5.7 ± 1.5	-5.62 ± 0.04
DRP-110-60	58.2 ± 0.8	58.9 ± 0.6	-2.1 ± 3.1	-5.62 ± 0.04

Table 2: Properties of the calibration curves in FIG. 6 for 3 identical SC-ISEs. The subscripts Asc and Desc refer to calibration curves in order of increasing concentrations and decreasing concentrations respectively. The detection limit was determined by the intersection point between best fit lines of the linear ranges from 10^{-1} to 10^{-5} M, and 10^{-6} to 10^{-7} M respectively.

[0067] Electrochemical impedance spectroscopy: Impedance spectroscopy of electropolymerized PEDOT:PSS on screen printed carbon electrodes after immersion into 0.1 M KCl are shown in FIG. 7. The range of frequencies investigated and the amplitude used are the same as that in FIG. 5. The PEDOT:PSS was subjected to different treatments corresponding to heat, moisture and solvent similar to the ISM cocktail deposition process. It was either exposed to heat at 60 °C, immersed once before in 0.1 M KCl, or exposed to THF which was allowed to evaporate before impedance spectroscopy was applied. Despite applying the treatments in different permutations, the spectra of each separate PEDOT:PSS layer remained unchanged from its original, capacitive behaviour. Overall, the performance of the

SC-ISEs with the most bubbles DRP-110-60 are highly similar to the model DRP-110-RT system, and SC-ISE parameters are not adversely affected.

[0068] Improved potential stability and reproducibility of electrodes with bubbles

[0069] The potential responses for DRP-110-60 and DRP-110-RT-Thick in solutions containing both KCl and NaCl are shown in FIG. 8. KCl was alternated between an initial concentration of 10^{-3} M and 10^{-5} M, while NaCl was kept constant at 10^{-1} M. While exposed to the solution of 10^{-1} M NaCl and 10^{-3} M KCl, all SC-ISEs were able to maintain a stable potential. However, upon reducing KCl to 10^{-5} M, the selectivity limit of the ISM was exceeded. As seen in the case of all SC-ISEs, the potential of all electrodes drifts over time. Some drift is expected as the SC-ISE is operating in a nonequilibrium regime. Upon returning the SC-ISEs to the initial solution with 10^{-3} M KCl, there is a clear deviation in the behaviour of each set of SC-ISEs. The DRP-110-RT-Thick showed shifted potentials from the initial set point of 0 mV. This extent of the shift was also dependent on the drift experienced while exposed to 10^{-5} M KCl, with greater drifts in 10^{-5} M KCl leading to greater shifts. In comparison, the DRP-110-60 electrodes show good reproducibility of the initial potential at 10^{-3} M KCl. While the 3 identical electrodes showed differences in their drift when in 10^{-5} M KCl, they were able to reproduce the set point of 0 mV when reintroduced to the initial solution.

[0070] At 18 h, the 3 DRP-110-RT-Thick showed a drifted potential of 25.4 ± 15.5 mV. In contrast, the potentials measured in 10^{-3} KCl are much more reproducible with DRP-110-60, and 3 SC-ISEs showed a drifted potential of 1.0 ± 0.6 mV at 18 h. The DRP-110-60 also showed high stability of the potential when in 10^{-3} M KCl, unlike some of the DRP-110-RT-Thick which showed drift in the opposite direction.

[0071] The drift directions of the DRP-110-RT-Thick and their shifted potentials show similarity that is indicative of the water layer within the SC-ISEs. The drifting potentials and the different traces between 3 identical electrodes in FIG. 8 show the poor stability and reproducibility of the potential due to change in concentration of the water layer.

[0072] In contrast, the improved stability and reproducibility of the potential for DRP-110-60 are attributed to the increased charge transfer resistance due to the bubbles in the ISM. The increased resistance results in a much slower rate of change of the internal water layer composition when the selectivity of the ISM is exceeded. As a result, even after 3 h of exposure, the initial set point of 0 mV can be reproduced. The bubbles in the ISM hence can be shown to greatly improve the performance of SC-ISEs by tailoring ion fluxes through the SC-ISE, even with the formation of a water layer. The modification step is simple and elegant, and also does not require additional chemical changes to the SC-ISE.

[0073] While the disclosure has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A layer structure (100) for an ion selective electrode sensor (200), the layer structure (100) comprising:

a porous ion selective membrane (110);

a solid contact layer (120);

an electrical conductor (130) disposed on an electrode (140), which is connectable to an electronic circuit (150);

wherein the solid contact layer (120) is disposed between the porous ion selective membrane (110) and the electrical conductor (130), and

wherein a porosity of the porous ion selective membrane (110) is higher in a first region than in a second region, wherein the first region is closer to the solid contact layer (120) than the second region.

2. The layer structure (100) of claim 1, wherein a porosity of the porous ion selective membrane (110) gradually decreases with a distance from the solid contact layer (120) along a thickness of the porous ion selective membrane (110).

3. The layer structure (100) of claim 1 or claim 2, wherein the solid contact layer (120) comprises polyaniline (PANI), poly-3-4-ethylenedioxythiophene polystyrene sulfonate (PEDOT:PSS), carbon particles, poly(octyl thiophene), polypyrrole, or a combination thereof.

4. The layer structure (100) of any one of claims 1 to 3, wherein the porous ion selective membrane (110) comprises polyvinyl chloride.

5. The layer structure (100) of any one of claims 1 to 4, wherein the porous ion selective membrane (110) comprises an ionophore.

6. The layer structure (100) of any one of claims 1 to 5, wherein the electrical conductor (130) comprises silver.

7. An ion selective electrode sensor (200) comprising

a substrate (210);

the layer structure (100) of any one of the previous claims disposed on a first portion of the substrate (210); and

a reference electrode (220) disposed on a second portion of the substrate (210).

8. The ion selective electrode sensor (200) of claim 7, wherein the ion selective electrode sensor (200) is free of a counter electrode.

9. A method of fabricating the layer structure for an ion selective electrode sensor (300) of any one of claims 1 to 6, the method comprising:

providing an electrical conductor (130) disposed on an electrode (140), which is connectable to an electronic circuit (310);

disposing a solid contact layer (120) on the electrical conductor (320);

heating the disposed solid contact layer (330);

disposing an ion selective membrane from a solution comprising a solvent and a membrane precursor on the heated disposed solid contact layer to form the layer structure (340), and allowing a porous ion selective membrane (110) to be formed, wherein a porosity of the porous ion selective membrane (110) is higher in a first region than in a second region, and wherein the first region is closer to the solid contact layer (120) than the second region (350).

10. The method of claim 9, wherein the step of disposing the ion selective membrane from a solution is repeated about 1 to 10 times.

11. The method of claim 9 or claim 10, wherein a final step of disposing the ion selective membrane from a solution is carried out at room temperature.

12. The method of any one of claims 9 to 11, wherein the heating involves heating the disposed solid contact layer to a temperature of at least 40 °C, or to the boiling point of the solvent.

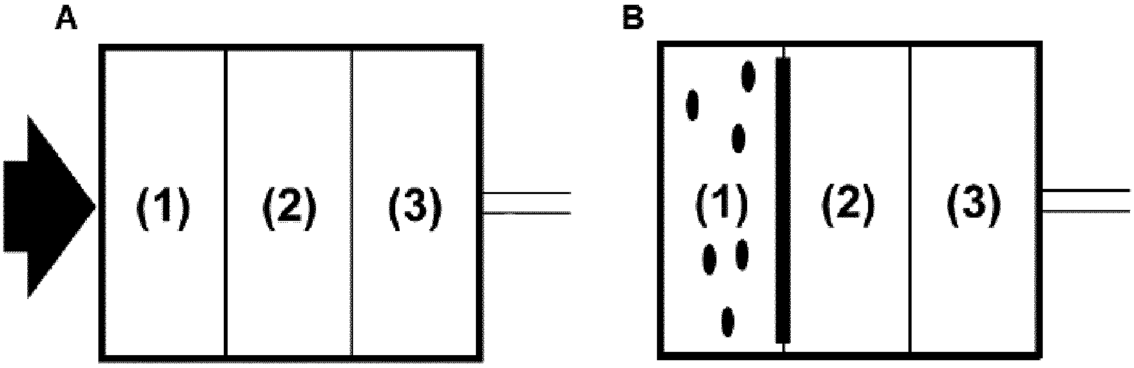

FIG. 1

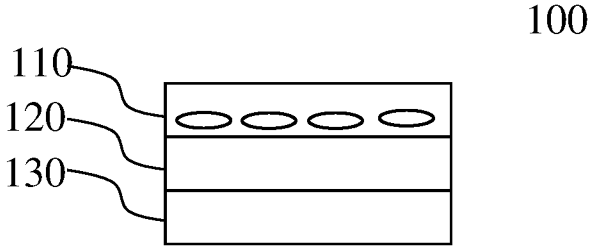

FIG. 2A

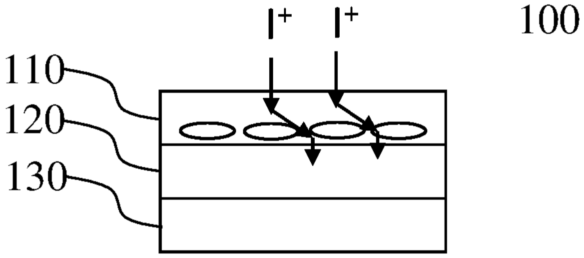

FIG. 2B

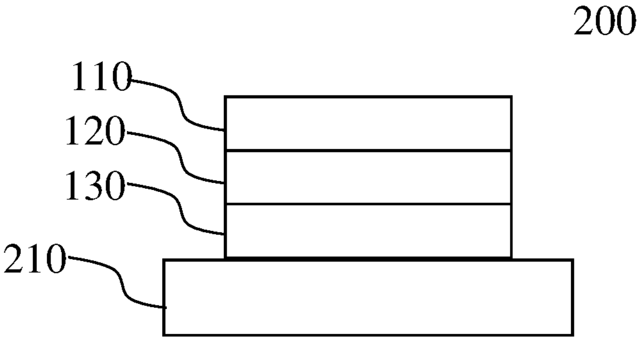

FIG. 2C

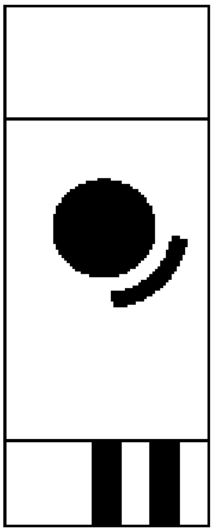

FIG. 3

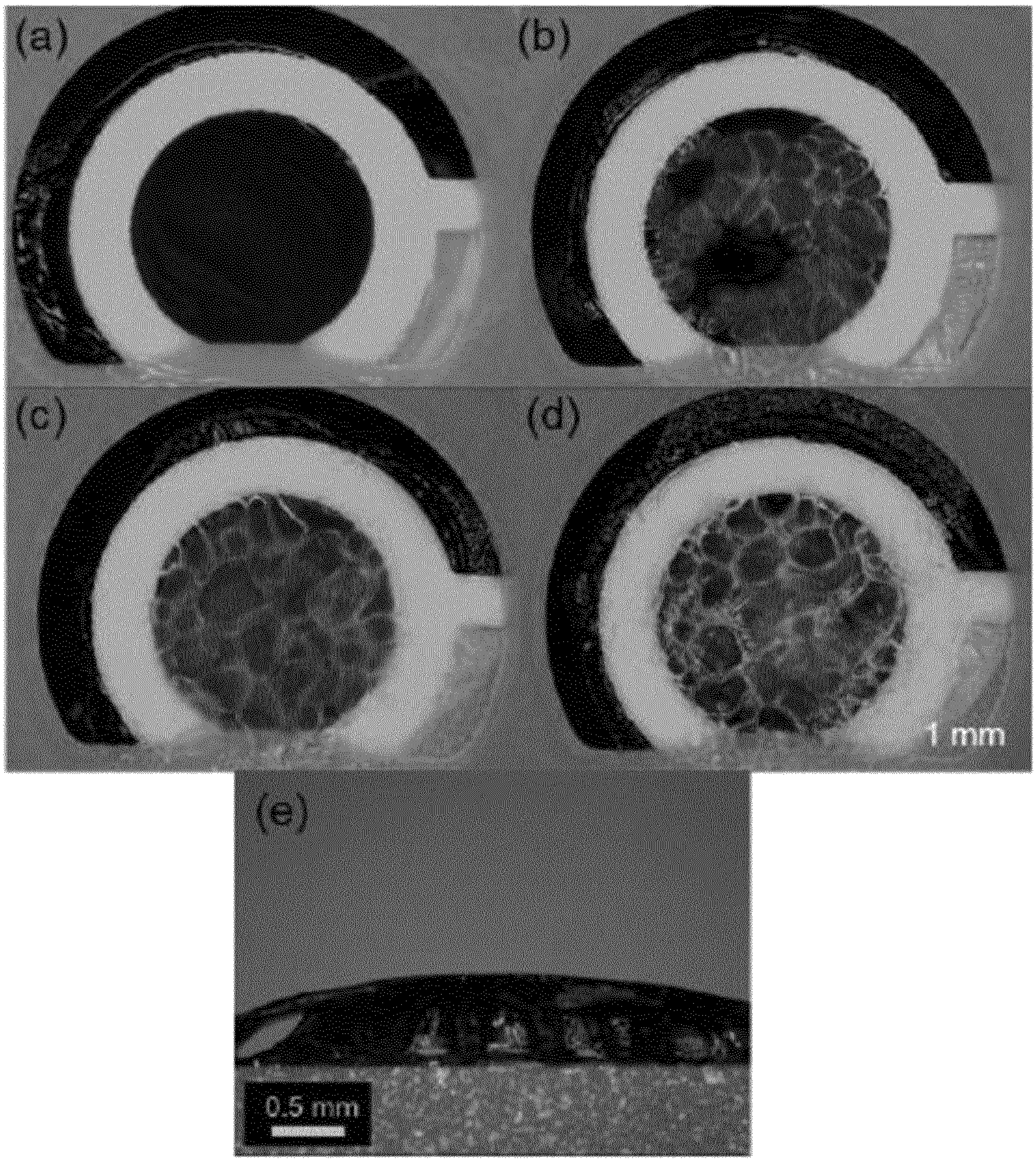

FIG. 4

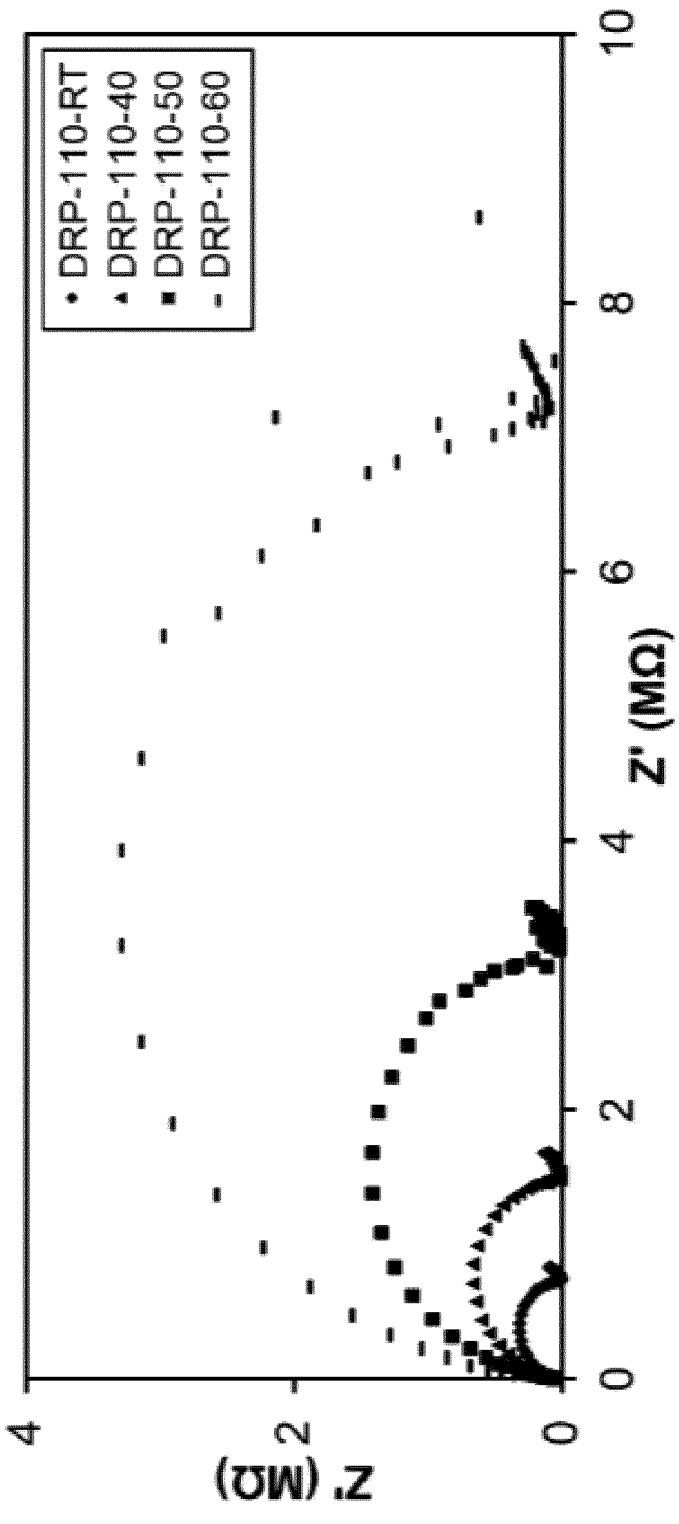

FIG. 5

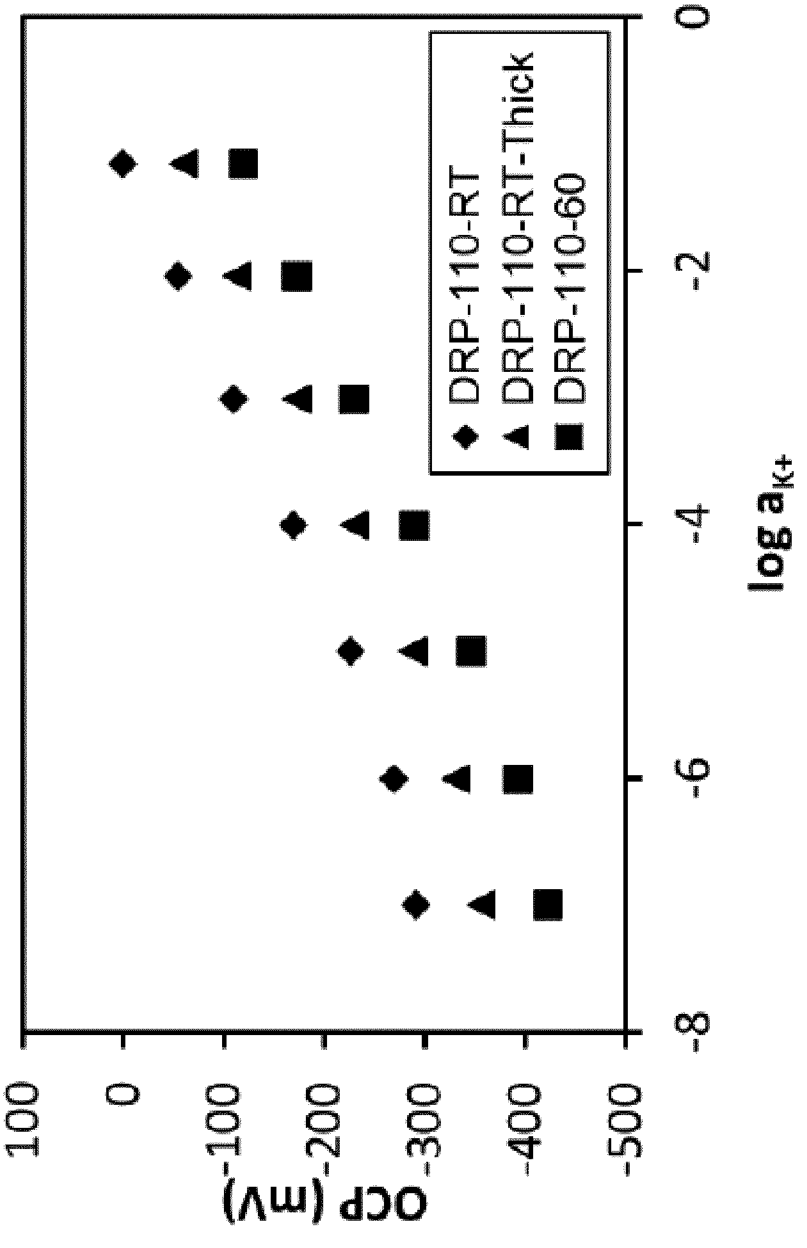
OCP (mV)
100
0
-100
-200
-300
-400
-500
log a_{K+}
-8
-6
-4
-2
0
DRP-110-RT
DRP-110-RT-Thick
DRP-110-60

FIG. 6

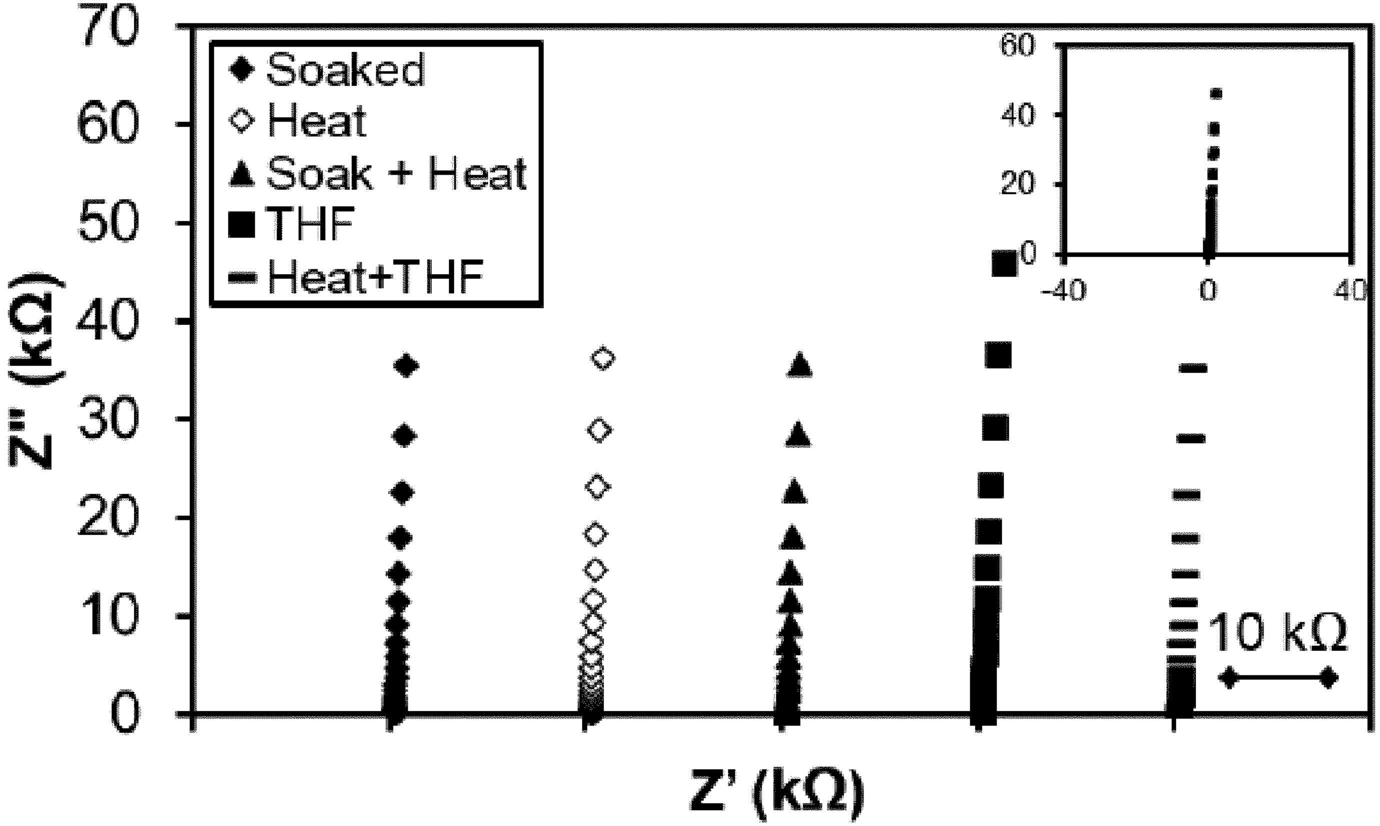
70
60
50
40
30
20
10
0
Z" (kΩ)
Z' (kΩ)
◆ Soaked
◇ Heat
▲ Soak + Heat
■ THF
▬ Heat+THF
60
40
20
0
-40
0
40
10 kΩ

FIG. 7

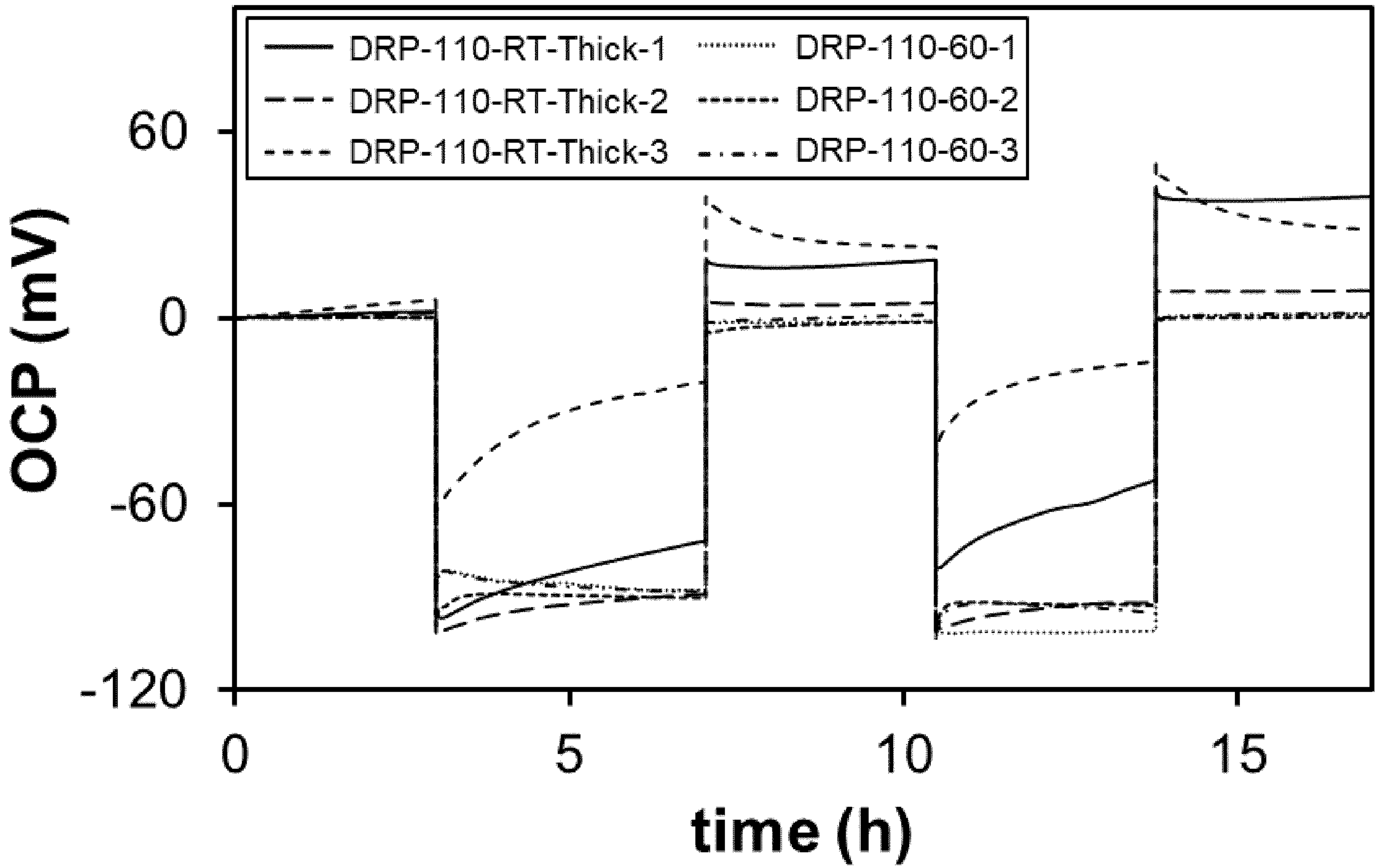
DRP-110-RT-Thick-1
DRP-110-RT-Thick-2
DRP-110-RT-Thick-3
DRP-110-60-1
DRP-110-60-2
DRP-110-60-3
OCP (mV)
60
0
-60
-120
0
5
10
15
time (h)

FIG. 8

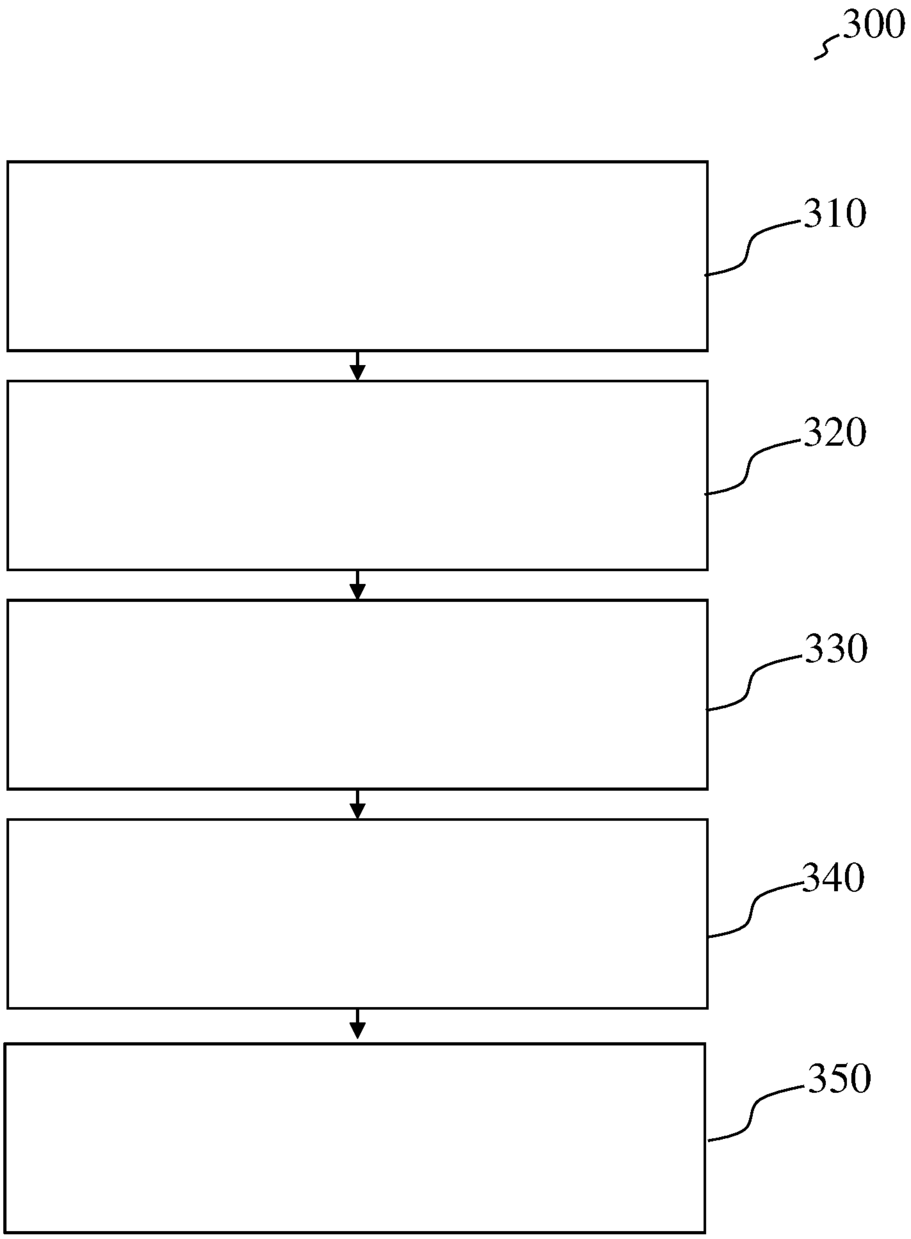

FIG. 9

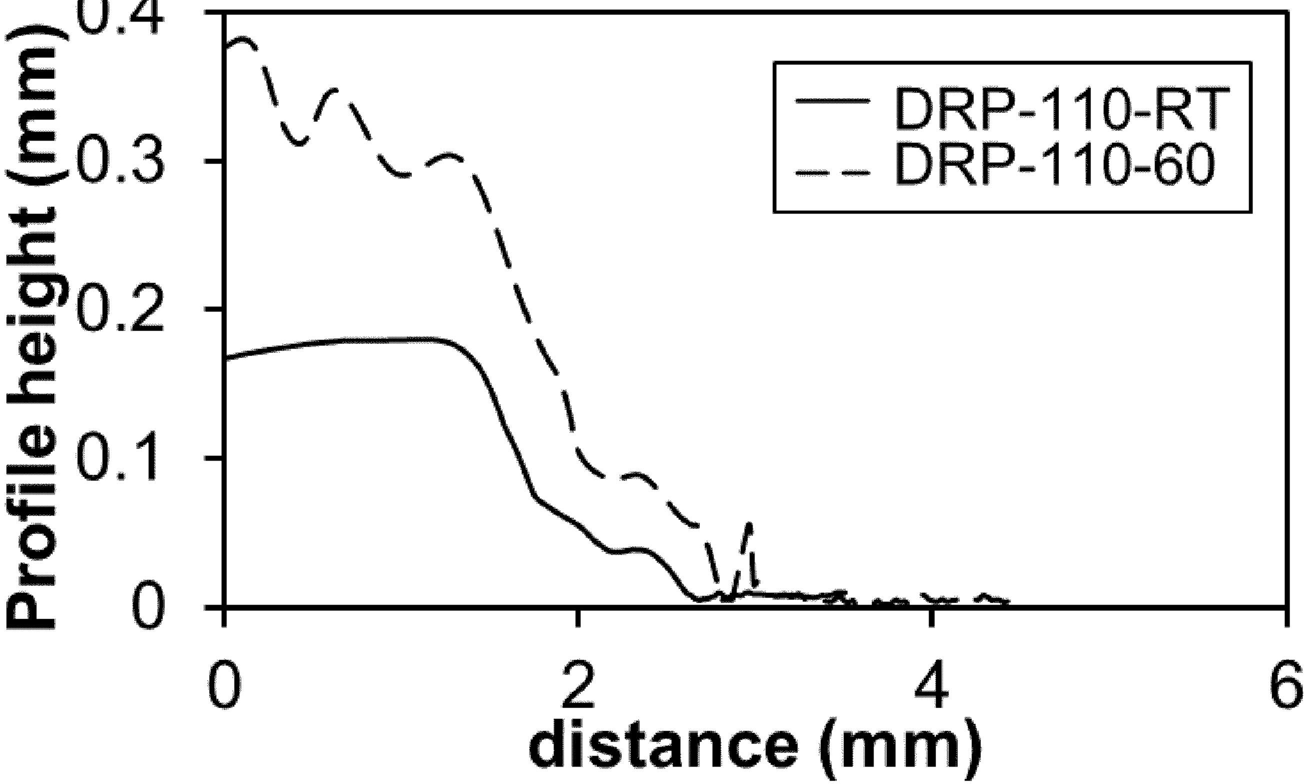
Profile height (mm)
0.4
0.3
0.2
0.1
0
0
2
4
6
distance (mm)
DRP-110-RT
DRP-110-60

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/065898

A. CLASSIFICATION OF SUBJECT MATTER

INV. G01N27/333
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	HE NING ET AL: "Influence of hydrophobization of the polyazulene ion-to-electron transducer on the potential stability of calcium-selective solid-contact electrodes", SENSORS AND ACTUATORS B: CHEMICAL, ELSEVIER BV, NL, vol. 207, 20 October 2014 (2014-10-20), pages 918-925, XP029104887, ISSN: 0925-4005, DOI: 10.1016/J.SNB.2014.10.048 the whole document -----	1-12
A	CN 110 711 503 A (UNIV SHANGHAI JIAOTONG) 21 January 2020 (2020-01-21) the whole document ----- -/--	1-12

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
8 February 2022

Date of mailing of the international search report
22/02/2022

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2
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Fax: (+31-70) 340-3016

Authorized officer
De Masi, Rita

1

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 112 717 731 A (HAINAN YEGUO FOODS CO LTD; UNIV SHANGHAI JIAOTONG) 30 April 2021 (2021-04-30) the whole document -----	1-12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2021/065898

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 110711503	A	21-01-2020	NONE	
CN 112717731	A	30-04-2021	NONE	