Disposable Planar Reference Electrode Based on Carbon Nanotubes and Poly-Acrylate Membrane

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In this technical note we report a new all-solid-state planar reference electrode based on single-walled carbon nanotubes and photocured poly(*n*-butylacrylate) (poly-nBA) membrane containing the Ag/AgCl/Cl^- ion system. Single-walled carbon nanotubes functionalised with octadecylamide (SWCNT-ODA) and deposited by drop-casting onto a disposable screen-printed electrode is an excellent all-solid-state transducer. The novel potentiometric planar reference electrode shows low potential variability (calibration slopes inferior to 2 mV/dec) for a wide range of chemical species (i.e. ions, small molecules, proteins) in a wide calibration range, redox pairs, changes in pH and changes in ambient light. Potentiometric medium-term signal stability (-0.9 ± 0.2 mV/h) and electrochemical impedance characterisation confirm the correct solid-contact between SWCNT-ODA layer and photocured poly-nBA membrane. Overall, the materials used and the simple fabrication by screen-printing and drop-casting enable a high throughput and highly parallel and cost-effective mass manufacture of the new disposable reference electrode. Moreover, the reference electrode has a long shelf life, characteristic that can be of special interest in decentralised and multiplexing potentiometric analysis.

Keywords: *screen-printing, all-solid-state reference electrode, carbon nanotubes, miniaturisation*

The simple and portable instrumentation employed in potentiometry, together with the miniaturisation of potentiometric systems, can provide analytical solutions to problems which still today remain mostly unsolved such as truly decentralised and multiplexing analysis.[1] All-solid-state ion-selective electrodes (ISEs) have been miniaturised using thin-film,[2] thick-film,[3] and micro-cavity techniques;[4, 5] however, the miniaturisation of reliable and cost-effective reference electrodes (RE) remains a crucial challenge for the fabrication of total miniaturised potentiometric systems. The first miniaturised REs to be reported were created by miniaturising the widely used Ag/AgCl liquid-junction RE.[6] However, a miniaturised liquid-junction RE faces several hurdles such as ion bleeding, reservoir ageing and high fabrication costs. Therefore, all-solid-state designs are eagerly sought in order to obtain mechanically robust, reliable and cost-effective miniaturised REs.[7] There are few examples of all-solid-state miniaturised REs in the literature. Lee et al. reported the use of a polyurethane polymer as an insensitive membrane for planar REs, but gave no details regarding medium- and long-term stability.[8] Ag/AgCl solid layer covered with materials with suppressed or compensated anion and cation exchange have been reported by Tymecki et al.[9] and Maminska et al.[10] The mechanism is based on the constant potential created when an invariable concentration of Cl^- ions is maintained in the Ag/AgCl redox system. In order to embed Cl^- ions in contact with a Ag/AgCl layer, Tymecki et al. used a screen-printed insulator paste and Maminska et al. used an electroneutral membrane based on polyvinyl chloride (PVC) and ionic liquids (ILs). Both could suffer from undesired signal interferences caused by Ag+ ions in the former (inherent to reference membranes based on Ag/AgCl system) and lipophilic species in the latter. Recently, conducting polymers (CPs) have been used in planar all-solid-state REs.[11, 12] It is well known that the use of solid transducers provides potentiometric electrodes with the necessary stability; however, CPs are not universal solid-contact potentiometric transducers because some show light and chemical sensitivity.[13] Kisiel et al. reported PVC reference membranes containing dispersed Ag, AgCl and KCl salts and covering a CP transducing layer. The Ag/AgCl/Cl^- ion system embedded inside the membrane yielded insensitive potentiometric responses and, at the same time, protected the CP from redox interferences.[14] Nonetheless, they did not address the light sensitivity issue and it is also well known that an inner water layer can be formed between the CP and the membrane interface.[15] Recently, single-walled carbon nanotubes (SWCNTs) have been reported as excellent transducers not only for ISEs,[16, 17] but also for all-solid-state REs.[18] SWCNT-based REs showed light insensitivity in the short-term for the first time, opening the way to their miniaturisation. To our understanding, the use of SWCNTs and polymeric membranes in REs has significant advantages in terms of applicability, given that the whole all-solid-state potentiometric system (ISE and RE) can be readily fabricated using the same transducer, membrane polymer and fabrication methodology. Regarding the polymeric membrane, polyacrylic membranes have been reported as improving the analytical performance characteristics of ISEs[19] and REs[18, 20] thanks to the low ion diffusion coefficients compared with plasticised PVC membranes. Moreover, we recently found that photocured poly(*n*-butylacrylate) (poly-nBA) was the best polyacrylic polymer out of three other common polyacrylic polymers for SWCNTs-based REs because it produced a mechanically robust membrane, with lower water percolation and gave excellent analytical performance characteristics.[18] Therefore, the fabrication of a planar all-solid-state RE using SWCNTs and poly-nBA can be seen as the first step towards the easy fabrication of a disposable potentiometric cell with enhanced analytical performance.

On the other hand, screen-printing is widely known as a versatile, straightforward, reproducible and cost-effective technique for the development of disposable all-solid-state sensors[21] and also for REs.[9] SWCNTs have not been applied yet in screen-printed inks due to the adverse effects of the presence of binders and plasticisers, which can reduce the transduction capacity of SWCNTs. The limited dispersion of pristine SWCNTs in any kind of solvent makes the functionalisation of SWCNTs indispensable. SWCNTs have been homogeneously dispersed in a variety of organic solvent by grafting the octadecylamine group onto the structure of the SWCNT (SWCNT-ODA).[22] As a result, SWCNTs-ODA can be readily drop-casted onto the electrical conductor layer without further treatment.

In this study we report a new disposable planar RE based on a SWCNT-ODA transducer layer and a polyacrylate membrane containing Ag, AgCl and KCl salts as the reference membrane. The new planar RE has been fabricated with simple and scalable deposition techniques and materials that aim for low-cost mass-manufacture and yet excellent analytical performance characteristics. So that SWCNTs can be readily used in the new planar design, we have deposited a homogeneous layer of SWCNT-ODA by means of simple and scalable drop-casting. We have studied the planar RE's emf variability to various chemical and biological interferences, pH, redox pairs and light. The potentiometric stability and electrochemical characterisation of the planar RE have been evaluated in order to study the electrode characteristics and assess the transduction between the conductive ink/SWCNTs-ODA/polyacrylic membrane solid-contacts. The disposable planar RE proposed here is a step forward in decentralised or multiplexing low-cost potentiometric analysis.

EXPERIMENTAL SECTION

Reagents. The salts $NaHCO_3$, Na_2SO_4, Na_2HPO_4, NaH_2PO_4, sodium pyruvate, glucose, urea and albumin were purchased in analytical grade form from Sigma-Aldrich. KCl, NaCl, LiCl, NH_4Cl, $MgCl_2$, $CaCl_2$, $NaNO_3$, NaOAc, tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH500), tetrahydrofuran (THF), cross-linker 1,6-hexanediol diacrylate (HDDA), photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPP) and n-butyl acrylate (nBA) monomer were purchased in analytical and selectophore grades from Fluka. AgCl was precipitated and stored as described herein.[18] Single-walled carbon nanotubes with >90 % wt. purity were purchased from HeJi, Inc. To solubilise the SWCNTs in THF, the long-chain molecule octadecylamine (ODA) was grafted to the SWCNTs (see Supporting Information for details).[22] All the solutions were prepared using MQ-Water (18,2 MΩ s^{-1}).

Disposable planar electrode development. Screen-printed electrodes were fabricated using a DEK-248 (DEK International) screen-printer. Ink 7102 conductor paste based on carbon and graphite was provided by DuPont Limited and directly screen-printed onto polyethylene terephthalate (PET) Melinex ST726 film substrate (175 μm thick) provided by Thyssenkrupp Plastic Iberica. The ink was cured in a Digiheat 150L oven (JP Selecta S.A.) at 120 ºC. The polyurethane squeegee used was provided by DEK International (model SQA152 with a 45º contact angle and a hardness factor of 70). A PET tape coated with acrylic adhesive on one side (Arcare 8565, Adhesives Research Inc) was used to protect the conducting paths.[23] SWCNTs-ODA were dissolved in THF (1 mg/mL), of which 25 μL were subsequently deposited by drop-casting onto the carbon ink sensing area (2.54 mm^2). The SWCNT-ODA layer was left to dry overnight at room temperature. The poly-nBA reference membrane cocktail was prepared as described herein.[18] 1 μL of the reference membrane was drop-casted over the SWCNT-ODA layer and photo-polymerization was carried out using a UV lamp (4W) for 5 min under argon flow.

Potentiometric measurements. Electromotive forces (EMF) were measured at room temperature (22 ± 2 °C) in stirred solutions with a Lawson Labs, Inc. high-input impedance voltmeter. All experiments were recorded against a double-junction Ag/AgCl/KCl (3 M) RE (type 6.0729.100, Metrohm AG) containing a 1 M LiOAc electrolyte bridge. Emf variability tests were performed by immersing the planar REs in the sample solution and stepwise decreasing the concentration of the specific species in the testing solution. The emf variability study was performed after the planar REs had been conditioned for 12 h in 10^{-3} M KCl. The response time was calculated as the time needed to attain 95% of the final response. Sensitivity to pH was recorded in a 10^{-2} M KCl solution with either HCl or NaOH added. Sensitivity to redox species was recorded in 10^{-4} M of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox species in the molar ratios 0.1, 1 and 10. Light sensitivity was assessed by exposing the potentiometric cell to room light and alternatively covering the whole potentiometric system with an opaque box.

Electrochemical impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) was performed by using an Autolab general purpose electrochemical system (AUTOLAB, Eco Chemie, B.V.). The planar electrode under study was connected as the working electrode in a one-compartment three-electrode cell in 0.1 M KCl at room temperature (22 ± 2 °C). The RE was an Ag/AgCl/KCl (3 M) single junction (Model 6.0733.100, Metrohm), and the auxiliary electrode was a glassy carbon rod. The impedance spectra were recorded in the frequency range 100 kHz-10 Hz at open circuit potential. The electrodes that consisted only of the layer of SWCNT-ODA were studied using an excitation amplitude of 10 mV, whereas an amplitude of 100 mV was used for the planar REs.

Scanning electron microscopy. A FEI Quanta model 600 environmental electron microscope (ESEM) with an Everhart-Thornley detector (Hillsboro) was used for the morphological characterization of the planar electrodes. See Supporting Information for details.

RESULTS AND DISCUSSION

Disposable Planar Reference Electrode Development. Figure 1 depicts the layers and the final design of the planar RE. We studied the morphology and thickness of each layer with ESEM (see Figure S2, Supporting Information): the screen-printed conductive carbon ink has a rough surface and a thickness of ~14 μm, the drop-casted SWCNT-ODA layer is flat and homogeneous with a thickness of ~30 μm and the drop-casted poly-nBA reference membrane layer is flat and ~270 μm thick. Screen-printing, drop-casting and the materials used for the fabrication of the planar all-solid-state REs enable a high throughput and a highly parallel and cost-effective mass manufacture.[21] However, it is difficult to reproducibly deposit the same amount of salts in each membrane by drop-casting. The RE active area was miniaturised to only 2.54 mm^2.

The use of SWCNTs-ODA as solid-contact transducers in a potentiometric sensor is reported here for the first time. Their solubility in organic solvents is advantageous since it allows an easy, rapid, reproducible and scalable deposition of a solid-contact transduction layer. We measured the potentiometric signal of freshly prepared planar REs with and without SWCNTs-ODA in their contact with a 10^{-3} M KCl aqueous solution.[15] This test was designed to assess the role of SWCNTs-ODA in the potentiometric signal generation and it can not be considered a conditioning or stability tests because in the short-term salt leaching or water percolation are not significantly observed, but these factors can play a role in conditioning and medium-term stability tests, as it is discussed in the EIS study below. The solid line in the inset in Figure 2 shows how SWCNT-based planar REs attain a 95% stable potential signal only after 3 min of the first solution contact. Attaining stability does not mean that the SWCNTs-ODA based disposable reference electrode can produce optimum insensitive results after only 3 min, since the membrane has to be fully conditioned. The signal from planar REs without SWCNTs-ODA took at least one hour to reach stability (Figure 2, dashed line). The planar REs without SWCNTs-ODA show the same exponential function shape (capacitive behaviour) drift every time the potentiometric measurement is stopped and subsequently started (off/on line in Figure 2), which is not the case for SWCNTs-ODA based REs. The response observed in coated-wire type REs is associated with a capacitive charge and discharge, which denotes an inadequate solid contact between the reference membrane and the conductor ink[15] and which prevents a rapid and stable measurement of the potentiometric signal after conditioning the membrane layer. In the light of these results, we conclude that an SWCNT-ODA layer is necessary for the effective transduction of the potentiometric response between the conductor ink and the reference membrane containing Ag, AgCl and KCl salts. Previous studies[18] proved that the Ag/AgCl/Cl^- ion system embedded in the membrane has an active effect on the generation of a stable potentiometric signal.

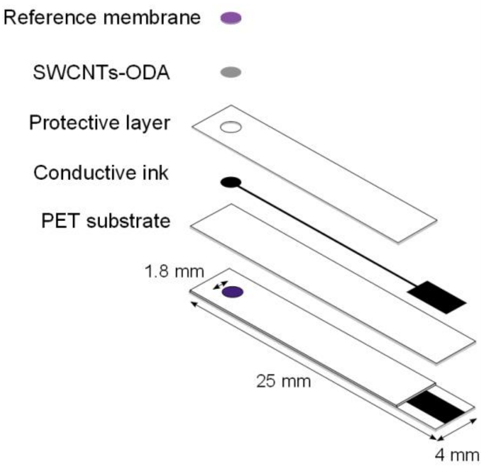

Figure 1. Scheme of the different layers and the final design (bottom) of the planar RE based on SWCNTs-ODA and a poly(n-BA) membrane

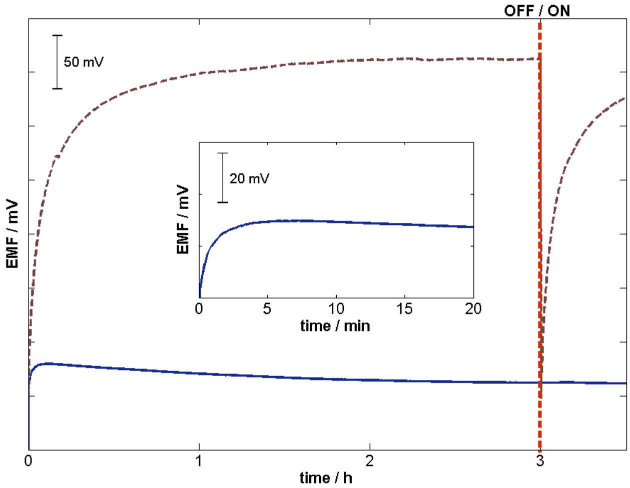

Figure 2. Potentiometric response of freshly prepared planar REs with (solid line and inset) and without (dashed line) SWCNTs-ODA as solid transducers in their contact with a 10^{-3} M KCl aqueous solution. The OFF/ON vertical line shows when the potentiometric measurement is stopped and subsequently started.

Electrochemical Impedance Spectroscopy (EIS) Characterisation. Following the planar RE morphological characterisation, we employed EIS to study the electrical properties of solid materials that are part of the planar RE.[24] First, we studied the electrode consisting only of the layer of SWCNTs-ODA deposited onto the screen-printed conductive ink in order to assess the electrical properties of this layer. The Nyquist plot was characterised by a segment of a semicircle at high frequencies followed by a diffusive line (Figure 3A). The experimental data from the SWCNT-ODA electrode was successfully fitted (average error, $\chi^2 = 7.3 \cdot 10^{-3}$) to the Warburg equivalent circuit (Figure 3A inset), formed by the electrolyte resistance (R_e = 6 kΩ), the geometric capacitance (C_g = 38.3 nF) created at the SWCNTs-ODA/electrolyte interface in parallel with a Warburg impedance ($Z_w = 1.9 \cdot 10^{-6}$ Ω) and a charge transfer resistance (R_{ct} = 36.4 kΩ), both associated with the transport and diffusion of ions from the solution into the SWCNT-ODA layer.[17]

EIS spectra corresponding to the new planar RE showed a high frequency depressed semicircle originated by the membrane resistance in parallel with the membrane geometric capacitance and a medium to low frequency diffusion line related to the Warburg impedance associated with the diffusion through the bulk of the membrane (Figure 3B). The experimental data was fitted to the equivalent circuit in Figure 3A inset ($\chi^2 = 5 \cdot 10^{-2}$). We observed a change in membrane properties with increasing contact of the electrodes in 0.1 M KCl solution; the membrane resistance was lowered from 3.7 MΩ to 250 kΩ, the geometric capacitance increased from 5.7 to 15.6 pF and the Warburg impedance increased from $0.4 \cdot 10^{-6}$ to $0.6 \cdot 10^{-6}$ Ω from the first contact in water to 12 h conditioning, respectively. The RE membrane contains a large amount of hydrophilic salts. The high salt content inside the membrane promotes water percolation through the bulk membrane,[18] which produces droplets surrounding the salt grains throughout the bulk membrane. The higher mobility of the ions in the droplets means that they form alternative ionic pathways to the high membrane resistance, thus gradually decreasing the high-frequency semicircle as the immersion time in 0.1 M KCl solution increases (Figure 3B inset).

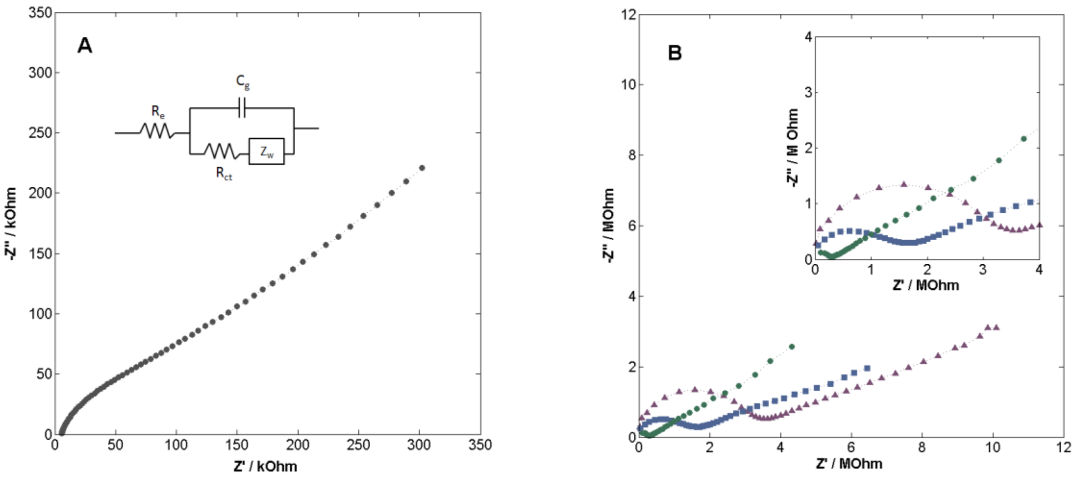

Figure 3. (A) Nyquist plots recorded for SWCNTs-ODA onto conductive carbon ink and (B) planar REs based on SWCNTs-ODA and poly(n-butyl acrylate) membrane in 0.1 M KCl solution. Dots in (B) correspond to signal recorded in the first contact with 0.1 M KCl solution (purple triangles), after 15 min (blue squares) and after overnight exposure (green circles). Inset magnifies the depressed semicircle obtained at increasing aqueous solution exposition

Potentiometric Performance Characteristics. The emf variability of the disposable planar RE to a wide variety of chemical substances was tested in a broad concentration range between 10^{-1} and 10^{-7} M against a conventional double-junction RE. The new planar RE yielded calibration slopes that were always lower than 2 mV/dec. Indeed, the new planar RE shows low emf variability to ions of different charges and hydrophilicity, to small molecules (glucose, urea), and large charged proteins (albumin). Experimental results also show that the planar RE is not affected by changes in ionic strength from 0.6 M to 0.6 μM. We tested the planar reference electrodes for all the salts in Figure 4 at 10^{-3} M concentration (n = 3 for each salt). With the data set obtained for one electrode (see Figure S3 and Table S1, Supporting Information) and using a one-way analysis of variance (ANOVA), we have calculated the standard deviation in terms of the repeatability within the same salt s_{repeat} = 1.2 mV (n = 45) and the standard deviation in terms of the precision between salts $s_{between}$ = 4.3 mV (n = 15). Clearly, the obtained potential window for the planar RE depends to some extent on the type of test samples to be analysed. However the precision level attained could be acceptable considering the disposable character of the planar electrodes and that they have an intended use in field samples, where the uncertainty values are usually larger than in the chemical laboratory. A non-significant response of the planar RE to pH and redox species variations was observed (see Figure 5). pH sensitivity was examined by changing the pH from 4 to 10 in a background 10^{-2} M KCl solution, and redox species sensitivity was tested in 0.1, 1 and 10 molar ratios of the redox pair $Fe(CN)^{3-}/Fe(CN)^{4-}$ in 10^{-4} M total concentration. The reduced signal variations observed in the pH and redox assays can be attributed to the exposure of the membrane embedded Ag and AgCl salts to the sample and to the formation of H^+ during the photopolymerisation process. New approaches[25] can increase the homogeneous distribution of ionic species inside the membrane, thus approaching to more robust and reproducible all-solid-state designs. Tolerance to ambient changes in the short-term range was tested by exposing the planar RE to ambient light and subsequently covering the potentiometric cell with an opaque box; no light sensitivity was observed in these tests (see Figure 5). Although the light sensitivity of AgCl can produce changes in the RE performance over a long-term exposure, the results show that short-term exposure does not affect the potentiometric signal. This is very relevant for disposable sensors that are to be used in decentralised measurements.

Here, it should be mentioned that the planar RE's optimal medium-term stability and emf variability (results shown below) are met after 12 h conditioning in 10^{-3} M KCl. In the light of EIS study results, it is apparent that the ion mobility throughout the bulk membrane has a key effect on the optimal performance of the RE. The planar RE's need for conditioning is similar as in polymer membrane ISEs and may be a drawback when thinking about the possible applications of disposable sensors. We performed emf variability tests with unconditioned planar REs (see Table S2 in Supporting Information), which showed short stabilisation time and insensitivity to ionic species but sensitivity to pH (-27.0 ± 3.7 mV/dec). Therefore, it is feasible to use the new SPRE for short-term measurements using pH buffered media in on-site measurements. For applications were high stability and pH insensitivity are required, the use of pre-conditioned planar RE is recommended.

The planar RE showed a medium-term stability (10 h) of -0.9 ± 0.2 mV/h (n=3) in 10^{-3} M KCl aqueous solution (see Figure S4, Supporting Information). Long-term stability tests showed that after 12 h conditioning, the potentiometric signal was stable over more than 4 days (see Figure S5, Supporting Information). Different batches of planar RE were prepared and their potentiometric signal at 0.1 M KCl ranged from 250 to 350 mV (referred to the double-junction Ag/AgCl/KCl (3 M) reference electrode). The differences in emf signal can be attributed to the heterogeneity of the membrane and to the home-made fabrication process. These results indicate that at least one calibration point is necessary for the standardisation of the potentiometric signal, which is also currently necessary for ISEs based on CNTs.

The performance characteristics of planar REs reported here are very similar to those obtained with previously reported rod-type all-solid-state REs based on SWCNTs and photocured poly(n-BA) reference membrane,[18] indicating that screen-printed support, SWCNTs-ODA and the design proposed in this study can yield planar REs with excellent performance characteristics. What is more, the new planar REs do not need special maintenance apart from keeping them away from prolonged light exposure. The shelf life of planar REs was studied over 8 months; during this time planar REs were kept in a dark and dry atmosphere and were periodically tested against variations in KCl concentration, without loss of their performance characteristics (see Table 1). The reported results make the new planar RE especially suited for decentralised potentiometric measurements that require stringent analytical and operational requirements.[26]

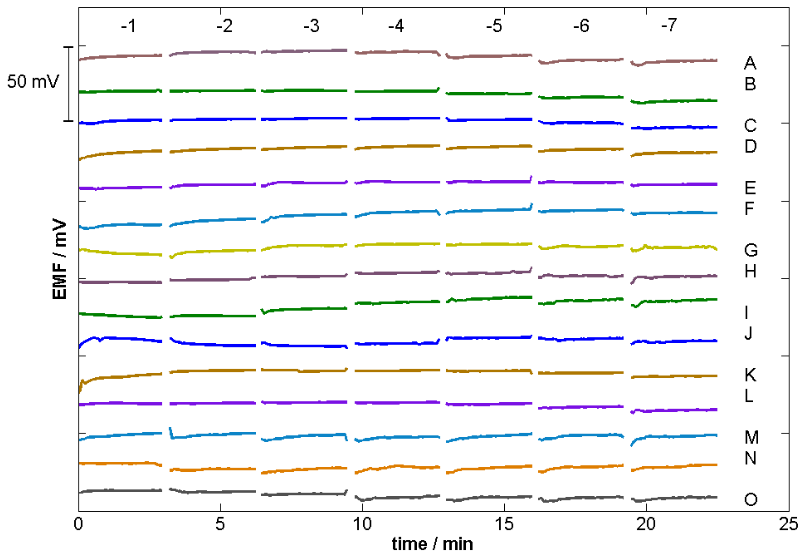

Figure 4. Potentiometric response of the planar RE to calibrations in (A) KCl, (B) NaCl, (C) LiCl, (D) NH_4Cl, (E) $MgCl_2$, (F) $CaCl_2$, (G) $NaNO_3$, (H) NaAcO, (I) $NaHCO_3$, (J) phosphate buffer solution (pH = 7), (K) Na_2SO_4, (L) sodium pyruvate, (M) glucose, (N) urea and (O) albumin from 10^{-1} to 10^{-7} M. The responses have been vertically shifted about 20 mV for clarity of presentation. Logarithmic concentration values are displayed above each segment

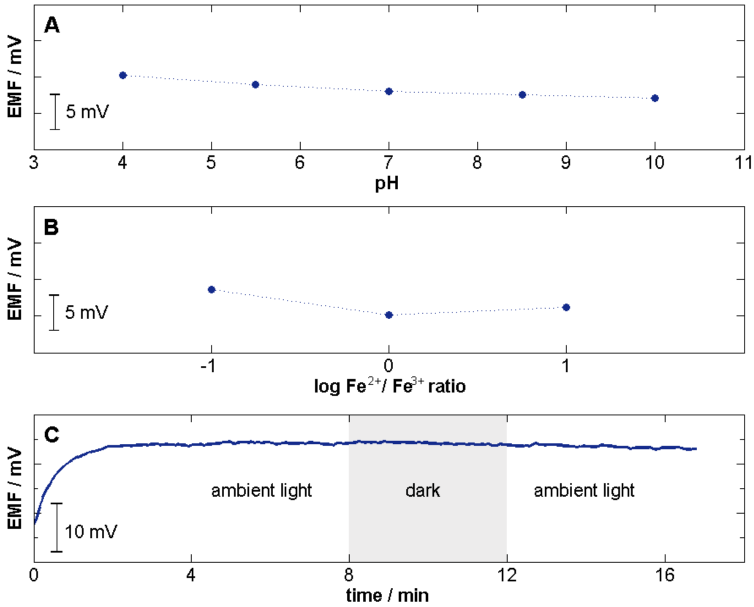

Figure 5. (A) pH, (B) 10^{-4} M $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox species and (C) light sensitivity of planar REs based on SWCNTs and poly(n-BA) reference membranes in 10^{-2} M KCl

Table 1. Planar RE's shelf life-time study. Planar REs were stored in dry and dark conditions without any maintenance. n is the number of planar REs tested

Shelf-life / months	**n**	**Emf variability[a] / mV/dec**
0.25	3	-0.6 ± 0.2
2	3	-0.3 ± 0.2
2.5	3	1.2 ± 0.8
4	3	0.6 ± 1.2
5	3	1.7 ± 0.3
8	3	0.5 ± 0.8

[a] Calculated for calibrations from 10^{-1} to 10^{-7} M KCl.

CONCLUSIONS

A disposable all-solid-state RE with outstanding performance and reduced fabrication costs has been developed using the screen-printing technique and by drop-casting an SWCNT-ODA transducer layer and photocured poly(n-BA) reference membrane. The SWCNT-ODA based planar RE was found to be insensitive (slopes inferior to 2 mV/dec) to a wide range of chemical concentrations (from 10^{-1} M to 10^{-7} M) of various cations and anions, small charged molecules, proteins, pHs, redox species, and ambient light. Moreover, the new planar RE has been stored in dry and dark conditions for 8 months without losing any of its analytical properties. Medium-term potentiometric stability in 10^{-3} M KCl aqueous solution (-0.9 ± 0.2 mV/h) and EIS characterisation shows that the constant potential generated at the reference membrane is effectively transduced by the SWCNT-ODA layer. The use of SWCNTs-ODA has been shown to be indispensable and is strongly recommended for achieving rapid and prolongated stability. The new SWCNT-ODA based planar RE represents a step forward in applying solid-contact potentiometric sensors to on-site measurements. Furthermore, the low cost of screen-printed sensors makes them ideal for use as disposable sensors. However, it is still necessary to extensively condition the reference membrane and the deposition of the reference membrane is not reproducible, thus calibration for the standardisation of potential is still necessary. Further steps will involve using planar REs in a disposable planar potentiometric system for the determination of analytes in complex samples.

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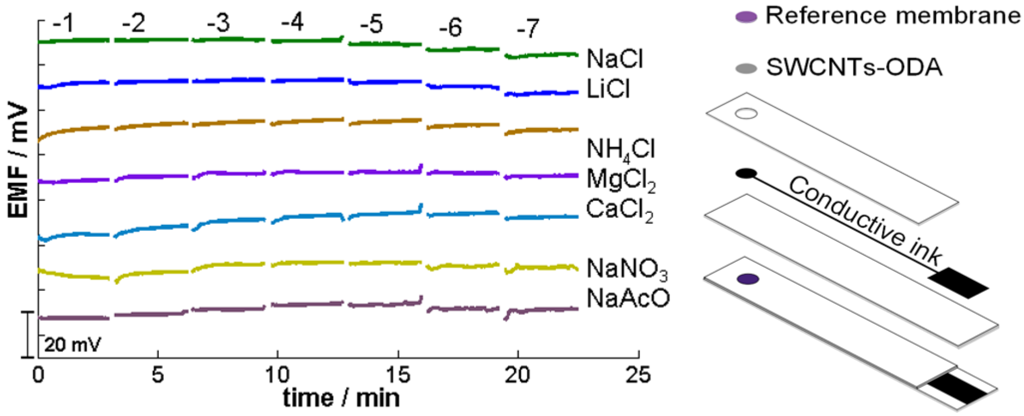
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Reference membrane
SWCNTs-ODA
Conductive ink