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ORIGINAL PAPER

Solid-state reference electrodes based on carbon nanotubes and polyacrylate membranes

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Abstract A novel potentiometric solid-state reference electrode containing single-walled carbon nanotubes as the transducer layer between a polyacrylate membrane and the conductor is reported here. Single-walled carbon nanotubes act as an efficient transducer of the constant potentiometric signal originating from the reference membrane containing the Ag/AgCl/Cl^{-} ions system, and they are needed to obtain a stable reference potentiometric signal. Furthermore, we have taken advantage of the light insensitivity of single-walled carbon nanotubes to improve the analytical performance characteristics of previously reported solid-state reference electrodes. Four different polyacrylate polymers have been selected in order to identify the most efficient reservoir for the Ag/AgCl system. Finally, two different arrangements have been assessed: (1) a solid-state reference electrode using photo-polymerised *n*-butyl acrylate polymer and (2) a thermo-polymerised methyl methacrylate:*n*-butyl acrylate (1:10) polymer. The sensitivity to various salts, pH and light, as well as time of response and stability, has been tested: the best results were obtained using single-walled carbon nanotubes and photo-polymerised *n*-butyl acrylate polymer. Water transport plays an important role in the potentiometric performance of acrylate membranes, so a new screening test method has been developed to qualitatively assess the difference in water percolation between the polyacrylic membranes studied. The results presented here open the way for the true miniaturisation of potentiometric systems using the excellent properties of single-walled carbon nanotubes.

Keywords Solid-state reference electrodes · Carbon nanotubes · Polyacrylate membrane · Water transport

Introduction

Recent advances in potentiometry have led to extremely low detection limits and high selectivity together with important operational features such as portability and simplicity, thus placing this technique at the forefront of the electrochemical methodologies that are able to perform in situ analysis [1]. However, further steps towards the true miniaturisation of potentiometric sensors are necessary so that they can be put to general use. One of these steps is the development of reliable solid-state reference electrodes (SSREs) that allow the construction of a fully miniaturised potentiometric cell including miniaturised indicator and reference electrodes.

The first polymer-based SSRE appeared due to the necessity of finding alternatives to solid-state Ag/AgCl pseudo-reference electrodes, which only work at constant sample chloride activity. First liquid junction-free SSRE prototypes only functioned under ideal or extremely well-defined conditions, which reduced the number of applications they could be used for [2, 3]. Later, Lee et al. reported the insensitivity of some polyurethane polymers as membranes for coated-wire type of SSRE [4], but medium- and long-term stability tests were not detailed. These early ideas were subsequently developed by Mamińska et al. [5] and

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Mattinnen et al. [6]. Both groups reported on PVC-based electroneutral membranes capable of being miniaturised and on the use of a solid redox-type transducers (Ag/AgCl or conducting polymers) so a better signal stability could be attained in comparison with coated-wire-type SSREs. However, these SSREs rely on the formation of a constant potential at an electroneutral membrane layer, and unfortunately, sample ions and lipophilic species entering the membrane may be the origin of interferences.

An alternative approach is to use conducting polymers (CPs) with suppressed or compensated anion and cation exchange in direct contact with the sample solution [7–9]. However, SSREs based on CPs are directly affected by redox species in solution [10] and show some of the drawbacks inherent in the use of CPs such as the necessity of tuning the doping conditions for different CPs or the marked light sensitivity of some CPs [11], which makes indispensable the use of protective systems that isolate them from changes in ambient light intensity.

The use of a polymeric protective layer containing the Ag/AgCl/Cl^- ions system or some components of it has been repetitively proposed in order to obtain constant potentials. The approach is not trivial due to the difficulties in preserving constant salts concentration in a solid state, while maintaining the conductive properties of the polymeric layer [12]. Tymecki et al. proposed the miniaturisation of SSREs by encapsulating chloride salts in a screen-printed insulator paste in contact with Ag/AgCl ink [13]. The reported stability of this planar SSRE was excellent, but response to Ag^+, Pb^{2+} and Fe^{3+} was observed due to the formation of insoluble species at the solid electrolyte/solution interface. Again, nonresponsive polymer materials showed promising insensitivity when encapsulating the Ag/AgCl/Cl^- ions system [14], although it has been argued that similar results could be difficult to reproduce in miniaturised configurations [12]. Other lipophilic materials, such as ionic liquids (ILs), have also been proposed for the entrapment of Ag/AgCl salts. ILs-SSREs showed promising results, and only the acute tendency of hydrophobic species (e.g. non-ionic species and surfactants) to enter the bulk membrane and the finite solubility of toxic IL in the sample solution hinder their on-field applications [15]. Recently, Kisiel et al. attained a high degree of solidification of the reference system by dispersing the Ag/AgCl/Cl^- ions system into strong hardening polymers such as polyvinyl chloride (PVC) or poly(*n*-butyl acrylate) [10, 16–18]. Alternatively, the solidification of the reference electrolyte on its own has been proposed as a valid alternative for applications in the food industry, where high temperature and pressures are attained during sterilisation [19]. Excessive electrolyte leakage into the sample solution was only ameliorated by optimised ceramic materials acting as liquid junction.

To date, the redox materials Ag/AgCl and CPs have been the only transducers used in SSREs. Conducting polymers perform as excellent redox transducers, but some of them display practical limitations, such as light sensitivity, the formation of a water layer at the interface between the transducer and the polymeric membrane and the formation of unwanted redox reactions [20]. Therefore, new solid-state transducing materials can be of great interest in order to develop novel SSREs with enhanced analytical and operational characteristics. Single-walled carbon nanotubes (SWCNTs) have been shown to be excellent ion-to-electron transducers for all-solid-state ISEs and thus represent an excellent alternative to CPs [21]. Our group recently demonstrated that the transduction performance of SWCNTs is mediated by their low resistance and their large bulk double-layer capacitance [22]. As a result, SWCNTs provide stable and rapid potentiometric responses, are chemically stable, are not affected by light and prevent the formation of undesirable inner water layers at the membrane–transducer interface [23].

The choice of the protective layer which shields the transducer from interferences and creates a constant potential simultaneously is generalised nowadays in SSREs. Moreover, it has been sought as an advantage that the same materials that will constitute the potentiometric cell could be used in both the solid-sate ISE and RE [5, 17, 24] or that the production method for both electrodes is compatible [13]. Polymeric membranes are largely used today in solid-state ISEs: polyacrylic polymers which have been reported to have better analytical performance characteristics in comparison with plasticised membranes based on its low ion and water diffusion coefficients [25]. Therefore, the use of novel polyacrylic polymers is attractive because it represents new alternatives in the fabrication of SSREs and solid-state potentiometric systems, which could be ultimately miniaturised.

The aim of the present article is to develop a new SSRE containing SWCNTs as ion-to-electron transducer and polyacrylic membranes for encapsulating the Ag/AgCl/Cl^- ions system. SWCNTs have been used here for the first time as transducer layer in SSREs in order to improve the analytical performance characteristics of the proposed SSREs with respect to previously reported CPs-based SSREs. Given the excellent properties of polyacrylic polymers, the best reservoir layers have been selected among four different polyacrylic polymers in order to obtain SSREs with excellent analytical performance characteristics. Water percolation through the membrane has been assessed with a novel screening method that allows us a rapid and qualitative water percolation comparison between four different polyacrylic membranes.

Experimental section

Reagents

Tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH500), tetrahydrofuran (THF), 2,2′-azobis(2-methylpropionitrile) (AIBN), methyl methacrylate (MMA), *n*-butyl acrylate (nBA) monomers, KCl, NaCl and $NaNO_3$ were purchased in Selectophore grade from Fluka. Sodium dodecyl sulphate (SDS), cross-linker 1,6-hexanediol diacrylate (HDDA), photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPP) and regioregular poly(octylthiophene) (POT) were purchased from Aldrich. AgCl was precipitated by mixing 3 M $AgNO_3$ and 3 M KCl solutions. The sediment formed was filtered on a soft filter, washed and dried in oven at 80 °C, for at least 1 h. AgCl was stored in a dark place until use. Single-walled carbon nanotubes with >90% weight purity were purchased from HeJi, Inc. and subsequently purified and carboxilated using protocols available in the literature [26]. Milli-Q PLUS (Millipore Corporation) water was used to prepare all the aqueous solutions. Sigladur glassy carbon (GC) and Cu rods with 3 mm diameter were obtained from HTW (Germany) and RS Components (Spain), respectively.

Electrode fabrication

The reference electrode was prepared by pre-processing the surface of the distal end of a glassy carbon rod onto which the SWCNTs and the reference membrane were then deposited. The GC distal end was polished using a sheet of abrasive paper (Buehler Carbimet 600/P1200) and subsequently treated using alumina of different grain sizes (30, 5 and 1 μm Buehler Micropolish II). SWCNT dispersion was homogenised by tip-sonication for 60 min (amplitude 60%, cycle 0.5, Ultraschallprozessor UP200S, Dr. Hielscher); then, carboxylated SWCNTs were deposited onto the distal end of the GC rod by spraying 10 mL of an aqueous dispersion containing 25 mg of carboxylated SWCNT and 100 mg of SDS. Finally, SDS is removed by heating the electrodes at 300 °C for 1 h, yielding a ~30 μm layer of SWCNTs. Figure 1 displays a schematic representation of the SWCNT-based SSRE. Then, the SWCNTs layer was covered with the reference membranes as described below.

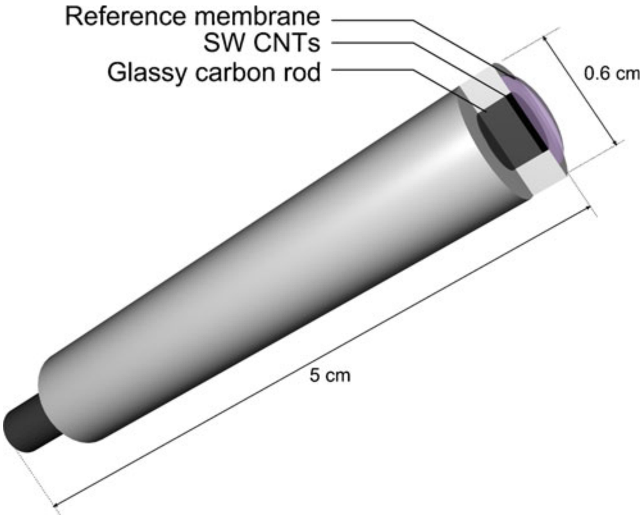


Fig. 1 Schematic representation of the SWCNT-based SSREs

Preparation of polymeric membranes

Four different polymeric membranes were prepared: thermo-polymerised nBA, thermo-polymerised MMA:nBA, photo-polymerised nBA and photo-polymerised MMA:nBA. Thermo-polymerised nBA was synthesised as described elsewhere [27]. Thermo-polymerised MMA:nBA (thermo-MMA:nBA) was synthesised by mixing 500 μL of MMA monomer, 4.500 μL of nBA monomer and 22 mg of AIBN initiator. The mixture was thoroughly degassed with N_2 and heated at 100 °C for 14 h. Finally, the reaction mixture was heated for 1 h (100 °C) under low pressure (water pump) to eliminate non-reacted monomers. To prepare the reference membrane cocktail, 200 mg of the chosen polymer, 34 mg of KCl, 13 mg of AgCl (with traces of Ag) and 5 mg of ETH500 were dispersed in 1 mL of THF. One hundred microlitres of the cocktail membrane were drop-cast onto the electrodes and left to dry overnight.

A cross-linking mixture was used to prepare photo-polymerised poly(*n*-butyl acrylate) (photo-nBA) membranes which contained 42.7 mg HDDA cross-linker, 457.2 mg DMPP photo-initiator and 3.3 mL of *n*-butyl acrylate. Photocured reference membrane cocktails were prepared with 180 μL of nBA monomer for photo-nBA, or 160 μL of nBA monomer and 20 μL of MMA monomer for photo-MMA:nBA, plus 20 μL of cross-linking mixture, 34 mg of KCl, 13 mg of AgCl (with traces of Ag) and 5 mg of ETH500. Twenty microliters of the photo-polymerised nBA or MMA:nBA reference cocktails were drop-cast onto the GC/SWCNTs electrodes, which were then placed upside-down. Photo-polymerisation was carried out using a UV lamp (4 W) for 8 min under argon flow.

Potentiometric testing of all-solid-state reference electrodes

Potentiometric measurements were performed against a conventional double-junction Ag/AgCl/KCl (3 M) reference electrode (type 6.0729.100, Metrohm AG) containing a 1 M LiOAc electrolyte bridge reference electrode. Electromotive forces (EMF) were measured at room temperature (22±2 °C) using a EMF16 multichannel data acquisition setup and software (Lawson Laboratories, Inc.). The pump systems 700 Dosino and 711 Liquino (Metrohm AG) were used to obtain sequential calibrations from 10^{-1} to 10^{-7} M for KCl, NaCl and $NaNO_3$. pH sensitivity measurements were performed in a 0.1 M KCl background solution using a Crison MM40 pH meter. To measure light sensitivity, the potentiometric signal was first recorded in the dark, then in room light and finally in the dark using an opaque box. Response time is calculated as the time needed to attain the 95% of the final response ($t_{95\%}$). All data reported was calculated with three electrodes.

Polymer characterisation

The four polymers described above were characterised by differential scanning calorimetry (DSC) using a Mettler DSC-821e differential scanning calorimeter. The samples weighing between 5 and 10 mg were placed in covered Al pans under N_2, to obtain the DSC curves, which in turn provided glass transition temperatures (T_g). The copolymers synthesised were also examined by proton nuclear magnetic resonance (NMR). NMR studies were carried out with a 400 MHz VARIAN Mercury VX400 NMR instrument. Samples were dissolved in deuterated chloroform, and the chemical shifts from 0 to 10 ppm were recorded. NMR spectra were used to calculate the cross-linked monomer ratios (Table 1) and polymer purity.

Detection of water percolation

In order to rapidly detect the percolation of water through the polymeric membranes, we used a Cu rod instead of the GC rod. The distal ends of the Cu rods (3 mm ∅) were exposed to a 16 V DC electric field in a distilled water bath to obtain a homogeneous Cu/Cu^{2+} surface. Once the Cu/Cu^{2+} surface was dry, 100 μL of each of the four reference membranes was deposited, letting it dry the necessary time for each membrane. Finally, the electrode was immersed in 3 M or 0.01 M KCl aqueous solutions, and the percolation of water through the polymeric membranes was assessed by direct observation of the $Cu_2Cl(OH)_3$ on the Cu rod surface over 24 h. The observable green species were characterised as $Cu_2Cl(OH)_3$ with a Bruker D8 Discover X-Ray diffraction instrument. Blank experiments performed in the absence of Cl^- salts or Cu/Cu^{2+} surface direct water exposure demonstrated that $Cu_2Cl(OH)_3$ was only formed when the Cu/Cu^{2+} surface was exposed to Cl^- anions together with H_2O molecules.

Results and discussion

Solid-state reference electrodes based on SWCNTs

SWCNTs have been used here for the first time in a SSRE so the advantageous properties of SWCNTs (i.e. SWCNTs are hydrophobic, and the stable potential created is not affected by UV/Vis light [21]) are exploited to improve the analytical performance of previously reported SSREs. Two different technologies merge in the present SSREs: (1) SWCNTs as excellent ion-to-electron transducer which promote signal stability [21] and (2) polyacrylic membranes that encapsulate Ag, AgCl and KCl salts, creating a constant and reproducible potential [16]. To compare the transduction ability of SWCNTs with CPs, we initially developed SSREs with SWCNTs and photo-nBA reference membrane to test whether the analytical performance of the new SWCNT-based SSREs is comparable to previously reported polypyrrole/photo-nBA-based SSREs [16].

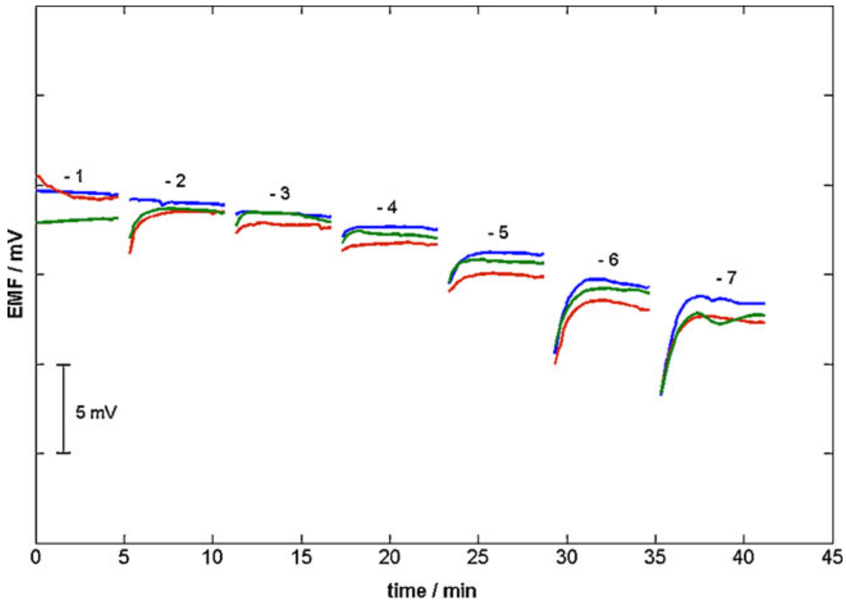
The SSREs were initially characterised by recording their electrode potential following their first contact with a KCl 3 M conditioning solution. Twenty-four-hour conditioning was found to be crucial for the stability of photo-nBA SSREs. The sensitivity of photo-nBA-based SSREs was assessed by recording the potentiometric signal when the types of anion (Cl^- or NO_3^-), cation (Na^+ or K^+) and salt concentration were varied in the test solution. The calibration plots obtained with photo-nBA SSREs are shown in Fig. 2: The recorded slopes were 0.7±1.7 mV/dec for KCl, 1.0±0.2 mV/dec for NaCl and 0.5±0.4 mV/dec for $NaNO_3$. Response times ($t_{95\%}$) varied from 1 min at low concentration to less than 30 s for higher than 10^{-5} M concentrations. Medium-term stability was recorded in 0.01 M KCl solution, obtaining a drift of −1.1±0.2 mV/h (Fig. 3, red line). Next,

Table 1 Studied physical characteristics of the polyacrylic polymers

	T_g (°C)	Monomer feed ratio MMA:nBA	Final monomer ratio MMA:nBA[a]	Polymer physical properties
Thermo-nBA	−51.5	0:10	0:10	Soft and sticky
Thermo-MMA:nBA	−42.6	1.1:10	1.2:10	Elastic and tacky
Photo-nBA	−50.4	0:10	0:10	Rubbery
Photo-MMA:nBA	−46.1	1.1:10	0.5:10	Rubbery

[a] Determined by NMR

Fig. 2 Potentiometric response of SWCNT-based photo-nBA SSREs to subsequent calibrations for KCl (*green*), NaCl (*red*) and $NaNO_3$ (*blue*) from 10^{-1} to 10^{-7} M (logarithmic values are displayed above each segment)

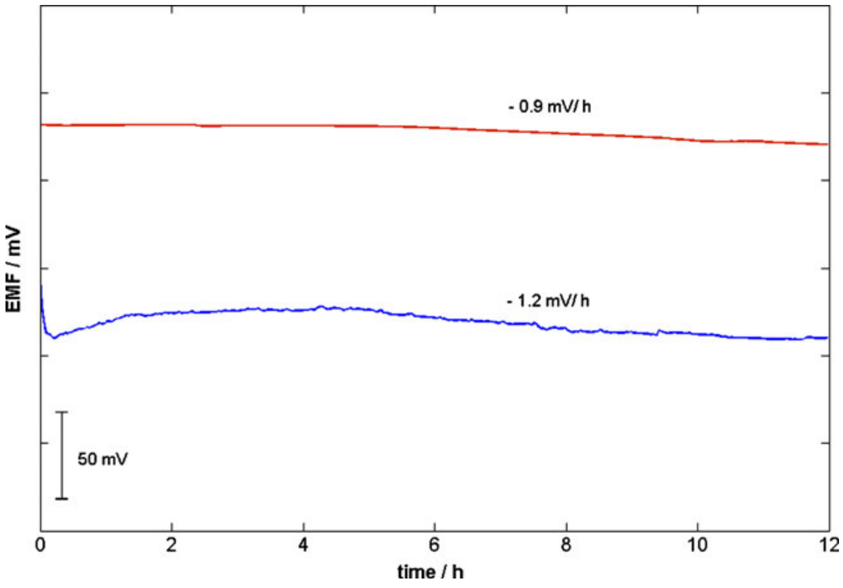


pH and light variations have been studied in order to determine to what extent they may affect the potential of the SSRE when measuring real samples in in situ analysis. SSREs based on SWCNTs and photo-nBA show no significant variations in potential from pH 5 to 11 (Fig. 4, red dots) and in the presence/absence of room light (Fig. 5, red line).

In the light of the experimental results obtained, we conclude that photo-nBA-based SSREs perform to a similar level with both SWCNTs and polypyrrole. The first two columns in Table 2 present the potentiometric performance characteristics of the SWCNTs and polypyrrole-based SSREs using photo-nBA as reference membrane matrix. Sensitivity to KCl, NaCl, $NaNO_3$ and pH are comparable for SWCNTs and polypyrrole-based SSREs. Only medium-term stability was reported to be lower for POT-based SSREs (0.2 mV/h), although it should be taken into account that this value was obtained in a more concentrated solution (0.1 M KCl). What is more, we show here for the first time the insensitivity of a novel SSRE to light exposure, which provides an advantage over other SSREs since light insensitivity is a key aspect in on-field potentiometric measurements.

Knowing that a SWCNTs layer is an excellent solid transducer for this kind of SSRE, we went a step further by investigating the fabrication of SWCNTs-based SSREs with other polyacrylic reference membranes. By doing this, we wanted to (1) develop a SSREs fabricated with polyacrylic membranes which have been already used in solid-state

Fig. 3 Medium-term stability of SWCNTs-based photo-nBA (*red*) and thermo-MMA:nBA (*blue*) SSREs in 10^{-2} M KCl



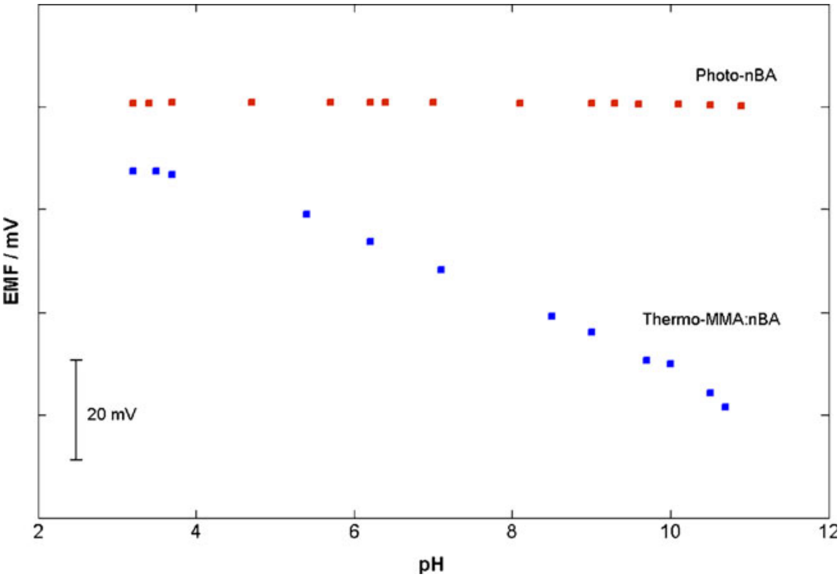


Fig. 4 pH response of SWCNTs-based photo-nBA (*red*) or thermo-MMA:nBA (*blue*) SSREs in 10^{-2} M KCl

ISEs [28–31] and (2) to obtain more insights on the behaviour of polyacrylic polymers as reservoirs for the Ag/AgCl system. We initially selected four polymers for this study: thermo-nBA, thermo-MMA:nBA, photo-nBA and photo-MMA:nBA. These polyacrylic polymers are either produced by UV photocuring or by thermic synthesis and incorporating in their matrix variable amounts of MMA and nBA monomers.

Selecting polyacrylic polymers for SWCNTs-based solid-state reference electrodes

In previous articles, Kisiel et al. used photo-polymerised and thermo-polymerised poly-nBA as membrane materials in SSREs [16, 18]. They found that the physical properties of the polyacrylate polymer influenced the performance of the reference membranes [18]. In the present study, the physical properties of thermo-nBA, thermo-MMA:nBA, photo-nBA and photo-MMA:nBA were compared by evaluating their T_g and monomer composition. To our knowledge, the comparison between these four widely used polyacrylic polymers has not been reported before.

Table 1 summarises all the results obtained in the characterisation of the four polyacrylic polymers. The T_g of a polymer is the temperature at which the transition from flexible rubber state to rigid solid (glass) occurs. The molecular chains of polymers with low T_g become flexible

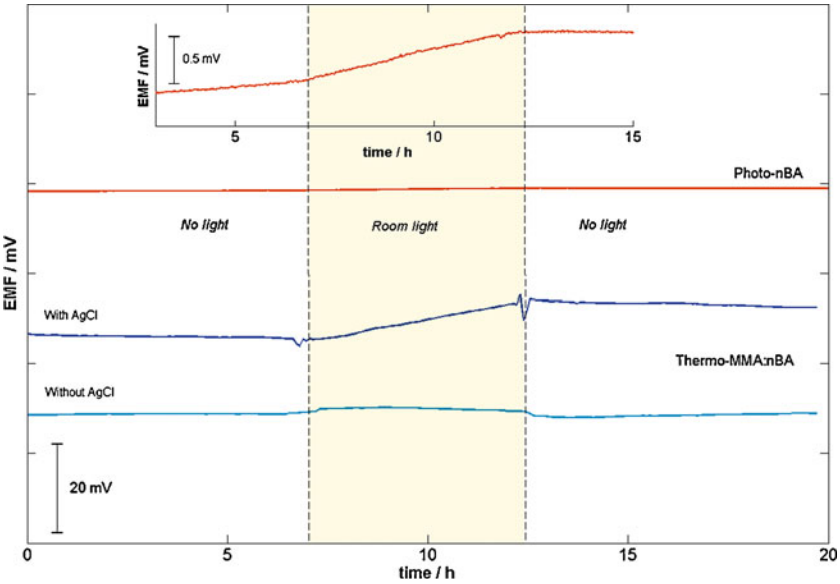


Fig. 5 Light sensitivity of SWCNTs-based photo-nBA (*red*) containing Ag, AgCl and KCl salts; thermo-MMA:nBA with (*dark blue*) and without AgCl (*light blue*) SSREs

Table 2 Potentiometric performance characteristics of SSREs using polymeric reservoir matrices for the Ag/AgCl system and using SWCNTs or CPs as solid-state transducers [10, 16, 18]

Polymeric reservoir matrix		Photo-nBA	Photo-nBA[a]	Thermo-MMA.nBA	Thermo-nBA[c]	PVC-DOS[a]	PVC-DOS[a]
Transducer		SWCNTs	Polypyrrole	SWCNTs	POT	PPy(PSS)	PEDOT(PSS)
Conditioning protocol (conditioning solution/time)		3 M KCl/24 h	3 M KCl/12 h	3 M KCl/12 h+10^{-2} M KCl/12 h	3 M KCl/48 h	3 M KCl/12 h	3 M KCl/12 h
Mid-term stability in 10^{-2} M KCl (mV/h)		-1.1 ± 0.2	0.2[c]	-1.2 ± 0.4	nd	nd	nd
Sensitivity (mV/dec log a)[b]	KCl	0.7 ± 1.7	0.7 ± 0.1	0.1 ± 0.6	1	0.1	-0.1
	NaCl	1.0 ± 0.2	0.9 ± 0.1	0.1 ± 1.1	0	0.7	-0.2
	$NaNO_3$	0.5 ± 0.4	0.9 ± 0.2	-0.3 ± 1.0	-1	0	0.4
Sensitivity (mV/pH unit)[d]	pH	-0.1 ± 0.1	0.0	-6 ± 1	nd	1[e]	nd
Sensitivity (mV/min)	Light	0.1 ± 0.1	nd	0.6 ± 0.2	nd	nd	nd

[a] For the concentration range between 0.1 and 10^{-5} M

[b] For the concentration range between 0.1 and 10^{-7} M

[c] Thermo-nBA microspheres composite. Overnight measurement carried out in 0.1 M KCl

[d] For the pH range between 3 and 10

[e] For the pH range between 2 and 6

enough at room temperature to allow mobility of the electrolytes within the matrix, which is necessary in reference membranes. DSC results clearly show that when MMA monomer is added to the polymer chain the regularity decreases, which in turn increases the T_g. Similar results were obtained in previous studies with polyacrylate polymers [32, 33]. Monomer copolymer ratios were studied by NMR spectroscopy [32], which showed that the incorporation of MMA monomers into the final polymeric membrane was favoured in thermo-polymerisation but was hindered for photo-polymerisation. The NMR results agree with the DSC results: the higher the content of polymerised MMA, the more positive the T_g.

The four reference membranes used in this work are heterogeneous and contain a high amount of hydrophilic salts, so it is expected that molecular water can enter the bulk membrane and form water islands or channels when it encounters the hydrophilic surfaces of the dispersed salts. Previous studies have studied water uptake in PVC and polyacrylic membranes by several approaches [34–38]. However, these methods for detecting water uptake are cumbersome or not feasible in heterogeneous reference membranes. Therefore, a simple, relatively fast and visual screening test has been used here for the first time to compare the water percolation of the four types of reference membranes. This test is based on the oxidation of Cu to Cu^{2+} and its subsequent complexation with Cl^- ions and H_2O, which forms green $Cu_2Cl(OH)_3$. Visual detection of green $Cu_2Cl(OH)_3$ indicates the presence of a water layer at the reference membrane/Cu interface. Reference membrane cocktails were prepared with the four polymers, deposited onto bare Cu electrode bodies and immersed in 3 M KCl solutions. After overnight exposure, green $Cu_2Cl(OH)_3$ were clearly observed in the thermo-nBA, the thermo-MMA:nBA and the photo-MMA:nBA polymer membranes. However, $Cu_2Cl(OH)_3$ was not observed in photo-nBA electrodes. Moreover, it was observed that water percolation also changed the volume and physical properties of the photo-nBA membrane, that is, the photo-nBA reference membrane swelled and partially lost its hydrophobic characteristics. Visual observations indicate that photo-nBA membrane is less prone to water percolation and promotes the accumulation of water molecules surrounding the salt grains. In contrast, the addition of MMA in the polymer chain and also the thermal synthesis produce membranes that did not swell, which suggests that they allow water molecules to be transported through the macromolecular structure of the polymers [13].

Taking the polymer's characterisation results into consideration, thermo-MMA:nBA appears to be an appealing polymer for the fabrication of SWCNTs-based SSREs: thermo-MMA:nBA presents T_g, physical properties (see Table 1), water percolation and salt distribution in its bulk that are significantly different from those already studied photo-nBA. In addition, thermo-MMA:nBA has been successfully used in SWCNTs-based ISEs [21, 28–31], so we know that its mechanical properties are compatible with SWCNTs, and it would be of great interest to be able to fabricate both the solid-state ISE and RE with the same polymeric matrix and fabrication procedure. We waived a further study of other membranes due to the following reasons: photo-MMA:nBA physical properties are very similar those of photo-nBA (see Table 1), so it would not add any significant novelty. On the other hand, thermo–nBA has already been studied to determine its ability to entrap Ag/AgCl and KCl salts in SSREs [18]: its softness and looser physical properties caused excessive salt leaching from the bulk membrane to the solution when dispersed salts were used, so only when using microspheres to entrap hydrophilic salts the SSRE showed acceptable insensitivity and stability.

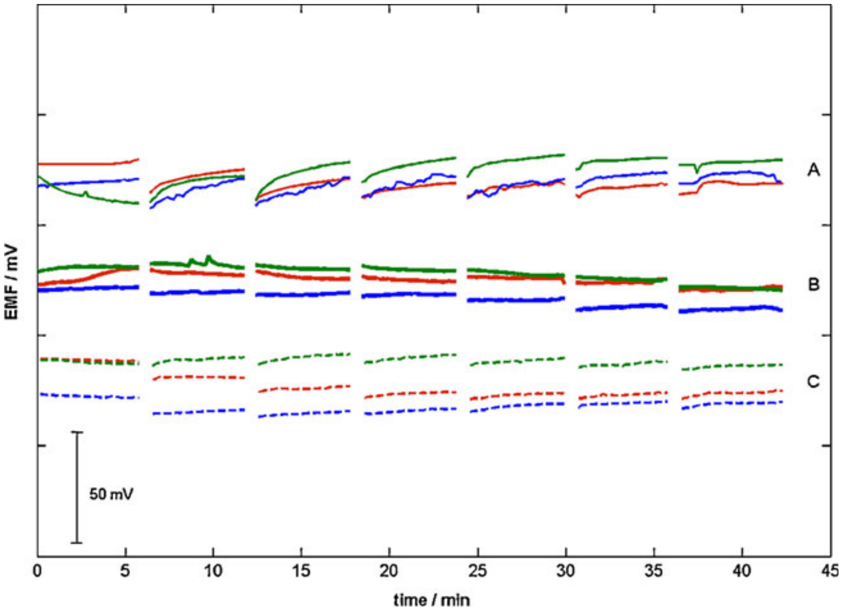
Solid-state reference electrode based on SWCNTs and thermo-MMA:nBA membrane

We first studied the conditioning protocol of the newly tested polymeric membrane: conditioning in 3 M KCl for 14 h yielded sensitivities to KCl, NaCl and $NaNO_3$ close to 3 mV/dec and a time of response of 4 min (curve A in Fig. 6). A shorter time of response was obtained after 14 h in a 3 M KCl solution, followed by 14 h in a 0.01 M KCl solution. These were the best conditions, and thermo-MMA: nBA SSREs produced the following results: slopes of 0.1± 0.6 mV/dec for KCl, 0.1±1.1 mV/dec for NaCl and −0.3± 1.0 mV/dec for $NaNO_3$ for concentration from 10^{-1} to 10^{-7} M (curve B in Fig. 6). Short response times ($t_{95\%}$ less than 30 s) were obtained over the whole operational range. Figure 3 shows the medium-term stability (12 h experiment) of the SWCNTs-based thermo-MMA:nBA SSRE, pointing to an initial positive drift followed by a signal plateau and a slight negative drift of −1.2±0.4 mV/h.

Since thermo-MMA:nBA membranes allow for intense water percolation, the thermo-MMA:nBA SSREs were further studied by keeping the electrodes in dry conditions for 1 week. During this time, water content inside the membrane is expected to significantly decrease. When we recorded the potentiometric response to variations in salt concentration immediately after being kept in dry conditions, the thermo-MMA:nBA SSREs showed drifts and long response times (4 min). The results improved after exposing the thermo-MMA:nBA SSRE to optimal conditioning described above: sensitivities to KCl, NaCl and $NaNO_3$ were then below 2 mV/dec, with times of response of 1 min and satisfactory medium-term stability (2 mV/h; see curve C in Fig. 6). Only a shift of 20 mV for the starting potentials of K^+ and Na^+ salts differentiated the results of thermo-MMA:nBA SSREs after 1 week storage in dry conditions. The latter results were promising, suggesting that it is possible to storage the thermo-MMA:nBA for a long time in dry conditions without maintenance, and only an appropriate conditioning protocol is needed to yield insensitivity to KCl, NaCl and $NaNO_3$.

Thermo-MMA.nBA showed a linear response of −6± 1 mV/pH unit from pH 3 to 11 (see Fig. 4, blue dots). The varying dispersion of the salts in the bulk membrane, the different membrane lipophilicity and different water percolation through the membrane can cause the response to changes in pH. Thermo-MMA:nBA SSREs showed practically no drift in dark conditions; however, when the potentiometric cell was exposed to daylight, a constant lineal drift of 0.6±0.2 mV/min appeared (see Fig. 5, dark blue line). When AgCl was removed from the reference thermo-MMA:nBA membrane, we observed only a 1 mV jump of potential when the potentiometric cell was exposed to daylight (see Fig. 5, light blue line). These results corroborate that AgCl is the agent causing light sensitivity. The photovoltaic effect forces the thermo-MMA:nBA SSRE to be integrated into dark cartridges to protect it from changes in ambient light.

Fig. 6 Potentiometric response of SWCNT-based thermo-MMA:nBA SSRE to subsequent calibrations for KCl (*green*), NaCl (*red*) and $NaNO_3$ (*blue*) from 10^{-1} to 10^{-7} M (logarithmic values are displayed above each segment): (*A*) conditioned in 3 M KCl for 14 h; (*B*) conditioned in 3 M KCl for 14 h and 10^{-2} M KCl for 14 h; (*C*) after 1 week kept dry and conditioned in 0.01 M KCl for 14 h



Role of SWCNTs and polyacrylic reference membranes

In order to study the role of SWCNTs as efficient transducer of the potentiometric signal, we have compared the analytical parameters found for SWCNTs-based SSREs (i.e. using photo-nBA and thermo-MMA:nBA membranes) with comparable studies previously reported on CPs-based SSREs by Kisiel et al. [10, 16, 18] (see Table 2). SWCNTs-based SSREs show comparable analytical performance values in terms of KCl, NaCl, $NaNO_3$ and pH insensitivity. Reported mid-term stability values for polypyrrole/photo-nBA-based SSREs are lower than for SWCNTs/photo-nBA SSREs, although one should take into account that mid-term stability can vary depending on solution concentration and stirring conditions. In this article, we report for the first time on a SWCNTs/photo-nBA SSRE being insensitive to light exposure. In short, we show that SWCNTs are a suitable transducer for SSREs, especially for on-field applications.

The role of the silver/silver chloride system contained in the reference membrane was investigated by removing the silver chloride and silver ion from the thermo-MMA:nBA reference membranes. It was found that reference membranes without AgCl responded to salt concentration variations. In another experiment, Ag/AgCl and KCl salts were all removed from the thermo-MMA:nBA reference membrane, while the membrane electroneutrality was assured following the method by Mattinnen et al. [6]: it was observed that electrodes in their first contact with water had no response to low KCl concentration (10^{-7} to 10^{-4} M), but signal started drifting at high KCl concentrations (10^{-4} to 10^{-2} M). After overnight conditioning in 10^{-3} M KCl, electrodes showed response to KCl concentration variations. These results show that thermo-MMA:nBA membrane is permeable to ions, and these ions can interfere in the potential stability of the SSRE. Therefore, it is clear that dispersed Ag/AgCl and KCl salts play an active role in maintaining a stable membrane potential.

Besides, photo-nBA and thermo-MMA:nBA polymers were proved to act as efficient solid reservoirs. Insensitivity to changes in the sample electrolyte concentration was observed after 1 month dry storage for both photo-nBA and thermo-MMA:nBA; insensitivity to KCl, NaCl and $NaNO_3$ never exceeded 2 mV/dec, results that are not significantly different from those shown in Figs. 2 and 6 for photo-nBA and thermo-MMA:nBA SWCNTs-based SSREs, respectively.

Conclusions

A new set of SSREs has been developed using SWCNTs as the ion-to-electron transducer and polyacrylic polymers as the Ag/AgCl system reservoir. SWCNTs transducer layer is shown to be comparable, and in some cases superior, to other solid transducers for the fabrication of SSREs. The best results were obtained with photo-nBA reference membrane SWCNTs-based SSRE: satisfactory medium-term stability and insensitivity to changes in KCl, NaCl, $NaNO_3$ and pH was observed. Besides, it did not respond to changes in room light, which has not been reported before for similar SSREs. Newly applied thermo-MMA:nBA showed response to pH and light in SWCNTs-based SSRE. New techniques (such as encapsulating components within polyacrylate microspheres [18]) would add value to this first study on the use of thermo-MMA:nBA in SWCNTs-based SSREs.

The high water percolation through the reference membranes has been qualitatively assessed, and it was found that thermo-MMA:nBA is more prone to water percolation than photo-nBA. This is in agreement with DSC and NMR results: photo-nBA is less prone to water percolation because it is a more ordered polymer (T_g=−50.4 °C), while the addition of 10% MMA monomer to the poly-nBA chain decreases the order of the polyacrylate matrix (T_g=−42.6 °C).

Polyacrylic membranes have been shown to be effective solid reservoirs, so it is possible to storage the SWCNTs-based SSREs for a long time in dry conditions without maintenance, and only proposed conditioning protocols have to be followed to obtain the reported insensitivity values. This new type of SWCNTs-based SSRE is simple to fabricate and miniaturise since it only contains SWCNTs as the transducer layer and a polyacrylic polymer to entrap the Ag/AgCl system. Moreover, using the same polyacrylic polymer in both the SSRE and the ISE simplifies the process of fabricating the entire potentiometric cell.

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