

Synthesis and characterization of high-integrity solid-contact polymeric ion sensors

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Received: 6 April 2008 / Accepted: 22 May 2008 / Published online: 27 June 2008
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Abstract High-integrity solid-contact (SC) polymeric ion sensors have been produced by using spin casting and electropolymerization techniques in the preparation of the SC employing the conductive polymer, poly(3-octylthiophene) (POT). The physical and chemical integrity of the POT SCs have been evaluated using scanning electron microscopy (SEM), atomic force microscopy (AFM), secondary ion mass spectrometry (SIMS), and X-ray photoelectron spectroscopy (XPS). Furthermore, the electrochemical stability of SC polymeric ion sensors has been investigated using electrochemical impedance spectroscopy (EIS). The results of this study demonstrate that electropolymerization and spin casting methods also comprising annealing of the synthesized SC film are capable of producing SCs that are relatively free of imperfections such as pores and pinholes. This leads to electrochemically stable and robust polymeric ion sensors where the SC/sensor interface is resistant to the formation of a detrimental water layer that normally gives rise to spurious ion fluxes and a degradation in the sensitivity and selectivity of the SC polymeric ion sensor.

Keywords Solid contact ion-selective electrode ·
Conductive polymer · Surface analysis ·
Polymeric membrane ion-selective electrode

Introduction

Ion-selective electrodes (ISEs) are currently utilized in a wide variety of applications ranging from the analysis of intracellular electrolyte concentrations [1] in biology to monitoring the calcium content of dairy products as part of quality control measures in the food industry [2, 3]. Importantly, ISEs have also been used to measure and monitor the concentration of bioanalytes [4] and vital electrolytes in bodily fluids [5, 6], and it has been estimated that well over a billion ISE measurements are made every year in clinical laboratories alone [7]. A key advantage of using ISEs is that they are capable of making reliable, rapid, and real-time measurements in point-of-care clinical applications [3].

Solid-contact (SC) ISEs can be used in virtually every application where their liquid-contact counterparts are deployed—perhaps with even more versatility—since their usage and storage are not confined to a vertical orientation, and factors such as the evaporation and leaching of the internal filling solution do not have to be considered [6]. This versatility coupled with their potential for miniaturization lends this class of ISE amenable to exciting applications such as the use of these concentration sensitive devices in the detection of ultratrace amounts of total analyte (e.g., attomole quantities [8]) in confined volumes, which may also be coupled to innovative bioassays employing nanoparticle-tagged biomolecules [9, 10].

Despite the advantages over other types of ISEs, polymeric SC ISEs are not yet as highly utilized as their

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liquid-contact counterparts. This is due primarily to a historic instability and irreproducibility in the standard potentials of SC ISEs, showing a variation between electrodes of the same type as well as within the lifetime of a single electrode [11–13]. These spurious measurements are believed to originate either from the formation of a water layer at the SC/polymeric sensing membrane interface [14–16], or through an ill-defined and erratic potential at the SC/ISE membrane buried interface that can be eliminated by using a conductive polymer SC as an ion-to-electron transducer [17]. The evolution of such a water layer has been studied by a variety of techniques including potentiometry [16], electrochemical impedance spectroscopy (EIS), and neutron reflectometry [14]. A previous EIS study by the authors [14] revealed a decrease in the convoluted contact resistance at the SC/ISE membrane-buried interface coupled with the bulk membrane resistance (i.e., so-called bulk membrane-contact resistance) when the SC ISE was exposed to aqueous electrolyte for prolonged periods of time [14].

These findings are consistent with the separation of a water layer comprising transported ions and water at the SC/ISE membrane interface, resulting in an electrolyte reservoir between the membrane and the SC [14, 15]. The presence of a water layer at the membrane/contact interface would facilitate spontaneous and undesired charge transfer between the two contacts, causing spurious ion fluxes and a degradation in the potentiometric response characteristics of the SC ISE. In addition, this gives rise to a reduced contact resistance between the SC and ISE membrane, manifesting itself as the observed diminution in the bulk membrane-contact resistance of the SC ISE.

Despite extensive previous research on SC ISEs, the critical physicochemical factors controlling the behavior of these sensors are not yet fully understood. For example, an unoxidized drop-cast conductive polymer SC sensor without redox buffering ability can obviate the water layer and associated sensor drift, while electropolymerization of the conducting polymer SC will produce a spurious water layer in the presence of certain background electrolytes [15, 18], but not in the presence of others. Conversely, a drop-cast SC polymeric film with a high degree of hydrophobicity, as reflected by its contact angle with water, will not show any potentiometric response characteristics commensurate with the formation of a water layer, but will sometimes display inferior stability, selectivity, and detection limit, presumably due to the presence of physical imperfections such as pores and pinholes in the SC film [18] that can accommodate local pools of water. Henceforth, the production of robust, stable, and reliable SC ISEs is presently a “hit or miss” technology.

In this work, the authors have aspired to develop high-quality poly(3-octylthiophene) (POT) SC ISEs, and to

optimize the SCs for superior sensor performance. Significantly, POT was chosen in this study as it has proven to be an excellent SC yielding nanomolar detection limits with SC ISEs for a variety of ions [19], noting that the seminal work of Bobacka et al. [20] demonstrated that POT provides a highly stable ion-to-electron transduction process, and that POT’s hydrophobic nature ameliorates the formation of detrimental water layers at the SC/ISE membrane buried interface (De Marco et al. 2008, submitted for publication). Since the drop casting of POT SCs has proven to be a “hit or miss” technique, we have focused on spin casting and electropolymerization as methods of synthesizing high-quality and high integrity SC ISEs. To ascertain the chemical integrity of the POT SCs, we have undertaken surface analyses of the SCs using X-ray photoelectron spectrometry (XPS) and secondary ion mass spectrometry (SIMS), while the physical integrity of the films, as evidenced by an absence of pores and pinholes in the POT SCs, has been studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Finally, the electrochemical robustness and stability of SC ISEs has been investigated using electrochemical impedance spectroscopy (EIS).

Materials and methods

Materials

High molecular weight poly(vinylchloride), dioctyl sebacate (DOS), Ca ionophore IV, and sodium tetraphenylborate (NaTPB) were Selectophore[®] reagents obtained from Fluka. Anhydrous lithium perchlorate, anhydrous propylene carbonate, 3-octylthiophene, regioregular poly(3-octylthiophene-2,5-diyl) (POT), and inhibitor-free tetrahydrofuran (THF, 99.8%) were obtained from Sigma-Aldrich. Analytical grade chloroform was obtained from Selby, while xylene was obtained from Chem Supply. Analytical grade anhydrous CaCl₂ and Ca(NO₃)₂ were obtained from Merck and the Ajax Chemical Co., respectively, and Milli-Q water was used in the preparation of all aqueous solutions.

The dichloromethane, analytical grade nitric acid, laboratory grade acetone, and ethanol used as washing agents were obtained from Chem Supply, Ajax Chemical Co., APS Chemicals, and CSR Distilleries, respectively.

Two types of substrates were used in this project—gold substrates (individual electrodes, and electrodes embedded in resin) and polished silicon wafers. The individual gold electrodes had dimensions of 0.5 cm×1.0 cm, and were used in ex-situ SIMS surface analyses of POT SCs. The electrodes used in the electropolymerization of POT were made of gold (area=0.5 cm×1.0 cm) possessing a backside silver epoxy contact, and the entire assembly was embedded

in epoxy resin. The electrodes used in spin casting of POT films consisted of gold discs (1.5 cm in diameter) attached to a steel substrate using a silver epoxy solid contact, and the entire assembly was embedded in epoxy resin.

The pre-polished silicon wafers comprising squares with dimensions of 10×10 mm and a nanometer scale smoothness were used in the AFM studies, and were sourced from University Wafer (1" single side polished, Mech Grade).

Preparation of polymer ISE membranes

Solutions

The calcium-selective PVC solutions were made by dissolving high molecular weight PVC (32.5 wt%), DOS (65.9 wt%), Ca Ionophore IV (1 wt%), and NaTPB (0.6 wt%) in inhibitor-free THF (2 ml per 200 mg of membrane). The solutions were thoroughly mixed and degassed by placing sealed vials of the solution in an ultrasonic bath for 5 min.

POT solutions in either xylene or chloroform (0.25 mM) for drop casting and spin casting were made by dissolving POT in an appropriate volume of solvent. Sealed vials of the solutions were placed in an ultrasonic bath for 5 min to enhance the dissolution of the POT flakes and to degas the POT stock solutions.

The 0.1 M LiClO_4 /0.2 M 3-octylthiophene in propylene carbonate electrolyte used in the electropolymerization of POT was prepared by dissolving LiClO_4 and 3-octylthiophene in the propylene carbonate solvent. The resultant solution was shaken well and allowed to stand overnight to ensure the complete dissolution of LiClO_4 and 3-octylthiophene.

Surface preparation of electrode substrates

In order to characterize the surface morphology of the thin POT SC films, it was essential to ensure that the substrate on which the film was cast or grown was both clean and relatively flat, so that any measurements made would truly reflect the state of the film.

The gold substrates were polished using 4,000 grit SiC paper (Struers™) mounted on a polishing wheel and lubricated using a continuous flow of water to remove any visible surface scratches. Prior to use, the gold substrates were polished using a Struers™ diamond polishing spray (1 μm particles) applied to a felt pad mounted on a polishing wheel, and lubricated using Struers™ red lubricant. The polished gold substrates were rinsed with dichloromethane, followed by a series of solvents (2 min per solvent in an ultrasonic bath) in acetone, ethanol, de-ionized water, 10^{-4} M nitric acid, and Milli-Q water. This rigorous cleaning program removed as many surface contaminants as possible including those introduced by the polishing procedure.

The pre-polished silicon wafers were prepared by bathing in ethanol (1 h in an ultrasonic bath), Milli-Q water (1 h in an ultrasonic bath) prior to placement in an ozone cleaner (30 min per side).

Preparation of POT SCs

Drop-cast, spin-cast, and electropolymerized POT films were prepared as described below. Coated specimens were also annealed in a N_2 environment at about 70 °C for an hour for comparison with the as-prepared films.

Spin-cast films were obtained by seven applications of 0.25-mM POT solution onto the desired substrate. Each application was designed to deliver the equivalent of $4/\pi$ μl of polymer solution per square millimeter of substrate. This volume-to-area ratio was chosen partly because it corresponds to that used in a previous study undertaken in our laboratory (typical applications are 100 μl of 0.25 mM polymer solution to electrodes of 1 cm in diameter) [14], and also because the application of a significantly higher ratio tended to result in the solution flowing over the edges of the substrate.

Spin-cast films were fabricated using a Laurell Technologies WS-400B spin coater. The POT solutions were cast onto the substrate and spun for 30 s and allowed to stand for 30 s prior to the next application of POT. Following SIMS depth profiling (to be discussed later), it was decided that subsequent AFM, SEM, and EIS evaluation of solution-cast POT films should be based on POT films made from 0.25-mM POT in xylene as this combination yielded the best uniformity and thickness of all synthesized films. For the same reason, it was also decided that subsequent spin casting of the POT films should be undertaken at 5,000 rpm for 30 s per application, allowing 30 s between applications to ensure drying of the spin-cast film.

Electrodeposition of POT was carried out under galvanostatic conditions from the propylene carbonate solution of 0.2 M 3-octylthiophene/0.1 M LiClO_4 [21]. With this procedure [21], the POT films were formed on a gold working electrode using a current density of 4 mA cm^{-2} . The counter electrode was a platinum mesh electrode, and the reference electrode was an Ag/AgCl double junction electrode (Orion) whose outer filling solution was replaced with the propylene carbonate electrolyte solution. The overall charge passed through the electrode was limited to 100 mC cm^{-2} . The electropolymerization was carried out using a Princeton Applied Research PARSTAT 2262 portable potentiostat.

The electropolymerized films were “purple-black” in color and appeared smooth and shiny. However, it was noted that the films did not adhere well to the gold electrodes and could only be rinsed by swirling them gently in a beaker of ethanol or water as even a low-pressure stream of solvent from a wash bottle would cause

dislodgement of the polymer film from the electrode surface.

SC-ISE fabrication

For the ISEs made with solution-cast POT films, PVC tubing was fitted around the electrode body prior to the casting of the POT and PVC membranes. The tubing was trimmed level with the electrode face, and then POT films were cast onto the electrode as detailed below. When the POT layers were dry, a suitable volume of ISE polymer solution (in accordance to the previously defined ratio of $4/\pi$ μl solution per square millimeter of substrate) was cast onto the electrode.

The ISEs with electropolymerized POT films did not have PVC tubing fitted around the electrode body due to the positioning of the electrode wires at the side of the epoxy disc. Again, a suitable volume of PVC/Ca ionophore solution was cast on top of the POT film, and care was taken to ensure that the entire electrode surface was covered with PVC ISE film.

EIS

Electrochemical impedance spectroscopy studies were undertaken on an EG & G Princeton Applied Research PARSTAT 2262 electrochemical impedance analyzer. All EIS spectra were collected using an excitation potential of 10 mV root mean square (rms) and a frequency range of 100 kHz to 1 mHz utilizing four-point data averaging statistics. Using a conventional three electrode cell, the EIS experiment was maintained at 20 ± 1 °C and contained a 0.1 M solution of CaCl_2 in all measurements. A Metrohm™ Au-tip ISE working electrode (used in drop-cast SC ISEs) or home-made gold disc electrode that was 1.5 cm in diameter (used in spin-cast SC ISEs), a platinum counter electrode, and a silver/silver chloride Orion™ double-junction reference electrode were used in the measurements.

Surface analysis

SIMS

SIMS analysis was undertaken at ANSTO using a Cameca IMS 5f instrument. A Cs^+ ion beam (beam current 200 nA; beam diameter 40 μm) was rastered over regions measuring 250×250 μm .

The electropolymerized POT films were rinsed in ethanol and Milli-Q water and allowed to dry prior to SIMS analysis. Five depth profiles were obtained from different regions of each specimen (four from the corners of the specimen and one from the centre). The signals corresponding to Au, C, S, Li, O, and Cl were recorded.

Two ISEs constructed with spin-cast POT (seven layers, 0.25 mM in xylene, 3,000 rpm) and PVC/Ca-ionophore membranes, and two electrodes with electrodeposited POT and PVC/Ca-ionophore membranes were also prepared. One of the spin-cast POT ISEs and one of the electrodeposited POT ISEs were treated overnight in 0.1 M CaCl_2 solution, and the other spin-cast POT ISE and electrodeposited POT ISE were treated overnight in 0.1 M $\text{Ca}(\text{NO}_3)_2$ solution. The treated electrodes were rinsed with Milli-Q water and dried in air, and the POT/ISE electrode was peeled from the gold substrate. Elemental analysis was carried out by sputtering through the POT layer to the PVC membrane to detect the formation of any salt residues at the POT/PVC interface. The signals corresponding to Au, C, S, Li, O, Cl, Ca, and N were recorded. The results were compared against those for the gold electrodes that had been coated with spin-cast and electrodeposited POT, but not treated in solution.

A sputter rate was calculated from the time taken to sputter through the electrodeposited POT film and by performing profilometry over the sputtered region (result not shown). The sputter rate for POT was calculated to be

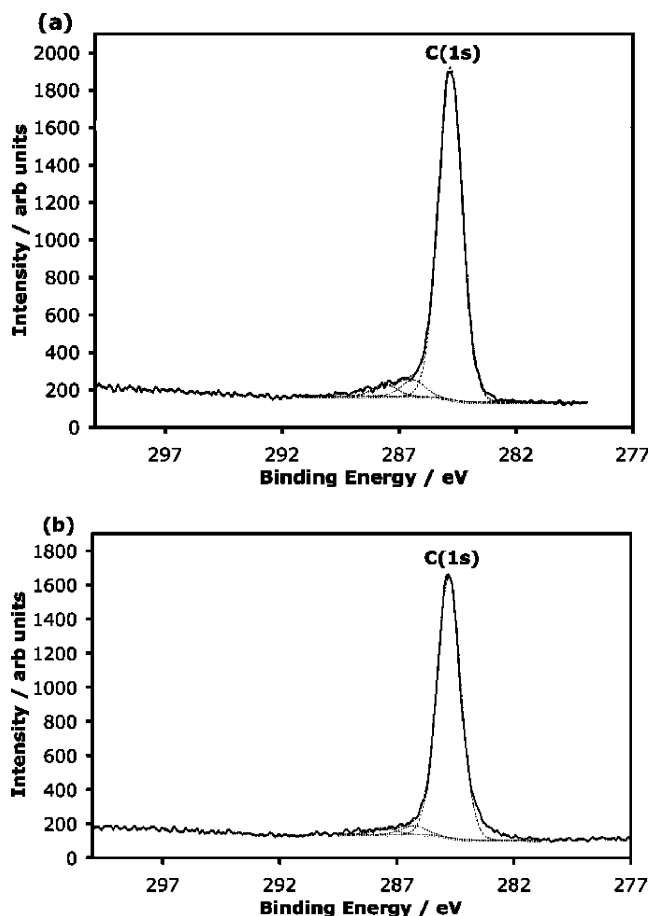


Fig. 1 XPS spectra of the C(1s) core atomic orbital for the following POT SC films: **a** solution cast; and **b** electropolymerized

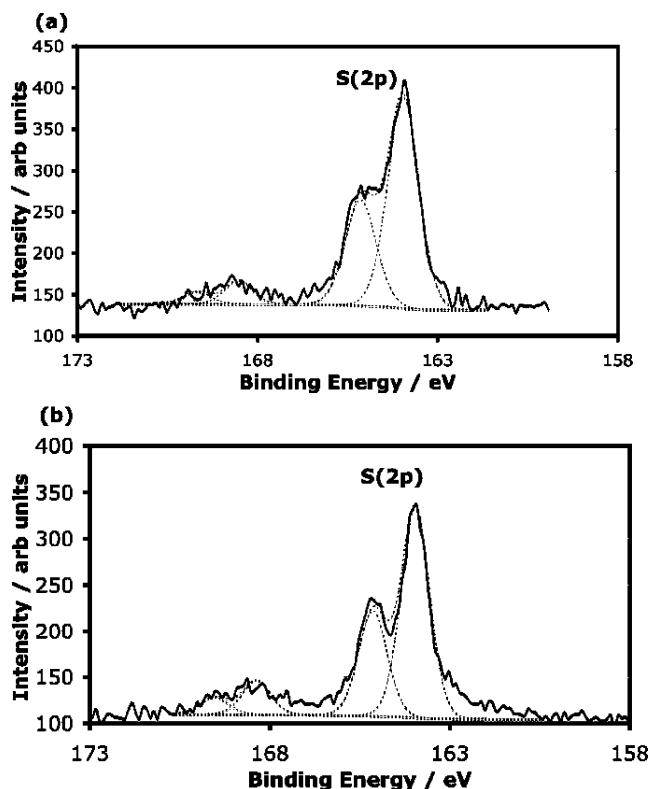


Fig. 2 XPS spectra of the S(2p) core atomic orbital for the following POT SC films: **a** solution cast; and **b** electropolymerized

6.49 nm/s for a beam current of 200 nA and a beam diameter of 40 μm .

AFM

The decision to prepare the spin-cast films for AFM examination onto silicon rather than gold wafers was made following the SIMS depth profiling work. It was found that the spin-cast POT films were approximately 40 nm thick, while AFM studies of a cleaned and polished gold electrode indicated that the gold substrates had uneven surfaces, with an estimated rms roughness of over 10 nm. It was deemed inappropriate to investigate the morphology of a film that was cast onto a substrate that had topographical variations that are comparable to the film thickness. Accordingly, polished silicon was used as the substrate in this AFM study since it is both stable to relatively high temperatures and is topo-

graphically smooth (sub-nanometer roughness—see http://www.universitywafer.com/Wafers__Services/Silicon_on_Insulator_Wafers/silicon_on_insulator_wafers.html).

AFM measurements were carried out under ambient conditions in Tapping Mode™ on a Digital Instruments Dimension 3000 atomic force microscope. Post-measurement analysis of AFM images was undertaken using the Gwyddion software (see <http://gwyddion.net>).

SEM

The morphology of as-prepared and annealed POT films obtained by spin casting and electrodeposition was also examined and compared using SEM. POT films spin-cast onto Si wafers (both N₂-annealed and as prepared) and POT films electrodeposited onto gold electrodes (both N₂-annealed and as prepared), which had been previously examined by AFM, were used for comparison.

All specimens were carbon coated prior to analysis to eliminate sample charging effects. The films were examined under a 15-kV beam in a Philips XL-30 SEM with EDAX capabilities.

XPS

Ex-situ XPS surface analysis of electrodes was conducted on samples rinsed with Milli-Q water and allowed to dry in air. XPS analysis on the films was undertaken using a Kratos AXIS Ultra DLD spectrometer housed at the University of South Australia. The samples were analyzed using monochromatic Al K α radiation (13 kV, 10 mA), noting that survey spectra were collected over an energy range of 0–1,100 eV using a pass energy of 160 eV and a step size of 0.5 eV, while high-resolution spectra were collected with a pass energy of 20 eV and a step size of 0.1 eV. The analyzer chamber was $<10^{-9}$ hPa during surface analyses.

Results and discussion

This research has utilized a multi-technique surface analysis approach to evaluate the physical, chemical, and electrochemical integrity of SC ISEs using several state-of-the-art

Table 1 XPS binding energies (eV) of POT solid-contacts prepared using solution casting and electrodeposition techniques

Level	Solution cast	Solution cast + ion etching	Electrodeposited	Electrodeposited + ion etching
C(1s)	284.8; 286.4; 287.6	284.7; 286.0; 287.5	284.8; 286.3; 287.6	284.8; 286.2; 287.4
O(1s)	530.9	n.d.	530.4	531.2
S(2p _{3/2})	164.0; 168.5	163.5	164.0; 168.4	163.5
S(2p _{1/2})	165.1; 169.7	164.9	165.2; 169.6	164.7

Table 2 Average thicknesses (t_{ave}) and standard deviations (SD) of POT SC films measured using SIMS depth profiling at 5 different locations utilizing either a spin casting method at different rotations speeds, a spin

casting method as a function of the POT concentration at a fixed rotation speed, a spin casting method with a chloroform or xylene solvent at a fixed rotation speed, or an electropolymerization technique

Spin-casting parameter	[POT] (mM)	Solvent	Rotation speed (rpm)	t_{ave} (nm)	SD (nm)
Solvent	0.25	Chloroform	3,000	16.1	2.7
	0.25	Xylene	3,000	8.9	0.9
Rotation speed	0.25	Xylene	500	10.7	6.9
	0.25	Xylene	1,000	14.3	4.7
	0.25	Xylene	3,000	8.9	0.9
	0.25	Xylene	5,000	41.3	1.9
[POT]	0.15	Xylene	3,000	9.5	0.8
	0.25	Xylene	3,000	8.9	0.9
	0.35	Xylene	3,000	10.7	6.4
N/A (Electropolymerization)	0.2 M octyl thiophene in 0.1 M LiClO ₄	Propylene carbonate	N/A	7.7 μ m	1.2 μ m

techniques. First, EIS is a powerful electrode kinetic technique that provided in depth information about the dielectric properties of the SC sensors, particularly the influence of continuous layers and localized regions of water in pores and pin holes in the SCs, on the contact resistance at the SC/ion sensing membrane interface. Notably, previous work [14, 21] has shown that EIS is an excellent technique for detecting water layers in SC ISEs, as evidenced by a diminution in the contact resistance at the

SC/ISE membrane interface upon wetting of this region, and therefore provides a simple and affordable methodology for screening of the integrity and quality of the SC ISEs. Next, ex-situ XPS and SIMS provided complementary surface analysis data yielding insights into the influence of the chemical and physical factors that control the behavior of all SC polymeric ISEs. Note that XPS has an excellent power for structure elucidation in the outer 1–10 nm of the sample for elements above 1 at.%, while SIMS used ion etching and

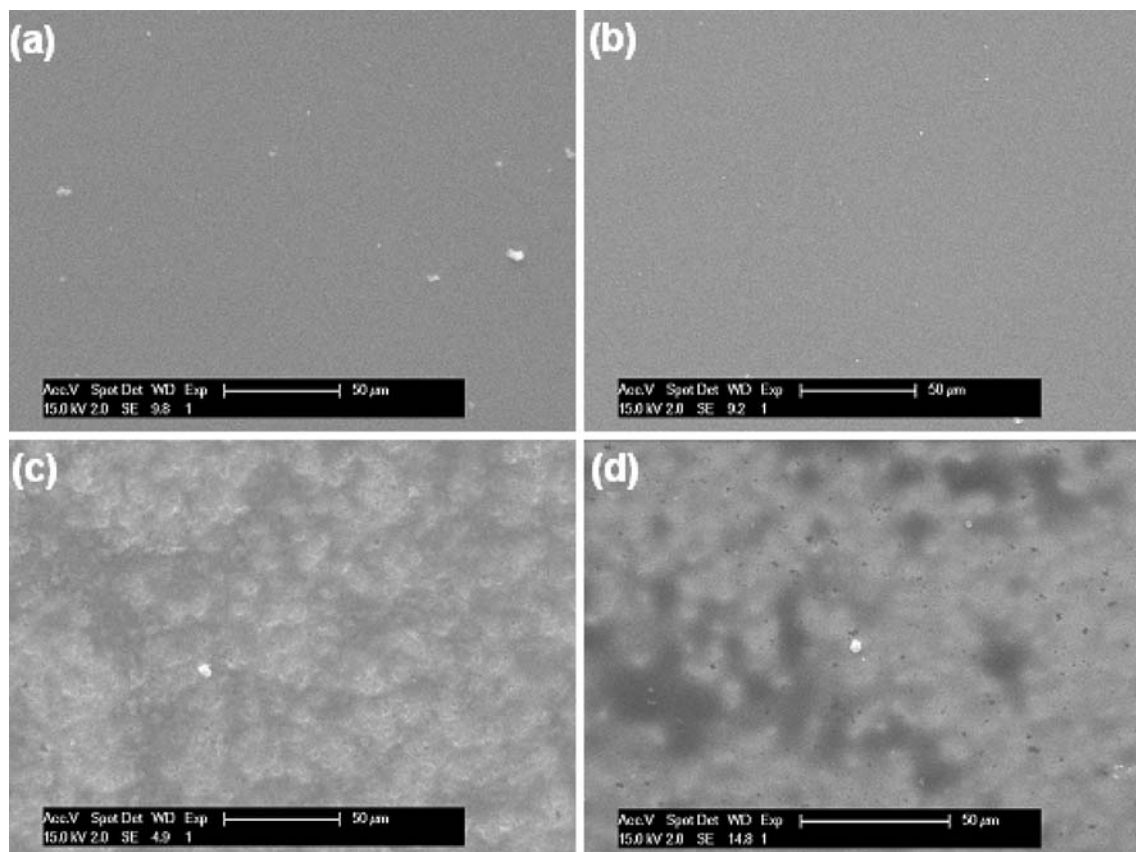


Fig. 3 SEM micrographs of the following POT SC films: **a** spin-cast (as prepared); **b** spin-cast and annealed at 70 °C; **c** electropolymerized (as prepared); **d** electropolymerized and annealed at 70 °C

mass spectrometry to detect subatomic percentages of dopant species in the 1- to 100-nm depth range. Last, SEM and AFM enabled a high-resolution imaging of the topography of the solid contacts in all solid-state polymeric ISEs, noting that SEM can provide a spatial resolution in the submicron range, while AFM was used to provide a nanoscale spatial resolution.

XPS analysis

Figure 1a and b presents the C(1s) XPS spectra for the native surfaces of solution cast and electropolymerized POT films, respectively, while Fig. 2a and b shows the corresponding S(2p) XPS spectra for the same surfaces. Furthermore, the XPS binding energies of the corresponding core atomic orbitals are presented in Table 1.

In both cases, the C(1s) spectra revealed a major peak at about 284.6 eV that is ascribable to C in hydrocarbons [22], while the small high-binding energy shoulders at approximately 286.4 and 287.6 eV may be attributed to C in C–S

and C=S functionalities [22], which is expected for poly(3-octylthiophene) or POT.

Similarly, the S(2p) spectra in both cases showed a pair of S(2p_{3/2}) and S(2p_{1/2}) spin-orbit split components corresponding to S in thiophene (viz., at 164 and 165.1 eV) as well as S in sulfone (viz., at 168.5 and 169.7 eV) [22]; the minor sulfone species (a few percent of the overall S(2p) intensity) symbolizes that this is a minor component of the sulfur surface species. Moreover, the similarity in intensities for the sulfone species on both the solution cast and electropolymerized surfaces (compare Fig. 2a and b) is symbolic of the partial aerial oxidation of POT to sulfone, not the electrochemical oxidation of POT to highly degraded and structurally defective sulfone-based films [21]. This hypothesis is supported by the observation that both POT surfaces, when subjected to a short burst of argon ion etching to remove the native surface film, were completely free of the oxidized or sulfone S(2p) XPS peaks (see Table 1).

An equally important XPS result for the electropolymerized POT was the absence of any carbonate functionalities in

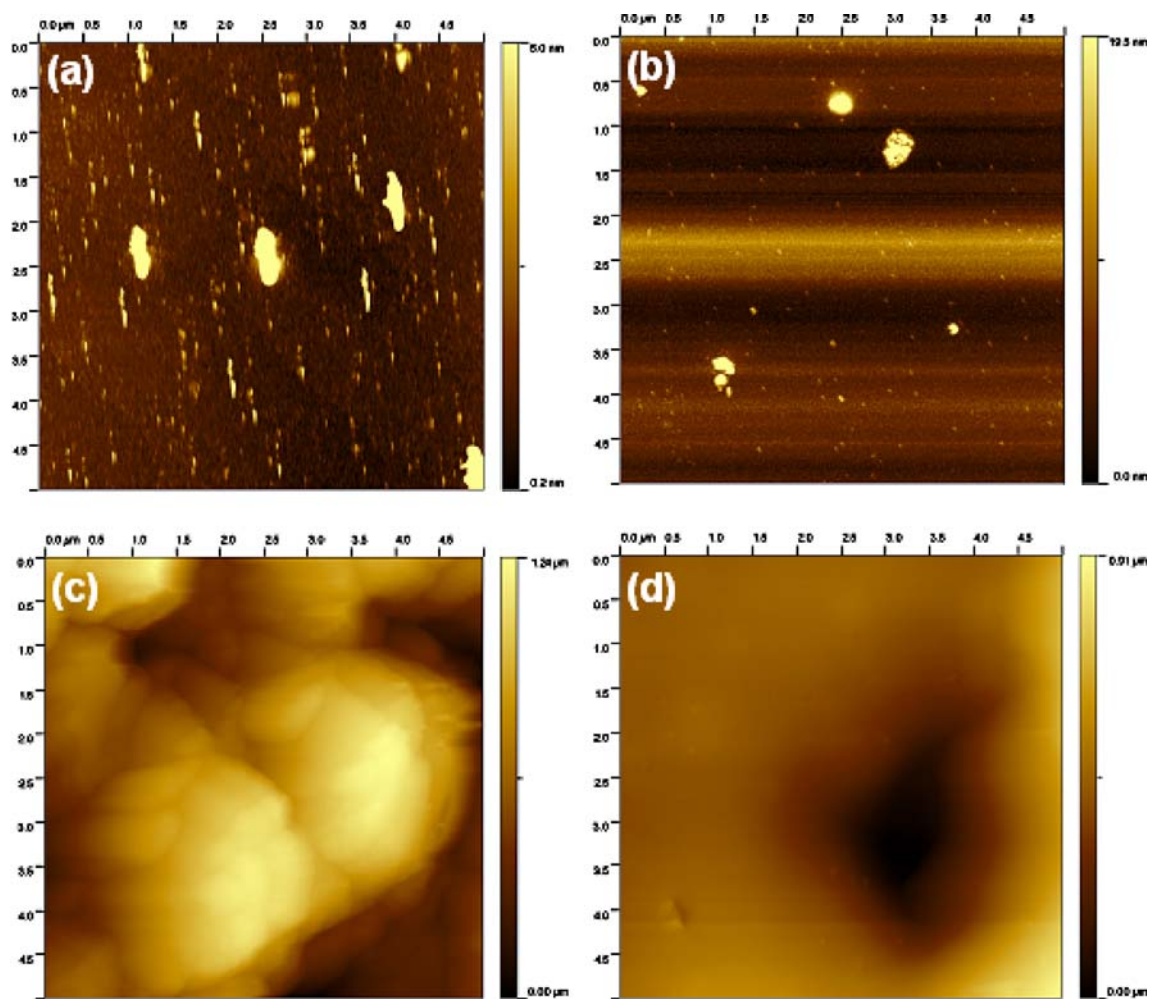


Fig. 4 AFM Tapping Mode micrographs of the following POT SC films: **a** spin-cast (as prepared); **b** spin-cast and annealed at 70 °C; **c** electropolymerized (as prepared); **d** electropolymerized and annealed at 70 °C

the C(1s) XPS spectra, as well as the absence of Li and Cl at the POT surface, either before or after argon ion sputtering. This result verifies that there has been no carryover of electrolyte into the electropolymerized POT SC.

The aforementioned XPS results demonstrate that it is possible to prepare unoxidized and chemically stable POT films using either a solution casting (drop or spin casting) or electropolymerization technique. This has important ramifications for sensor miniaturization, showing it is possible to either solution cast or electrodeposit chemically stable POT onto a microelectrode substrate.

SIMS analysis

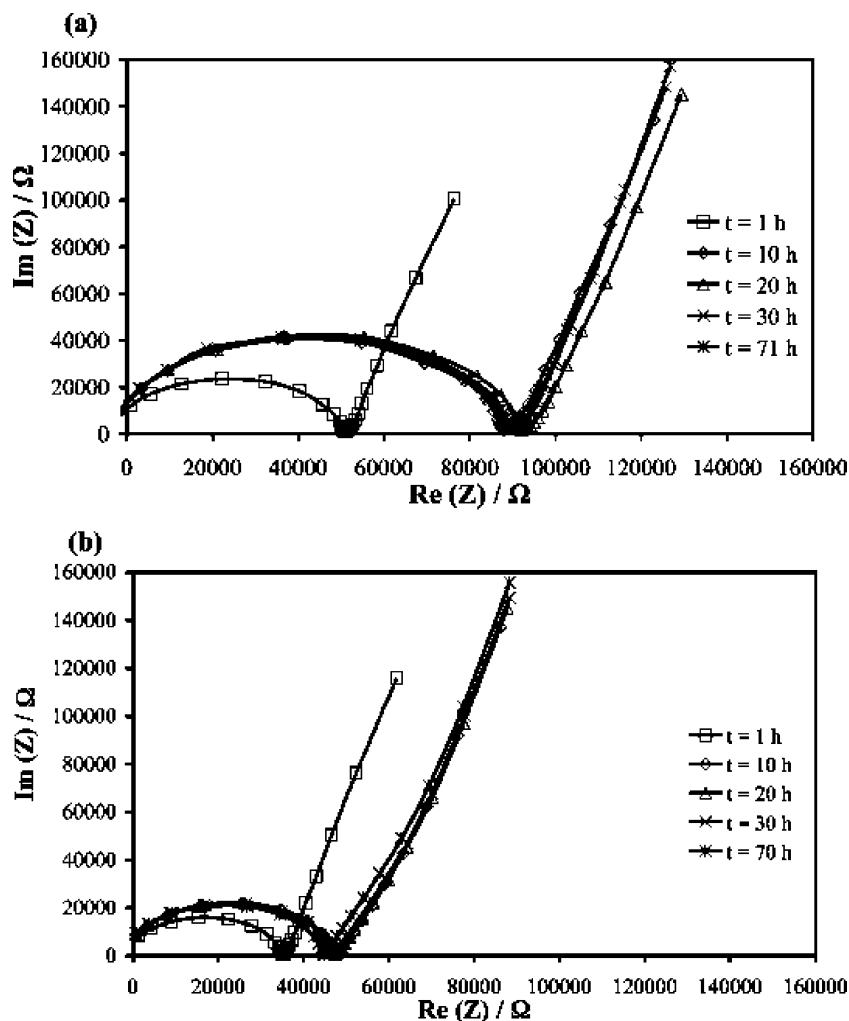
Depth profiling was carried out on electropolymerized POT films and POT films that had been spin-cast onto gold electrodes using a range of solution concentrations (0.15–0.35 mM), solvents (chloroform and xylene) and rotation speeds (500–5,000 rpm). Five depth profiles were obtained from different regions on each specimen (four from the corners and one in the centre of each specimen). The MCs^+

signals corresponding to $M = Au, C,$ and S were used to monitor the thickness of the POT films, and the corresponding film thicknesses (t_{ave}) and standard deviations (SD) are summarized in Table 2.

The depth profiling measurements indicated that the thickest and most even film was prepared by spin casting at 5,000 rpm from 0.25 mM POT in xylene. Films cast at lower rotation speeds tended to be relatively uneven, and prior to SIMS analysis, it was evident to the naked eye that the spin-cast film at 500 rpm was concave (as evidenced by the POT purple coloration on the outer portions of the electrode, and a clear and transparent film at the inner part of the electrode). Although the POT film cast from the chloroform solution gave a thicker film compared to one cast from the xylene solution, the relative variation in film thickness was reduced with the xylene spin-cast film. This was ascribed to the slower evaporation rate of xylene, allowing the films to grow more slowly and evenly on the substrate during the flash evaporation of the solvent while spin casting.

The electropolymerized POT film prepared with the chronopotentiometric method used in this study (see the

Fig. 5 EIS Nyquist plots for drop-cast POT SC ISEs using either **a** drop-cast POT (as prepared) or **b** drop-cast POT after annealing



“Materials and methods” section titled Preparation of POT SCs) was considerably thicker than the nanoscale spin-cast POT films (compare tens of nanometers with 7.7 μm), but the electropolymerized films provided a similar uniformity in thickness (expressed as a relative SD of approximately 10–15%) compared to the spin-cast films. Nevertheless, it is possible to prepare a thinner film by reducing the current as well as the rate of mass transfer of 3-octylthiophene to the electrode surface using a rotating disc electrode [20]. Although this aspect was investigated in a brief and exploratory way in the present study, the alternate POT films were either of a similar or inferior physical integrity to the present films, so a surface study of the films prepared in this study was deemed appropriate.

In summary, SIMS data suggest that physically robust films that are relatively free of pores and pinholes may be prepared at a rotation speed of 5,000 rpm using a 0.25-mM solution of POT in xylene, and it appears that electro-deposited films are also suitable for use in SC ISEs.

It is significant to note that a comparison of SIMS depth profiles for membranes peeled away from the gold substrate

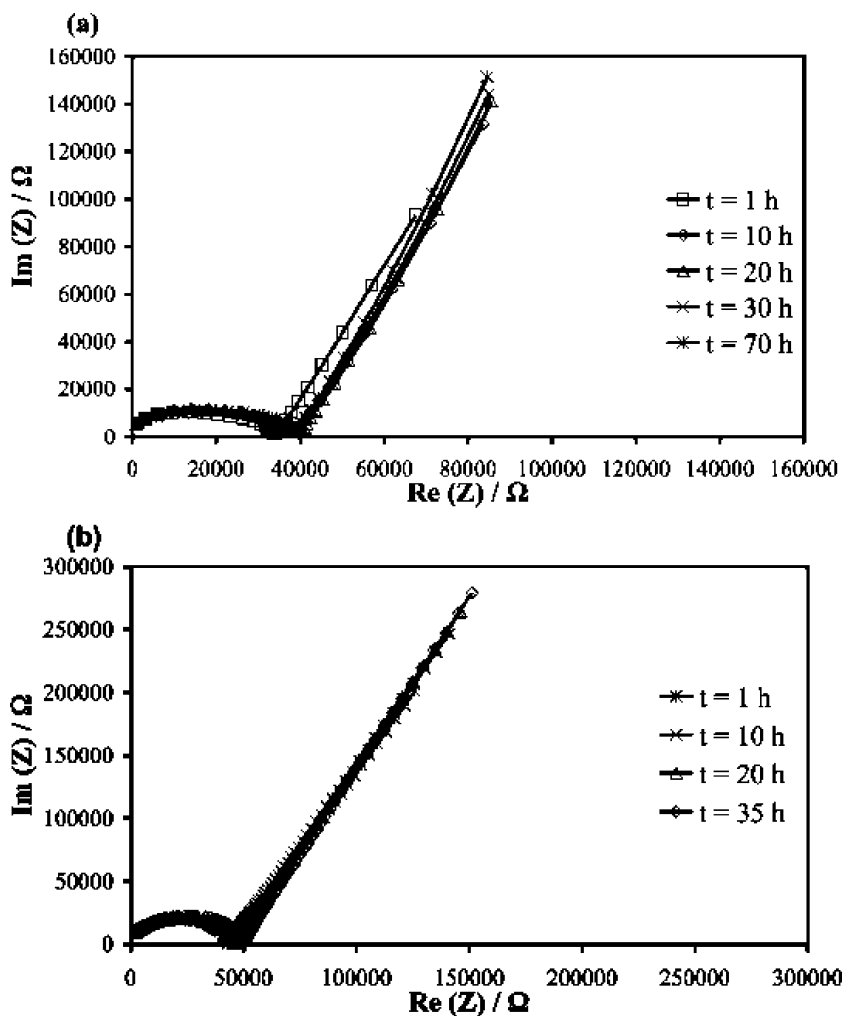
and etched from the conductive POT contact to the insulating PVC membrane interface (results not shown) in both untreated samples and those exposed to 0.1 M CaCl_2 and 0.1 M $\text{Ca}(\text{NO}_3)_2$ for 24 h failed to detect a surplus of Ca, Cl, and N ion signals at the POT/ISE membrane boundary, as should occur and was observed recently [14] if a water layer formed in a coated-wire electrode. This demonstrates that spin-cast and electropolymerized POT SCs are capable of resisting the formation of undesirable water layers in SC ISEs.

SEM and AFM examination

Figure 3a to b presents SEM micrographs for Si surfaces that had been spin-coated with POT using the aforementioned optimal conditions before (a) and after (b) annealing in a nitrogen atmosphere at 70°C for 1 h, while Fig. 3c and d present the corresponding SEM images of electropolymerized POT on a gold substrate electrode.

It is evident in the SEM results that the spin-cast film is relatively smooth and defect-free, with annealing generally smoothing any island inclusions in the film, while the

Fig. 6 EIS Nyquist plots for spin-cast POT SC ISEs using either a spin-cast POT (as prepared) or (b) spin-cast POT after annealing

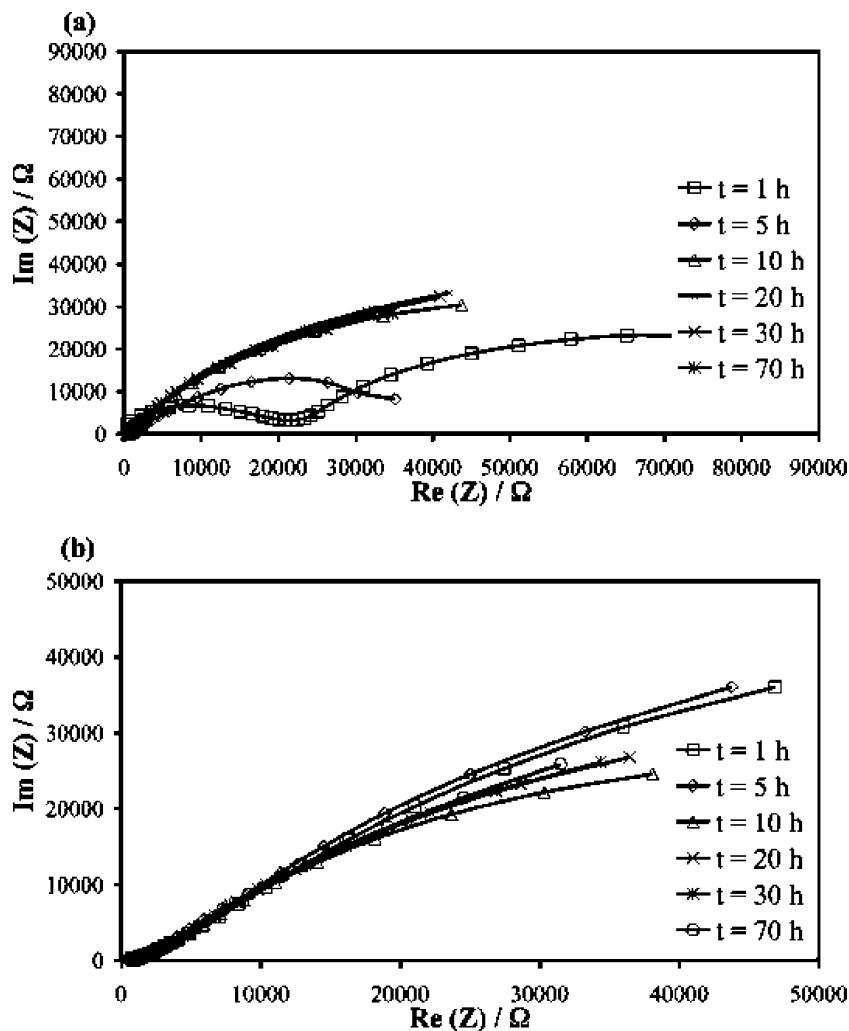


electropolymerized POT film is rough on the micron scale, showing signs of porosity, particularly with the annealed film.

Since AFM is capable of providing a nanoscale resolution for the topography of the POT films, we also undertook Tapping Mode™ AFM imaging of the spin-cast (see Fig. 4a and b) and electropolymerized (see Fig. 4c and d) films. Again, spin casting yielded smoother and more uniform films, while electropolymerization formed a highly porous SC on the nanoscale, but its localized porosity diminished significantly upon annealing at 70 °C.

Significantly, AFM determinations of the rms roughness of the synthesized POT SCs showed that the spin-cast films were relatively flat before and after annealing (viz., rms roughness of 2.8 to 2.3 nm), while the straight electropolymerized films were extremely rough (viz., rms roughness of 270 nm) but smoothed considerably upon annealing (viz., rms roughness of 24 nm). Notwithstanding, the electropolymerized and annealed film is still relatively rough, and is therefore susceptible to the formation of pores and pinholes that might act as repositories for water droplets at the SC/ISE membrane interface.

Fig. 7 EIS Nyquist plots for electropolymerized POT SC ISEs using either **a** electropolymerized POT (as prepared) or **b** electropolymerized POT after annealing



It must be noted that the formation of water droplets at the SC/ISE membrane-buried interface is expected to produce localized repositories of ions (on the nano-to-microscale) that may avoid detection in SIMS depth profiling of $250 \times 250 \mu\text{m}$ raster areas, as was observed in a recent study of a methyl methacrylate/decyl methacrylate copolymer ISE on a gold substrate (De Marco et al. 2008, submitted for publication). Accordingly, a non-detection of a water layer by SIMS does not exclude the possibility of localized repositories of water and ions.

EIS studies

Previous EIS research [14, 21] has shown that a poor SC ISE displays a contact resistance at the SC/membrane interface that, when wetted by water and electrolyte, reveals a diminution in the composite of the bulk membrane-contact resistance as the water layer is established. Accordingly, EIS provides a sensitive electrochemical technique for probing the water layers in SC ISEs since, even if localized repositories of water are formed at pores

and pinholes, it may be detected by this technique [14], whereas alternative methods such as potentiometry involve the measurement of an average phase boundary potential that cannot sensitively detect such a localized event.

Figure 5a and b presents EIS Nyquist plots for a drop-cast POT SC Ca ISE on continuous exposure to 0.1 M CaCl_2 for (a) as prepared POT and (b) annealed POT films, and the high frequency bulk membrane-contact resistance (small semi-circle on the left-hand side) showed the usual increase in impedance on exposure to solution (De Marco et al. 2008, submitted for publication), but it did not reveal a statistically significant diminution in resistance (i.e., $>\pm 5\%$ relative or the EIS uncertainty) on continuous exposure to electrolyte (after 10 h) symbolizing that the drop-cast POT SC had prevented the formation of a deleterious water layer at the SC/ISE membrane interface.

Similarly, Fig. 6a and b for a spin-cast film without (a) and with (b) annealing showed a relative absence of a water layer, as evidenced by the stability in the bulk membrane-contact resistance once the electrode had equilibrated with water after approximately 10 h.

Last, the electropolymerized POT SC Ca ISE (see Fig. 7a and b) showed a similar behavior to the drop-cast and spin-cast films (i.e., the impedance response stabilized after equilibration in the electrolyte after 10 h); however, the membrane-contact resistance, charge transfer resistance, and Warburg resistance time constants had all merged into one with this system, presumably due to an additional time constant for the POT SC arising from its extreme thickness (about 8 μm) compared to drop-cast and spin-cast POT SCs (tens of nanometers in thickness), but equivalent circuit modeling to deconvolute this complex data (not shown) inferred that the bulk membrane-contact resistance had apparently stabilized after about 10 h of exposure to the electrolyte.

Previous research using neutron reflectometry [14, 21] demonstrated an interfacial amalgamation of the POT SC with the PVC ISE membrane due to dissolution and diffusion of POT into the PVC membrane during the solvent casting of the ISE. Accordingly, it is likely that this POT/PVC amalgam will fill the pores and pinholes in the electropolymerized POT SC (as observed using SEM and AFM), providing an ability to ameliorate against water layer formation. Nevertheless, it is the authors' view that these physical imperfections will compromise significantly the strength of the adhesive bond at the metal/POT/PVC interface, and this will allow the formation of detrimental localized water droplets on continuous use in solution.

In summary, it is evident that stable POT SC ISEs can be prepared using either a drop-casting, spin-casting or electropolymerization technique in the fabrication of the POT SC; however, the highest quality, both chemically and physically, POT SCs are produced using an optimal spin casting technique. Accordingly, we recommend the use of a

spin-casting method in the preparation of the POT SC since a lack of imperfections in the assembled POT film (i.e., pores and pinholes) will prevent the deposition of localized regions of water at the SC/ISE membrane interface

Conclusions

The results of this study demonstrate that high-quality POT SCs, which are relatively free of physical imperfections such as pores and pinholes, may be prepared by employing a spin-casting technique in conjunction with film annealing in an inert atmosphere, and this approach may be used to circumvent the formation of an undesirable water layer at the SC/ISE interface. Despite the relatively high porosity and roughness of electropolymerized POT SCs, annealing reduces significantly the porosity of these films, and EIS has shown that these films are electrochemically stable and may also be used in the fabrication of good SC ISEs. Either way, this research has important ramifications for SC ISEs; it is possible to prepare robust and stable SC ISEs that are free from the usual degradation in analytical performance (i.e., selectivity and sensitivity) associated with the spurious and uncontrollable ion fluxes encountered when a water layer is present at the SC/ISE interface.

It is also evident that a combination of surface analysis (i.e., XPS, SIMS, SEM, and AFM) and electrochemical (i.e., EIS) techniques provides a powerful research methodology for the characterization of SC ISEs. Accordingly, this research strategy may be used in the future development of optimal methods for the preparation of functional SC ISEs.

Acknowledgments The authors acknowledge the financial support of the Australian Research Council (LX0454397 and DP0665400), Australian Institute of Nuclear Science and Engineering, National Institutes of Health (EB002189) and Swiss National Foundation. We also thank Mr. Armand Atanacio at ANSTO for assistance with the SIMS research, and Mr. Chris Bassell at the University of South Australia for assistance with the XPS analyses.

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