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Synchrotron Radiation/Fourier Transform-Infrared Microspectroscopy Study of Undesirable Water Inclusions in Solid-Contact Polymeric Ion-Selective Electrodes

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This paper reports on three-dimensional synchrotron radiation/Fourier transform-infrared microspectroscopy (SR/FT-IRM) imaging studies of water inclusions at the buried interface of solid-contact-ion-selective electrodes (SC-ISEs). It is our intention to describe a nondestructive method that may be used in surface studies of the buried interfaces of materials, especially multilayers of polymers. Herein, we demonstrate the power of SR/FT-IRM for studying water inclusions at the buried interfaces of SC-ISEs. A poly(methyl methacrylate)–poly(decyl methacrylate) [PMMA–PDMA] copolymer revealed the presence of micrometer sized inclusions of water at the gold/membrane interface, while a coupling of a hydrophobic solid contact of poly(3-octylthiophene 2,5-diyl) (POT) prevented the accumulation of water at the buried interface. A similar study with a poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) [PEDOT/PSS] solid contact also revealed an absence of distinct micrometer-sized pools of water; however, there were signs of absorption of water accompanied by swelling of the PEDOT/PSS underlayer, and these membrane zones are enriched with respect to water.

Robust miniaturized ion-selective electrodes (ISEs) are of high significance in modern analytical and clinical chemistry.^{1–3} To achieve the required potential stability, miniaturized hydrogel-based liquid contacts are used between the sensing membrane and the inner electrode.^{1,3} This complicated design requires complex manufacturing steps and long conditioning periods in order to rehydrate the inner layer. Consequently, ISEs without such a liquid layer [i.e., with an inner solid contact (SC)] are highly desirable. Since their inferior potential stability can pose a problem

with SC-ISEs, a considerable amount of research has been undertaken to characterize the interfacial region of these devices.^{2,4–6}

Detrimental to the stability of SC-ISEs is the formation of a water layer at the buried interface of the electrode substrate/ion selective membrane.^{7–10} A water film often results in drifting ISE potentials by acting as a reservoir for electrochemically active or pH altering species such as H₂O, O₂, and CO₂ along with ionic species transported across the membrane.^{2,7,11} In a previous study, a combination of surface analysis tools was used in the elucidation⁷ and elimination⁴ of the detrimental water layer in SC-ISEs. These studies demonstrated that a system incorporating a poly(vinyl chloride) (PVC) ion-sensing membrane in direct contact with an inert metal was susceptible to the formation of a continuous water layer.⁷ Likewise, a water-repellent poly(methyl methacrylate)–poly(decyl methacrylate) (PMMA–PDMA) copolymer ion-sensing membrane resulted in water “pooling” at the buried interface on the inert metal substrate, most likely in areas surrounding physical imperfections.⁴ Most significantly, the adoption of a PMMA–PDMA copolymer together with a hydrophobic poly(3-octylthiophene 2,5-diyl) (POT) solid contact as the ion-to-electron-transducer provided an excellent strategy for eliminating the detrimental water layer.^{4,12,13}

Previous studies^{4,7} used surface analysis techniques such as neutron reflectometry (NR), scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS) to identify localized

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zones of water at the PMMA–PDMA/metal interface; however, this evidence is inferred through the apparent interfacial roughening in the NR data, along with the fact that the SEM and SIMS studies were conducted on metal coupons after scraping the strongly adhered PMMA–PDMA film away from the electrode substrate, which in all likelihood destroyed the buried interface. Consequently, a direct and nondestructive surface analysis method that identifies water at the buried interface is required for the reliable characterization of this system.

This paper introduces synchrotron radiation/Fourier transform-infrared microspectroscopy (SR/FT-IRM) as a method for visualizing the existence of localized water at the buried interface of PMMA–PDMA SC-ISEs. IRM is a microanalytical and imaging technique which achieves analytical contrast via the intramolecular vibrational modes.¹⁴ Highly focused SR in the IR region of the electromagnetic spectrum is about 1000 times brighter than a conventional laboratory source and is capable of providing considerably enhanced signal-to-noise ratios,¹⁴ as well as an enhanced spatial resolution when considering micrometer-sized fluid inclusions.¹⁵ The study of inclusions via SR/FT-IRM is a well established technique that is often applied to studies of fluid inclusions in minerals, particularly as a means of identifying rock samples as potential oil sources.^{14,15} Hence, previous research was performed with great success providing both structural information and unequivocal evidence for the existence of fluid inclusions¹⁵ using this nondestructive method. On this basis, SR/FT-IRM has been chosen for this study since it is a powerful technique for the location of chemical and physical heterogeneities in materials, as well as determinations of their association with localized inclusions. Hence, this study should have important implications in the field of materials science; since SR/FT-IRM has the potential to glean important insights into the water distribution of hydrogels and new gel-based materials, it will allow the location of organic inclusions such as proteins in natural biomaterials as a means to understanding the physical and mechanical properties of these unique materials, and it will enable a probing of fluid permeation in important porous natural materials such as zeolites, etc. Accordingly, it is anticipated that SR/FT-IRM will be an excellent method for identifying localized zones of water at the buried interface of SC ISEs, as well as any localized differences in the IR spectra accompanying the polymer and/or metallic substrate.

EXPERIMENTAL DETAILS

Herein, a similar study to the previous ex situ SIMS experiment on PMMA/PDMA⁴ entailing exposure to solution for an extended period of time (500 h) was performed on ISE membranes; with the exception that a much thinner membrane (10 μm) was used to enable faster water transportation, this polymer film was not peeled to reveal the buried interface, with reflectance SR/FT-IRM measurements undertaken on the unperturbed thin film immediately following exposure to solution. All measurements were performed after blotting the treated membranes on tissue to remove excess surface water or dry the membranes. Importantly, the gold surfaces were prepared using standard methods for the

fabrication of conventional SC-ISEs. As compared to the previous ex situ SIMS study, SR/FT-IRM allows a study of the ISE buried interface without inducing physical damage in both the membrane and the interfacial region between the membrane and the electrode substrate.

Reagents. Calcium ionophore IV or *N,N*-dicyclohexyl-*N',N'*-dioctadecyl-3-oxapentanediamide, sodium tetrakis [3,5-bis(trifluoromethyl) phenyl] borate (NaTFPB) (Selectophore), and regioregular poly(3-octylthiophene 2,5-diyl) (POT) as well as high conductivity grade poly (3,4-ethylenedioxythiophene)/poly (styrenesulfonate) (PEDOT/PSS) were obtained from Sigma-Aldrich, Australia. Analytical grade reagent chloroform was sourced from Selby, while laboratory grade dichloromethane was obtained from Chem. Supply. The washing solvents of acetone and ethanol were laboratory grade and were obtained from APS chemicals and CSR Distilleries, respectively. Analytical grade nitric acid used in electrode washings was sourced from the Ajax Chemical Co. Analytical grade CaCl_2 was obtained from Merck. The monomers, methyl methacrylate, 99.5%, (MMA) and *n*-decyl methacrylate (DMA), 99%, were obtained from Polysciences, Inc. The polymerization initiator 2,2'-azobis(isobutyronitrile) (AIBN), 98%, was sourced from Sigma-Aldrich. Ethyl acetate and 1,4-dioxane used in the copolymer synthesis were reagent grade as sourced from Chem. Supply. Milli-Q water was used to prepare all aqueous solutions unless otherwise specified.

Gold Substrate Electrodes. Solid gold coupons (5 \times 10 \times 0.5 mm), obtained from Precious Metals Engineering Western Australia, were polished using alumina nanoparticles (0.01 μm in diameter) and copious quantities of water in conjunction with a rotating polishing pad. Polishing pads and alumina nanoparticles were all obtained from Metrohm. After polishing, the electrodes were rinsed with vast quantities of Milli-Q water and bathed for 5 min at a time, under sonication, in acetone, nitric acid (10⁻⁴ M), Milli-Q water, and finally dichloromethane. The electrodes were thoroughly rinsed with Milli-Q water and completely air-dried after each cleaning step. A hydrogen flame was used to anneal the gold surfaces, which were subsequently cooled in Milli-Q water.

Ion-Selective Electrode (ISE) Membrane and Solid Contact Preparation and Deposition. Synthesis of the poly methyl methacrylate/poly decyl methacrylate (PMMA/PDMA) copolymer was carried out using the method of Qin et al.¹⁶ A calcium selective copolymer cocktail was prepared by dissolving the PMMA–PDMA copolymer (97.7 wt %), calcium ionophore IV or *N,N*-dicyclohexyl-*N',N'*-dioctadecyl-3-oxapentanediamide (1.7 wt %), and NaTFPB (0.6 wt %) together in dichloromethane (1% w/v). The casting solution for POT was prepared by dissolving the polymer in chloroform (0.005% w/v). The commercially available PEDOT/PSS polymer was obtained as an aqueous suspension and was used as supplied.

Electrodes coated with a sole layer of PMMA–PDMA copolymer were prepared by casting the copolymer cocktail onto a gold substrate using a cocktail volume of 63 μL [this lower volume gave a thinner film (10 μm) that enabled mass transportation of water to the buried interface in the time frame of these experiments]. Following membrane deposition, the ISEs were annealed overnight at 80 $^\circ\text{C}$ in a nitrogen saturated environment. All

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electrodes utilizing conductive polymer underlayers in combination with the copolymer membrane were treated in the same manner, however, under varied casting and annealing conditions, as described below. For the system utilizing POT as a solid contact, the electrode was coated 6 times with the POT solution using a total volume of POT solution of 6.3 μL . The electrodes were subsequently annealed in an inert environment at 80 $^{\circ}\text{C}$ overnight. The PEDOT/PSS solid contact system required spin coating of the aqueous PEDOT/PSS suspension at 3000 rpm for 2 min followed by annealing for 2 h at 200 $^{\circ}\text{C}$ under an inert atmosphere prior to membrane deposition.

Synchrotron Radiation/Fourier Transform-Infrared Microspectroscopy (SR/FT-IRM). ISEs were bathed in a 0.1 M calcium chloride solution for approximately 3 days. Following bathing, the ISEs were rinsed in a jet of ultrahigh purity water and quickly blown dry with nitrogen to remove any excess surface water. Measurements were made immediately after the samples had been removed from the electrolyte to ensure that all measurements were made prior to the membranes drying out. The results obtained from those bathed in solution were also compared to identical samples that had not been exposed to solution.

All SR-FTIR measurements were carried out at the IR beamline (2BM1) of the Australian synchrotron, Melbourne, Australia. The spectra were recorded with a Bruker Vertex V80 vacuum FT-IR spectrometer and Bruker Hyperion 2000 IR microscope (Bruker Optik GmbH, Ettlingen, Germany) in conjunction with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen and IR radiation emitted from a bending magnet of the synchrotron storage ring. The microscope and spectrometer were controlled through the Bruker Opus software, version 6.5. The general range of measurements was from 3800 to 700 cm^{-1} at a spectral resolution of 8 cm^{-1} . The spectra were measured with a beam aperture of $10 \times 10 \mu\text{m}$ in place. Spectral collections were made in the reflection mode with 16 scan data averaging statistics. The measurements were all made in the mapping mode, which consisted of running individual measurements in a prespecified grid size (9×9 scan positions) in a region of interest on the sample (see Figure S1, Supporting Information). Certain bands of interest in the IR spectra were later chosen for integration, and an intensity map was generated showing the intensity of the integrated band correlated back to its position in the measured grid.

RESULTS AND DISCUSSION

The IRM instrument at the Australian Synchrotron is a conventional and commercially available instrument that may be utilized in either a reflectance or transmission mode. Either way, IRM spectra are representative of bulk chemical compositions of small irradiated volumes of the sample during high resolution chemical mapping, noting that the reflected beam experiences a double pass through the polymer film (once for the incoming and once for the outgoing beams), while the transmission mode involves a single pass through the bulk material. In the present study, IRM is performed in the reflectance mode since the polished gold substrates are highly reflective and nontransparent to infrared radiation. The primary advantage of the use of SR from the bending magnet beamline at the Australian Synchrotron is that the highly collimated and polarized beam provides a superior

spatial resolution of several micrometers and a 100-fold enhancement in beam intensity, as compared to a conventional laboratory global light source. These important features of SR enable high resolution and high quality infrared microspectroscopy imaging of materials.

Most significantly, since the PMMA–PDMA copolymer is known to be water repellent and unsuitable for water sorption at measurable levels in the bulk membrane,⁴ the detection (or nondetection) of water by reflectance SR-IRM is symbolic of the presence (or absence) of localized zones of water at the buried interface of a solid-contact ISE employing PMMA–PDMA as the sensing membrane.

Figure 1 presents the optical micrograph of an area of interest taken from a Ca^{2+} -selective copolymer membrane coated onto a gold coupon ($5 \times 10 \times 0.5 \text{ mm}$) after exposure to solution, along with the corresponding 3-D intensity map of the integrated OH bending mode of water [$\delta(\text{OH}) \approx 1645 \text{ cm}^{-1}$]. The data reveals a region on the sample, corresponding to the blurred region in the microscopic image of the membrane, where there is a significant increase in the intensity of the integrated $\delta(\text{OH})$ peak. This region is indicative of a high amount of interfacial water, which is due to localized or droplet-like inclusions of water at the buried interface. When compared to all measurement sites on a dry sample, the integrated peak intensity in the bathed sample at 1645 cm^{-1} , corresponding to the OH bending mode of water, was absent from the IR spectrum of any of the regions on the dry sample.

Interestingly, the image of the ISE shown in Figure 1 reveals a degree of surface roughness that is only evident on a microscopic level. Apparently, the corresponding 3-D map shows that the water is accumulating in a region on the sample, which is ascribable to physical (e.g., microscopic surface roughness, poor adhesion, etc.) and/or chemical imperfections (e.g., ionic impurities) at the substrate/membrane interface. Either scenario would generate sites at which water could accumulate.

Further credence for the above-mentioned interpretation is the previous and complementary small angle neutron scattering (SANS)⁴ study of water sorption in the PMMA–PDMA copolymer membrane, which showed negligible levels of neutron scattering from nanosized scatterers in the membrane such as water nanodroplets; highlighting that water was not taken up by the bulk membrane, so the water inclusions must be formed at the buried interface.

The present study on PMMA–PDMA has been extended to a system also incorporating a POT solid contact. A comparable SR/FT-IRM study of a system incorporating POT as a conductive polymer SC (image and map not shown) showed an absence of water in the numerous randomly sampled regions of over 100 spot analyses. This result is not unexpected since the hydrophobic POT film inhibits the accumulation of water at the buried interface by providing an effective barrier of a hydrophobic substrate over the metal electrode surface that prevents water deposition at chemical and/or physical imperfections. Significantly, this result validates previous surface studies⁴ showing that a POT/PMMA–PDMA copolymer ISE eliminates water pools at the buried interface of the ISE.

In this study, the authors have used the sharp water $\delta(\text{OH})$ band at 1645 cm^{-1} over the broad and more intense water $\nu(\text{OH})$

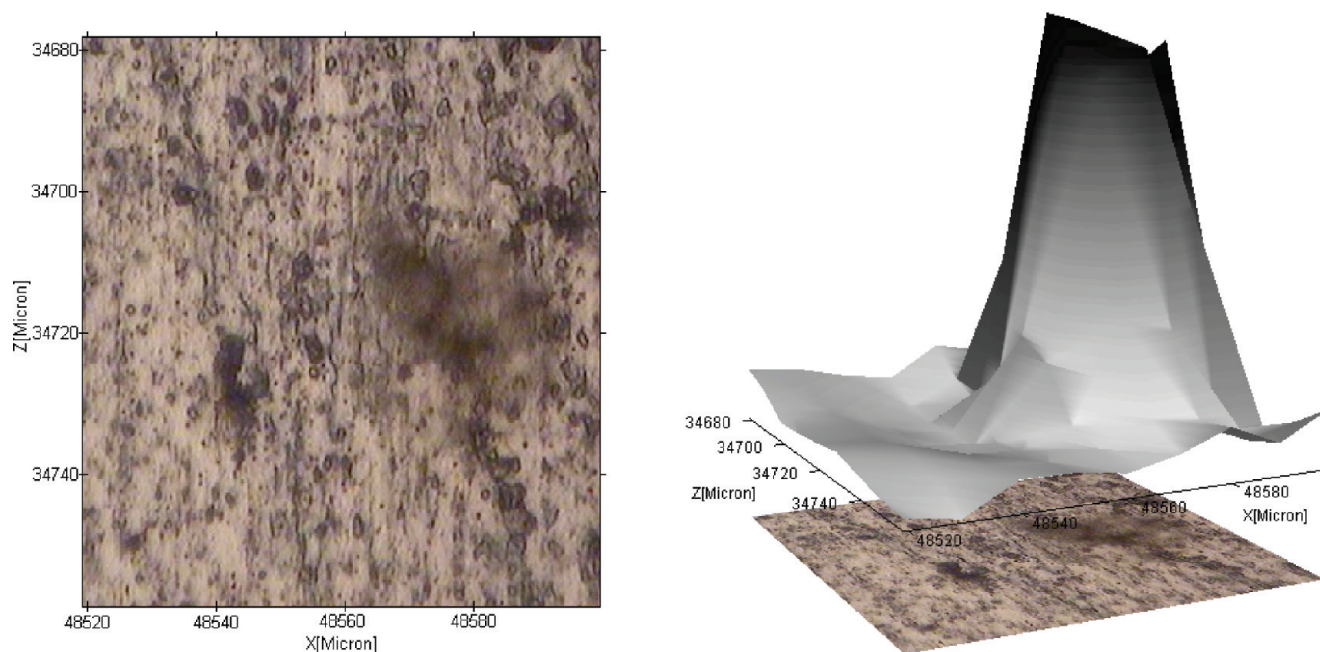


Figure 1. Optical micrograph of a PMMA-PDMA Ca^{2+} -selective membrane coated onto gold and exposed to solution (left), as well as the corresponding three-dimensional intensity map of the integrated OH bending mode of water (right).

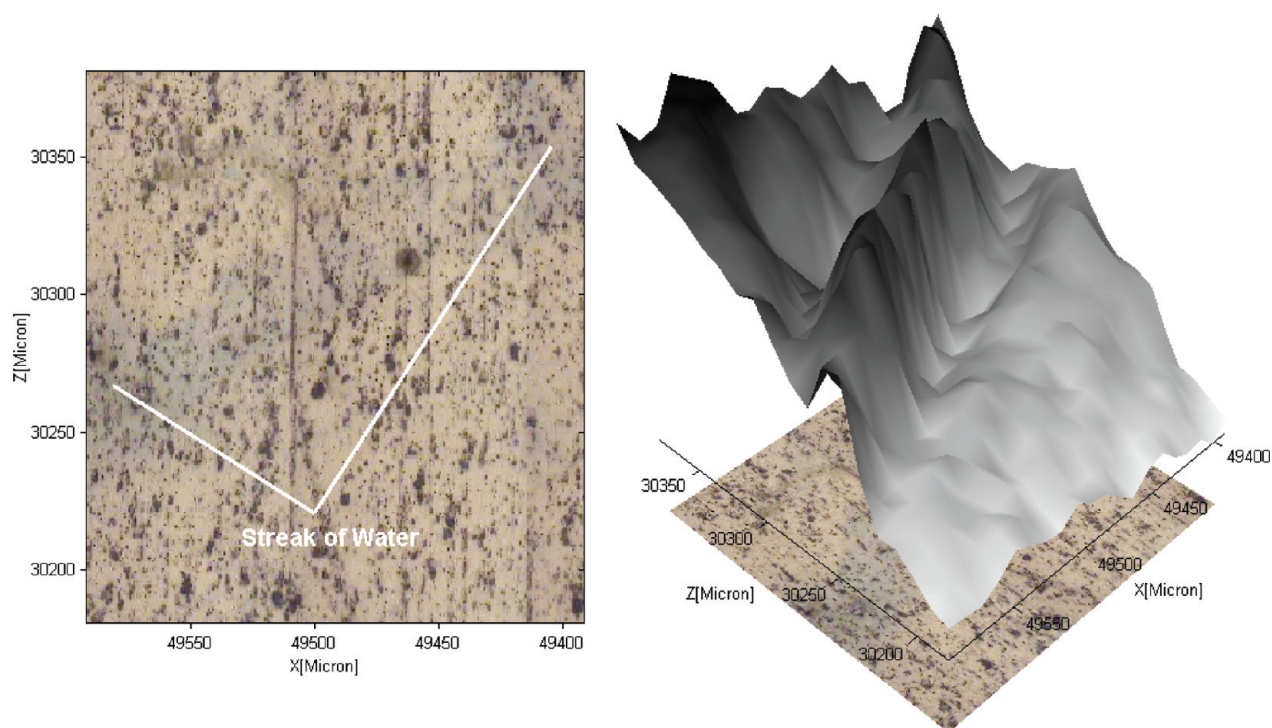


Figure 2. Optical micrograph of a region of interest for a solid contact ISE system comprising PMMA-PDMA calcium selective membrane coated on a PEDOT/PSS conductive polymer layer on a gold substrate after exposure to solution (left), as well as three-dimensional intensity map of the integrated OH bending mode of water (right).

band at 3500 cm^{-1} since the presence of broad reflectance interference fringes in the background spectra of the dry and wet samples made it very difficult to decipher the membrane signal from the background while examining the broad $\nu(\text{OH})$ band. Furthermore, the IRM maps of the $\delta(\text{OH})$ data for the dry samples or treated sample that is free of water inclusions (e.g., POT/PMMA-PDMA) [not shown] revealed featureless maps, actually comprising noise spikes on the low background signals. Accordingly, we have demonstrated a relative absence

of water in dry samples, as well as the treated POT/PMMA-PDMA sample, by showing representative overlay spectra for the $\delta(\text{OH})$ band in Figures S2–S4 in the Supporting Information.

Since a combination of a hydrophobic ion selective membrane (e.g., PMMA-PDMA copolymer) with a hydrophobic solid contact (e.g., POT) displayed an ability to eliminate water inclusions, we decided to carry out a comparable study of the hydrophobic ion selective copolymer membrane in conjunction

with the relatively hydrophilic SC of poly (3,4-ethylenedioxythiophene)/poly (styrenesulfonate) [PEDOT/PSS], so as to gauge if this system may also be used in the production of SC ISEs that are devoid of deleterious water layers. Figure 2 presents an optical micrograph of an interesting region on a PEDOT/PSS/copolymer ISE after exposure to solution, along with the corresponding 3-D intensity map of the integrated OH bending mode of water (1645 cm^{-1}). Notably, a distinct trail of water (marked) is visible in the 3D intensity map, which is evident as a gray and hazy streak in the optical micrograph. Indeed, this outcome suggests a swelling and roughening of the PEDOT/PSS/copolymer interface, especially when a hydrophobic membrane is coupled with the hydrophilic SC. In this context, water transported through the membrane probably exists in a miscible form within the PEDOT/PSS and does not separate into droplets, with the dark streak in the optical micrograph corresponding to areas where water has been transported to the ion selective membrane/PEDOT/PSS interface and is absorbed relatively evenly into the hydrophilic PEDOT/PSS layer in much the same way as water is absorbed into a sponge. Accordingly, it is likely that PEDOT will behave analogously to a hydrogel and will provide a transient transmembrane flux of ions and a concomitant degradation in the sensitivity and selectivity of the PEDOT SC-ISE. Significantly, such a thick hydrogel is unable to display a sensitivity in water layer testing but will still display degraded potentiometric response characteristics, noting that this potentiometric behavior was observed elsewhere by Sundfors et al.¹⁷

CONCLUSIONS

The results of this study demonstrate the power of SR/FT-IRM as a research tool for studying the buried interface of multilayered materials. The use of high-resolution 3-dimensional mapping enables a visual depiction of the location and nature of fluid inclusions at interfaces, in this case, demonstrated by a study of water in polymeric ISEs.

Specifically, this work has confirmed unequivocally that PMMA–PDMA copolymer is susceptible to the pooling of water

droplets at the buried interface of the electrode. Additionally, the use of a hydrophobic conducting polymer SC such as POT inhibits the deposition of water by removing possible sites for water accumulation. Different results are evident when a hydrophilic conducting polymer SC such as PEDOT/PSS is used in conjunction with a hydrophobic PMMA–PDMA copolymer membrane. Evidently, the PEDOT/PSS SC leads to the formation of water in a miscible state within the PEDOT/PSS underlayer, akin to a hydrogel, instead of a separate and thin water layer.

Most significantly, SR/FT-IRM is suitable for studies of other polymeric ISEs such as silicone rubbers, polyurethanes, polyvinyl chlorides, etc. on alternate electrode substrates such as nanostructured carbons, doped silicon, platinum, etc. and may be used in the elucidation of novel mechanistic information about these important electrochemical sensors.

The aforementioned outcomes present valuable insights into the physical behavior of technologically important materials such as ISE membranes exposed to fluid media for prolonged periods. Parallels between the physicochemical information obtained via SR/FT-IRM and the chemical behavior of the functional material can undoubtedly be drawn to achieve an enhanced understanding of the material systems under consideration.

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SUPPORTING INFORMATION AVAILABLE

More detailed information relating to the experimental conditions utilized and ISE fabrication. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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