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Evidence of a Water Layer in Solid-Contact Polymeric Ion Sensors

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Abstract

This paper presents the very first direct structural evidence for the formation of a 100 ± 10 Å water layer in coated-wire polymeric membrane ion-selective electrodes (ISEs).

Solid-state ion selective electrodes (ISEs) utilizing a polymeric sensing membrane have shown great promise for use in mainstream analytical chemistry. Such solid-state polymeric ISEs do not require an inner filling solution (normally required in liquid contact ISEs) and are suited superbly for miniaturization as coated-wire electrodes (CWEs)^{1,2}. The CWEs also exhibited rapid response times and a long life out of solution², which are desirable qualities for any ion sensor. Small sensors enable novel applications in systems that contain minute amounts of analyte, such as intracellular measurements^{3–5} where improvements can be made on existing technologies, and in lab-on-a-chip technologies, where a considerable reduction in the size of components can lead to advantages over traditional analytical techniques^{6–9}.

Miniaturized polymeric ion sensors provide exciting opportunities for the application of these concentration sensitive devices in the detection of ultratrace amounts of total analyte (e.g., attomole quantities¹⁰), which may also be coupled to novel bioassays utilizing nanoparticle tagged biomolecules^{11, 12}.

The underlying problem associated with solid-state polymeric ISEs or CWEs is their susceptibility to a decline in stability and relatively mediocre detection limits and selectivities over lengthened periods of time in solution. The degradation in sensor response has recently been ascribed to the existence of a water layer between the membrane and the electrode substrate, which behaves unintentionally as an electrolyte reservoir that re-equilibrates on each and every change in sample composition^{13, 14}. In recent times, the presence of a hydrophobic conductive polymer or redox mediator, acting as a redox buffering underlayer, has been shown to be important not only for the ion-to-electron transduction process^{15, 16}, noting that this ion-

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[†]Electronic Supplementary Information (ESI) available: [Experimental details, neutron reflectometry (NR) cell design, theoretically modelled NR data for PVC with and without a water layer, and NR best-fit data]. See <http://dx.doi.org/10.1039/b000000x/>

to-electron transduction concept had been established with silver sulfide solid-state sensors in early work by Rhodes and Buck¹⁷. Furthermore, inhibition of the deterioration in sensitivity and stability of all solid state polymeric ISEs^{15, 16, 18–20} is due to an elimination of the water reservoir that tends to form at the electrode substrate/sensing membrane interface. Furthermore, the solid-contact allows the elimination of the liquid contact utilized in conventional polymeric membrane ISEs, obviating spurious ion fluxes and the need to control and optimize the filling solution in the liquid contact to achieve low detection limit sensors (see references^{21–23}).

Neutron reflectometry (NR) is an excellent surface analysis technique for investigating in-situ the nanostructures of surfaces, interfaces and thin films, and can be used to monitor the development of water layers at the solid contact/ion sensing membrane interface of CWE ISEs²⁴. With NR, it is necessary to prepare molecularly thin and atomically flat films [tens to hundreds of Å in thickness and a few Å root mean square (rms) in roughness], so as to enable sufficient reflectivity (via reduced roughness) and to minimize the number of interference fringes arising from the coherent neutron scattering of successive layers of polymeric material (through diminished thickness) in the thin film. If the prerequisites are satisfied then it is possible to derive atomic scale information about the physical nature of thin films. Theoretical modelling of the NR reflectivity data for a 120 Å thick water layer beneath a 200 Å thick ISE layer (see Fig. S1 in the supplementary information) reveals that, for perfectly resolved and atomically flat layers, the water layer produces a series of interference fringes that are interspersed with the corresponding interference fringes for the ISE film, thereby confirming that NR can be used to detect water layers in CWEs.

In this communication, the authors present the very first structural and spectroscopic evidence, as deduced using NR, electrochemical impedance spectroscopy (EIS), and secondary ion mass spectrometry (SIMS), for the formation of water layers at the metal substrate/membrane interface of CWE Ag⁺ and Ca²⁺ ISEs, noting that these ISEs were chosen as model systems in this study due to their excellent response attributes.

Fig. 1(a) presents a snap-shot of EIS complex-plane impedance plots as a function of exposure for a CWE Ag⁺ ISE soaking in 10⁻³M AgNO₃ for 48 hours. The data reveals a high frequency semi-circle that is ascribable to the bulk membrane resistance coupled with a spurious resistance such as the contact resistance between the membrane and the gold substrate electrode. From Fig. 1(b), it is evident that, during conditioning, the bulk membrane resistance-contact resistance rises sharply until approximately 3 hours, and diminishes gradually until about 20 hours, at which point it stabilizes. The initial increase in resistance has been explained by ion trapping whereby hydrophilic ionic impurities are dissolved into water nanodroplets in the membrane creating electrical discontinuities²⁵. The EIS trend after 3 hours may be interpreted in terms of the establishment of a water layer comprising both water and transported ions, and the wet ISE membrane/gold interface ultimately yields a lower contact resistance manifested as a diminished bulk membrane resistance-contact resistance at high frequency. Significantly, a conventional liquid contact polymeric membrane ISE shows the initial increase in resistance, but not the eventual decline in resistance that is consistent with the presence of an interfacial water layer.

X-ray reflectometry (XR) was used to determine the thickness and integrity of the spin cast ISE films, so as to ascertain their suitability in subsequent NR measurements. Accordingly, Fig. 2 shows the XR curve for a molecularly thin Ag⁺-selective plasticized PVC film, as measured in air without conditioning. Fitting of the reflectivity data to a single-layer film model yielded a PVC film thickness of 217 Å and a surface roughness of 11 Å rms. The blurring of the interference fringes in the X-ray reflectivity data at Q values above 0.25 Å⁻¹ is indicative of slight roughening of the polymer coating, as the atomically smooth silicon wafer possesses a surface roughness of a few Å rms. Subsequent work on unplasticized copolymer ISEs

(unpublished findings) has shown that this surface roughening of a spin cast film is due to the high volatility of the tetrahydrofuran (THF) casting solvent, which promotes the deposition of a non-uniform film. Nevertheless, the XR data show that the THF spin cast film is adequate for measurements on the NR instrument used in this study that possesses a Q range from 0 to $0.25 \text{ \AA}^{-1}$.

Note that electrochemical studies on molecularly thin films like the one proposed in the present study are experimentally viable, as a previous potentiometric study of a valinomycin-based bilayer membrane revealed a classical Nernstian response to potassium over a wide dynamic range ²⁶.

Unfortunately, the NR profile of the PVC film in air cannot be contrasted to the ones in the electrolyte, as the disparate contrasts in neutron scattering length density (NSLD) of the polymer against air as well as D_2O or D_2O/H_2O or H_2O cannot be compared. Furthermore, as the NSLDs for air and PVC are too similar, there is insufficient neutron scattering contrast to meaningfully extract information from this featureless NR profile.

The in-situ NR data for the PVC Ag^+ -selective film [see Fig. 3 and Fig. 4 for the reflectivity and NSLD curves, respectively] required a fitting of two physically dissimilar films with roughening factors. This can be explained by the scattering of neutrons from the polydisperse nanodroplets of water in the membrane, and the presence of an interior film (100–120 $\text{\AA}$ thick) possessing a NSLD akin to a composite of water and polydisperse nanodroplets of organic liquid (e.g., membrane plasticizer exuded into the water layer ²⁵). Furthermore, the NSLD values for the water infused materials (i.e., water layer with exuded plasticizer and polymer with water nanodroplets) varied in accordance with changes in the contrast in NSLD values for D_2O to D_2O/H_2O to H_2O . This is strong evidence for the reliability of the NR fits. Also noteworthy is the fact that the XR thickness of the original polymer film is congruent with the NR fitted data for the electrolyte treated samples. Unfortunately, the NR results for the Ag^+ ISE bathed in $10^{-3} \text{ M } AgNO_3$ in D_2O , a mixture of D_2O/H_2O , along with H_2O [see the reflectivity curves in Figures 3(a) to 3(c) and NSLD curves in Figures 4(a) to 4(c)], together with the NR best fit parameters (see Table S1 in the supplementary information), revealed a smearing of the interference fringes. Similar to the interpretation of the NR data, this can be explained by a roughening of the films, along with an apparent loss of contrast in NSLD values. Clearly, the blurring at the interface between the PVC and water layer, as evidenced in the NSLD profiles, is ascribable to roughening of the films due to neutron scattering from the polydisperse water inclusions in the PVC layer and polydisperse plasticizer nanodroplets in the water layer (see Fig. 5). Furthermore, the fitted data for the films provided apparent NSLDs for the PVC film akin to a composite of the plasticized PVC film and inclusions of water, and a water layer consistent with the presence of exuded organic material (i.e., plasticizer) from the membrane. This is symbolic of the permeation of water nanodroplets into the PVC film and plasticizer into the water layer; well known phenomena that have been studied extensively by various researchers ^{25, 27–31} where it was shown that the water droplets are nanoscaled ²⁷. This phenomenon is responsible for the polymer's NSLD value approaching that of the aqueous electrolyte, as well as the observed smearing of the interference fringes due to roughening as neutrons scatter off the polydisperse water and/or plasticizer nanodroplets along with the surrounding polymer matrix and/or water layer. Also, the H_2O NR data (see Fig. 3 (c)) showed signs of a time dependency over the duration of the NR measurement (i.e., about 20 hours), as evidenced by a slight increase in reflectivity between Q values of 0.175 and $0.225 \text{ \AA}^{-1}$. This time dependency is responsible for the slight deviation between the fitted and experimental reflectivity data at higher Q values.

Following conditioning of CWE Ca^{2+} ISEs in separate solutions of 0.1 M $Ca(NO_3)_2$, 0.1 M $CaCl_2$ and 0.1 M $NaCl$ with subsequent peeling of the ISE membrane to expose the underlying

Au substrate electrode, SIMS depth profiling revealed a surplus of cation (i.e., Ca^{2+} and Na^+) and anion (i.e., Cl^- and NO_3^-), as compared to the control Au sample, symbolizing the transportation of water and ions to the metallic electrode/membrane interface (see Table 1 for average $^{133}\text{Cs}^+\text{M}^+$ counts for static SIMS profiles of these substrates). Note the following important points: 1) the control Au sample comprised a CWE that had not been exposed to electrolyte; 2) the SIMS intensities represented raw ion counts without consideration of elemental sensitivity factors; and 3) the relatively high experimental uncertainty of the SIMS ion counts (i.e., 10–20% relative) did not permit a comparison of the relative permeation rates of ions through the ISE membrane. Clearly, the water layer acts as a reservoir for membrane transported ions, and provides a source of uncontrollable and spurious ion fluxes that manifest themselves in the same way as transmembrane fluxes do in the non-optimized filling solutions of liquid-contact polymeric ISEs¹⁴. Without doubt, this is a critical problem that must be resolved if solid-contact ISEs are to be used widely in analytical chemistry.

Fig. 5 presents a schematic diagram of a polymeric CWE ISE, particularly as it relates to the Ag^+ ISE investigated in the in-situ NR study of the evolution of water layers in CWE ISEs. In the model, the presence of polydisperse water nanodroplets are proposed, as suggested elsewhere by Li et al.³⁰ and supported strongly in this work by the NSLD data and smearing of the interference fringes for the fitted polymer ISE film in the NR reflectivity data. Furthermore, the interfacial water layer is infused by polydisperse nanodroplets of the membrane plasticizer, as evidenced by an intermediate NSLD for water and the organic plasticizer, and this phenomenon has been observed by other investigators^{25, 31} who noted membrane exudation of plasticizer into the electrolyte, so the plasticizer is also expected to migrate into the water layer of the CWE ISE.

Conclusions

This work has provided the first experimental evidence for the formation of a water layer in CWE ISEs, as depicted in Fig. 5. Significantly, this undesirable water layer acts as an intermediate electrolyte reservoir manifesting itself in the same way as a non-optimized filling solution in a liquid contact ISE, thereby providing spurious ion fluxes that degrade the detection limit and selectivity of CWE ISEs.

The outcome of this research has important ramifications for solid-contact polymeric ISEs; it is necessary to develop strategies to eliminate the formation of a detrimental water layer at the electrode substrate/ISE membrane interface if the superior response characteristics of an all-solid-state polymeric ISEs are to be achieved.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. EIS data for a gold CWE Ca^{2+} ISE conditioned in 10^{-3}M CaCl_2 over a prolonged period: (a) complex-plane impedance plot; (b) bulk membrane resistance as a function of time.

Fig. 2.

XR reflectivity curve in air for a molecularly thin spin cast film of Ag^+ ISE deposited onto atomically smooth silicon. Note, R is the neutron reflectivity, Q is the magnitude of the neutron scattering vector, and ρ is the scattering length density (SLD).

Fig. 3. NR reflectivity curves for a molecularly thin spin cast film of Ag^+ -selective membrane deposited onto an atomically smooth silicon wafer in 10^{-3} M AgNO_3 in (a) D_2O , (b) $\text{D}_2\text{O}/\text{H}_2\text{O}$ and (c) H_2O .

Fig. 4. NR NSLD curves for a molecularly thin spin cast film of Ag ISE deposited onto an atomically smooth silicon wafer in 10^{-3} M AgNO_3 in (a) D₂O, (b) D₂O/H₂O and (c) H₂O.

Fig. 5. Schematic diagram depicting the physical structure in a CWE ISE membrane, noting the formation of a water layer comprising exuded plasticizer (i.e., M) and a membrane phase saturated with polydisperse water (i.e., A).

Table 1

SIMS spectral intensities for $^{133}\text{Cs}^{\text{N}}\text{M}^+$ species sputtered from the Au substrate (normalized against the $^{133}\text{Cs}^+$ signal for each sample) for CWE Ca^{2+} ISEs. In each case except for the Au control sample, the CWE ISE was exposed to 0.1 M solutions of the electrolyte for 24 hours. The plateau region of each SIMS elemental depth profile was averaged, and the mean values are provided for multiple spot analyses. The number of replicates [N] and relative standard deviation (%RSD) are provided in parentheses.

Sample	$^{133}\text{Cs}^{23}\text{Na}^+$	$^{133}\text{Cs}^{14}\text{N}^+$	$^{133}\text{Cs}^{35}\text{Cl}^+$	$^{133}\text{Cs}^{40}\text{Ca}^+$
Au [N=4]	4059 (61)	527 (22)	129 (48)	4787 (45)
Au PVC $\text{Ca}(\text{NO}_3)_2$ [N=4]		1627 (8)		22298 (21)
Au PVC CaCl_2 [N=4]			1729 (5)	30357 (10)
Au PVC NaCl [N=3]	29785 (49)		1366 (20)	