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Short communication

A near edge X-ray absorption fine structure (NEXAFS) study of the response mechanism of the iron (III) chalcogenide glass membrane ion-selective electrode

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ABSTRACT

We have utilized synchrotron radiation-X-ray photoelectron spectroscopy (SR-XPS) and near edge X-ray absorption fine structure (NEXAFS) to demonstrate unequivocally that the modified surface layer (MSL) of the iron chalcogenide glass ion-selective electrode (ISE) comprises a mixture of iron(II) and iron(III) redox states, as proposed in previous theories to explain the mixed electron transfer and ion exchange response mechanism of this analytically important ISE.

1. Introduction

Potentiometric chalcogenide glass membrane sensors have attracted considerable attention for the analysis of metals due to their high durability, sensitivity and suitability for industrial and environmental monitoring [1]. Chalcogenide glass materials comprise chalcogen elements, which are located in Group 6 of the Periodic Table (i.e. sulfur, selenium, etc.). One of the most widely used Fe(III) ISEs is based on a chalcogenide glass membrane [$Fe_{2.5}(Se_{60}Ge_{28}Sb_{12})_{97.5}$]. Early work by Vlasov, Bychkov and Legin [2,3] demonstrated Nernstian response with the Fe(III) ISE in unbuffered iron(III) solutions down to 10^{-6} M Fe^{3+}. Further studies by De Marco and Mackey [4] showed that the Fe^{3+} ISE can be calibrated down to pFe ~ 23 in citrate and salicylate buffers. Other research has shown that careful preparation of the electrode and a hydrodynamic flow regime (i.e., continuous flow analysis) minimizes membrane fouling allowing trace analyses of metals in seawater [5]. However, as discussed previously [6], a hindrance to the widespread application of the iron(III) chalcogenide glass ISE has been contradictions in the literature about a physicochemical rationale for its response mechanism. Most agree that the mechanism is probably electronic rather than ionic; however, there are several inconsistencies related to slopes of iron (III) ISE response curves with most researchers reporting slopes of 30–50 mV/decade change in the activity of iron (III)(aFe^{III}) in unbuffered iron(III) standards [7–9] which is much lower than the Nernstian prediction of 59.16 mV/decade for a one electron charge transfer process. Previously, De Marco and Pejcic [4] undertook a detailed experimental and theoretical study of the response mechanism of the iron(III) ISE in saline media to explain the Nernstian slope of 30 mV/decade over a range of 10^{-23}–10^{-1} M in saline iron (III) citrate standards, unbuffered iron (III) standards and UV-oxidized and organic free seawater [6]. The observed slope of 30 mV/decade was inconsistent with the expected value for trivalent ion-exchange of Fe(III), (i.e., 19.72 mV/decade), or the one predicted for a one electron transfer process (slope = 59.16 mV/decade) [7,10,11]. Instead, De Marco and co-workers [4,12] inferred theoretically a mixed reaction mechanism involving both electron transfer and ion-exchange processes.

This study utilized synchrotron radiation-X-ray photoelectron spectroscopy (SR-XPS) and near edge X-ray absorption fine structure (NEXAFS) to probe the modified surface layer (MSL) of the electrode, so as to characterize the surface reaction products after exposure of the membrane to various calibration media. Moreover, SR-XPS was used to confirm the surface composition of the MSL, while NEXAFS was used to elucidate the chemical states of iron in the MSL of the iron(III) chalcogenide glass ISE, providing unequivocal evidence for a combined electron transfer and ion exchange response mechanism of this ISE in aqueous media.

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2. Material and methods

2.1. Electrode preparation and solutions

The chalcogenide glass membrane [$Fe_{2.5}(Se_{60}Ge_{28}Sb_{12})_{97.5}$] was prepared using the method of Koenig and Grabner [7]. A synthetic brine was prepared by dissolving 0.6 M NaCl in Milli-Q water, and a sodium citrate buffer was prepared using 10^{-4} M ferric chloride ($FeCl_3$), 10^{-2} M sodium citrate ($Na_3C_6H_5O_7.2H_2O$), 10^{-3} M sodium hydrogen carbonate ($NaHCO_3$) and 0.6 M sodium chloride (NaCl). All polyethylene storage containers were soaked overnight in dilute hydrochloric acid (1 M) followed by rinsing with large volumes of Milli-Q water.

2.2. SR-XPS/NEXAFS measurements

SR-XPS/NEXAFS measurements were performed at the soft X-ray spectroscopy beamline (141D) at the Australian Synchrotron. SR-XPS was performed at a photon energy that was about 130 eV above the absorption edge of the probed element, as well as a pass energy of 5 eV using a dwell time of 0.1 s and a step size of 0.1 eV. The instrument was calibrated using the Au($4f_{7/2}$) peak at a binding energy of 85.15 eV, with the C(1 s) peak from adventitious hydrocarbons at 284.6 eV used as an internal standard to correct for surface charging effects. Samples were mounted on a stainless steel sample holder using double-sided conductive carbon tape, and pumped to a background pressure of 10^{-7} hPa in the load lock chamber of the end station. Both the beamline and end station were maintained at ultrahigh vacuum at a pressure of about 10^{-10} hPa in the analysis chamber. The insertion device for the beamline is an elliptically polarized undulator (Apple II) providing an energy range of 100–2500 eV at a resolution of 5000 and 10,000 (ΔE/E). The OmniVac and PreVac end station was equipped with a SPECS Phoibos 150 Hemispherical Analyzer complete with a retarding grid analyzer. The data was acquired by SpecsLab 2.32-r11458 software (SPECS GmbH).

NEXAFS spectroscopy was also conducted on this soft X-ray beamline. The Apple II undulator was set to output horizontally polarized light that was passed through a Peterson plane grating monochromator (1200 lines mm^{-1}). NEXAFS spectra were recorded using a SPECS Phoibos 150 Hemispherical Analyzer incorporating an extended 9 channel detector. The spectra were acquired for iron (700–730 eV) *L-edge* in the fluorescence yield (FY) and total electron yield (TEY) modes. The data was acquired by SpecsLab 2.32-r11458 software (SPECS GmbH). NEXAFS spectra were normalised against the incident photon flux [13].

3. Results and discussion

The surface composition of the chalcogenide glass membrane following exposure to brine and citrate buffer was probed by SR-XPS. Chemical information pertaining to the surface reaction products was obtained by examining the binding energies, intensities and shapes of the SR-XPS peaks (results not shown), noting that a polished membrane was used as a control sample.

In all cases, SR-XPS identified two carbon species with peaks at ~285 and ~287 eV ascribable to contamination from the analysis chamber of the instrument via adventitious hydrocarbons, as well as alcohol used in the rinsing and drying of membranes [14]. Similarly, Ge(3d) spectra for the chalcogenide membrane before and after exposure to solution revealed the presence of a broad peak indicative of at least two Ge species with the main peak at ~30.5 eV along with a high binding energy shoulder at ~32.1 eV consistent with Ge in GeSe or $GeSe_2$ and GeO_2 respectively, which agrees with previous literature about rapid atmospheric oxidation of GeSe [14,15].

With all membranes, Sb(3d) spectra revealed Sb($3d_{5/2}$) and Sb($3d_{3/2}$) spin–orbit split components at ~530 and ~539 eV respectively, with these peaks attributable to Sb_2Se_3/Sb_2O_3 [14]. However, high resolution SR-XPS spectra of Fe(2p) on all membranes revealed that, even with the enhanced sensitivity of SR-XPS, this surface analysis technique failed to detect iron in the surface region of all the treated membranes, with the lack of iron in the surface region attributable to the iron deficient MSL of the ISE [4]. Again, with all membranes, the O(1 s) peaks at ~531 and ~533 eV are attributable to metal oxide (i.e., GeO_2 and Sb_2O_3) and water respectively [4,14], and the Se($3d_{5/2}$) and Se($3d_{3/2}$) peaks at ~54.5 and ~55.5 eV are characteristic of Se^{2-} species [4].

In summary, SR-XPS confirms that the MSL of the iron chalcogenide glass ISE is composed predominantly of GeSe, $GeSe_2$ and Sb_2Se_3 phases, which upon exposure to air after polishing or solution after treatment, undergo oxidation to GeO_2 and Sb_2O_3 with a diminution of Fe to below the detection of XPS, which is due to leaching of soluble Fe(II) and Fe(III) upon oxidation of FeSe [4,7]. Furthermore, Koenig and Grabner [7] along with De Marco and Pejcic [4] detected bulk iron in the iron(III) ISE after XPS depth profiling to about 8 nm, which represents the thickness of this Fe deficient MSL.

The inability of SR-XPS to detect sub-atomic percentages of Fe in the surface layers of the iron(III) chalcogenide glass membrane is internally consistent with an iron deficient MSL. Previous research using electrochemical impedance spectroscopy (EIS) and XPS [4] inferred a combined electron transfer and ion exchange reaction mechanism at the electrode MSL (see Fig. 1). In the previous work [4], it was inferred from the EIS and XPS data on the Fe(III) ISE that there were two surface films comprising an outer surface layer (OSL) and an iron deficient MSL. For an electron transfer mechanism, it is essential that the electrode MSL comprises the Fe(II)/Fe(III) redox couple, as was inferred in the previous EIS study of this system [4]. However, since the previous XPS study [4] and the present SR-XPS study have failed to detect iron in the MSL of treated membranes, it was necessary to employ a surface analysis technique with enhanced elemental sensitivity to shed insights into the Fe(III) reaction mechanism of this electrode.

Accordingly, we have utilized NEXAFS of the Fe(2p) level or *L-edge*, so as to detect Fe and its chemical states in the MSL of the iron(III) chalcogenide glass ISE. With NEXAFS, when the incident beam energy approaches and resonates with the Fe *L-edge*, the photoabsorption cross-section or probability of excitation of the Fe *L-edge* increases by several orders of magnitude, and this substantially boosts the analytical sensitivity of NEXAFS. Furthermore, since the Fe *L-edge* NEXAFS excited photoelectrons experience scattering with Fe's neighbouring atoms within the MSL, the “fine structure” on the NEXAFS absorption edge is symbolic of the chemical environment of the iron atom. Accordingly, NEXAFS is a powerful surface analysis technique that, not only permits detection of Fe species in the Fe depleted electrode MSL, but it also allows elucidation of the chemical states of the Fe species in the MSL — as opposed to high surface sensitivity techniques like secondary ion mass spectrometry (SIMS) that allow detection of low surface concentrations, but cannot deduce the chemical state information of NEXAFS.

Fig. 2 presents the TEY NEXAFS spectra of the Fe(2p) level or Fe *L-edge* for polished and solution treated iron(III) ISEs. Significantly, the Fe($2p_{3/2}$) NEXAFS spectrum of the polished chalcogenide membrane or control displayed a large peak at 708.0 eV with a weaker partially resolved peak at approximately 710.5 eV, which is distinctive for Fe^{2+} [15,16]. This is internally consistent with a chalcogenide membrane that has been doped with iron(II), which is the chemical state of iron in a conventionally fused membrane. By contrast, the brine and citrate buffer treated membranes revealed the presence of Fe^{3+} as evidenced by a shoulder at 707.8 eV with a major peak at 709.6 eV, which is commensurate with iron as Fe^{3+} [16,17]. Hence, with a membrane exposed to brine and citrate solutions, the spectra are indicative of a mixture of Fe^{2+} and Fe^{3+} since Fe^{3+} alone would have yielded an intensity ratio of the ~708 eV to ~710 eV peaks of 1 to 2 instead of the observed intensity ratio of about 1 to 1 [15–17], which is ascribable to a convolution of doublet peaks for the two Fe oxidation states. This result is the first time that NEXAFS spectroscopy has observed directly the presence of both Fe(II) and Fe(III) in the MSL of the iron chalcogenide glass membrane,