

Silver and lead all-plastic sensors—polyaniline vs. poly(3,4-ethylenedioxythiophene) solid contact

Agata Michalska · Marcin Wojciechowski ·
Wojciech Jędral · Ewa Bulska · Krzysztof Maksymiuk

Received: 27 February 2008 / Accepted: 15 April 2008 / Published online: 28 May 2008
© Springer-Verlag 2008

Abstract Silver and lead selective all-plastic ion-selective electrodes were obtained using poly(vinyl chloride)-based membranes and either poly(3,4-ethylenedioxythiophene) or polyaniline dispersion cast on an insulating plastic support as transducer and electrical lead. The effect of interactions of applied conducting polymer with analyte ions on potentiometric responses was evaluated and correlated with changes in elemental composition and element distribution within the ion-selective membrane and the conducting polymer transducer revealed in course of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) experiments. In the case of silver selective electrodes, potentiometric responses obtained are much dependent on the oxidation state of the polymer placed beneath the ion-selective membrane. For semi-oxidized polymer (poly(3,4-ethylenedioxythiophene)-based electrodes, linear responses with detection limit equal to $10^{-5.4}$ M were obtained. For a more oxidized polyaniline (of higher conductivity), although the electrodes were pretreated exactly in the same way and tested in parallel, super Nernstian potential slope was recorded within the AgNO_3 activities range from 10^{-6} to 10^{-7} M. These responses were consistent with results of LA-ICP-MS, revealing profoundly higher silver signals intensities for poly(3,4-ethylenedioxythiophene) underlying silver selective membrane. It seems highly probable that silver is accumulated in this polymer layer as Ag^0 due to spontaneous redox reaction leading to oxidation of the polymer; however, this process requires also the presence of silver ions at the interface. In fact, when reduced

(deprotonated) polyaniline was used as transducer, the potentiometric responses of the sensor were, within the range of experimental error, the same as obtained for poly(3,4-ethylenedioxythiophene)-based sensor. On the other hand, for lead(II) selective sensors, the difference in responses of electrodes prepared using poly(3,4-ethylenedioxythiophene) or polyaniline was less pronounced, which is in accordance with the elemental composition of these sensors.

Keywords All-solid-state potentiometric sensor · All-plastic ion-selective electrode · Polyaniline · Poly(3,4-ethylenedioxythiophene)

Introduction

Elimination of internal solution from ion-selective electrode arrangement is attractive mostly due to many practical reasons. However, exclusion of the solution phase from the sensor construction usually requires incorporation of a (solid) transducer to ensure stability of electrode potentials. In recent years, conducting polymers (CPs), available also commercially in variety of products, have gained significant attention as transducer phase of potentiometric sensors. This is fully confirmed by attractive analytical parameters of obtained devices that are well comparable, in all aspects, with modern internal-solution ion-selective electrodes [1, 2].

Choosing the right conducting polymer transducer for particular potentiometric sensor is important, however often underestimated issue [1–6]. Especially oxidation state of the polymer, presence of ions (dopants, components) are important factors affecting potentiometric responses of these sensors; however, not many studies have been performed towards comparison of different polymers used

A. Michalska (✉) · M. Wojciechowski · W. Jędral ·
E. Bulska · K. Maksymiuk
Department of Chemistry, Warsaw University,
Pasteura 1, 02-093 Warsaw, Poland
e-mail: agatam@chem.uw.edu.pl

for similar applications [4, 5]. Various factors can be taken into account while choosing CP: polymer layer deposition procedure (e.g. electropolymerization vs. solution casting), properties of the resulting layer (hydrophobicity, ion contents, oxidation state, redox capacity), lifetime of the conducting polymer layer, adhesion to other sensor layers etc. Among others, interactions between conducting polymer (understood as a complex of polymer backbone, dopant ions and/or other ions possibly present in the polymer commercial composition) and analyte ions, reaching polymer layer through the ion-selective membrane, can significantly affect potentiometric responses of the sensors. These can be of different nature—redox reactions; complexation, ion-exchange, precipitate formation processes can occur. Description of these interactions in general terms is difficult as they are often case specific-analyte ion-applied conducting polymer composition.

This report is limited to comparison of polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT)-conducting polymers, both commercially available in the form of watery suspension and used as solid contacts for ion-selective electrodes [1, 2, 7–11].

In this study, all-plastic sensors were used [12–14]. This variation of solid contact arrangement, proposed a few years ago, applies a conducting polymer layer on insulating plastic support, partially as a transducer and partially as electrical lead.

Herein silver(I) or lead(II) selective sensors with plastic solvent polymeric poly(vinyl chloride) (PVC)-based membranes were chosen as models to demonstrate different effects related to the interactions of analyte ions with the transducer layer.

Potentiometric responses obtained were supplemented with results of ions-profiles studies performed by inductively coupled plasma mass spectrometry (ICP-MS) measurements coupled with laser ablation (LA-ICP-MS) [15–18].

The aim of this study was to compare sensors prepared using either polyaniline or poly(3,4-ethylenedioxythiophene) dispersion and prepared (except for the conducting polymer used) exactly in the same way and tested in parallel. This approach was applied to highlight conducting polymer effect on recorded responses, primarily dynamic range and selectivity.

Experimental

Apparatus

In the potentiometric experiments, a multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA, 19355, USA), was used; stable potential readings recorded were used to construct calibration graphs. The pumps systems 700 Dosino and 711

Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solutions. In voltammetric experiment galvanostat-potentiostat CH-Instruments model 660A (Austin, TX, USA) and conventional three electrode cell, with platinum sheet as counter electrode, was used.

An inductively coupled plasma mass spectrometer ELAN 9000 (Perkin Elmer, Germany) equipped with the laser ablation system LSX-200+ (CETAC, USA) was used. The LSX-200+ combines a stable, environmentally sealed 266 nm ultraviolet laser (Nd-YAG, solid state, Q-switched) with a high sampling efficiency, variable 1–20 Hz pulse repetition rate and maximum energy up to 6 mJ/pulse. Samples were inserted in a cell on X, Y, Z translation stage. The exact position of the sample was observed with a charge-coupled device camera as a viewing system under PC control. The LSX-200+ is centrally controlled by Cetac Windows software that allows selective ablation of chosen areas of investigated samples. The applied laser energy was 3.2 mJ/pulse, repetition rate was 5 Hz, spot size was 100 μm . The distribution of selected elements within the ion-selective membrane thickness was followed, and the signal intensities for each element in different membranes were compared. Note that the quantitative analysis of the membranes' components was not aimed. The penetration depth was estimated taking into account actual thickness of LA-ICP-MS sample (determined post-experiment) and sensor analysis time.

In potentiometric and voltammetric experiments, a double junction Ag/AgCl reference electrode with 1 M lithium acetate in outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. The recorded potential values were corrected for the liquid junction potential calculated according to Henderson approximation.

Reagents

Tetrahydrofuran (THF), PVC, 2-nitrophenyl octyl ether (oNPOE), bis(2-ethylhexyl sebacate) (DOS), sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), tert-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) (lead ionophore IV), (*O,O'*-bis[2-methylthio]ethyl)-tert-butylcalix[4]arene (silver ionophore IV) were from Fluka AG (Buchs, Switzerland).

Doubly distilled and freshly deionized water (resistance 18.2 M Ω cm, Milli-Qplus, Millipore, Austria) was used throughout this work. All measurements were performed in solution of unaltered neutral, pH. All used salts were of analytical grade and were obtained from POCh (Gliwice, Poland) with the exception of: PEDOT water suspension Baytron P obtained from Bayer AG (Leverkusen, Germany) and PANI water suspension DW1032 obtained from Ormecon GmbH (Ammersbeck, Germany).

Ion-selective membrane

Lead-selective membrane contained (in wt.%): 1% of lead ionophore IV, 0.7% of NaTFPB, 64.3% oNPOE and 34% PVC, total of 200 mg of membrane components were dissolved in 2 mL of THF. Silver selective membranes contained (in wt.%) 2% of silver ionophore, 1% of NaTFPB, 70% of DOS, 27% of PVC, total of 200 mg of membrane components were dissolved in 2 mL of THF.

Preparation of all-plastic sensors

All-plastic sensors were prepared on acetate transparency sheets as described earlier [12, 13, 14], using 60 μL of either poly(3,4-ethylenedioxythiophene) or polyaniline. After drying of applied conducting polymer (resulting in a layer of thickness close to 0.01 mm), a strip of polytetrafluoroethylene (PTFE) adhesive was applied to isolate the transducer and the electrical lead part of the CP layer.

If not stated otherwise, on the prepared layers of conducting polymers, THF-based cocktails of ion-selective membranes were applied.

In a control experiment, deprotonated polyaniline layer was applied as a transducer part of all-plastic sensors—in this case, after applying PTFE tape, the transducer part of PANI was immersed in 0.1 M NaOH solution of 10 min (leading to visible change of PANI color from green to dark blue). Then the transducer part of PANI was well rinsed with water and left to dry in lab atmosphere and used as other PANI or PEDOT electrodes.

Onto the transducer part of future sensor, 20 μL of either lead or silver selective membrane cocktail was applied. The applied cocktail solvent was allowed to evaporate in laboratory atmosphere overnight. The thickness of dried ion-selective membranes (measured with micrometricaliper) was 0.03 mm.

Before the measurement, the part of the sensor with ion-selective membrane on it was conditioned first for 2 h in distilled water and then for 1.5 h in 10^{-3} M solution of primary ion nitrate.

A target for LA-ICP-MS were all-plastic sensors prepared exactly in the same way as those used in potentiometric measurements.

PANI layers for linear sweep voltammetry experiment were prepared by casting 10 μL of PANI dispersion on glassy carbon electrodes (diameter 3 mm) placed in upside down position; after drying of CP layers, these were either used directly in experiments, left in contact with 10^{-3} M AgNO_3 for 1 h and tested electrochemically or deprotonated in 0.1 M NaOH for 10 min, rinsed, dried in laboratory atmosphere and left in contact with 10^{-3} M AgNO_3 for 1 h. Voltammetric experiments were conducted in (silver ions free) 0.1 M KNO_3 .

Results and discussion

Although both conducting polymers applied to prepare all-plastic sensors were obtained in the form of aqueous dispersions, their oxidation state or conductivity differs significantly. According to the producers' specifications, Baytron P is characterized with conductivity close 10^{-5} S/cm; on the other hand, Ormecon polyaniline DW1032 is characterized with conductivity 200 S/cm. Baytron P specification acknowledges high presence of sodium polystyrenesulfonate in the dispersion, whereas Ormecon dispersion contains (among others) toluenesulfonate ions.

Silver selective all-plastic sensors

Figure 1 presents potentiometric responses of silver selective all-plastic sensors prepared using either PANI- or PEDOT-conducting polymers. As it can be seen from Fig. 1, both PANI and PEDOT all-plastic sensors were characterized with similar potentiometric responses within AgNO_3 activities from 0.1 to 10^{-5} M. The slopes of these part of characteristic were equal to 58.2 ± 0.5 mV/dec ($R^2=0.999$) and 60.7 ± 1.9 mV/dec ($R^2=0.995$) for PANI and PEDOT sensors, respectively. However, for lower activities, a pronounced difference was observed in E vs. $\log a \text{Ag}^+$ dependencies. For PANI-based sensor change of silver ions activity from 10^{-6} to 10^{-7} M corresponded to potential change slightly lower than 100 mV, pointing to super-Nernstian type of behavior of the electrode. On the other hand, for PEDOT based electrode, within low activities

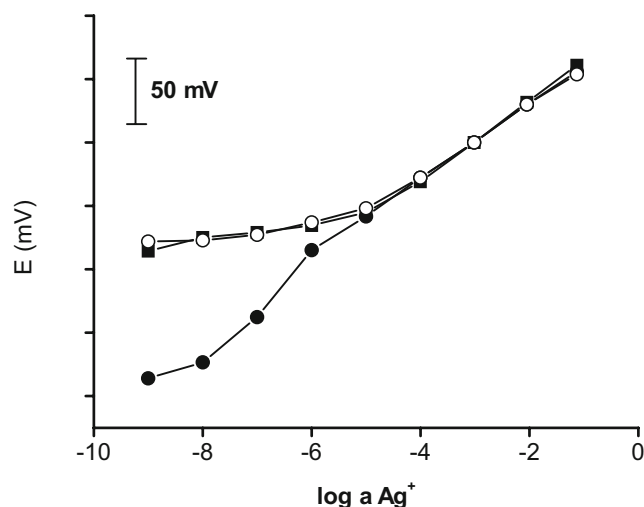


Fig. 1 Open circuit potentiometric responses of silver selective all-plastic sensors prepared using: (filled square) poly(3,4-ethylenedioxythiophene), (filled circle) polyaniline, (unfilled circle) polyaniline deprotonated (reduced) before casting of silver selective membrane. For easy comparison all curves were shifted to give equal potential at $\log a \text{Ag}^+ = -3$

range, the potential was practically independent of Ag^+ activity changes with detection limit equal to $10^{-5.4}$ M.

The high stability of PANI based Ag^+ -selective (in principle disposable) sensors should be highlighted: for activities higher than 10^{-6} mol/dm³ reproducibility of potentials recorded in subsequent calibrations was within the range of ± 1.5 mV. For lower activities higher changes in recorded potentials were observed; however, this effect was not unexpected taking into consideration broad activities range in which electrodes were tested (from 0.1 to 10^{-9} mol/dm³) [16].

Accordingly to the response patterns, selectivity coefficients obtained for tested sensors also differ significantly, Table 1. As it can be seen from Table 1 PANI based sensor was characterized with nearly three orders of magnitude lower selectivity coefficients compared to PEDOT-based electrode tested in parallel. Moreover, in the case of H^+ interferences, PANI-based sensor selectivity coefficient obtained was close to unbiased selectivity coefficient value reported earlier [19].

This pronounced difference in potentiometric responses for sensors with the same membrane in terms of composition and thickness, pretreated in the same way and tested in parallel point out to pronounced influence of applied conducting polymer transducer on potentiometric responses.

One of the possible reasons of observed differences can lay in different oxidation state of the two polymers used to prepare all-plastic sensors. As shown not only by our earlier results [20] but also by others [21–25], silver ions in solution tend to react spontaneously with semi-oxidized or reduced conducting polymers yielding oxidation of polymer on expense of deposition of metallic silver within the phase. It seems reasonable to expect that this phenomenon can occur also within the all-solid state conducting polymer based sensors on the interface of silver-selective membrane and semi-oxidized conducting polymer, and in the CP phase. This process can lead to accumulation of silver (metallic but at first of silver ions diffusing through the ion-selective membrane to the “reaction zone”) within the polymer close to the interface with ion-selective membrane and ultimately to classical (i.e. μM) detection limit of the

Table 1 Mean potentiometric selectivity coefficients

Ion J	$\log K_{\text{Ag},j}^{\text{pot}} \pm \text{SD}$ for sensor with transducer part:		
	PEDOT	PANI	Deprotonated PANI
H^+	-3.1 ± 0.7	-5.7 ± 0.1	-3.0 ± 0.3
Na^+	-3.5 ± 0.5	-6.0 ± 0.2	-3.1 ± 0.7

$\log K_{\text{Ag},j}^{\text{pot}} \pm \text{SD}$ obtained within the activities range from 10^{-1} to 10^{-4} mol/dm³, separate solution method, for all-plastic silver selective electrodes based on different conducting polymers, using experimental electrode slope

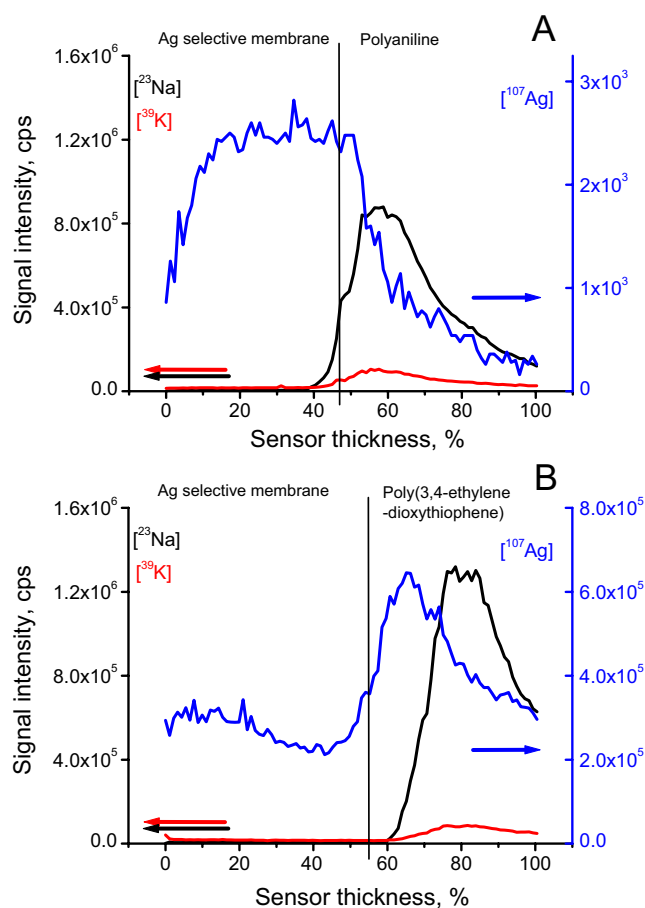


Fig. 2 Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested silver-selective electrode: **A** sensor prepared using polyaniline, **B** sensor prepared using poly(3,4-ethylenedioxythiophene). Black lines correspond to total signal, red lines to potassium signal, blue lines to silver signal. Vertical line visualizes approximated interface between silver selective membrane and underlying conducting polymer. Note y-axes scales difference

sensor applying semi-oxidized conducting polymer [2, 6], like PEDOT in the studied case.

To verify the above hypothesis, the LA-ICP-MS was used to evaluate the elements distribution through the investigated all-plastic sensor membranes. Obtained element's distribution profiles within the membrane thickness and underlying conducting polymer (recorded in one experiment) are presented in Fig. 2.

For PANI-based sensor, LA-ICP-MS data revealed presence of silver within the ion-selective membrane (signal intensities close to $2.5 \cdot 10^3$ cps); recorded silver signals were quite stable within the thickness of ion-selective membrane. There were practically no sodium or potassium within this phase. The change in the penetrated phase from ion-selective membrane to the PANI layer was marked by quite rapid increase of both sodium and potassium signal intensities. These elements are components of conducting polymer solution as indicated by

LA-ICP-MS experiment performed for “electrical lead” part of the conducting polymer (results not shown). However, silver signals intensities decreased rapidly to values close to zero while going through this phase, suggesting that there was a little silver inside the conducting polymer (in the region where relatively high ^{39}K and ^{23}Na signals intensities were recorded).

This picture suggests that for PANI based sensor majority of silver is present in the ion-selective membrane, while sodium and potassium are remaining within the conducting polymer. The composition of the transducer layer (relatively high contents of interferents and some of analyte) correlates well with the presence of super-Nernstian potential jump on the E vs. $\log a \text{Ag}^+$ dependence [e.g. 6].

A quite different picture was obtained for PEDOT based sensor. In the membrane, close to sensor outer surface ^{107}Ag signals intensities were close to $3 \cdot 10^5$ cps, i.e. were significantly higher compared to values recorded for the same membrane placed over PANI. Going deeper into the sensor silver signals intensities slightly decreased close to the membrane-conducting polymer boundary. Then silver signals intensities rise abruptly at about 55% to 60% of sensor thickness, i.e. at the region that corresponds to the outer layer of the conducting polymer, to the level of more than $6 \cdot 10^5$ cps, being orders of magnitude higher than silver intensities recorded for similar region of PANI based sensor. After reaching the maximum, silver signals intensities decrease slowly while going throughout the CP part of the sensor to reach—deep in the polymer—values close to $3 \cdot 10^5$ cps. As expected, within the conducting polymer, both potassium and sodium signal intensities increased compared to the ion-selective membrane layer; however, this increase was gradual and maximal intensities of the two elements were observed at the penetration depth where silver signal intensities were already decreasing. The profiles recorded for polymer phase of PEDOT sensor suggest that silver can be accumulated replacing sodium/potassium within the transducer part of the polymer (no silver was present in the electrical lead part of the sensor—results not shown).

Taking into consideration earlier reports [20–25] it seems highly probable that accumulation of silver ions in the (semi-oxidized) PEDOT layer is enhanced by spontaneous reduction of silver ions to Ag^0 . This process requires removal of sodium/potassium ions from the polymer phase or exchange of these for silver(I) ions. Ultimate consequence of the process is high contents of silver (ions and metal) beneath the ion-selective membrane of PEDOT based all-plastic sensor after conditioning, which results (in the case of first of the two silver species) in micromolar detection limit of this type sensors.

The above considerations were supported by results of potentiometric studies of all-plastic sensor prepared using

PANI, which was deprotonated (i.e. reduced) in the transducer part of the electrode by relatively short contact with NaOH solution, before application of silver-selective membrane. The occurrence of this process can be monitored visually by change of the color of transducer part of the PANI (while on acetate sheet) from green to dark blue [26]. As it can be seen from Fig. 1 the sensor prepared using deprotonated PANI as transducer was characterized with potentiometric responses the same (within the range of experimental error) as PEDOT based one. Linear potentiometric dependence of recorded potentials on logarithm of silver ions activity was obtained within the activities range from 0.1 to 10^{-5} M with slope equal to 55.4 ± 1.2 mV/dec ($R^2=0.998$) and detection limit equal to $10^{-5.6}$ M. Also the selectivity coefficients, Table 1, recorded for deprotonated PANI electrode were within the limit of experimental error equal to values obtained for PEDOT based sensor.

The results obtained for deprotonated PANI transducer support the thesis that oxidation state of the polymer–transducer can influence the response pattern of the sensor in the case when spontaneous redox reaction between the transducer and analyte ion can occur. Moreover less oxidized state of the CP stimulates incorporation of cations (Ag^+) from the sample solution.

Also results of linear sweep voltammetry experiment performed on glassy carbon electrodes have supported this statement. The current vs. potential curves were recorded within potentials range from 0.4 to 0.9 V for PANI film (results not shown) in silver ions free KNO_3 . Regardless if PANI was or was not in contact with silver(I) ions no peaks were recorded. However, for deprotonated (reduced) PANI that has been left in contact with Ag^+ ions prior to this experiment, a pronounced current peak was recorded at +0.52 V, which can correspond to electrochemical oxidation of Ag^0 spontaneously accumulated on/within the polymer.

Interestingly, these results are in line with electrochemical intuition suggesting using as transducer a more oxidized polymer (which is usually coupled with higher redox capacity of the layer) as potentially leading to better performance of the sensor in terms of analytical characteristic (detection limit, selectivity and stability) which is in good accordance with previously published reports [e.g. 6].

Lead selective all-plastic sensors

Figure 3 presents potentiometric responses of lead selective all-plastic sensors prepared using either PANI or PEDOT conducting polymers. PEDOT sensors were characterized with linear responses within the activity range from 10^{-2} to 10^{-8} M with slope equal to 29.1 ± 0.7 mV/dec ($R^2=0.997$) and detection limit equal to $10^{-8.1}$ M. PANI-based electrodes were characterized with linear responses within

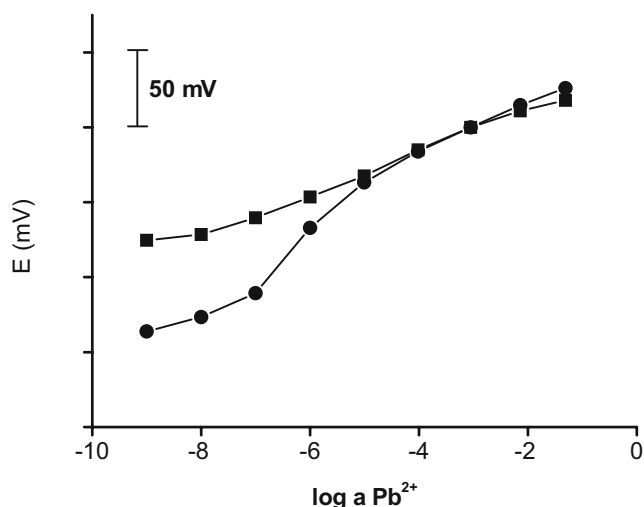


Fig. 3 Open circuit potentiometric responses of lead selective all-plastic sensors prepared using: (*filled square*) poly(3,4-ethylenedioxythiophene), (*filled circle*) polyaniline. For easy comparison, all curves were shifted to give equal potential at $\log a \text{Pb}^{2+} = -4$

activities range from 10^{-1} to 10^{-5} with slope equal to 33.9 ± 1.5 mV/dec ($R^2 = 0.994$). Dilution of $\text{Pb}(\text{NO}_3)_2$ solution from 10^{-6} to 10^{-7} M resulted in the case of PANI sensor in about 90 mV potential decrease.

Selectivity coefficients obtained for tested lead(II) sensors are gathered in Table 2. Accordingly to potentiometric characteristic recorded, PEDOT-based sensor were characterized with higher values of $K_{\text{Pb},\text{J}}$ compared to electrodes using PANI tested in parallel. Nevertheless, log of selectivity coefficients obtained for PANI sensors were lower compared to unbiased values reported for internal-solution electrode [27], suggesting (together with position on activity scale and magnitude of super-Nernstian potential shift) some accumulation of lead ions in the transducer phase (but still smaller than recorded for PEDOT). There should be noted that the redox potential of $\text{Pb}^{2+}/\text{Pb}^0$ redox couple is almost 1 V lower compared to the silver counter part. Therefore, spontaneous deposition of lead within studied conducting polymer is hardly possible.

The results of LA-ICP-MS experiments are presented in Fig. 4. For both sensors lead signals intensities within the

Table 2 Mean potentiometric selectivity coefficients

Ion J	$\log K_{\text{Pb},\text{J}}^{\text{pot}} \pm \text{SD}$ for sensor with transducer part:	
	PEDOT	PANI
H^+	-2.8 ± 0.1	-4.8 ± 0.3
Na^+	-2.9 ± 0.5	-4.3 ± 0.8

$\log K_{\text{Pb},\text{J}}^{\text{pot}} \pm \text{SD}$ obtained within the activities range from 10^{-2} to 10^{-4} mol/dm³, separate solution method, for all-plastic lead selective electrodes based on different conducting polymers, using experimental electrode slope

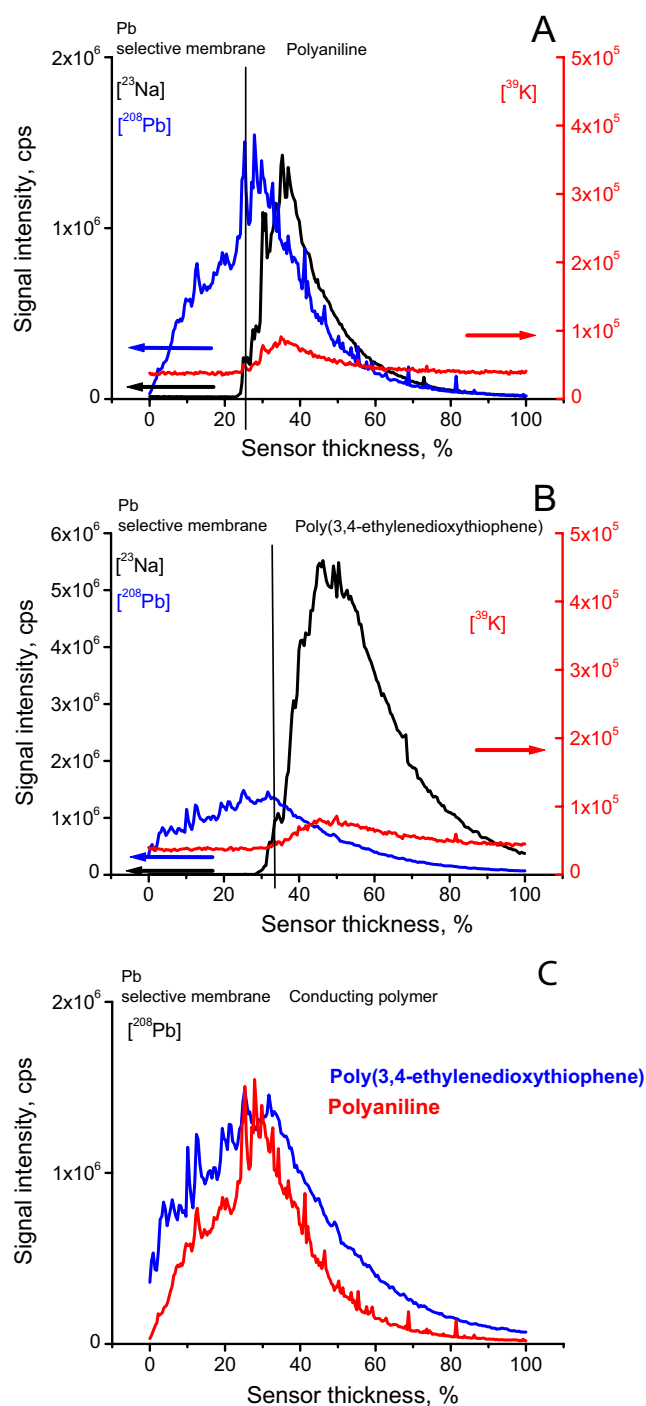


Fig. 4 Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested lead-selective electrode: **A** sensor prepared using polyaniline, **B** sensor prepared using poly(3,4-ethylenedioxythiophene). *Black lines* corresponds to sodium signal, *red lines* to potassium signal, *blue lines* to lead signal. *Vertical line* visualizes approximated interface between lead selective membrane and underlying conducting polymer. Note y-axes scales difference. **C** comparison of lead signals intensities recorded for polyaniline and poly(3,4-ethylenedioxythiophene)

ion-selective membrane were similar, slightly increasing while going into membrane-conducting polymer interface to reach about $1 \cdot 10^6$ or $1.4 \cdot 10^6$ cps, close to this interface, for PANI- and PEDOT-based sensor, respectively. For both sensors, lead signals were recorded also for the conducting polymer phase (marked by the potassium signals intensity increase, in both cases); however, lead signal intensities were gradually decreasing in the conducting polymer phase. Comparison of lead signal intensities recorded presented in Fig. 4c shows that somewhat higher counts per second values, both in the ion-selective membrane and in conducting polymer phase, were—as expected on the basis of potentiometric responses shown in Fig. 3—obtained for PEDOT-based sensor, suggesting higher contents of lead in this case. Higher contents of lead in the sensor phases of PEDOT all-plastic electrode results in linear responses within whole tested activity range, on the other hand for PANI sensor lower contents of lead, especially in the conducting polymer phase yields super-Nernstian behavior for activities lower than 10^{-6} M. Interestingly, for both types of sensors, practically no sodium was present in the ion-selective membrane phase; however, relatively high sodium intensities were recorded for conducting polymer parts of the sensors. Higher sodium signal intensities were obtained for PEDOT-based electrode; in contrary to PEDOT-based silver selective sensor, high sodium intensities were recorded already close to the membrane-conducting polymer interface. In the case of Pb^{2+} selective sensor, sodium intensities within the PEDOT layer were also higher compared to that recorded for Ag^+ selective electrode. For PANI-based sensor, high sodium signal intensities were also observed close to the ion-selective membrane-conducting polymer interface; however, in this case, the magnitude of signals was more comparable with that recorded for PANI-based Ag electrode.

A more similar picture of elements contents and distribution in both PANI and PEDOT lead sensor phases compared to Ag^+ -selective counterparts suggests similar mechanism of interactions between lead ions and conducting polymers applied, being independent of the oxidation state of applied CP transducer. In the case of PEDOT, it seems probable that ion-exchange properties of poly(4-styrenesulphonate) ions used to stabilize the conducting polymer suspension [28] are responsible for effective decrease of free lead ions activity within the PEDOT phase leading to enhanced detection limit of the sensor. Unfortunately, composition of PANI suspension is not known beyond the presence of toluenesulfonate ions in it. However, it is interesting to speculate about similar mechanism in the case of polyaniline based electrode, possibly due to the presence of different components, different binding parameters (kinetic and equilibrium) applies, yielding lower lead activity in the PANI film for exactly the same sensor pretreatment.

Conclusions

Herein, presented results confirm that careful choice of conducting polymer transducer is important factor while preparing all-solid state sensor. Both for silver and lead selective electrodes, polyaniline results in super Nernstian type behavior observed for activities lower than 10^{-6} M and higher selectivity coefficients. In the case of silver sensor, this effect is related to higher oxidation state of the polymer (coupled with higher conductivity). In the case of lead electrode, most probably, ions stabilizing suspension or dopant ions present in the commercially available polymer dispersion are responsible for the observed behavior.

Although these experiments were limited to all-plastic sensor, the results obtained can be useful for more general considerations related to all-solid-state sensors with conducting polymer underlying ion-selective membranes.

Acknowledgements Baytron P was obtained on courtesy of Bayer AG. This work was supported from scientific research funds (Poland) within the research project N204 242234 for years 2008-2011 (AM, WJ, KM) and from the project 120000-5011/68-BW-175616 at Warsaw University (MW).

References

1. Bobacka J (2006) *Electroanalysis* 18:7–18
2. Michalska A (2006) *Anal Bioanal Chem* 384:391–406
3. Lindfors T, Ivaska A (2004) *Anal Chem* 76:4387–4394
4. Sjöberg-Erola P, Bobacka J, Lewenstam A, Ivaska A (2007) *Sens Actuators B* 127:545–553
5. Vázquez M, Bobacka J, Ivaska A, Lewenstam A (2002) *Sens Actuators B* 82:7–13
6. Michalska A, Skompska M, Mieczkowski J, Zagórska M, Maksymiuk K (2006) *Electroanalysis* 18:763–771
7. Bobacka J, Lahtinen T, Nordman J, Häggström S, Rissanen K, Lewenstam A, Ivaska A (2001) *Electroanalysis* 13:723–726
8. Bobacka J, Lahtinen T, Koskinen H, Rissanen K, Lewenstam A, Ivaska A (2002) *Electroanalysis* 14:1353–1357
9. Bobacka J, Väänänen V, Lewenstam A, Ivaska A (2004) *Talanta* 63:135–138
10. Vázquez M, Danielsson P, Bobacka J, Lewenstam A, Ivaska A (2004) *Sens Actuators B* 97:182–189
11. Perea H, Fordyce K, Shvarev A (2007) *Anal Chem* 79:4564–4573
12. Michalska A, Maksymiuk K (2004) *Anal Chim Acta* 523:97–105
13. Michalska A, Ocypa M, Maksymiuk K (2005) *Electroanalysis* 17:327–333
14. Kisiel A, Michalska A, Maksymiuk K (2007) *Bioelectrochemistry* 71:75–80
15. Michalska A, Wojciechowski M, Bulska E, Maksymiuk K (2008) *Electrochem Commun* 10:61–65
16. Rzewuska A, Wojciechowski M, Bulska E, Hall EAH, Maksymiuk K, Michalska A (2008) *Anal Chem* 80:321–327
17. Lyczewska M, Wojciechowski M, Bulska E, Hall EAH, Maksymiuk K, Michalska A (2007) *Electroanalysis* 19:393–397
18. Konopka A, Sokalski T, Lewenstam A, Maj-Zurawska M (2006) *Electroanalysis* 18:2232–2242

19. Ceresa A, Radu A, Peper S, Bakker E, Pretsch E (2002) *Anal Chem* 72:4027–4036
20. Ocypta M, Ptasińska M, Michalska A, Maksymiuk K, Hall EAH (2006) *J Electroanal Chem* 596:157–168
21. Zhang AQ, Cui CQ, Lee JY, Loh FC (1995) *J Electrochem Soc* 142:1097–1113
22. Ivanov S, Tsakova V (2005) *Electrochim Acta* 50:5616–5623
23. Clarke TC, Geiss RH, Kwak JF, Street GB (1978) *J Chem Soc Chem Commun* 489–490 doi:[10.1039/C39780000489](https://doi.org/10.1039/C39780000489)
24. Pałys BJ, Skompska M, Jackowska K (1997) *J Electroanal Chem* 433:41–48
25. Lebedev MY, Lauritzen MV, Curzon AE, Holdcroft S (1998) *Chem Mater* 10:156–163
26. Lindfors T, Harju L, Ivaska A (2006) *Anal Chem* 78:3019–3026
27. Sokalski T, Ceresa A, Fibbioli M, Zwickl T, Bakker E, Pretsch E (1999) *Anal Chem* 71:1210–1214
28. Li W, Teasdale PR, Zhang S, John R, Zhao H (2003) *Anal Chem* 75:2578–2583