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Element profiles in galvanostatically polarized K$^+$-selective all-solid-state sensors with poly(vinyl chloride)-based membranes

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Abstract The influence of galvanostatic polarization on ion concentration profiles in all-solid-state ion-selective sensors was studied. As a model system K$^+$-selective electrode with poly(vinyl chloride)-based membrane, ionophore–valinomycin and polypyrrole doped by chloride ions as ion-to-electron transducer was selected. The ion exchanger—a typical component of ion-selective membrane—was replaced by lipophilic salt: tetradodecylammonium tetrakis(4-chlorophenyl) borate to avoid spontaneous extraction of potassium ions. Potassium, sodium, and chlorine distribution within the sensor phases were studied using laser ablation micro-sampling followed by inductively coupled plasma mass spectrometry measurements. The experiments revealed accumulation of potassium ions in course of cathodic galvanostatic polarization, with concentration decreasing by moving inside the ion-selective membrane. The surface content of K$^+$ ions was found to be linearly dependent on applied current. Influence of sequential anodic galvanostatic polarization or open circuit conditioning applied after cathodic polarization revealed only limited recovery of the initial concentration profiles in the membrane.

Keywords Potassium selective electrode · Chronopotentiometry · LA ICP MS · Elements distribution profile · Polypyrrole

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Introduction

In the field of potentiometric ion-selective sensors, significant development has been observed in recent years related both to improvement of analytical parameters: lower detection limit, better selectivity, as well as to simpler construction and miniaturization [1–3]. The latter issue is strictly connected with development of all-solid-state sensors, where the internal solution and internal reference electrode are replaced by an ion-to-electron transducing layer, one of the most promising transducer materials are conducting polymers [4–6].

Although the role of potentiometric sensors with ion-selective membranes rapidly increases in modern electro-analysis, their advantages are not fully explored by working exclusively under open circuit conditions. Additional superior benefits related to this class of sensors can be exposed under conditions of external polarization. Therefore, dynamically emerging research area concerns application of potential or current controlled methods for ion-selective electrodes (e.g., first works [7, 8]). However, a significant problem limiting effective usage of such methods is influence of large ohmic resistance of typical ion-selective plastic membranes. From this point of view, particularly promising are galvanostatic methods, where the ohmic potential drop influence can be easily measured and separated. Moreover, a precise current aided control of ion fluxes in the membrane during measurement or conditioning step is helpful in compensation of undesired primary ions release into the sample, thus leading to lowering detection limit, both for internal solution [9–12] and all-solid-state sensors [13–15]. Bakker and Shvarev have proposed a working mode with short galvanostatic pulses (pulstrodes), which resulted in adjustable selectivity and enhanced sensitivity [16, 17]. This method is especially

useful for determination of biologically important multi-charged ions [18], where open-circuit potentiometry gives either drifts due to spontaneous extraction of ions or slopes equal to just a few mV per decade (under equilibrium conditions). Current-based methods are also helpful in obtaining unbiased selectivity coefficients [19, 20].

Chronopotentiometry is beneficial not only for improvement of analytical parameters of ion-selective electrodes, but also can be an effective diagnostic tool to study properties of ion-selective sensors properties, their components and interfaces. Bobacka [21, 22], by using a simple equivalent circuit model, has shown that current reversal chronopotentiometry can bring information about membrane resistance, equilibrium potential of the electrode, as well as redox capacitance of the conducting polymer solid contact. In recent papers, Lindner et al. [23, 24] have presented a mathematical model providing calculations of concentration polarization related to transport of ionophore and cation–ionophore complexes in the galvanostatically polarized membranes. This model enables also determination of diffusion coefficients of these species.

Additional benefit of chronopotentiometry results from recording separate responses from different sensors components only by varying the experimental conditions as electrolysis time, applied current or electrolyte concentration in solution. For relatively concentrated solution and low current/short electrolysis time, concentration polarization effects, both in solution and sensor components (membrane and solid contact) can be neglected. In such a case, information about capacitance of the solid contact or interfaces can be derived from linear dependences of potential on time, as shown by Bobacka [21]. However, for high-electrolyte concentration but higher currents/longer times than in previous case, concentration polarization in the membrane becomes important, and diffusion-like phenomena on chronopotentiograms can be observed. On the other hand, if electrolyte concentration decreases, concentration polarization effects in solution predominate [15] and under such conditions low detection limit of the sensor can be affected by applied current.

An important but still unresolved problem is ion transport nature and ion concentration profiles within the membrane under chronopotentiometric conditions; therefore, it requires supplementary information which can be hopefully delivered by modern instrumental techniques. Lindner et al. [25–29] have visualized concentration profiles in the membrane using VIS spectroscopy. However, such studies require a dedicated, tailored instrumentation, moreover, changes in the membrane composition compared to that used in ion-selective membranes (as incorporation of chromoionophore) are necessary.

In our recent preliminary communications [30], we have described a new approach enabling visualization of ele-ments distribution profiles in the galvanostatically polarized membranes using the laser ablation inductively coupled plasma mass spectrometry (LA ICP MS). By using laser microsampling, an original membrane of composition typical for application in ion-selective electrodes can be used and information about ion transport of primary ions and interfering ones could be obtained in one experimental run.

The above-mentioned paper has concerned membranes of classical internal solution sensors. The aim of the present communication is to show results obtained for an all-solid state sensor, under galvanostic polarization conditions, with additional highlight of ion-selective membrane/conducting polymer interface. Suitability of LA ICP MS technique to study concentration profiles in all-solid-state ion sensors with polypyrrole solid contact, under open circuit conditions, has been proven by Konopka et al. [31].

In our work, as a model example, electrodes with poly (vinyl chloride)-based potassium selective membranes containing ionophore valinomycin, and polypyrrole solid contact were selected.

Experimental

Apparatus

An inductively coupled plasma mass spectrometer ELAN 9000 (Perkin Elmer, Germany) equipped with the laser ablation system LSX-200+ (CETAC, USA) was used, experimental details were described in [32]. At each pulse, a small amount of the membrane was evaporated, transported to ICP and then analyzed by mass spectrometry. Depending on the exposure time and energy of the laser beam, micro-amount of membrane material from different depths can be collected. Thus, the relation: signal intensity vs. evaporation time can be converted to a dependence of intensity of the signal (recorded for elements of interest) on the distance inside from the membrane surface.

Electrochemical experiments were carried out using potentiostat/galvanostat CH 660 (CH Instruments, USA), in one-compartment cell with working all-solid-state ion-selective electrode described below and platinum counter electrode (surface area 2 cm^2). As reference electrode Ag/AgCl Möller Glasbläserei (Zürich, Switzerland) with 1 M lithium acetate in outer sleeve was used.

Reagents

Tetrahydrofuran (THF), poly(vinyl chloride) (PVC), bis (2-ethylhexyl) sebacate (DOS), tetradodecylammonium tetrakis(4-chlorophenyl) borate (ETH 500) and ionophore valinomycin were from Fluka AG (Buchs, Switzerland).

Doubly distilled and freshly deionised water (resistance 18.2 MΩcm, Milli-Qplus, Millipore, Austria) was used throughout this work. All other reagents were of analytical grade and were obtained from POCh (Gliwice, Poland) with the exception of monomer pyrrole, obtained from Aldrich (Steinheim, Germany). Distilled pyrrole was stored in a refrigerator and prior to its use was purified by passing through an alumina gel mini-column.

All-solid-state electrodes

Home-made electrodes with exchangeable glassy carbon disks tips of surface area 0.07 cm^2 were used to prepare all-solid-state ion-selective electrodes. This construction enabled LA ICP MS studies of the membrane and polypyrrole layer without removing the membrane from the electrode surface. The substrate electrodes were polished with Al_2O_3, 0.3 μm.

These electrodes were coated with a polypyrrole film obtained in course of potentiostatic electrodeposition at 0.9 V, passing charge 100 mC, from aqueous solution containing 0.05 M pyrrole and 0.1 M NaCl, to yield polypyrrole doped with chloride anions.

The ion-selective membrane contained (in wt%): 3.5% of valinomycin, 2.2% of ETH 500, 64.8% DOS, and 29.5% PVC. Total 93 mg of membrane components were dissolved in 3 ml of THF and applied as described below.

Polypyrrole films obtained as described above were placed in a position with the polymer film facing up. The top of the electrode was covered with pipetted 50 μl THF solution of membrane components, resulting in c.a. 100-μm-thick membrane. The obtained electrodes were conditioned in water for 24 h.

If not stated otherwise, the all-solid-state electrodes were then polarized galvanostatically for 180 s in 0.05 M K_2SO_4 solution, using currents of various magnitude and direction (cathodic and/or anodic).

After polarization, the glassy carbon disks with the ion-selective membrane and polypyrrole transducer were dismounted from the electrode body, well rinsed with water and tissue dried. Then, they were immediately placed in a holder of LA ICP MS chamber in upside down position, i.e., the outer PVC membrane was facing the laser beam. Each LA ICP MS profile determination was repeated a few times (at least in triplicate) from various parts of the membrane.

Results and discussion

The composition of ion-selective membranes of electrodes used in chronopotentiometric mode should be different from those used in classical open-circuit potentiometry [16]. The ion-exchanger should be replaced with a salt of lipophilic both cation and anion to avoid spontaneous accumulation of ions, accompanying galvanostatic process. In this work, the lipophilic salt applied was tetradodecylammonium tetrakis(4-chlorophenyl) borate (ETH 500). The membranes prior to galvanostatic experiment were conditioned in water; therefore, they did not contain primary ions (K^+) before current application.

The polypyrrole transducer was polymerized from NaCl solution (instead of typical KCl) to avoid presence of K^+ ions in the polymer and thus to avoid influence on K^+ amount in the membrane. Moreover, carrying out polymerization using different electrolyte from that in galvanostatic experiment opens possibility to follow independently ions contents changes both in the conducting polymer and in the membrane, using LA ICP MS method.

In course of galvanostatic experiment, the conducting polymer layer was either oxidized or reduced. The maximal current used in the process was $1.2 \cdot 10^{-6}$ A, thus the flowing charge was close to $2 \cdot 10^{-4}$ C, i.e., about 2% of the oxidation charge accumulated in the polypyrrole layer. Therefore, the change of polypyrrole oxidation state during chronopotentiometric experiment was negligibly small.

Figure 1 presents examples of chronopotentiometric curves recorded for potassium all-solid-state sensors, for two values of cathodic current. The cathodic polarization is expected to stimulate K^+ ions incorporation into the membrane. Potentials recorded for higher currents are much lower, due to influence of ohmic resistance of the membrane. From the potential difference at the beginning of the measurement (ΔE), the approximate resistance value can be estimated from ΔE/(current difference), and the obtained value is close to 1 MΩ, a typical value for the used PVC-based membrane.
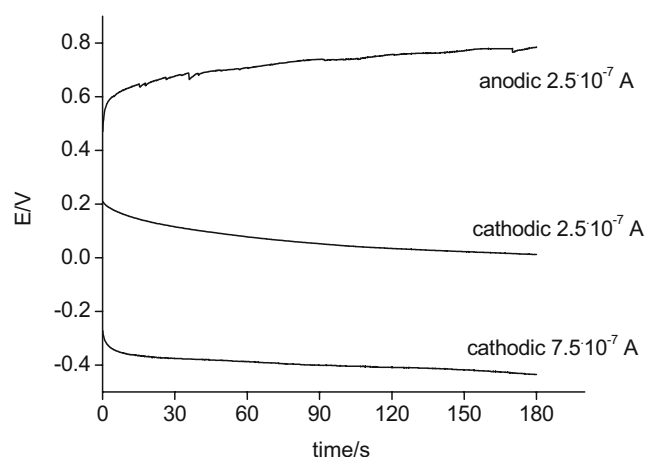
Fig. 1 Chronopotentiometric curves recorded for all-solid-state K^+-selective electrodes

Chronopotentiometric curves (Fig. 1) are significantly bent pointing to diffusion limitations in current flow, resulting in concentration polarization effects. Moreover, for the higher cathodic current, the potential decrease at the end of experiment becomes faster suggesting lowering of free ionophore concentration close to the membrane surface.

For a simple case of linear diffusion limited process, the concentration change at an interface can be described by the formula [33]:

$$c(0,t) = c^0 \pm \frac{2I}{nFA(D\pi)^{1/2}} t^{1/2} \qquad (1)$$

where c^0 and $c(0,t)$ are concentrations of transferred species in bulk and at the interface, respectively, I is applied current, n = number of electrons, F = Faraday's constant, A = electrode surface area, D = diffusion coefficient of transferred species, and t = time. The $\pm$ sign depends on flux direction of transferred species.

Equation 1 enables rough estimation of concentration polarization effects (migration neglected). For K^+ ions in the electrolyte solution ($c^0 = 10^{-4}$ mol·cm^{-3}, $D = 2 \cdot 10^{-5}$ cm^{2}s^{-1} [34], $n = 1$) and cathodic current $I = 7.5 \cdot 10^{-7}$ A, the relative change of K^+ concentration (solution close to the membrane vs. solution bulk) is below 0.5%. On the other hand, for free ionophore ($c^0 \sim 7\ 10^{-5}$ mol cm^{-3}, $D = 2 \cdot 10^{-8}$ cm^{2}s^{-1} [23], $n = 1$) and the same current and electrolysis time, the change (interface vs. membrane bulk) is approaching 15%, pointing to significant concentration polarization effect, visible on the chronopotentiometric curve (Fig. 1).

However, more significant changes of concentration should relate to K^+ ions in the membrane, because the membrane is initially void of these ions. Information about potassium ions distribution can be collected directly from LA ICP MS experiments. Figure 2 presents exemplary results—dependence of signals of elements ^{39}K, ^{23}Na, and ^{35}Cl within the sensor on the distance from the membrane surface. These signals were expected to bring information about cations incorporation form the solution to the membrane (^{39}K), from the polypyrrole layer to the membrane (^{23}Na) and anion transfer (^{35}Cl). Although chlorine is present both in PVC and polypyrrole (doping chloride ions), it is uniformly distributed in both phases. Thus, any deviations from this distribution can suggest interfacial transfer. The "sensor thickness" value 0 corresponds to the membrane/solution interface. Inside membrane, the sodium signal is rather low (the membrane did not contain sodium ions), but then a sharp increase is observed, corresponding to approaching the polypyrrole layer containing Na$^+$ cations (accumulated from the polymerization solution). A similar sharp signal intensity change marking the membrane/polypyrrole interface was visible for ^{35}Cl.
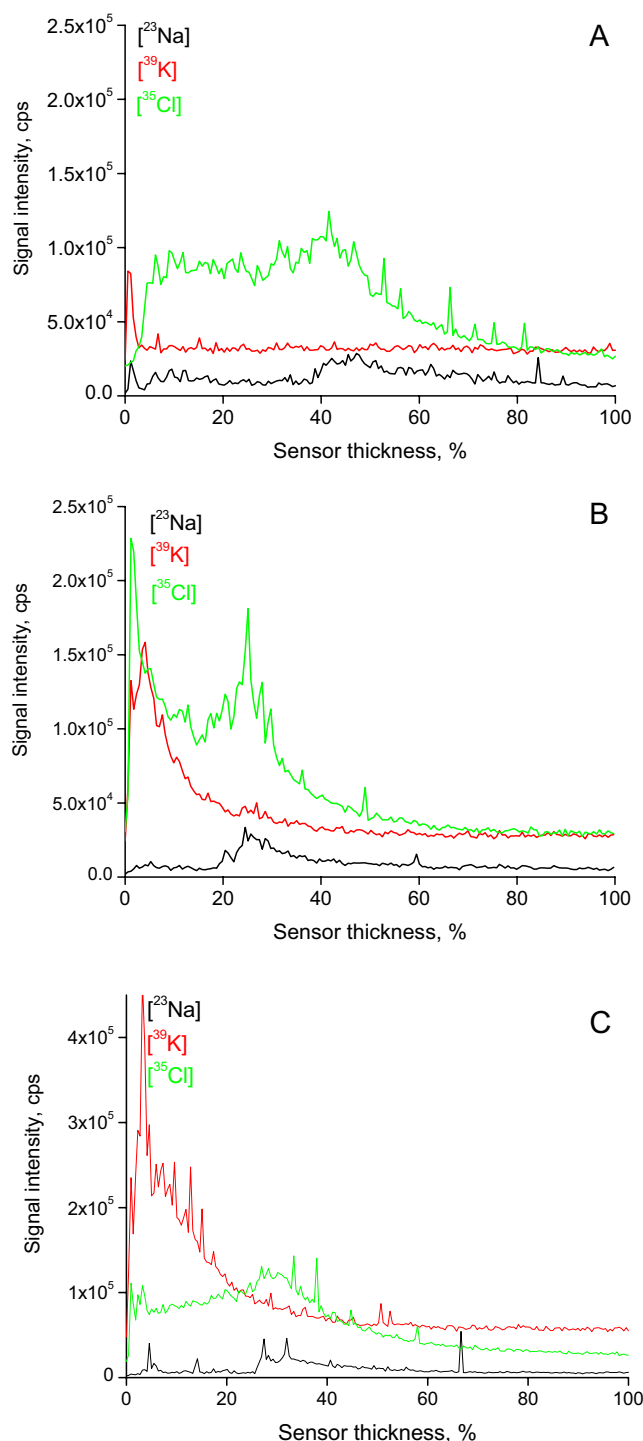
Fig. 2 Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested all-solid state potassium electrodes: **a** as prepared sensor (no current applied), **b** sensor polarized with cathodic current 2.5 10^{-7} A, **c** sensor polarized with cathodic current 7.5 10^{-7} A. *Black lines* correspond to sodium signal, *red lines* to potassium signal, *green lines* to chlorine signal

One should be aware of possible limitations and errors related with this method and available parameters, resulting e.g., in membrane fractionation or conical crater formation inside the membrane. The influence of such errors was
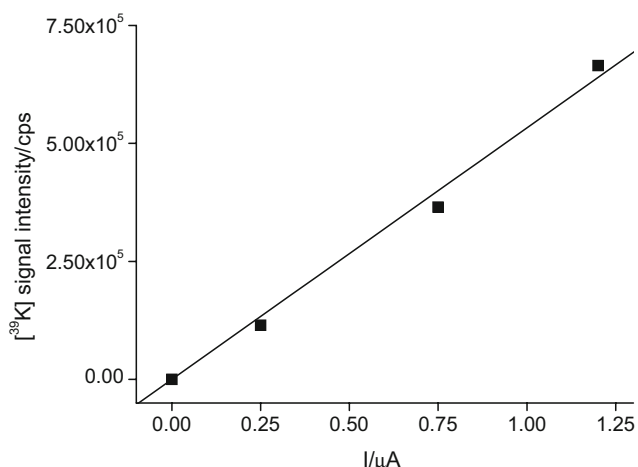
Fig. 3 Dependence of the membrane surface signal intensity of ^{39}K on cathodic current

reduced by comparing the results for non-polarized (blank) and polarized membranes, and by repeating ablation from various parts of the same membrane.

For a non-polarized membrane (only conditioned in water) a low level of potassium was observed, which can be regarded as a background level (Fig. 2a). After cathodic chronopotentiometric polarization (I=2.5 10^{-7} A, Fig. 2b) significantly higher amount of potassium was recorded, especially close to the membrane/solution interface and then the signal was lowering in the membrane bulk. This result confirms the hypothesis of the galvanostatically forced incorporation of K^+ ions into the membrane. Since the membrane did not contain removable ions, the charge carriers at the polypyrrole/membrane interface should be chloride ions released from polypyrrole to the membrane, ensuring eleectroneutrality of reduced conducting polymer. Figure 2b confirms the role of chloride ions showing a peak of Cl signal at the distance corresponding to the membrane/polypyrrole interface.

For higher currents, qualitatively similar results were obtained (results for I=7.5 10^{-7} A were shown, Fig. 2c), only the signal of potassium, particularly at the membrane/solution interface was increasing with rising current magnitude. Using Eq. 1 and assuming for K^+ in the membrane c^0=0, the surface concentration of K^+ ions in the membrane ($c(0,t)$) should be linearly dependent on applied current magnitude. Since the ICP MS signal is proportional to the concentration of the element in the membrane, a linear dependence of ^{39}K signal on I will be expected. Figure 3 shows such dependence confirming this assumption, even for high currents where ionophore depletion close to the membrane/solution interface is significant. In such a case, also free K^+ ions, non-complexed by the ionophore, are expected to be transferred across the membrane. Since results concerning the membrane surface were taken into consideration, positive errors

resulting from conical crater formation are of negligible significance in this case.

In the case of anodic polarization, the shape of chronopotentiometric curves is significantly dependent on the magnitude of applied current (Fig. 1). For I=2.5 10^{-7} A, a curve of similar shape as for cathodic process (but with potential increase) was recorded, while for higher current ($7.5 \cdot 10^{-7}$ A) a relatively stable potential around + 3V was achieved (results not shown). The latter effect can result from limitations in charge transfer across the interfaces because this process should be accompanied either by anions transfer from the membrane to the conducting polymer (transferable anions are not available in the membrane) or incorporation of Na^+ cations from polypyrrole to the membrane (present in limited amount because the anion-exchanging form of polypyrrole was applied). These expectations were confirmed by LA ICP MS results (Fig. 4). The potassium signal is much lower than in case of
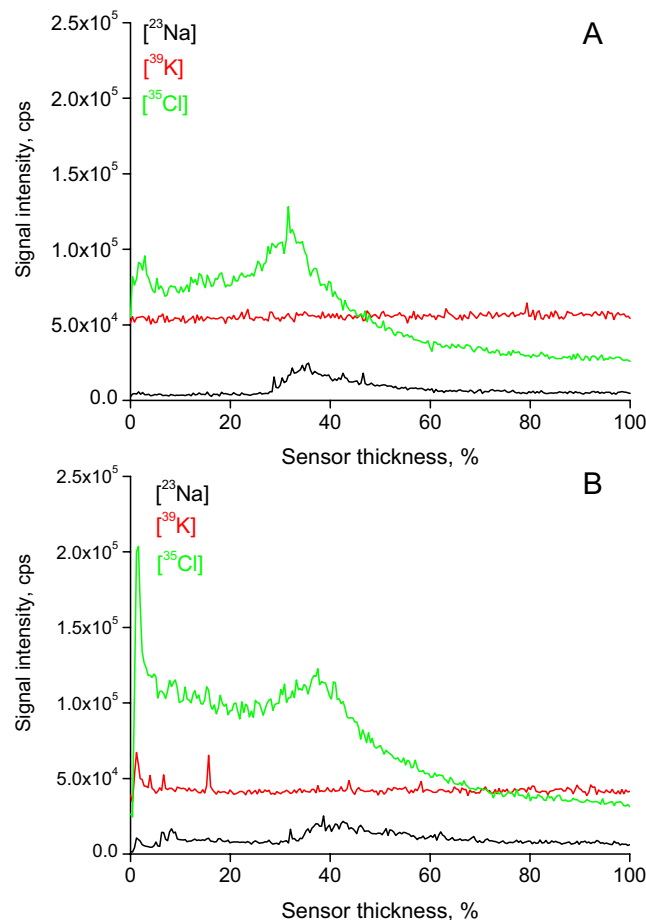
Fig. 4 Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested all-solid state potassium electrodes: **a** sensor polarized with anodic current 2.5 10^{-7} A, **b** sensor polarized with anodic current 7.5 10^{-7} A. *Black lines* correspond to sodium signal, *red lines* to potassium signal, *green lines* to chlorine signal
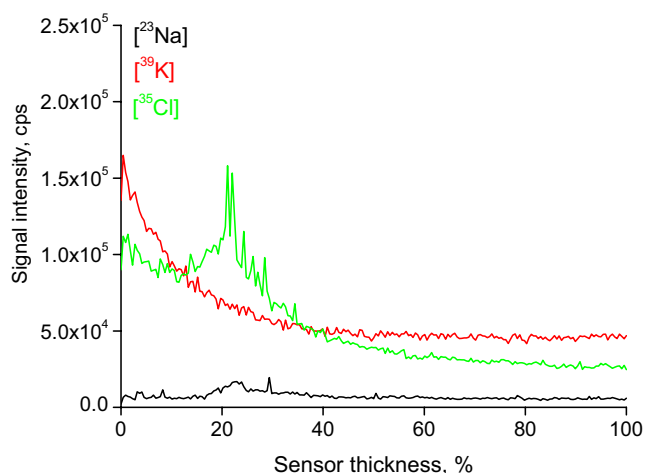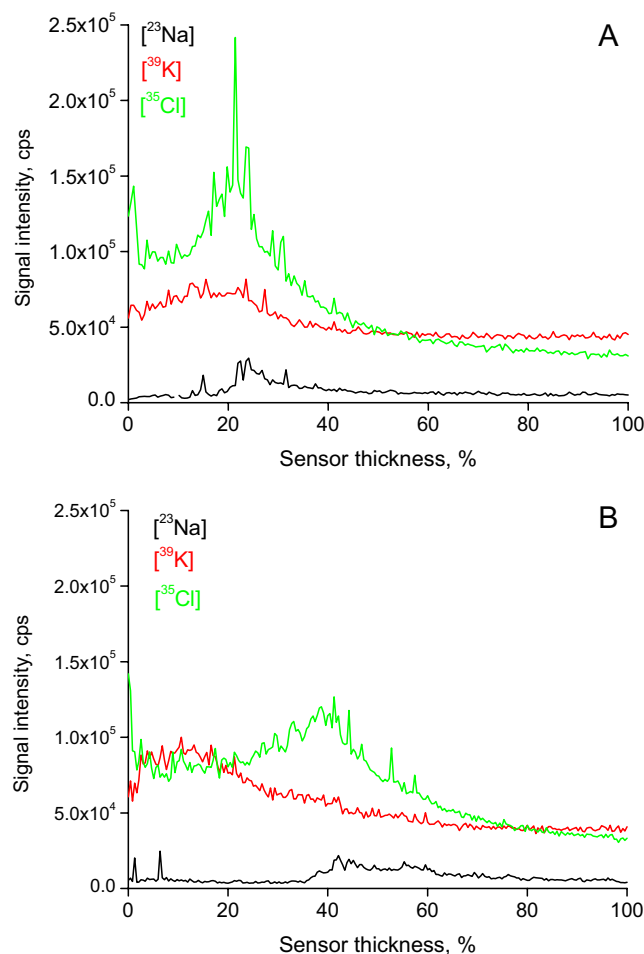
Fig. 5 Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested all-solid state potassium electrode polarized first with cathodic current, and then with anodic current, both equal to $7.5 \ 10^{-7}$ A. *Black line* corresponds to sodium signal, *red line* to potassium signal, *green line* to chlorine signal

cathodic polarization, although slightly higher compared to the non-polarized membrane. On the other hand, no significant changes in sodium profile at the polymer/ solution interface were recorded, where Na^+ transfers from the conducting polymer to the membrane would be expected. Moreover, no distinct changes of ^{32}S signal were noticed, proving no significant incorporation of sulfate anions from solution (results not shown). Therefore, the studied sensor, previously not contacted with K^+ ions, seems to operate as a rectifying device, easily passing cathodic current (incorporation of K^+ ions preferred in the membrane), but being a barrier for higher anodic currents.

Multiple application of an all-solid-state sensor working in galvanostatic mode requires possibility of fast and complete recovery of its initial state, as before current application. Shvarev and Bakker [16] have used appropriate potentiostatic polarization after galvanostatic pulse application; however, in the present case, the problem seems more significant due to more advanced electrolysis (higher currents, longer time). Therefore, in the next experiment, the extent of initial membrane state recovery was checked using anodic polarization just after cathodic one, with the same current magnitude and polarization time. Figure 5 presents LA ICP MS results obtained directly after cathodic/anodic polarization using current $7.5 \ 10^{-7}$ A, with polarization time 180 s in each step. This plot shows presence of considerable potassium amount in the membrane outer part; however, lower than after cathodic polarization only (160,000 cps vs. ~400,000 cps close to the membrane surface). On the other hand, a stronger chlorine signal was recorded close to the membrane/ polypyrrole interface, confirming the role of chloride ions in ion transfer. This result confirms that initial state (lack of K^+ cations) cannot be achieved in this way, probably much

longer polarization is required. This effect can result from strong interactions of K^+ ions with valinomycin, stimulating ions incorporation over their release back into the solution. Therefore, the membrane composition becomes a kind of "fingerprint" of the membrane history.

Another valuable application of chronopotentiometry for all-solid-state ion-selective sensors can be galvanostatic conditioning, resulting in inducing appropriate concentration gradients, necessary to obtain desirable potentiometric characteristic under open circuit conditions [14]. An important issue in this case would be open circuit stability of obtained concentration profiles. The electrodes after cathodic polarization and LA ICP MS experiment were left in the ambient atmosphere with no contact with solution. Then the LA ICP MS experiment was repeated.

Fig. 6 Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested all-solid state potassium electrodes after some time post polarization: **a** the sensor polarized with anodic current $2.5 \ 10^{-7}$ A and left for 2 h, **b** the sensor polarized with anodic current $7.5 \ 10^{-7}$ A and left for 1 h and 15 min. *Black lines* correspond to sodium signal, *red lines* to potassium signal, *green lines* to chlorine signal

For all studied membranes after 1–2 h waiting, significant changes in the element distribution recorded by LA ICP MS results were observed. Exemplary plots of exactly the same systems as in Fig. 2, for two cathodic current values and two waiting times, are presented in Fig. 6. The ^{39}K concentration profile becomes more elevated (compared to Fig. 2), the maximum concentration moves more into the membrane, and the concentration close to the membrane surface is considerably lower than just after polarization. The maximal values are similar for both cases, although different polarizing current were applied. This effect can be explained by shorter relaxation time in case of higher current. Taking into account the diffusion coefficient value of K$^+$–valinomycin complex ($D = 2 \cdot 10^{-8}$ cm^{2}s^{-1} [23]) and approximate thickness of the membrane $L = 100$ µm, the time required to obtain significant changes in K$^+$ ions distribution in the membrane (L^2/D) is around 2 ÷ 3 h, consistent with our results obtained from LA ICP MS measurements.

It should be underlined that in such a case, the relaxation process is possible without contact with bathing solution because the membrane is still wet. These results denote also that potential benefits from galvanostatically established concentration profiles are available for potentiometric analysis only for a short time period after chronopotentiometric conditioning, in the range of minutes.

Conclusions

Within this work, it was proved that LA ICP MS enables visualization of element distribution in galvanostatically polarized K$^+$-selective all-solid-state sensors. As expected, significant asymmetry was observed related to applied current direction. For cathodically polarized electrodes K$^+$ ions were easily incorporated into the membrane and their concentration in the membrane, close to the solution phase, was linearly dependent on the applied current. However, for anodic polarization of K$^+$ ions-free membrane, ion transfer is significantly limited resulting in high anodic overpotential.

The mass spectrometry measurements of the microsamples ablated by laser beam from the membranes proved also to be useful tool to study the recovery of the membrane state after cathodic polarization. Both anodic polarization and open circuit conditioning experiments confirmed slow regaining of the initial state. This is disadvantageous effect for multiple application of the sensor in galvanostatic mode, but it may be promising in case of galvanostatic conditioning of potentiometric sensors, inducing concentration gradients useful from the point of view of desirable analytical parameters.

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