



Experimental study on stability of different solid contact arrangements of ion-selective electrodes

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ABSTRACT

Comparison of potentials stability of different types of solid contact lead selective electrodes is presented. Conducting polymer based sensors (hydrophilic and conducting – poly(3,4-ethylenedioxythiophene) or hydrophobic and semiconducting-polyoctylthiophene) were studied in parallel with coated wire and hydrogel (poly(hydroxyethylmethacrylate)) contact electrodes. The within day and between days potential stability was compared, highlighting the effect of sensor storing conditions. The obtained results clearly demonstrate that different conclusions on stability of sensors' potential can be drawn depending on experimental protocol applied. Polyoctylthiophene based contacts show superior within day stability with no influence of dry storage. On the other hand, a chronopotentiometric method of stability evaluation clearly prefers poly(3,4-ethylenedioxythiophene) based sensors, pointing to smallest resistance and polarizability. It is clearly shown that the choice of experimental conditions applied to test stability can favor particular type of contact used.

The inductively coupled plasma mass spectrometry with laser ablation (LA-ICP-MS) experiments conducted for different arrangements tested has shown that for poly(3,4-ethylenedioxythiophene) and poly(hydroxyethylmethacrylate) type contacts longer contact time with lead(II) solution results in changes in the elemental composition of the transducer layer. On the other hand, in line with high stability observed under potentiometric conditions, no changes were seen for polyoctylthiophene based transducer.

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1. Introduction

In recent years there is a pronounced interest in solid-state ion-selective electrodes, with clear emphasis on use of conducting polymers (CPs) as solid contacts (ion-to-electron transducer) [1,2]. Coupled ionic and electronic conductivity of CPs resulting in pronounced stability of sensors has attracted much scientific attention leading to sensors of both high stability and optimized analytical parameters. An additional advantage is that conducting polymers are nowadays available commercially in the form of water-based dispersions [3–9] or solid materials that can be dissolved in common solvents [10–17]. They can be cast on substrate electrodes yielding (after drying) a solid contact layer.

Depending on applications envisaged, conducting polymers of different properties can be used as solid contacts, e.g. polymers containing ion-exchangers as doping ions [6,9,18], polymers doped with complexing ligands [19] or those containing dopants forming precipitates with analyte ions [20]. Thus, apart from maintaining charge-transfer equilibrium at the back side of the membrane, addi-

tional benefits can arise from lowering free analyte ion activity in the polymer phase, leading to detection limits and selectivities comparable to those of similar systems with tailored internal solution [6,9,18–20].

On the other hand, using more lipophilic, solution processable conducting polymers, e.g. polyoctylthiophene or other alkylthiophenes [10–16], can be also advantageous. These materials, usually applied in neutral, low electronic and ionic conductivity form, are less prone to undergo spontaneous charging/discharging processes [21,22] and thus they do not create significant (undesired) ion-fluxes through ion-selective membranes. Moreover, high lipophilicity of these materials is believed to help to prevent unwanted water layer formation within the sensor [23,24]. On the other hand, the electrical capacitance of this type of layers is significantly lower compared to more oxidized polymers, which can also affect signal stability.

Some benefits of application of CPs in solid contact electrodes are unquestionable and clearly seen when (as usually done) CP based sensors are compared to other arrangements (coated wire or hydrogel [25,26]) in one set of experiments. However, different CP systems are rarely compared to each other. Moreover, different approaches for studying sensor stability have been proposed and are in use. They range from recording potential values in

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different solution activities (or calibrating the sensor) for a couple of days [27,28], recording potential in solutions of constant activity for longer time (water layer tests) [24], using current based electrochemical techniques (impedance spectroscopy and/or chronopotentiometry) [29] or looking at changes in absorption spectra of polymer layers underneath ion-selective membrane [30]. Depending on the method used, and moreover, depending on sensor pretreatment before test, different results can be obtained, making comparison between different systems difficult [18]. Thus, it seemed important to compare different internal solution free sensors under the same experimental conditions (both pretreatment and test set-up) in a parallel experiment. In our opinion, comparison of different sensors and methods used to evaluate stability can add value to the field, it seems also important to check if coherent results are obtained using different experimental approaches. One of the important issues is the effect of polymer capacitance and possible water uptake on sensors stability, thus the experimental conditions were chosen to highlight these effects. It should be stressed that there is not much data in the literature on within day or between days stability of solid-state contact sensors [1,2]. Moreover, results concerning changes of sensors performance with time of its use are still limited. However, both issues are vitally important for practical application of sensors.

In this study sensors with different solid contacts were compared: polymer layers obtained from different materials including polymers of various oxidation states: (i) aqueous dispersion of semi-oxidized conducting polymer (poly(3,4-ethylenedioxythiophene) – prepared using commercially available water-based dispersion, Baytron, stabilized with poly(4-styrenesulfonate) ions) and (ii) more lipophilic, semi-conductor state, polyoctylthiophene (commercially available polymer – solution cast from chloroform) as well as (iii) poly(hydroxyethylmethacrylate) (pHEMA) contact and (iv) coated wire arrangement. As a model system lead selective electrodes with poly(vinyl chloride) (PCV) based membranes were chosen.

It can be expected that potential instability is related also to changes in the transducer elemental composition occurring as a result of undesired ion-fluxes through ion-selective membrane. Thus, the electrochemical data were supplemented with results of ions-profiles studies performed by ICP-MS measurements coupled with laser ablation (LA-ICP-MS) [9,18,31–36].

2. Experimental

2.1. Apparatus

In the potentiometric experiments a multi-channel data acquisition set-up and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) were used, stable potential readings recorded were used to construct calibration graphs. Pumps systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solutions. In voltammetric experiments 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), described earlier [9,18,31–36], was used. 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 and transducer thickness were followed and the signal intensities for each element in different sensors were compared. Note that the quantitative analysis of the membranes' components was not aimed.

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.

2.2. Reagents

Tetrahydrofuran (THF), poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (oNPOE), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), lead ionophore IV tert-butylcalix [4]arene-tetrakis(N,N-dimethylthioacetamide) were from Fluka AG (Buchs, Switzerland), hydroxyethylmethacrylate and 2,2-dimethoxy-2-diphenylacetophenone (DMPP) were from Aldrich (Germany).

Doubly distilled and freshly deionized water (resistance 18.2 M Ωcm , 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). Conducting polymers used were obtained from: poly(3,4-ethylenedioxythiophene) (PEDOT) water dispersion stabilized with poly(4-styrenesulfonate) ions – Baytron P – Bayer AG (Leverkusen, Germany) and polyoctylthiophene (POT) from Aldrich (Germany).

2.3. Preparation of solid contact sensors

Glassy carbon (GC) electrodes of area 0.07 cm² were used as substrates. They were polished with Al₂O₃, 0.3 μm and rinsed well in water.

Coated wire (CW) sensors were obtained by covering prepared as described above GC layers with ion-selective membrane cocktail.

Polyoctylthiophene (POT) layers were prepared by applying 20 μl ($2 \times 10 \mu\text{l}$) of polymer solution in chloroform (2.75 mg ml⁻¹) on the GC electrode, prepared as described above placed in upside down position. After drying of CP solvent ion-selective membrane was applied.

Poly(3,4-ethylenedioxythiophene) (PEDOT) layers were obtained by applying 10 μl of as obtained water-based polymer dispersion on top of GC electrode, prepared as described above, placed in upside down position. After drying CP layer was further covered with ion-selective membrane.

Before preparation of poly(hydroxyethylmethacrylate) (pHEMA) layers on prepared as described above GC electrodes, silver layers were deposited (potentiostatically at –0.5 V, reduction charge was equal to 0.05 C), then the silver coated GC electrodes were immersed in 0.1 M FeCl₃ solution for 15 min, yielding a Ag/AgCl layer on GC substrate. Then 15 μl of hydroxyethylmethacrylate solution containing 2% (w/w) of DMPP was applied on electrodes placed in upside down position and photopolymerized using UV light for 5 min under nitrogen atmosphere. Thus obtained pHEMA layers were conditioned in 0.1 M KCl for 1.5 h before covering with ion-selective membrane.

2.4. Ion-selective membrane

Lead selective membrane contained (in wt%): 1.5% of lead ionophore IV, 0.8% of NaTFPB, 65.1% oNPOE and 32.6% PVC; total 200 mg of membrane components were dissolved in 2 ml of THF.

20 μl of membrane cocktail were applied on electrode resulting in membrane of thickness ca 200 μm .

2.5. Sensors samples for LA-ICP-MS

Sensor to be targets for LA-ICP-MS elements distributions studies were prepared in the same way as electrochemically tested

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