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Plastic reference electrodes and plastic potentiometric cells with dispersion cast poly(3,4-ethylenedioxythiophene) and poly(vinyl chloride) based membranes

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Abstract

A simple procedure of preparing low cost, planar and disposable reference electrodes for potentiometric applications is presented. This method is essentially the same as used for obtaining all-plastic ion-selective electrodes and thus promising for simple fabrication of complete cells. Commercially available aqueous dispersion of poly(3,4-ethylenedioxythiophene) doped by poly(4-styrenesulfonate) ions (PEDOT-PSS, Baytron P) is simply cast on a non-conducting plastic support (transparent foil for laser printers). This layer is covered by a non-selective poly(vinyl chloride) based membrane containing solid AgCl and KCl, added to obtain a stable potential. The conducting polymer layer plays a double role, of electrical contact and ion-to-electron transducer, enhancing the potential stability.

The reference electrodes obtained exhibit independence of the kind and concentration of electrolyte applied as well as very low sensitivity to interferences: redox reactants and H^+ ions; they are also characterized by both potential stability and low polarisability, sufficient for potentiometric applications.

Cells of plastic electrodes (indicator and reference ones) are tested using an arrangement with Pb^{2+} or Ca^{2+} selective sensors. Potentiometric characteristic of such cells is satisfactory, well comparable with that using a classical electrode arrangement.

Keywords: Reference electrode; Poly(3,4-ethylenedioxythiophene); All-plastic ion-selective electrode; Lead ion sensor; Calcium ion sensor

1. Introduction

The research interest in the field of potentiometry is most often oriented towards the ion-sensing element (half-cell), in recent years a considerable progress in this field has been achieved. The improvement concerns lower detection limit, extension of linear response range to lower activities, reaching more favorable selectivities, simplifying all-solid-state construction, miniaturization, making sensors disposable etc. [1–4]. On the other hand, among reference electrodes still classical constructions dominate, based on well known systems: Ag/AgCl and Hg/Hg_2Cl_2. This results mainly from major advantages related to reliability and long term stability of these electrodes, which compensate for some drawbacks attributed mainly to the presence of the liquid phase and toxic metals (Hg). The liquid component is related not only to risk of leakage, some maintenance requirements and problems with miniaturization or shape tailoring. Such electrodes are also not compatible with modern potentiometric sensor systems, the indicator and the above mentioned reference electrodes cannot be produced in one step using the same fabrication method.

Some non-classical all-solid-state constructions have been proposed in recent years, based, e.g., on screen printing [5–8], field effect transistor technology [9–11] or usage of conjugate conducting polymers [12–16]. An important requirement for proper functioning of a reference electrode is presence of a buffered redox system and an appropriate junction between the electrode medium with buffering ions and the sample. In the case of solid-state systems the role of junction is usually played by a plastic polymeric membrane. The dependence of the membrane potential on a sample composition is reduced or eliminated by exposing non-selectivity of the membrane. It can be assured in the absence of an ionophore, using a lipophilic salt in the

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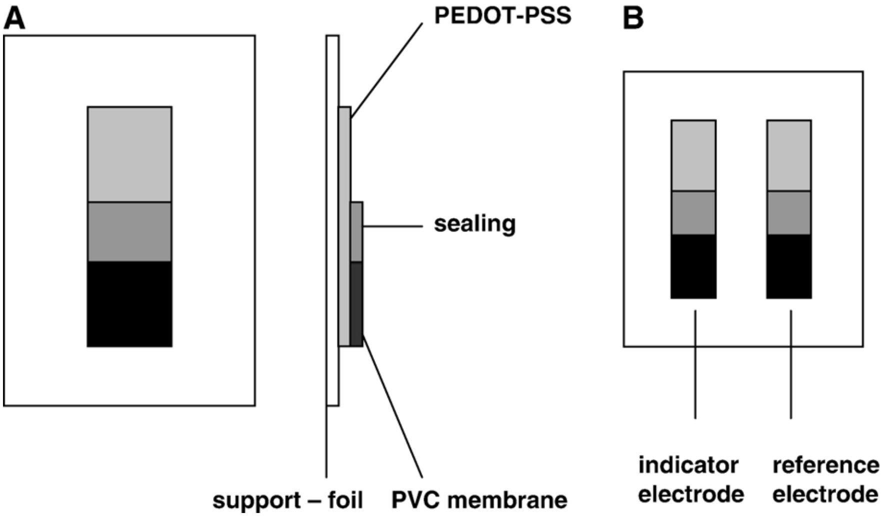

Fig. 1. Schematic representation of (A) a plastic electrode with dispersion cast PEDOT-PSS layer and PVC based membrane, and (B) a cell with plastic electrodes.

membrane phase (with cation and anions operating as cation- and anion-exchangers, respectively). In an ideal case the cation- and anion-exchange properties of the membrane compensate.

Recently, we have proposed a promising arrangement of reference electrodes, where a non-selective poly(vinyl chloride) (PVC) based membrane with lipophilic cations and anions is coated on an electrode first covered by a conducting polymer (CP) (polypyrrole or poly(3,4-ethylenedioxythiophene) (PEDOT)) [16]. The role of the conducting polymer was to operate as ion-to-electron transducer, assuring stable and reversible ion transfer between the membrane and CP, and electron transfer between the CP and the electrode support. The PVC based membrane contained also dispersion of solid AgCl/Ag couple and solid KCl, to additionally stabilize the potential.

Electropolymerisation of conducting polymer layers, regardless it is used in reference or ion sensitive electrodes, can be easily applied in laboratory conditions. However, this is not the optimal method for mass production of sensors or cells. In such a case a solution or suspension based CP is a promising option, resulting in a simplified method of fabrication.

Recently, a new concept of simplified construction of all-plastic ion-selective electrodes has been proposed [17,18]. In such arrangement a plastic support (e.g. a foil used for laser printing of overheads) is covered by aqueous suspension of conducting PEDOT, using the line patterning method [19]. After drying, a part of the CP layer is coated by a typical ion-selective PVC based membrane. In this arrangement, the CP layer plays a double role: of an ion-to-electron transducer and electrical contact. Then, the CP layer is coated by a membrane. Properties of such low-cost, planar and disposable electrodes, in terms of detection limit and selectivity, are comparable with those of modern classical electrodes with internal solution.

Development of all-plastic technology for sensors with ultimate objective of making plastic potentiometric cells requires the reference electrodes to be obtained using the same method. Hence, the aim of this work was to prepare plastic reference electrodes and study their properties. The approach was analogous to that described above [17,18], the most significant difference relates to application of a non-selective PVC based membrane, assuring potential independent of sample composition and concentration.

For application in potentiometric cells with ion-selective electrodes one of the most important properties of reference electrodes is stable and reliable potential, independent of kind of the electrolyte and concentration in a wide range, as well as independent of the presence of possible interferents (redox reactants, H^+/OH^- ions). Therefore in testing of proposed plastic reference electrodes we focus on these properties. In the second part of the paper, tests involving exemplary cells with plastic electrodes will be briefly reported, using Pb^{2+} and Ca^{2+} selective sensors as indicator electrodes.

2. Experimental

2.1. Apparatus and electrodes

For electrochemical experiments, a galvanostat–potentiostat CH-Instruments model 660A (Austin, TX, USA) was used and a conventional three electrode cell, with platinum counter electrode and Ag/AgCl with 1 M KCl in gel phase as reference electrode. In these tests, the studied plastic reference electrodes served as working ones. In the potentiometric experiments a multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) were used. The pumps system 700 Dosino and 711 Liquino (Methrom, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solutions.

For potentiometric measurements the double junction Ag/AgCl reference electrode with 1 M CH_3COOLi in the outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. Here, the plastic electrodes served as indicators.

The plastic electrodes were prepared by coating a laser printer foil (Laser/Copier Transparencies Plain, type C, Xerox) using the method described in [17]. After drying, the obtained polymer film (PEDOT-PSS) was covered by a PVC based membrane [17], using the membrane composition typical either for a reference electrode or indicator electrodes (Pb^{2+}, Ca^{2+}), Fig. 1.

2.2. Reagents

Aqueous dispersion of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) anions, Baytron P (Bayer, Germany) was used as obtained.

Tetrahydrofuran (THF), poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis(4-chlorophenyl) borate (KTChP), tridodecylmethylammonium chloride (MTDDA-Cl), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), 2-nitrophenyl octyl ether (oNPOE), lead ionophore IV (tert-butylcalix[4]arene-tetrakis(*N*,*N*-dimethylthioacetamide) and calcium ionophore ETH 5234 were from Fluka AG (Switzerland).

Other used salts were of analytical grade and were from POCh (Gliwice, Poland).

Doubly distilled and freshly deionised water, resistance 18.2 MΩcm, Milli-Qplus (Millipore, Austria) was used throughout this work. Silver chloride was precipitated by mixing 3 M $AgNO_3$ and 3 M KCl solutions. The sediment formed was filtered on a soft filter, washed and dried in oven at 80 °C, for at least 1 h. Then, it was stored in a dark place until use.

2.3. Solvent polymeric plastic membranes

The membrane used for reference electrodes fabrication contained (in wt.%) 0.9% of potassium tetrakis(4-chlorophenyl) borate (KTChP), 1.1% of tridodecylmethylammonium chloride (MTDDA-Cl) (molar ratio KTChP:MTDDA-Cl is 1:1), 68% of bis(2-ethylhexyl) sebacate (DOS) and 30% of poly(vinyl chloride) (PVC); total 200 mg of membrane components were dissolved in 2 mL of THF. To 250 µL aliquot of the above cocktail 40.4 mg of ground KCl and 15.3 mg of powdered AgCl (with traces of spontaneously formed metallic Ag) in molar ratio KCl/AgCl equal to 5:1 was added, to yield a suspension. The suspension was applied (with 30 µL volume) onto one end of dry PEDOT-PSS layer obtained on a plastic foil. Following 8–12 h drying under ambient conditions, electrodes were conditioned in KCl solution (see details in the Results and discussion section). Estimated thickness of the membranes was 200 µm.

The membrane used for Pb^{2+} selective electrodes contained (in wt.%): 0.4% of lead ionophore IV, 0.15% of NaTFPB, 62.3% oNPOE and 37.15% PVC. Calcium selective membrane contained (in wt.%) 0.7% of NaTFPB, 1% ETH 5234, 67.0% oNPOE and 31.3% PCV. Total 200 mg of membrane components were dissolved in 2 mL of THF. The membrane cocktail (30 µL) was applied as described above. After drying, the plastic ion-selective electrodes were conditioned for 2 h in 1 mM $Pb(NO_3)_2$ solution or for 1 h in 1 mM $CaCl_2$ solution (Pb and Ca sensor, respectively).

Although Baytron P layers easily redissolve in contact with aqueous solutions, after covering with a PVC based membrane, they were quite stable for a longer time (hours).

The potential values recorded vs. classical reference electrode were corrected for the liquid junction potential, calculated according to Henderson approximation. Mean ion activities were calculated according to Debeye–Hückel theory [20].

3. Results and discussion

3.1. Plastic reference electrodes

The composition of a PVC based membrane coated on a PEDOT-PSS layer, for a reference half-cell, was tailored to expose both non-selectivity and a defined stable potential. This membrane contains highly lipophilic cation and anion components, to eliminate ion exchange between the sample and solution and to lower the membrane resistance. The role of dispersed AgCl with traces of metallic Ag and solid KCl dispersion is redox buffering for the half-cell reaction in the membrane phase: $AgCl+e \leftrightarrows Ag+Cl^-$.

The influence of the electrolyte cation in the sample solution on the recorded potential was checked. The measurements were carried out for a series of chloride solutions (KCl, NaCl, $CaCl_2$, $MgCl_2$), the potentiometric characteristics (dependence of potential on logarithm of electrolyte activity) were recorded after 1 h conditioning in 3 M KCl solution. The obtained potentials were only slightly dependent on the kind and concentration of the electrolyte used, the difference for various cations (the same electrolyte concentration) did not exceed 5 mV. All the slopes of potential vs. logarithm of activity were close or lower than 1 mV/dec., see Table 1. These near-zero slopes are satisfactory from the point of view of reference electrodes properties. Similar results (potentials and low slopes) were obtained, comparing solutions of various anions: NaCl and $NaNO_3$. Table 1 presents slopes of potentiometric characteristics for various electrolytes and conditioning procedures.

The prepared electrodes were conditioned in KCl solutions of different concentration. The recorded data reveal the influence of both conditioning time and concentration of the conditioning solution on the potential of plastic reference electrodes. After 12 h conditioning in 3 M KCl the potential values were about 50 mV higher than after 12 h pre-treatment in 0.1 M KCl.

The best results (most stable potentials, the lowest influence of electrolyte concentration) were obtained after conditioning in concentrated, 3 M, KCl solution. 1 h conditioning was found sufficient to obtain stable and reproducible data. Therefore, other results presented in this work, were obtained using this conditioning procedure. Despite the application of suspensions-

Table 1
Slopes of potentiometric characteristics of plastic reference electrodes

Solution	Concentration range/M	Conditioning solution, conditioning time	Slope (mV/dec.)± SD[a]
KCl	$10^{-6}÷10^{-1}$	3 M KCl, 1 h	−0.3±0.1
KCl	$10^{-5}÷10^{-1}$	0.1 M KCl, 12 h	3.4±0.4
NaCl	$10^{-6}÷10^{-1}$	3 M KCl, 1 h	−1.1±0.3
NaCl	$10^{-5}÷10^{-1}$	0.1 M KCl, 12 h	−2.2±0.4
KCl	$10^{-5}÷1$	3 KCl, 12 h	~0
$CaCl_2$	$10^{-6}÷10^{-1}$	3 M KCl, 1 h	−0.9±0.4
$MgCl_2$	$10^{-6}÷10^{-1}$	3 M KCl, 1 h	~0
$NaNO_3$	$10^{-5}÷10^{-1}$	0.1 M KCl, 12 h	2.6±0.8

[a] SD: standard deviation, for one electrode tested in a solution series.

containing membrane, reproducibility of potentials of 4–5 electrode batches (all electrodes were conditioned simultaneously in the same solution) was within a few mV. For different electrode batches the reproducibility was in the range ±10 mV. For an exemplary electrode the potential drift observed in 1 M KCl solution for 1 h, was lower than 0.4 mV. The stability tests for a longer time scale were not carried out, because plastic electrodes of this type are intended to be disposable, thus the long term stability does not apply here.

An important requirement for reference electrodes is insensitivity of the potential to possible interferents. From the point of view of CP applications the most severe ones are redox reactants and H^+ ions. The influence of redox interferents was checked by measuring potentials in solutions containing a redox couple: $Fe(CN)_6^{3-/4-}$ of equal concentrations of oxidized and reduced forms, ranging from 10^{-5} to 10^{-2} M, Fig. 2. The presence of this redox couple results in only a small potential shift to lower values, over 10 mV, and almost independent of the redox couple concentration, if higher than 10^{-4} M. The change of concentration ratio Fe(III)/Fe(II) for the constant summary concentration of both forms did not noticeably affect the recorded potential.

The influence of changing pH on potentiometric responses of the plastic reference electrode was tested in acidic solutions within pH from 2 to 6. The solution pH value was varied by adding concentrated HCl. The obtained results point to the independence of the potential of pH, the recorded slope is close to 0.3 mV/pH unit.

Other electrochemical properties of plastic reference electrodes were tested using electrochemical impedance spectroscopy (EIS) and chronopotentiometry. The EIS spectra were recorded within a frequency range from 10^5 to 10^{-3} Hz, at a potential of 0.300 V, using a voltage amplitude of 50 mV. An exemplary Bode plot, recorded in 0.1 M KCl solution is shown in Fig. 3. In a wide frequency range (below 10^4 Hz) a purely resistive behaviour is observed, with a phase angle close to 0. The resistance, 1.5×10^5 Ω, can result either from the membrane resistance and resistance of other components of the electrode. Analogous experiments carried out for electrodes with the same membrane, coated on an electropolymerised PEDOT layer, revealed a lower resistance value [16]. This means that the plastic planar arrangement with the CP obtained by casting from aqueous dispersion highly contributes to the resistance of the electrode. For frequencies higher than 10^4 Hz, a gradual decrease of the impedance is visible, accompanied by a decreasing phase angle down to −70° at a frequency of 10^5 Hz. This points to the growing role of the system's capacitive behaviour. Since the impedance related to capacitive properties is lower than 10^5 Ω for frequencies higher than 10^5 Hz, the approximate value of capacitance (calculated as 1/(angular frequency × impedance)) is close to 10^{-10} F. This value is typical for geometric capacitance of PVC based membranes [21].

An important parameter characterizing reference electrodes is polarisability. Although under zero-current and potentiometric conditions this parameter does not seem crucial, a relatively low polarisability is important to record stable potentials. Polarisability was studied under galvanostatic conditions. Fig. 4 presents a chronopotentiometric curve recorded for cathodic/

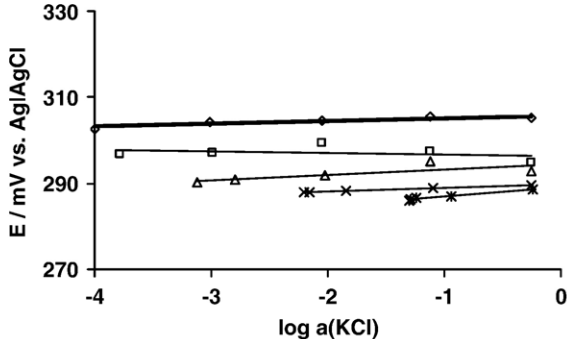

Fig. 2. Potentiometric characteristics of plastic reference electrodes in solutions containing $Fe(CN)_6^{3-/4-}$ redox couple of concentration: 0 (diamonds), 1×10^{-5} M (squares), 1×10^{-4} M (triangles), 1×10^{-3} M (crosses) and 1×10^{-2} M (stars). Measurements were carried out after 1 h conditioning in 3 M KCl solution. Activity a(KCl) relates to molar concentration [KCl]/M.

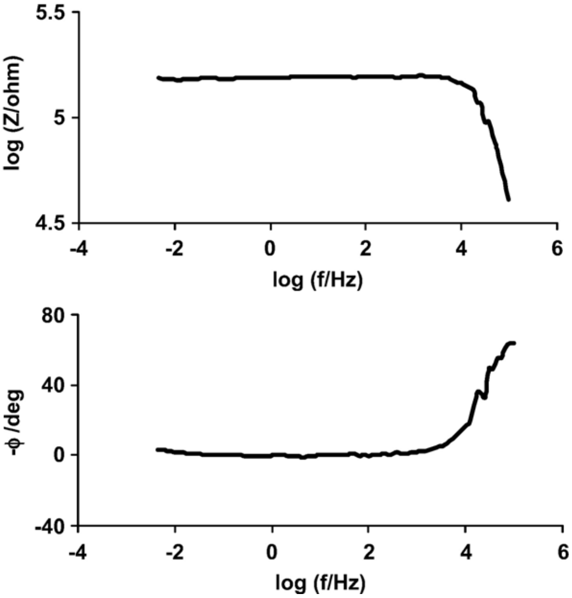

Fig. 3. Bode plot of a plastic reference electrode (applied as a working one) in 0.1 M KCl. Dependence of the logarithm of impedance module (top part) and negative value of phase angle, ϕ (bottom part) on logarithm of frequency. Applied potential: 0.300 V, amplitude: 50 mV.

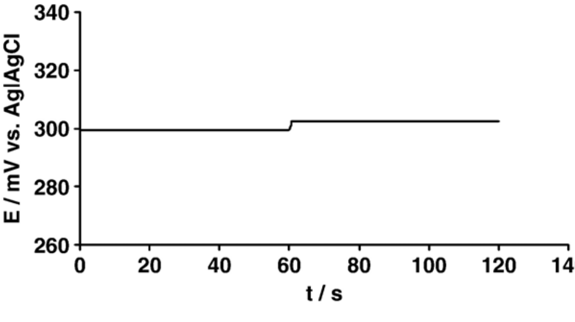

Fig. 4. Chronopotentiometric curve recorded for a plastic reference electrode in 0.1 M KCl solution. Applied cathodic/anodic current: 1×10^{-8} A.

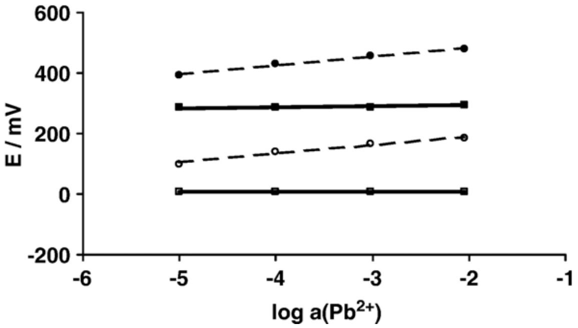

Fig. 5. Potentiometric characteristics recorded in $Pb(NO_3)_2$ solutions for: plastic Pb^{2+} selective electrode (dashed line) recorded vs. classical (filled circles) and plastic (open circles) reference electrode; of a plastic reference electrode (solid line) recorded vs. classical (top line) and another plastic reference electrode (bottom line). Activity a(Pb^{2+}) relates to molar concentration $[Pb(NO_3)_2]$/M.

anodic current $i=10^{-8}$ A in 0.1 M KCl solution. The applied current is very low; however, quite high compared to potentiometric conditions with high impedance voltmeter. The recorded potential is stable both in cathodic and anodic polarisation mode, the potential drift is below 1 mV/min. From this potential drift, $\Delta E/\Delta t$, the low frequency capacitance of the studied system, C, can be evaluated, using the equation [21]:

$$\frac{\Delta E}{\Delta t}=\frac{i}{C} \qquad (1)$$

This value, in the range of 10^{-4} F, results from redox capacitance of the conducting polymer contact [18]. In the case of a PVC based membrane, coated directly on an electrode support (as a metal or glassy carbon, coated wire arrangement), the capacitance is usually much lower, in the range of 10^{-6}–10^{-7} F [21]. A higher capacitance value, resulting from the PEDOT layer presence, is beneficial for potential stability of the electrode.

Change of current polarity from cathodic to anodic results in small potential increase. From this potential jump, the ohmic resistance, R, of the electrode can be estimated:

$$R=\frac{\Delta E}{2i} \qquad (2)$$

This resistance is $(1.5\pm0.2)\times10^5\,\Omega$, within the limit of experimental error equal to that obtained from EIS measurement.

3.2. Potentiometric cells with plastic electrodes

One of the highest advantages of plastic reference electrodes is compatibility with plastic indicator electrodes, both electrodes can be prepared using a similar technique. The same method of fabrication of plastic ion-selective electrodes [17] and reference electrodes, described in the present paper, can be used for simple preparation of complete cells with plastic disposable electrodes.

As model systems, cells with Pb^{2+} and Ca^{2+} selective indicator electrodes were applied. Fig. 5 presents the potentiometric characteristics of Pb^{2+} plastic sensor and plastic reference electrode, measured against a classical reference electrode. For Pb^{2+} selective electrode a Nernstian slope (29.9 mV/dec., $R^2=0.99$) was obtained for the Pb(II) activity corresponding to the concentration range from 10^{-2} to 10^{-5} M $Pb(NO_3)_2$. The potential of the plastic reference electrodes in these solutions (measured against the classical reference electrode) was practically constant (slope: 0.8 mV/dec.). Fig. 5 presents also the characteristics of Pb^{2+} selective electrode measured against a plastic reference electrode as well as potential difference of two plastic reference electrodes. In the case of two reference electrodes, the obtained potential difference is, as expected, equal to zero, with slope 0.7 mV/dec. For the cell: plastic Pb^{2+} indicator electrode, plastic reference electrode, a linear dependence was recorded with the slope close to Nernstian (28.7 mV/dec., $R^2=0.98$).

The second example is related to a cell with Ca^{2+} selective plastic sensor. Potentials of this electrode were measured against the plastic reference electrode, in a wider concentration range from 0.1 to 10^{-8} M. The obtained potentiometric characteristic is presented in Fig. 6, it is similar to that measured for this electrode vs. a classical reference electrode [17]. In the activity range, corresponding to concentrations 0.1–10^{-4} M, a linear dependence with close to Nernstian slope (27.3 mV/dec., $R^2=0.99$) was recorded. For lower concentrations, down to 10^{-6} M, a super-Nernstian behaviour was observed. This effect is owing to membrane oriented flux of Ca^{2+} cations, resulting from Ca^{2+} interactions with PSS^- anions, doping the conducting polymer [17]. For more diluted solutions the potential is only slightly dependent on Ca^{2+} activity.

Selectivity coefficients, $K^{pot}_{Ca,J}$, were determined in this cell using a separate solution method, the recorded potentials are presented in Fig. 6. The following mean values of $\log K^{pot}_{Ca,J}\pm SD$ were obtained within interferent activity range from 0.1 to 10^{-3} M (slope of the dependence recorded in interferent ion solutions is included in brackets): $\log K^{pot}_{Ca,Mg}=-6.63\pm0.2$ (28.5); $\log K^{pot}_{Ca,Na}=-5.51\pm0.3$ (48.8); $\log K^{pot}_{Ca,K}=-6.0\pm0.2$ (50.6). These data are

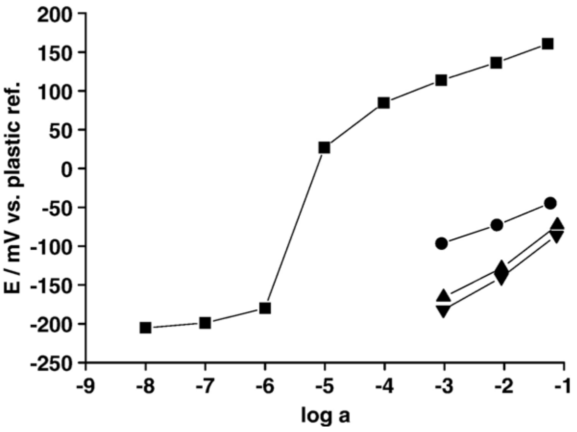

Fig. 6. Potentiometric characteristic of plastic Ca^{2+}-selective electrode vs. plastic reference electrode in $CaCl_2$ (■), $MgCl_2$ (●), NaCl (▲) and KCl (▼) solutions. Activity relates to molar concentration of corresponding salt.

worse or comparable with literature values obtained for tailored internal solution electrodes [22]: −8.6±0.3, −6.4±0.3 and −5.6±0.8, for Mg^{2+}, Na^+ and K^+, respectively. However, obtained selectivity coefficients are still satisfactory for typical analytical applications. These results show also that the plastic reference electrode does not interfere in the responses of the indicator one, even at low analyte concentrations.

The above results confirm analytical applicability of plastic indicator and reference electrodes in this simple and disposable solution-free arrangement.

4. Conclusions

The same concept of plastic electrodes based on dispersion cast poly(3,4-ethylenedioxythiophene) can be used to obtain both ion-selective and reference electrodes. The role of PEDOT is to be an electrical contact and to stabilise the electrode potential owing to high redox capacitance of the polymer. The difference in manufacturing method relates only to poly(vinyl chloride) based outer membrane composition. Despite of simple preparation method, obtained reference electrodes are characterized by a stable potential insensitive to electrolyte kind and concentration, to influence of redox reactants and pH changes. These reference electrodes are promising for use in potentiometric cells with either ion-selective electrodes or biosensors.

Owing to compatibility: plastic indicator vs. plastic reference electrodes, complete cells can be prepared, fabricating both electrodes in similar steps, on the same plastic support. Potentiometric characteristics, checked on example of cells with Pb^{2+} and Ca^{2+} selective electrodes, reveal suitability of such systems for analytical applications.

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References

[1] E. Bakker, Y. Qin, Electrochemical sensors, Anal. Chem. 78 (2006) 3965–3984.
[2] E. Bakker, E. Pretsch, Potentiometric sensors for trace-level analysis, Trends Anal. Chem. 24 (2005) 199–207.
[3] J. Bobacka, Conducting polymer-based solid-state ion-selective electrodes, Electroanalysis 18 (2006) 7–18.
[4] A. Michalska, Optimizing the analytical performance and construction of ion-selective electrodes with conducting polymer-based ion-to-electron transducers, Anal. Bioanal. Chem. 384 (2006) 391–406.
[5] D. Desmond, B. Lane, J. Alderman, J.D. Glennon, D. Diamond, D.W.M. Arrigan, Evaluation of miniaturised solid state reference electrodes on a silicon based component, Sens. Actuators, B, Chem. 44 (1997) 389–396.
[6] H.J. Lee, U.S. Hong, D.K. Lee, J.H. Shin, H. Nam, G.S. Cha, Solvent-processible polymer membrane-based liquid junction-free reference electrode, Anal. Chem. 70 (1998) 3377–3383.
[7] Ł. Tymecki, E. Zwierkowska, R. Koncki, Screen-printed reference electrodes for potentiometric measurements, Anal. Chim. Acta 526 (2004) 3–11.
[8] J. Ha, S.M. Martin, Y. Jeon, I.J. Yoon, R.B. Brown, H. Nam, G.S. Cha, A polymeric junction membrane for solid-state reference electrodes, Anal. Chim. Acta 549 (2005) 59–66.
[9] J.H. Shin, H.J. Lee, C.Y. Kim, B.K. Oh, K.L. Rho, H. Nam, G.S. Cha, ISFET-based differential pCO_2 sensors employing a low-resistance gas-permeable membrane, Anal. Chem. 68 (1996) 3166–3172.
[10] M. Chudy, W. Wróblewski, Z. Brzózka, Towards REFET, Sens. Actuators, B, Chem. 57 (1999) 47–50.
[11] A. Errachid, J. Bausells, N. Jaffrezic-Renault, A simple REFET for pH detection in differential mode, Sens. Actuators, B, Chem 60 (1999) 43–48.
[12] N.L. Pickup, M. Lam, D. Milojevic, R.Y. Bi, J.S. Shapiro, D.K.Y. Wong, Investigations of the feasibility of constructing a polypyrrole-mercury/mercury chloride reference electrode, Polymer 38 (1997) 2561–2565.
[13] K.-M. Mangold, S. Schäfer, K. Jüttner, Reference electrodes based on conducting polymers, Fresenius' J. Anal. Chem 367 (2000) 340–342.
[14] K.-M. Mangold, S. Schäfer, K. Jüttner, Reference electrodes based on conducting polymer bilayers, Synth. Met. 119 (2001) 345–346.
[15] T. Blaz, J. Migdalski, A. Lewenstam, Junction-less reference electrode for potentiometric measurements obtained by buffering pH in a conducting polymer matrix, Analyst 130 (2005) 637–643.
[16] A. Kisiel, H. Marcisz, A. Michalska, K. Maksymiuk, All-solid-state reference electrodes based on conducting polymers, Analyst 130 (2005) 1655–1662.
[17] A. Michalska, K. Maksymiuk, All-plastic, disposable, low detection limit ion-selective electrodes, Anal. Chim. Acta 523 (2004) 97–105.
[18] A. Michalska, M. Ocypa, K. Maksymiuk, Highly selective all-plastic, disposable Cu^{2+}-selective electrodes, Electroanalysis 17 (2005) 327–333.
[19] A.G. MacDiarmid, Synthetic metals: a novel role for organic polymers, Synth. Met 125 (2002) 11–22.
[20] P.C. Meier, Two-parameter Debye–Hückel approximation for the evaluation of mean activity coefficients of 109 electrolytes, Anal. Chim. Acta 136 (1982) 363–368.
[21] J. Bobacka, Potential stability of all-solid-state ion-selective electrodes using conducting polymers as ion-to-electron transducers, Anal. Chem. 71 (1999) 4932–4937.
[22] T. Sokalski, A. Ceresa, M. Fibbioli, T. Zwickl, E. Bakker, E. Pretsch, Lowering the detection limit of solvent polymeric ion-selective membrane electrodes. 2. Influence of composition of sample and internal electrolyte solution, Anal. Chem 71 (1999) 1210–1214.