A simple way to modify selectivity of sodium sensitive electrodes by using organic conductive crystals

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Abstract

An ion-selective membrane is an essential element in the construction of ion-selective electrodes. In this work, some investigations concerned on influence of an ion-selective membrane composition on sodium-selective electrode properties are presented. Several coated-disc sodium-selective electrodes were prepared with the use of sodium ionophore III or sodium ionophore VI, or mixture of these two selective carriers. Membranes with the same compositions were also used to obtain sensors with solid contact transducer layer consisted of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its sodium radical salt (NaTCNQ). In other polymeric membranes, a whole or some part of ionophore was replaced by NaTCNQ in order to assess the effect of its presence on sodium single-piece electrode characteristics. All kinds of prepared electrodes were tested using potentiometric and chronopotentiometric studies, and significant impact of membrane composition on electrode parameters was observed. Among investigated sensors, TCNQ/NaTCNQ-contacted all-solid-state electrodes exhibited the best analytical and electrical performance due to the presence of the intermediate layer, which simplifies the ion-to-electron transduction process between the ion-sensing membrane and the glassy carbon electrode. Exemplary, these electrodes with sodium ionophore III had a close-to-Nernstian slope (58.63 mV/pNa) in the range from 10^{-5} – 10^{-1} -M NaCl and revealed detection limit of $10^{-5.2}$ M. However, the mixing of sodium ionophores III and VI in one polymeric membrane led to improved sensitivity and limit of detection (58.79 mV/pNa and $10^{-5.4}$ M, respectively). The highest capacitance observed for electrodes with TCNQ/NaTCNQ based on intermediate layer was 139 μ F.

Keywords Ionophore · Selectivity change · Sodium-selective electrode · 7,7,8,8-Tetracyanoquinodimethane

Introduction

The most important element of an ion-selective electrode (ISE) is an ion-selective membrane (ISM) responsible for forming the potentiometric response. A typical cation-selective liquid membrane consists of an ionophore, lipophilic salt, water-immiscible plasticizer, and a polymer matrix. A life span of electrode depends largely on the lipophilicity of the membrane, because during its use, the slow elution of membrane components into aqueous solution is observed [1].

The ionophore, which is the carrier of the ions, selectively and reversibly binds the determined ions forming a complex

compound with them. During complexation process, ions are transported between the water phase (sample) and the organic phase (membrane). This phenomenon enables to notice the potential change at the membrane/sample interface, which forms grounds for potentiometric measurements. However, the rest of membrane ingredients affect the formation of the complex compound as well, thus the membrane composition should be optimized [1, 2]. Nevertheless, the ionophore has the greatest influence on the binding of primary or interfering ions, thereby defining the electrode selectivity, which is one of the most important sensor parameter [3, 4].

In conventional ISEs, the sensing membrane is placed at the end of a plastic tube filled with an internal solution and inner reference electrode is immersed therein. However, such electrodes with liquid contact have some inconveniences that limit their practical use and render impossible applications in mobile analytical systems. The polymer-based membrane separates sample solution from the internal reference system, thus differences in the ionic strength between the sample and

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the inner filling can result in the osmotic pressure and water transport between these solutions, and in consequence, signal interferences. Moreover, conventional ISEs have to be fabricated and used with care, and their miniaturization is restricted due to the indispensable liquid contact volume. These disadvantages have been overcome by replacing conventional ISEs with all-solid-state ion-selective electrodes (ASS-ISEs). In this group of potentiometric sensors, liquid contact was substituted by solid contact (SC) layer placed between the ISM and an electrical substrate. Such construction comes to meet the demand for ISE application in various fields due to ability of miniaturization, easy maintenance, low cost of production and analysis processes, and small sample volume [5, 6].

Materials that are used as effective ion-to-electron transducers should be characterized by a high redox or a double-layer capacitance [7, 8]. There are many examples of conducting polymer (CP) [9–12], metal nanoparticle [13], or carbon nanomaterial (CNM) [14–19] applications as SC layers. Noteworthy is also the intermediate layer consisting of a redox buffer based on the Co(III) and Co(II) complexes of 1,10-phenanthroline, the use of which allowed to obtain high reproducibility of the ISEs potential [20]. Although CPs generally improve sensor sensitivity, linear range, and detection limit, they suffer from light, gases, or pH interferences [21]. Introduction of nanomaterial-based SC significantly changes for the better not only analytical but also electrical parameters of electrodes and especially stability of the potentiometric response [13–19]. This desirable effect is caused by the unique properties of nanomaterials, e.g., high hydrophobicity, good conductivity, and large surface area. The high double-layer capacitance of the polymeric membrane/nanomaterial based on layer interface increases stability of the measured response, electrodes reproducibility, and capability for long-term use [22]. Despite of influence on sensor characteristics, the application of CNMs leaves electrode selectivity unchanged. For instance, potassium sensors modified with platinum nanoparticles (PtNPs) [13], carbon black (CB) [17], or CB supporting platinum nanoparticle (CB-PtNP) [18] intermediate layer, presented similar values of selectivity coefficients. Although the dissolution of the CP in ISM in the solid-state single-piece electrode (SP-ISEs) can change electrode selectivity [12], the CP-contacted potentiometric sensor shows selectivity close to conventional ISEs or slightly better [10]. Nevertheless, the application of ionic liquids as polymer-sensing membrane additives or SC elements [23, 24] or recently reported combination of organic crystals with their radical salt in SC layer [25–27] positively affects the selectivity of ISEs.

In order to shed the light on the last group, in this work, the influence of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its sodium salt (NaTCNQ) application on single-piece and all-solid-state ISE parameters is studied. TCNQ is strong π -

electron acceptor and may form radical anion salts and charge transfer complexes. One of the most interesting properties of such compounds is high electrical conductivity [28]. Therefore, TCNQ and its compounds have been successfully applied in electrochemical sensors with voltammetric [29] or potentiometric detection [30]. Herein, the effect of TCNQ/NaTCNQ presence was tested with the use of two sodium-selective ionophores, which were applied separately, as well as simultaneously in one polymeric membrane solution. Potentiometric and chronopotentiometric measurements were carried out in order to evaluate analytical and electrical parameters of studied sensors, respectively. Infrared (IR) spectroscopic studies were performed to characterize prepared ISMs.

Experimental

Materials

TCNQ 98%, sodium ionophore III (*N,N,N',N'*-tetracyclohexyl-1,2-phenylene-dioxyacetamide, ETH 2120), sodium ionophore VI (bis[(12-crown-4)methyl]dodecylmethylmalonate), potassium tetrakis(p-chlorophenyl)borate (KTPCIPB), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), sodium tetraphenylborate (NaTPB), *o*-nitrophenyl octyl ether (*o*-NPOE), poly(vinyl chloride) (PVC) of high molecular weight, tetrahydrofuran (THF), methanol, and acetone were the selectophore reagents purchased from Sigma-Aldrich. All other chemicals used were of analytical-reagent grade. Distilled and deionized water was used to prepare the aqueous solutions. NaTCNQ was obtained by chemical synthesis carried out according to the method proposed by Melby et al. [31].

Electrode preparation

In order to assess the impact of NaTCNQ presence and membrane composition on the parameters of sodium sensors, four groups of electrodes were prepared: coated disc electrodes (CD-ISEs), solid-state single-piece electrodes, all-solid-state electrodes, and ionophore-free solid-state single-piece electrodes. All studied electrodes were obtained applying a drop-casting method by dropping the appropriate membrane solution onto bare or modified electrodes surface. In the first stage, the glassy carbon disc (GCD) electrodes (Mineral, Poland) were carefully polished using 0.3- μ m alumina slurry. Then electrodes were sonicated several times with water and methanol and in the end rinsed with intense water stream. All studied electrodes were prepared using the same GCD substrate electrodes consisting of GC rods enveloped in PEEK (polyetheretherketone) bodies (GC area = 7 mm²).

Next, above-mentioned groups of electrodes were prepared and three various membrane compositions were proposed for

each group. Two different sodium ionophores or their mixture were used to prepare coated disc electrodes by dropping suitable membrane solution onto the bare GCD surface. In the second group, membrane cocktails contained sodium ionophore (III, VI or III, and VI), NaTCNQ, lipophilic salt, plasticizer, and PVC. NaTCNQ was added to ISMs as a supplementary ingredient in order to obtain solid-state single-piece electrodes. The mass percentages of ionophores in these membranes were smaller than in preceding membranes due to the presence of NaTCNQ with unchanged content of lipophilic salt. Similarly to the previous group, sodium-selective membrane was deposited on unmodified glassy carbon electrodes. Other sensors—all-solid-state sodium-selective electrodes were prepared with the use of primary membrane solutions (applied for the group of CD-ISEs) but dropped onto the SC transducer layer, which were obtained by casting GCD surface with a 15 μL of TCNQ/NaTCNQ acetone suspension. And finally in the last group of sensors (ionophore-free solid-state single-piece electrodes), no ionophore was used to prepare membrane solution, but only NaTCNQ and different lipophilic salts were added to polymer matrix and plasticizer. As for the other SP-ISEs and CD-ISEs, no intermediate layer was introduced and membrane was dropped directly on the GCD electrodes. All precisely defined membrane compositions and electrode symbols are listed in Table 1.

The bare GCD electrodes or GCD electrodes modified with TCNQ/NaTCNQ layer were twice coated using 30- μL THF solutions of membrane components. The process of preparing sensors with sodium ionophores is schematically shown in Fig. 1. Ionophore-free single-piece electrodes were prepared in the same way as shown for SP-ISEs, but using membrane solutions without ionophores and therefore were omitted in

the picture. After coverage of electrodes with the ISM, they were left to complete solvent evaporation at room temperature for 24 h. Three identical electrodes of each kind were prepared and investigated. Before every measurement, sensors were conditioned in 0.01-M NaCl solution for 1 day. All electrodes were separately stored and conditioned.

Apparatus

The measurements of the electromotive force (EMF) of an indicator electrode, a reference electrode (Ag/AgCl/3-M KCl electrode type 6.0733.100- Ω Metrohm, Switzerland), and an auxiliary electrode (platinum electrode) cell were performed with a 16-channel mV-meter (Lawson Labs., Inc., Malvern, PA). The activity coefficients necessary to convert the concentrations to activities were calculated according to the extended Debye-Hückel equation [32].

The chronopotentiometry measurements were carried out using an Autolab General Purpose Electrochemical System (AUT302N.FRA-2-AUTOLAB, Eco Chemie, The Netherlands) connected to a one-compartment, three-electrode cell. Tested ISE was used as a working electrode. An Ag/AgCl/3-M KCl electrode type 6.0733.100- Ω Metrohm, Switzerland was connected as the reference electrode and a glassy carbon rod as the auxiliary one.

The composition of the ISMs applied in studied sensors was investigated by IR spectroscopic studies. Spectra of all types of membranes were measured on a Bruker VERTEX 70 v vacuum FT-IR spectrometer using attenuated total reflectance (ATR) technique. They were collected in the mid-infrared (MIR) region (4000–500 cm^{-1}) after 128 scans at 4- cm^{-1} resolution.

Table 1 Composition of studied polymer-based membranes

No electrode	SC	Membrane composition (wt%)							
		Ionophore		NaTCNQ	Ionic additive			o-NPOE	PVC
		III	VI		NaTFPB	KTpCIPB	NaTPB		
CD-ISEs	1a	–	1.35	–	1.15	–	–	66.50	31
	1b	–	–	1.62	–	–	–	66.23	31
	1c	–	0.67	0.81	–	–	–	66.37	31
SP-ISEs	2a	–	0.67	–	0.28	1.15	–	66.90	31
	2b	–	–	0.81	0.28	1.15	–	66.76	31
	2c	–	0.45	0.54	0.18	1.15	–	66.68	31
ASS-ISEs	3a	+	1.35	–	–	1.15	–	66.50	31
	3b	+	–	1.62	–	1.15	–	66.23	31
	3c	+	0.67	0.81	–	1.15	–	66.37	31
ionophore-free SP-ISEs	4a	–	–	–	1.3	0.65	–	65.05	33
	4b	–	–	–	1.3	–	0.65	65.05	33
	4c	–	–	–	1.3	–	0.65	65.05	33

Fig. 1 Schematic illustration of studied sodium-selective electrode preparation using drop casting method (CD-ISEs—coated disc ion-selective electrodes, ASS-ISEs—all-solid-state ion-selective electrodes, SP-ISEs—single-piece ion-selective electrodes)

Results and discussion

Mid-infrared spectroscopic studies of ion-selective membranes

ATR-FTIR spectroscopy was used in this work in order to verify the composition of all polymeric membranes used to prepare studied sodium sensors, and achieved spectra of membranes with and without sodium ionophore III are presented in Fig. 2. The results obtained for membranes with sodium ionophore VI as well as the ionophore mixtures are analogous;

Fig. 2 FT-IR analysis of the PVC membranes with (1a, 2a, 3a) and without (4a) ETH 2120 in the range of 4000–500 cm^{-1} (the range between 4000 and 3500 cm^{-1} was omitted in the picture due to lack of bands)

hence, only the spectra for membranes removed from the electrodes 1a, 2a, 3a, and 4a are shown.

Comparison and analysis of the presented spectra do not indicate any significant differences between them except the spectrum 3a collected for the membrane taken off from electrode together with TCNQ/NaTCNQ layer. In this case, the additional vibrational bands specific to TCNQ^- appeared at 2190 and 2159 cm^{-1} and are associated with nitrile group ($\text{C}\equiv\text{N}$) stretching. The presence of band at 823 cm^{-1} related to $\text{C}\equiv\text{C}-\text{H}$ bending vibration also confirms the presence of NaTCNQ [33]. It would be expected that such bands should as well occur for membranes in which sodium salt of TCNQ was added instead of ionophore (2a and 4a). Nonetheless, the amounts of NaTCNQ used in SP-ISEs were much lower than in ASS-ISEs, thus the tested membranes contained much less NaTCNQ than the sample obtained from electrode 3a. Although wherever the NaTCNQ completely replaced the ionophore, slight bands at ca. 2000 cm^{-1} were observed.

Similarly, due to a very low content of ionophore in the polymer matrix, it may not seem possible to deduce explicitly the presence of ETH 2120 individually from the obtained spectra. However, small absorption bands in the range from 1620 to 1750 cm^{-1} for spectra 1a and 3a may be connected with $\text{C}=\text{O}$ stretching vibration derived from sodium ionophore III. And what is more, in the band of $\text{C}-\text{O}$ stretching which appears at ca. 1164 cm^{-1} associated with the presence of plasticizer (o-NPOE) in the membrane matrix, additional shoulder is appeared at 1125 cm^{-1} but only for spectra 1a, 2a, and 3a, i.e., samples containing ETH 2120. Since the ionophore molecule has such $\text{C}-\text{O}$ bond as well, it can be assumed that this shoulder originated from sodium ionophore III (ETH 2120).

It is noteworthy to mention that a small amount of lipophilic salt in investigated membranes and overlapping bands make difficult a specific description the bands related to NaTFPB presence. Both lipophilic salt and plasticizer showed the common bands derived from C=C aromatic stretching vibration at ca. 1607 and 1581 cm^{-1} . On the other hand, the presence of o-NPOE in samples is confirmed unequivocally by the strong stretching N=O bands observed at 1523 cm^{-1} . Moreover, plasticizer and PVC reveal the common aliphatic stretch bands of C—H at 2925 and 2855 cm^{-1} and band related to C—H bending in the range from 1350 to 1250 cm^{-1} , though the presence of C—Cl stretching vibration in 700 to 600- cm^{-1} region definitely indicates the matrix made of poly(vinyl chloride).

Analytical and electrical parameters of sensors

The potentiometric response of prepared electrodes was examined in the sodium ion concentration range from 10^{-6} to 10^{-1} M. The dependency of measured potential on $\log a_{\text{Na}^+}$ for all studied electrodes is presented in Fig. 3. Some significant differences in electrode behavior can be observed. The obtained calibration plot slope values calculated for linear range of

Na^+ activity, standard potential values, and detection limits evaluated as the intersection of the two slope lines are listed in Table 2. Three identical sensors of each type were prepared, so the electrode-to-electrode reproducibility of analytical parameters was also investigated and presented as a standard deviation (SD).

The sensor sensitivity corresponding to the slope of the calibration curve was dependent on the type of electrode. Taking into account the first group of electrodes, it can be noted that mixing of two ionophores (1c) allowed to obtain sensors with better sensitivity and E^0 potential stability than those with ionophores used separately (1a and 1b). Nevertheless, coated disc electrodes behaved quite poorly due to lack of intermediate layer with ionic and electronic conductivity. However, replacing some amount of ionophore by NaTCNQ salt in the membrane composition improved the reproducibility of the electrodes. In the case of membrane with ionophore III, and ionophore III mixed with VI (2a and 2c), the SP-ISE sensitivity was also improved compared to coated-disc electrodes (without NaTCNQ, 1a and 1c, respectively) in the same range of linearity. Electrodes with solid-contact transducer layer exhibited the best analytical parameters compared to the other sensors due to the

Fig. 3 The potentiometric responses of each type of prepared electrodes recorded in sodium chloride solutions after 72 h conditioning in 0.01-M NaCl. The chart number is simultaneously the number of the group of

tested sensors (1—CD-ISEs, 2—SP-ISEs, 3—ASS-ISEs, 4—ionophore-free SP-ISEs), while the particular electrodes are marked as: ■ (a), ● (b), and ▲ (c)

Table 2 Metrological parameters of all studied electrodes determined after 72-h conditioning time (number of electrodes $n = 3$)

Electrode		Parameter $\pm$ SD						
		Slope (mV/dec)	E^0 (mV)	Linear range (M)	Detection limit (M)	R_{total} (k Ω)	dE_{dc}/dt ($\mu\text{V s}^{-1}$)	C (μF)
CD-ISEs	1a	56.97 $\pm$ 0.64	371 $\pm$ 16	$10^{-4.5}$ – 10^{-1}	$10^{-5.1 \pm 0.1}$	1177 $\pm$ 56	738 $\pm$ 63	1.36 $\pm$ 0.12
	1b	57.78 $\pm$ 0.77	409 $\pm$ 20	$10^{-4.5}$ – 10^{-1}	$10^{-4.8 \pm 0.2}$	780 $\pm$ 15	832 $\pm$ 78	1.21 $\pm$ 0.13
	1c	57.90 $\pm$ 0.34	401 $\pm$ 11	$10^{-4.5}$ – 10^{-1}	$10^{-4.9 \pm 0.1}$	1053 $\pm$ 31	785 $\pm$ 38	1.28 $\pm$ 0.06
SP-ISEs	2a	58.41 $\pm$ 0.11	316 $\pm$ 12	$10^{-4.5}$ – 10^{-1}	$10^{-5.0 \pm 0.2}$	774 $\pm$ 45	169 $\pm$ 11	5.95 $\pm$ 0.40
	2b	57.16 $\pm$ 0.07	341 $\pm$ 15	$10^{-4.5}$ – 10^{-1}	$10^{-4.7 \pm 0.1}$	850 $\pm$ 11	593 $\pm$ 63	1.70 $\pm$ 0.18
	2c	58.19 $\pm$ 0.19	326 $\pm$ 3	$10^{-4.5}$ – 10^{-1}	$10^{-4.9 \pm 0.1}$	1319 $\pm$ 8	305 $\pm$ 46	3.28 $\pm$ 0.14
ASS-ISEs	3a	58.63 $\pm$ 0.05	262.1 $\pm$ 0.5	$10^{-5.0}$ – 10^{-1}	$10^{-5.2 \pm 0.1}$	328 $\pm$ 8	7.24 $\pm$ 0.57	139 $\pm$ 11
	3b	58.77 $\pm$ 0.09	233.6 $\pm$ 0.6	$10^{-5.0}$ – 10^{-1}	$10^{-5.3 \pm 0.1}$	424 $\pm$ 13	16.1 $\pm$ 1.0	62.3 $\pm$ 3.9
	3c	58.79 $\pm$ 0.15	253.5 $\pm$ 0.4	$10^{-5.0}$ – 10^{-1}	$10^{-5.4 \pm 0.1}$	254 $\pm$ 7	13.5 $\pm$ 1.0	74.7 $\pm$ 5.7
ionophore-free SP-ISEs	4a	51.03 $\pm$ 0.59	193 $\pm$ 41	$10^{-4.0}$ – 10^{-1}	$10^{-4.7 \pm 0.2}$	1912 $\pm$ 98	853 $\pm$ 53	1.18 $\pm$ 0.07
	4b	54.33 $\pm$ 0.55	283 $\pm$ 32	$10^{-4.5}$ – 10^{-1}	$10^{-5.1 \pm 0.1}$	859 $\pm$ 37	800 $\pm$ 40	1.25 $\pm$ 0.06
	4c	49.11 $\pm$ 2.24	238 $\pm$ 43	$10^{-3.0}$ – 10^{-1}	$10^{-3.7 \pm 0.2}$	3562 $\pm$ 223	1322 $\pm$ 56	0.76 $\pm$ 0.03

presence of TCNQ/NaTCNQ intermediate layer and good-defined phase boundary potential. Analytical parameters of other previously reported sodium-selective electrodes with ion-to-electron transducer layer are presented in Table 3. It can be observed, that TCNQ/NaTCNQ-contacted electrodes showed comparable parameters to earlier presented sodium sensors. The SD of E^0 represents the reproducibility from electrode to electrode. It is worth noting that the studied ASS-ISEs were characterized by the comparable reproducibility as sensors modified with Co(II)/Co(III) redox buffer layer [20] or CNMs [19]. Considering the ionophore-free membranes, electrodes with KTpCIPB showed the best characteristics and electrodes with NaTPB the worst.

On the one hand, it seems that all studied sensors have similar properties; nevertheless, distinct differences between them have been observed only during long conditioning time. Exemplary changes in electrode response are shown in Fig. 4 (one sensor was selected from each tested group). After a month of soaking in 0.01-M NaCl solution, only 3a, 3b, and 3c sensors still presented a linear response in the same range of

Na^+ activity. For other electrodes, the linear range has been shortened, especially for sensors denoted as 4c. Here, the membrane was consisted on PVC, *o*-NPOE, NaTCNQ, and NaTPB. As it was shown in [35], if the membrane solution with similar composition is dropped directly onto glassy carbon substrate, the leaching of the lipophilic salt is observed resulting in the decline of potentiometric response. The diversity in repeatability of the other sensors is also worth emphasizing. As expected, the coated disc electrodes were characterized with the poorest stability due to the lack of reversible transfer of ion and electron across the “blocked” interface between the ISM and glassy carbon electrode. In the first group of electrodes, the smallest deviation from the standard potential value after this time was observed for sensor 1c with two ionophores-based membrane and it was equal 9.6 mV, whereas for electrode 1a and 1b, 17.0 and 28.2 mV, respectively. The standard potential values of electrodes with membrane where some part or all of the ionophore was replaced by NaTCNQ were changed, and SDs of E^0 were equal to 15.0 (2a), 20.1 (2b), 8.3 (2c), and 15.1 (4a), 11.3 (4b), and 39.5 mV

Table 3 Characteristic of various reported Na^+ -selective solid contact electrodes

Ref.	Sodium ionophore	Intermediate layer	Slope (mV/dec)	Linear range (M)	Detection limit (M)
[10]	ETH 227	Poly(pyrrole)	58.3	$2 \cdot 10^{-5}$ – $6 \cdot 10^{-1}$	–
[25]	IV	TCNQ	58.68	10^{-6} – 10^{-1}	$10^{-6.3}$
		NaTCNQ	58.78	$10^{-5.8}$ – 10^{-1}	$10^{-6.1}$
[27]	IV	TCNQ:NaTCNQ:CB (1:1:1)	58.08	$10^{-4.5}$ – 10^{-1}	$10^{-5.1}$
		TCNQ:NaTCNQ:CB (1:0.2:0.8)	59.10	10^{-6} – 10^{-1}	$10^{-6.2}$
[34]	IV	CB-Printex XE2-B	57.10	10^{-5} – 10^{-1}	$9 \cdot 10^{-6}$
[35]	ETH 2120	CB-Printex U	59.14	10^{-6} – 10^{-1}	$10^{-6.2}$
		Poly(N-methylpyrrole)	58.54	10^{-6} – 10^{-5}	$10^{-5.5}$

Fig. 4 EMF dependence on Na^+ activities for all tested electrodes with mean potential values and standard deviations recorded over 1 month of electrode conditioning. The chart number is simultaneously the number

of the group of tested sensors (1—CD-ISEs, 2—SP-ISEs, 3—ASS-ISEs, 4—ionophore-free SP-ISEs), while the particular electrodes are marked as: ■ (a), ● (b), and ▲ (c)

(4c) after 1 month of conditioning in 0.01-M NaCl. The most repeatable potentiometric response was observed for sensors with TCNQ/NaTCNQ intermediate layer and at the same time E^0 values alerted only of 2.3, 1.4, and 3.1 mV for 3a, 3b, and 3c electrodes, respectively.

One of the reasons for the instability of electrode potential in time may be the formation of a thin water layer between the polymeric membrane and the underlying substrate, and, as a consequence membrane detachment. Possible presence of such undesirable aqueous film was assessed by potentiometric water layer test [36]. As it was shown in Fig. 5, first the electrode response was recorded during conditioning in 0.01-M NaCl solution. After 2.5-h, solution was changed to 0.01-M KCl and potential of electrodes was measured for the same period of time. Then solution of interfering ion was replaced by solution of primary ion again. In the case of coated disc electrode (1a), the observed potential drift confirmed the formation of water layer at the Na^+ -ISM/GCD interface. Under the same experimental conditions, SP-ISE (2a) presented more stable potential, but the best characteristic was achieved for ASS-ISE (3a). Such result demonstrated that the presence of NaTCNQ suppressed the water layer in examined sensors due to its hydrophobic character. Observed effect

is consistent with those previously reported for potentiometric sensors modified with organic crystals [25, 27].

All prepared sensors were also investigated using current-reversal chronopotentiometry measurements in order to evaluate

Fig. 5 Water layer test determined for 1a (CD-ISE), 2a (SP-ISE), and 3a (ASS-ISE) electrodes in 0.01-M NaCl and 0.01-M KCl solution. For clarity, the response curves have been shifted in relation to each other

the electric characteristic of electrodes [11]. The potential responses of electrodes recorded during polarization by applying a current (I) of +1 nA for 60 s and −1 nA over another 60 s are presented in Fig. 6. The chronopotentiometric tests were carried out in 0.01-M NaCl solution and allowed to determine the electrical parameters of sensors. The total resistance of electrode $R_{\text{total}} = \Delta E_{\text{dc}} / 2I$ was calculated based on the signal jump (ΔE_{dc}) observed in the potential response after the change of current polarity. The potential drift of electrode was derived from $\Delta E_{\text{dc}} / \Delta t$ ratio and was related with the capacitance C according to $\Delta E_{\text{dc}} / \Delta t = I / C$ equation. All electric parameters of developed electrodes calculated using chronopotentiometric studies are also presented in Table 2.

As expected, all-solid-state electrodes exhibited the smallest resistance compared to other tested electrodes, thus the presence of SC transducer facilitated sodium ions transport. In turn, in the case of non-ionophore membranes, the highest resistances were detected, due to the absence of compounds forming sodium complexes in PVC matrix. Slight differences in (1a, 1b, 1c and 2a, 2b, 2c) sensor capacitance, respectively, were caused by replacement the certain amount of ionophore by small quantities of NaTCNQ conductive salt.

The best potential stability and the highest electrode capacitance were measured for TCNQ/NaTCNQ-contacted sensors. As regards capacitance, these estimated values are slightly better or similar to those reported for carbon nanotubes (60 μF) [16], CB (51 μF) [17], PtNPs (82 μF) [13], and graphene (83 μF) [14], but lower than those obtained for CP (204 μF) [11] or colloid-imprinted mesoporous carbon (1.0 mF) [15] used as intermediate layer. Nevertheless, TCNQ and its radical sodium salt may act as redox reaction transducer. The resulting capacitances were comparable to those previously reported for sensors modified with TCNQ or NaTCNQ separately (154 and 132 μF , respectively) [25].

Selectivity

Undoubtedly, one of the most important properties of ISEs is the ability to react only to the chosen ion despite of the presence of other accompanying ions. Selectivity describes the attractiveness of the practical usage of ISE and its capability to distinguish primary ion from other interfering ions and is expressed by the potentiometric selectivity coefficient. Low values of selectivity coefficient are the most advantageous,

Fig. 6 Exemplary chronopotentiograms for tested electrodes recorded in 0.01-M NaCl by applying current +1 and −1 nA successively three times. The chart number is simultaneously the number of the group of

tested sensors (1—CD-ISEs, 2—SP-ISEs, 3—ASS-ISEs, 4—ionophore-free SP-ISEs), while the particular electrodes are marked as: □ (a), ○ (b), and △ (c)

because they indicate better electrode selectivity to the particular ion.

The selectivity coefficients values were calculated using the separate solution method (SSM) [37] by measuring the potentiometric response in the chloride solutions of main cation (i : Na^+) and interfering cations (j : Ca^{2+} , Mg^{2+} , Li^+ , NH_4^+ , K^+). Response functions were extrapolated to the activity of ions equal to 1 M ($a_i = a_j = 1$ M). The obtained results presented in Fig. 7 indicate that the membrane composition, kind of ionophore, as well as the introduction of NaTCNQ as membrane or SC component affects the sensors selectivity.

Taking into account the electrodes covered with membranes not containing the ionophore, but only NaTCNQ and lipophilic salt, it can be assumed that in the case of ions carrier absence the lipophilic component acts as ion exchanger [1]. Due to its ion-exchange properties, the lipophilic salt causes the extraction of all cations between solution and membrane phases. Merely results determined for electrode 4a are shown in the Fig. 7 due to the usage of NaTFPB in ionophore-based membranes also, however, similar characteristics were observed for the remaining lipophilic salts. The obtained selectivity coefficients sequence for each of these electrodes was $\text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$, and this order is in a good agreement with the Hofmeister series [38].

Only the addition of the ionophore to the ISM causes distinct differences in electrode selectivity. Electrode behavior depends on the type of ionophore used, therefore 1a and 1b sensors exhibited diversity of selectivity coefficients values [3, 4]. High sensitivity of 1a electrode to calcium ions can be explained by the fact that ETH 2120 added to membrane in which o-NPOE is used as plasticizer shows a clear lack of selectivity for sodium cations [39]. Nevertheless, such effect was reduced by introducing another sodium ions carrier to this ISM. Mixing of two ionophores in one ISM solution reduced

or raised selectivity coefficients compared to those obtained for membranes in which these ionophores were used separately. The selectivity coefficients evaluated for the electrode 1c are the resultant of those calculated for electrodes 1a and 1b.

Replacing a certain amount of ionophore with NaTCNQ salt (electrodes 2a, 2b, and 2c) caused a worsening of selectivity. The values of selectivity coefficients increased in relation to these calculated for the corresponding electrodes from the first group. Such change in selectivity behavior can be caused by insufficient quantity of selective carriers in ISM then the process of sodium ion-ionophore complex formation takes place on a smaller scale.

The introduction of TCNQ/NaTCNQ SC layer led to a reduction of the selectivity coefficient values compared to other groups of sensors. In this case, the improvement of selectivity may be due to the properties of intermediate layer. The applied SC can accumulate and release primary ions and therefore can inhibit the flow of primary ions from the membrane into interfering ions solution. The presence of sodium ions at the sample/membrane interface allows an undisturbed ion exchange process with interfering ion participation to be observed. This way, the potentiometric response in such samples is not overvalued, which significantly influences the selectivity behavior. Similar dependence was previously observed for sodium sensors modified with SC layer based on CNMs mixed with TCNQ and NaTCNQ and covered with ISM-containing sodium ionophore IV [27].

TCNQ/NaTCNQ-contacted electrodes showed the most reproducible potentiometric response during selectivity measurements. The SD of the standard potential of electrodes determined on the basis of the calibration performed in NaCl solutions between the successive measurement in interfering ions was 2.2, 2.6, and 1.1 mV for electrodes 3a, 3b, and 3c, respectively. Whereas, the same parameter obtained under the

Fig. 7 The selectivity coefficients $\log K_{i,j}^{\text{pot}}$ of investigated sensors determined by separate solution method (1a, 1b, and 1c—CD-ISEs; 2a, 2b, and 2c—SP-ISEs; 3a, 3b and 3c—ASS-ISEs; 4a—ionophore-free SP-ISE with NaTFPB)

same experimental conditions for the remaining sodium sensors was in turn 14.8 (1a), 16.0 (1b), 10.2 (1c), 11.2 (2a), 12.6 (2b), and 8.1 mV (2c).

Conclusion

The effect of sodium-selective membrane composition was studied through preparing sensors with the use of sodium ionophore III, sodium ionophore VI, and NaTCNQ. The membrane composition affects not only the observed selectivity coefficients but also the analytical and electrical parameters of electrodes. TCNQ/NaTCNQ-contacted Na^+ -ISEs showed the best characteristics. Such sensors exhibited better detection limits, more reproducible standard potential values, and lower potential drift compared to coated disc or single-piece electrodes.

Nevertheless, type of ionophore influences not only the sensor resistance but also capacitance. Elimination of ion carrier from ISM resulted in the weakest analytical and metrological parameters of electrodes. Moreover, partially replacement of ionic sites with sodium salt of TCNQ causes the deterioration of selectivity, since NaTCNQ does not act as ion exchanger and does not participate in potential formation. However, the introduction of TCNQ/NaTCNQ SC transducer slightly improved sensors selectivity compared to coated disc electrodes with membrane containing the same concentration of ionic sites. It can be assumed that such SC layer inhibits the flow of primary ions from the membrane into the solutions of interfering ions and thus does not overestimate the recorded potentiometric response. This in turn contributes to obtain better values of selectivity coefficients. Nonetheless, the phenomenon of improved selectivity is highly desirable considering the practical application of potentiometric sensors.

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References

- Bakker E, Bühlmann P, Pretsch E (1997) Carrier based ion-selective electrodes and bulk optodes. 1. General characteristics. *Chem Rev* 97:3083–3132
- Bühlmann P, Pretsch E, Bakker E (1998) Carrier-based ion-selective electrodes and bulk optodes. 2. Ionophores for potentiometric and optical sensors. *Chem Rev* 98:1593–1687
- Maruizumi T, Wegmann D, Suter G, Ammann D, Simon W (1986) Neutral carrier-based Na^+ -selective electrode for application in blood serum. *Microchim Acta* 1:331–336
- Shono T, Okahara M, Ikeda I, Kimura K, Tamura H (1982) Sodium-selective PVC membrane electrodes based on bis(12-crown-4)s. *J Electroanal Chem* 132:99–105
- Lindner E, Gyurcsányi RE (2009) Quality control criteria for solid-contact, solvent polymeric membrane ion-selective electrodes. *J Solid State Electrochem* 13:51–68
- Bieg C, Fuchsberger K, Stelzle M (2017) Introduction to polymer-based solid-contact ion-selective electrodes-basic concepts, practical considerations, and current research topics. *Anal Bioanal Chem* 409:45–61
- Bakker E (2016) Electroanalysis with membrane electrodes and liquid-liquid interfaces. *Anal Chem* 88:395–413
- Hu J, Stein A, Bühlmann P (2016) Rational design of all-solid-state ion-selective electrodes and reference electrodes. *TrAC Trends Anal Chem* 76:102–114
- Bobacka J, Ivaska A, Lewenstam A (2008) Potentiometric ion sensors. *Chem Rev* 108:329–351
- Michalska A, Hulanicki A, Lewenstam A (1997) All-solid-state potentiometric sensors for potassium and sodium based on poly(pyrrole) solid contact. *Microchem J* 57:59–64
- Bobacka J (1999) Potential stability of all-solid-state ion-selective electrodes using conducting polymers as ion-to-electron transducers. *Anal Chem* 71:4932–4937
- Bobacka J (2006) Conducting polymer-based solid-state ion-selective electrodes. *Electroanalysis* 18:7–18
- Paczosa-Bator B, Cabaj L, Piech R, Skupień K (2012) Platinum nanoparticles intermediate layer in solid-state selective electrodes. *Analyst* 137:5272–5277
- Li F, Ye J, Zhou M, Gan S, Zhang Q, Han D, Niu L (2012) All-solid-state potassium-selective electrode using graphene as the solid contact. *Analyst* 137:618–623
- Hu J, Zou XU, Stein A, Bühlmann P (2014) Ion-selective electrodes with colloid-imprinted mesoporous carbon as solid contact. *Anal Chem* 86:7111–7118
- Crespo GA, Macho S, Rius FX (2008) Ion-selective electrodes using carbon nanotubes as ion-to-electron transducers. *Anal Chem* 80:1316–1322
- Paczosa-Bator B (2012) All-solid-state selective electrodes using carbon black. *Talanta* 93:424–427
- Paczosa-Bator B, Cabaj L, Piech R, Skupień K (2013) Potentiometric sensors with carbon black supporting platinum nanoparticles. *Anal Chem* 85:10255–10261
- Paczosa-Bator B (2015) Ion-selective electrodes with superhydrophobic polymer/carbon nanocomposites as solid contact. *Carbon* 95:879–887
- Zou XU, Cheong JH, Tait BJ, Bühlmann P (2013) Solid contact ion-selective electrodes with a well-controlled Co(II)/Co(III) redox buffer layer. *Anal Chem* 85:9350–9355
- Lindfors T (2009) Light sensitivity and potential stability of electrically conducting polymers commonly used in solid contact ion-selective electrodes. *J Solid State Electrochem* 13:77–89
- Yin T, Qin W (2013) Applications of nanomaterials in potentiometric sensors. *TrAC Trends Anal Chem* 51:79–86
- Wardak C (2015) Solid contact cadmium ion-selective electrode based on ionic liquid and carbon nanotubes. *Sensors Actuators B Chem* 209:131–137
- Wardak C, Lenik J (2013) Application of ionic liquid to the construction of Cu(II) ion-selective electrode with solid contact. *Sensors Actuators B Chem* 189:52–59
- Paczosa-Bator B, Pięk M, Piech R (2015) Application of nanostructured TCNQ to potentiometric ion-selective K^+ and Na^+ electrodes. *Anal Chem* 87:1718–1725

26. Pięk M, Fendrych K, Smajdor J, Piech R, Paczosa-Bator B (2017) High selective potentiometric sensor for determination of nanomolar concentration of Cu(II) using a polymeric electrode modified by a graphene/7,7,8,8-tetracyanoquinodimethane nanoparticles. *Talanta* 170:41–48
27. Pięk M, Piech R, Paczosa-Bator B (2016) The complex crystal of NaTCNQ–TCNQ supported on different carbon materials as ion-to-electron transducer in all-solid-state sodium-selective electrode. *J Electrochem Soc* 163:B573–B579
28. Starodub VA, Starodub TN (2014) Radical anion salts and charge transfer complexes based on tetracyanoquinodimethane and other strong π -electron acceptors. *Russ Chem Rev* 83:391–438
29. Wooster TJ, Bond AM, Honeychurch MJ (2003) An analogy of an ion-selective electrode sensor based on the voltammetry of micro-crystals of tetracyanoquinodimethane or tetrathiafulvalene adhered to an electrode surface. *Anal Chem* 75:586–592
30. Sharp M, Johansson G (1971) Ion-selective electrodes based on 7,7,8,8-tetracyanoquinodimethane-radical salts. *Anal Chim Acta* 54:13–21
31. Melby LR, Harder RJ, Hertler WR, Mahler W, Benson RE, Mochel WE (1962) Anion-radical derivatives and complexes of 7,7,8,8-tetracyanoquinodimethane. *J Am Chem Soc* 84:3374–3387
32. Koryta J, Dvořák J, Kavan L (1993) Principles of electrochemistry, 2nd edn. Wiley, Chichester, p 38
33. Ramanathan R, Walia S, Kandjani AE, Balendran S, Mohammadtaheri M, Bhargava SK, Kalantar-Zadeh K, Bansal V (2014) Low-temperature fabrication of alkali metal-organic charge transfer complexes on cotton textile for optoelectronics and gas sensing. *Langmuir* 31:1581–1587
34. Paczosa-Bator B, Cabaj L, Raś M, Baś B, Piech R (2014) Potentiometric sensor platform based on a carbon black modified electrodes. *Int J Electrochem Sci* 9:2816–2823
35. Paczosa-Bator B, Piech R, Cabaj L (2012) The influence of an intermediate layer on the composition stability of a polymeric ion-selective membrane. *Electrochim Acta* 85:104–109
36. Fibbioli M, Morf WE, Badertscher M, De Rooij NF, Pretsch E (2000) Potential drifts of solid-contacted ion-selective electrodes due to zero-current ion fluxes through the sensor membrane. *Electroanalysis* 12:1286–1292
37. Bakker E, Pretsch E, Bühlmann P (2000) Selectivity of potentiometric ion sensors. *Anal Chem* 72:1127–1133
38. Hofmeister F (1888) Zur lehre von der wirkung der salze. *Arch Exp Pathol Pharmacol* 24:247–260
39. Nägele M, Mi Y, Bakker E, Pretsch E (1998) Influence of lipophilic inert electrolytes on the selectivity of polymer membrane electrodes. *Anal Chem* 70:1686–1691