



Critical assessment of graphene as ion-to-electron transducer for all-solid-state potentiometric sensors

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ABSTRACT

Carboxy-functionalized graphene was used as a solid contact for potassium ion-selective electrodes with poly(vinyl chloride) based membrane. Transducer layers were obtained simply by application of a dispersion of graphene derivative in water. Analytical performance of thus obtained sensors was compared with that of all-solid-state sensors with typical transducer materials: poly(octylthiophene) applied as chloroform solution, conducting polymers available as aqueous dispersions of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) ions or polyaniline. It was found that all sensors tested were characterized with similar analytical parameters. Carboxy-functionalized graphene contact layer was in some respect similar to polyaniline one, what most probably results from the presence of pH sensitive groups in both materials.

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1. Introduction

Conducting-polymers (CPs) are established solid contact materials, ion-to-electron transducers applied in all-solid state ion selective electrodes [1,2]. The unique properties, especially coupled ionic and electronic conductivity of CPs resulting in pronounced stability of sensors have attracted much scientific attention leading to sensors of both high stability and optimized analytical parameters. Initially, conducting polymers intended to be transducer layers were electropolymerized directly on the substrate [1,2], later solution processable/dispersable polymers were preferred [3]. Clear benefits of simplicity of the application of conducting polymers, either in the form of water based dispersions [4–11] or from other solvents [12–19], has led to ongoing discussion on superiority of water vs. organic solvents based polymers solutions/dispersion with emphasis on analytical properties of resulting sensors. The key issue here is possibility of accumulation of electrolyte aqueous solution at the backside of the membrane, resulting in ion-fluxes affecting analytical performance of the electrode [10,20–24]. Earlier reports highlighted benefits of application of semiconducting, quite lipophilic conducting polymers, e.g. poly(octylthiophene), as assuring absence of water layer in sensor phases. However, more recent studies clearly show, using both advanced experimental methods [25] and potentiometric studies [11], that water dispersible conducting polymers, e.g. poly(3,4-ethylenedioxythiophene) doped with

poly(4-styrenesulfonate) ions, result in the absence of water layer, possibly accumulating some water and electrolyte ions similarly as hydrogels.

Despite the unquestionable profits of conducting polymers application as transducers, the field is open for other materials that can assure stable potential readings of all-solid state potentiometric sensors. The clear interest recently is in the application of nanostructured materials including conducting polymers nanoparticles [7,8,10,26] or microcapsules [27–29], carbon nanotubes [30–32], nanostructured carbon [33] or gold [34–36] and very recently graphene [37].

Graphene can be attractive material for application as a transducer in potentiometric sensors, especially if graphene derivatives containing functional groups, e.g. carboxy-functionalized graphene, able to exchange ions with ion-selective membrane layer are considered, as earlier shown for conducting polymers [1,2] or more recently for carbon nanotubes [38]. The additional benefit of these derivatives is that they can be prepared as water based suspension and in this form applied on top of a substrate electrode. This, however, again, opens the question on the possible effect of relative hydrophilicity of graphene derivative applied on stability of potential and electrochemical parameters characterizing thus obtained all-solid-state sensors. These issues have not been thoroughly discussed in the literature.

In this report we are experimentally comparing, in one parallel study, all-solid-state potassium sensors (with poly(vinyl chloride) based membranes) applying as transducer layer poly(octylthiophene), polyaniline and poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) ions as well as carboxy-functionalized graphene with classical coated wire (coated disk) arrangement.

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2. Experimental

2.1. Reagents, electrodes and apparatus

All reagents used were analytical grade salts and were from POCh (Poland) or Sigma. Doubly distilled and freshly deionised water (resistance 18.2 M Ω cm, Milli-Qplus, Millipore, Austria) was used throughout this work.

Glassy carbon (GC) electrodes of surface area 0.07 cm² were used, before application of graphene layer the electrodes were polished using sand paper of fine grit. The double junction silver/silver chloride reference electrode with 1 M lithium acetate in the outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. In electrochemical impedance spectroscopy (EIS) experiments conventional three electrode cell, with platinum sheet as counter electrode, was used.

In the potentiometric experiments and electrochemical measurements experimental setup described earlier e.g. Ref. [39] was used. The recorded potential values were corrected for the liquid junction potential calculated according to Henderson approximation.

X-ray photoelectron spectroscopy (XPS) experiments were performed in a PHI 5000 VersaProbe—Scanning ESCA Microprobe (ULVAC-PHI, Japan/USA) instrument at a base pressure below 5×10^{-9} mbar. Monochromatic Al K α radiation was used and the X-ray beam, focused to a diameter of 100 μ m, was scanned on a 250×250 μ m surface, at an operating power of 25 W. Photoelectron survey spectra were acquired using a hemispherical analyzer at pass energy 117.4 eV with a 0.4 eV energy step, core-level spectra were acquired at pass energy 23.5 eV with a 0.1 eV energy step. All spectra were acquired with 90° between X-ray source and analyzer and with the use of low energy electrons and low energy argon ions for charge neutralization. After subtraction of the Shirley-type background, the core-level spectra were decomposed into their components with mixed Gaussian–Lorentzian (30:70) shape lines using the CasaXPS software. Quantification calculations were conducted with using sensitivity factors supplied by PHI. Spectra were calibrated against 284.6 eV for C 1s region corresponding to C–C bonds.

2.2. Reagents

Tetrahydrofuran (THF), chloroform, regioregular poly(ocetylthiophene) (POT), poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), valinomycin, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) were from Fluka AG (Buchs, Switzerland) or from Aldrich (Germany). Aqueous dispersion of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) was obtained from Bayer AG (currently it is available from H.C. Starck). PANI aqueous suspension D1012W-1 was obtained from Ormecon GmbH (Germany).

2.3. Carboxy-functionalized graphene derivative

Carboxy-functionalized graphene derivative (CF-G) has been synthesized according to the previously reported method [40]. Shortly, graphite oxide has been obtained via the modified Hummer's method [41] without the use of silver nitrate and then reacted with the N,N-dimethylacetamide dimethyl acetal (2 times the molar equivalent of oxygen content of graphite oxide, at 150 °C, in bis(2-methoxyethyl)ether, under inert atmosphere). The obtained material has been extensively washed and subsequently reacted with aqueous potassium hydroxide solution to yield carboxy-functionalized graphene derivative (G4 in Ref. [40]).

2.4. Preparation of solid contact electrodes

Carboxy-functionalized graphene as water suspension (2.2 mg/ml) was applied on top of glassy carbon electrodes while substrate facing up, 20 μ l of carboxy-functionalized graphene was applied per electrode in 5 μ l portions and left for water evaporation in laboratory atmosphere. After application of the final portion the electrodes were left for 5 h for water evaporation at room temperature. Thickness of obtained layer was close to 3 μ m.

For comparison POT transducer sensors were also used, they were prepared by applying 10 μ l of polymer solution in chloroform (2.5 mg/ml) instead of CF-G and left for evaporation of POT solvent, at room temperature. Similarly, PEDOT or PANI transducer layers were obtained by applying 10 μ l of polymer water suspension on substrate electrode facing up and leaving for solvent evaporation (5 h), at room temperature. Thickness of obtained layer was close to 3 μ m.

Coated wire (CW) (in fact coated disk, however, the traditional name was preferred throughout the report) sensors were obtained applying the membrane directly on polished electrode support.

2.5. Ion-selective membranes

Potassium selective electrodes, K-ISE, membranes contained (by weight): 1.2% NaTFPB, 2.8% valinomycin, 64.4% DOS and 31.6% PVC. Total 200 mg were dissolved in 1.5 ml of THF. Thickness of obtained membrane was close to 200 μ m.

30 μ l of the membrane cocktail was applied on the top of electrodes prepared as described above (in 10 μ l aliquots), when the electrode (either unmodified glassy carbon, alternatively glassy carbon modified with carboxy-functionalized graphene, PANI, PEDOT or POT) was placed in up-side down position and left for 5 h for water or THF evaporation, respectively, yielding CW-ISE, CF-G-ISE, PANI-ISE, PEDOT-ISE or POT-ISE, respectively. As lowering of the detection limit was not aimed in this study, all tested sensors were conditioned before measurements for at least 12 h and were stored in-between measurements in 10^{-3} M KCl solution.

3. Results and discussion

Results of XPS analysis of CF-G allowed atomic composition determination (Table 1, Fig. 1). The nitrogen content, 1.2 atomic percentage is a proof of non quantitative amide groups saponification in course of CF-G preparation. The presence of CON(CH₃)₂ moieties in the obtained material is further confirmed by careful analysis of high resolution of C(1 s) region. Components ascribed to C–N (285.4 eV) and N–C=O (286.6 eV) signals were found. To evaluate the abundance of COOH groups grafted onto the surface of graphene sheets, the decrease of nitrogen content between graphene amide and carboxylic derivative can be used. The drop from 3.1% to 1.2% atomic nitrogen content can be translated into 61% yield of saponification reaction and consequently it can be concluded that the carboxylic group density is 1 moiety per 38 carbons atoms constituting graphene sheet (with still remaining

Table 1
Results of XPS analysis of as prepared CF-G films.

Atomic %			
C	O	N	K
74.4	22.6	1.2	1.8

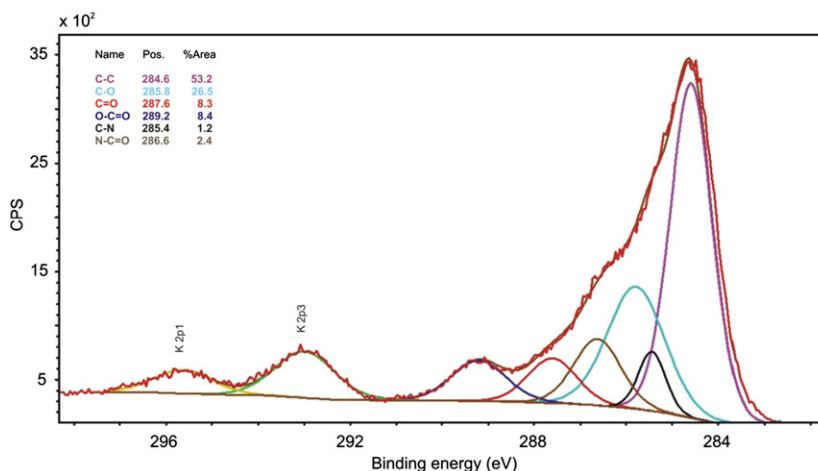


Fig. 1. The result of XPS studies of as prepared carboxyl-functionalized graphene.

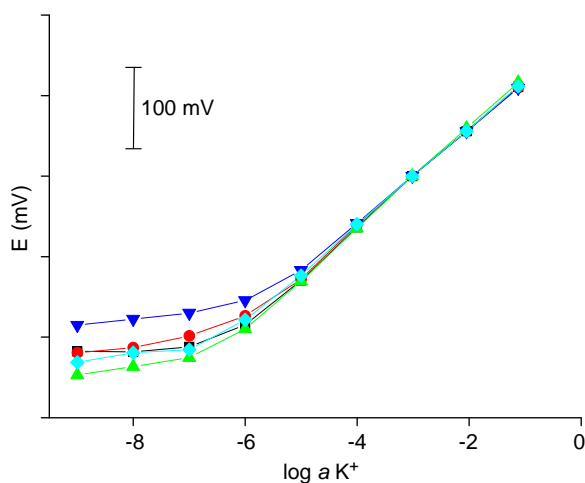


Fig. 2. Calibration lines obtained for tested potentiometric sensors: (■) coated wire or all-solid state sensors with (●) polyaniline, (▲) carboxy-functionalized graphene, (◆) poly(octylthiophene) or (▼) poly(3,4-ethylenedioxythiophene) transducer layers. For easy comparison all curves were shifted to give equal potential at $\log a K^+ = -3$.

1 amide group per 59 carbons atoms). It should be stressed that no detail data on composition of graphene applied previously as solid contact layer was presented [37].

Potentiometric responses of tested sensors are presented in Fig. 2 and calibration parameters are gathered in Table 2. The tested sensors were showing similar Nernstian responses, within the range of experimental error with exception of PEDOT contact sensor. The presence of PEDOT transducer layer has resulted in slope of characteristic lower than Nernstian and equal to 55.2 ± 1.7 mV/dec, the lowest among tested electrodes. This type sensors were also characterized with the highest, among tested, detection limit equal to $10^{-6.3}$ M. This can be result of ability of conducting polymer doping poly(4-styrenesulfonate) anions to bind potassium cations, thus enriching transducer layer with primary ions [7], which affects responses in low activity range. For CW type sensor the linear response range was slightly longer compared to PEDOT transducer sensor and its detection limit was equal to $10^{-6.5}$ M, i.e. it was similar to the value reported earlier for all-plastic electrodes using the same conducting polymer [7]. A similar value of detection limit ($10^{-6.6}$ M) was obtained for PANI solid contact electrode, which is expected taking into account that PANI applied as transducer was also obtained from aqueous dispersion stabilized with polyelectrolyte ions [10].

Sensors prepared using a virtually ion-free, conducting polymer in reduced form, poly(octylthiophene), have been characterized by slightly lower detection limit equal to $10^{-6.8}$ M. Yet lower detection limit, equal to $10^{-7.1}$ M, was obtained for carboxy-functionalized graphene transducer, this value is significantly lower compared to reported previously for graphene based contact sensor, equal to 10^{-5} M [37]. The obtained detection limit, lower compared to obtained for other transducers applied from aqueous dispersions: PEDOT and PANI, can be related to lower accumulation of analyte ions in the CF-G compared to conducting polymers. In the latter case presence of polyelectrolyte, ion-exchanger stabilizing the suspension of PEDOT or PANI in solution, is ultimately resulting in high primary ion loadings of the transducer phase [11]. The lower detection limit obtained for CF-G transducer, compared to other systems tested in parallel, is promising for the application of graphene as a transducer layer in potentiometric sensors.

The selectivity coefficients calculated for tested sensors (Table 2), were similar within the range of experimental error for ion-selective electrodes containing any of the tested transducers and similar to previously reported values for K^+ selective electrodes using valinomycin as an ionophore [7,30,34,37]. This is according to expectations as selectivity, for fully saturated membranes, i.e. classical membranes, is determined by the properties of the membrane as such.

Fig. 3 presents results of chronopotentiometric tests performed for all-solid-state sensors, resistivity and capacitance calculated as described earlier [42] are gathered in Table 2. As it can be seen from Fig. 3 introduction of transducer layer significantly lowered the potential jump observed when the current polarity was changed, compared to coated wire electrode. This is reflected by values of resistance of sensors (Table 2), the value characterizing the coated wire electrode is the highest among obtained for tested sensors and is close to 10 MΩ. Sensors with transducers obtained from aqueous dispersion of conducting polymers, PANI or PEDOT, were characterized with similar and lowest resistance among tested sensors, close to 1 MΩ. Taking into account high ions contents in the two layers and relatively high conductivity of these polymers (compared e.g. to POT) [7,10] this value probably reflects the resistance of ion-selective membrane. Slightly bigger value was characterizing sensors with POT layer applied as a transducer. This can be attributed to weak semiconducting properties of undoped POT layer, resulting in a relatively higher resistance of this layer. The value characterizing CF-G transducer sensor was yet higher compared to POT contact layer sensor, which probably result from low ionic contents of

Table 2

Selectivity coefficients, $\log K_{R_j}^{\text{pot}} \pm \text{SD}$ obtained within the activities range from 10^{-1} to 10^{-3} M, separate solution method (the values were determined using experimental electrodes characteristic slopes), slopes of calibration lines, calculated detection limits and electrical parameters of sensors determined from the results of chronopotentiometric tests using current $\pm 10^{-9}$ A, for tested potassium selective electrodes.

	CW	CF-G	PEDOT	PANI	POT
Ion J	$\log K_{R_j}^{\text{pot}} \pm \text{SD}$				
Mg ²⁺	-3.5 ± 0.3	-3.7 ± 0.3	-3.6 ± 0.2	-3.6 ± 0.3	-3.4 ± 0.4
Ca ²⁺	-3.5 ± 0.3	-3.7 ± 0.3	-3.5 ± 0.3	-3.6 ± 0.3	-3.4 ± 0.4
H ⁺	-4.5 ± 0.2	-4.6 ± 0.1	-4.2 ± 0.3	-4.6 ± 0.3	-4.5 ± 0.3
Na ⁺	-3.4 ± 0.2	-3.5 ± 0.2	-3.1 ± 0.2	-3.5 ± 0.1	-3.1 ± 0.1
–	Calibration line parameters				
Slope ± SD (mV/dec) (range [M])	61.2 ± 0.7 (10 ⁻¹ –10 ⁻⁶)	60.0 ± 1.8 (10 ⁻¹ –10 ⁻⁷)	55.2 ± 1.7 (10 ⁻¹ –10 ⁻⁶)	59.2 ± 1.2 (10 ⁻¹ –10 ⁻⁶)	59.8 ± 0.5 (10 ⁻¹ –10 ⁻⁷)
Detection limit [M]	10 ^{-6.5}	10 ^{-7.1}	10 ^{-6.3}	10 ^{-6.6}	10 ^{-6.8}
–	Sensor electrochemical parameters (from chronopotentiometric studies)				
Resistance [Ω]	8.8 × 10 ⁶	3.0 × 10 ⁶	1.8 × 10 ⁶	1.1 × 10 ⁶	2.5 × 10 ⁶
Capacitance [F]	2 × 10 ⁻⁶	3 × 10 ⁻⁵	9 × 10 ⁻⁵	2 × 10 ⁻⁵	1 × 10 ⁻⁴

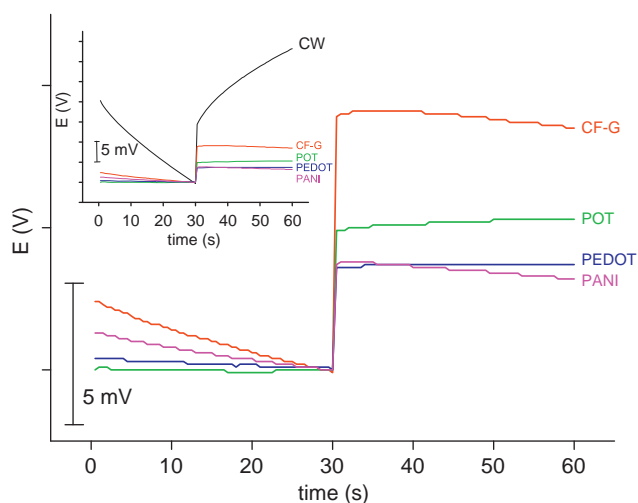


Fig. 3. Chronopotentiometric test of solid contact electrodes, passing current: $\pm 10^{-9}$ A, in 10^{-1} M KCl (inset: chronopotentiometric responses in the scale showing also CW type sensor).

carboxy-functionalized graphene. Nevertheless the value obtained for this CF-G transducer sensor was significantly lower compared to coated wire type electrode tested in parallel. Interestingly, also recorded dependence of potential on time was significantly different for coated wire sensor and electrode using carboxy-functionalized graphene as solid contact (Fig. 3). In the latter case the potential dependence on time was significantly less pronounced, it was more comparable to that for sensor with PANI transducer. Thus, the capacitance values calculated for CF-G and PANI sensors were comparable within the range of experimental error and were close to 3×10^{-5} and 2×10^{-5} F, respectively, and were one order of magnitude higher than the value obtained for coated wire type sensor (Table 2). Herein reported capacity value obtained for carboxy-functionalized graphene contact is well comparable with those reported for carbon-nanotube sensors [30] or graphene transducers [37]. However, the resistivity reported in this work for CF-G transducer sensors is one order of magnitude lower than values given in either of the above reports.

It is interesting to speculate on the origin of similarity between CF-G and PANI transducer layer properties under chronopotentiometric test—it seems probable that the similarity can be related to possibility of expulsion/binding hydrogen ions within the phase. Interestingly, similar effect was reported earlier for carbon nanotubes transducer sensors, however, applying significantly ($100 \times$) higher current [30]. Although the mechanism of this is

expected to be different for the two solid contact layers, both contain “potentially” exchangeable hydrogen cations, either in carboxyl group or in the polymer backbone. Possibly, using significantly higher current some exchange of hydrogen ions between carbon nanotube based transducer and ion-selective membrane could be induced too. In our studies increase of polarizing current to 10^{-8} A did not result in change of the responses recorded (results not shown). Clearly more detail studies are required, however, these are beyond the scope of this report.

POT and PEDOT transducer sensors were characterized with similar values of capacitance close to 10^{-4} F, which are comparable with results of other experiments with the two layers [e.g. Ref. [11]].

Fig. 4 shows results of electrochemical impedance spectroscopy measurements carried out in 0.1 M KCl solution, presented in the form of Bode plots. The impedance spectra were recorded within frequency range from 0.01 to 10^4 Hz, at potential 0.5 V with amplitude 50 mV.

For all the studied sensors: with PANI, POT, PEDOT and carboxy-functionalized graphene solid contact as well as for coated wire electrode, in the frequency range from 0.1 to 10^3 Hz the impedance was almost independent of frequency and phase angle was equal or close to zero. This denotes that recorded impedance was practically equal to resistance. The resistance sequence (the highest for coated wire electrode, the lowest for the electrodes with conducting polymer solid contact) is consistent with chronopotentiometric results (Fig. 3). This resistance corresponds to ohmic resistance of the membrane and additionally hindered charge transfer, particularly in the case of coated wire electrode, it can contribute to apparent elevated resistance [43].

For frequencies higher than 10^3 Hz the impedance starts to decrease with rising frequency and the negative value of the phase angle significantly increases. This points to growing role of a capacitive element, in this case geometric capacitance of the PVC based membrane, connected parallel to ohmic resistance [42]. The geometric capacitance, C_g , estimated from the impedance, Z , recorded for phase angle close to -90° , can be calculated from

$$C_g = \frac{1}{2\pi f Z} \quad (1)$$

where f is frequency. The estimated C_g is around 10^{-11} F, consistent with other data reported for PVC based membranes [42].

At frequencies lower than 0.1 Hz, for the coated wire electrode, the impedance increases with lowering frequency, while for other electrodes the impedance is practically constant. This increase for coated wire sensor results from low capacitance at the electrode support/membrane interface (compared to arrangement with

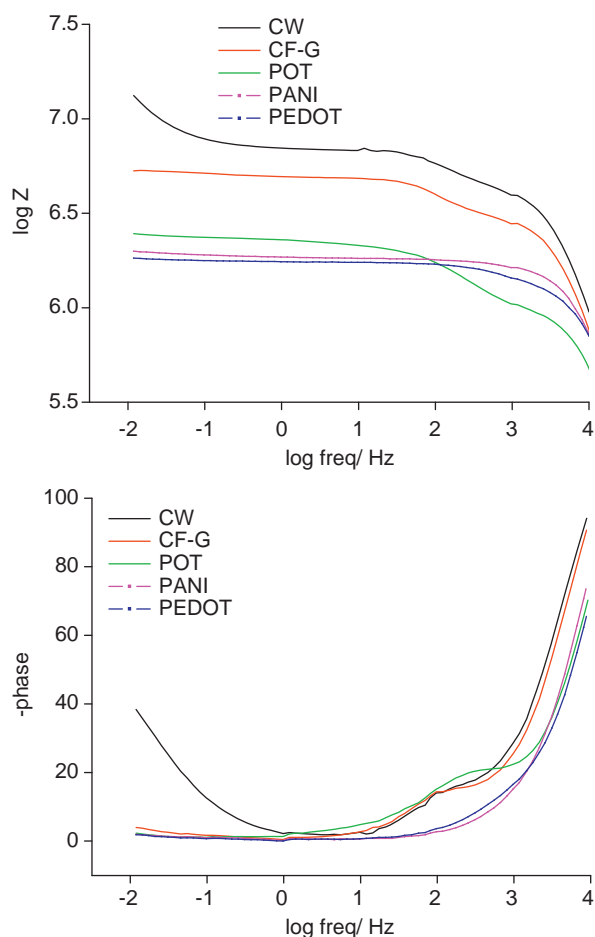


Fig. 4. Electrochemical impedance spectra recorded for K-selective electrodes with different type solid contact applied as well as coated wire type sensors, recorded in 10^{-1} M KCl solution, using 50 mV amplitude at potential 0.5 V.

conducting polymer or carboxy-functionalized graphene solid contact), manifested also in relatively high slope of the chrono-potentiometric plot (Fig. 3).

Stability of all-solid-state sensors with carboxy-functionalized graphene were the subject of detail studies. Potentiometric tests performed during 3 weeks revealed high stability of potential values recorded (Fig. 5). The standard deviation of mean value of potential values recorded within the activity range from 10^{-4} to 10^{-1} M was close to 4 mV, slightly higher standard deviations were obtained for lower activities, reaching values close to 15 mV for activities below the detection limit. As it can be seen from Fig. 5 the obtained stability is significantly higher compared to results of parallel experiment conducted for coated wire type sensor. The obtained results are highly promising for application of functionalized graphene as transducer layer in potentiometric sensors.

Fig. 6 presents the result of other commonly used test allowing insight in sensor stability, called water layer test [20]. It is looking at the formation of electrolyte layer beneath the ion-selective membrane. As it can be seen from Fig. 6, carboxy-functionalized graphene solid contact electrode was characterized with high stability of potential values recorded – no drifts – both in primary ion solution and in interfering ion solution, similarly as observed earlier for conducting polymers based sensors, e.g. Ref. [11]. The herein presented results clearly show that there is no water layer within the structure of the CF-G transducer based sensor, thus the outcome of this test is significantly different from results

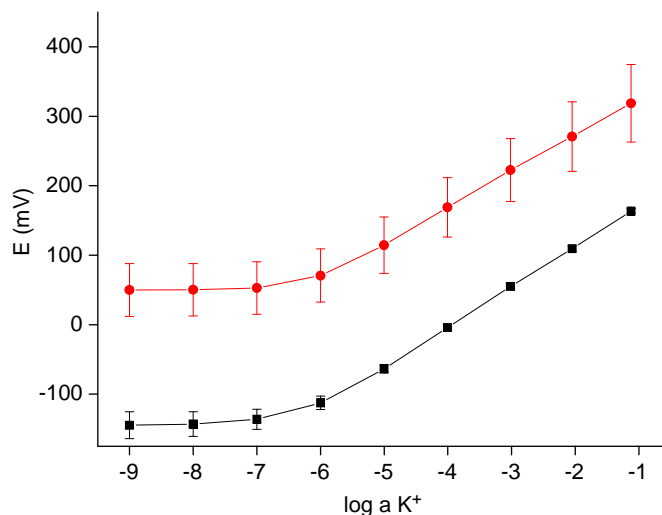


Fig. 5. The mean potential values \pm SD recorded over 19 day tests (repeated calibrations): (■) carboxy-functionalized graphene (CF-G) transducer sensor, (●) coated wire type electrode.

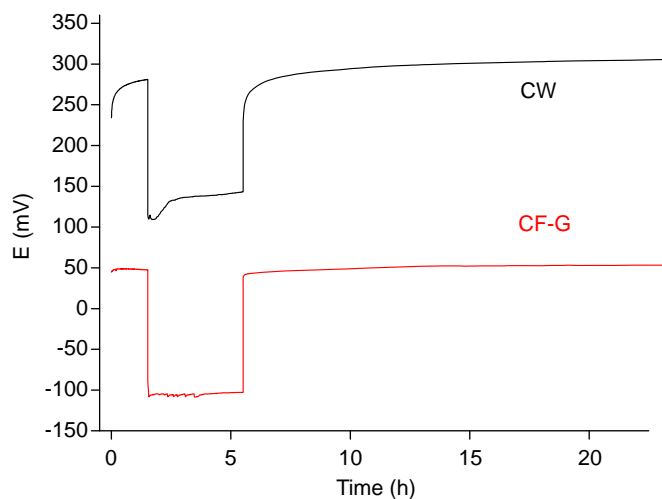


Fig. 6. The aqueous layer test experiment performed for carboxy-functionalized graphene (CF-G) solid contact electrode and coated wire type electrode. The experiment was performed in 10^{-3} M KCl, 10^{-3} M NaCl and 10^{-3} M KCl again.

presented by Li et al. [37], where the presence of water layer in the carboxy-functionalized graphene transducer based sensor was postulated. A significantly different picture was obtained for coated wire type sensor tested in parallel – both initially in K^+ ions solution, in Na^+ ions and again in K^+ ions solution -for this type sensor potential drifts were observed, similarly as reported earlier for this type of electrodes [e.g. Refs. [34,37]].

High stability of potential readings obtained for carboxy-functionalized graphene transducer based sensors (Figs. 5 and 6), clearly shows that application of aqueous dispersion is not imposing any constrain on sensor performance. This is in good agreement with the results obtained for other materials available as aqueous dispersion, e.g. PEDOT or PANI [11], as well as with recent reports when carboxy-functionalized graphene was directly applied as potentiometric membrane [44].

4. Conclusions

Results presented above clearly show that carboxy-functionalized graphene layers applied as a solid contact in potentiometric

sensors, instead of typically applied conducting polymer film, can effectively work as ion-to-electron transducers. Analytical parameters of carboxy-functionalized graphene contact ion-selective electrodes are comparable with those of other all-solid-state arrangements. Potential readings stability is much improved compared to that of coated wire electrodes (using the same type membrane) tested in parallel and is well comparable with the other systems tested in our group, including highly reliable POT solid contact potassium-selective electrodes.

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