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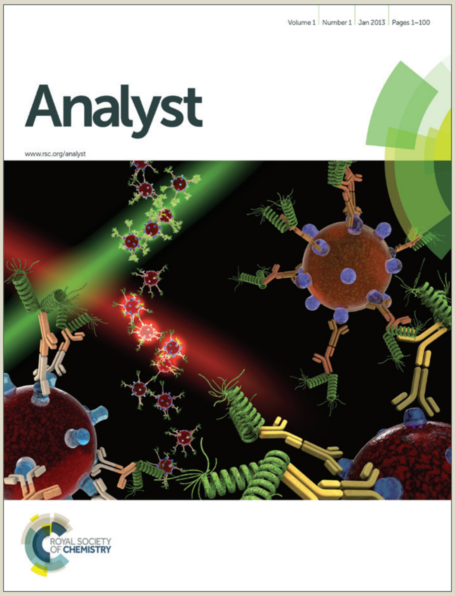

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Spray coated all-solid-state potentiometric sensors

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Abstract

A novel fully spray coating based method of preparation of all-solid-state ion-selective electrodes of simplified construction is proposed. This method is alternative for screen-printed electrodes used sometimes in potentiometric applications. The benefits of herein proposed approach include fully automatic sensor preparation as well as minimized use of chemicals allowing production of low cost sensors that can be applied as disposables.

A spray coated carbon nanotubes layer on inert support was used both as electrical lead and as transducer, to simplify sensor layout and to avoid possible problems of changing in time composition of this layer, as previously observed in the case of screen-printed supporting electrodes in potentiometric applications.

The ion-selective poly(vinyl chloride) based membrane and the insulator layer were spray-coated, too. Obtained sensors, as model system potassium-selective sensors were prepared, were characterized with analytical parameters well comparable with those of conventional all-solid-state ion-selective electrodes. The applicability of herein proposed approach to prepare also other ion-selective electrodes was tested on example of H^+ and Cl^- sensor.

Introduction

Internal solution free ion-selective electrodes have nowadays established position in the potentiometry [1]. All-solid-state ion-selective electrodes (ASS-ISEs) can offer analytical parameters well comparable with those of conventional internal solution containing potentiometric sensors, including stability of potential values recorded in time [1,2]. In principle ASS-ISEs can be a low cost, easy to produce, miniature, reliable and disposable alternative to conventional potentiometric sensors; however, this idea has not been fully accomplished in practice, yet. The classical set up of ASS-ISEs applies a macroscopic inert substrate electrode [1,2], which is further modified by application of a transducer layer (required to achieve high stability of potential readings in time) and an ion-selective membrane. The cost and size of supporting electrode and the manual operations required to obtain ASS-ISEs hinder mass scale preparation of cost-effective, miniature, disposable sensors.

Application of simple low cost methods leads to substantial improvements in electronics and related fields offering a simple, disposable elements [e.g.3]. In this respect screen-printed electrodes are of interest, too. They allow not only miniaturization but also custom tailored arrangements of electrodes and they are successfully used e.g. in amperometric sensing; a range of screen-printed electrodes for this purpose is available commercially [4]. Although application of screen-printing technique to automatize production of sensors containing sparingly soluble salts dispersed within electrochemically inactive matrix (analogues of sparingly-soluble salts membranes) has been reported [e.g. 5], this approach for obvious reasons is applicable only to a few systems.

Screen-printed *substrate* electrodes have been also used to prepare potentiometric sensors. This approach requires modification of screen-printed substrate with conducting polymers (CPs) [6,7,8] or carbon nanotubes (CNTs) [9], i.e. materials typically applied as ion-to-electron transducers for ASS-ISEs. Both CNTs and CPs are often applied by drop casting of their solution / dispersion [7,8,9]. CPs layers can be also obtained by direct electropolymerization on screen-printed substrate [e.g.6]. The next step is usually manual drop casting of solution / dispersion of an ion-solution membrane cocktail [6-9]. Thus, similarly as for classical ASS-ISEs, a few manual operations are necessary to prepare a potentiometric sensor, even though the substrate electrodes can be produced automatically, increasing cost and material consumption hinder practical application as disposable electrodes.

The obtained sensors (as model mainly K^+-selective electrodes were prepared) are usually characterized with analytical parameters slightly worse (detection limit, selectivity) when compared with arrangements using classical ASS-ISEs [6-9]. Although this deviation from typical (the best achievable) parameters in principle is acceptable for many applications, usage of screen-printed electrodes in potentiometry is limited, in contrary to their popularity in e.g. amperometry. Clearly one of the reasons lies in the combination of nature of screen-printing method and time scale of potentiometric vs. amperometric measurements. The latter are usually completed within seconds or a few minutes at the most. On the other hand, potentiometric measurements, even using nominally disposable electrodes, take significantly longer – due to nature of technique (calibration required, signal stabilization). Occasionally, even disposable sensors are required to work continuously for a few hours or days. In this time scale unwanted spontaneous processes occurring within the screen-printed layer, e.g. hydrolysis of the applied paint components, can occur and adversely affect the performance of the sensor. These processes usually result in formation of species that can partition into the ion-selective membrane ultimately affecting the analytical parameters of the sensors [e.g.[6]]. In short time scale (e.g. in amperometric measurements) these effects are insignificant; however, can be severe in potentiometric experiment time scales, especially as the details of the composition of the screen-printing paste is usually unknown. The other issue that increases in significance in longer time scale is adhesion of layers constituting the sensor. In the case of screen-printed substrate electrode, to solve this problem introduction of adhesive admixture to the membrane composition was required [[7,8]].

The issue of adhesion of the PVC based membrane to the substrate (in the case of internal solution free sensors and optical sensors) has been discussed in literature for many years now, mainly looking at SiO_2 based substrates [e.g.[10],[11],[12],[13],[14]]. In this respect Kapton (polyimide) support, in the arrangement using gold tracks as electrical lead/substrate, covered with hydrogel layer and then by solvent cast PVC membrane [[15]] has been found a promising material for miniature, planar potentiometric sensors for bio-medical applications [[16]] already 20 years ago.

The above mentioned issues related to application of screen-printed sensors in potentiometry, have stimulated search for alternative approaches that can lead to planar, low-cost, and potentially disposable ion-selective electrodes. There is a clear research interest in development of such sensors, especially in recent years. This has led for example to application of ink-jet printing for sensor development [[17]].

Also alternative approaches have been studied, their common feature is manual application of a conducting material (as e.g. suspension), most often conducting polymer [[18],[19],[20]], graphene [[21]] or carbon nanotubes [[22]] that play a role of both substrate and transducer on inert supporting material: acetate foil [18,19,20,21] or paper [22]. Alternatively semi-manual methods using aerograph, manually operated type devices are used to obtain e.g. carbon nanotubes layers [22,23]. Sometimes this step is also followed by additional manual treatment (washing) of the obtained layer [e.g.22]. The next manual step required is drop casting an ion-selective membrane cocktail [18-22]. Definitely, this approach is free from risk related to unknown and unstable (in time, in water environment) composition of the substrate layer; however, the manual operations required still hinder mass scale production. Moreover, these are potentially less reproducible and more material consuming compared to automatic alternatives, highlighting the need for alternative approach.

On the other hand, electronic devices (e.g. field effect transistors or solar cells) benefit from spray coating method of (conducting) layers application [e.g. 24,25,26]. This method, to our best knowledge, has not been applied to prepare ion-selective membrane layers, or to prepare potentiometric sensors, yet. Among layers that can be spray coated on different substrates, including plastic and glass, are carbon nanotubes (CNTs) of high electrical conductivity [e.g. 27]. The CNTs layers thus obtained conveniently can be used as electrical lead and substrate/ transducer of potentiometric sensors. From the potentiometric application point of view it is also important that spray coated layers do not contain any binders, thickening agent or any material that can undergo uncontrolled changes during even long time contact with water based sample. Moreover, spray coating offers higher reproducibility and better control of resulting layers compared to manual (e.g. paintbrush [22] or drop casting [18-21]) application, and the usage of materials can be minimized, too. Spray coating – due to mild conditions of the process – can be applicable to the (sensitive) ion-selective membrane as well. The demand of preparing all layers of a sensor in the same technology can be achieved, moreover, in automatized procedure.

In this work, we report for the first time on ion-selective electrodes prepared using solely a spray coating method. As an electrical lead support and transducer - spray coated CNTs layers were used. The ion-selective membrane was also coated by spraying membrane cocktail over (part of) the CNTs layer. As an insulating layer (PVC protective layer) – separating the part of CNTs used as electrical lead, from the substrate layer, a plasticized poly(vinyl chloride) (PVC) film was spray coated. As a model system, potassium-, hydrogen ion- and chloride-selective electrodes using plasticized PVC membranes were prepared.

Experimental

Chemicals

Tetrahydrofuran (THF), poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS), valinomycin, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), potassium tetrakis(4-chlorophenyl)borate (KTChPB), tridodecylamine, tridodecylmethylammonium chloride (TDDM-Cl), multiwalled carbon nanotubes (MWCNTs) were from Fluka AG (Buchs, Switzerland) or from Aldrich (Germany).

All reagents used were analytical grade salts (Aldrich (Germany). Deionised water (resistance 18.2 MΩcm, Milli-Qplus, Millipore) was used throughout this work.

As a substrate layers for spray coating either polyimide - Kapton® HM (DuPont) or polyethylene terephthalate (PET) Hostaphan® (Mitsubishi) sheets were used.

Apparatus

Spray coating

For spray coating the layers a pneumatically controlled Krautzberger M10 spray head was used, with nitrogen as atomizing gas. Samples were placed on a hotplate under the spray gun and coated with the different materials at different sample to nozzle distances. In case of the CNT layer the coating was done in several cycles with breaks in between to allow a drying of the layers. Otherwise big droplet formation would be present on the sample causing inhomogeneous layers. Thickness of layers is defined by the number of spray cycles as thickness is increasing linearly with spray time. In case of the CNT layer the coating was made in several cycles with breaks in between to allow drying of the layers. This was not necessary for the ion-selective membrane/ PVC protective layer as the THF used as solvent was evaporating much faster, allowing a continuous coating of the substrates. The patterns were achieved by the use of different shadow masks resembling the pattern needed for each layer. Like in optical lithography these shadow masks block the sprayed material in areas where it is not desired. A new pattern can be implemented quickly by just replacing the shadow mask. A drawback of spray coating when used in small scale with a stationary setup is the amount of material needed. If the spray head is not moved across the sample, only the centre of the sprayed area shows homogenous layer thickness. However, this can be overcome easily by the use of non-stationary spraying devices and/or up scaling the fabrication for example in roll-to-roll processes.

Electrochemical measurements

In the potentiometric experiments and electrochemical measurements, an experimental setup described earlier e.g. [28] was used. The recorded potential values were corrected for the liquid junction potential calculated according to Henderson approximation. The glass electrode used was from Moeller AG, Switzerland.

Ion-selective membranes

K^+-selective membranes contained (by weight): 1.2 % NaTFPB, 2.8 % valinomycin, 64.4 % DOS and 31.6 % PVC. Total 200 mg were dissolved in 20 ml of THF.

The insulation mask membrane contained (by weight): 40 % PVC and 60 % DOS. Total 400 mg were dissolved in 40 ml of THF.

H^+-selective membrane contained (by weight): 1.0 % of tridodecyl amine, 0.6 % KTChPB, 63.8 % DOS and 34.6 % of PVC. Total 200 mg were dissolved in 20 ml of THF.

Cl^--selective membrane contained (by weight): 5 % TDDM-Cl, 32.9 % PVC and 62.1 % DOS. Total 200 mg were dissolved in 20 ml of THF.

Fabrication of CNT ink

6 g of sodium dodecyl sulfate (SDS) were dissolved in 60 ml water and stirred for 1 hour. Subsequently 30 mg of MWCNT (0,05 wt %) were added and the mixture was sonicated with a horn sonicator (Branson Digital Sonifier 450) three times for 5 minutes each with 5 minutes breaks in between for cooling. Then, the solution was centrifuged for 1.5 hours at 15000 rpm. After centrifugation the top 75 % of the solution was used as ink.

Substrate preparation

About 50 mm x 20 mm PET or Kapton sheets were put in an ultrasonic bath with isopropanol for 20 minutes and dry blowed with nitrogen. Before spray coating both kinds of substrates were put into an oxygen plasma (150 W, TePla 100-E) for 1 minute to increase wettability.

Spray coating of CNTs layers

The substrates were put onto a hot plate and heated up to 30°C and then coated with 1 bar atomizing gas pressure and 25 cm nozzle to substrate distance 25 times for 30 seconds with 15 seconds drying steps in. A line pattern with 4 mm width and 30 mm length was fabricated by using a shadow mask. After spray coating, the substrates were dried for one hour at room temperature. To remove the SDS, the substrates were put in water for 15 minutes, afterwards in isopropanol for 10 minutes and finally blown dry with nitrogen.

Spray coating of ion-selective membrane/ PVC protective layer

On top of the CNT electrode a circle with 4 mm diameter of the ion-selective membrane was deposited with a substrate to nozzle distance of 15 cm and 1 bar atomizing gas pressure for 40 s at room temperature, resulting in a layer with a thickness close to 40 µm.

As last step the PVC protective layer was deposited on top with a substrate to nozzle distance of 17 cm and 1 bar atomizing gas pressure for 60 s also at room temperature, as well resulting in a layer thickness close to 60 µm. During this step the ion-selective membrane was covered by a circular shadow mask with a 3mm diameter, forming an active window of 7.06 mm². The 0.5 mm overlap of both layers ensures that no gap between the membrane and the protective layer is present. Thus obtained ion-selective electrodes before measurement were conditioned in 10^{-3} M KCl for 1 h. In-between measurements electrodes were stored in air.

Results and Discussion

The spray coating of substrate with CNTs has resulted in conducting layers characterized with resistivity close to 40 kOhm/square. They were composed of a porous network of tangled carbon nanotubes, as shown in Fig. 1. The thickness of the spray coated layer was about 200 nm. Thus obtained MWCNTs layers can be used as substrate to obtain ion-selective electrodes by spray coating ion-selective membrane and insulating PVC film, Fig. 1.

Potentiometric responses of spray coated potassium selective electrodes are shown in Fig. 2. For sensors prepared on Kapton as well as on PET linear responses within the activities range from 0.1 to 10^{-6} M with Nernstian slope equal to 59.8 ± 0.4 mV/dec ($R^2 = 0.9998$) and 59.6 ± 0.5 mV/dec ($R^2 = 0.9996$), respectively, and the detection limits (DLs) equal to $10^{-6.5}$ M were obtained. Spray coated sensors characteristics obtained are well comparable with those of classical ASS-ISEs potassium sensors reported, including those examined in our group [e.g. [2]]. They are also well comparable with planar arrangements based on screen-printed substrates and CNTs transducer [[9]] or manually coated layers of graphene/ CNTs used both as transducer and electrical lead [[21]], and show more favorable DLs compared to paper based sensors using CNTs as transducer and electrical lead [[22]].

The obtained logarithms of selectivity coefficients ± SD, for activities range from 0.1 to 10^{-4} M (separate solution method, using experimental slope values) were: log $K_{K,Na}$ -3.3 ± 0.4 and -2.8 ± 0.3; log $K_{K,Mg}$ -4.4 ± 0.4 and -3.4 ± 0.3; log $K_{K,Ca}$ -4.6 ± 0.3 and -3.6 ± 0.4; log $K_{K,H}$ -4.5 ± 0.3 and -4.0 ± 0.6, for Kapton and PET substrate, respectively. Although selectivity coefficients obtained are well comparable with those obtained for other (nominally disposable) systems [e.g. [18,22]] prepared using PVC based membranes, there were some differences between sensors prepared using Kapton and PET substrates. Despite the sensors were pretreated/ tested in parallel, repeatedly Kapton substrate based sensors prove to be characterized by somewhat higher selectivity for divalent interfering ions compared to PET. In our opinion this effect, consistently seen in tested sensors, can be related to the substrate effect, especially as relatively thin ion-selective membrane were used (c.a. 4 times thinner compared to standard membrane thickness used [e.g.[2]].

The preliminary conclusions drawn from conducted experiments related to reproducibility of automatic manufacturing production method are highly encouraging. The differences in E^0 potential value between sensors prepared in one manufacturing batch (regardless type of the substrate used) were in the range of a few mV. The response time of spray coated sensors was dependent on activity of sample solution, however, it was observed that sensors prepared using Kapton substrate were characterized with shorter responses time compared to PET ones, reaching about 20 s and about 70 s, respectively; as shown in Fig. S1 for electrolyte concentration change from 10^{-2} to 10^{-3} M.

The reproducibility of potential readings of nominally disposable spray coated made potentiometric sensors (within day) was tested in a non-optimized setup – simply in a beaker. Mean values ± SD of potentials recorded for each activity during four consecutive calibrations performed within the broad KCl activity range (from 0.1 to 10^{-9} M) are presented in Fig. 2. Fig. 2 clearly shows that both supports used result in sensors characterized with similar and high reproducibility of potential values recorded (SD of values recorded $\leq$ 9 mV). The results presented clearly confirm that although herein proposed system is prepared using relatively small amount of chemicals per sensor (relatively thin layers of automatically applied materials) the sensor offers sufficient long term stability to enable multiple measurements.

Moreover, the potentiometric performance of sensors tested both shortly after preparation (e.g. < 2 weeks, including the transport between cooperating groups laboratories) or after significantly longer storage (in fridge, due to valinomycin ionophore used) was the same within the range of experimental error, which is promising for practical applications.

The reproducibility of potential values is well comparable with that obtained by us in similar tests performed for traditional sensors (glassy carbon supporting electrode) with one of the most trusted transducer – poly(3-octylthiophene) [[29]]. This result is highly promising form the point of view of possible practical application of the simplified sensors herein proposed.

The stability of potentiometric responses within longer time period was also studied. Although such tests are generally rarely performed for nominally disposable sensors, in our opinion this is an important long term stability test for any new proposed arrangement. The

SD of mean value of potentials recorded were changing with electrolyte concentration, lower SD values were obtained for linear range of responses (close to 7 mV), somewhat higher values were obtained for lower activities, Fig. S2.

The usual set of tests applied for novel type potentiometric all-solid-state sensors includes impedance spectroscopy [2]. Fig. 3 presents complex plane impedance plots for sensors with Kapton and PET support, respectively. For the Kapton support, the spectrum contains a single semicircle at higher frequencies followed by a linear part recorded at lower frequencies (slope close to 45 degrees) and then the slope of dependence increases with decreasing frequency. For the PET substrate the picture is more complicated suggesting overlapping of two semicircles at high frequencies. This effect can result from additional resistance in the presence of the PET support. It can be noticed that the shapes of plots for Z' higher than $6\cdot10^5$ Ω (Kapton) and $3\cdot10^5$ Ω (PET) are similar. The plot obtained for PET support seems to be shifted to $3\cdot10^5$ Ω higher resistances compared to the Kapton one, suggesting the same properties in the case of both supports, related to the membrane, CNT transducer, and their interface. The shape of the EIS response suggests that it can be analyzed using the simplified equivalent circuit, proposed in [21] for the glassy carbon and plastic electrodes with CNT layer, Fig.3. This circuit consists of solution resistance, R_S, and parallel connected R and C_g, representing the membrane resistance (as the most resistive component of the sensor) and geometric capacitance of the sensor (membrane), respectively. Z_W represents Warburg impedance resulting from diffusion limitations in the membrane, while C_b corresponds to bulk capacitance of the CNT layer responsible for its transducing properties. For the data presented, Fig. S3 shows the results of a fitting procedure which was applied to the experimental data for the sensor with Kapton support, leading to good concordance with experimental data. The R resistance and C_g are typical values obtained for PVC based membrane ($4.8\cdot10^5$ Ω and $1.7\cdot10^{-10}$ F, respectively), while C_b around $2\cdot10^{-6}$ F is typical for carbon supports [30]. Similar (within the range of experimental error) values of the R and C_b were obtained also form chronopotentiometric experiment (results not shown).

The same methodology was used to prepare H^+-selective electrodes (on PET substrate) using tridodecylamine as ionophore. Thus obtained sensors were characterized with linear responses of slope equal to 53.7 ± 1.1 mV/dec ($R^2 = 0.997$) for hydrochloric acid concentration change from 0.1 to 10^{-5} M. Thus obtained sensor was used to determine H^+ concentration of 3 different branches of orange juices. The results obtained using herein prepared nominally disposable H^+ sensitive sensor were within the range of experimental error comparable with that of performed in parallel experiment with glass electrode determination in unoptimized experimental setup – in beaker measurements (3.83 and 3.85; 3.72 and 3.74; 3.91 and 3.95, for spray-coated and glass H^+ selective electrode, respectively). These results clearly show that herein proposed sensors can be used as cost effective devices (relatively low chemicals consumptions to prepare sensor) in analysis of real samples.

As model anion-selective sensor Cl^--selective electrode was also prepared (on PET substrate). Thus obtained sensors were characterized with linear responses within the KCl concentration range from 0.1 to 10^{-5} M with slope equal to -56.3 ± 1.3 mV/dec ($R^2 = 0.994$). The selectivity of thus obtained sensor was tested for model interferens Br^- and NO_3^- anions. Obtained selectivity coeffcients (for ions that are known to be severe interferents for chloride-ion selective sensor; separate solution method within the activity range from 10^{-1} to 10^{-3} M) were equal to log $K_{Cl,Br}$ 1.3 and log $K_{Cl,NO3}$ 1.6. These values are more favorable than reported earlier for other classical size all-solid-state chloride-selective electrode of the similar membrane [[31]], clearly showing that herein proposed method can be used to prepare sensors responding to different ions.

Conclusions

The results presented above clearly show that the novel, automatized method of preparation of potentiometric sensors herein proposed – spray coating - is a simple and efficient method of production leading to reliable potentiometric sensors. The construction proposed – carbon nanotubes used as support and transducer - resulted in sensor of analytical performance well comparable with that of traditional solid state ion-selective electrodes based on glassy carbon support. Elimination of manual application of membrane is advantageous from sensors mass scale production point of view.

Acknowledgements

Financial support from National Centre of Science project, based on decision DEC-2013/09//B/ST4/00098 is gratefully acknowledged (AM & KM).

EJ acknowledges support from Foundation for Polish Science Ventures Programme co-financed by the EU European Regional Development Fund.

Dr Mariana Gniadek assistance in obtaining SEM pictures of CNTs spray coated layers is kindly acknowledged.

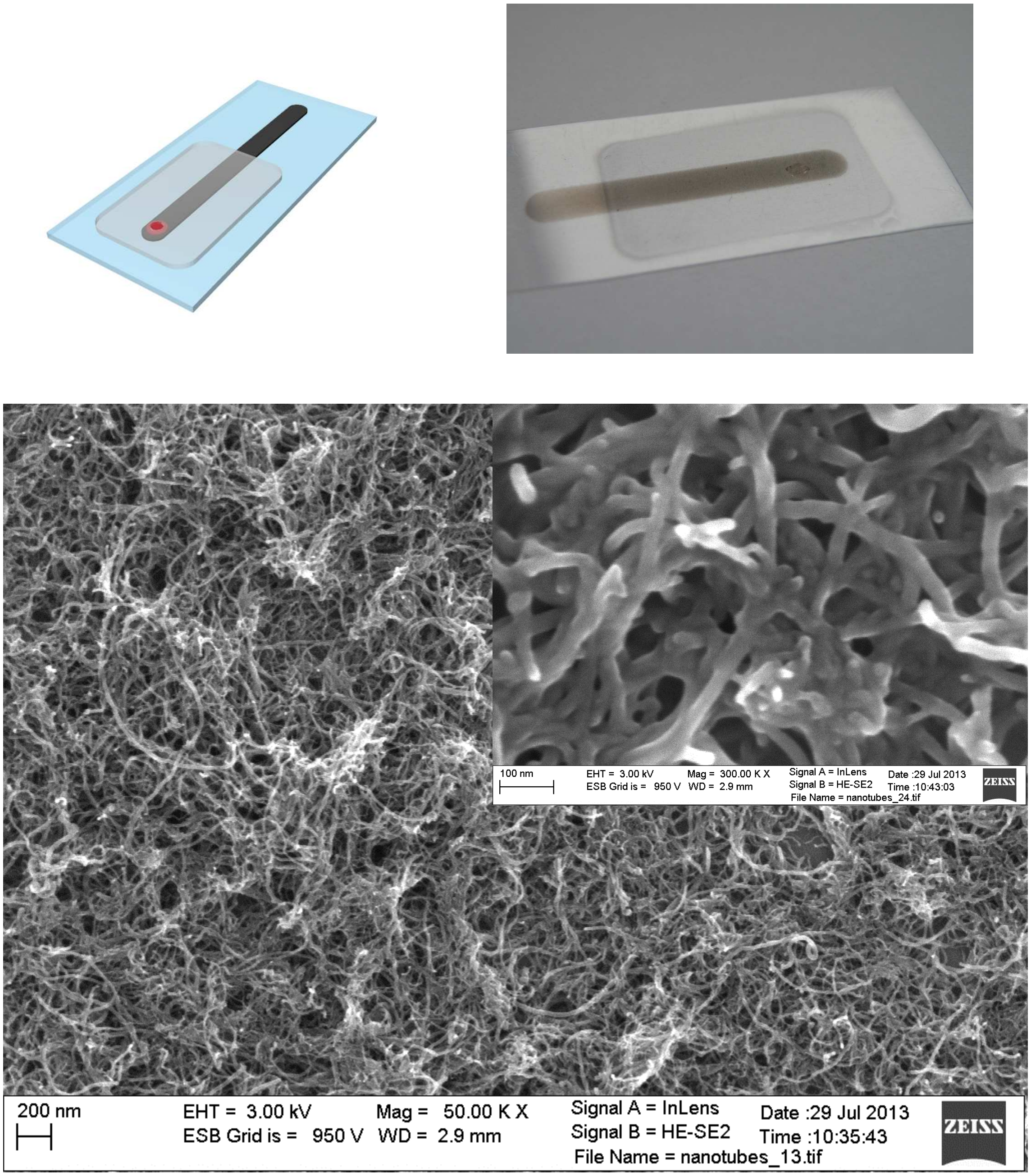

Fig. 1. SEM pictures of spray coated layers of CNTs on glass substrate and the schematic representation of spray coated ion-selective electrodes: substrate (blue), spray coated layer of carbon nanotubes (black), PVC layer – insulation of CNTs (grey), d) PVC ion-selective membrane (red) and picture of prepared electrode.

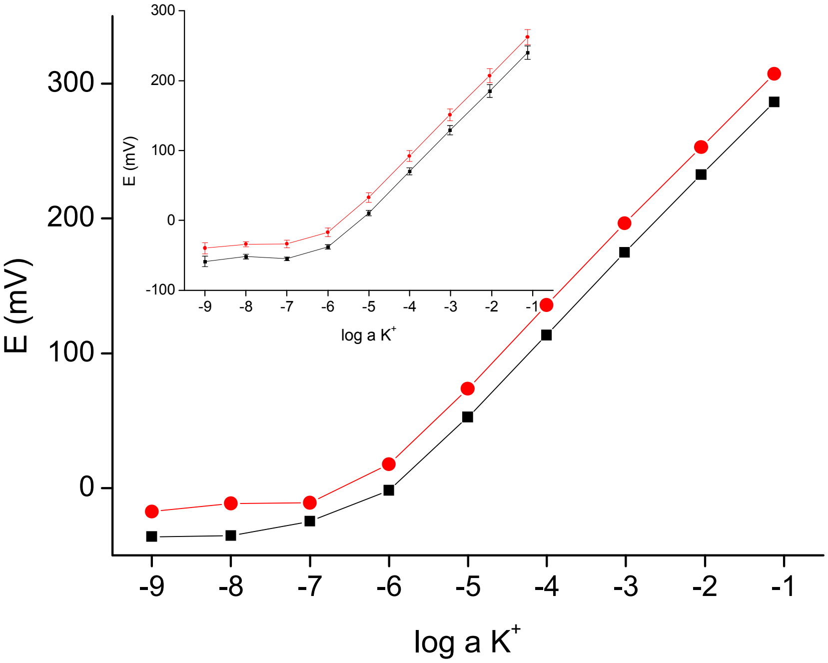

Fig. 2. Potentiometric responses of spray coated ion-selective electrodes prepared using: (■) PET or (●) Kapton substrate, recorded in KCl solutions. Inset: Mean potential values ± SD recorded in course of 4 calibrations performed during one day for spray coated sensors using either: (■) PET or (●) Kapton, substrate.

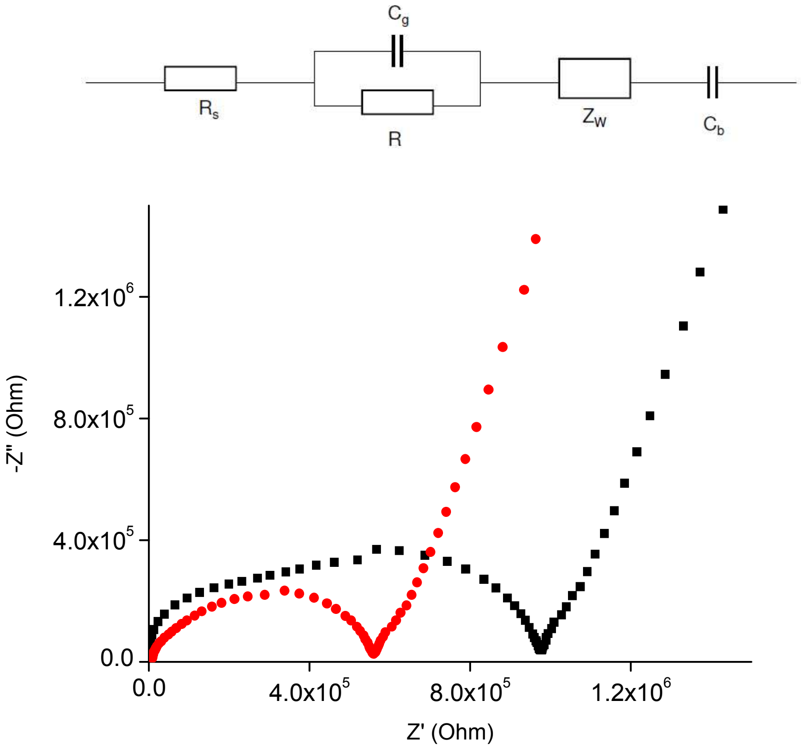

Fig. 3. Complex plane impedance plots of tested spray coated K$^+$- electrodes prepared using (■) PET or (●) Kapton, recorded in 0.1 M KCl solution, using 50 mV amplitude at 0.3 V potential, in the frequency range from 0.01 Hz to 10^5 Hz and equivalent circuit proposed for the Kapton support electrode.

References

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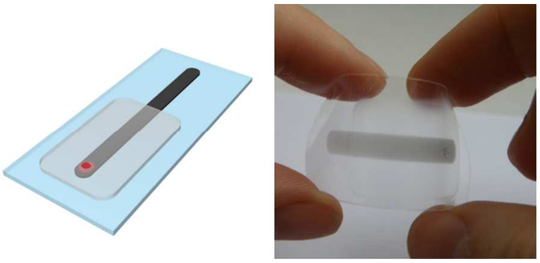
[1] J. Bobacka, *Electroanalysis*, 2006, **18**, 7.
[2] A. Michalska, *Electroanalysis,* 2012, **24**, 1253.
[3] A. C. Siegel, S. T. Phillips, M. D. Dickey, N. Lu, Z. Suo, G. M. Whitesides, *Adv. Funct. Mater.*, 2010, **20**, 28.
[4] K. C. Honeychurch, J. P. Hart, *Trends in Analytical Chemistry,* 2003, **22**, 456.
[5] R. Koncki, Ł. Tymecki, E. Zwierkowska, S. Głab, *Fresenius J. Anal. Chem.,* 2000, **367**, 393.
[6] R. Zielińska, E. Mulik, A. Michalska, S. Achmatowicz, M. Maj-Żurawska, *Anal. Chim. Acta,* 2002, **451**, 243.
[7] R. Paciorek, P. Bieganowski, M. Maj-Żurawska, *Sensors and Actuators* B, 2005, **108**, 840.
[8] R. Paciorek, P. D. van der Wal, N. F. de Rooij, M. Maj-Żurawska, *Electroanalysis,* 2003, **15**, 1314.
[9] F. X. Rius-Ruiz, G. A. Crespo, D. Bejarano-Nosas, P. Blondeau, J. Riu, F. X. Rius, *Anal. Chem.,* 2011, **83**, 8810.
[10] E. Wang, M. E. Meyerhoff, *Anal. Lett.,* 1993, **26**, 1519.
[11] T. Satchwill, D. J. Harrison, *J. Electroanal Chem.*, 1986, **202**, 75.
[12] K. Wygłądacz, M. Durnaś, P. Parzuchowski, Z. Brzózka, E. Malinowska, *Sensors and Actuators B,* 2003, **95**, 366.
[13] L. Y. Heng, E.A.H. Hall, *Anal. Chim. Acta,* 2001, **443**, 25.
[14] E. Malinowska, V. Oklejas, R. W. Hower, R. B. Brown, M. E. Meyerhoff, *Sensors and Actuators B,* 1996, **33**, 161.
[15] V.V. Cosofret, E. Lindner, T.A. Johnson, M. R. Neuman, *Talanta*, 1994, **41**, 931.
[16] V. V. Cosofret, M. Erdosy, E. Lindner, T. A. Johnson, R. P. Buck, W. J. Kao, M. R. Neuman, J. M. Anderson, *Anal. Lett.*, 1994, **27**, 3039.
[17] K. Abe, K. Suzuki, D. Citterio, *Anal. Chem.,* 2008, **80**, 6928.
[18] A. Michalska, K. Maksymiuk, *Anal. Chim. Acta*, 2004, **523**, 97.
[19] A. Michalska, M. Ocypa, K. Maksymiuk, *Electroanalysis*, 2005, **17**, 327.
[20] A. Michalska, M. Wojciechowski, W. Jędral, E. Bulska, K. Maksymiuk, *J Solid State Electrochem.*, 2009, **13**, 99.
[21] E. Jaworska, W. Lewandowski, J. Mieczkowski, K. Maksymiuk, A. Michalska, *Analyst*, 2013, **138**, 2363.
[22] M. Novell, M. Parrilla, G. A. Crespo, F. X. Rius, F. J. Andrade, *Anal. Chem.*, 2012, **84**, 4695.
[23] P. Yáñez-Sedeño, J. M. Pingarrón, J. Riu, F. X. Rius, *Trends in Analytical Chemistry*, 2010, **29**, 939.
[24] A. M. Münzer, M. Heimgreiter, K. Melzer, A. Weise, B. Fabel, A. Abdellah, P. Lugli, G. Scarpa *J. Mater. Chem. B*, 2013, **1**, 3797.
[25] J. G. Tait, B. J. Worfolk, S.A. Maloney, T. C. Hauger, A.L. Elias, J. M. Buriak, K. D. Harris, *Solar Energy Materials & Solar Cells*, 2013, **110**, 98.
[26] E. Ramasamy, W. J. Lee, D. Y. Lee, J. S.Song, *Electrochem. Commun.*, 2008, **10**, 1087.
[27] M. Kaempgen, G. S. Duesberg, S. Roth, *Applied Surface Science*, 2005, **252**, 425.
[28] E. Jaworska, A. Kisiel, K. Maksymiuk, A. Michalska, *Anal. Chem.*, 2011, **83**, 438.
[29] E. Jaworska, M. Wójcik, A. Kisiel, J. Mieczkowski, A. Michalska, *Talanta*, 2011, **85**, 1986.
[30] E. Jaworska, W. Lewandowski, J. Mieczkowski, K. Maksymiuk, A. Michalska, *Talanta*, 2012, **97**, 414.
[31] A. Hulanicki, A. Michalska, *Electroanalysis*, 1995, **7**, 692.



A novel fully spray coating based method of preparation of all-solid-state ion-selective electrodes of simplified construction is proposed.