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Mandjoukov, Bojidar; Lindfors, Tom

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# Planar, low-cost, flexible, and fully laminated graphene paper pseudo-reference and potassium-selective electrodes

Bojidar Mandjoukov<sup>1</sup>, Tom Lindfors<sup>\*</sup>

Åbo Akademi University, Laboratory of Molecular Science and Engineering, Henriksgatan 2, 20500 Åbo, Finland

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## ABSTRACT

We report for the first time a one-step fabrication by lamination of inexpensive graphene paper (GP) based Ag/AgCl pseudo-reference (RE) and K<sup>+</sup>-selective coated-film electrodes forming the novelty of this work. Contrary to our previous work about laminated GP solid-contact electrodes, the electrode fabrication in this work does not require manual drop casting steps after the lamination, simplifying the fabrication and making it suitable for mass production. We also eliminated the need of the solid contact and simplified the electrode construction by placing the plasticized potassium-selective PVC membrane (ISM) directly on the GP functioning as combined electrode substrate and ion-to-electron transducer. Both Ag/AgCl and the ISMs were pre-deposited on rectangular GP sheets (10 × 100 mm<sup>2</sup>) before placing them inside laminating pouches and feeding them through an office laminator after which the electrodes were ready for use. Five batches of 32 pseudo-REs had a very good  $E^0$  reproducibility of  $\pm 2.8$  mV. The K<sup>+</sup>-electrodes had a slope and detection limit of  $57.4 \pm 0.3$  mV/pK ( $n = 4$ ) and  $6 \times 10^{-7}$  M, and the  $E^0$  reproducibility was in the best case only  $\pm 1.2$  mV matching the performance of non-laminated K<sup>+</sup>-electrodes. This work demonstrates that the ISMs are compatible with the lamination where the temperature can momentarily rise to ca. 130 °C.

## 1. Introduction

Solid-contact ion-selective electrodes (SCISEs) where the ion-to-electron transducer is placed between the electrically conducting substrate and the ion-selective membrane (ISM) have become the main direction in ion-selective electrode research. This is because of their several advantages over conventional ion-selective electrodes with a liquid contact [1], such as the possibility of fabricating the SCISEs in different geometries on flexible substrates suitable for wearable applications and the compatibility of the SCISE concept with fabrication techniques suitable for mass production, e.g., ink jet printing [2] and lamination [3] making it superior to the conventional ISEs. Despite of these advantages the SCISEs suffer still from insufficient reproducibility of the standard potential ( $E^0$ ) hampering their commercialization [4,5], but also from the lack of a reliable solid-state reference electrode (RE) that can be integrated with the SCISE to one measuring unit.

The solid-state REs can be divided into three main groups [6]. The first consists of pseudo-REs where a silver surface or wire is coated with AgCl that requires that the chloride concentration in the sample solution

is constant or it is controlled [7]. In the second approach Ag/AgCl is coated with KCl that is incorporated in a polymeric binder such as poly(vinyl acetate) [6,8]. This approach has shown to reduce the leakage of KCl into the sample solution compared to conventional REs with liquid salt bridges, but on the cost of an equilibration time of several days [8]. The third RE type mimics the SCISEs by using solid-state transducers typically coated with a plasticized poly(vinyl chloride) (PVC) membrane containing lipophilic salts that are insoluble in the sample solution. An example of this is an early work by Kisiel et al. where a plasticized PVC membrane containing hydrophobic salts was applied on top of poly(3,4-ethylenedioxythiophene) functioning as ion-to-electron transducer [9,10]. The salts then formed a lipophilic ion pair ( $C^+A^-$ ) that prevented the extraction of cations and anions from the sample solution making the PVC membrane insensitive to inorganic ions and thus providing the solid-state RE with a stable potential. Recently biocompatible and plasticizer-free fluorosilicones doped with ionic liquids have also shown to be suitable as solid-state REs [11]. They had a stable potential with a very low potential drift of only 20  $\mu$ V/h over 8 days.

Several types of planar solid-state REs [2,7,9,12–30] and ISEs [2,9,

<sup>\*</sup> Corresponding author.

E-mail address: [tom.lindfors@abo.fi](mailto:tom.lindfors@abo.fi) (T. Lindfors).

<sup>1</sup> Present address: University of Tartu, Department of Geology, Ravila 14a, 50411 Tartu linn, Tartumaa, Estonia

[18,27,31–38] have been fabricated on rigid substrate materials such as silicon [13,14,18], glass [14,17], alumina [16,18,20,21,23,26] and polycarbonate [31], but also on more flexible substrates like paper [2,7,12,24,25,28,29,33] coated with carbon nanotubes [27,38], heat-sealing [15,35] and laser printer films [9,36,37], polyimide [22,32], polyester [19] and polyethylene terephthalate (PET) [7,30]. For planar and flexible Ag/AgCl reference electrodes, the Ag/AgCl layer is usually applied by screen-printing of a Ag/AgCl paste on the flexible substrate material [15,19,22,28,29]. Other methods include stencil-printing of Ag/AgCl inks [24], electrochemical deposition of AgCl on prefabricated Ag stripes [25], chlorination of Ag by immersing it into a sodium hypochlorite solution [7,30], and inkjet printing of first Ag and on top of it another layer of FeCl<sub>3</sub> to transform silver to AgCl [2]. The solid-state RE has been only in rare cases integrated with a solid-state ISE into a single measuring unit [2]. Most of the fabrication procedures of the solid-state REs involve multiple processing steps and the fabrication is therefore complex, time-consuming, and not compatible with mass production.

In contrast, lamination is a simple, fast and cost-efficient fabrication method for disposable solid-state REs [2,15] and ISEs [3,33–35] that has been used only to a limited extent. Mroz et al. fabricated a planar disposable RE by first depositing a screen-printed Ag/AgCl layer on a heat-sealing film and after curing it at 80 °C for 1 h, a carbon contact (for the potentiometer) was printed on the upper end of the Ag/AgCl layer [15]. A filter paper functioning as a KCl reservoir was then placed on top of the lower end of the Ag/AgCl layer before encapsulating the structure by lamination with another heat-sealing film leaving a hole for the Ag/AgCl layer covered with the KCl impregnated filter paper. The same technology was used to make planar and disposable ISEs with different variations of the double matrix technology using a filter paper coated with silver [33–35]. However, for all solid-state ISEs, the ion-selective membrane (ISM) was added after the lamination on the Ag-coated filter paper in an additional manual drop casting step making the fabrication more complex.

We have recently used inexpensive and electrically conducting graphene paper (GP) to fabricate laminated planar, low-cost (< €1) and flexible K<sup>+</sup>-selective solid-contact electrodes showing performance on par with the state of the art SCISEs [3]. However, in that work, both the solid contact and the ISM were manually deposited on the GP after the lamination like in [33–35]. In this paper, we have therefore developed a novel fully laminated concept of fabricating graphene paper based solid-state pseudo-REs and K<sup>+</sup>-selective coated-film electrodes having a plasticized poly(vinyl chloride) (PVC) based ISM. Compared to our previous work about laminated SCISEs, the concept presented here does not require the solid contact for the K<sup>+</sup>-electrodes, thus simplifying the electrode construction by placing the ISMs directly on the GP, which functions as a combined electrode substrate and ion-to-electron transducer. The pseudo-REs and the K<sup>+</sup>-selective electrodes are laminated in a single step making them suitable for mass production and at the same time eliminating the need of manually drop casting the ISM after the lamination. This has not been reported previously to the best of our knowledge. A potentiometric cell with a disposable solid-state RE and an ISE – suitable for example to low-income countries – can easily be assembled by non-experts with an inexpensive office laminator in combination with a handheld voltmeter with a sufficiently high input impedance and buffer solutions for the ISE.

## 2. Material and methods

### 2.1. Chemicals and materials

Graphene paper was purchased from Graphene Supermarket (SKU GRAPH-SHEET-8×8–10) as a 10 pack of 25 μm thick conductive graphene paper sheets (8'×8') consisting of graphene nanoplatelets (97%) held together with a binder (3%). The GP sheets had according to the manufacturer a resistance of  $2.8 \times 10^{-2} \Omega/\text{square}$ , a tensile strength of 30 MPa and a density of 2 g cm<sup>-3</sup>. They can be easily cut to a desired size

with scissors or a craft knife. All laminations in this work was done with an inexpensive A4 office hot laminator (Exibel) by using 125 μm thick laminating pouches made of polyethylene terephthalate (PET, Exibel). Ag/AgCl (60/40) paste for screen printing was purchased from Sigma-Aldrich. The ISM for the K<sup>+</sup>-selective electrodes consisted of 32.9% (m/m) high molecular weight PVC, 65.7% bis(2-ethylhexyl) sebacate as plasticizer, 1.06% valinomycin (potassium ionophore I) and 0.34% potassium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate as ion-exchanger (ionic additive). All membrane components were of Selectophore grade bought from Merck (Supelco®).

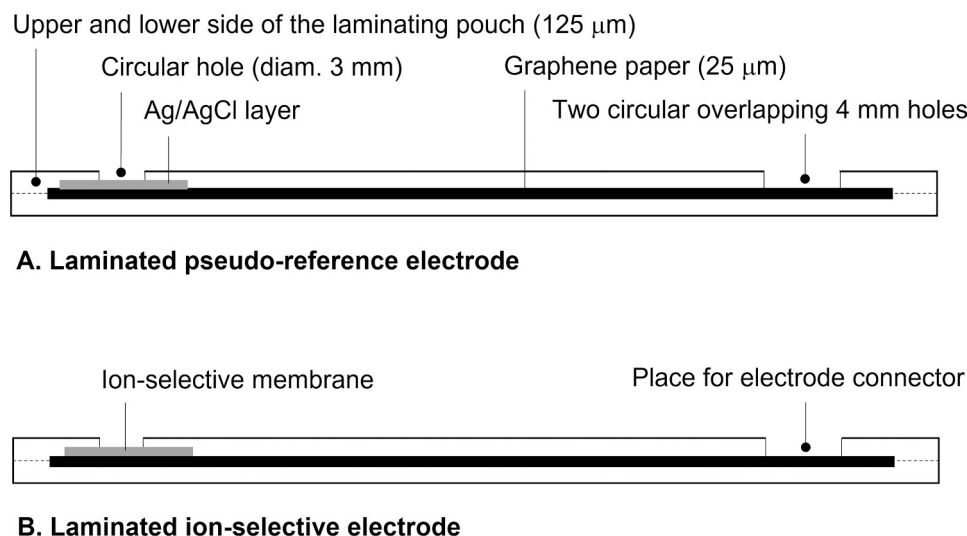
### 2.2. Lamination of graphene paper pseudo-reference and K<sup>+</sup>-selective electrodes

Schematic side views of the laminated electrodes are shown in Fig. 1. For the lamination of pseudo-REs in Fig. 1A, the GP was first cut to rectangular pieces of 10 mm × 100 mm and then argon plasma cleaned for 10 min before applying one or two layers of the Ag/AgCl paste on one end of the GP with a few millimeters wide paint brush. After that the Ag/AgCl coated GPs were cured for 10 min at 80 °C before the lamination of the pseudo-REs was carried out. The lamination followed the procedure described in [3]. First, places for several rectangular GPs were marked on the outside of the upper side of the A4 sized laminating pouch. Circular holes with a diameter of 3 mm were then made on this side with a sharp hole punch on one end of the marked rectangular areas and two slightly overlapping 4 mm holes on the other end for flat electrode connectors (Fig. 1). The Ag/AgCl coated GPs were then carefully placed correctly on the inside of the lower sheet of the laminating pouch (matching the marks on the upper one) leaving enough space between the individual papers. The Ag/AgCl coated GPs (i.e., the pseudo-REs) are ready to use after feeding them through the hot laminator encapsulating the electrodes inside the laminating pouch. Pseudo-REs can be prepared quickly with lamination since it takes only ca. one minute to feed the lamination sheet through the laminator. The heat activated adhesive on the inner sides of the laminating pouch ensures that they are glued together with the Ag/AgCl coated GPs leaving uncovered circular openings (describe above) only for the Ag/AgCl surface and the uncoated GP (for the electrode connectors). Finally, the individual pseudo-REs were separated from each other with scissors [3].

The K<sup>+</sup>-selective membranes were fabricated by first solution casting the membrane solution (20 wt% in THF) into Petri dishes yielding ISMs with a mean thickness of ca. 110 μm. The ISMs were then carefully removed from the glass substrate after letting them dry for at least 16 h. ISMs with a 6 mm diameter were then punched out from the cast master membranes with a hole punch and placed on rectangular GP pieces prior to the lamination (Fig. 1B) as described above for the pseudo-REs. The lamination of the K<sup>+</sup>-selective electrodes was then performed in the same way as for the pseudo-REs and the individual ISEs were ready for use after being separated from each other.

### 2.3. Characterization of the graphene paper pseudo-reference electrodes

The potentiometric response to chloride ions of the pseudo-REs was studied in  $10^{-5}$  –  $10^{-1}$  M KCl solutions vs. a commercial double junction Ag/AgCl/3 M KCl/1.0 M LiOAc reference electrode, which was used in all potentiometric measurements in this paper. The electrodes were not conditioned before the measurements or between subsequent measurements and they can be storage in the dry state (not in solution) between the measurements. Furthermore, all potentials reported in this work were corrected for the liquid junction potentials with Henderson equation, the activity coefficients were calculated according to the Debye-Hückel equation and the  $E^0$  values reported correspond to extrapolation of the linear potential response to  $a_i = 1$ , i.e. to  $\log a_i = 0$ . After calibrating the pseudo-REs in KCl solutions their initial potential stability was measured in a 0.1 M KCl solution for 17 h. Their gas and light sensitivity were determined in a 0.01 M NaCl solution by measuring the



**Fig. 1.** Schematic side view of the construction of the flexible graphene paper based (A) laminated Ag/AgCl pseudo-reference electrode and (B) laminated  $K^+$ -selective electrode.

electrode potentials when air (containing oxygen), nitrogen and carbon dioxide gas was purged through the solution in this sequence, which was repeated three times. To study the *light sensitivity*, the electrode potentials were measured when the pseudo-REs were exposed to room light, darkness, and intense cold light (Leica CLS 150XE light source,  $> 1.6 \times 10^5$  lx), in this sequence that was repeated three times. A 16-channel Lawson high input impedance voltmeter ( $10^{15} \Omega$ , Lawson Laboratories, Malvern, PA, USA) were used in all potentiometric measurements in this work. The influence of interfering electrolytes on the potential of the pseudo-REs was studied in a  $10^{-2}$  M NaCl solution into which  $10^{-3}$  M and  $10^{-2}$  M  $LiNO_3$ ,  $NaNO_3$ ,  $KNO_3$ ,  $Ca(NO_3)_2$ ,  $Mg(NO_3)_2$  and  $HNO_3$  (all with  $10^{-2}$  M NaCl as the background electrolyte) was added with a micropipette under stirring.

#### 2.4. Characterization of the $K^+$ -selective electrodes

The *potentiometric response* of the plasticized PVC based  $K^+$ -selective electrodes were measured in  $10^{-9}$  –  $10^{-1}$  M  $KNO_3$  solutions with  $10^{-3}$  M NaCl as the background electrolyte. The linear part of the calibration graphs of all  $K^+$ -selective electrodes and pseudo-REs were fitted to a straight line with linear regression. To construct the calibration graphs, we calculated first the mean potentials and standard deviations (SD) of all  $n$  electrodes at every concentration (activity) for each electrode batch. The calibration graphs were then plotted for each electrode batch based on the mean potentials and their SDs. After that straight lines were fitted to the linear part of the calibration graphs with Origin 2020b without applying weighting to the individual potentials. Almost the same fitting results were obtained when we used instrumental weighting, which gives more weight to potentials with lower SD. *Selectivity coefficients* for the electrodes were determined with the separate solution method in  $10^{-2}$  M solutions of  $Mg(NO_3)_2$ ,  $Ca(NO_3)_2$ ,  $HNO_3$ ,  $LiNO_3$  and  $NaNO_3$ . The *light sensitivity* was measured in the same way as for the pseudo-REs.

### 3. Results and discussion

#### 3.1. Laminated graphene paper pseudo-reference electrodes

The working principle of the Ag/AgCl pseudo-REs can be derived from its half-cell reaction:



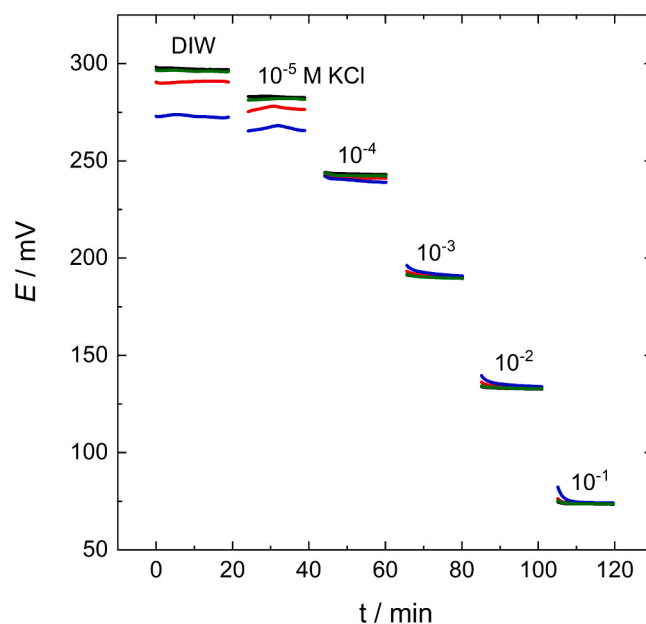
Derivation of the Nernst equation from the half-cell reaction at 25 °C

gives:

$$E = E^0 - 0.0592 \times \log a_{Cl^-} \quad (2)$$

where  $E$ ,  $E^0$  and  $a_{Cl^-}$  are the electrode potential and standard reduction potentials in volts, and the activity of chloride, respectively. Ideally functioning Ag/AgCl pseudo-REs should therefore have an electrode slope of  $-59.2$  mV/decade in chloride solutions at 25 °C.

First, we wanted to study if the laminated pseudo-REs prepared with one and two layers of Ag/Ag/AgCl paste obeyed the Nernst equation. Freshly prepared electrodes were therefore calibrated in  $10^{-5}$  –  $10^{-1}$  M KCl solutions from low concentration to high. Fig. 2 shows the potential traces measured during the calibration of four identically prepared pseudo-REs (with one layer of Ag/AgCl) and Fig. 3a their corresponding calibration graphs. The potential traces show that the electrodes responded quickly to the changes in the chloride ion activity indicating



**Fig. 2.** The potential vs. time traces of four laminated Ag/AgCl graphene paper pseudo-reference electrode in  $10^{-5}$  –  $10^{-1}$  M KCl solutions measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode. The potential vs. time traces in deionized water is denoted as DIW.

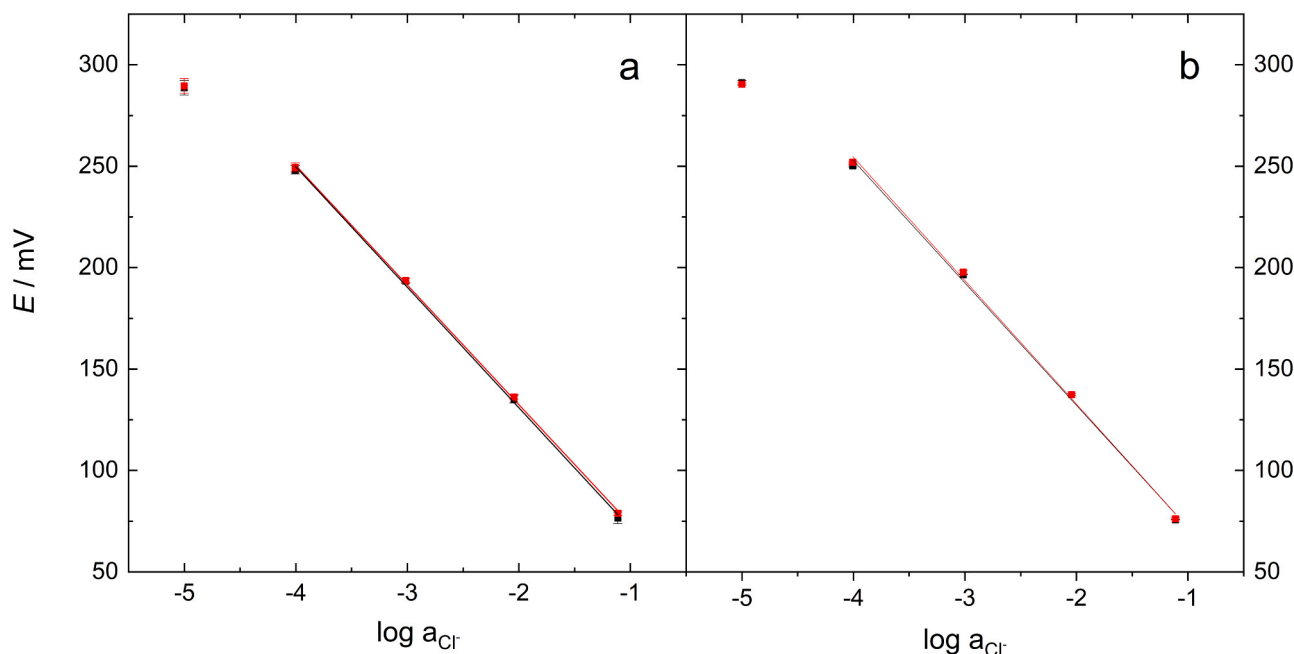


Fig. 3. Potentiometric responses of four identically fabricated laminated Ag/AgCl graphene paper pseudo-reference electrodes measured in  $10^{-5}$ – $10^{-1}$  M KCl before (a) and after (b) exposure to the initial potential stability test in 0.1 M KCl shown in Fig. 4. The Ag/AgCl layer was applied on graphene paper with a small brush either once (black squares) or twice (red squares). All potentials were measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.

that the half-cell reaction is highly reversible with high exchange current density. The pseudo-REs fabricated with both one and two layers of Ag/AgCl had a Nernstian slope of  $-59.4 \pm 1.2$  ( $n = 4$ ;  $r^2 = 0.9992$ ) and  $-59.0 \pm 0.8$  mV/decade ( $n = 4$ ;  $r^2 = 0.9996$ ), and a very good  $E^0$  reproducibility of  $12.2 \pm 3.2$  mV and  $14.6 \pm 2.2$  mV, respectively, verifying that fully functional GP based Ag/AgCl pseudo-REs can be fabricated with a standard office lamination from relatively inexpensive starting materials. The solubility product of AgCl ( $K_{sp} = 10^{-9.5}$ ;  $\mu = 0.1$  M) predicts that the solubility of AgCl is ca.  $1.8 \times 10^{-5}$  M, which limits the Nernstian concentration range of the pseudo-REs to chloride concentrations above ca.  $5 \times 10^{-5}$  M. This is in good accordance with linear range shown in Fig. 3a.

After the initial calibration of the pseudo-REs in Fig. 3a, we measured the potential stability of the pseudo-REs in 0.1 M KCl over 17 h (Fig. 4). As the figure shows, a very good potential reproducibility with a very low potential drift was obtained during the test period of 17 h. The average potential and their reproducibility for eight identically prepared pseudo-REs was  $75.4 \pm 2.4$  mV ( $n = 8$ ) in the very beginning of the test improving to  $73.4 \pm 0.7$  mV,  $72.9 \pm 0.4$  and  $72.8 \pm 0.4$  mV after 2, 6 and 17 h in 0.1 M KCl. The corresponding potential drifts – calculated from the mean values of the potentials – were  $1.0$  mV  $h^{-1}$  (from 0–2 h),  $125$   $\mu$ V  $h^{-1}$  (2–6 h),  $9$   $\mu$ V  $h^{-1}$  (6–17 h) indicating that the pseudo-REs are suitable for both short-term measurements (disposable electrodes) and measurement up to at least 17 h. We did not study the long-term potential stability of the pseudo-REs due to time limitations, but it is expected that they show good stability with low potential drift even for longer times than 17 h.

After the potential stability test, the electrodes were calibrated once again in KCl solutions (Fig. 3b) giving slopes of  $-60.3 \pm 1.9$  ( $n = 4$ ; one AgCl layer) and  $-60.9 \pm 1.7$  mV/decade ( $n = 4$ ; two layers), and  $E^0$  reproducibilities of  $11.5 \pm 5.2$  mV ( $r^2 = 0.9980$ ) and  $11.0 \pm 4.8$  mV ( $r^2 = 0.9984$ ), respectively, which are basically the same as obtained before the potential stability test (Fig. 3a). It shows that the performance of the pseudo-REs is unaffected for at least 17 h. Fig. S1 reveals also that the Ag/AgCl surface is intact without any visually observable changes (e.g., cracks) after the second calibration in KCl solutions. Since there was practically no difference in the performance between the pseudo-RE prepared with one and two Ag/AgCl layers, we decided to fabricate

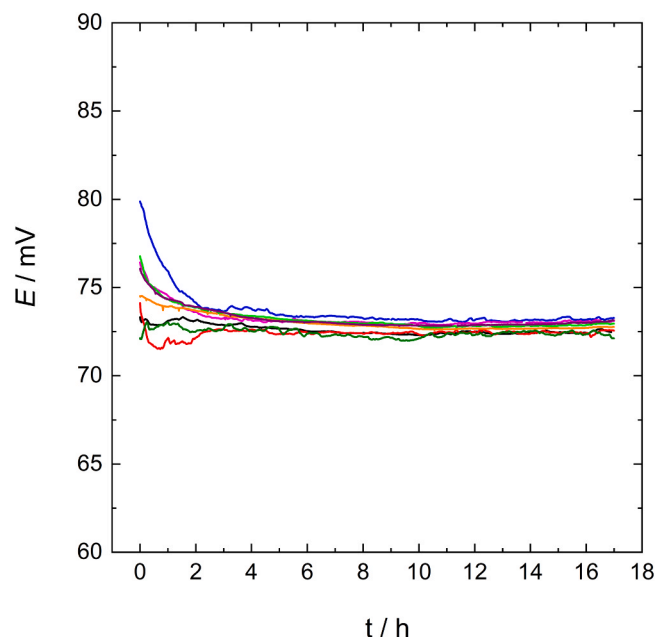
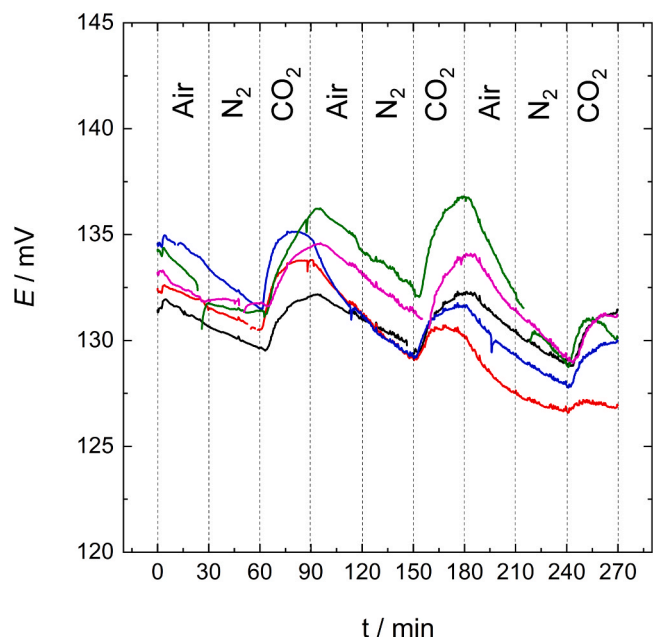


Fig. 4. The initial potential stability of eight laminated Ag/AgCl graphene paper pseudo-reference electrodes measured in 0.1 M KCl for 17 h against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.

the pseudo-REs for all other measurements from now on with only one layer, which saves time and consumes less Ag/AgCl paste.

The potentiometric response of the pseudo-REs to oxygen and carbon dioxide was measured by purging air, nitrogen, and carbon dioxide gas through a solution of 0.01 M NaCl (Fig. 5). The results reveal that the electrodes are practically insensitive to oxygen but give a potential response of ca. 2–5 mV to carbon dioxide that decreases the pH of the measuring solution (see also Fig. 7 later). AgCl should be insensitive to pH changes and although the exact reason for the minor potentiometric response to carbon dioxide is currently unclear, it can be speculated that

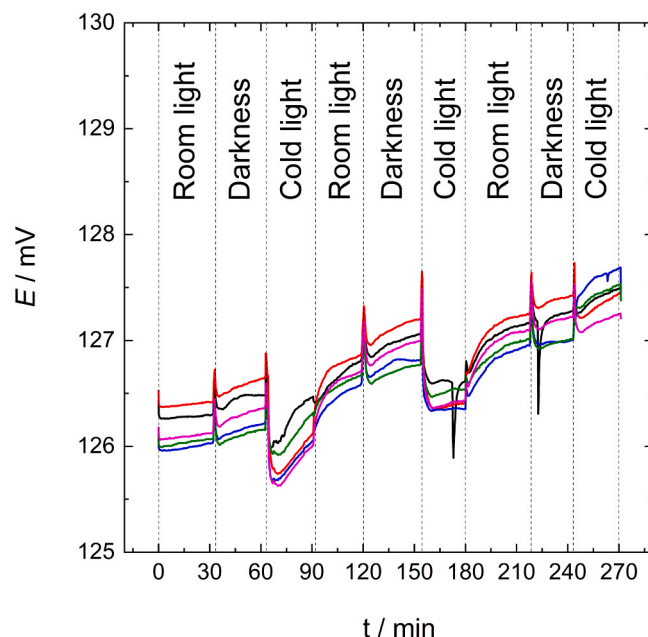


**Fig. 5.** Potentiometric  $O_2$  and  $CO_2$  sensitivity of five identically fabricated laminated Ag/AgCl graphene paper pseudo-reference electrodes measured in 0.01 M NaCl by purging it three times with air (containing  $O_2$ ), pure  $N_2$  and  $CO_2$  gas in this sequence. All potentials were measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.

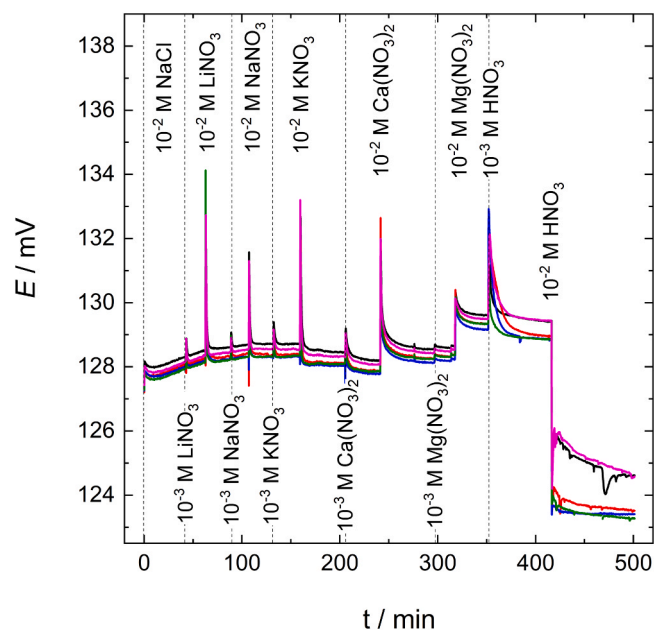
it is connected to minor changes in the ionic strength caused by the formation of  $H^+$  and  $HCO_3^-$  due to the dissociation of the formed  $H_2CO_3$ . This may also influence the liquid junction potential of the double junction Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode against which the potentials of the pseudo-REs were measured. However, by purging carbon dioxide gas through the 0.01 M NaCl can be considered as an extreme case raising the  $CO_2$  concentration to levels that are unlikely in real measurements where the carbon dioxide levels are usually rather constant. Therefore, it is likely that the minor  $CO_2$  sensitivity of the pseudo-REs will not limit their use.

It is known that AgCl is sensitive to light to a very minor extent. We exposed therefore the pseudo-REs to room light, darkness, and very intense cold light (Fig. 6). The latter is an extreme situation hardly happening in real measurements. Fig. 6 reveals that the potential is practically unchanged when switching from room light to darkness, but exposure to intense cold light induces a potential change of less than 0.5 mV. It can therefore be concluded that the pseudo-REs are insensitive to light under normal illumination conditions and very little affected even under extreme conditions.

The influence of interfering electrolytes on the potential of the pseudo-REs was studied in a solution of 0.01 M NaCl. We added to this solution  $10^{-3}$  M and  $10^{-2}$  M concentrations of nitrate salts of  $Li^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and  $H^+$  (containing 0.01 M NaCl) and measured the potential simultaneously (Fig. 7). Sodium nitrate was also studied to determine the influence of nitrate ions on the electrode potential when the cation ( $Na^+$ ) is kept unchanged. Fig. 7 shows that  $10^{-3}$  and  $10^{-2}$  M concentrations of  $LiNO_3$ ,  $NaNO_3$ ,  $KNO_3$  and  $Ca(NO_3)_2$  did not affect the potential of the pseudo-REs, but a minor increase of the potential of ca. 1 mV was observed for  $10^{-2}$  M  $Mg(NO_3)_2$  and  $10^{-3}$  M  $HNO_3$ . On the other hand, the potential decreased ca. 5 mV for  $10^{-2}$  M  $HNO_3$ , which we currently do not know the exact reason for. We speculate that minor changes in ionic strength affecting the activity coefficient of  $Cl^-$  may be the reason for the minor decrease in potential. We note, however, that a pH response was also observed for  $CO_2$  as explained above, but in that case the potential increased with 2–5 mV. The results in Fig. 7 reveal that the pseudo-REs are insensitive to clinically relevant concentrations



**Fig. 6.** The light sensitivity of five identically fabricated laminated Ag/AgCl graphene paper pseudo-reference electrodes exposed to room light, darkness, and intense cold light (ca.  $1.6 \times 10^5$  lx) in 0.01 M NaCl. All potentials were measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.



**Fig. 7.** Potentiometric responses of five identically fabricated laminated Ag/AgCl graphene paper pseudo-reference electrodes in  $10^{-2}$  M NaCl exposed to possible interfering electrolytes with  $10^{-3}$  M and  $10^{-2}$  M concentrations of  $LiNO_3$ ,  $NaNO_3$ ,  $KNO_3$ ,  $Ca(NO_3)_2$ ,  $Mg(NO_3)_2$  and  $HNO_3$ . All added electrolytes had  $10^{-2}$  M NaCl as the background electrolyte and the potentials were measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.

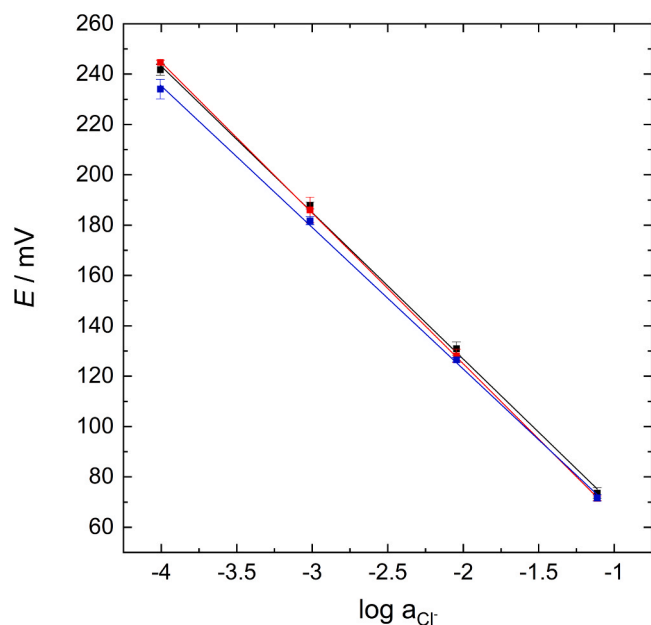
of  $Li^+$  (0.4 – 1.2 mM),  $K^+$  (3.6 – 5.2 mM),  $Ca^{2+}$  (2.1 – 2.6 mM),  $Mg^{2+}$  (0.85 – 1.1 mM) and most likely also to  $Na^+$  (0.096 – 0.106 mM) and pH (7.35 – 7.45) showing that the pseudo-RE developed in this work could be used as reference electrode in blood analysis.

Finally, we wanted to study the  $E^0$  reproducibility of the pseudo-REs

by preparing three identical electrode batches with eight laminated electrodes in each batch ( $n = 3 \times 8 = 24$ ). Fig. 8 shows that the laminated pseudo-REs had a very reproducible potential in  $10^{-4} - 10^{-1}$  M KCl solutions. The three electrode batches had mean electrode slopes of  $-58.2 \pm 1.1$  ( $r^2 = 0.9992$ ),  $-59.9 \pm 0.2$  ( $r^2 = 0.9999$ ) and  $-56.2 \pm 1.0$  mV/decade ( $r^2 = 0.9994$ ) and mean standard potentials ( $E^0$ ) of  $10.5 \pm 3.0$ ,  $5.2 \pm 0.6$  and  $10.4 \pm 2.7$  mV. Table 1 summarizes the numerical mean values of the pseudo-RE slopes and standard potentials of five batches with all together 32 electrodes that was fabricated in this work. The table shows that the laminated pseudo-REs had a very good  $E^0$  reproducibility of  $10.8 \pm 2.8$  mV and a Nernstian electrode slope of  $-59.1 \pm 1.6$  mV/decade making them to a viable option for mass production.

### 3.2. Laminated graphene paper $K^+$ -selective electrodes

We have previously reported the fabrication of laminated  $K^+$ -selective electrodes [3] for which the polyaniline solid contact and the plasticized PVC based ISM was drop cast on the GP substrate after the lamination. In this work, we wanted to develop a fully laminated ISE concept where the ISE can be fabricated in only one lamination step without any additional post-fabrication steps. We decided also to simplify the ISE design from a two layer to a one layer design mimicking coated-wire electrodes (CWE) [39]. The laminated ISEs were therefore fabricated by placing only a pre-made  $K^+$ -selective plasticized PVC-ISM containing valinomycin as the ionophore directly on top of the GP surface before the lamination. It is well-known that carbon nanotubes and graphene can act as ion-to-electron transducers. The  $K^+$ -selective ISM contacting the GP had an area of ca.  $29 \text{ mm}^2$  which is much higher than for most solid-state ISEs and therefore it can be speculated that a relatively high interfacial capacitance can be achieved resulting in ISEs with stable potentials. However, there is a risk that the high temperature in hot lamination (ca.  $130^\circ\text{C}$ ) degrades valinomycin, which could simultaneously degrade the performance of the ISEs by lowering their selectivity against interfering ions or in the worst case make them



**Fig. 8.** Reproducibility study showing three identically prepared electrode batches of laminated Ag/AgCl graphene paper pseudo-reference electrodes measured in  $10^{-4}$ - $10^{-1}$  M KCl. Each batch contain eight identically prepared laminated Ag/AgCl graphene paper pseudo-reference electrodes and the graph includes therefore data for twenty-four laminated reference electrodes. All potentials were measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.

**Table 1**

Potentiometric slopes and standard reduction potentials ( $E^0$ ) for five electrode batches of laminated Ag/AgCl graphene paper pseudo-reference electrodes with totally thirty-two electrodes calibrated in  $10^{-4} - 10^{-1}$  M KCl solutions measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.

Batch #	Fig #	n	Slope <sup>a</sup>	$E^0$ <sup>a</sup>
			(mV/dec)	(mV)
1	3a	4	-59.4	12.2
2 <sup>b</sup>	3a	4	-59.0	14.6
1 <sup>c</sup>	3b	4	-60.3	11.5
2 <sup>b,c</sup>	3b	4	-60.9	11.0
3	8	8	-58.2	10.5
4	8	8	-59.9	5.2
5	8	8	-56.2	10.4
Average		32	$-59.1 \pm 1.6$	$10.8 \pm 2.8$

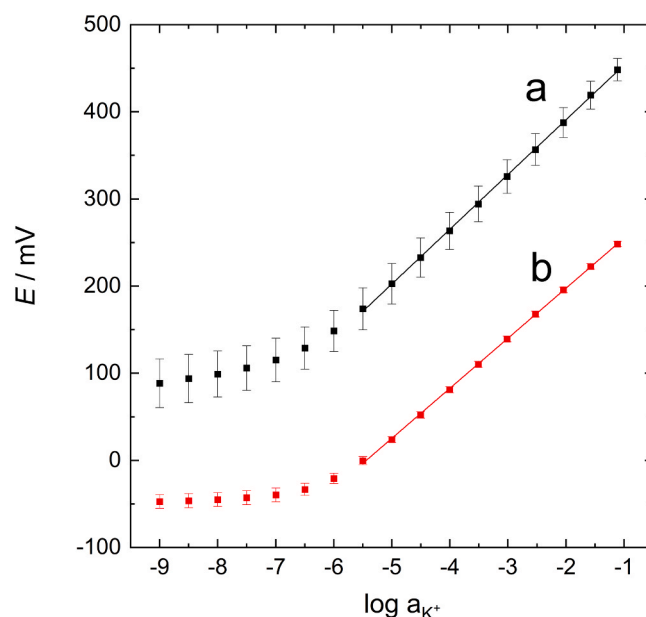
<sup>a</sup> Mean values of  $n$  electrodes.

<sup>b</sup> The Ag/AgCl layer was applied twice on the graphene paper.

<sup>c</sup> Second calibration after the potential stability test shown in Fig. 4.

non-selective to  $K^+$ .

Fig. 9 shows the calibration graphs of four identical, freshly prepared and unconditioned laminated  $K^+$ -selective electrodes (graph a). The electrodes had a slightly super-Nernstian potentiometric response of  $62.8 \pm 0.4$  mV/decade and a detection limit of ca.  $10^{-6}$  M showing that the plasticized PVC membranes containing valinomycin are compatible with the momentarily high temperature that the electrodes are exposed to in hot lamination. However, the potentials of unconditioned electrodes had a high SD of ca. 15–30 mV, which is usually observed for CWEs. During conditioning the electrode potentials were drifting ca. 150 mV to lower potentials but showed a very low SD of ca. 3 mV for the potentials in the linear response range ( $10^{-5.5} - 10^{-1}$  M  $\text{KNO}_3$ ) and slightly higher for lower  $K^+$  activities. The conditioned  $K^+$ -selective laminated electrodes ( $n = 4$ ) had a near-Nernstian slope of  $57.4 \pm 0.3$  mV/decade ( $r^2 = 0.9997$ ), a detection limit of ca.  $6 \times 10^{-7}$  M and a very good  $E^0$  reproducibility of only  $\pm 1.2$  mV. Only ISM with the same weight was chosen for the lamination of the  $K^+$ -selective electrodes that could explain the high  $E^0$  reproducibility. The ISMs were punched from master membranes that were prepared by solution casting



**Fig. 9.** Potentiometric responses of four identically fabricated laminated graphene paper  $K^+$ -selective electrodes measured in  $10^{-9}$ - $10^{-1}$  M  $\text{KNO}_3$  with  $10^{-3}$  M NaCl as the ionic background. (a) Unconditioned and (b) fully conditioned electrodes. All potentials were measured against a commercial Ag/AgCl/3 M KCl//1.0 M LiOAc reference electrode.

of the ISM solution into Petri dishes. Due to capillary forces acting at the edge of the Petri dish, the ISMs will be thicker at the edges than in the middle of the master membranes. To exclude possible variations in the ISM thickness, we did not punch individual ISMs close to the edges of the master membrane. A further study of the  $E^0$  reproducibility of the  $K^+$ -selective electrodes was not included in this work due to time limitations, but we are planning to study it in a separate work.

The logarithmic selectivity coefficients ( $\log K_{K^+}^{pot}$ ) of the laminated  $K^+$ -selective electrodes against  $Na^+$ ,  $Li^+$ ,  $H^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  were  $-3.37 \pm 0.02$ ,  $-3.66 \pm 0.05$ ,  $-4.04 \pm 0.03$ ,  $-4.02 \pm 0.05$  and  $-4.59 \pm 0.08$  ( $n = 4$ ), respectively, further confirming that the selectivity of the electrodes were not compromised by the hot lamination. Neither did the electrodes show light sensitivity when exposed to room light, darkness and intense cold light, which is an advantage compared to some conducting polymer based solid contact materials that can be highly light sensitive, such as poly(3-octylthiophene) [40].

#### 4. Conclusions

We show in this paper that planar, low-cost ( $< \text{€}1$ ) and flexible laminated graphene paper Ag/AgCl pseudo-REs aimed for single use can be fabricated with high  $E^0$  reproducibility of  $10.8 \pm 2.8$  mV ( $n = 32$ ) measured against a commercial double junction Ag/AgCl reference electrode. Multiple pseudo-REs with a very good batch-to-batch reproducibility can be quickly fabricated in a single lamination step making them suitable for mass production. They had practically no light sensitivity and were also insensitive to clinically relevant concentrations of inorganic ions, such as  $Li^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ , which makes them potentially useful in blood analysis where the chloride level is rather constant. However, the requirement of a constant chloride concentration is also a limitation of the pseudo-reference electrodes presented in this work. In a follow up paper, we are planning to modify the Ag/AgCl layer with a coating making the electrodes insensitive to fluctuations in the chloride concentration.

We also report a one-step fabrication by lamination of fully laminated  $K^+$ -selective coated-film electrodes that did not require a solid contact or any additional post-processing steps (drop casting) after the lamination. The planar and flexible ISEs showed close to Nernstian electrode slope of  $57.4 \pm 0.3$  mV/pK with a detection limit of  $6 \times 10^{-7}$  M and in the best case a very good  $E^0$  reproducibility of only  $\pm 1.2$  mV. The results reveal that valinomycin, the  $K^+$ -selective ionophore used in this study, does not degrade during the momentarily high temperature it is exposed to during the hot lamination. In a future study, we aim to integrate the pseudo-RE and the  $K^+$ -selective electrode to a single measuring unit by using hot lamination.

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#### CRediT authorship contribution statement

**Bojidar Mandjoukov:** Investigation, Methodology, Validation, Formal analysis, Writing – review & editing. **Tom Lindfors:** Conceptualization, Methodology, Validation, Supervision, Writing – original draft, Writing – review & editing, Resources, Project administration.

#### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Bojidar Mandjoukov reports financial support was provided by Excellence in Analytical Chemistry (EACH) Erasmus Mundus Joint Master

Degree.

#### Data Availability

Data will be made available on request.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.snb.2023.135190](https://doi.org/10.1016/j.snb.2023.135190).

#### References

- [1] Y. Shao, Y. Ying, J. Ping, Recent advances in solid-contact ion-selective electrodes: functional materials, transduction mechanisms, and development trends, *Chem. Soc. Rev.* 49 (2020) 4405–4465, <https://doi.org/10.10039/c9cs00587k>.
- [2] N. Ruecha, O. Chailapakul, K. Suzuki, D. Citterio, Fully Inkjet-Printed Paper-Based Potentiometric Ion-Sensing Devices, *Anal. Chem.* 89 (2017) 10608–10616, <https://doi.org/10.1021/acs.analchem.7b03177>.
- [3] M. Rutkowska, T. Lindfors, Z. Boeva, M. Strawski, Low-cost flexible laminated graphene paper solid-contact ion-selective electrodes, *Sens. Actuators B Chem.* 337 (2021), 129808, <https://doi.org/10.1016/j.snb.2021.129808>.
- [4] N. He, S. Papp, T. Lindfors, L. Höfler, R.M. Latonen, R.E. Gyurcsányi, Pre-polarized hydrophobic conducting polymer solid-contact ion selective electrodes with improved potential reproducibility, *Anal. Chem.* 89 (2017) 2598–2605, <https://doi.org/10.1021/acs.analchem.6b04885>.
- [5] S. Papp, M. Bojtár, R.E. Gyurcsányi, T. Lindfors, Potential Reproducibility of Potassium-Selective Electrodes Having Perfluorinated Alkanoate Side Chain Functionalized Poly(3,4-ethylenedioxythiophene) as a Hydrophobic Solid Contact, *Anal. Chem.* 91 (2019) 9111–9118, <https://doi.org/10.1021/acs.analchem.9b01587>.
- [6] B.K. Trout, C.R. Rousseau, X.I.N. Dong, E.L. Anderson, P. Buhlmann, Recent progress in the development of improved reference electrodes for electrochemistry, *Anal. Sci.* 38 (2022) 71–83, <https://doi.org/10.2116/analsci.21SAR11>.
- [7] E. da Silva, S. Miserere, L.T. Kubota, A. Merkoci, Simple On-Plastic/Paper Inkjet-Printed Solid-State Ag/AgCl Pseudoreference Electrode, *Anal. Chem.* 86 (2014) 10531–10534, <https://doi.org/10.1021/ac503029q>.
- [8] Z. Mousavi, K. Granholm, T. Sokalski, A. Lewenstam, An analytical quality solid-state composite reference electrode, *Analyst* 138 (2013) 5216–5220, <https://doi.org/10.1039/c3an00852e>.
- [9] A. Kisiel, A. Michalska, K. Maksymiuk, Plastic reference electrodes and plastic potentiometric cells with dispersion cast poly(3,4-ethylenedioxythiophene) and poly(vinyl chloride) based membranes, *Bioelectrochemistry* 71 (2007) 75–80, <https://doi.org/10.1016/j.bioelechem.2006.09.006>.
- [10] U. Mattinen, J. Bobacka, A. Lewenstam, Solid-Contact Reference Electrodes Based on Lipophilic Salts, *Electroanalysis* 21 (2009) 1955–1960, <https://doi.org/10.1002/elan.200904615>.
- [11] X.V. Chen, A. Stein, P. Buhlmann, Reference Electrodes Based on Ionic Liquid-Doped Reference Membranes with Biocompatible Silicone Matrixes, *ACS Sens.* 5 (2020) 1717–1725, <https://doi.org/10.1021/acssensors.0c00363>.
- [12] C. Diekmann, C. Dumschat, K. Cammann, M. Knoll, Disposable reference electrode, *Sens. Actuators B Chem.* 24 (1995) 276–278, [https://doi.org/10.1016/0925-4005\(95\)85059-7](https://doi.org/10.1016/0925-4005(95)85059-7).
- [13] D. Desmond, B. Lane, J. Alderman, J.D. Glennon, D. Diamond, D.W.M. Arrigan, Evaluation of miniaturised solid state reference electrodes on a silicon based component, *Sens. Actuators B Chem.* 44 (1997) 389–396, [https://doi.org/10.1016/S0925-4005\(97\)00231-1](https://doi.org/10.1016/S0925-4005(97)00231-1).
- [14] H. Suzuki, T. Hirakawa, S. Sasaki, I. Karube, Micromachined liquid-junction Ag/AgCl reference electrode, *Sens. Actuators B Chem.* 46 (1998) 146–154, [https://doi.org/10.1016/S0925-4005\(98\)00110-5](https://doi.org/10.1016/S0925-4005(98)00110-5).
- [15] A. Mroz, M. Borchardt, C. Diekmann, K. Cammann, M. Knoll, C. Dumschat, Disposable reference electrode, *Analyst* 123 (6) (1998) 1373, <https://doi.org/10.1039/a708992i>.
- [16] H.J. Lee, U.S. Hong, D.K. Lee, J.H. Shin, H. Nam, G.S. Cha, Solvent-processible polymer membrane-based liquid junction-free reference electrode, *Anal. Chem.* 70 (1998) 3377–3383, <https://doi.org/10.1021/ac980265k>.
- [17] H. Suzuki, H. Shiroishi, S. Sasaki, I. Karube, Microfabricated liquid junction Ag/AgCl reference electrode and its application to a one-chip potentiometric sensor, *Anal. Chem.* 71 (1999) 5069–5075, <https://doi.org/10.1021/ac990437t>.
- [18] H.J. Yoon, J.H. Shin, S.D. Lee, H. Nam, G.S. Cha, T.D. Strong, et al., Solid-state ion sensors with a liquid junction-free polymer membrane-based reference electrode for blood analysis, *Sens. Actuators B Chem.* 64 (2000) 8–14, [https://doi.org/10.1016/S0925-4005\(99\)00476-1](https://doi.org/10.1016/S0925-4005(99)00476-1).
- [19] L. Tymecki, Z. Zwierkowska, R. Koncki, Screen-printed reference electrodes for potentiometric measurements, *Anal. Chim. Acta* 526 (2004) 3–11, <https://doi.org/10.1016/j.aca.2004.08.056>.
- [20] W.Y. Liao, T.C. Chou, Fabrication of a planar-form screen-printed solid electrolyte modified Ag/AgCl reference electrode for application in a potentiometric biosensor, *Anal. Chem.* 78 (2006) 4219–4223, <https://doi.org/10.1021/ac051562+>.
- [21] J.K. Atkinson, M. Glanc, P. Boltryk, M. Sophocleous, E. Garcia-Breijo, An investigation into the effect of fabrication parameter variation on the



- characteristics of screen-printed thick-film silver/silver chloride reference electrodes, *Microelectron Int.* 28 (2011) 49–52, <https://doi.org/10.1108/13565361111127368>.
- [22] I. Shitanda, H. Kiryu, M. Itagaki, Improvement in the long-term stability of screen-printed planar type solid-state Ag/AgCl reference electrode by introducing poly (dimethylsiloxane) liquid junction, *Electrochim Acta.* 58 (2011) 528–531, <https://doi.org/10.1016/j.electacta.2011.09.086>.
- [23] A. Cranny, N.R. Harris, M. Nie, J.A. Wharton, R.J.K. Wood, K.R. Stokes, Screen-printed potentiometric Ag/AgCl chloride sensors: Lifetime performance and their use in soil salt measurements, *Sens Actuators A Phys.* 169 (2011) 288–294, <https://doi.org/10.1016/j.sna.2011.01.016>.
- [24] W.J. Lan, E.J. Maxwell, C. Parolo, D.K. Bwambok, A.B. Subramaniam, G. M. Whitesides, Paper-based electroanalytical devices with an integrated, stable reference electrode, *Lab a Chip* 13 (2013) 4103–4108, <https://doi.org/10.1039/c3lc50771h>.
- [25] A. Määttänen, U. Vanamo, P. Ihalainen, P. Pulkkinen, H. Tenhu, J. Bobacka, et al., A low-cost paper-based inkjet-printed platform for electrochemical analyses, *Sens Actuators B Chem.* 177 (2013) 153–162, <https://doi.org/10.1016/j.snb.2012.10.113>.
- [26] M. Glanc, M. Sophocleous, J.K. Atkinson, E. Garcia-Brejjo, The effect on performance of fabrication parameter variations of thick-film screen printed silver/silver chloride potentiometric reference electrodes, *Sens Actuators A Phys.* 197 (2013) 1–8, <https://doi.org/10.1016/j.sna.2013.03.036>.
- [27] M. Novell, T. Guinovart, P. Blondeau, F.X. Rius, F.J. Andrade, A paper-based potentiometric cell for decentralized monitoring of Li levels in whole blood, *Lab a Chip* 14 (2014) 1308–1314, <https://doi.org/10.1039/c3lc51098k>.
- [28] I. Shitanda, M. Komoda, Y. Hoshi, M. Itagaki, An instantly usable paper-based screen-printed solid-state KCl/Ag/AgCl reference electrode with long-term stability, *Analyst* 140 (2015) 6481–6484, <https://doi.org/10.1039/c5an00617a>.
- [29] I. Shitanda, M. Komoda, Y. Hoshi, M. Itagaki, Screen-printed Paper-based Three-electrode System with Long-term Stable and Instantaneously Usable Reference Electrode, *Chem. Lett.* 47 (2018) 1502–1504, <https://doi.org/10.1246/cl.180809>.
- [30] A. Bananezhad, M. Jovic, L.F. Villalobos, K.V. Agrawal, M.R. Ganjali, H.H. Girault, Large-scale fabrication of flexible solid-state reference electrodes, *J. Electroanal Chem.* 847 (2019), <https://doi.org/10.1016/j.jelechem.2019.113241>.
- [31] U. Lemke, K. Cammann, Coated film electrodes, *Fresen J. Anal. Chem.* 335 (1989) 852–854, <https://doi.org/10.1007/bf01204100>.
- [32] E. Lindner, V.V. Cosofret, S. Ufer, T.A. Johnson, R.B. Ash, H.T. Nagle, et al., In-vivo and in-vitro testing of micromechanically fabricated planar sensors designed for applications in cardiology, *Fresenius J. Anal. Chem.* 346 (1993) 584–588, <https://doi.org/10.1007/bf00321250>.
- [33] M. Borchardt, C. Diekmann, C. Dumschat, K. Cammann, M. Knoll, Disposable sodium electrodes, *Talanta* 41 (1994) 1025–1028, [https://doi.org/10.1016/0039-9140\(94\)e0107-3](https://doi.org/10.1016/0039-9140(94)e0107-3).
- [34] M. Borchardt, C. Dumschat, K. Cammann, M. Knoll, Disposable ion-selective electrodes, *Sens Actuators B Chem.* 25 (1995) 721–723, [https://doi.org/10.1016/0925-4005\(95\)85159-3](https://doi.org/10.1016/0925-4005(95)85159-3).
- [35] F. Wendzinski, M. Borchardt, B. Romberg, M. Knoi, Application of double matrix membrane technology for ion-selective electrodes, *Anal. Lett.* 36 (2003) 21–39, <https://doi.org/10.1081/al-120017261>.
- [36] A. Michalska, K. Maksymiuk, All-plastic, disposable, low detection limit ion-selective electrodes, *Anal. Chim. Acta* 523 (2004) 97–105, <https://doi.org/10.1016/j.aca.2004.07.020>.
- [37] A. Michalska, M. Ocyka, K. Maksymiuk, Highly selective all-plastic, disposable, Cu<sup>2+</sup>-selective electrodes, *Electroanalysis* 17 (2005) 327–333, <https://doi.org/10.1002/elan.200403107>.
- [38] M. Novell, M. Parrilla, G.A. Crespo, F.X. Rius, F.J. Andrade, Paper-Based Ion-Selective Potentiometric Sensors, *Anal. Chem.* 84 (2012) 4695–4702, <https://doi.org/10.1021/ac202979j>.
- [39] R.W. Cattrall, H. Freiser, Coated wire ion selective electrodes, *Anal. Chem.* 43 (1971) 1905–1906.
- [40] T. Lindfors, Light sensitivity and potential stability of electrically conducting polymers commonly used in solid contact ion-selective electrodes, *J. Solid State Electrochem* 13 (2009) 77–89, <https://doi.org/10.1007/s10008-008-0561-z>.

**Bojidar Manjoukov** received his BSc in 2020 from Sofia University (Bulgaria) and his MSc in 2022 from Åbo Akademi University (Finland) within the Erasmus Mundus joint Master's programme Excellence in Analytical Chemistry (EACH). He is since September 2022 a PhD student at the Department of Geology at University of Tartu (Estonia).

**Tom Lindfors** is Associate Professor in Analytical Chemistry at the Laboratory of Molecular Science and Engineering at Åbo Akademi University (Finland). His research interests cover calibration-free solid-state ion-selective electrodes, graphene based composite materials, electrically conducting polymers, water uptake of polymeric ion-selective membrane materials and barrier properties of carbon materials.