

All-Solid-State Reference Electrode with Heterogeneous Membrane

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 **Supporting Information**

ABSTRACT: Novel reference electrodes with a solid contact coated by a heterogeneous polymer membrane are described. The electrodes are obtained using Ag nanoparticles, AgBr, KBr suspended in tetrahydrofuran solution of PVC and DOS and deposited on Ag substrate, or another substrate covered with Ag, by drop casting. After a short period of soaking in a KBr solution, stable and reproducible formal potentials of -157 ± 2 mV (vs Ag/AgCl/3 M KCl) were observed, and the solid-contact reference electrodes were ready to use. It is shown that the described reference electrodes are relatively insensitive to the changes in the sample matrix, the concentrations of ions, the pH and the redox potential. These electrodes can also be fabricated in miniaturized form, and thus used to produce miniaturized multielectrode probes.



The application of a conducting polymer as a solid contact (SC) for ion-selective electrodes (ISEs) with polymeric (e.g., PVC) membranes has opened a new avenue in potentiometry.^{1,2} Different all-solid-state indicator and reference electrodes have since then been reported, and interest in solid contact ion-selective electrodes (SC-ISEs) is a mainstream of potentiometry today.^{3–6} Solid contact reference electrodes (SC-REF), owing to their high metrological demands and distinctively different design techniques, occupy a know-how niche of their own.⁷

A significant technical challenge is in selecting the materials and procedures that would be compatible in production for both SC-ISEs and SC-REFs. In the case of all-solid-state PVC electrodes, obviously advantageous would be the application of the same material, for example, conducting polymer and PVC.^{6,8,9} Some benefits can be gained by using organic salts and ionic liquids dispersed in PCV or inorganic salts in inert polymer binders.^{10–16} So far, the electrochemical mechanism of all-solid-state reference electrodes is not sufficiently elucidated, which prompts the researcher to use trial-error methods. A general electrochemical rationale points to a condition of the equitransferent liquid junctions.¹⁷ However, in the case SC-REF, one has the asymmetric junction between the solid contact and solution, and applicability of the equitransferent condition is challenged. To understand the mechanism of SC-REF, the concept of pseudoreference electrode,^{8,18} and a “stable-in-a matrix” diffusion potential¹⁹ can be useful, but it appears that a more comprehensive interpretation is needed. At the moment though, further developments primarily depend on the practical purpose, the scope of applications and technical inventiveness.

For both theoretical and practical reasons, the most popular reference electrodes are silver chloride electrode systems (e.g., Ag/AgCl/KCl) used in different configurations.^{7,16,20–25} An inventive approach was the introduction of a composite membrane made of polyvinyl acetate containing a very large loading of KCl (1:1 w/w KCl/PVA).^{10,11} Very recently,

Polypropylene (PP) has been successfully used as the binding polymer for the same purpose with the advantage of production by injection molding.¹⁶ In this report, we show that a composite based on poly(vinyl chloride) (PVC) membrane containing nanoparticles of Ag, AgBr, KBr, and potassium bromoargentates allows the design of a solid-contact reference electrode.²⁶ In general, even the conventional Ag/AgBr electrodes are rarely used²⁵ and, to our knowledge, the system reported has never been explicitly described.

Our technical note sees an avenue for a new class of the reference electrodes with heterogeneous membranes. We show that, by conventional drop casting, it is possible to obtain all-solid-state reference electrodes coupled with excellent analytical properties.

EXPERIMENTAL SECTION

Reagents. Bis(2-ethylhexyl) sebacate (DOS), tetrabutylammonium tetrabutylborate (QB), and poly(vinyl chloride) high molecular weight (PVC) were purchased from Fluka (Buchs, Switzerland). Silver nanowires of diameter 175 nm \times L 20–50 μm as 0.5% suspension in isopropanol obtained from Sigma-Aldrich (Steinheim, Germany) were used as received. Tetrahydrofuran (THF) purchased from Sigma-Aldrich was distilled before use.

The other compounds used were obtained as p.a. form POCh, Poland and Merck, Germany and used as received. The gases were obtained from Linde Gas, Poland.

Water redistilled from quartz was used to prepare the solutions. All solutions with concentrations lower than 0.01 mol dm^{-3} were prepared just before use.

Preparation of Reference Electrode Cocktails. Silver bromide was precipitated from 3 M silver nitrate with the 3 M potassium bromide solution. Precipitated salt was filtered

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(without washing) and dried at 100 °C. Potassium bromide p.a. was dried at 300 °C and ground to a fine powder. Next, silver bromide and potassium bromide were mixed in molar ratio 1:5, and the mixture was thoroughly ground again and exposed to light to allow for photochemical decomposition of AgBr. The presence of metallic silver nanoparticles was proved by XPS and AgBr KBr by XRD analysis. Bis(2-ethylhexyl)-sebacate (DOS) and poly(vinyl chloride) (PVC) of total mass 3.3 g and 35–50 weight% of PVC were dissolved in 25 mL of freshly distilled THF.

Three types of THF solutions containing bromide salts (cocktails) were used.

The first contained 0.336 g of AgBr/KBr in 1.5 mL of the solution. This cocktail (owing to the small amount of Ag nanoparticles produced during the photochemical reaction) is depicted and referred to below as “REF-Br-photo”.

In the second cocktail type, the metallic silver content was increased. To prepare this cocktail, 1 mL of silver nanowire suspension in 2-propanol was evaporated to obtain the volume of less than 0.05 mL. Next, 0.336 g of freshly dried and thoroughly ground mixture of AgBr/KBr and 1.5 mL of the PVC/DOS solution were added. The reference membranes prepared from such a cocktail are called “REF-Br-nano”.

The third type of reference cocktail contained an additional amount of metallic silver formed during the redox reaction of AgBr with reducing agent, for example, QB. To prepare this cocktail, QB was added to the solution containing the AgBr/KBr suspension. The amount of QB introduced to 1.5 mL of suspension containing 0.336 g AgBr/KBr was varied from 1 to 25 mg. After QB addition, the cocktail color changed from light yellow to dark brown owing to the formation of metallic Ag, as proved by XPS. The reference membranes prepared from such cocktails are called “REF-Br-QB”.

Regarding the major components, the typical composition of the above three membranes used in our studies was (in % w/w): 15.2 (AgBr), 47.8 (KBr), 23.1 (DOS), and 13.9 (PVC).

Preparation of the Reference Electrodes. Before membrane casting, each cocktail was vigorously mixed and a cloudy mixture of 100–200 μL was deposited on the silver substrate as well as on the glassy carbon (GC) or the gold substrate covered with Ag and (for comparison) on the pure GC or Au. The electrodeposition of a silver layer on the GC or Au substrates was done in 0.05 M AgNO₃ solution using an Autolab PGSTAT-100 Analyzer (Ecco Chemie, Nederlands) in the three-electrode electrochemical cell. The silver chloride electrode Ag/AgCl/satd KCl with a bridge filled with the 1 M KNO₃ solution was used as the reference electrode. A Pt sheet with an area of about 2 cm² was used as an auxiliary electrode. The deposition potential was adjusted to a current density of 1.5–3 mA/cm² and a typical deposition time was 1000 s.

Prior to Ag electrodeposition, the GC or Au electrodes were polished with 0.3 μm aluminum oxide and subsequently sonicated (for at least 5 min) in water, 0.1 M KOH in ethanol, bidistilled water, 5% nitric acid, and finally rinsed with bidistilled water and dried. These substrates with a deposited silver layer are denoted in the text as GC/Ag or Au/Ag. Before the reference membrane casting, the surfaces of the Ag, GC/Ag, or Au/Ag were rinsed with methanol and THF. The reference cocktails were allowed to dry for at least 24 h, and after that the quality of the dry REF-Br membranes was inspected using an optical microscope to check for possible faults (namely, adhesion to the substrate, compactness of the membrane layer, the presence of cracks, and uncovered substrate areas),

and to select the membranes without faults for further experiments.

Apparatus. The potentiometric measurements were performed using a homemade 16-channel setup. The input impedance was greater than 10¹³ Ohms and the input current was lower than 20 fA for each of the 16 inputs as well as for the reference electrode input. The multichannel potential-meter was coupled with a personal computer equipped with a 16-bit resolution data acquisition card PCI DAS 6014 (Computer Boards; U.S.) and custom-made software. In typical conditions, the potential resolution was better than 0.02 mV.

In the potentiometric measurements the double junction REF251 (Metrohm; Switzerland) reference electrodes were used. All the experiments were performed at room temperature (22–24 °C). Stirring up to 500 rpm did not significantly affect the readouts.

RESULTS AND DISCUSSION

1. The rate of standard potential stabilization and its repeatability. Freshly prepared electrodes with dry REF-Br membranes were immersed in 2 M KBr and their potential changes were recorded. The shortest soaking time (usually several tens of seconds) was needed for electrodes with REF-Br-nano membranes. A longer soaking (several hundreds of seconds) was required for the electrodes with REF-Br-photo membranes, while the longest was for the electrodes with REF-Br-QB membranes. The short-time behavior of the electrodes is similar for the metallic silver and the substrates with a deposited silver layer on nonsilver electronically conducting substrates, for example, glassy carbon, as shown in Figure 1.

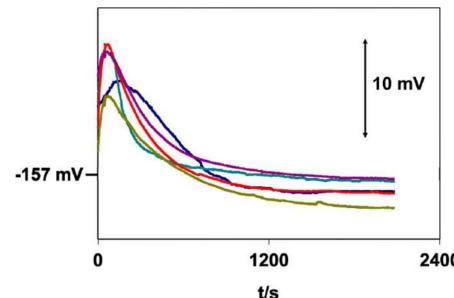


Figure 1. Potential changes of the five electrodes with REF-Br-photo reference membranes (measured vs Ag/AgCl/3 M KCl electrode) recorded from the moment when freshly prepared and dry electrodes were dipped in 2 M KBr solution. The membranes tested were deposited on three Ag substrates (red, violet and green lines) and two GC substrates covered with silver (blue and navy blue lines).

The results show the convergence of the short-time potentials, for the five electrodes used, to less than 3 mV after a few minutes of soaking. The mean potential after 20 min is -157.63 ± 1.09 mV. (More data can be found in Supporting Information, Table S-1.)

2. Long-Term Potential Stability of the Electrodes with REF-Br Reference Membranes. For several hundreds of all the types of REF-Br membranes studied, the stable and reproducible potential readouts collected are all located in a rather narrow potential range to the mean potential -157 ± 10 mV. No systematic lifetime experiments were undertaken. However, for the same subtypes of electrodes, typically in a series of 5–16 electrodes, the potentials were reproducible within ± 2 mV during continuous measurement for 10 days in 2

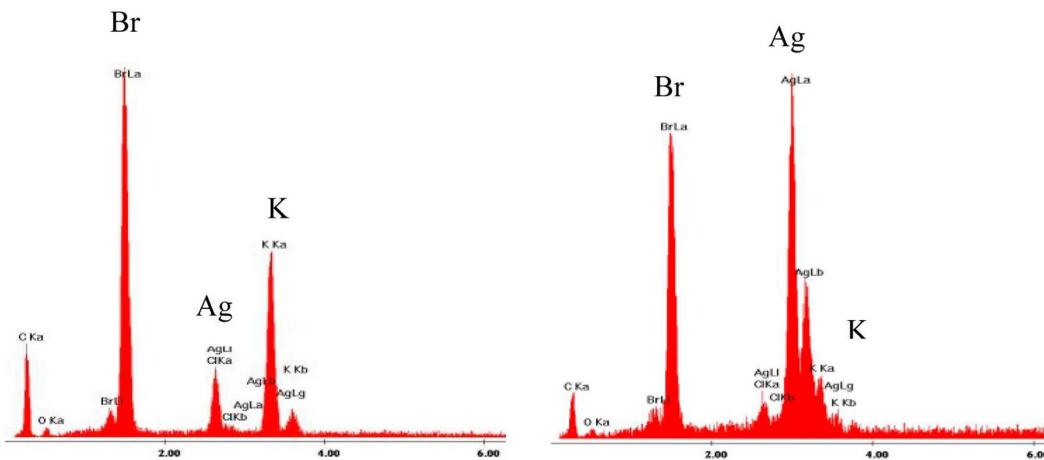


Figure 2. EDAX spectra taken for REF-Br photo membrane on the membrane separated from the Ag substrate. The spectra were recorded for the side remaining in contact with the solution (left side) and for the other side of the membrane in contact with Ag substrate (right side).

M KBr (**Figure S-1**). These were the electrodes with the reference membranes deposited on Ag substrate embedded in a PVC body. This design facilitates the adhesion of PVC membrane to the PVC body which is advantageous to the electrodes' lifetime.

3. Substrate Influence on the Standard Potential Value and Its Stability. Excellent potential reproducibility and long-term potential stability were observed for all REF-Br membranes deposited on silver substrate or with GC or Au substrate covered with the silver layer. The membrane was unattached from the substrate and the presence of silver, potassium, and bromide was analyzed by SEM/EDAX on both sides of the membrane, **Figure 2**.

The largest amount of silver and bromide were determined on the side of the membrane in contact with Ag substrate, whereas for the other side, mainly bromide and potassium signals were detected.

If the reference membranes were placed directly on GC or Au substrate, unpredictable and unstable potential values were recorded (see **Table S-2**).

4. EIS Spectra for Electrodes with REF-Br Membranes Deposited on Silver or Nonsilver Substrate. The influence of the Ag phase was inspected by electrochemical impedance spectroscopy (EIS).

A striking difference in the impedance spectra for electrodes with reference membranes deposited on Ag substrate or nonsilver substrate was observed. Namely, the difference is manifested by a disappearance of a low-frequency branch for the membranes deposited on Ag substrate which is present if the substrate is a nonsilver one. The EIS results indicate a slower electrochemical process rate in the membrane without dispersed Ag. The appearance of Warburg type behavior at lower frequencies can be attributed to a slower ion-transport in the membrane. It can be hypothesized that dispersed silver facilitates the overall electrochemical process.

The EIS spectra illustrating this effect, recorded for electrodes with REF-Br-photo membranes deposited on a bare GC substrate and for the GC substrate covered with Ag are presented in **Figure S-2**.

5. Mechanism of the Br-REF Response. Undoubtedly, the fact that the metallic silver, both as the layer on the substrate and in the form of dispersed nanosilver in the membrane, significantly contribute to stabilizing the potential of the REF-Br systems is of general importance to solid contact

ion-sensor technology with heterogeneous membranes. The composite-like heterogeneous membrane serves as the reservoir of Ag, AgBr, KBr, and respective silver bromide complexes. The coexistence of these three solid phases coupled through the contact with the respective ions (silver, potassium bromoargentate, and bromide ions) saturating pores and slow electrolyte outflow from the membrane is the prerequisite of the stability observed. Interestingly, the mean standard potential of the REF-Br electrodes (-157 mV vs Ag/AgCl/3 M KCl ($E^0 = +210$ mV vs NHE)) indicates that the composite reference electrode works as the analogue of the Ag/AgBr reference electrode immersed in the heterogeneous membrane, which plays the role of a stable electrolyte bridge. The bridge provides a stable electrochemical matrix, in respect to the coexistence of the phases, ion concentrations, single ion diffusion, and activity coefficients. Generalized mathematical interpretation which reduces potential stability of the REF-Br electrodes to the fundamental Gibbs' Phase Rule and E^0 set by Ag⁺/Ag redox pair will be provided by the authors in a separate paper.

From the technical perspective, though, the system in focus is sufficiently attractive to be of choice in different analytical applications as shown below.

6. Calibration of the REF-Br Electrodes in KBr and MX Solutions. A crucial question regarding the conceptual and analytical validity of the REF-Br is their insensitivity toward bromides. **Figure 3** shows the potential changes of the five

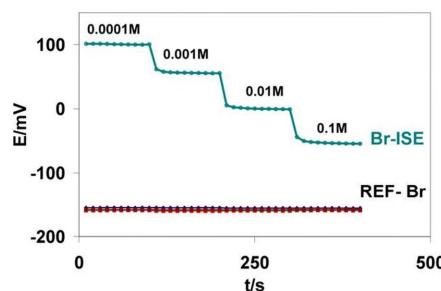


Figure 3. Potential changes of the five electrodes with REF-Br-photo membranes deposited on Ag substrate and Br-ISE (with AgBr/Ag₂S solid state membrane) during calibration in KBr solutions in the concentration range 0.0001–0.1 M. The potential of each REF electrode in the calibration does not change more than 1 mV.

electrodes with REF-Br-photo membranes as well as Br-ISE recorded during calibration with KBr solution. A striking difference provides direct proof of the invention reported.

Negligible potential changes were observed for electrodes with REF-Br-nano, REF-Br-QB, and REF-Br-photo reference membranes during up-down-up as well as down-up-down calibrations in KCl solutions with concentration ranging from 1 M up to 10^{-5} M. As an example, the potential values measured during up-down-up calibration are presented in Table S-3. Similar results were also obtained during calibration in LiCl, NaCl, KBr, KNO_3 , and CaCl_2 solutions. The influence of lipophilic ions was also checked using the representative perchlorate ion. No statistically significant effect was observed between the calibrations performed in chloride and perchlorate salts, see Figures S-3 and S-4.

7. Redox Sensitivity of the Electrodes with REF-Br Membranes.

The presence of elemental silver can induce undesirable redox sensitivity of the REF-Br membranes. Therefore, all the membranes were studied in the calibration using the mixture of $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}[\text{Fe}(\text{CN})_6]$ with total concentration 0.01 M but different molar ratios. Before and after redox calibration, additional measurements in 2 M KBr were performed to check the potential stability. The redox insensitivity was proved for all the REF-Br membranes and different substrates, as shown in Table S-4. The redox effect was not observed as well in the solutions saturated with O_2 , CO_2 , and Ar (Figure S-5).

8. Potential Stability of the REF-Br Electrodes during Prolonged Contact with Deionized Water.

For every reference electrode, the test of its behavior in water is most challenging and analytically relevant. For this reason, all the electrodes equipped with REF-Br-nano, REF-Br-QB, or REF-Br-photo reference membranes were tested in deionized water. After a due period of soaking, the potential of the REF-Br electrodes was measured for 10 min versus the commercial silver chloride reference electrode (Metrohm). A very good potential stability was observed, and the potentials measured were practically invariant at least for several hours of contact with water (or even up to a few days for some of the electrodes). The results are summarized in Table S-5.

9. Multisolution Calibration Experiment. To judge the performance of the reference electrodes in real analysis, a multisolution calibration was carried out following the protocol shown by Mousavi et al.¹⁵ The potential of the electrodes with REF-Br-nano, REF-Br-QB, and REF-Br-photo reference membranes was measured in several solutions to check the influence of ion concentration, pH and ion mobility. The potential in each solution was recorded for 10 min. After each test, the electrodes were rinsed with deionized water and immersed in the subsequent solution. The exemplary results obtained for electrodes with REF-Br-photo reference membranes deposited on Ag substrates and the potential values measured at the end of each 10 min period are shown in Figures 4 and S-6 and collected in Table S-6.

10. Influence of pH: Potential Stability of the Electrodes with REF-Br Reference Membranes during Acid–Base Titration.

To check the pH influence on the potential of the reference electrodes, the REF-Br-photo reference membranes and pH-ISE were employed in the titration of 1 mL of 0.1 M NaOH with 0.1 M HCl, Figure 5. As required, both reference membranes are insensitive to pH changes in the course of the titration performed.

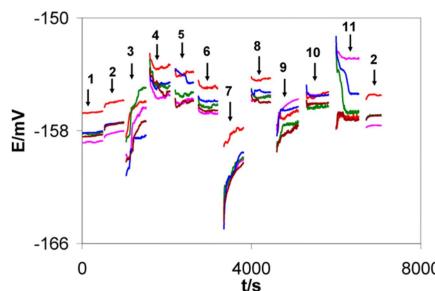


Figure 4. Multi Solution Protocol carried out for five identical REF electrodes with Br-photo membranes deposited on Ag substrate in the following solutions sequence: (1) 2 M KBr, (2) 3 M KCl, (3) H_2O , (4) 0.01 M NaCl, (5) 0.01 M KCl, (6) 0.1 M KCl, (7) 0.01 M HCl, (8) 0.1 M NaCl, (9) 0.1 M NaHCO_3 , (10) 0.1 M KBr, and (11) 0.001 M KOH. Potential changes were recorded from the moment the electrodes were contacted with indicated solutions.

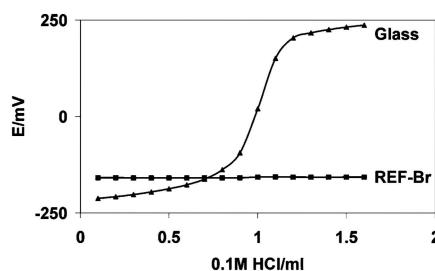


Figure 5. Potential changes of the two reference electrodes with REF-Br-photo membranes deposited on Ag substrate and pH-sensitive glass electrode recorded during titration of 1 mL of 0.1 M NaOH (diluted to 20 mL) with 0.1 M HCl.

11. Performance of the Microcell with REF-Br Reference and Potassium-Ion Selective Electrodes.

In this measurement, a homemade multielectrode platform with a body made of epoxy resin was used. The platform contained five gold wire electrodes (Au 99.99 obtained from Johnson Matthey Company) with a diameter of 0.8 mm. The external diameter of the epoxy body was 8 mm.^{27–29} All the gold discs were electrochemically covered with silver, and the REF-Br-photo membranes and potassium-selective membranes were deposited by solution cast on selected discs. Negligible potential changes were recorded for both electrodes with REF-Br-photo membranes used and close to theoretical potential changes were recorded for K-ISE, Figure S-7. These results indicate that employing the reference electrodes described here for designing a complete multielectrode microcell is feasible. Moreover, the junctionless REF-Br reference electrode is used in two roles as the external reference electrode and the internal solid-contact of the ion-selective electrode. Interestingly, a similar dual role has been reported by the authors before.³⁰ However, in that case, the same conducting polymer film was employed either as the solid contact or as the electroactive membrane of an ion-selective electrode.

CONCLUSIONS

A simple procedure for obtaining analytical quality solid-state reference electrodes by a solution cast method is shown. It is made possible by applying a cocktail containing the mixture of KBr, AgBr, and Ag nanoparticles suspended in PVC/DOS/THF solution and drop casting of the cocktail on Ag substrates. The soaking in 2 M KBr for approximately several hundred

seconds is sufficient to activate the electrodes characterized with reproducible and stable potential. This potential is in the range of -157 ± 2 mV versus silver chloride electrode, which indicates that the operation mechanism is similar to that of the silver bromide reference electrode, but not the same owing to the role played by the composite heterogeneous membrane. Carefully designed tests to check the performance of the reference electrodes proved the insensitivity of the REF-Br electrodes to repeated and challenging changes in the solution composition, pH, concentration, mobility, and lipophilicity of ions, as well as the presence of redox species. Electrodes of this type possess comparable properties to high-quality commercially available reference electrodes. Additionally, as all-solid-state electrodes, they can be fabricated in miniaturized form and thus be applied when designing miniaturized multielectrode platforms and probes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.analchem.6b02762](https://doi.org/10.1021/acs.analchem.6b02762).

Six additional tables, Tables S1–S6, and seven figures, Figures S-1–S-7 (on pages S-2–S-7). The tables contain data on short-time responses (S-1), influence of the contact (S-2), chloride ion effect (S-3), and the influence of redox potential (S-4), soaking in water (S-5) and in different electrolyte solutions (S-6). The figures illustrate the influence of the electrode body (S-1), electrochemical impedance (S-2), influence of chloride ions (S-3) and perchlorate ions (S-4), influence of redox potential change by gas saturation (S-5), influence of electrolyte solutions (S-6), and measurement using solid-contact electrodes in a microcell (S-7; [PDF](#)).

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Notes

The authors declare no competing financial interest.

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