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All-solid-state electrochemical platform for potentiometric measurements

Zekra Mousavi[a], Kim Granholm[a], Tomasz Sokalski[a], Andrzej Lewenstam[a,b,*]

[a] Process Chemistry Centre, c/o Laboratory of Analytical Chemistry, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo-Turku, Finland
[b] AGH – University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30, 30-059 Krakow, Poland

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ABSTRACT

A unique concept of all-solid-state electrochemical platform is presented in this paper. The electrochemically active composite body of the platform, in conjunction with an internal reference element, serves both as a reference electrode and an encasement for the indicator electrode(s). The solid-state composite reference electrode is simple to manufacture, mechanically processable, maintenance free, and has significantly reduced leakage of inorganic salt. This analytical-quality reference electrode combined with solid-state indicator electrodes makes a novel and attractive proposition for an all-solid-state electrochemical device.

The platform can contain different types of electrochemical indicator electrodes, such as ion-selective electrodes, glassy carbon, gold, or platinum electrodes. As an example, in this work anionic- (chloride) and cationic- (potassium) selective platforms were prepared and successfully tested in potentiometric measurements.

1. Introduction

The recent development of potentiometric ion sensors has mainly been dedicated to the elimination the inner filling solution, which is an electrolyte solution providing an ion-to-electron transduction. This internal solution in conventional ion-selective electrodes (ISEs) can be replaced for example with a conducting polymer as solid-contact (SC), i.e. the material with mixed conductivity. An application of a conducting polymer as a solid contact was first shown by Lewenstam et al. [1]. The solid-state indicator electrodes have many advantages such as a robust design and ease of miniaturization and mass production. However, one problem is still remaining. In order to have a complete all-solid-state potentiometric system, the reference electrode should also have an all-solid-state construction. There are several papers describing solid-state reference electrodes [2–14]. However, the traditional reference electrodes with internal solution are still superior in terms of continuous, prolonged, and intensive usage. In our previous papers we introduced new analytical-quality solid-state composite reference electrodes which were on par or even better than the conventional reference electrodes [15,16]. In this paper, we demonstrate a way for using the solid-state composite material of the reference electrode as the body/encasement for one or several indicator electrodes. Platforms having integrated multielectrode constructions have been introduced earlier [17,18]. However, in these setups the epoxy resin platform body was electrochemically inactive. In addition, the solid-state reference electrode based on a conducting polymer doped with pH buffering ligand is technologically advantageous, but its application is limited by narrow pH insensitivity range [5].

In our novel concept presented in this paper, the composite material of the reference electrode which is electrochemically active serves also as the body/encasement for the indicator electrode(s).

1.1. The concept of electrochemical platform

The platform schematically illustrated in Fig. 1, is a solid and completely stand-alone electrochemical device which integrates the composite reference electrode and a solid-state indicator electrode in a single body. The concept is novel because the platform body exhibits a double role and acts both as a reference electrode (in conjunction with an internal reference element) and also as a physical encasement for the whole device. The solid-state

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[*] Corresponding author at: Process Chemistry Centre, c/o Laboratory of Analytical Chemistry, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo-Turku, Finland. Tel.: +358 405010860.

E-mail addresses: tomasz.sokalski@abo.fi (T. Sokalski), andrzej.lewenstam@abo.fi, andrzej.lewenstam@gmail.com (A. Lewenstam).

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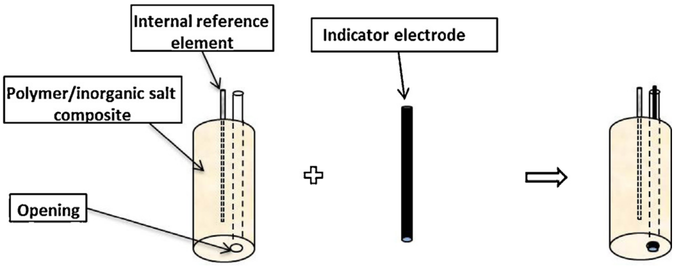

Fig. 1. Schematic illustration of the all-solid-state electrochemical platform.

reference electrode part is based on a polymer/inorganic salt composite that can be prepared either by chemical polymerization [15] or injection molding method [16]. Various combinations of indicator electrodes, such as ion-selective electrodes for potentiometric measurements, or glassy carbon, gold, and platinum electrodes for other electrochemical measurements can be used.

2. Experimental

2.1. Chemicals

Vinyl acetate monomer (VAc, ≥99%), 2,2-dimethoxy-2-phenylacetophenone (DMPP, 99%), poly(sodium 4-styrenesulfonate) (NaPSS; MW ~ 70,000), and 3,4-ethylenedioxythiophene (EDOT, 97%) were purchased from Aldrich. Potassium chloride (KCl, ≥99%) was purchased from Fluka. Polyvinyl acetate (PVAc) powder was obtained from Wacker (Vinnapas B60 Finely ground). Polyvinyl chloride (PVC) of high molecular weight, Potassium ionophore I (valinomycin), potassium tetrakis(4-chlorophenyl)borate (KTpClPB), bis(2-ethylhexyl) sebacate (DOS), 2-nitrophenyl octyl ether (o-NPOE), tridodecylmethylammonium chloride (TDMACl), and tetrahydrofuran (THF, >99.5%) were Selectophore reagents from Fluka. Distilled and deionized water (ELGA, 18.2 MΩ cm) was used to prepare the aqueous solutions.

2.2. Preparation of the platforms

The platform was prepared using the design shown in Fig. 1. For preparing the body and reference part of the platform, a plastic tube was first fixed on one side of a glass vial using a small amount of glue. Then, the mixture of KCl, PVAc powder, VAc monomer, and the photo-initiator DMPP was poured into the vial and the polymerization was carried out using a UV lamp as it is described in our earlier paper [15]. A silver/silver chloride (Ag/AgCl) wire was inserted into the mixture, in the center of vial. When the polymerization was done, the bottom part of the vial was removed to reveal a slot that is used for inserting the indicator electrode (Fig. 1). The platform was conditioned in 3 M KCl solution until a stable potential for the reference electrode part was achieved [15]. The dimensions of the platform were: diameter 1.5 cm, height 3 cm. The platform can be made bigger or smaller than the given example.

A chloride or potassium ion-selective electrode (Cl- or K-ISE) was prepared and used as the indicator electrode in the platform.

In preparation of Cl-ISE, the conducting polymer poly(3,4-ethylenedioxythiophene) doped with chloride, i.e. PEDOT(Cl), was first deposited on a glassy carbon (GC) rod (diameter = 2 mm). The GC rod had a very tight PVC ring around one of the ends where the ion-selective membrane (ISM) was applied later. The galvanostatic electrochemical polymerization was carried out in deaerated aqueous solution containing 0.01 M EDOT and 0.1 M KCl in one compartment two-electrode cell connected to an Autolab General Purpose System (AUT20.FRA2-Autolab, Eco Chemie, B.V., The Netherlands). A constant current of 0.006 mA (0.2 mA/cm^2) was applied for 714 s. A GC rod was used as the auxiliary electrode. The reference electrode was Ag/AgCl/3 M KCl. After depositing the polymer, the resulting GC/PEDOT(Cl) electrode was rinsed with deionized water, conditioned in 0.01 M KCl solution for at least one day, and then allowed to dry before adding the chloride ion-selective membrane (Cl-ISM). A Cl-ISE was prepared by coating the GC/PEDOT(Cl) electrode with 20 μL of Cl-ISM cocktail containing the following composition in % (w/w): 34% PVC, 51% o-NPOE, and 15% TDMACl. These components were dissolved in THF (dry fraction of the membrane cocktail is ca. 22%).

In the preparation of K-ISE, 0.01 M EDOT and 0.1 M NaPSS aqueous solution was used for the electrochemically deposition of PEDOT(PSS) on a GC rod using the galvanostatic method as described above. The resulting GC/PEDOT(PSS) electrode was conditioned in 0.01 M KCl solution before adding a 20 μL of K-ISM cocktail on it. Composition of the K-ISM cocktail in % (w/w) was: 1.2 valinomycin, 0.4 KTpClPB, 66.4 DOS, and 32 PVC. These components were dissolved in THF (dry fraction of the membrane cocktail is ca. 23%).

After being conditioned and calibrated in KCl solutions, the resulting Cl- or K-ISE was inserted in the slot at the bottom of the platform body and fixed using epoxy glue (Fig. 1). When the glue was dry, the resulting chloride-selective platform or potassium-selective platform was conditioned in 0.01 M KCl solution before further measurements.

2.3. Performance of the platforms

The performance of the prepared chloride-selective platform was checked by carrying out conventional calibrations in 10^{-1}–10^{-8} M KCl solutions. The platform was also used for the determination of chloride ion concentration in two synthetic KCl samples. To evaluate the behavior of the reference part of the platform in real samples, the potential of different indicator electrodes was measured versus the platform solid-state reference electrode in a river water sample. The water sample was taken from Aura River in Turku/Finland. The results from these measurements were compared with results obtained using a commercial Ag/AgCl/3 M KCl reference electrode (model 6.0733.100, Metrohm, Switzerland).For comparison purpose, commercial solid-state chloride-ion-selective electrode (Cl-ISE, Thermo Scientific Orion 9417BN) and a Ag/AgCl disk electrode were also used in the potentiometric measurements. To prepare the Ag/AgCl disk electrode, a silver disk (3 mm diameter) with a PVC body was chlorinated galvanostatically from 1 M KCl by passing a current of 0.1 mA for 2 h using a galvanostat (Coulometer type E211, Metrohm, Herisau, Switzerland).

The potentiometric measurements were performed using a 16-channel millivoltmeter (Lawson Labs. Inc., Malvern, PA, USA). The calibrations were done by automatic dilution of stock solution using two Metrohm Dosino 700 instruments equipped with burets of 50 mL capacity (Herisau, Switzerland). The pumps were programmed to dilute the sample solution with fresh deionized water. The activity coefficients were calculated according to the Deby-Hückel approximation. All the potentiometric experiments were performed at room temperature (23 ± 2 °C).

3. Results and discussion

3.1. Calibration measurements

Results from the potentiometric sensitivity of the chloride-selective platform that was conditioned for 3 days in 0.01 M KCl, and the commercial Cl-ISE toward Cl$^-$ ions are shown in Fig. 2. The calibration test started at 10^{-1} M KCl and continued