



Potentiometric layered membranes



Anna Kisiel^a, Emilia Woźnica^a, Marcin Wojciechowski^{a,b}, Ewa Bulska^{a,b},
Krzysztof Maksymiuk^a, Agata Michalska^{a,*}

^a Faculty of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

^b Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland

ARTICLE INFO

Article history:

Available online 19 October 2014

Keywords:

Layered membranes
Ion-selective electrodes
Potentiometry
Polyacrylate membranes
Potassium-ions sensor
Copper-ions sensor

ABSTRACT

In this work a new concept of potentiometric layered membranes is introduced. In most cases described so far a potentiometric membrane is made of one polymer (or one copolymer) used with ion-exchanger and ionophore, for some polymers/copolymers optionally used with a plasticizer of choice. Application of just one polymer (or copolymer) with additives as membrane material is the classical concept of potentiometry. On the other hand, in potentiometry often different materials are applied as ion-selective membranes, resulting in receptor layers characterized with different parameters including ion-transport, although they contain the same ionophore and ion-exchanger.

From the point of view of optimization of the sensor performance, especially for practical applications, it would be beneficial to control the ion diffusion rate in the membrane, for example to prevent the unwanted (as leading to impaired performance) accumulation of the analyte ions close to the outer membrane surface, but on the other hand, to prevent or to slow down the full saturation of the membrane phase with primary ions. Achieving this goal with single membrane composition (based on one polymer/copolymer) is, however, difficult. This can be done, for example, by using a membrane being an ordered composition of different thin layers, arranged in such a way that diffusion coefficients gradually change through the membrane thickness. This novel approach is presented here by introducing the layered membranes concept.

The novel structured potentiometric membranes are composed of a sequence of layers of tailored polymers containing the same contents of ionophore and ion-exchanger. Thus, due to consecutive changes in properties of polymers applied, the primary ion diffusion rate can be controlled through the membrane allowing improvement of the sensor performance.

© 2014 Elsevier B.V. All rights reserved.

Potentiometric sensors are sensitive to the analyte activity changes in the solution layer adjacent to the ion-selective membrane phase; however, the performance of ion-selective electrodes is also highly dependent on the diffusion processes occurring within the membrane phase [1].

Most of the ion-selective membranes, directly after preparation, contain no ions for which they are primary sensitive, thus the natural and spontaneous process is incorporation of these ions to the membrane during conditioning and/or use of the sensor, resulting (similarly as other processes, for example coextraction) in ion-fluxes through the membrane [e.g., 1].

Ion diffusion through the membrane influences not only achievable detection limits and selectivities, but also generally the performance of the sensor (slope of characteristic, reversibility of

responses) and electrical resistance of the membrane phase. Thus, it also influences possibility of tuning electrochemical responses [2,3]. There is no doubt that careful tailoring of ion fluxes through the membrane is essential to improve the sensor performance [e.g., 2,3]. These issues have been addressed in many research in last twenty years. Most of so far proposed methods successfully applied to improve or to optimize potentiometric responses took advantage of controlled ion-fluxes through the membrane. However, to achieve the desired ion transport and ion-fluxes *in the membrane*, most often conditions *external to the membrane* were applied. The gradients within the membrane were created through tailoring composition of the solution contacting the membrane [e.g., 2,4,5] or applying galvanostatic polarization [e.g., 3,6,7]. Some attempts were focused on membrane material to affect the membrane bulk properties, for example change of characteristic of the membrane material (different polymer, different plasticizer, different proportion of plasticizer to the polymer) [e.g., 5,8,9], or significantly changing membrane thickness [5,10], but these works

* Corresponding author. Tel.: +48 228220211.

E-mail address: agatam@chem.uw.edu.pl (A. Michalska).

were still using one define material (or one define composition) as a membrane. Generally, it follows from the above studies that for membranes prepared using ion-exchanger of counter ions different than primary ions, membranes of lower diffusion coefficients result in more favorable analytical characteristic (e.g., lower detection limits).

The traditional approach – one material applied as a receptor layer – results sometimes in problems related to the membrane performance. Generally, ion diffusion coefficients in the membrane are at least two orders of magnitude lower compared to those in the solution what results in different effects. Among others relatively long time is required to achieve full membrane saturation with primary ions, on the other hand, on the electrolyte/membrane interface significant accumulation can occur [11–13]. These effects increase in significance with lowering diffusion coefficient of ions within the membrane, for example when traditional PVC-based membranes are replaced with polyacrylate counterparts. For typically used plasticized poly(vinyl chloride) membranes ions diffusion coefficients are generally in order of 10^{-8} cm²/s [14]. Lower diffusion coefficients characterize polyacrylate ion-selective membranes, typically reported values are in order of 10^{-11} cm²/s [15,16], resulting usually in more favorable analytical parameters [12,16] but also highlighting problems related to accumulation of ions [11,13]. Accumulation of high (compared to ion-exchanger) amount of analyte ions in the membrane can result in impaired potentiometric responses [11] and/or lost selectivity of the sensor as seen, for example in the case of silver-selective or copper-selective sensors prepared using polyacrylate based membranes (for copper-selective sensor, the logarithm of selectivity coefficient for sodium ions, $\log K_{Cu, Na} = +3.7$) [13].

A solution to above problems could be application of structured membranes characterized with diffusion coefficient changing through the membrane thickness due to different properties of consecutively applied layers. The concept of layered potentiometric membranes to our best knowledge has not been used earlier, however a gradual change of diffusion coefficient – e.g. higher value of diffusion coefficient at the sample/solution interface region and lower within the membrane bulk, in principle can not only prevent accumulation of ions in the outer membrane surface but also help to improve the membrane performance.

The herein proposed approach can be successful if two general conditions are fulfilled: the ionophore and ion-exchanger contents of the individual layers are constant through the membrane, each layer material is characterized by a certain ion-diffusion coefficient, moreover, the excellent adhesion between all layers is necessary. Taking these requirements into account a natural candidate to prepare structured potentiometric membranes are polyacrylate polymers. Due to availability of different monomers belonging to this group, polymers of different properties could be easily prepared [e.g., 8,17,18]. Thus, a range of polymers with gradually changing, for example ion-transport properties, could be prepared and this could be arranged in a define order to form a layered structure. Moreover, previous reports clearly show [e.g., 8,19] that different polyacrylate layers can be applied one over another, yielding excellent adhesion of adjacent layers due to the presence of acrylate groups and copolymerization. As the differences in ion-diffusion rate through the polymers are achieved due to change in the polymer/copolymer composition, keeping constant the contents of ion-exchanger and ionophore of choice, the risk of intermixing of layers components is void.

In this report we introduce a novel concept of structured, layered potentiometric membranes. It takes advantage of possibility of merging different polyacrylate layers during photopolymerization resulting in one structured potentiometric receptor layer. Individual layers are prepared from tailored acrylate copolymers/polymers with gradually changing applied acrylates composition – resulting

in gradual change of ion diffusion coefficient within the membrane. This concept can help to overcome problems related to practical applications of ion-selective membranes, for example unwanted accumulation of primary ions within the membrane outer layer.

Thus, the novel type potentiometric membranes prepared can potentially offer a reasonable degree of “control” of ions fluxes through the phase. As a model systems potassium ion-selective electrodes were chosen to highlight the effect of applied ion-exchanger counter ion (either sodium or potassium ion-exchanger was applied). Also copper ion-selective electrodes were prepared – as this is proven challenging system when polyacrylates are taken into account [13]. All sensors have been prepared using photopolymerized membranes.

The obtained structures (as well as individual – component – membranes) were characterized potentiometrically, using electrochemical impedance spectroscopy and by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) aided insight into the layers [14,20,21].

1. Experimental

1.1. Apparatus

In the potentiometric experiments a multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) were used. The pump systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solution.

The double junction silver/silver chloride reference electrode with 1 M lithium acetate in the outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. The recorded potential values were corrected for the liquid junction potential calculated according to the Henderson approximation.

To test electrochemical properties of obtained electrodes galvanostat–potentiostat CH-Instruments model 660A (Austin, TX, USA) and conventional three-electrode cell, with platinum sheet as a counter electrode and above described reference electrode were used.

An inductively coupled plasma mass spectrometer ELAN 9000 (PerkinElmer, Germany) equipped with the laser ablation system LSX-213 (CETAC, USA) was used. The parameters of laser ablation were: laser energy was 3.2 mJ/pulse, repetition rate was 5 Hz, and spot size was 100 μm. The penetration depth was estimated taking into account actual thickness of the membrane (measured after experiment, using micrometer screw) and analysis time. Each LA-ICP-MS analysis was done in triplicate at different points of the membrane. The diffusion coefficients were calculated taking into account recorded intensities vs. time profiles, recalculated to intensities vs. distance as described in details earlier [14], using formula there given.

As a support for all-solid-state ion-selective electrodes glassy carbon (GC) electrodes, prepared for experiments as usually [e.g., 20,21], were used.

1.2. Reagents

Copper selective ionophore – *o*-xylylenebis(*N,N*-diisobutyl-dithiocarbamate), potassium selective ionophore–valinomycin, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), potassium tetrakis(4-chlorophenyl)borate (KTChP); 1,6-hexanedioldiacrylate (HDDA), 2,2-dimethoxy-2-diphenylacetophenone (DMPP) lauryl acrylate (La), hexyl acrylate (Hex), regioregular poly(3-octylthiophene-2,5-diyl) (POT), tetrahydrofuran (THF), chloroform were from Sigma–Aldrich (Germany).

Download English Version:

<https://daneshyari.com/en/article/742520>

Download Persian Version:

<https://daneshyari.com/article/742520>

[Daneshyari.com](https://daneshyari.com)