



Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: [www.elsevier.com/locate/aca](http://www.elsevier.com/locate/aca)

# Solid contact ion sensor with conducting polymer layer copolymerized with the ion-selective membrane for determination of calcium in blood serum



Natalia Abramova <sup>a, b</sup>, Javier Moral-Vico <sup>c</sup>, Jordi Soley <sup>a</sup>, Cristina Ocaña <sup>a</sup>, Andrey Bratov <sup>a, \*</sup>

<sup>a</sup> BioMEMS Group, Instituto de Microelectrónica de Barcelona, Centro Nacional de Microelectrónica (CSIC), Campus U.A.B., 08193, Bellaterra, Barcelona, Spain

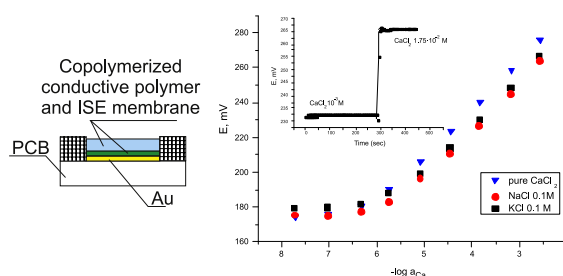
<sup>b</sup> Lab. Artificial Sensors Syst., ITMO University, Kronverskiy pr. 49, 197101, St. Petersburg, Russia

<sup>c</sup> Department of Chemical, Biological and Environmental Engineering, Escola d'Enginyeria, Universitat Autònoma de Barcelona, 08193, Bellaterra, Barcelona, Spain

## HIGHLIGHTS

- A new approach of solid contact ion selective electrodes (ISE) fabrication is tested.
- Conductive polymer layer is copolymerized with ion-selective membrane.
- The ISE design prevents formation of water layer at the boundary between two polymers.
- The ISE shows enhanced stability and life-time.
- The sensor may be used for calcium ion determination in blood serum.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 2 June 2016

Received in revised form

13 September 2016

Accepted 14 September 2016

Available online 21 September 2016

### Keywords:

Solid-contact ion selective electrode

Conducting polymer

Calcium ions

Blood serum

## ABSTRACT

A new solid contact ion selective electrode with intermediate conducting polymer (CP) layer formed by electropolymerization on a gold electrode of a bifunctional monomer, *n*-phenyl-ethylenediamine-methacrylamide (NPEDMA), which contains a methacrylamide group attached to aniline, is presented. The conducting polymer was studied by means of optical spectroscopy, cyclic voltammetry and potentiometric measurements.  $\text{Ca}^{2+}$ -ion-selective membrane based on acrylated urethane polymer was shown to co-polymerize with the CP forming highly adhesive boundary that prevents formation of water layers between the CP and membrane, thus enhancing the stability and life-time of the sensor. The designed ion-selective electrode was successfully used for determination of total calcium ion concentration in blood serum samples.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Potentiometric ion sensors or ion-selective electrodes (ISEs) are an important electrochemical sensors subgroup. ISEs based on polymeric membranes containing neutral or charged carriers (ionophores) are available for the determination of a large number

\* Corresponding author.

E-mail address: [andrei.bratov@imb-cnm.csic.es](mailto:andrei.bratov@imb-cnm.csic.es) (A. Bratov).

of inorganic and organic ions [1]. Solid-type ion sensors are of interest in industrial and medical applications as replacement for traditional ion-selective electrodes with liquid inner contact. These sensors can be easily miniaturised and are of potentially lower cost. They generally consist of a polymer ion-selective membrane, typically polyvinylchloride (PVC), impregnated with certain plasticizer and ionophore, deposited onto a solid inner electrode. If the sensor is formed by direct contact between ion-selective membrane and electronic conductor (metal), it is called a coated wire electrode (CWE). The main drawback of the CWE [1] is obviously the poor potential stability resulting from the blocked interface between the purely electronic conductor (metal) and the purely ionic conductor (ion-selective membrane). Solid-contact ISEs with improved potential stability have, therefore, been produced by utilising electroactive materials possessing redox functionality and showing mixed electronic and ionic conductivity that serve as ion-to-electron transducers between the electronic conductor and the ion-selective membrane. Among different electroactive materials that may be used for this purpose, redox conducting polymers based on electropolymerized or chemically polymerized derivatives of pyrrole, thiophene and aniline are the most generally used [2,3].

Conducting polymers in ISEs design can either form a part of the ion selective membrane, by mixing it with other membrane components, or placed as an intermediate layer between a metal electrode and an ion selective membrane, acting as ion-to-electron conductivity transducers in both cases. Both approaches are shown to improve the long-term potential stability compared to coated-wire electrodes [4,5]. In the first case the conducting polymer (CP) is normally dissolved in organic solvents, e.g. tetrahydrofuran (THF), chloroform and dichloromethane (DCM) [6] before mixing it with ion-selective membrane components and in the second case a CP film is deposited chemically or electrochemically onto a metal electrode support [7] covered afterwards with an ISE polymer membrane.

Most of the reported solid-type ion sensors with conductive polymers use PVC as a membrane polymer matrix [8]. One of the primary causes of failure in these sensors is penetration of water through the membrane. Due to water uptake thin aqueous layers or pools of water can be formed at the electrode interfaces resulting in potential instability and poor membrane adhesion to the solid contact [9].

Photocurable polymers, which may be regarded as an alternative material for membrane matrices for ISFETs, solid contact electrode (SCE) and coated wire electrode (CWE), were introduced by different research groups in the middle of 1980s, early 1990s. Application of photocured polymers permits to use standard photolithographic processes to form ion-sensitive membranes. This may be beneficial for mass production of ion sensors permitting to reduce their fabrication costs. Another positive feature of this class of organic polymers is the opportunity to obtain an ISE membrane without leaching of its main components using ionophore, lipophilic additives, and plasticizer that are copolymerized within the membrane matrix. This approach was applied some years ago by the group of D. Reinhoudt for modified polysiloxanes membranes [10,11] and by D. Harrison and co-workers [12] for PVC. However, the synthesis of these copolymerized compounds seems to require much effort.

Among different photocurable polymer systems, urethane acrylate based compositions present certain advantages as fast curing rates, and compatibility with common plasticizers and ionophores. Ion sensors based on these membranes, which are selective to a wide variety of ions have been reported [13,14]. PVC-based membranes compared to polyurethane have a limited durability when ISEs are used in biological samples (e.g. for clinical ion analysis) due to high

protein adsorption on the sensor surface resulting in biofouling and sensor degradation [15,16]. Besides, ISE with polyurethane membranes are less susceptible to protein adsorption and can be successfully applied for measurements in biological samples [13]. Another positive feature of these membranes is that they may be chemically “anchored” to the solid surface. Earlier we have successfully employed this strategy for deposition of photocurable ion sensitive membranes on ISFETs, the surface of which was grafted with silane containing methacrylic group [13].

Starting from the paper of Fogt et al., published in 1985 [17], it is universally assumed that ISFETs with a polymer membrane deposited directly over a silicon oxide or silicon nitride gate inevitably suffer from the interference caused by penetration of the carbon dioxide and organic acids from a water solution to the membrane organic phase, changing pH at the membrane/silicon oxide interface. In the case when the membrane was chemically attached to the grafted gate surface no influence of organic acids and CO<sub>2</sub> on the behaviour of ISFETs with polymeric membranes, characteristic of this type of sensors [18], which means that no water layer was formed at the membrane/solid substrate interface.

Polyaniline (PANI) is one of the most widely used CP for ISE applications [19,20]. PANI properties can be tuned by adding other moieties to the monomer, generating a PANI derivative, which may result more suitable for the ISE application. Here we present a study of a bifunctional monomer, *n*-phenyl-ethylenediamine-methacrylamide (NPEDMA) [21], which contains a methacrylamide group attached to aniline, used as an intermediate layer for a solid-contact ISE with a polymer membrane. When polymerized, its surface presents a high density of methacrylamide groups that can be used as reactive sites for a better bonding and stronger adhesion to the acrylate membrane. NPEDMA monomer polymerization can be performed, as in the case of PANI, by chemical oxidation or electrochemical deposition.

The objective of this work was to obtain sensors with a stable and durable solid contact preventing the formation of a water layer at the ISE membrane/solid contact interface. To achieve this we present an approach that explores for the first time copolymerization of the conducting polymer layer with the polyurethane acrylate ISE membrane matrix, containing the usual additives (ionophore and ion-exchanger), during a single photopolymerization step, thus chemically binding the membrane to the conductive polymer. To this end, electropolymerized P-NPEDMA layers on thin film gold electrodes were used.

It must be noted that it is not for the first time that conducting polymer and membrane polymer matrix components are copolymerized. All-solid-state ion-selective potentiometric electrodes have been reported [22] in which polyacrylate-based membrane components and a conducting polymer poly(3,4-ethylenedioxythiophene), end capped with methacrylate groups, were copolymerized on a glassy carbon electrode surface forming a single phase membrane matrix. However, this approach can not prevent the formation of a water layer between the membrane and a glassy carbon solid contact.

## 2. Materials and methods

### 2.1. Conducting polymer films preparation

Aniline (ACS reagent, ≥99.5%) and acetonitrile (anhydrous, 99.8%) were purchased from Sigma-Aldrich. 4-dodecylbenzenesulfonic acid (DBS) (tech. ~90%) was purchased from Fluka. *N*-phenyl-ethylenediamine-methacrylamide (NPEDMA) was synthesized as presented in Ref. [21]. The purity of monomer is 92% confirmed by gas chromatography.

All solutions were prepared using ultrapure deionized water of resistivity not less than 18 MΩ cm from a Milli-Q system (Millipore,

Download English Version:

<https://daneshyari.com/en/article/5131220>

Download Persian Version:

<https://daneshyari.com/article/5131220>

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