



Calcium-selective electrodes based on photo-cured polyurethane-acrylate membranes covalently attached to methacrylate functionalized poly(3,4-ethylenedioxythiophene) as solid-contact

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ABSTRACT

We report here the fabrication of solid-contact calcium-selective electrodes (Ca²⁺-SCISEs) made of a polyurethane acrylate ion-selective membrane (ISM) that was covalently attached to the underlying ion-to-electron transducer (solid-contact). Methacrylate-functionalized poly(3,4-ethylenedioxythiophene) (Meth-PEDOT) and Meth-PEDOT films containing either multiwalled carbon nanotubes (MWCNT) or carboxylated MWCNT (cMWCNT) were used as solid contacts. The solid contacts were deposited by drop-casting on screen-printed electrodes and characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potentiometry. Covalent binding between the solid contact and the ISM was obtained via photopolymerization in order to increase the robustness of the Ca²⁺-SCISEs. The performance of the Ca²⁺-SCISEs was studied by measuring their potentiometric response and their sensitivity to light, oxygen and carbon dioxide. Meth-PEDOT was found to be a promising solid-contact material to develop low-cost and easy to prepare ISEs.

1. Introduction

Over the years, the synthesis and characterization of conducting polymers has attracted attention due to their unique electronic and optical properties [1,2] in many applications such as electrochromic devices [3–5], light emitting diodes [6–8], energy storage devices [9–11], biosensors [12–14] and all-solid-state ion sensors [15–18]. Among electronically conducting polymers, there is a considerable interest in using poly(3,4-ethylenedioxythiophene) (PEDOT) because of its low oxidation potential, high stability in ambient environments [19,20], mechanical flexibility and stable oxidized form [21]. Furthermore, addition of electrically conducting nanomaterials (e.g. graphene or carbon nanotubes) to PEDOT is known to improve the electrical conductivity by better connecting individual conducting PEDOT domains in the composite film [22,23].

In this work, methacrylate-functionalized PEDOT (Meth-PEDOT), Meth-PEDOT containing MWCNT (Meth-PEDOT-MWCNT) and cMWCNT (Meth-PEDOT-cMWCNT) were used as the ion-to-electron transducer in potentiometric solid-contact calcium-selective electrodes (Ca²⁺-SCISEs). In recent years, the classical liquid contact ISEs are being replaced by SCISEs due to the possibility of robust

miniaturization [24], low-cost production and compatibility with mass production by standard microfabrication techniques [25]. Most of the reported SCISEs with conductive polymers use plasticized poly(vinyl chloride) (PVC) as the ion-selective membrane (ISM) [26–28]. However, the PVC-based ISEs suffer from diffusion of water through the ISM and the possible formation of a water layer or water pools at the ISM/solid-contact (SC) or SC/substrate interfaces resulting in poor potential stability and weakening of the ISM adhesion to the substrate [29,30].

Photocurable membranes are alternative materials to PVC-ISMs. Several ISEs using photocurable ISMs have been developed since their introduction in the middle of 1980s and 1990s [31,32]. Photo-cured polymeric systems show many advantages over PVC-ISMs such as the possibility to use standard photolithography processes, which may be beneficial for mass production of ISEs, and the opportunity to obtain ISMs with low leaching rates of the active components [33]. Urethane-acrylate ISMs are one of the most used photo-cured membrane types because of their fast curing rates and their compatibility with common plasticizers and ionophores [34]. In addition, this type of ISMs present high durability and reduced biofouling when SCISEs are used in biological samples [35] and they may possibly be chemically “anchored” to the solid electrode substrate [32]. However, it must be noted that it is

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not the first time that Meth-PEDOT and ISM matrix are copolymerized. Rzewuska et al. reported SCISEs based on the copolymerization of polyacrylate-based membrane and Meth-PEDOT on a glassy carbon electrode surface forming a single phase membrane matrix [36]. However, in this approach the polymerization time was 5 min and in our previous studies we observed that when the polymerization time increases the selectivity of the SCISEs becomes worse due to the sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate photobleaching [37].

The main aim of this work is electrochemical characterization of Meth-PEDOT, Meth-PEDOT-MWCNT and Meth-PEDOT-cMWCNT and their application as ion-to-electron transducers in polyurethane (PU) based Ca^{2+} -SCISEs. In this paper, we present a simple, low-cost and robust method for preparing Ca^{2+} -SCISEs, which might be beneficial for different fields such as ranching where they require easy to use and semiautomatic analytical systems with very low costs per analysis. The end-capped methacrylate groups of Meth-PEDOT functioned as reactive sites for obtaining better bonding and stronger adhesion to the PU-acrylate ISM during the copolymerization process. This was expected to enhance the durability of the Ca^{2+} -SCISEs.

2. Experimental

2.1. Chemicals

Tetramethacrylate end-capped poly(3,4-ethylenedioxythiophene) solution (Meth-PEDOT, 0.5 wt% dispersion in propylene carbonate carbonate and p-toluenesulfonate as charge compensating ion), KCl, KNO_3 , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$ and carboxylated MWCNTs were obtained from Sigma Aldrich. MWCNTs were obtained from DropSens (Oviedo, Spain). Calcium Ionophore II (ETH 129), bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis(p-chlorophenyl)borate (KTPClPB), ETH500 and hexafluorobutyl acrylate (HFBuA) were obtained from Fluka. Aliphatic urethane diacrylate (oligomer Ebecryl 270), cross-linker and hexanediol diacrylate (HDDA) were from UCB Chemicals and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (IRG 651) from Ciba-Geigy. All other chemicals used were analytical reagent grade and all solutions were prepared using ultrapure deionized water with the resistivity of 18.2 M Ω cm (Milli-Q system, Millipore, Billerica, MA). Screen-printed electrodes (SPEs) with silver ink and flash gold ($d = 2$ mm) prepared on PET polymer substrates were supplied by FAE (FAE S.A., Spain).

2.2. Meth-PEDOT, Meth-PEDOT-MWCNT/cMWCNT deposition

5.0 μL ($2 \times 2.5 \mu\text{L}$) of Meth-PEDOT solution containing either 0.2–0.5 wt% MWCNT or cMWCNT solution was drop-cast on the screen-printed electrodes to form SC layers of Meth-PEDOT-MWCNT and Meth-PEDOT-cMWCNT. After that, the electrodes were placed on a heating plate at 50 °C to increase the evaporation rate of the propylene carbonate solvent. All further experiments were performed at room temperature.

2.3. Ca^{2+} -selective ISM deposition

The photocurable ISM composition was prepared as presented previously [38]. Briefly, the main polymer composition was prepared by mixing the aliphatic urethane diacrylate oligomer Ebecryl 270 with the reactive diluent HDDA and the photoinitiator Irgacure 651 in the ratio (w/w) of 81:17:2. In the next step, 0.3 g of the main polymer composition was dissolved in 0.2 ml THF and the plasticizers DOS and HFBuA, Ca^{2+} -ionophore II and lipophilic salts were then added to this solution. This ISM solution was placed in an ultrasonic bath until it was homogeneous and then left unstirred for several hours to allow evaporation of THF from the solution. This resulted in the following ISM composition: main polymer mixture (56.5 wt%), DOS (20.0 wt%), HFBuA (20.0 wt%), Ca^{2+} -ionophore II (1.0%), KTPClPB (0.5 wt%) and ETH

500 (2.0 wt%).

ISM were deposited on the screen-printed electrode substrates (Ag and Au) by applying the ISM solution with a microsyringe on the Meth-PEDOT, Meth-PEDOT-MWCNT and Meth-PEDOT-cMWCNT solid-contact layers. After the ISM deposition, the electrodes were exposed to 365 nm UV light for 20 s using a UV Curing Light Lamp 8141 (Düren, Germany) to form covalent bonds between the ISMs and the acrylate groups of SCs. A scheme of the copolymerization process is shown in Fig. S1. Crosslinking between the PU-ISM and polyaniline functionalized with methacrylate groups was confirmed by FTIR-ATR analysis in previous studies [32]. Therefore, we assume that crosslinking occurs also between the PU-ISM and the Meth-PEDOT used in this work. The thicknesses of the ISM was ca. 200 μm , as measured with a micrometer screw gauge (resolution: 1 μm) after the polymerization process.

2.4. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)

Cyclic voltammograms and impedance spectra were recorded by using a one-compartment three-electrode cell connected to the Autolab potentiostat equipped with a frequency response analyzer (AUT20. FRA2-AUTOLAB, Eco Chemie, B.V., The Netherlands). The screen-printed electrodes, a glassy carbon rod and a double junction Ag/AgCl/3 M KCl//0.1 M LiOAc served as the working (WE), auxiliary (AE) and reference electrode (RE), respectively. CVs were recorded between -0.5 V and $+0.4$ V in 0.1 M KNO_3 at a scan rate $\nu = 0.01$ Vs $^{-1}$. The impedance spectra were measured at the open circuit potential (E_{dc}) in 0.1 M KNO_3 within the frequency range ($f = 10$ kHz – 0.01 Hz) using an excitation signal amplitude $\Delta E_{\text{ac}} = 10$ mV. The impedance spectra were fitted to equivalent circuits with the ZView software (Scribner Associates Inc., USA).

2.5. Chronopotentiometric measurements

Constant-current chronopotentiograms were recorded in 0.1 M CaCl_2 with the Autolab potentiostat described above by passing a constant current of ± 1 nA through the Ca^{2+} -SCISEs for 60 s [39].

2.6. Potentiometric measurements

The potentiometric response of the Ca^{2+} -SCISEs was measured in a Faraday's cage with a 16-channel potentiometer (Lawson Labs, Inc., input impedance: 10^{15} Ω) and by using the double junction Ag/AgCl/3 M KCl//0.1 M LiOAc as the RE. The Ca^{2+} -SCISEs were preconditioned under stirring in 10^{-3} M CaCl_2 for 3 days prior to the potentiometric measurements. Calibration plots were obtained in CaCl_2 solutions from 10^{-7} M to 10^{-2} M by stirring the solutions for 2 min at each concentration. The activity coefficients were calculated according to the Debye-Hückel equation.

The selectivity coefficients towards Na^+ , K^+ , Mg^{2+} , NH_4^+ and Li^+ ions were determined at 0.1 M concentrations of interfering ions with the mixed solution method recommended by IUPAC [40]. The potentiometric aqueous layer tests were performed by recording the Ca^{2+} -SCISE potentials in 0.1 M CaCl_2 , 0.1 M NaCl and 0.1 M CaCl_2 solutions (in this order). The CO_2 and O_2 sensitivities of the Ca^{2+} -SCISEs were obtained by measuring the potential of the Ca^{2+} -SCISEs in a 0.1 M CaCl_2 solution that was purged with pure O_2 , N_2 and CO_2 gas in the following sequence: N_2 (1 h), O_2 (1 h), N_2 (1 h), CO_2 (1 h), N_2 (1 h). The light sensitivity was measured in 0.1 M CaCl_2 solution by monitoring the Ca^{2+} -SCISE potentials as the illumination of the electrode surfaces changed in the following order: darkness (30 min), ambient room light (30 min), cold light (30 min), ambient room light (30 min) and darkness (30 min). The Leica CLS 150 XE cold light source (150 W, 21 V) was directed through the electrolyte solution towards the Ca^{2+} -SCISEs surfaces.

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