

Electrochemical control of the standard potential of solid-contact ion-selective electrodes having a conducting polymer as ion-to-electron transducer



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ABSTRACT

This work addresses the well-known problem of variations in the standard potential (E°) of solid-contact ion-selective electrodes (SC-ISEs) that have a conducting polymer (CP) as ion-to-electron transducer covered by a polymeric ion-selective membrane. Poly(3,4-ethylene dioxythiophene) doped with poly(sodium 4-styrenesulfonate), i.e. PEDOT(PSS), was electrodeposited on glassy carbon (GC) disk electrodes and used as the solid contact for three different types of PVC-based membranes in order to elucidate the possibility to electrochemically control E° for this type of SC-ISE. The GC/PEDOT(PSS) electrode was thus coated with potassium-selective membranes with and without the lipophilic salt tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH-500) and by a cation-sensitive membrane without ionophore. The results show that the standard potential of the studied types of SC-ISEs can be shifted by applying a potential that deviates from the open-circuit potential of the electrode in the chosen electrolyte solution or by applying current pulses in the nA range.

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1. Introduction

Calibration-free measurements with potentiometric ion sensors would require: (i) selectivity for the primary ion over interfering ions, (ii) close to theoretical slope and (iii) reproducible standard potential (E°) [1]. It is the last requirement that hits to the core of the problem, especially for solid-contact ion-selective electrodes (SC-ISEs) having a conducting polymer as the ion-to-electron transducer [2,3]. Lindner and Gyurcsányi have stated that the quality of a solid contact is indeed better assessed from the reproducibility of the standard potential than the reproducibility of the calibration slope [4].

Recently Niu's group [5] reported a new solid-contact arrangement based on modified monolayer-protected Au nanoclusters doped with tetrakis(4-chlorophenyl)borate resulting in exceptionally stable and reproducible E° . Michalska et al. [6] have compared the stabilities of different solid-contact arrangements with each other, but the lack of a generally applied test protocol for SC-ISEs has been pointed out [4,7]. A water layer at the back side of the ion-selective membrane is known to be one source of potential drift in SC-ISEs, and thus the use of hydrophobic solid-contact materials such as a self-assembled lipophilic monolayer with a redox

active compound can reduce the potential drift [8]. Also hydrophobic semiconducting polymers, such as poly(3-octylthiophene), was found to improve the reproducibility of the standard potential [9]. In their recent article dealing with potential stability of conducting polymers Shiskanova et al. [10] emphasize the importance of a suitable cleaning step for the substrate, compactness of the polymer film covering the substrate and appropriate post-polymerization treatment, like conditioning under constant potential. Pretreatment with cyclic voltammetry was found useful by Mousavi et al. [11] in the case of conducting polymer-based Ag^+ sensors. Also, an adequate capacitance of the solid contact is recognized as a requirement for stable potentials [12], for which reason also different carbon-based solid-contact arrangements with large surface area have been found appropriate [13–15]. Novel transducer materials have been reviewed recently [3].

Already two decades ago it was found that introducing a layer of conducting polymer (CP) between an electronically conducting substrate and an ionically conducting ion-selective membrane stabilizes the sensor response compared to coated wire arrangements with a blocked interface [16], and despite new transducer materials, conducting polymers have remained popular. An interesting feature of CP-based SC-ISEs is that the calibration slope may be retained although the standard potential varies between different electrodes and with time. Such instability of the standard potential of SC-ISEs can be due to minor variations in the transducer layer induced by e.g. manual production [17], changes in its composition due to chemical instability [4] or slow spontaneous

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charging/discharging processes followed by or caused by ion fluxes through the membrane [18–20].

The CP as solid contact is expected to undergo similar processes as if it was in direct contact with solution as the ion-selective membrane is permeable to ions, water, CO₂ and oxygen [20]. The potentiometric signal of the CP itself is dictated by its redox state and ionic equilibrium that are influenced both by polymerization conditions and by the composition of the contacting solution [21,22]. Therefore drifts in potential can be expected whenever the composition of the electrolyte solution changes [6,20]. Applying potential [22] or current [23] on the CP prior to open circuit measurements is recognized to shift the position of the calibration slope. Polarization with direct current has been used also to tune the linear range of SC-ISEs with CP as solid contact [23].

In the present work we explore the possibility to adjust the standard potential (E°) for SC-ISEs by applying a potential or current.

2. Experimental

2.1. Chemicals

Valinomycin, potassium tetrakis(4-chlorophenyl)borate (KTP-CIB), potassium tetrakis [3,5-bis(trifluoromethyl)-phenyl]borate (KTFPB), tetradecylammonium tetrakis(4-chlorophenyl)borate (ETH-500), bis(2-ethylhexyl)sebacate (DOS), 2-nitrophenyl octyl ether (o-NPOE), poly (vinyl chloride) (PVC) and tetrahydrofuran (THF) were from Fluka and of Selectophore grade. Poly(sodium 4-styrenesulfonate) (NaPSS) $M_w \sim 70,000$, 3,4-ethylene-dioxythiophene (97%) and KCl ($\geq 99.5\%$) were purchased from Sigma–Aldrich. Deionized water (ELGA Purelab Ultra) was used throughout the experiments.

2.2. Electrodes

Disk shaped working electrodes were prepared by fitting a glassy carbon (GC) rod (Sigradur G, HTW Hochtemperatur – Werkstoffe GmbH, D-86672, Thierhaupten, Germany) in a PVC cylinder. The GC disk electrodes were carefully polished with 0.3 μm Al₂O₃ powder and cleaned chemically by immersion in 1 M HNO₃ followed by ultrasonic cleaning in ethanol and de-ionized water. A Metrohm double junction Ag/AgCl/3 M KCl reference with 0.1 M NaPSS bridge was used for electropolymerization of PEDOT(PSS) films and with 1 M lithium acetate (LiAc) bridge for potentiometric calibrations and for potential adjustments between calibrations. For long term stability measurements comprising E° adjustment a double junction Ag/AgCl/3MKCl/0.1 M KCl electrode was used. The counter electrode was a GC rod. Potential differences between used reference electrodes were taken into account when comparing results.

Polymerization of PEDOT(PSS) films on GC disk electrodes (area = 0.07 cm²) was done galvanostatically with an Autolab General Purpose Electrochemical System (PGSTAT20, FRA2, AUTOLAB, Eco Chemie, B.V., the Netherlands) in a conventional three electrode cell under nitrogen atmosphere by applying a 0.014 mA current (0.2 mA/cm²) for 714 s in 0.1 M NaPSS + 0.01 M EDOT solution that was stirred overnight to guarantee proper dissolution of the monomer prior to electropolymerization [12]. After polymerization, the GC/PEDOT(PSS) electrodes were conditioned in 0.1 M KCl for one day, after which they were let dry in air before drop-casting of the membrane cocktail.

Three different membrane cocktails were prepared using THF as solvent, resulting in the following membrane compositions (after evaporation of THF): (i) a potassium selective membrane without ETH-500 (1% valinomycin, 0.5%, KTFPB, 33.3% PVC, 65.2% DOS),

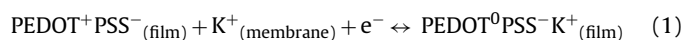
(ii) a potassium selective membrane with ETH-500 (1% valinomycin, 0.5% KTFPB, 1% ETH-500, 32.5% PVC and 65% DOS) and (iii) a cation-sensitive membrane without ionophore (1% KTPCIB, 33% PVC and 66% o-NPOE). The dry content of each membrane cocktail was 15 wt%. Two replicate GC/PEDOT(PSS) electrodes were covered with each membrane by drop-casting 100 μl of the prepared cocktail on the electrode surface. THF was let to evaporate resulting in SC-ISEs with membrane compositions (i), (ii) and (iii), which will be called SC-ISE(i), SC-ISE(ii) and SC-ISE(iii), respectively. The SC-ISEs were conditioned in 0.1 M KCl for 3 days before and always in between measurements.

2.3. Measurements

Chronoamperometric and chronopotentiometric studies were carried out on the SC-ISEs immersed in 0.1 M KCl by using a conventional one-compartment three-electrode cell connected to an IVIUMSTAT (Ivium Technologies, The Netherlands). The electrochemical cell was placed inside a grounded faraday cage. Chronoamperometry was performed by applying a constant potential (for 17–66 h) deviating approximately 100 mV from the initially measured open-circuit potential (OCP) for the SC-ISE. After this, the OCP was measured for at least 10 h with a potentiometer (Lawson EMF16 Interface potentiometer, Lawson Labs, Inc.) to observe the induced changes in standard potential and possible drift, or a calibration was performed to check the slope. Chronopotentiometric measurements were performed by applying ten 5-min current pulses of +1 nA (total charge = 3 μC). Each 5-min current pulse was followed by 5 min relaxation time at open circuit. Before the series of current pulse was started, the OCP was recorded to confirm that the initial potential of each SC-ISE was stable. After the pulse sequence, OCP was recorded for 24 h to observe the effect of the applied current pulses on the standard potential and possible drift. Corresponding experiments were done using negative (–1 nA) current pulses. Electrodes were also treated with one single 50-min current pulse of +1 nA (total charge = 3 μC) followed by recording the OCP for at least 24 h. For SC-ISE (i) also longer pulses of (100 min, +1 nA) and (50 min, –1 nA) were applied. Before chronoamperometric and chronopotentiometric measurements, all SC-ISEs were calibrated in 10^{–1} M KCl–10^{–8} M KCl solutions to check that the electrodes were working properly.

3. Results and discussion

The possibility to tune and adjust the standard potential (E°) of SC-ISEs by applying a potential or current is based on the hypothesis that the overall open-circuit potential of the SC-ISE is influenced by the redox state and the ionic content of the CP-transducer layer [21]. PEDOT(PSS) was chosen as model transducer because it is electrochemically stable in its oxidized (doped) state and it is known to perform well in combination with PVC-based ion-selective membranes [12,24]. The bulky immobile polymeric doping anion (PSS[–]) in PEDOT(PSS) is known to result in a cationic response [12,22]. Thus for the SC-ISEs studied, the ion-to-electron transduction is expected to occur primarily according to Eq. (1):



where the sub-script “film” refers to the PEDOT(PSS) layer and the sub-script “membrane” refers to the PVC-based K⁺-selective membrane (i) and (ii) or cation sensitive membrane (iii). In open-circuit potentiometry, where the measurement instrument has a very high input impedance, the net current flowing during the measurement in order to achieve ion-to electron transduction is usually negligible and does not significantly alter the redox state of the bulk of PEDOT(PSS) [12]. However at a higher value of an applied current the change in the redox state of the PEDOT(PSS) transducer

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