



# Optimization of capacitance of conducting polymer solid contact in ion-selective electrodes



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## ABSTRACT

All-solid-state ion-selective electrodes with conducting polymer solid contact represent good analytical parameters, comparable with those of classical sensors with internal filling solution. One of parameters characterizing quality of the solid contact, related to ion-to-electron transduction, is the electrical capacitance. However, in many cases this capacitance is lower than for the solid contact only, in the absence of ion-selective membrane. This effect can be disadvantageous, particularly for sensors working under polarization conditions, in galvanostatic mode.

The capacitance reduction effect was studied on example of model systems of anion- and cation-selective electrodes with poly(3,4-ethylenedioxythiophene) solid contact with anion- or cation-exchange properties. Basing on results obtained for these membranes and contacts as well as some model calculations, the reasons of reduced capacitance were ascribed to low amount of ions transferrable across the solid contact/membrane interface. This effect can result from low concentration of mobile ions in the conducting polymer contact or concentration polarization effects. Procedures or pretreatment methods were proposed to minimize the effect of capacitance decrease.

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## 1. Introduction

Ion-selective electrodes (ISE) are established tool of potentiometric analysis of great practical significance in industry, environment protection, medical applications etc. In these applications areas typically “classical” ion-selective electrodes with internal solutions are used, characterized by excellent analytical parameters, concerning linear characteristics, selectivity, stability as well as detection limits. However, significant drawback of these electrodes relates to the presence of an internal liquid phase, requiring operation in vertical position, refilling and hindering miniaturization and shape tailoring.

From practical applications point of view much more promising are all-solid-state constructions of ISEs, where the internal solution is replaced by a solid contact (ion-to-electron transducer) located between the ion-selective membrane and the electrode support [1]. As solid contacts typically conducting polymers as usually polypyrrole [2], polyaniline [3] poly(3,4-ethylenedioxythiophene) (PEDOT) [4,5] or other polythiophenes [6], mainly poly(3-octylthiophene) [7,8] are used, offering good parameters of ISEs for potentiometric applications. Alternatively, redox-active self-

assembling monolayers [9], polypyrrole microcapsules filled with electrolyte solution [10] and carbon materials of large surface area were used [11,12,13]. Recently also nanomaterials were found to be promising for such purposes, e.g. gold [14,15] or platinum nanoparticles [16], carbon nanotubes [17,18], graphene/reduced graphene oxide [19,20,21] as well as composite systems, e.g. PEDOT with carbon nanotubes [22].

A good solid contact should form a well adhesive layer, both to the electrode support and the membrane material and should prevent formation of a thin aqueous layer between the membrane and solid contact. Thus the solid contact should be either highly lipophilic, a typical example is poly(3-octylthiophene), or highly hydrophilic, as e.g. PEDOT doped by polystyrenesulfonate ions (PEDOT(PSS)), with pores filled with aqueous solution. In the latter case properties of electrodes with this contact resemble those of ISEs with inner filling solution.

The main quantitative parameter characterizing the usefulness of a solid contact is electrical capacitance, being a measure of stability of the electrode potential under influence of a small external current. A good solid contact should exhibit the capacitance significantly higher than that of coated wire arrangement, where a membrane is placed directly on the electrode substrate. The origin of high capacitance can be usually ascribed e.g. to double layer capacitance for large surface/volume ratio of the solid contact, as for carbon materials and metal nanoparticles,

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or oxidation/reduction processes of the solid contact material in the absence of mass-transfer limitations (“redox” capacitance”), typical for conducting polymers.

Requirement for high capacitance solid contacts is immensely higher in the case of ISEs working under polarization conditions, e.g. in galvanostatic mode. Recently applications of typical electrochemical techniques become popular as a method to improve analytical parameters of ISEs or to extend possibilities of applications of these sensor to other analytes, e.g. multi-charge ions for which unstable potentiometric responses are usually obtained. Among the new methods particularly advantageous are pulse chronopotentiometric methods [23,24], including “flash-titration” [25], enabling reversible and reproducible tailoring of ion fluxes, resulting in reliable determination of many non-electroactive ions. However, for such applications either internal solutions or solid contacts of high capacitance are required to reduce changes of the potential assigned to changes of the solid contact composition/redox state. For instance, for a sensor with typical conducting polymer solid contact of capacitance 1 mF, applying a current 1  $\mu\text{A}$  results in potential change related to the solid contact (calculated as ratio of the current and the capacitance) equal to  $1\text{ mV s}^{-1}$ . For all-solid-state ISEs the capacitances are close to  $10^{-5}$ – $10^{-4}\text{ F}$  for noble metal nanoparticles used as the solid contact [15,16] or polypyrrole microcapsules [10],  $10^{-4}\text{ F}$  for graphene [21] and  $10^{-3}$  for carbon nanotubes [18,26], i.e. they are higher than for coated wire arrangement (no solid contact). Quite high capacitance, around  $10^{-2}\text{ F}$  was recorded for polypyrrole microcapsules filled with solution containing redox active  $\text{Fe}(\text{CN})_6^{4-}$  ions [10]. Generally, sufficiently high capacitance value, needed e.g. in galvanostatic methods, can be expected for rather thick layers of conducting polymers.

One of the best solid contact material in the group of conducting polymers is PEDOT, characterized by high stability, high mass transfer rate within the polymer phase, facile deposition of thick layers by electropolymerization and significant redox capacitance. Due to its properties, it can be also regarded as a model solid contact to study the response mechanism of all-solid-state ISEs. Basing on data obtained for this polymer, Bobacka has proposed a simple, useful method of solid contact capacitance determination using chronopotentiometry [4].

Although the stabilizing role of solid contacts is significant, there are no many papers describing mechanisms of ion-to-electron transduction in ISEs with such contacts. Bobacka et al. used current reversal chronopotentiometry [27] and impedance spectroscopy [18,28] Veder et al. [29] carried out XPS and NEXAFS studies of poly(3-octylthiophene) pointing to partial oxidation of POT coupled with incorporation of cation-exchanging sites from the membrane.

Literature data reveal, including also pioneering paper of Bobacka [4] that usually the recorded capacitance of solid contacts in ISEs is significantly lower than the capacitance of the same material and the same quantity, but in the absence of the ion-selective membrane (e.g. [22,30]). This can be a significant disadvantage, since only a part of potentially available capacitance of the solid contact in ISE can be used for the electrode potential stabilization. In some cases the reported capacitance was similar to that observed in the absence of the membrane, however, this was found only in the case of low capacitance materials ( $\sim 10^{-5}\text{ F}$ ) [15] Mattinen et al. [12] have carried out impedance studies of PEDOT in the presence of aqueous or organic electrolyte solutions, simulating a membrane. It was found that the low frequency impedance is low (i.e. capacitance is high) in case of contact of cation- or anion-exchanging PEDOT with solution containing mobile cations or anions, respectively.

In this paper we are aiming to study the effect of capacitance decrease in real conditions in the presence of ion-selective

membranes. Basing on example of PEDOT solid contact and changing the concentration of ion-exchanger in the membrane, PEDOT film thickness as well as preconditioning procedures, we will be attempting to extend explanation of this behavior. Although we are not focused on analytical parameters optimization or studying their changes, our aim was also to propose conditions and pretreatment methods to increase the available capacitance of the solid contact.

As mentioned above, reasonable explanation of capacitance reduction are limitations in ions flow to/from the conducting polymer in the presence of the membrane. Therefore, to show the role of ions kind and their charge, PEDOT films with cation- or anion-exchanging properties are tested, doped either by poly(4-styrenesulfonate) ions or mobile anions ( $\text{Cl}^-$  or  $\text{NO}_3^-$ ), respectively. As ion-selective membranes either cationic ( $\text{K}^+$ -selective) or anion ( $\text{Cl}^-$ -selective) membranes are used.

## 2. Experimental

### 2.1. Apparatus and reagents

In the open circuit potentiometric experiments a multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) was used, stable (within  $\pm 0.2\text{ mV}$ ) potential readings were recorded. In other electrochemical measurements galvanostat-potentiostat CH-Instruments model 760A (Austin, TX, USA) and conventional three-electrode cell was used. The pumps systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solutions.

Tetrahydrofuran (THF), PVC, bis(2-ethylhexyl) sebacate (DOS), potassium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (KTFPB), methyl tridodecylammonium chloride and ionophore valinomycin were from Fluka AG (Buchs, Switzerland).

Doubly distilled and freshly deionised water (resistance  $18.2\text{ M}\Omega\text{cm}$ , Milli-Qplus, Millipore, Austria) was used throughout this work. All other reagents were of analytical grade and were obtained from POCh (Gliwice, Poland) with the exception of monomer 3,4-ethylenedioxythiophene (EDOT), obtained from Sigma (Steinheim, Germany).

### 2.2. Potassium-selective membranes

The potassium-selective membrane ( $\text{ISM-K}^+$ ) contained 0.5% (m/m) of KTFPB, 1.0% of valinomycin, 33.3% of poly(vinyl chloride) and 65.2% of plasticizer – DOS (composition A). Total 100 mg of membrane components were dissolved in 1 ml of THF and applied as described below. Alternatively, 1.9% of KTFPB, 3.9% of valinomycin, 31.5% of poly(vinyl chloride) and 62.7% of plasticizer – DOS were used, dissolved in 1 ml THF (composition B).

### 2.3. Chloride-selective membranes

The chloride-selective membrane ( $\text{ISM-Cl}^-$ ) contained 5% (m/m) of methyl tridodecylammonium chloride, 30.0% of poly(vinyl chloride) and 65.0% of plasticizer – DOS. Total 100 mg of membrane components were dissolved in 1 ml of THF and applied as described below.

### 2.4. Electrodes

Glassy carbon disc electrodes of area  $0.07\text{ cm}^2$  were used in experiments with PEDOT/membrane electrodes. The substrate electrodes were polished with  $\text{Al}_2\text{O}_3$ ,  $0.3\ \mu\text{m}$ . A mirror smooth polishing was avoided to prevent peeling off the relatively thick polymer film. The double junction silver/silver chloride reference

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