



Conducting polymers - mechanisms of cationic sensitivity and the methods of inducing thereof



Jan Migdalski*, Teresa Błaż, Andrzej Lewenstam

AGH - University of Science and Technology, Faculty of Materials Science and Ceramics, PL-30059 Krakow, Poland

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ABSTRACT

Different methods for inducing open-circuit cationic sensitivity of the conducting polymer (CP) films doped with Metal Complexing Ligands (MCL) are presented. Selected MCLs have the $R-(MCG-H)_p(SO_3H)_n$ structure and contain bulky organic group (R), “n” sulphonate groups responsible for CP doping and “p” metal complexing groups (-MCG-H) responsible for formation of the complexes with a narrow group of cations. MCLs molecules introduced to CP layer as bulky doping anions are immobilized inside CP layer and preserve their chemical properties known from water chemistry. Similarly, as ionophores, they can form complexes inside CP membrane with selected cations only. It was shown that formation of the complex inside the polymer layer is necessary for inducing preferred open-circuit sensitivity of the CP membrane. Various, efficient methods of the CP-MCL film sensitization towards calcium, magnesium as well as copper, cadmium, lead or zinc cations are presented.

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1. Introduction

Conducting Polymers (CP), owing to their mixed ionic/electronic conductivity, are used as ion-to-electron transducers (solid contact, mediating layer) in all-solid-state chemical sensors and biosensors [1–11]. Several examples of direct CPs application as potentiometric membranes were also described [12–24]. The CPs role is to couple the electron charge transfer at metallic/CP interphase and ionic transfer at the CP/ISE membrane or CP/solution interface. Although application of conducting polymers is covered in several reviews [25–32], and numerous causal reports, it is necessary to summarize the present information to build up concerted know-how that would be useful for every practitioner.

Successful application of conducting polymers in sensor technology, as a solid-contact or an ion-selective membrane, demands detailed understating of the sensitivity mechanism. For this reason we first present the theoretical background. On this platform we show then empirical procedures of inducing open-circuit sensitivity of the CPs by the goal-oriented methods of synthesis and prior-to-application treatment enhancing preferred ion-sensitivity.

The aim of this paper is to add precise and mostly new information on ionic open-circuit sensitivity of conducting polymers that

clear up procedures, which enables deep understanding of the art of making conducting polymers sensitive for the preferred cations, characterized with preferably Nernstian response.

The factors affecting selectivity of CP films response was considered by Michalska and Migdalski [33–35]. According to our assumption, selective and CP oxidation state independent open-circuit sensitivity can be expected if:

- preferred cations will be selectively bounded inside CP layer and
- preferred cation loading will be CP oxidation state independent.

To fulfil this assumption the CP films were doped with bulky anions from the group of Metal Complexing Ligands (MCL), such as Calcion, Sulphosalicylic acid, Tiron, Calcon, Kalces or Arsenazo-I [33,34,36–40]. All selected MCLs with big molecular weight were introduced to CP film as doping anions and being bulky molecules were strongly immobilized inside CP layer. Similarly as ionophores, MCLs can form complexes with only a narrow group of cations. Composition of MCLs can be shown as $R-(MCG-H)_p(SO_3H)_n$, where symbol R denotes bulky organic group of MCL, and MCG-H is a non-anionic part of the MCL, responsible for selective binding of cations via ion-exchange with protons present.

Free MCL ligand $[R-(MCG-H)-SO_3^-]$ and MCL-Me complex $[R-(MCG-Me)-SO_3^-]$ are both anions and both can dope conducting polymer. This means that loading with complexed cations, as well as preferred cationic sensitivity should be CP oxidation state independent.

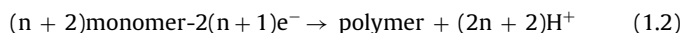
* Corresponding author.

E-mail address: migdal@agh.edu.pl (J. Migdalski).

Since protons are released during complex formation according to reaction (1.1):



elevated pH is favorable for such process. Unfortunately, according to [41], also freshly electrodeposited CP is saturated with protons according to scheme (1.2)



It means that effective methods of the CP-MCL film deprotonation are highly awaited prior to and during complex formation. For these reasons soaking with alkaline solutions of the preferred cations was the first method of choice which we have used for inducing preferred cationic sensitivity of the CP-MCL films towards calcium or magnesium ions.

The results described in [33,34,36–40] have proved that MCL introduced to CP film as doping anions retain their complexing properties. It was confirmed also [34,37], that formation of complex inside the CP-MCL film is necessary for inducing preferred cationic sensitivity. For example, calcium sensitivity of the polypyrrole films doped with Calcion ligands can not be induced by soaking PPy-Calcion films in the calcium chloride solution with neutral pH, even if soaking period was extended up to few months [33,38]. On the other hand, expected calcium sensitivity with almost theoretical slope value and quite good selectivity was observed after short soaking in calcium hydroxide solution [33]. According to [42] formation of calcium complex proceed in strong alkaline solution only, with $pH > 11.5$. Soaking with alkaline solution of the preferred cation seems to be the best method for inducing preferred sensitivity of the CP-MCL films. In fact, in many cases stable open-circuit response towards calcium or magnesium ions with a close to theoretical slope value was observed after short soaking of the CP-MCL films in the saturated calcium or magnesium hydroxide solutions. Usually, longer soaking time was needed to induce magnesium sensitivity, because of lower magnesium ion concentration in the saturated magnesium hydroxide solution (respectively, $0.013 \text{ mol L}^{-1} \text{ Ca}^{+2}$ and $0.00016 \text{ mol L}^{-1} \text{ Mg}^{+2}$ for saturated calcium and magnesium hydroxides, values calculated on the base of solubility constant). It was shown also that CP-MCLs films doped with Arsenazo, Calcon, Eriochrome Black or Tiron and made calcium or magnesium sensitive had satisfactory selectivity towards alkaline cations, whereas potential changes caused by calcium or magnesium addition were similar [34]. Such selectivity pattern was expected, because selected MCLs can form complexes with both calcium and magnesium ions.

It was also proved, that contradictory to CP membranes doped with bulky anions without complexing properties, cationic sensitivity of the CP-MCL membranes were preserved after CP oxidation [34,37].

Direct soaking in alkaline solutions of calcium or magnesium hydroxides or in a mixture of calcium or magnesium salts with adequate hydroxides was also the reliable method of inducing calcium or magnesium sensitivity of the CP films doped with Heparin or Adenosine triphosphate [43,44], whereas some more complicated soaking procedures must be used for inducing magnesium or calcium sensitivity of the CP films doped with adenosine diphosphate [45] or Taurine [46]

Inducing sensitivity towards heavy metals cations like copper, cadmium, zinc or lead was much more difficult task and simple soaking procedure was not effective. In practice, preferred copper sensitivity was observed only for few percent of the polypyrrole films doped with SSA or Tiron after long term soaking in dilute copper sulphate solution, $pH \sim 4.5$ [36]. For these reasons more sophisticated, unfailing methods were worked out by us and are described in this article. Such cation sensitive and selective CP films

can be treated as the first material of choice that allows significant progress in sensor technology, making sensors maintenance free and enhancing their analytical properties. In consequence, application of conducting polymers and more up-to-date materials as ion-to-electron transducers can be more effective. This is of special importance owing to a new wave of interest in nanostructures used to enhance properties of the sensors.

2. Experimental

2.1. Chemicals

Pyrrrole (Py, Merck) and 1-Methylpyrrole (MPy, Merck) was purified by double distillation under argon gas and then stored under argon at low temperature and protected from light.

3,4-ethylenedioxythiophene (EDOT, Merck) was used as received.

The following Metal Complexing Ligands (MCL) were used:

- 2-(*o*-Arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic sodium salt, $C_{16}H_{11}O_{11}N_2S_2AsNa_2$, (Arsenazo I)
- [1-(1-Hydroxy-2 naphthylazo)-2-naphthol-4-sulphonic]sodium salt, $C_{20}H_{13}N_2NaO_5S$, (Calcon)
- 1-Hydroxy-4-sulphobenzoic acid p.a., $C_7H_6O_6S \cdot H_2O$ (SSA)
- 3,3'-Bis[*N,N*-bis(carboxymethyl) aminomethyl]-*o*-cresolsulfonephthalein tetrasodium salt, $C_{31}H_{28}N_2Na_4O_{13}S$, (Xylenol Orange tetrasodium salt)

Prior to electropolymerization, sodium cations were removed from MCLs sodium salt with a DOWEX 50WX8 50/100 ion exchanger.

Electrodeposition of the CP-MCL films was performed from following solutions:

0.025 mol L^{-1} Arsenazo-I, $pH = 1.6$

0.02 mol L^{-1} Calcon, $pH = 1.9$

0.1 mol L^{-1} SSA, $pH = 1$

0.025 mol L^{-1} Xylenol Orange, $pH = 2.5$

containing additionally 0.1 mol L^{-1} Py, 0.1 mol L^{-1} MPy or 0.01 mol L^{-1} EDOT.

$CaCl_2$ p.a. (POCh), $MgCl_2$ p.a. (POCh), $CuSO_4$ p.a. (Merck), $CuCl_2$ p.a. (Merck), $CdCl_2$ p.a. (Merck), $CdSO_4$ p.a. (Merck), $ZnSO_4$ p.a. (Merck), $Zn(NO_3)_2$ p.a. (Merck), MgO p.a. (POCh), CaO p.a. (POCh), $NaOH$ p.a. (POCh), $NaCl$ p.a. (Merck), $Na_2C_2O_4$ p.a. (POCh), H_2SO_4 p.a. (POCh), CH_3OH p.a. (POCh) were used as received.

Water re-distilled from quartz was used to prepare solutions. All solutions at concentrations lower than 0.01 mol L^{-1} were prepared just before use.

2.2. Instrumentation

The electrochemical polymerization was performed using an EA-9 C electrochemical analyzer (MTM, Poland) or Aulolab PGSTAT-100 Analyser (Ecco Chemie, Nederland). The polymerization was performed in a single-compartment, three-electrode electrochemical cell. The working electrode, to be covered with CP film, was a disc electrode of an area of about $0.03\text{--}0.07 \text{ cm}^2$ made of platinum (Pt), gold (Au) or glassy carbon (GC). For Energy-Dispersive X-ray spectroscopy (EDAX) and X-Ray Photoelectron Spectroscopy (XPS) measurements CP-MCL films were deposited on Pt or ITO sheets with an area of about $0.5\text{--}1 \text{ cm}^2$. The reference electrode was an Ag/AgCl/sat. KCl electrode, which was connected to the cell

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