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Switchable Potentiometric Sensing Probes

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Abstract:

We present ion-selective electrodes on the basis of thin polymeric membrane (about 200 nm) deposited onto poly(3-octylthiophene) layer for use as potentiometric sensors. The influence of the membrane thickness on the resulting lower detection limit, membrane selectivity and response time is studied. Thin membranes allow one to detect cations and anions with a single electrode by means of electrochemical switching.

Key words: ion-selective electrode, thin membrane, poly(3-octylthiophene), transmembrane ion fluxes, switchable cation/anion response.

Introduction

Ion-selective electrodes (ISEs) with polymeric membrane form an important group of chemical sensors that are widely used in clinical diagnostics [1] and environmental analysis [1]. The application scope of ISEs was significantly enlarged by discovering numerous of ion-to-electron transducing materials (conducting polymers, carbon-based composites, redox probes etc. [2]), allowing one to produce electrodes without an internal filling solution, achieving reliable solid-contact ISEs. While the elimination of the internal filling solution increases the durability of the electrodes and facilitates their miniaturization, it also opens up the opportunity to drastically decrease the ion-sensing film thickness (down to 200 nm [3]) by using a spin-coating technique for its deposition on electrode surface.

Thin membrane configuration has been recently successfully adopted by dynamic electrochemistry techniques when the membrane is being interrogated by either controlled current or potential pulses. In particular, ISEs with thin polymeric films deposited onto some conducting polymers (poly(3-octylthiophene) (POT) [3-5] or poly(3,4-ethylenedioxythiophene) (PEDOT) [6]) were used in ion transfer voltammetry for a selective detection of a range of compounds (heparin [4], perchlorate [5], calcium [6]) and multi-cation mixtures [3]. However, it is apparent that a decrease in membrane thickness of an ISE may be beneficial also for zero-current potentiometric measurements but this remains unexplored. Therefore, the goal of this work is to study the applicability of thin membranes in potentiometry.

Elimination of time-dependent mass transport in the membrane

What could be the advantages of thin film configuration in potentiometry? It is clear that the use of thin ion-sensing films should allow one to completely eliminate the preconditioning step during electrode fabrication. The expected equilibration time should be about several milliseconds for a film with thickness of 200 nm and diffusion coefficient of 10^{-8} cm^2 s^{-1} while the preconditioning step of conventional ISEs with membrane thickness of 200 μm requires time of about several hours. Moreover, a thin membrane configuration should virtually diminish or even completely eliminate the potential drifts that originate from time dependent mass transport processes in the membrane. It is well-known that these processes define the observed values of the lower detection limit. Selectivity coefficients determined according to IUPAC recommendations over highly discriminating ions are usually overestimated by many orders of magnitude and depend on the specific measuring conditions, such as experimental time and concentration of primary and/or interfering ions. The main reason for this behavior is an incomplete ion-exchange at the sample–membrane interface, resulting in mass transport processes in the membrane phase and an increase of primary ion concentration at the sample side of the interface. To overcome this important problem, different approaches have been proposed over the years including preconditioning the membrane with a discriminated ion instead of the analyte ion [7] or extrapolation of the time-dependent electrode responses in solutions of interfering ions [8].

ISEs with a thin membrane should allow one to determine directly unbiased selectivity coefficients due to the fast equilibration time and more rapidly accomplish a complete ion-exchange at the sample–membrane interface upon contact with interfering ion solution.

Switchable cation/anion response

At the same time a thin membrane configuration can give a rare opportunity to detect cations and anions with a single electrode. This can be achieved by electrochemical switching. An idealized mechanism of switching between cationic and anionic potentiometric responses is illustrated in Figure 1.

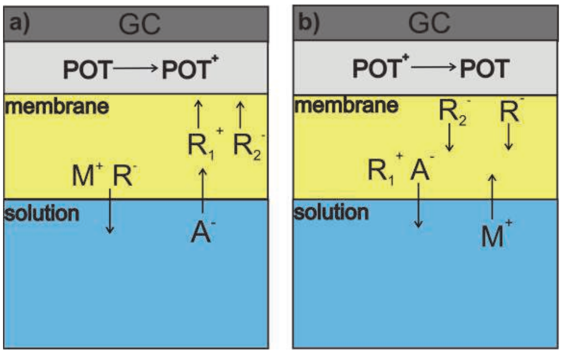

Fig. 1 Mechanism of switching between cationic and anionic potentiometric responses for thin membrane containing cation-exchanger (R^-) and lipophilic electrolyte ($R_1^+R_2^-$) backside contacted with POT as a result of applying (a) oxidation and (b) reduction current pulses.

A freshly prepared electrode with a membrane containing cation-exchanger (R^-) and lipophilic electrolyte ($R_1^+R_2^-$) backside contacted with POT by virtue of the presence of an excess of anionic sites in the membrane exhibits a cationic M^+ potentiometric response. As POT is oxidized to POT^+, it starts to form ion pairs with the lipophilic anions (R^- and R_2^-) present in the membrane, resulting in the expulsion of M^+ from the membrane. This process eventually results in the extraction of A^- to balance free cationic sites (R_1^+) that are being liberated (Figure 1a). Consequently, as the A^- concentration in the organic phase is constant and determined by the concentration of cationic sites (R_1^+), the phase boundary potential of the electrodes will now depend on the A^- activity change in the aqueous phase. At the same time, during the reduction of POT^+ to electrically neutral POT, one should expect the opposite processes (see Figure 1b), namely, the expulsion of A^- from the membrane and the extraction of M^+ from the solution to counterbalance the liberated anionic sites (R^- and R_2^-). As a result of this electrochemical modulation one may restore the cationic potentiometric response.

Conclusions

It is apparent that the use of thin membrane configuration can be very beneficial in potentiometric measurements for both improving ISEs performance characteristics and providing new sensing modes.

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