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Highly-stable Li^+ ion-selective electrodes based on noble metal nanostructured layers as solid-contacts

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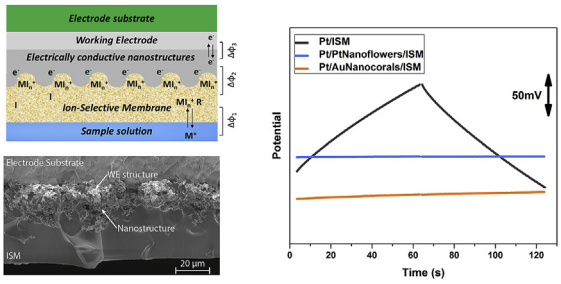
HIGHLIGHTS

- All-solid-state Li^+-ISEs with noble metal nanostructured layers as solid-contacts are developed.
- The gold and platinum nanostructures are prepared by a one-step electrodeposition procedure.
- The fabricated sensors offer Nernstian behavior, short response time and exceptional potential stability.
- High selectivity is achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Nowadays the development of stable and highly efficient Solid-Contact Ion-Selective Electrodes (SC-ISEs) attracts much attention in the research community because of the great expansion of portable analytical devices. In this work, we present highly stable Li^+ all-solid-state ISEs exploiting noble metals nanostructures as ion-to-electron transducers. The detection of lithium is essential for therapeutic drug monitoring of bipolar patients. In addition, greater environmental exposure to this ion is occurring due to the large diffusion of lithium-ion batteries. However, only a limited number of SC Li^+ ISEs already exists in literature based on Conductive Polymers (CPs) and carbon nanotubes. The use of noble metals for ion-to-electron transduction offers considerable advantages over CPs and carbon materials, including fast and conformal one-step deposition by electrochemical means, non-toxicity and high stability. We investigate for the first time the use of gold nanocorals obtained by means of a one-step electrodeposition process to improve sensor performance and we compare it to all-solid-state ISEs based on electrodeposited platinum nanoflowers. In addition, the effect of substrate electrode material, membrane thickness and conditioning concentration on the potentiometric response is carefully analysed. Scanning Electron Microscopy (SEM) and Current Reversal Chronopotentiometry (CRC) techniques are used to characterize the morphology and the electrochemical behaviour of the different ISEs. The use of nanostructured gold and platinum contacts allows the increase of the SC capacitance by one or two orders of magnitude, respectively, with respect to the flat metal, while the SC resistance is significantly reduced. We show that the microfabricated sensors offer Nernstian behaviour (58.7±0.8 mV/decade) in the activity range from 10^{-5} to 0.1 M, with short response time (~15 s) and small potential drift during CRC measurements ($\frac{dE}{dt} = 3 \times 10^{-5} \pm 2 \times 10^{-5}$ V/s). The exceptional response stability is verified also when no potential is applied. The sensor shows high selectivity towards all clinically important ions, with values very similar to conventional ISEs. Furthermore, to our knowledge, the selectivity towards Ca^{+2} is the best ever reported for SC-ISEs. In conclusion, the present study opens up new interesting perspectives

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towards the development of simple and reproducible fabrication protocols to obtain high-quality and high-stability all-solid-state ISEs.

1. Introduction

Solid-Contact Ion-Selective Electrodes (SC-ISEs) have received considerable attention over the past 50 years towards next-generation portable and miniaturized ion-sensors with integrated steering circuits and read-out electronics [1]. Accurate and quantitative measurements of ions in solution are crucial in several different applications, including medical analysis [2,3], environmental [4] and water quality [5] monitoring, cosmetics [6], agriculture [7] and process control [8,9]. The first all solid-state ISE without internal reference solution was proposed in 1970 by Hirata and Date [10], followed by Cattrall et al. [11] the year after. Both systems were based on coated-wire electrodes. Poor reliability was achieved by Hirata and Catrall mainly because of the purely capacitive interface and the reduced contact area that caused large potential instabilities. Since then, several advances have been made thanks to the use of new SC materials and to better understanding of transport phenomena and water accumulation in the membrane. However, these systems still require major improvements since they suffer from some important limitations including the need of calibration, limited selectivity and potential drift. The most critical aspect is certainly represented by potential stability. There are mainly two possible causes of potential drift: the formation of a water layer at the ISM/SC interface and the small but non-zero current required for OCP measurements. In the first case, the sensor is generally sensitive to osmolality variations. Membrane delamination can eventually occur during operation because of poor adhesion to the substrate [1,12].

So far, the most promising candidates for commercial SC-ISEs are Conductive Polymers (CPs) and nanostructures with high double layer capacitance [13–15]. Nanostructured materials offer several advantages with respect to CPs, including the possibility to achieve high conductivity, the absence of possible side-reactions and the insensitivity to pH and light [1,16]. They exploit the electrical double layer that is formed at the membrane/electrode interface for ion-to-electron transduction: the accumulation of ions on one side of the interface thanks to the role of the ISM attracts electrons or holes on the other side; this leads to the formation of an asymmetric capacitor. In these systems the interfacial potential is not related to redox reactions, as in the case of CPs, or to ion partitioning, as in conventional ISEs, but to the amount of charge accumulated in the double layer. Thanks to their large surface area and their hydrophobic behaviour, nanostructured materials enable the achievement of good adhesion, avoiding the risk of water absorption. Moreover, they are typically characterized by high capacitance values. This property is crucial to reduce polarization effects due to the small but non-zero currents required for the measurement. For a more detailed description we refer the reader to [17]. Both carbon and noble metals nanostructures have been successfully investigated as SCs for ISEs: carbon nanotubes [18–21], fullerene [22,23], porous carbon [24–26], graphene [21,27–30], different polymer/carbon composites [31,32], platinum nanoparticles supported on carbon black [33], platinum nanopetals [34], gold nanodendrites [16], gold nanoclusters [35], nanoporous gold films [36] and gold nanoparticles [37,38]. An example of a SC-ISE based on MoO_2 microspheres has also been reported [39].

Many examples of portable SCs ion-sensors already exist in literature for most ions of clinical relevance. The research has focused mainly on cystic fibrosis and physical exercise monitoring. The most investigated ions are K^+ [23,34,37,40–48], Na^+ [45,49–52], Cl^- [47,53], NH^{4+} [48,54–56] and H^+ [48,52,57–59]. On the contrary, a very limited number of studies have been carried out in order to sense lithium ions.

Lithium salts represent the oldest yet effective drugs to treat psychiatric patients suffering of Bipolar Disorder (BD) in order to keep under control maniac episodes [60]. BD is a serious and potentially mortal disease, which cannot be cured, but only treated with specific drugs. It is characterized by episodes of depressed and maniac mood, separated by periods of normal mood. Maniac and depressed conditions can cause insomnia or hypersomnia, excessive weight loss/gain, suicidal thoughts, aboulia [61,62]. The risk of suicide is 30 times higher than in general population [63]. Consequently, after diagnosis, there is an urgent need of stabilization therapy [64]. Unfortunately, the therapeutic range of this compound is very narrow (0.5–1.5 mM) [65]. Moreover, dietary variations, interaction with other medicines as well as individual variability have a strong effect on the determination of the right dose [66]. The consequences of overdose can be extremely severe. They include drowsiness, ataxia, myoclonic twitching and chronic toxicity that can lead to irreversible damages to kidneys, liver and brain, and eventually to death [66]. Hence, Therapeutic Drug Monitoring (TDM) is crucial to optimize the dose for each patient [67]. More specifically, lithium concentration in serum must be controlled at least every week (standardized 12h or 24h Li^+ serum concentration) at the beginning of the treatment or after any change in the dose. The time interval between subsequent check-ups can be enlarged only in absence of any complications. On the contrary, the frequency of serum lithium analyses should be increased accordingly. Check-ups every three month must be performed during maintenance [60].

Lithium quantification in clinical laboratories is routinely performed by atomic absorption spectrometry, flame emission photometry or conventional ISEs [68]. The possibility to use colorimetry [65] and photometry [69,70] has also been reported in literature [68]. Obviously, all these techniques require highly qualified personnel and expensive equipment. In this regard, all-solid-state SC-ISEs constitute ideal candidates for the development of low-cost and easy-to-use sensors for decentralized monitoring of lithium that would avoid frequent check-ups in hospital to the patients. Novell et al. have reported the fabrication of a paper-based Li^+ ion-selective sensor using carbon nanotubes as SCs [71]. Coldur et al. have fabricated a miniaturized Li^+ ISE with improved selectivity using a graphite composite to achieve ion-to-electron transduction [72]. In the following years they have also reported the determination of lithium under flowing conditions towards the development of automatic and LOC analytical devices [73]. All these sensing systems open up new interesting perspectives, but some limitations must still be tackled, including biocompatibility and toxicity, reproducibility and simplicity of the fabrication process.

Other possible applications of lithium sensors may also arise from the expanding use of lithium-ion batteries that is likely to bring greater environmental exposure through leaching of landfill [74].

In this paper, we present highly stable Li^+ ISEs based on noble