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Functional Layers for Chemical Sensors Based on Conducting Polypyrrole

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SUMMARY: Functional thin layers based on polypyrrole were used in electrochemical sensors as mixed conducting interfaces between ion-selective membranes and the wiring. In particular, new types of ion-selective electrodes for potentiometric measurement of pH value and concentration of sulfate ions in solutions were developed. The resulting electrodes do not need any inner liquid junction. First determinations of the sensor parameters sensitivity, selectivity and long term stability indicate a good performance of the prepared sensors. The results imply that interfaces, containing polypyrrole, could be an interesting basis for the construction of a new type of all-solid-state ion-selective electrodes.

Introduction

The interest in intrinsically conducting polymers (ICP) has increased during the last decade owing to new fields of application in electronics and corrosion prevention. The mixed conductivity (electronic and ionic conductivity), showed by these polymers, is of special interest for applications in chemical sensors, including ion-selective electrodes (ISE)[1-4).
For many types of ISE inner liquid junctions have been necessary, although liquids inside the electrodes give rise to divers disadvantages[5). Therefore, a lot of efforts have been made to construct ISE without any inner liquid junction, so-called all-solid-state electrodes, however, most of them work with unsatisfactory performance[6).

First promising attempts to use ICP for inner solid junctions in ISE are known for electrodes, containing a PVC membrane selective for chloride, nitrate, calcium, and alkali metal ions, respectively[7,8). However, to the authors knowledge no comparable applications of ICP to the most widely used pH glass electrodes and to ISE, which are selective to multivalent anions, e.g. sulphate ions, can be found from the literature. To shorten this gap, the presented work deals with the construction and testing of new types of all-solid-state pH glass electrodes and sulphate selective PVC membrane electrodes using an ICP for the inner solid junction.

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Preparation

Owing to its high conductivity, remarkable stability, simple preparation, and well known properties[4)], polypyrrole (PPy) in the oxidized doped state was the ICP used in all experiments. The general construction of the new sensors is presented in Fig. 1. Two new types of ion-selective electrodes were prepared using this construction.

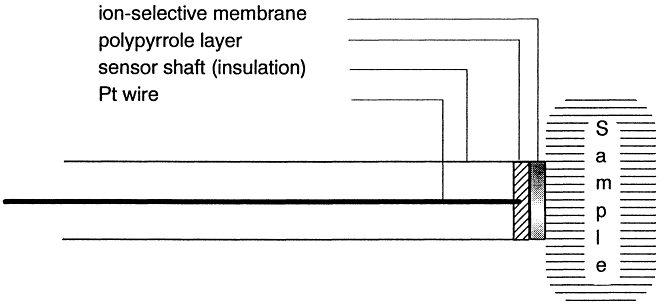

Fig. 1: Schematic diagram of an electrochemical all-solid-state sensor, using polypyrrole as contact layer.

The first type is a sulphate ion-selective electrode with a PVC membrane, containing the sulphate sensitive ionophore 3-decyl-1,5,8-triazacyclodecan-2,4-dion. The solid junction was prepared by electrochemical deposition of PPy on the Pt wire from aqueous pyrrole (Fluka, purum) solutions in a first step, and deposition of the PVC (high moleculare, Fluka, selectophore®) membrane on the PPy layer by solution casting in a next step[9)].

The second type is a pH electrode with a H^+ selective glass membrane[10)]. Its preparation was much more difficult, because neither an electrochemical deposition of PPy on the glass membrane nor a deposition of the glass membrane on the PPy layer, by e.g. casting, were applicable. Chemical precipitation of PPy direct on the inner surface of the glass membrane did not result in sufficiently stable junctions. The problem was solved by the deposition of PPy powder between the Pt wire and the glass membrane from a suspension, containing an ion-exchange material (IEM). The PPy was prepared chemically by oxidation of pyrrole (Fluka, purum) with $FeCl_3$ (Fluka, puriss. p.a.) in aqueous solution at room temperature. The obtained junctions are mechanically stable and show sufficiently high electrical conductivities.

Results and Discussion

First measurements have been carried out to determine some interesting properties of the new sensor. Typical results at room temperature are given below.

Sulphate Ion-Selective Electrode

The prepared sulphate ion-selective sensors[9] show a linear potential response in the range of sulphate concentration 10^{-4}-10^{-2} mol/l (Fig. 2). In this range the slope of the response is about -26 mV/mol·l^{-1}, and therefore close to the theoretical Nernstian value valid for negatively charged divalent ions. Investigations of the long-term stability up to 150 days show only a small drift of the sensor signal (Fig. 2). In the presence of interfering nitrate ions, the selectivity of the new sensor with respect to sulphate ions is higher (potentiometric selectivity coefficient, log $K^{pot}[SO_4^{2-}, NO_3^-]$: -0.24) than the corresponding selectivity reported for other sulphate sensors (log $K^{pot}[SO_4^{2-}, NO_3^-]$: 4.3, 4.9, 4.1)[9, 11].

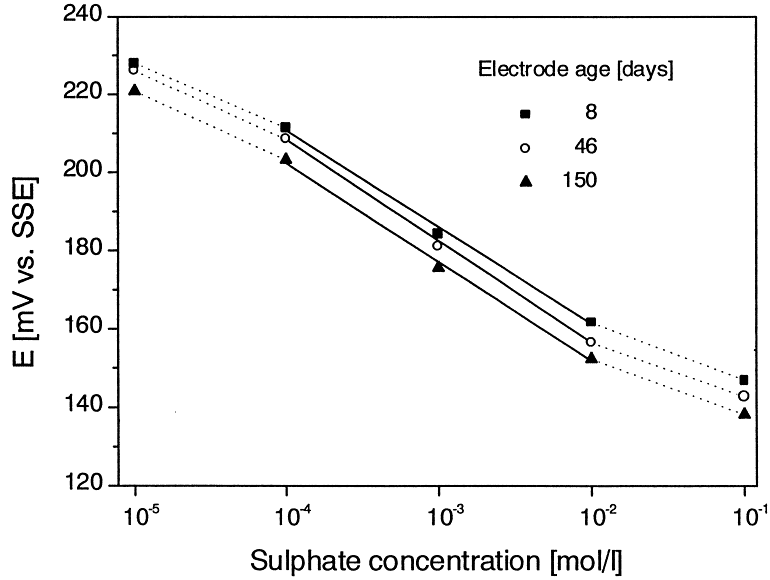

Fig. 2: Potential (E) of an all-solid-state sulphate sensor *vs*. sulphate concentration of solution at different ages of the sensor, measured *vs*. saturated Ag-AgCl reference electrode (SSE).

pH Glass Electrode

All prepared pH sensors show a linear potential response in the pH range 2-11. In this range the slope of the response is about -57 mV/pH, and therefore close to the theoretical Nernstian value valid for positively charged univalent ions. The long-term stability is surprisingly high (Fig. 3, 5). The lifetime of the pH sensor exceeds one year for most examples.

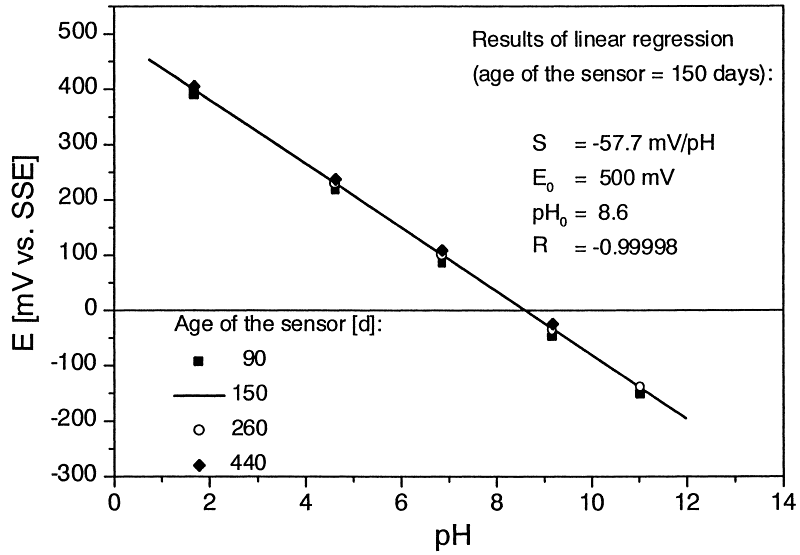

Fig. 3: Potential of an all-solid-state pH sensor as a function of pH ($E = S \cdot pH + E_0$) at different ages of the sensor.

A comparison of the long-term stabilities of three differently constructed all-solid-state pH glass electrodes is given in Fig. 5. The electrodes P1 and P2 (Ø 6 mm) contain a solid mixture of PPy and IEM as interfacial layer. P2 is miniaturized (Ø 2 mm) and much more simply constructed than P1 (see Fig. 4). The third electrode I1 was prepared for comparison. It has the same construction than P1, but the interfacial layer does not contain PPy, it consist of the IEM only. Fig. 5 demonstrates that the two electrodes with interfaces containing PPy (P1, P2) show a higher long-term stability than the one without it (I1), even if the PPy containing electrode is smaller and much more simply constructed (P2) than the electrode without PPy (I1). The high stability of the sensor response of P1 is remarkable for an all-solid-state pH glass electrode.

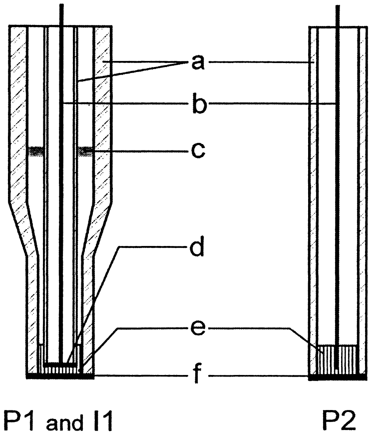

Fig. 4: Schematic diagram of three differently constructed all-solid-state pH sensors; a – sensor shaft (insulating glass); b – Pt wire; c – spacer; d – Pt disc; e – IEM (I1) and PPy-IEM (P1, P2) interfacial layer, respectively; f – H^+ selective glass membrane.

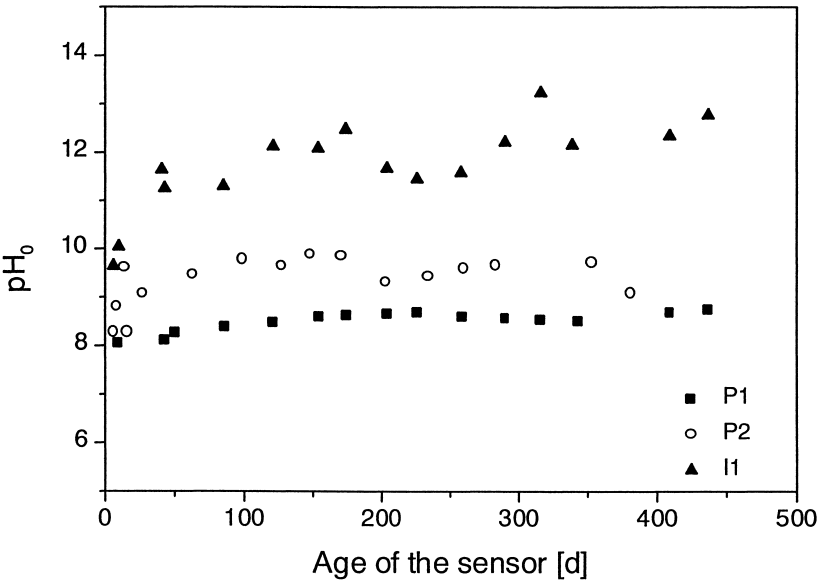

Fig. 5: pH at E = 0 mV (pH_O) vs. age of the sensors for three differently constructed all-solid-state pH sensors; P1, I1: PPy-IEM and IEM interfacial layer, respectively (Ø 6 mm); P2: PPy-IEM interfacial layer, simplified construction (Ø 2 mm).

Conclusion and Outlook

The presented all-solid-state electrodes could result in an interesting alternative to conventional ion-selective electrodes for the measurement of pH and sulphate ions in solutions. The use of mixed conductive interfaces, containing PPy, between the ion-sensitive part and the wiring of the electrodes seems to be responsible for the observed high reproducibility and long-term stability of the sensor response. Currently, further attempts are made to improve the construction of the sensors. Moreover, the stability of the solid-state junction at elevated temperatures is under investigation.

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