Macromol. Symp. **2004**, *210*, 385-391

Mixed Conducting Polymers on Ion-Conducting Sensor Glasses – Charge Transfer in the System Polymer/Glass

Heimo Jahn, Heiner Kaden, Monika Berthold*

Kurt-Schwabe Institute for Measuring and Sensor Technology Meinsberg,
Fabrikstraße 69, 04720 Ziegra-Knobelsdorf, Germany
E-mail: jahn@ksi-meinsberg.de

Summary: Mixed ion/electron conducting polymer layers based on polypyrrole have been used as internal reference electrodes in all-solid-state pH glass electrodes. The effect of the nature and composition of the polymer used and of the deposition technique applied on the performance of the resulting sensor has been studied. For this purpose, crucial sensor properties, e.g. parameters of the calibration function, response behaviour and complex impedance, have been determined experimentally at room temperature. The results show that several properties studied remained nearly uninfluenced by changes of the polymer composition. The zero potential point of the calibration line was found to be the most sensitive parameter. Principally, almost all mixed conducting polymers used seems to result in a stable charge transfer in the system polymer/glass.

Keywords: charge transfer; composites; conducting polymers; pH sensor; polymer/glass interface; polypyrroles

Introduction

The interface between a polymer film and a substrate controls the adhesion and the electrical behaviour of a variety of polymeric systems including coatings of polymers on glass fibre composites, in photovoltaic devices and coatings of conducting polymers on glasses. Intrinsically conducting polymers, amongst them polypyrrole (PPy), are interesting sensor materials, especially due to their mixed ionic and electronic conductivity. In previous works [1-6] we could show that mixed conducting polymer composites consisting of polypyrrole doped with $FeCl_3$ ($PPy[FeCl_3]$) and Nafion® are promising candidates for a new kind of internal reference systems in all-solid-state pH-sensitive glass membrane sensors. In this work the influence of the nature and composition of further mixed conducting polymers used in such reference systems on the performance of the resulting sensor has been studied.

DOI: 10.1002/masy.200450643

Experimental

The set-up of the all-solid-state pH-sensitive glass sensors studied is given in Fig. 1 schematically. The solid-state internal reference system of these sensors is based on a mixed conducting polymeric interlayer between the ion-sensitive glass and a metal wire replacing the conventionally used liquid-based reference system: Ag/AgCl/buffer solution.

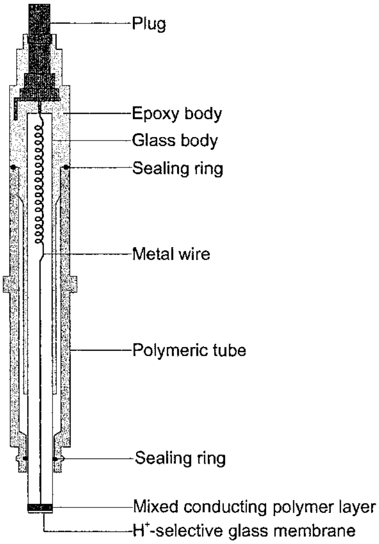

Figure 1. Schematic diagram of an all-solid-state pH glass sensor using a mixed conducting polymer layer as internal reference electrode.

Preparation

The preparation of the polymeric layer was performed by deposition of PPy on the inner side of the ion-sensitive glass membrane applying two different techniques:

(1) deposition from a suspension of PPy dispersed in a Nafion® solution [1, 6],
(2) direct precipitation from non-aqueous solutions of pyrrole employing an oxidizing agent.

In the case of the first way of preparation, chemically or electrochemically doped PPy was used. The doping agents applied were $FeCl_3$, $Fe(NO_3)_3$, $Na_2S_2O_8$ (chemical doping) or $NaClO_4$, polystyrenesulphonic acid sodium salt (NaPSS), Nafion® (electrochemical doping). Nafion in its protonated form (Nafion® 117) was utilized. In the case of the second way, $FeCl_3 \cdot 6H_2O$ or $H_3PMo_{12}O_{40} \cdot xH_2O$ were the oxidizing agents employed. The resulting polymer layers consist either of a PPy-Nafion® composite (technique 1) or of a composite containing PPy and the by-products of the reaction between pyrrole and the oxidizing agent (technique 2).

Measurements

Crucial characteristics of the resulting sensors, e.g. parameters of the calibration function (and their long-term stability), response behaviour and complex impedance, have been determined experimentally at room temperature (23 ± 3 °C). The measurements were carried out in a Faraday cage using an external Ag/AgCl reference electrode with saturated aqueous KCl filling (SSE). All potentiometric investigations were performed in the range $1.7 \leq pH \leq 9.2$. The response behaviour was determined by the method of quick change of buffer solutions[7]. Further, more detailed descriptions of the procedures of preparation and measurement have been given elsewhere [1, 5, 6].

Results and Discussion

The long-time behaviour of a critical parameter of the calibration function, the zero potential point (pH_0), is presented in dependence of quantitative (Fig. 2) and qualitative (Fig. 3) changes in the composition of PPy-Nafion® composites used and in the technique of polymer deposition applied (Fig. 4). As can be seen in the given figures both the change of the PPy/Nafion® ratio as well as the use of different dopants of the PPy applied in the composite are reflected by the values of this parameter. The minima observed during the first two weeks after preparation of the solid contacts indicates strong initial interactions between the components of the system PPy-Nafion®/glass for all PPy[$FeCl_3$]/Nafion ratios studied (Fig. 2). However, the long-term stability of pH_0 after this “conditioning” period was high. The most stable values were obtained for polymers containing 50 wt.% PPy. The long-term stability of pH_0 for PPy-Nafion® layers with generally 50 wt.% PPy but with varying dopants (Fig. 3) has been found to be high over very long

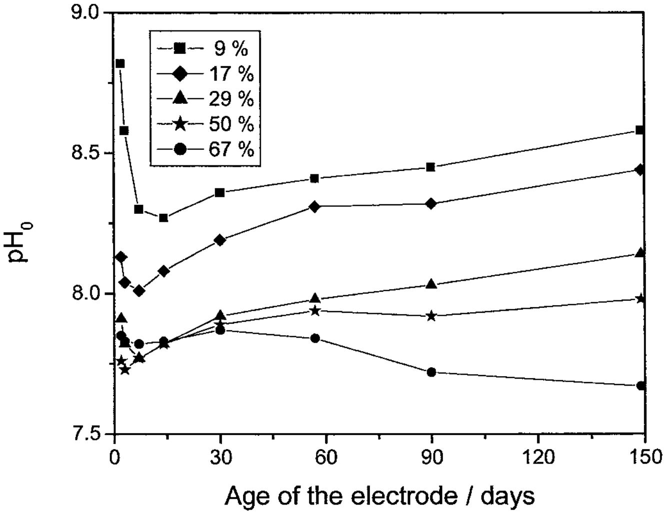

Figure 2. The influence of the PPy content (wt.%) of the mixed conducting PPy[$FeCl_3$]-Nafion® layer on the long-time behaviour of the zero potential point (pH_0) of the pH sensor at 25 °C.

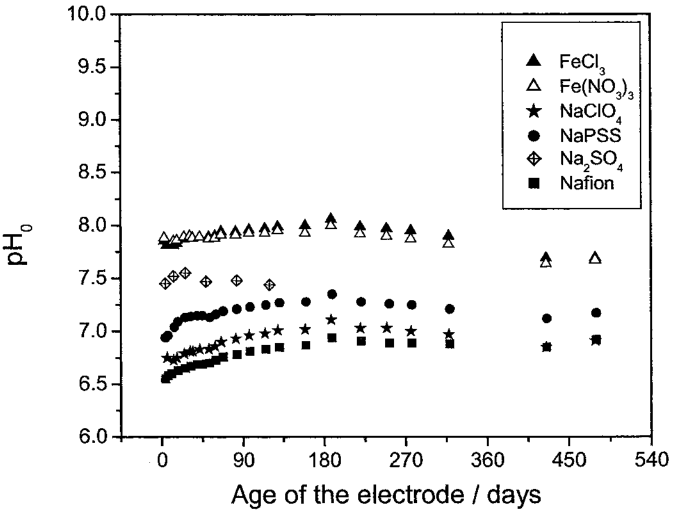

Figure 3. The effect of the dopant of PPy on the long-term stability of pH_0 for electrodes using PPy-Nafion® composites (50/50 w/w) as polymer layer.

periods (up to 16 month) in all cases studied. The direct precipitation of PPy from non-aqueous solutions of pyrrole (technique 2) employing the oxidizing agents $FeCl_3 \cdot 6H_2O$ and $H_3PMo_{12}O_{40} \cdot xH_2O$, respectively, resulted in solid contacts showing a relatively poor long-time behaviour compared to this based on PPy-Nafion® composites (Fig. 4). The differences in the absolute values of pH_0 for the various polymer layers are the consequence of the different doping agents used. In contrast to pH_0, the parameters slope and linearity of the calibration line have found to be nearly uninfluenced by the investigated changes in composition and technique of preparation. In the case of sensors based on directly precipitated PPy layers, however, an enlarged scatter of the values of these parameters was observed.

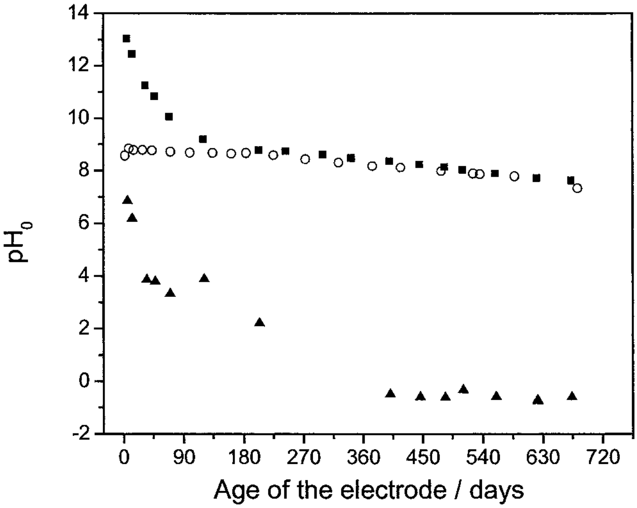

Figure 4. Comparison of the long-time behaviour of pH_0 for electrodes containing differently prepared polymer layers: PPy directly precipitated from non-aqueous solutions of $FeCl_3 \cdot 6H_2O$ (triangles) or $H_3PMo_{12}O_{40} \cdot xH_2O$ (squares), PPy[$FeCl_3$] applied as PPy-Nafion® composite containing 50 wt.% PPy (circles).

A typical example for the response *vs.* time dependence during pH changes of electrodes employing a PPy-Nafion® composite (50/50 w/w) based on PPy which was chemically doped by ferric nitrate (PPy[$Fe(NO_3)_3$] is given in Fig. 5. The response times for 95% of equilibration (t_{95})

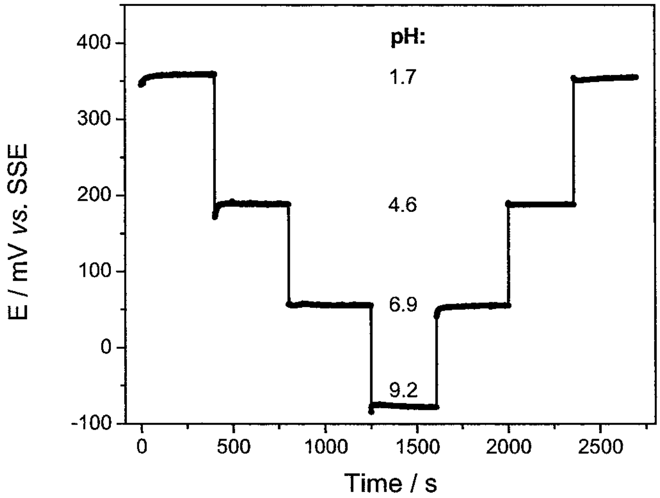

Figure 5. Response behaviour of a sensor with PPy[Fe(NO$_3$)$_3$]-Nafion®/ Pt as internal reference system during the change of pH of the test solution at 25 °C.

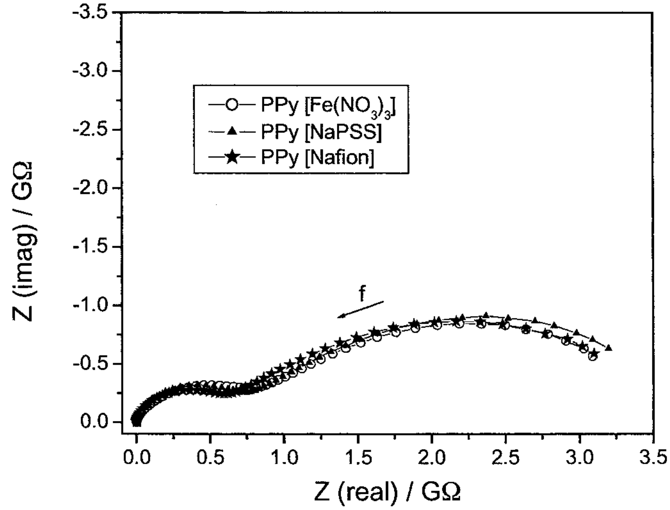

Figure 6. Nyquist plot of complex impedance of the system SSE, 1 M KCl/ **pH glass/ PPy-Nafion®**/ Pt containing differently doped PPy at 25 °C. Z (imag), Z (real): imaginary and real part of complex impedance. In direction of the arrow: higher frequencies f.

were estimated to be smaller than 10 s for all pH steps studied. This result is in good agreement with that found earlier ($t_{95} < 9$ s)[6] for a PPy[$FeCl_3$]-based sensor of the same type.

The complex impedance curves of three electrodes under investigation (Fig. 6) show two semicircles in the frequency range 0.001 Hz to 100 kHz. The impedance of the glass/polymer interface (included in right semicircle according to SANDIFER et al.[8]) is nearly uninfluenced by the dopant used.

Conclusions

It has been shown that the zero potential point was the parameter which was most sensitive to changes in the composition of the mixed conducting polymer layer. Further sensor characteristics like the slope and linearity of the calibration line, the response time as well as the impedance spectra were found to be nearly uninfluenced by the dopant applied. The long-term stability of the sensor response of the electrodes containing PPy-Nafion® composites was much higher than that of the electrodes containing directly precipitated PPy without admixture of Nafion®. Principally, almost all mixed conducting polymers used in this work exhibited a good performance as internal reference electrodes of pH selective glass sensors. This result indicates a stable charge transfer in the studied systems: Pt/mixed conducting polymer/ion-conducting glass.

[1] Ger. 10018750 (2000), Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V. Meinsberg, invs.: H. Kaden, H. Jahn, M. Berthold, K.-H. Lubert; Chem. Abstr. **2001**, *134*, 109879e.
[2] H. Jahn, M. Berthold, H. Kaden, *Macromol. Symp.* **2001**, *164*, 181.
[3] H. Kaden, H. Jahn, M. Berthold, K. Jüttner, K.-M. Mangold, S. Schäfer, *Chem. Eng. Technol.* **2001**, *24*, 1120.
[4] H. Jahn, M. Berthold, H. Kaden, in: „Dresdner Beiträge zur Sensorik", Vol. 16., J.P. Baselt, G. Gerlach, Eds., w.e.b. Universitätsverlag, Dresden 2002, pp.174-177.
[5] H. Kaden, H. Jahn, M. Berthold, *Solid State Ionics* (in press).
[6] H. Jahn, H. Kaden, *Microchim. Acta* (submitted for publication).
[7] H. Galster, „pH-Messung", VCH Verlagsgesellschaft, Weinheim 1990, p.152.
[8] J.R. Sandifer, R.B. Buck, *Electroanal. Chem. Interfac. Electrochem.* **1974**, *56*, 385.