ORIGINAL PAPER

New solid-state glass electrodes by using zinc oxide thin films as interface layer

W. Vonau · F. Gerlach · U. Enseleit · J. Spindler · T. Bachmann

Abstract Novel glass electrodes for the determination of cations with reversible internal solid contact are introduced. They are based on a semiconducting zinc oxide layer with a maximum thickness of 1 μm in contact with ion selective glasses on one side and with a metal layer on the other side. The metal oxide layer is thereby generated either by ultrasonic spray pyrolysis from zinc acetate solution, by electrochemical deposition from zinc nitrate solution or by spin coating from a dispersion of ZnO in an organic binder. A following activation in a palladium chloride solution allows the chemical reductive deposition of NiP as electronic conductor. Dipping-type and flow through electrodes as well as planar glass electrodes in thick film technology fabricated in the above-mentioned method are described. In this case gold electrodes are applied by screen printing on isolated steel substrates. The zinc oxide layers, created in different manners, are covered afterwards with cation selective glasses in thick film technology. They cause a stabilisation of the half-cell potentials of the all solid state indicator electrodes proved by suitable measurements.

Introduction

For a long time the fabrication of so-called all-solid-state glass electrodes for the determination of cation activities has been a research objective. This is related to several drawbacks of conventional glass electrodes, such as position dependence when these electrodes are stored and used, pressure and temperature dependence, limitations concerning the miniaturisation and mechanical fragility.

In the past there were different approaches for the construction of solid contacts for glass electrodes. These electrodes in their traditional setup with liquid internal electrolytes have been primarily used for pH measurements for a long period. For a considerable time such electrodes have also been available for the determination of activities of further monovalent cations [1].

Electrodes with solid state contacts have been made from metallised ion-conducting glasses (e.g. Corning 015, consisting of 72 wt% SiO_2, 24 wt% Na_2O and 6 wt% CaO) with discharge conductors consisting of silver [2, 3], amalgams [4] or alloys with low melting points [5, 6]. Glazing [7] and enamelling [8] of metallic base structures are also possible. Screen printing of pH glass on planar metal coated substrates is also described [9]. Last but not least, it was recommended to apply carbon black immobilised in polymers (e.g. elastomers) as contact material [10].

A main problem with metallised or carbon-coated oxide glass membrane electrodes is the lack of long-term stability of the half-cell potential owing to the irreversibility of charge

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carrier transfer at the phase interface metallic discharge/ selective glass. The same applies for electronic conducting semi-finished products coated with the special glass.

For this reason several efforts were undertaken to create a reversible phase boundary. Some examples are subsequently summarised:

– Starting from investigations in [11], where the preparation of laminated glasses is recommended, which consist of electrolytically conductive pH glasses and mixed conductive redox glasses, electrodes with ball-shaped membranes 0.3 mm thick and made of a pH-electrode glass (70.5 mol% SiO_2, 21.5 mol% Na_2O, 6.7 mol% CaO, 1.3 mol% UO_3) (outside) and mixed conductive glass (50 mol% SiO_2, 23 mol% Fe_2O_3, 22 mol% Na_2O, 5 mol% Al_2O_3) (inside) were fabricated. The latter glass was silvered in a chemically reductive way and formed together with the mixed conducting glass by means of the internal reference system [12].
– Cu wires were oxidised and coated with a cation selective glass consisting of SiO_2, LiO_2, CaO, Cs_2O, La_2O and BaO [13].
– Solid contact based on Na^+ containing Prussian blue (NaPB) as mixed-valent compound was used [14].
– Prefabricated flask-shaped glass electrodes were filled with solid $AgNO_3$ to be melted. Subsequent electrolysis was done using a Pt-wire (inside) and a Pt-net electrode at a current flow of 30 mA over periods of 1–50 min. There was a partial mechanical destruction of the membranes. Electrodes that survived the procedure were silvered chemically and showed a good potential stability. However, case-specific differences of the absolute electrode potentials could be observed [15].
– Polypyrrole (PPY) from the group of intrinsically mixed conducting polymers was used as contact material for planar pH membranes. The problem of poor adhesion on the glass surface was solved by using Nafion® as glue. This application resulted in solid-state pH electrodes of high long-term stability [16].

All attempts presented here and elsewhere [17] to fabricate solid-state glass electrodes with reversible internal discharge systems did not lead to sensing elements with a measuring performance comparable to conventional systems up to now. Furthermore, the sensor preparation often is very extensive.

Former investigations have shown that ZnO thin films with a thickness of less than 1 μm can be used as adhesion promoter between a glass substrate and a copper layer [18, 19]. Reinecke et al. [20] used ZnO as interface layer for planar electrochemical sensors based on electroless NiP-plating on dielectric substrates (glass, ceramic). The electroless deposition of NiP was possible, when the ZnO layer was activated in acidic $PdCl_2$ solution.

Zinc oxide is a wide-bandgap oxide semiconductor with a direct energy gap of about 3.37 eV. It can be used as transparent conductive oxide (TCO) thin film, e.g. for applications in solar cells [21], gas sensors [22] or light emitting diodes [23].

ZnO thin films can be produced by various techniques such as sputtering [24], reactive evaporation [25], spray pyrolysis [26–28] and electrochemically [29, 30].

In the current paper, a new approach is given to fabricate advantageous solid-state glass electrodes for different application fields using semiconducting zinc oxide layers between selective glass and metallic discharge. The new probes were tested comparatively to other state-of-the-art glass sensors.

Materials and methods

Preparation of solid-state glass electrodes

#### Glass electrode with metallic coating on the inside

The aim of the work, the creation of glass electrodes with reversible internal solid contacts using the n-type semiconductor zinc oxide, was approached in different ways. Depending on the used electrode system the ZnO films were deposited by spray pyrolysis, spin coating or electrochemical deposition.

Zinc oxide thin films were obtained inside glass electrodes in conventional design by ultrasonic spray pyrolysis technique. The overall dimensions of this tubing were an internal diameter of 10 mm and a length of 120 mm. As selective glass for cations, Corning 015, and as shaft glass, lead-free EMGO 360 (EMGO, Lommel, Belgium) were used.

The spray system is illustrated in Fig. 1. The tubing was heated by a cylindrical furnace and the deposition temperature was fixed at 693 K. As precursor a 0.1 mol/l zinc acetate dehydrate (Fluka, >99.5%) solution, diluted in methanol and distilled water (5.6:1 ratio, dynamic viscosity η=1.05 mPa) was used. The carrier gas was filtered air. As atomiser a medical nebulizer (Schill Medizintechnik, Probstzella, Germany) with an oscillator frequency f of 2.5 MHz and a particle size range of 1.5 to 5.7 μm was applied. The deposition was carried out five times in each case for 5 min. In addition, the cylindrical furnace was fixed onto a mobile stage, which gave an axial movement with a speed of 0.33 cm/s. This allowed the production of a uniform film along the electrode length. After deposition the films were annealed in a muffle furnace at a temperature of 723 K for 15 min in air atmosphere.

The glass electrode with ZnO coating on the inside was activated for electroless NiP deposition by immersing in an acidic $PdCl_2$ solution (pH=2.5, β=0.2 g/l) for 10 s. The

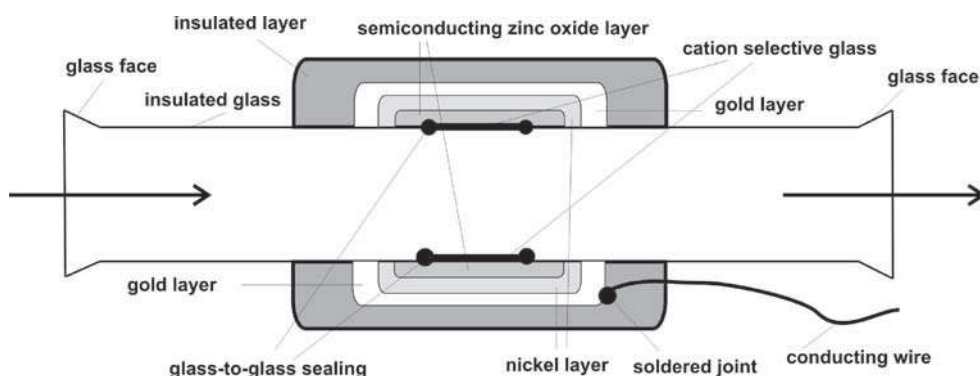**Fig. 1** Schematic drawing of the system for ultrasonic spray pyrolysis
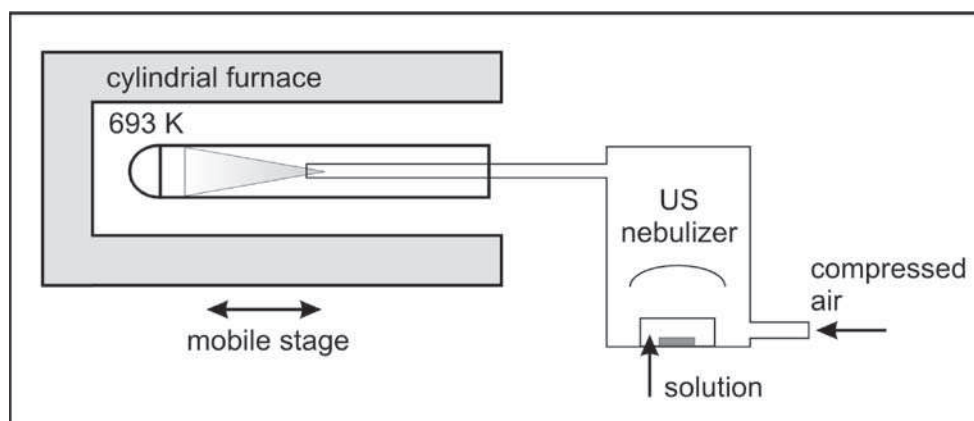
electroless NiP plating was carried out in an alkaline bath (pH=9.5) consisting of 15 g/l nickel(II) sulfate hexahydrate, 10 g/l citric acid, 2 g/l sodium tetraborate and 20 g/l sodium hypophosphate in distilled water at 328 K for 3 min.

Finally, the electrode was completed with an electrode head and cable in accordance with DIN standard 19262 [31].

Flow-through electrodes with metallic coating on the outside

All solid state flow-through cells were prepared. A schematic drawing of such a novel pH flow-through cell is shown in Fig. 2. It consists of a tube segment of pH selective glass that is fused between two shaft glass tubes with a diameter of 6 mm. Thereby it is advantageous when both connection regions do not possess a large bulge. Furthermore, the linear thermal expansion coefficient of both glass types should not differ strongly ($\Delta\alpha\leq 7$ 10^{-7} K^{-1}) to avoid cracks and tension. On the cation selective glass and beyond the junction of both glasses a zinc oxide and a nickel phosphorus layer with thicknesses of 50 nm (ZnO) and 200 nm (NiP) are applied. Through the interior space the analyte can flow continuously. A silver wire as dissipation was glued on the NiP layer by means of a two-component epoxide resin. For the determination of pH values the flow-through cell was completed with a silver chloride reference electrode.

The ZnO layer on the pH selective glass body of the flow-through cell was realised by spin coating. As raw material for the covering a paste was used, consisting of zinc oxide (β=3 g/l), ethyl cellulose (β= 1.5 g/l) and α-terpineol. Before coating the body the material of the flow through cell was cleaned in an ultrasonic bath and dried in a drying oven at 100 °C. Afterwards it was chucked in a rotating device and a rotational speed of 1,800 rpm was adjusted. The paste was then dropped on the pH selective glass with a pipette and thereafter inserted 3 min into a tube oven having a temperature of 400 °C. In a next step, the ZnO layer was stoved in a muffle furnace at 450 °C for 2 h. Thus closed zinc oxide layers could be generated. Activation and metallisation were carried out in accordance with electrodes with metallic internal discharge.

Planar all solid-state glass electrodes in thick film technology

A further attempt to develop potential stable solid-state glass electrodes with ZnO intermediate layer uses thick film technology for preparation.

Substrate basis for planar solid-state electrode systems with glass membranes (Fig. 3A) as function-determining sensor component is high-grade steel 1.4016 with a thickness of 1.5 mm. The angles were rounded off to decrease mechanical tensions of the printed layers. Multi-

Fig. 2 Schematic assembling of the solid-state pH flow-through cell

Fig. 3 Planar solid-state glass electrode. **A** Photograph, **B** schematic layer composition
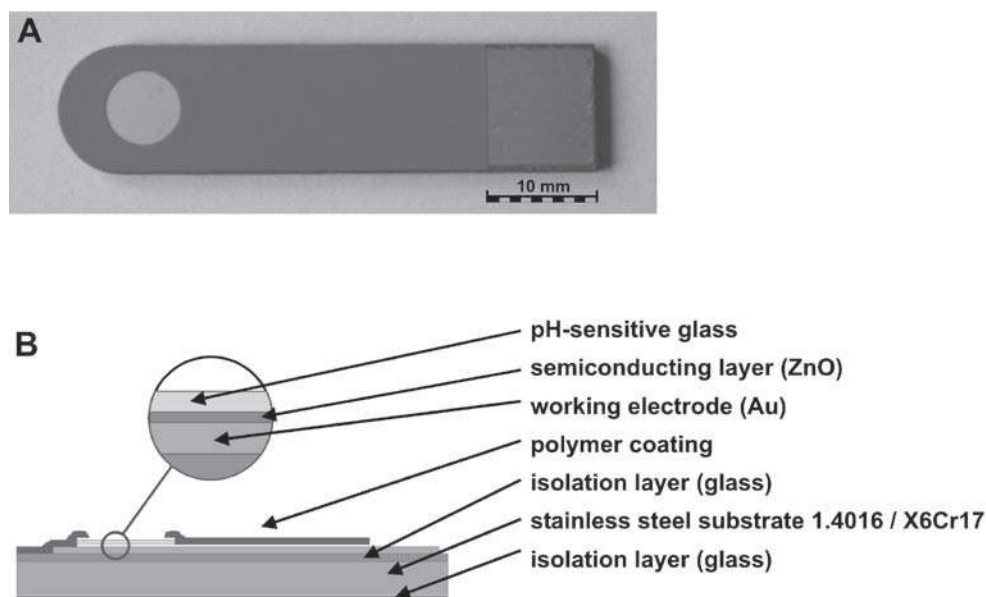
print with commercially available ceramic glasses, such as ESL 4924, ESL, King of Prussia, USA, leads to a sufficient insulation of the steel substrates.

Screen printing process was carried out by means of a semi-automatic screen printer (EKRA mat S30 (EKRA, Bönnigheim, Germany). The used sieve clothes applied on the sieve frame in a lining angle of 22.5° consisted of stainless steel. To generate close layers the technical thermal coefficients of expansion were adjusted and the paste formulations were optimised. The basic layer sequence is shown in Fig. 3B. On the prepared steel substrate several insulating glass layers were realised. A gold electrode and a gold contact pad (C5754, Heraeus, Hanau, Germany) were used for the signal conduction followed by a semiconducting

intermediate layer for the potential stabilisation and last but not least by the pH selective glass layer.

ZnO deposition was carried out electrochemically in a temperature-controlled measuring cell from an aqueous 0.1 mol/l $Zn(NO_3)_2$-solution at $j=-2$ mA/cm^2 for $t=$ 2.5 min and a temperature of $\vartheta=70$ °C. As reference electrode a saturated Ag/AgCl-electrode (SSE) and a platinum sheet as counter electrode were used. Simultaneously the gold electrode served as working electrode, and the conductive path of the thick film electrode was used for the current entry. During the electrochemical deposition the electrolyte was stirred with a magnetic stirrer.

Especially for the pH glasses a paste development was necessary to fabricate highly sensitive and at the same time

Fig. 4 XPS analysis of conventionally fabricated glass membrane and of a thick film glass membrane consisting of 72 wt% SiO_2, 24 wt% Na_2O and 6 wt% CaO
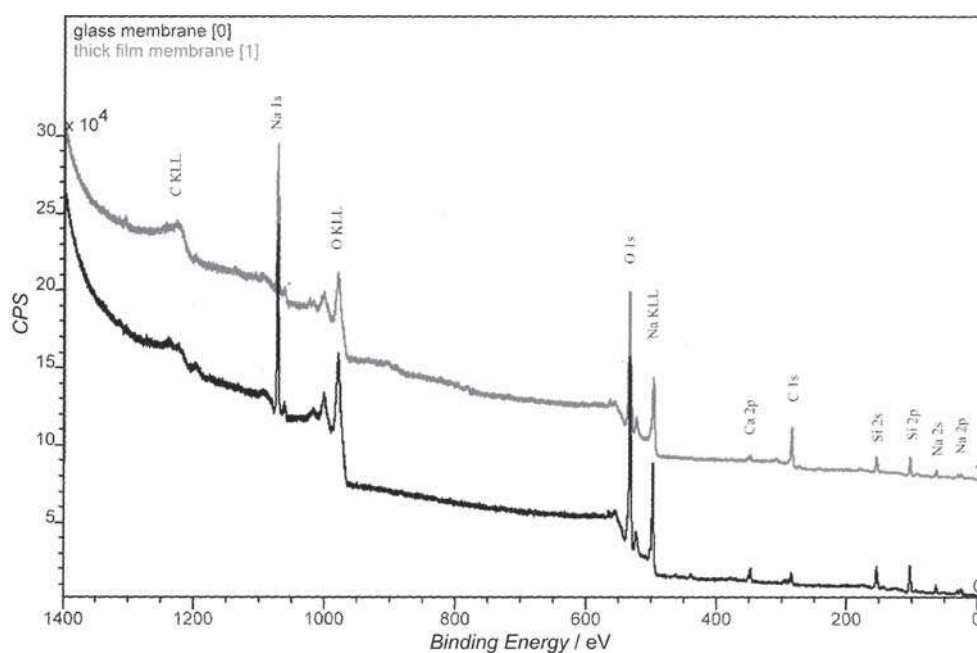
compact glass layers. From former projects [32] the demand for anhydrous systems was known, because pH glasses can change their structure due to glass corrosion and to the large specific surface of finely ground powders, which often leads to an impairment of pH sensitivity. The different layers of glass components during the optimisation process of pH sensitive glasses were characterised by means of X-ray photoelectron spectroscopy (XPS). The evidence of the identity of chemical compositions of membrane materials made by the glassblower and fabricated in thick film technology, which is important for the comparability of measured data, is provided in Fig. 4. Electrode and contact pads were masked by a polymer coating (ESL 242, ESL, King of Prussia, USA).

Structural and electrochemical characterisations

The structural properties of the ZnO and NiP films were studied using scanning electron microscopy (SEM) (QUANTA 200, FEI, Hillsboro, USA), XPS (SAGE HR 100, Specs, Berlin, Germany) and Atomic Force Microscopy, AFM (PicoSPM, Molecular Imaging, Phoenix, USA). For differential thermal analysis (DTA) the system Setsys 12 (Setaram, Caluire, France) was applied. The electrochemical and the sensor properties, respectively, were measured with a pH meter 764 Multi-Calimatic (Knick, Berlin, Germany). As reference system a saturated silver/silver chloride electrode (SSE) and for the determination of electrode resistances by electrochemical impedance spectroscopy (EIS) an electrochemical workstation Zahner IM6 (Zahner-Elektrik, Kronach, Germany) were used.

Results and discussion

Glass electrode with metallic coating on the inside

The zinc oxide films deposited by ultrasonic spray pyrolysis from a zinc acetate starting solution inside a glass electrode were characterised by AFM and XPS. Figure 5 shows an AFM shooting of a homogeneous 100-nm-thick ZnO layer created by fivefold deposition for 5 min each. The crystal structure can be clearly seen.

X-ray photoelectron spectroscopy investigations indicate with bond energies of $Zn2p_{3/2}$, $E_b=1022.4$ eV and $O1s$ $E_b=530.9$ eV the formation of zinc oxide. A DTA analysis with a scan rate of 1 K/min of the thermal conversion of zinc acetate to zinc oxide is shown in Fig. 6. The process can formally be described by Eq. 1.
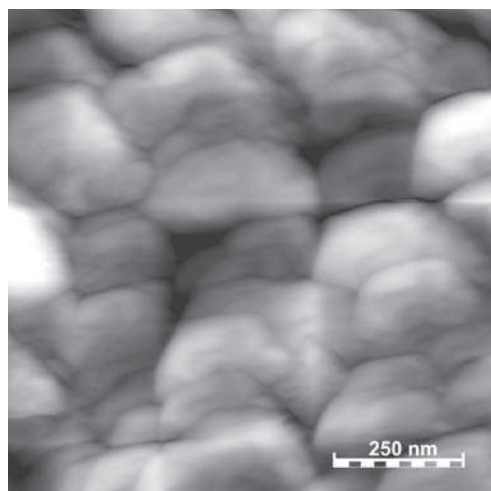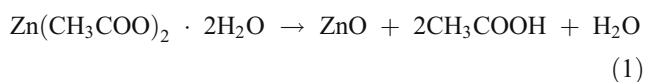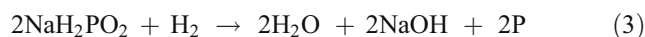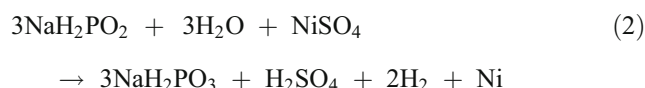
$$Zn(CH_3COO)_2 \cdot 2H_2O \rightarrow ZnO + 2CH_3COOH + H_2O \quad (1)$$

Fig. 5 2D-AFM-plot of the zinc oxide layer on top of the Corning 015 glass membrane (4 μm×4 μm×57 nm)

The currentless metallisation in a nickel sulfate electrolyte, which follows the activation of the surface in palladium chloride solution, leads to a deposition of a 200-nm-thick NiP film with a content of phosphorus of 8.5 at%, according to Eqs. 2 and 3.

$$3NaH_2PO_2 + 3H_2O + NiSO_4 \quad (2)$$
$$\rightarrow 3NaH_2PO_3 + H_2SO_4 + 2H_2 + Ni$$

$$2NaH_2PO_2 + H_2 \rightarrow 2H_2O + 2NaOH + 2P \quad (3)$$

With the tape test according to the German standard DIN 58196-6 [33] a very good adhesive strength of the rating K2 was found. Fig. 7 shows a photograph of the novel internally metallised glass electrode with zinc oxide as interface layer.
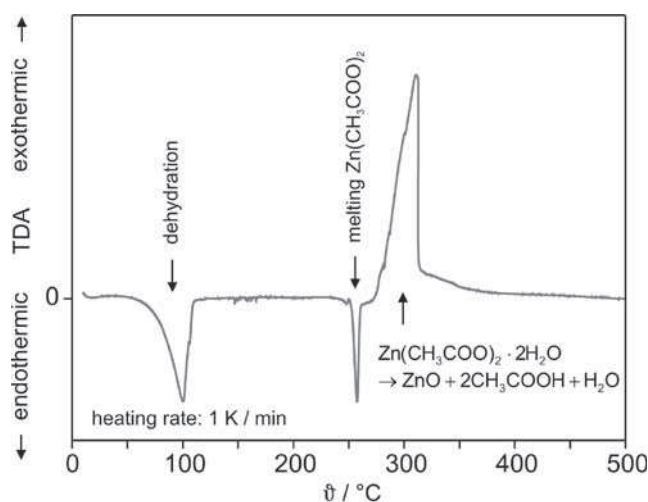

Fig. 6 DTA analysis of the zinc acetate dehydrate pyrolysis

The electrode function of the system NiP | ZnO | Corning 015 || test solution || SSE in different buffer solutions shows a linear dependency of the electrode potential on the pH value during a period of 2 months. The slope of 58 mV/pH at room temperature is in accordance with the Nernst equation and comparable with the values of glass electrodes with internal electrolytic solutions. The zero point of the measuring chains is in the optimum area of pH=7±0.5. After the preparation and after 185 days an unchanged electrode resistance of 300 MΩ was found.

Results of the investigation of response times of the novel glass electrodes are given in Fig. 8. With a t_{90} time of 17 s they are somewhat longer than those of conventional electrodes. This can be caused by a lower reaction rate (charge transfer until an adjustment of the thermodynamic equilibrium is achieved) through the interface solution | glass | ZnO | NiP. Zinc ions on interstitials are available as free charge carriers and thus as donators within the band gap of the n-type semiconductor ZnO [34].

These results of metallisation and electrochemical characterisation of pH selective electrodes based on Corning 015 glass show that an enhanced potential discharge by
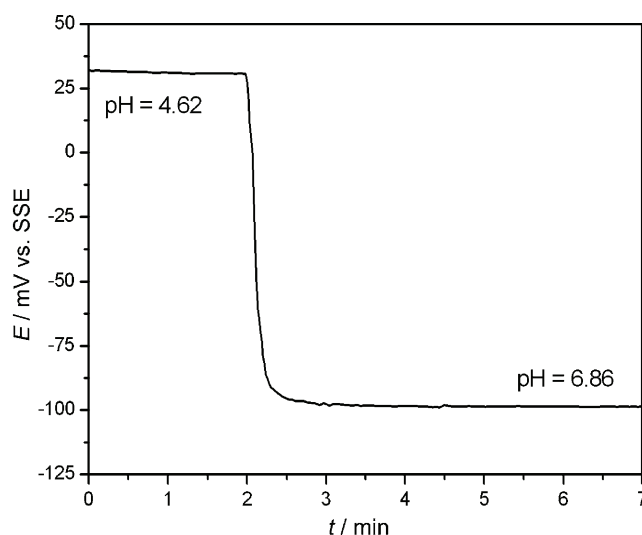

Fig. 8 Response time of the glass electrode at 25 °C

introducing a semiconducting interface layer of zinc oxide between electrode glass and NiP is technologically realisable and practically usable. It should be possible to use the novel internal discharge system also for other ion selective glass electrodes.

Flow-through electrodes with metallic coating on the outside

Investigations of the electrochemical behaviour of flow-through electrodes at $\vartheta=25$ °C show that they also can be used as potentiometric indicator electrodes for the pH determination. Figure 9 presents electrode functions of solid-state pH flow through cells in National Bureau of Standards (NBS) buffer solutions vs SSE. The measurement range of all tested electrodes with solid contact runs
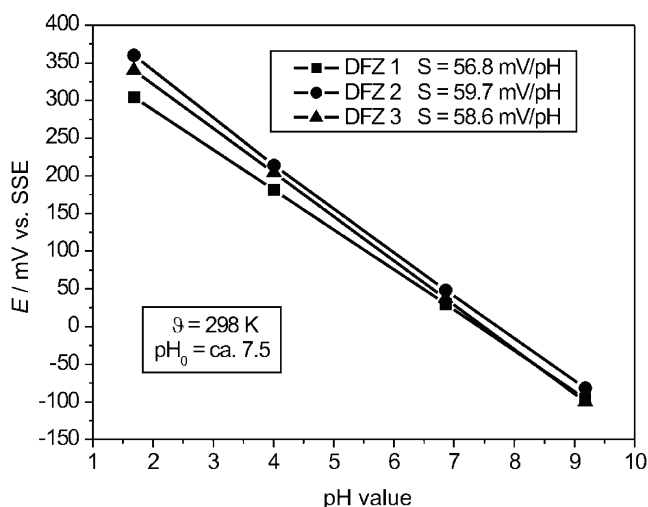

Fig. 7 Picture of the new glass electrode with internal metallic coating

Fig. 9 Electrode function at room temperature of solid-state pH flow-through measuring cells with NiP layer vs SSE

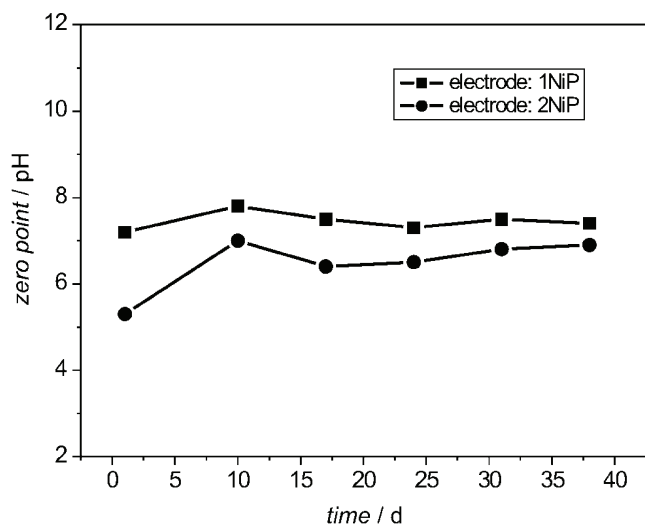**Fig. 10** Zero points of solid-state pH flow-through measuring cells at room temperature vs SSE depending on time

Fig. 12 Long-term behaviour of slopes of pH thick film electrodes vs SSE at room temperature

from pH=1 to pH=9 with a slope of dE/dpH=−56...−59 mV/pH.

By installing the mixed conducting zinc oxide layer as electrical mediator between electronically conducting NiP discharge and electrolytically conducting pH glass membrane the zero point of the measuring chain was stable during a period of 40 days (Fig. 10). The zero points of the measuring chains were found between pH=6 and pH=8.

Planar solid-state glass electrodes in thick film technology

The newly developed thick film sensors were characterised electrochemically concerning their sensor properties (slope, zero point, internal resistance and long-term drift). From the responding behaviour in NBS buffer solutions the electrode
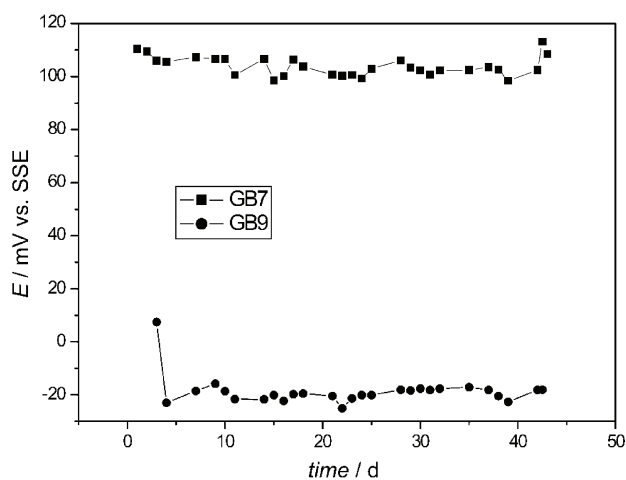
functions were determined similar to the procedure used for the cylindrical electrodes. The sensors showed Nernstian behaviour. After short running-in periods of about 10 min the sensors are ready for the measurement. A permanent storage in solutions, which is necessary for conventional glass electrodes, is not required for thick-film electrodes. However, they show a considerable variance of the values for the zero points, also within one and the same charge. This makes it problematic to apply the sensors with conventional pH measuring devices. On the other hand, potential changing over the time (Fig. 11), in part also caused by an alteration of reference electrodes, are small. Causation of these positive results compared to results from projects in the past was the consistent elimination of non-

Fig. 11 Drift measurements of two pH thick film sensors (GB7, GB 9) of one and the same fabrication charge without semiconducting interface layer in NBS-buffer of pH=6.86 vs SSE
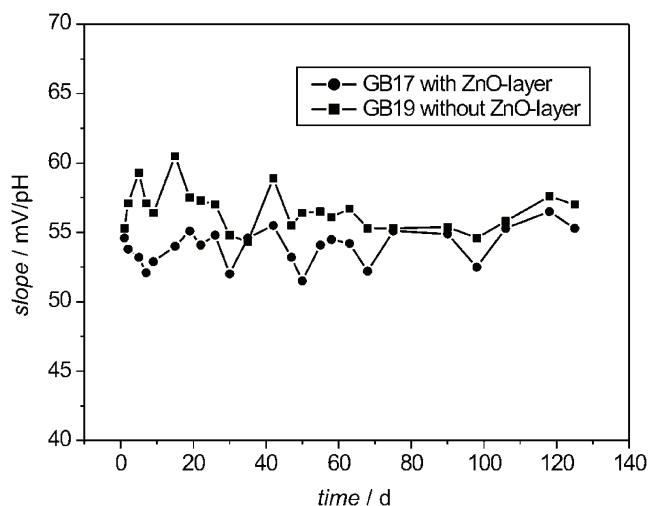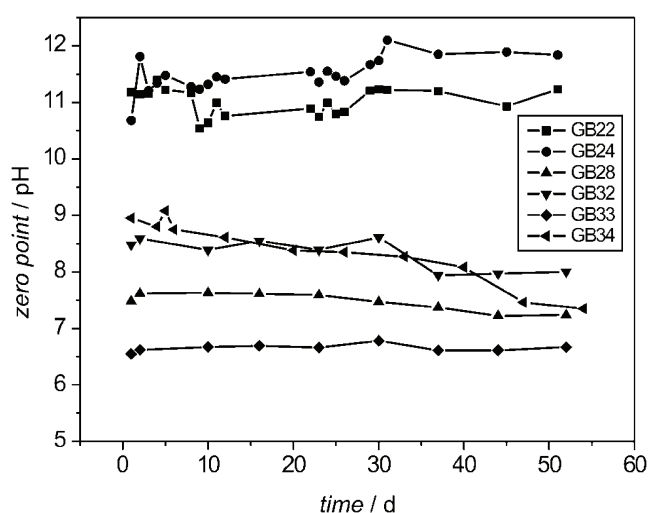

Fig. 13 Zero points of pH thick film sensors at room temperature vs SSE depending on time. Electrodes GB22, GB24—without ZnO-layer; electrodes GB32, GB34—coating at −2 mA/cm^2 for 10 min; electrodes GB33, GB28—coating at −2 mA/cm^2 for 2 min

glass-system components from the ion selective materials, especially concerning the paste preparation.

To reduce the broad distribution of the potentials of the thick-film electrodes, semiconducting zinc oxide layers were deposited on gold electrodes; the resulting sensors were also characterised electrochemically. The electrode function of pH electrodes in thick-film technology with and without ZnO layers was investigated over a period of up to 120 days (Fig. 12). The zinc oxide coating of the electrode GB17 in this figure was carried out electrochemically. Thereby it was shown that the integration of the mixed conducting ZnO layer has no significant influence on the slope of the thick-film electrode.

However, the existence of ZnO films as electrical mediator between electronically conducting gold discharge and ionically conducting pH glass membrane has a positive effect on stability and value of the zero points of the measuring chains (Fig. 13). The zero point of a pH measuring chain should be located preferably near pH=7. For the uncoated thick film electrodes (GB22 and GB24) it was found at pH values of 10 to 11. In addition, during a test period of 55 days it did not show a constant value. Using electrodes with ZnO layer leads to a zero-point shift to pH values of 8.5 to 6.5.

Likewise, the thickness of the metal oxide layer is of importance. Thus, the thick film electrodes, which have a ZnO layer with a thickness of about 50… 100 nm (GB28 and GB33, the electrochemical deposition was carried out at $j=-2$ mA/cm^2 in only 2 min), show higher potential stability during a period of 55 days and an appropriate zero point of the measuring chains in comparison with electrodes with thicker ZnO layers (GB32 and 34, 10-min deposition).

Conclusions

It can be shown that the insufficient electrochemical performance of internally metallised glass electrodes can be significantly improved if the electrodes contain ZnO layers in contact with selective glasses. The combination of electrolytically conducting glass and semiconducting zinc oxide leads to half-cells with reversible charge transfer. For the preparation of these indicator electrodes ultrasonic spray pyrolysis, spin coating and chemical deposition are possible procedures to obtain the ZnO layers. These should have a maximum thickness of 200 nm. Deposition of 200 nm NiP was found to be particularly suitable as a method for metallising the semiconducting layer in case of fabricating solid state glass electrodes in conventional design.

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