

Impedance investigations on heat-stressed, pH-sensitive glass membranes

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Abstract The behaviour of pH glass sensors is determined strongly by the kind and composition of glasses. For the heat stability, the kind and concentration of the alkaline oxide as modifier play an important role. It could be shown by potentiometric and impedimetric measurements that lithium oxide-containing glass membranes are much more stable than those with sodium oxide concerning the emf of the electrochemical cell. They tolerate several 5-h heat treatments at temperatures of 100°C. The impedance plots show differences in electrochemical kinetics between both glass membranes, which can be caused by different leaching due to differences in ionic radii of Li^+ and Na^+ , respectively.

Keywords Impedance · Heat · Glass membranes

Introduction

For ion-selective electrodes [1], single [2] or poly crystals [3] of hardly soluble salts, immobilized organic compounds [4–6], and different glasses [7] are used as materials for the indicator electrode. Practically important materials of the last group concern chalcogenid [8] and silicate glasses [9], which are used mainly for pH determination [10]. The sensing mechanism was described in principle already in 1906 [11]. The Mac Innes or CORNING 015 glass, one of the first glasses used for pH measurements and one of the few with published composition, contains 72 wt-% SiO_2 , 22 wt-% Na_2O , and 6 wt-% CaO [12]. The first pH glass

electrodes offered by the former company Corning Glass International (today: CORNING Inc., CANTON, NY) in 1930 were based on this glass. Since then, a variety of investigations has been made to improve the properties of the glasses by optimization of the glass compositions according to the application conditions [13]. The main topics were as follows:

- adjustment of the thermal expansion coefficient to that of the shaft glass,
- improvement of the glass blowing processibility, nowadays also with respect to the automation of the glass blowing process,
- decrease of the specific electrical resistance for electrode applications at low temperatures and to improve the mechanical membrane stability by increasing membrane thickness,
- improvement of the corrosion stability at extreme application conditions (strongly acidic or alkaline solutions, high temperature, long-term application)
- broadening of the measuring range,
- improvement of the selectivity against other ions.

The majority of experiments for optimizing the glass composition can be characterized as empirical. Nevertheless, it was found out relatively early that sodium oxide-containing glasses show the so-called alkaline error, which can be utilized also advantageously to fabricate sodium ion-sensitive electrodes [14]. In contrast to that, lithium oxide starts to substitute sodium oxide as the network modifier in pH glasses since the early 1940s of the last century. Today, both alkaline oxides can be found in commercial glass membranes as mixtures or alone. Novel admixtures with significant effects on the electrode properties contain small amounts of oxides of lanthanum, neodymium, uranium, niobium, and titanium. More recently, we reported on the long-term behaviour of

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Table 1 Components of the investigated glasses

Glass no.	Components	Thermal expansion coefficient (α)/K ⁻¹
1	SiO ₂ , Na ₂ O, CaO, UO ₃	11.5 10 ⁻⁶
2	SiO ₂ , BaO, Li ₂ O, UO ₃ , SnO ₂ , TiO ₂ , PbO, Cs ₂ O	9.50 10 ⁻⁶

sodium and lithium oxide-containing glass membranes [15]. It could be shown that the electrode function of lithium-containing glass electrodes was less influenced during the heat treatment and long-term experiments than that of the sodium oxide-containing electrodes. This observation was supported by the results of impedance investigations, which show a stronger leaching process in case of sodium oxide-containing glasses.

In this article, we report the results of impedance investigations on sodium or lithium oxide glass membranes with modified compositions under heat stress to characterize the corrosion process of the glass membranes at higher temperatures.

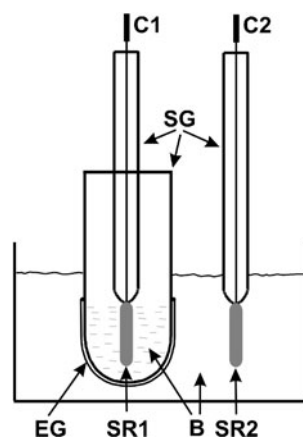
Experimental

Preparation of the glass membranes

For the investigation, two glasses with different compositions were prepared by mixing the corresponding oxides and carbonates in a ball mill. The glasses were melted in a covered platinum crucible at temperatures between 1,300°C and 1,400°C. The two glasses were prepared as bars from the slowly cooling melt. The linear thermal expansion coefficient was determined by means of a dilatometer (DIL 402 C, Erich NETZSCH GmbH & Co. Holding KG, Selb, Germany) in the temperature range between 20°C and 300°C (Table 1).

Further investigations were carried out on fingertip-formed membranes fused on shaft glass pipes. The electrode bodies were filled with buffer solution (pH 6.86+1 mol/L KCl) according to the National Bureau of Standards (NBS) which is also recommended by Deutsches Institut für Normung (DIN) [16] and contain an Ag/AgCl contact electrode (Fig. 1). The

Fig. 1 Setup for impedance and pH sensitivity measurements on glass electrodes. C1, C2: electric connectors; SG: shaft glass; EG: electrode glass; b: buffer solution + 1 molL⁻¹ KCl; SR1, SR2: Ag/AgCl reference electrodes



outer contact was provided by an electrode with identical construction without junction.

Characterization of the glass electrodes after heat treatments

The glass electrodes were treated cyclically at 100°C (5 h per cycle) in an NBS buffer solution (pH 6.86+1 mol/L KCl) for 35 h totally. Between each treatment, the electrode function was measured (see Section [Impedance investigations](#)).

Impedance investigations

The characterization of the corrosion state was carried out at 25°C after respective treatment in hot buffer solution (NBS standard, pH 6.86+1 mol/L KCl). Two silver chloride electrodes C1 (inner) and C2 (outer) were used in a symmetric arrangement. Additionally, the pH sensitivity was measured at 25°C in NBS standard buffer solutions (pH 4.01, 6.86, and 9.18, $c(\text{KCl})=1$ mol/L) between the heat treatments. The electrode function was calculated from these values by linear regression.

Results and discussion

Figures 2 and 3 show the results of investigations for pH-sensitive glasses no. 1 and 2 at $\vartheta=25^\circ\text{C}$ before and after heat treatment. In the plots, one depressed semicircle can be seen for fresh glass electrodes (Fig. 2, curve 1) and after heat treatment (curve 2). The Nyquist plots obtained for glass no. 1 show only a slight dependence on the heat treatment. The impedance increases slightly after each heat treatment but only at a small extent of approximately 25%. The effect of an increasing modulus of impedance can be shown more strikingly after a heat treatment of glass no. 2 (Fig. 3). For this glass, the modulus of impedance increases

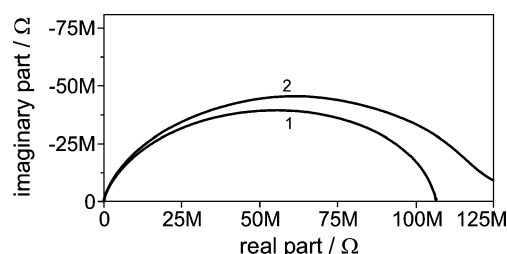


Fig. 2 Nyquist plots for measurements on glass no. 1. Curve 1: initial state; curve 2: after 23 h of buffer exposure with heat treatment

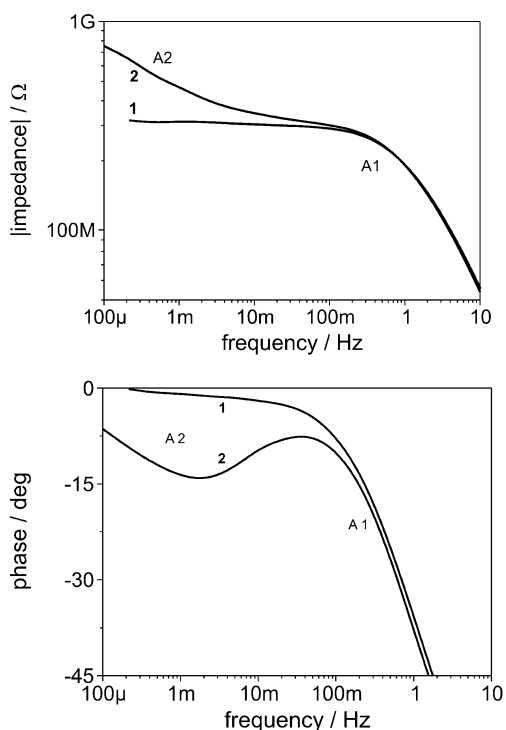


Fig. 3 Bode plots for measurements on glass no. 2. Curve 1: initial state; curve 2: after 23 h of buffer exposure with heat treatment. A1: range containing elements (R1//Cv1). A2: range containing elements (R2//Cv2) formed after heat treatment

markedly by approximately 135%. During exposure to the solution, a second region A2 is formed (to be seen in the low frequency range of the Bode plot). This suggests that the region A1 can be attributed to the bulk resistance, while the region A2 corresponds to the resistance of the surface layer of the glass. This behaviour is in agreement with the well-known five-layer model of the glass electrode [17].

The electrical behaviour of the glass electrode can be modelled by an equivalent circuit (R1//Cv1+R2//Cv2). The subcircuit (R1//Cv1) is attributed to the range A1 and (R2//Cv2) to that of A2, respectively. According to the model, the values for the parameters R, Cv, and e were calculated [18]. The parameter e, typical for electrochemical systems, is an exponent of Cv, which takes the nonideal behaviour of the capacity into account.

The R1, the Cv1, and the e1 values of glass no. 2, given in Table 2, are constant before and after heat treatment. The

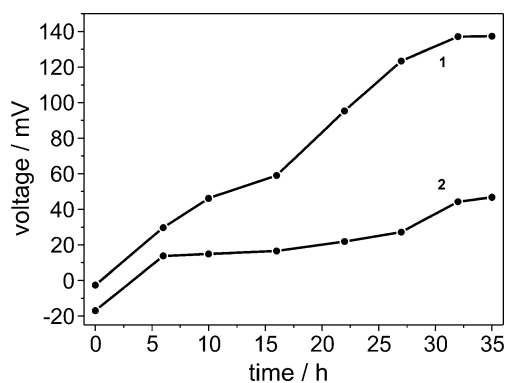


Fig. 4 Emf at pH 6.86 as a function of time of heat treatment. Curve 1: glass no. 1; curve 2: glass no. 2

region A2 is formed with increasing time of heat treatments. The surface layer resistance increases drastically and is much higher than the bulk resistance. On the other hand, the capacity increases also. That means, the thickness of the phase boundary layer is reduced. The e2 value (e2=0.75) is lower than that of a fresh electrode. This can be interpreted as an enhancement of inhomogeneity in the layer (Table 2).

The effect of heat treatment can also be reached by a long-term application at normal temperature. Therefore, the heat treatment can be regarded as an accelerated lifetime test [15].

In Fig. 4, the emf obtained by electrode function for pH 6.86 is plotted as a function of the duration of heat treatment at 100°C. In the case of sodium ion-containing glass no. 1 (curve 1), the drift of the emf after heat treatment is 140 mV, and for lithium ion-containing glass no. 2 (curve 2), it is 64 mV. As expected, these results show that lithium ion glasses are more stable against heat treatment than sodium ion glasses.

More recently, it could be shown on sodium and lithium ion-containing glasses with other compositions that the long-term application causes similar effects [15]. These corrosion phenomena were also described by Bachmann [19]. It seems to be that as compared to the sodium ion glass, the thicker leaching layer is a better buffer and stabilizes the condition for electrochemical reaction.

The solubility of the glass as well as the electric conductivity of sodium ion-containing glasses (glass no. 1) is higher than those of lithium ion glass (glass no. 2). This is in agreement with results reported in the literature

Table 2 Values of the circuit parameters for the circuit elements obtained by regression for glass no. 2

Exposure, time (h)	Fig.2, curve	Bulk resistance			Surface layer resistance		
		Range A1			Range A2		
		R1, (MΩ)	Cv1, (pF)	e1	R2, (MΩ)	Cv2, (pF)	e2
0	1	295	450	0.93	–	–	–
23	2	300	470	0.92	700	215,000	0.76

[20]. That is also the reason for higher deviation of the electrode function in the case of sodium ion-containing glass due to the heat treatment.

As compared to the sodium ion, the lower mobility of the lithium ions retards the leaching of lithium ions and their transport into the solution. Instead of that, an additional phase layer is formed on the surface of the glass, which could be confirmed by our impedance investigation. This phenomenon leads to a limited extension of the lifetime of the glass electrode. The heat treatment has the same effect on the glass as the long-term strain, which we reported more recently [15].

Conclusions

It is well known that heat stress changes the performance of pH glass electrodes. Due to corrosion drifting electrode function, prolonged response times and higher electrode resistances result from this treatment. These alterations depend on the duration of the heat treatment and can be monitored by impedance measurements on fresh and aged glass membranes. Differences in aging of sodium and lithium ion-containing glasses can be precisely monitored by this method. The total electrode resistance of sodium-containing glasses changes only slightly during the heat treatment. That of the lithium-containing glasses can be split into two parts concerning the bulk and the surface layer, respectively. Only the surface layer resistance increases with heat treatment. Regarding the glass composition, the extent of glass corrosion and the single steps of the corrosion process can be studied by analysis of the impedance plots.

Furthermore, a correlation exists between the amount of drift of the electrode function $E=f(\text{pH})$ after heat stress and

the glass composition. Concluding all, it could be confirmed that pH-selective glasses containing lithium instead of sodium are more stable against heat stress and also during long-term contact with the analyte.

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