Chapter 5
Glass Electrodes

This chapter is devoted to glass electrodes for the pH and metal ion measurements, as well as to RedOx-sensitive glass electrodes.

5.1 Materials of the Glass Electrode Membranes

Ion-selective electrodes with glass membranes are the oldest [1–5] (see also Sects. 1.2–1.4) and until now the most frequently used among other ISEs. This is because glass electrodes are by far the best sensors of the pH, and the pH is the most frequently measured parameter of the chemical composition of various types of samples. Besides measurements of the pH, measurements of activities of several metal cations (in the first place—Na^+) can also be performed with the respective glass electrodes.

Silicon dioxide (SiO_2) is the main component of the electrode glasses. Silicate glass membranes are very stable against aggressive chemicals like concentrated acids (except of HF) or organic solvents. Therefore, electrodes with glass membranes can be used under harsh conditions, including those in chemical and biochemical industries. Phosphoric glasses are also known but only seldom in use because these kinds of glasses are relatively soluble in water and therefore unstable in most real applications.

Although glasses are amorphous, a short-range ordering exists in glass membranes. In quartz, silicon dioxide forms tetrahedral lattice. A similar although less regular structure is characteristic also for the electrode glasses. As shown in Fig. 5.1, oxygen atoms are of two types: bridge and non-bridge atoms. The former are bound to two silicon atoms, the latter to only one silicon atom, while the other is a metal atom. The metal atoms in the structure originate from the respective metal oxides: Li_2O, Na_2O, and K_2O. Electrode glasses are always doped with some of these metal oxides because pure SiO_2 is non-conducting. Metal oxides are introduced into melted silicon dioxide, and the whole melt has to be cooled fast in order to maintain in the hard glass the uniform distribution of the components, which is characteristic of the melted oxide mixture.

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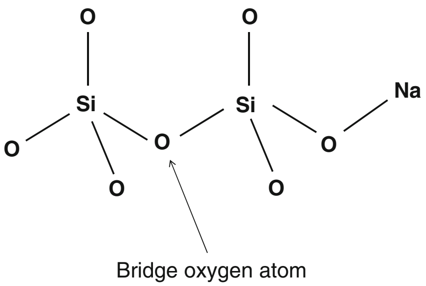

Fig. 5.1 Silicon dioxide tetrahedral lattice in glass. Most of oxygen atoms are bound to silicon atoms (*bridge oxygen atoms*), but some of oxygens are bound to a silicon atom and to a metal atom

When a glass membrane is in contact with an aqueous solution, water molecules enter glass and attack Si–O and also O–M bonds in ≡Si–O–Si≡ and ≡Si–O–M fragments. Hydrogen atoms partly replace silicon and metal atoms, producing ≡Si–O–H groups. These groups, in turn, are subjects for the water molecule attack as well and undergo the hydrolysis process, resulting in ≡Si–O^- groups and H_3O^+ ions released into solution, see Fig. 5.2. These both processes are reversible (this feature is not shown in Fig. 5.2 to avoid overloading) and govern the glass electrode response to pH and metal cations.

The respective ion-exchange sites in glass are represented by $(SiO_{3/2})O^-$ groups: the products of the partial dissociation of the ≡Si–O–H and Si–O–M groups. The ≡Si–O–H bond is much more covalent than the ≡Si–O–M bond. Therefore, hydrogen atoms are strongly preferred by the glass phase. This is why electrodes with membranes made of binary glasses containing only SiO_2 and Na_2O or Li_2O (the typical compositions are 22 mol % Na_2O, 78 mol % SiO_2 and 27 mol % Li_2O, 73 mol % SiO_2) show Nernstian response to the pH in an enormously broad range: from pH 1 to pH 9. Some multi-component glasses allow for pH measurements from pH − 1 to even 14, but in this case, the alkaline pH is adjusted by means of bases with large organic cations.

Some compositions of the pH-selective glass membranes are presented in Table 5.1, composed on the basis of a similar table by Belyustin [6]. As one can

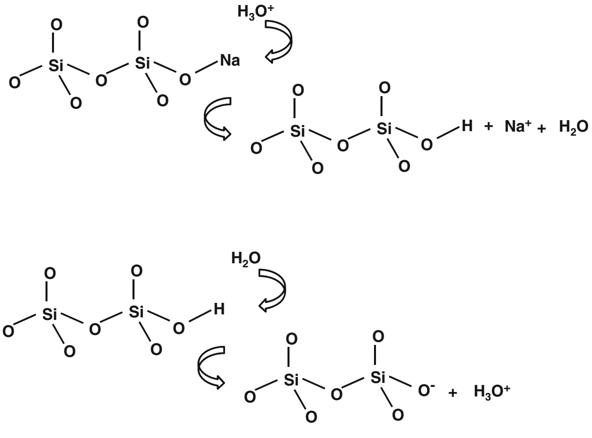

Fig. 5.2 Schematic illustration of the ion-exchange process (*top*) and the hydrolysis process (*bottom*)

Table 5.1 Compositions of glasses for the pH electrodes

Marking	Composition	Author, year, reference
Sodium silicate glasses (*wt. %*)		
"Hughes's glass"	20 Na_2O–8 CaO–72 SiO_2	Hughes 1928 [37]
McInnes and Dole glass, Corning 015	22 Na_2O–6 CaO–72 SiO_2	MacInnes, Dole 1929, 1930 [38, 39]
Lithium silicate glasses (*mol %*)		
LiCa	18.1 Li_2O–9.6 CaO–72.3 SiO_2	Sokolov, Passinskii 1932 [40]
LiBa	26 Li_2O–3.6 BaO–70.4 SiO_2	Avseevich 1938–1948 [41, 42]
LiMg	26.5 Li_2O–12.3 MgO–61.2 SiO_2	
LiCa	25 Li_2O–7 CaO–68 SiO_2	Cary, Baxter 1949 [43]
	Li_2O–Cs_2O–La_2O_3–SiO_2	Perley 1948, 1949 [44, 45]
Present day glasses for pH electrodes	21–33 Li_2O, 2–4 Cs_2O, 3–5 La_2O_3 (Nd_2O_3, Er_2O_3), 2–4 CaO (BaO)–SiO_2 (the rest)	Manufacturers all over the world

see, a large variety of the pH glass membrane compositions have been invented already by 1950s. Besides SiO_2 and Na_2O (Li_2O), glass membranes contain also alkaline earth metal oxides. More recent progress has been motivated by the success of the Perley's glass and relies on doping glass membranes with rare earth metal oxides.

Addition of Al_2O_3 or B_2O_3 to an electrode glass composition causes significant changes in the electrode selectivity. Qualitatively, the same kind of processes like those taking place with the ≡Si–O–H and Si–O–M groups also takes place with =Si–O–Al–H, =Si–O–B–H, and =Si–O–AlM, =Si–O–B–M groups: ion exchange and hydrolysis. However, quantitatively the situation is very different. Aluminum and boric hydroxides (when tetra-coordinated) are relatively strong acids, and glasses containing these dopants show dramatically lower selectivity to hydrogen ions than glasses for the pH control. This makes possible using the respective electrodes for measuring metal ion activities in solutions. However, the excess of the metal ions over hydrogen must be about 1,000; otherwise, the electrode responds to pH. Examples of the compositions for some metal cation sensing glass membranes are given in Table 5.2, composed on the basis of [6].

Kiprianov added halogen (fluoride) as LiF (up to 3.5 %) to the glass compositions [7, 8]. The resulting melts are less viscose, which is technologically advantageous. The selectivity to K^+ ions and the chemical robustness of the electrodes are improved as compared to the ISEs without fluoride in membranes.

Not only the surface of the glass undergoes hydration process. In fact, hydration spreads into the glass phase forming the so-called hydrated surface layers. There are two main types of surface layers: (1) a layer with smooth profile with a steep gradient of the metal (e.g., Na) concentration starting from the very glass/solution

Table 5.2 Compositions of glasses for metal ion sensing

Marking, target ions	Composition (mol %)	Author, year reference
Sodium (potassium) silicate glasses		
Schott, Na^+, K^+, Ag^+	Na_2O–B_2O_3–Al_2O_3–SiO_2 + additives	Horovitz, Schiller 1923–1925 [46, 47]
D_a and its options, Na^+	(11–25) Na_2O–(9–12) B_2O_3–(3–5) Al_2O_3–SiO_2 (the rest)	Schultz et al. 1953–1955 [48, 49]
Potassium analogs of D_a	(15–25) K_2O–(9–12) B_2O_3–(3–5) Al_2O_3–SiO_2 (the rest)	Schultz et al. 1955–1958 [50, 51]
NAS-1118, Na^+	11 Na_2O–18 Al_2O_3–71 SiO_2	Eisenman, since 1957, [52, 53]
NAS-2704, K^+	27 Na_2O–4 Al_2O_3–69 SiO_2	Eisenman, since 1957, [52, 53]
ESL-51, Na^+, Gomel Instrumentation Factory, Belarus	24 Na_2O–5 B_2O_3–9 Al_2O_3–62 SiO_2 and 21 Na_2O–3 B_2O_3–12 Al_2O_3–64 SiO_2	Schultz et al. [54]
Lithium silicate glasses		
39278, Na^+	26.2 Li_2O–12.4 Al_2O_3–61.4 SiO_2	Beckman [55]
BH-67A, Na^+	Li_2O–Al_2O_3–SiO_2	Electronic Instruments Ltd., UK [56]
ESL-10, Na^+, $^+$, Gomel Instrumentation Factory, Belarus	16 Li_2O–8 Al_2O_3–76 SiO_2	Belyustin et al. [57]

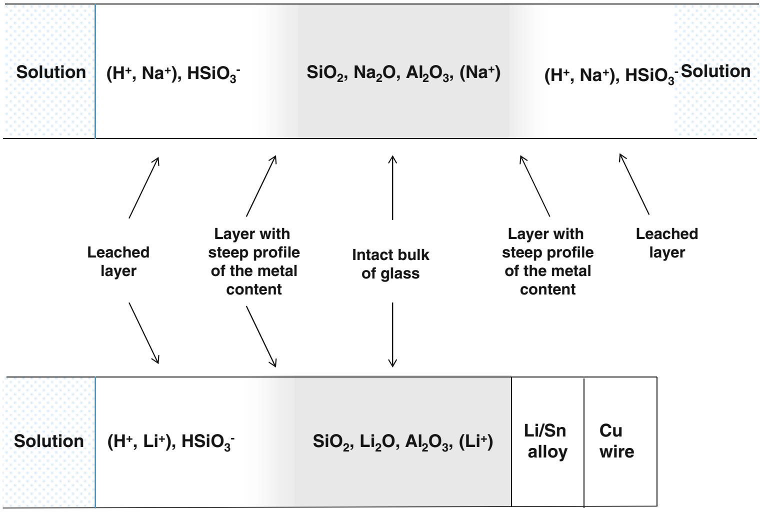

Fig. 5.3 Glass membranes of a classical glass electrode (*top*) and a solid-contact glass electrode (*bottom*). Species ensuring the conductivity are shown in parenthesis; the thickness of the surface layers is exaggerated for clarity

boundary and (2) a layer containing a relatively lengthy leached layer (5–100 nm in Li-glasses and up to 2–3 mcm in Na-glasses), with an underlying layer with a steep gradient of the metal concentration. These layers formed in a membrane of a classical glass electrode with internal solution, and that in a solid-contact glass electrode, are shown schematically in Fig. 5.3. For the discussion of solid-contact ISEs, see Sect. 8.2.

The conductivity of glasses is of ionic in nature, due to the diffusion of H^+ and Na^+ (Li^+) ions in the leached layers and Na^+ (Li^+) ions in the intact bulk of the glass membrane. Special type of glasses—electronically conducting glasses—is briefly discussed in Sect. 5.3.

5.2 The Theories of the pH and Metal Ion Glass Electrode Response and Selectivity

5.2.1 *The Nikolsky "Simple" Theory*

The so-called simple theory has been proposed by Nikolsky already in 1937 [3]. Below, we will briefly describe this theory like it was done by Nikolsky himself. The theory was aimed at rationalization of the following experimental observations, well established by that time:

1. glass electrodes show linear response to pH with the slope close to Nernstian value in a broad pH range:

$$\frac{\mathrm{dE}}{\mathrm{dpH}} \approx -\frac{\mathrm{RT}}{F} \tag{5.1}$$

2. the response deviates from linearity at high pH values (in alkaline region)
3. the magnitude of the deviations in alkaline region depends on the composition of glass
4. anions do not interfere with the electrode potential.

Observation (3) deserves special consideration. Table 5.1 provides with some details on this observation. One can see that the interference from an ion is determined by the ion's size. Glasses doped with lithium oxide, that is, the oxide of the smallest metal among other metals, suffer significant interference only from the lithium ion, while larger ions sodium and potassium show low interference. Glasses doped with sodium oxide discriminate K^+, but Li^+ and Na^+ interfere with the pH response. Now, glasses doped with potassium oxide discriminate only rather large cations like barium and tetraethylammonium. These facts suggest that the ability of an ion to interfere depends on its ability to enter the glass phase and replace the metal dopant atom in the membrane structure. This is nothing else as

Table 5.3 Dependence of the cation interference with the glass electrode response to pH on the nature of the metal oxide in the membrane

Metal oxide	Interfering ions	Discriminated ions
Li_2O	Li^+	Na^+, K^+
Na_2O	Li^+, Na^+	K^+
K_2O[a]	Li^+, Na^+, K^+	Ba^{2+}, Et_4N^+

[a] Nowadays, this kind of glasses is not in use for the pH measurements

ion-exchange process between the two phases: solution and membrane (Table 5.3).

By the mid-1930s, it was also known that glass electrodes are low polarizable. This suggests fast charge-transfer process at the membrane/solution interface. Thus, the ion-exchange process which makes possible the interfacial charge transfer must also be fast and must reach equilibrium within a short time period after the phases are put into contact.

In principle, adsorption of ions at the membrane surface could result in similar effects. However, according to the Freundlich equation describing the potential effect of ion adsorption, the electrode should respond as below:

$$\frac{\mathrm{dE}}{\mathrm{d}\ln C_H} = \left(1 - \frac{1}{n}\right)\frac{\mathrm{RT}}{F}. \tag{5.2}$$

Given the factor $1/n$ in Eq. (5.2) is normally about 0.6, the adsorption theory predicts the response with a half-Nernstian or even lower slope which is not confirmed by the experimental data.

Based on these considerations, Nikolsky assumed that the main reason for the glass electrode response to the pH is ion exchange at the membrane/solution interface, and the selectivity of this response originates from large shift of the respective equilibrium, see Eq. (5.3), in favor of hydrogen ions. The formal apparatus of the Nikolsky "simple" theory is presented below.

It is assumed that the interfacial ion exchange takes place and reaches equilibrium:

$$\mathrm{Na}^{+,\mathrm{glass}} + \mathrm{H}^{+,\mathrm{aq}} \leftrightarrow \mathrm{Na}^{+,\mathrm{aq}} + \mathrm{H}^{+,\mathrm{glass}} \tag{5.3}$$

Then, one can easily obtain for the boundary potential:

$$\begin{aligned} F\left(\varphi^{\mathrm{glass}} - \varphi^{\mathrm{aq}}\right) &= \mu_{\mathrm{H}^+}{}^{0,\mathrm{aq}} - \mu_{\mathrm{H}^+}{}^{0,\mathrm{glass}} + \mathrm{RT}\ln\frac{a_{\mathrm{H}^+}{}^{\mathrm{aq}}}{a_{\mathrm{H}^+}{}^{\mathrm{glass}}} \\ &= \mu_{\mathrm{Na}^+}{}^{0,\mathrm{aq}} - \mu_{\mathrm{Na}^+}{}^{0,\mathrm{glass}} + \mathrm{RT}\ln\frac{a_{\mathrm{Na}^+}{}^{\mathrm{aq}}}{a_{\mathrm{Na}^+}{}^{\mathrm{glass}}}. \end{aligned} \tag{5.4}$$

The equilibrium constant of the ion-exchange reaction (5.3) is as follows:

$$K_{\mathrm{H/Na}}{}^{\mathrm{exch}} = \exp\left(\mu_{\mathrm{H}^+}{}^{0,\mathrm{glass}} - \mu_{\mathrm{H}^+}{}^{0,\mathrm{aq}} + \mu_{\mathrm{Na}^+}{}^{0,\mathrm{aq}} - \mu_{\mathrm{Na}^+}{}^{0,\mathrm{glass}}/\mathrm{RT}\right) = \mathrm{Const}. \tag{5.5}$$

Next comes the assumption which Nikolsky himself considered as obvious: The sum of the concentrations (or that of the mole fractions of hydrogen and the metal ions) is constant and equals that of R^{-1} ion-exchange sites in glass:

$$N_0 = N_{H^+} + N_{Na^+}. \tag{5.6}$$

With full respect to Nikolsky, the author of this book does not consider this obvious. This assumption is true for the respective total values: total sites, total hydrogen, and total sodium (or other metal), whatever in associated forms, HR and NaR, or in ionic forms, R^-, H^+, and Na^+. When referred to only ionic forms, Eq. (5.6) is only true if the dissociation degrees of HR and NaR ion pairs are always equal. The latter suggests either equal dissociation constants of HR and NaR, which is hardly true, or very high dissociation constants of both HR and NaR so that the ionic forms strongly predominate over the associated forms. Otherwise, N_0 varies along the ion-exchange process. Anyway, assuming Eq. (5.6) is true, we obtain for the ratio of the cation activities in the glass phase:

$$\frac{a_{Na^+}{}^{\text{glass}}}{a_{H^+}{}^{\text{glass}}} = \frac{N_{Na^+}}{a_{H^+}{}^{\text{glass}}} = \frac{N_0 - N_{H^+}}{a_{H^+}{}^{\text{glass}}} f_{Na^+}{}^{\text{glass}} = K_{H/Na}{}^{\text{exch}} \frac{a_{Na^+}{}^{\text{aq}}}{a_{H^+}{}^{\text{aq}}}. \tag{5.7}$$

Here, $f_{Na^+}{}^{\text{glass}}, f_{H^+}{}^{\text{glass}}$ stand for the Na^+ and H^+ ion activity coefficients in the glass phase. Assuming both these values are equal to 1, that is, activities in the glass phase are replaced with the respective concentrations, we get

$$\frac{a_{H^+}{}^{\text{aq}}}{a_{H^+}{}^{\text{glass}}} = \frac{a_{H^+}{}^{\text{aq}} + K_{H/Na}{}^{\text{exch}} a_{Na^+}{}^{\text{aq}}}{N_0}. \tag{5.8}$$

The combination of Eqs. (5.4) and (5.8) yields

$$\left(\varphi^{\text{glass}} - \varphi^{\text{aq}}\right) = \frac{\mu_{H^+}{}^{0,\text{aq}} - \mu_{H^+}{}^{0,\text{glass}}}{F} + \frac{RT}{F} \ln \frac{a_{H^+}{}^{\text{aq}} + K_{H/Na}{}^{\text{exch}} a_{Na^+}{}^{\text{aq}}}{N_0}. \tag{5.9}$$

Now, we can write for the emf of a galvanic cell containing the glass electrode and a suitable reference electrode as shown in the equation below:

$$E = E^0 + \frac{RT}{F} \ln\left(a_{H^+}{}^{\text{aq}} + K_{H/Na}{}^{\text{exch}} a_{Na^+}{}^{\text{aq}}\right) \tag{5.10}$$

Equation (5.10) is the well-known Nikolsky equation. Equations by form the same as the one derived in [3] are the most frequently used in the ISE theory and practice, whatever is the nature of the membrane. However, the physical meaning of the selectivity coefficient (the parameter $K_{H/Na}$ or, more generally, $K_{I/J}$) is different dependent on the nature of the membrane (glass, polymeric, crystalline). According to the Nikolsky "simple" theory, the potentiometric selectivity

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[1] Here, the symbol R^- stands for ionogenic group in glass: ≡Si–O⁻ or =Al–O⁻ or =B–O⁻ or whatever else, dependent on the glass composition.

coefficient equals the ion-exchange constant at the membrane/solution interface. More advanced theories consider more factors influencing the selectivity.

5.2.2 The Eisenman Theory

In the transient part of the response, when the pH response vanishes at high pH and turns to a metal cation response, the experimental curves deviate from what should be according to the Nikolsky equation. The transient part is more expanded in comparison with that predicted by Eq. (5.10), see also Fig. 5.4. This fact motivated further experimental research into the mechanism and the evolution of the theoretical description of the glass electrode response. An important contribution was made by Eisenman [5, 9, 10]. Eisenman assumed power function for the dependence of the ion activities in glass on their mole fractions: $a_I{}^{\mathrm{glass}} = N_I^n$. Under this assumption, the equation for the EMF is

$$E = E^0 + n\frac{\mathrm{RT}}{F}\ln\left(\left(a_{\mathrm{H}^+}{}^{\mathrm{aq}}\right)^{1/n} + \left(K_{\mathrm{H/Na}}{}^{\mathrm{pot}} a_{\mathrm{Na}^+}{}^{\mathrm{aq}}\right)^{1/n}\right). \tag{5.11}$$

The n value is selected empirically in order to fit the experimental data.

The Eisenman theory differs from the Nikolsky “simple” theory also regarding the physical meaning of the selectivity coefficient. Eisenman has considered the overall membrane potential, including also the diffusion potential contribution [5, 10]. Therefore, the selectivity coefficient in Eq. (5.11) is dependent not only on the ion-exchange constant but also on the ion mobilities ratio:

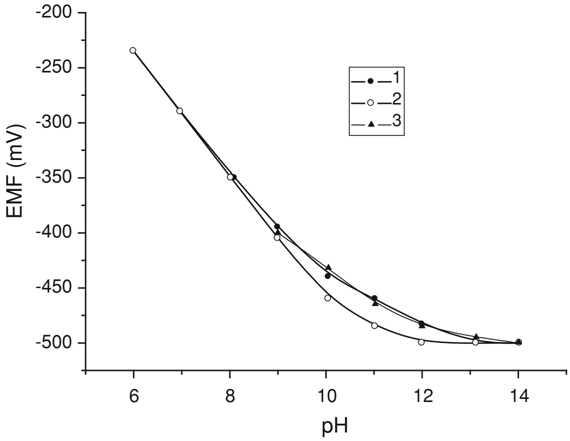

Fig. 5.4 Experimental and calculated curves for the pH electrode with membrane containing 22 % Na_2O, 9.4 % B_2O_3, and 68.6 % SiO_2 [18]. Sodium activity is $a_{\mathrm{Na}} = 2.14$. *Curve 1*: experimental values, *Curve 2*: calculated with Eq. (5.10) using $K_{\mathrm{H/Na}}{}^{\mathrm{exch}} = 1.4 \times 10^{-11}$, *Curve 3*: calculated with Eq. (5.15) using $\alpha_{\mathrm{H},1^{1/2}} K_{\mathrm{H/Na}}{}^{\mathrm{exch}} = 1.4 \times 10^{-11}, \alpha_{\mathrm{H},1} = 9 \times 10^{-4}$

$$K_{\mathrm{H/Na}}{}^{\mathrm{pot}} = \frac{u_{\mathrm{Na}}}{u_{\mathrm{H}}} K_{\mathrm{H/Na}}{}^{\mathrm{exch}}. \tag{5.12}$$

Since the ion mobilities are assumed constant, the consideration of the diffusion potential within the membrane does not alter the shape of the response curve. However, the difference in ion mobilities may contribute to the value of the selectivity coefficient as compared to only the ion-exchange constant.

It is worth to mention that before Eisenman, the same has been done by Stefanova [11]. Furthermore, several distinctively different mechanisms of ion transfer within the glass phase have been considered, aimed at rationalization of surprisingly high selectivity of silicate glasses to pH (higher than could be expected from low acidity of SiO_2) [12–15]. These papers, however, have been published only in Russian and for years remained unknown for the international scientific community, until Morf briefly analyzed these approaches in his book [16].

5.2.3 The Nikolsky–Shultz Generalized Theory

Nikolsky together with Shultz developed the so-called Nikolsky–Shultz generalized theory. This theory is known in two versions, based on two distinctively different approaches. Below, the Nikolsky–Shultz generalized theory is described like it was summarized by Belyustin [17]. Both versions of the generalized theory accounted for differences in the strength of the interactions between the ions and different ionogenic groups (ion-exchange sites) in glass. However, one approach relied mostly on quasi-thermodynamic improvements in the Nikolsky "simple" theory, while the other one directly considered the difference in the dissociation degrees for different ion-exchange sites.

Within the frames of the first approach, Nikolsky and Shultz introduced $\alpha_{\mathrm{H}^+,i}$, $\alpha_{\mathrm{M}^+,i}$ —the so-called partial activity coefficients. It was assumed that the ion activities in glass can be represented by the sums of the multiples of the respective partial activity coefficients and mole fractions of the respective sites:

$$a_{\mathrm{H}^+}{}^{\mathrm{glass}} = \sum_i \alpha_{\mathrm{H}^+,i} N_{\mathrm{H}^+,i},\ a_{\mathrm{M}^+}{}^{\mathrm{glass}} = \sum_i \alpha_{\mathrm{M}^+,i} N_{\mathrm{M}^+,i}.$$

Thus, for each of the i sorts of the ion-exchange sites in glass, the partial activity coefficients of H^+ and M^+ ions are different and however do not depend on $N_{\mathrm{H}^+,i}$, $N_{\mathrm{M}^+,i}$—the mole fractions of the cations bound to these kind of sites. Thus, the assumption on the constant values of the overall activity coefficients in glass utilized in the Nikolsky "simple" theory is replaced here by the assumption on the constancy of the partial activity coefficients. For each sort of the sites, the sum of the mole fractions referring to H^+ and M^+ ions is constant:

$$N_{\mathrm{H}^+,i} + N_{\mathrm{M}^+,i} = N_{0,i} = \mathrm{Const.} \tag{5.13}$$

The latter statement, like in the case of the Nikolsky "simple" theory, suggests equal dissociation degrees for H$^+$ and M$^+$ ions bounded to a particular sort of the sites. The final form obtained for the EMF using this approach is

$$E = E^0 + \frac{\mathrm{RT}}{F} \ln \sum_i \frac{a_{\mathrm{H}^+}{}^{\mathrm{aq}} + \alpha_{\mathrm{H}^+,i} K_{\mathrm{H/M}} a_{\mathrm{M}^+}{}^{\mathrm{aq}}}{\alpha_{\mathrm{H}^+,i} N_{0,i}}. \tag{5.14}$$

The physical meaning of the other approach is different and perfectly clear. Each ionogenic group in glass, whatever in H$^+$ or M$^+$ form, dissociates $R_iH \leftrightarrow \mathrm{R}_i^- + \mathrm{H}^+$ and $R_iM \leftrightarrow \mathrm{R}_i^- + \mathrm{M}^+$, and these dissociation equilibria are characterized by the respective dissociation constants:

$$k_{\mathrm{H}^+,i} = \frac{a_{R_i^-}{}^{\mathrm{glass}} a_{\mathrm{H}^+}{}^{\mathrm{glass}}}{a_{R_iH}{}^{\mathrm{glass}}}, k_{\mathrm{M}^+,i} = \frac{a_{R_i^-}{}^{\mathrm{glass}} a_{\mathrm{M}^+}{}^{\mathrm{glass}}}{a_{R_iM}{}^{\mathrm{glass}}}.$$

The values of $k_{H,i}$, $k_{M,i}$ are specific and may differ significantly. The approach results in equation

$$E = E^0 + 0.5\frac{\mathrm{RT}}{F} \ln\left(a_{\mathrm{H}^+}{}^{\mathrm{aq}} + K_{\mathrm{H/M}} a_{\mathrm{M}^+}{}^{\mathrm{aq}}\right) + 0.5\frac{\mathrm{RT}}{F} \sum_i \frac{a_{\mathrm{H}^+}{}^{\mathrm{aq}} + \alpha_{\mathrm{H}^+,i} K_{\mathrm{H/M}} a_{\mathrm{M}^+}{}^{\mathrm{aq}}}{k_{\mathrm{H}^+,i} N_{0,I}}. \tag{5.15}$$

This equation allowed for rational explanation of the expanded transient parts in the calibration curves (for one sort of anionic sites in glass), see Fig. 5.4, and also for step-wise EMF—pH curves in the case of two sorts of anionic sites, see Fig. 5.5 [18]:

5.2.4 The Baucke Theory, Comparison with the Nikolsky Theory

A different theory has been developed by Baucke [19–24]. Brief description of this theory is presented below, on the basis of [24]. According to the Baucke theory, glass electrodes work primarily due to a dissociation mechanism, that is, due to the hydrolysis process shown in Fig. 5.2, bottom. Baucke considers the following ionogenic groups in glass: ≡Si–O–H, ≡Si–O–Na, and ≡Si–O$^-$. Furthermore, the groups located at the glass surface are not the same as those in the glass bulk. At the surface, the ≡Si–O–H groups are hydrolyzed by water molecules producing hydrogen ions into the aqueous phase:

$$\equiv \mathrm{SiOH}^{\mathrm{surf}} + \mathrm{H_2O}^{\mathrm{aq}} \leftrightarrow \equiv \mathrm{SiO}^{-,\mathrm{surf}} + \mathrm{H_3O}^{+,\mathrm{aq}}. \tag{5.16}$$

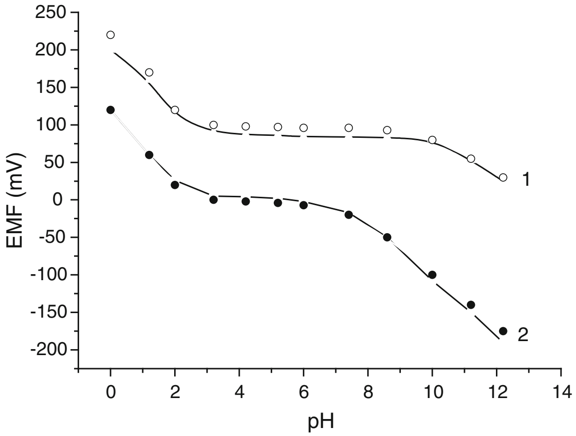

Fig. 5.5 Experimental (*circles*) and calculated using Eq. (5.15) (*solid lines*) step-wise E–pH curves for the electrodes with membranes containing 22 % Na_2O, 2 % Al_2O_3, and 76 % SiO_2 [18]. *Curve 1*: 21 % Na_2O, 2.4 % Al_2O_3; *curve 2*: 76.6 % SiO_2 (2). Sodium activity is $a_{Na} = 0.08$. Parameter values: $K_{H/Na}{}^{exch} = 1.4 \cdot 10^{-11}, \alpha_{H,1} = 1, \alpha_{H,2} = 10^{-10}$

The equilibrium constant of the reaction (5.16) is expressed as below:

$$K_{D,H} = \frac{a_R{}^{surf} a_{H_3O}{}^{aq}}{a_{RH}{}^{surf} a_{H_2O}{}^{aq}}. \tag{5.17}$$

Here, as before, R^- stands for $\equiv$Si–O$^-$ groups, however, located at the surface rather than in the glass bulk. The value of $K_{D,H}$ is smaller than that of the analogous homogeneous reaction in the bulk of the glass phase because the negative charge of the glass surface hinders the hydrogen ion coming out the glass phase.

The other process which is taken into account by Baucke is the formation of associates of metal cations from aqueous solution and $\equiv$Si–O$^-$ anions at the glass surface:

$$\equiv \text{SiO}^{-surf} + \text{M}^{+aq} \leftrightarrow \equiv \text{SiOM}^{surf}. \tag{5.18}$$

The respective association constant is

$$K_{A,M} = \frac{a_{RM}{}^{surf}}{a_R{}^{surf} a_M{}^{aq}}. \tag{5.19}$$

The equilibria (5.16) and (5.18) can be combined into a crossed equilibrium below:

$$\begin{array}{l} \text{M}^{+,aq} \\ + \\ \equiv \text{SiOH}^{surf} + \text{H}_2\text{O}^{aq} \leftrightarrow \equiv \text{SiO}^{-,surf} + \text{H}_3\text{O}^{+,aq} \\ \updownarrow \\ \text{SiOM}^{surf} \end{array} \tag{5.20}$$

Thus, the anionic form of the surface groups $\equiv$Si–O$^-$ binds the partial equilibria (5.16) and (5.18) together. Baucke therefore characterizes the selectivity by selectivity product: $K_{D,H}K_{A,M}$. Unfortunately, the two components of the selectivity product: $K_{D,H}$ and $K_{A,M}$ cannot be measured independently. However, the value of the selectivity product has been measured by ion bombardment for spectrochemical analysis (IBSCA) technique and proved to be very close to the respective value obtained from the potentiometric measurements. The interpretation of the latter, obviously, suggests an equation which describes the electrode response in mixed solutions. The respective equation for the membrane potential [20] is, formally, equivalent to the Nikolsky equation:

$$\varphi = \varphi^0 + \frac{\mathrm{RT}}{F}\ln\left(a_{\mathrm{H_3O}}{}^{\mathrm{aq}} + K_{D,H}K_{A,M}a_M{}^{\mathrm{aq}}\right). \tag{5.21}$$

It may appear that the physical meaning of the Baucke's selectivity product is critically different from that of the Nikolsky's selectivity coefficient (or ion-exchange constant in the Nikolsky "simple" theory). In fact, the key factor of the Baucke theory is $a_R{}^{\mathrm{surf}}$—the activity of the surface anionic groups eliminates from the selectivity product value:

$$K_{D,H}K_{A,M} = \frac{a_R{}^{\mathrm{surf}}a_{\mathrm{H_3O}}{}^{\mathrm{aq}}a_{\mathrm{RM}}{}^{\mathrm{surf}}}{a_{\mathrm{RH}}{}^{\mathrm{surf}}a_{\mathrm{H_2O}}{}^{\mathrm{aq}}a_R{}^{\mathrm{surf}}a_M{}^{\mathrm{aq}}} = \frac{a_{\mathrm{H_3O}}{}^{\mathrm{aq}}a_{\mathrm{RM}}{}^{\mathrm{surf}}}{a_{\mathrm{RH}}{}^{\mathrm{surf}}a_{\mathrm{H_2O}}{}^{\mathrm{aq}}a_M{}^{\mathrm{aq}}}. \tag{5.22}$$

This equilibrium constant refers to the reaction below:

$$\mathrm{RH}^{\mathrm{surf}} + \mathrm{H_2O}^{\mathrm{aq}} + \mathrm{M}^{+,\mathrm{aq}} \leftrightarrow \mathrm{RM}^{\mathrm{surf}} + \mathrm{H_3O}^{+,\mathrm{aq}}. \tag{5.23}$$

One can see that the reaction (5.23) considered in the Baucke theory is, effectively, an ion-exchange reaction. However, it is different from that considered by Nikolsky [3]. One source of difference comes from the consideration of associated rather than dissociated forms of hydrogen and metal cations on the glass surface. When it comes to the generalized Nikolsky–Shultz theory, this difference disappears (see Sect. 5.2.3). Another source of difference between the Nikolsky theory and the Baucke theory is that the reaction (5.23) directly accounts for the hydrolysis process at the glass surface, which is somewhat hidden in the Nikolsky's approach.

The direct consideration of the hydrolysis process at the glass/solution interface appears important novelty of the Baucke theory. Indeed, consideration of the hydrolysis as a process located at the surface allows obtaining the following expression for the electrode potential within the range of the pH response:

$$\varphi = \varphi^0 + \frac{\mathrm{RT}}{F}\ln\frac{a_R{}^{\mathrm{surf}}}{a_{\mathrm{RH}}{}^{\mathrm{surf}}a_{\mathrm{H_2O}}{}^{\mathrm{aq}}} + \frac{\mathrm{RT}}{F}\ln a_{\mathrm{H_3O}}{}^{\mathrm{aq}}. \tag{5.24}$$

Activities of water in the solution and that of $\equiv$Si–OH groups at the glass surface are virtually constant [19–24] but $a_R{}^{\mathrm{surf}}$—the surface activity of $\equiv$Si–O$^-$—varies with the variation in the solution composition. From the practical point of view, the respective contribution to the electrode slope is relatively small: of about −0.1 to −1 mV. However, from the academic viewpoint, the explanation of slightly sub-Nernstian slope of glass pH electrodes (which is a well-known experimental fact) is very significant and must be considered an important achievement.

Let us discuss why the Nikolsky's approach, whatever for full dissociation or for partial association, predicts full Nernstian slope within the pH or a metal ion response range. The concept of ion exchange suggests macroscopic equality of the quantities of ions exchanging between the contacting phases.[2] Therefore, a pure ion-exchange process like $\mathrm{H}^{+,\mathrm{glass}} \leftrightarrow \mathrm{H}^{+,\mathrm{aq}}$ or $\mathrm{Na}^{+,\mathrm{glass}} \leftrightarrow \mathrm{Na}^{+,\mathrm{aq}}$ can change neither the exchanging ion activity, nor the dissociation degree of the ionogenic groups in glass. The point is that consideration of processes *within phases*, not *at the surface*, inevitably results in the mass balance and in the macroscopic electroneutrality condition, presented below for H^{+}—response range in terms of the species concentrations (for better clarity):

$$C_R{}^{\mathrm{tot,glass}} = C_R{}^{\mathrm{glass}} + C_{\mathrm{RH}}{}^{\mathrm{glass}} C_R{}^{\mathrm{glass}} = C_H{}^{\mathrm{glass}} \tag{5.25}$$

The concentration of the associated form is proportional to the respective species concentrations and the association constant: $C_{\mathrm{RH}}{}^{\mathrm{glass}} = C_R{}^{\mathrm{glass}} C_{\mathrm{H}}{}^{\mathrm{glass}} K_{\mathrm{RH}}$. One can easily obtain for hydrogen ion concentration in the glass phase:

$$C_{\mathrm{H}}{}^{\mathrm{glass}} = \left(-1 + \sqrt{1 + 4C_R{}^{\mathrm{tot,glass}}}\right) 2K_{\mathrm{RH}}. \tag{5.26}$$

According to Eq. (5.26), the concentration of hydrogen ions in the glass phase equilibrated with an aqueous solution is constant whatever is the composition of the solution (within the pH response range), predicting the full Nernstian slope.

The same result can be obtained for the metal ion response range. As to the transient response range, within the Nikolsky approach, the variable slope originates from variable ratio of the hydrogen and the metal ion concentrations in the membrane phase. The response is therefore described by Eqs. (5.10) or (5.15)—dependent on whether the model assumes complete or incomplete dissociation.

Apparently, the Nikolsky approach although originally developed for glasses is more adequate for the ionophore-based membranes where the extraction and ion-exchange processes do affect the contacting phases, not only the surface of the membrane, even during the normal measurement procedures. On the other hand, the long-term kinetics of the glass electrode response reveals significant, sometimes even crucial, effects caused by processes deep in the glass phase [25–30].

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[2] It is important to mention that microscopic non-equality of ion exchange and the respective deviation from the electroneutrality within the space-charge region at the membrane/solution interface always takes place. Furthermore, the boundary potential originates from this minute non-equality, see Sect. 2.2. However, this microscopic non-equality does not affect the macroscopic compositions of the respective phases and even those of the surface layers outside the space-charge region.

The thickness of the layers modified by the ion-exchange processes is up to 20 μm [25–30]. Also, the enormous amount of studies performed using the Nikolsky's concept revealed practically and academically important regularities of the electrode properties as a function of the glass composition [6, 17].

Therefore, considering the Nikolsky theory and the Baucke theory as antagonistic to one another appears counter-productive. Rather, these two approaches are complementary to one another and must be unified under an umbrella of a generalized theory.

5.3 Glass Electrodes for RedOx Sensing

As mentioned above (see Sect. 5.1), the electrode glasses are, normally, ionic conductors. However, Pisarevskii showed that glasses doped with transient metal oxides (Fe^{II}/Fe^{III}, Ti^{III}/Ti^{IV}) are semiconductors of p-type or n-type dependent on the nature of the transient metal (Fe or Ti) and also on their concentrations [31–36]. These glasses possess significant electronic conductivity, and the electrodes with membranes made of these glasses can be used for RedOx sensing.

The concentrations of the respective transient metal oxides must be tuned to ensure the electronic conductivity and, at the same time, the glass-like state of the membrane (to suppress crystallinity), while the ionic conductivity is suppressed by the so-called mixed-alkali effect. The intrinsic electronic conductivity of these glasses allows for solid-contact construct of the electrode, with vacuum-sputtered silver on the internal side of the glass membrane. The electrode is stuffed with graphite to ensure contact between the sputtered silver layer and wire.

In a number of reversible RedOx systems like Fe^{2+}/Fe^{3+}, $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$, and quinone/hydroquinone glass, RedOx electrodes behave in the same way as platinum or other noble metals. These electrodes also work in systems like Eu^{2+}/Eu^{3+} and Ce^{3+}/Ce^{4+}—"difficult" for measurements with noble metal electrodes. On the other hand, glass RedOx electrodes are insensitive to oxygen and some other gases.

To describe the RedOx glass electrode behavior, Pisarevskii invented the concept of the RedOx selectivity, that is, the selectivity toward one RedOx system in the presence of other ones [32–35]. Obviously, under total equilibrium, no RedOx selectivity exists: The electrode potential is governed by the formal activity of electron in the sample, which, in turn, is a net effect of the interactions between all the RedOx systems involved. Therefore, the Pisarevskii's concept is intrinsically irreversible: The electrode is selective to the system which is faster than the others, and this is due to the catalytic properties of the electrode surface toward this particular system. The respective formalism is Nikolsky-like with the selectivity coefficient determined by equilibrium parameters: $E^{0,1}$, $E^{0,2}$—the standard potentials of the two "competing" RedOx systems and also by kinetic parameters: α—the transfer coefficient and $j^{0,1}$ $j^{0,2}$—the respective standard exchange current densities. The deviation of the potential caused by the presence of RedOx system 2 (mixed potential) from the equilibrium value obtained for pure system 1 obeys the equation below:

$$\Delta E = {E^{1,2}}_{\mathrm{mixed}} - E^{1} = \frac{\mathrm{RT}}{F}\frac{j^{0,2}}{j^{0,1}}\exp\frac{\alpha_2 F(E^{0,1} - E^{0,2})}{\mathrm{RT}}\left(\frac{a_{\mathrm{Ox},1}a_{\mathrm{Red},2}}{a_{\mathrm{Red},1}a_{\mathrm{Ox},2}}\right)^{\alpha_2}. \quad (5.27)$$

Equation (5.27) holds for the situations when $E^{0,1} - E^{0,2} > 4\mathrm{RT}/F$, $\Delta E < \mathrm{RT}/F$. One can see that if $j^{0,2} \ll j^{0,1}$ the presence of RedOx system 2 does not influence the electrode potential.

Glass RedOx electrodes show a pronounced selectivity to systems with low oxidation potential. This selectivity allows for measurements under ambient conditions because the atmospheric oxygen does not interfere with the electrode potential. The glass RedOx electrodes proved to be critically useful for a number of applications, like the measurements of the chemical or the biologic oxygen demand [32, 33, 35, 36].

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