SCIENCE FOR GLASS PRODUCTION

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INCREASING THE RESISTANCE OF ELECTRODE GLASSES TO FLUORINE-CONTAINING MEDIA

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The effect of ZrO_2, P_2O_5, and F^- ions on the resistance of electrode glass to fluorine-containing media is investigated. It is established that the most stable glasses have the minimum content of P_2O_5 (no more than 2.5%) and molar content of ZrO_2 to 3%. It is shown that for glass electrodes whose active part consists of experimental glass the electrode should be soaked for 3 – 7 days in a HF solution with concentration to 1000 mg/liter.

Key words: electrode glass, fluorine-containing media, stability in HF solutions, stabilization of mass loss, soaking.

Glass electrodes are the oldest and most commonly used ion-selective electrodes. They are more convenient and versatile than all other types.

Electrode glass is used to make the working (active) part of a glass electrode. Depending on its intended purpose the active part can be spherical, conical, needle-shaped, and so on. The shape most often used in industry is a sphere — beads 9 – 10 mm in diameter and 0.3 – 0.4 mm thick wall.

Glass electrodes are used to monitor the acidity (pH) of the medium in electrolytic solutions used in various areas of science, industry, agriculture, and public health. Even the first works studying glass electrodes found that the sensitivity to pH variation is different for glasses with different composition [1]. Water and acidic solutions leach from glass electrodes the main components of the glass, which are bound by ionic bonds and are replaced by hydrogen ions. The reaction products pass into solution, and a layer of hydrolyzed silica is formed and protects the glass from further destruction. Storing an electrode in water increases its service life. On the other hand alkali solutions as well as HF and H_3PO_4 solutions destroy the silicon-oxygen structural network and do not promote the formation of a protective layer.

The theory of glass electrodes is based on the idea that glass can act as an ion-exchanger that can enter into ionic interaction with a solution, for example, R^+ ions in the glass are exchanged with H^+ ions in the solution, which requires the presence of a substantial number of alkali ions in the glass [2]. Previously, irrespective of the purpose of glass electrodes, ÉS-1 sodium-potassium-silicate glass (technical name Corning-O15) was used with the composition (wt.%) 22.0 Na_2O, 6.0 CaO, and 72 SiO_2, close to the most low-melting eutectic in the system $Na_2O – CaO – SiO_2$ as well as lithium-barium-silicate and lithium-magnesium-silicate glasses [1 – 3]. These glasses all possess high electric resistance and are fabricated in the form of thin membranes.

Introducing barium, cesium, and lanthanum oxides into glass and replacing Na^+ with Li^+ in silicate glass greatly expands the range of H^+ functions [2]. For this reason, glass electrodes made of lithium-cesium-lanthanum silicate glasses, first obtained by the Leeds and Northrup Company (USA), have been widely used in recent years. The glasses in this system possess high electrode characteristics and high resistance to high pH and temperature, which made it possible to expand the range of applications of glass electrodes. An optimal glass composition for electrode glasses with the following composition (molar content, %) was proposed: 28.0 Li_2O, 3.0 Cs_2O, 4.0 La_2O_3, 65.0 SiO_2 (Perley glass) [4]. However, the stability of this glass in fluorine-containing media is very low.

In the Republic of Belarus glass electrodes for pH-metric and ionometric devices are manufactured by the Gomel’ Works for Measuring Instruments (GZIP). The assortment of electrodes is quite wide, but a number of requirements in glass electrodes remain unsatisfied. Specifically, this concerns glass electrodes which resist fluorine-containing me-

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dia. At the present time the Republic obtains such electrodes only from abroad, mainly the countries of Europe.

Since there is a need to expand the assortment of products, the problem of developing electrode glasses with high resistance to fluorine-containing media at HF concentration in solution 1000 mg/liter was studied.

The difficulty of solving this problem lies in the fact that silicate glasses in general are resistant to HF solutions. According to the effect on silicate glass HF and fluoride solutions are group-II reagents resistance to which is 100 time lower than to group-I reagents, i.e., to water and acids [1]. They attack the silicon-oxygen framework of the glass directly, as a result of which the surface layers are completely removed; the etch rate remains constant in time. The principle of etching of silicate glass is based on this mechanism. HF solutions actively interact not only with the silicon-oxygen base of the glass but also with alkali oxides and other modifiers. As a result the glass breaks down rapidly. The etch process accelerates in the presence of sulfuric acid, which transforms insoluble etch products into a soluble state.

The compound ZrO_2 occupies a special place among compounds capable of increasing the resistance of silicate glasses to fluorine-containing media; this compound increases the chemical resistance of glass to practically all reagents. However, according to the published data [5], introducing ZrO_2 in amounts above 2% (molar content) into electrode glasses degrades their electrode characteristics.

Phosphate glasses with P_2O_5 to 77% exhibit resistance to fluorine-containing media [1]. Phosphorus oxide is also used for obtaining silicate glasses which resist HF and fluorides [6, 7]. But the possibilities of introducing P_2O_5 into silicate glasses are also limited because such glasses become opacified as a result of the segregation phenomena and the appearance of structural nonuniformity.

Fluorine-containing compounds — fluorides of alkali and alkali-earth metals, whose introduction into silicate glasses increases resistance to HF and fluoride solutions — are also of interest [8 – 10]. When part of the oxygen in a glass network is replaced by an equivalent amount of fluorine an anionic component of mixed type is obtained. But, in general, the effect of fluorides is not unique. Fluorine increases the chemical resistance of unstable glasses and, conversely, lowers the chemical resistance when introduced into chemically stable glasses. For most glasses with electrode compositions, introducing fluorine degrades their resistance to water, acids, and alkali [9, 10]. Information on the effect of fluorine-containing additives on the change of the electrode characteristics of such glasses can be found only in [10].

Analysis of measurements of the electric conductivity of fluorine-containing alkali-silicate glasses showed a general tendency for the resistivity of the glasses to increase when a halogen is introduced, which makes these glasses impractical for manufacturing membranes, especially glass with a high fluorine content [8]. Electrodes have resistances 10 – 20 MΩ with mass content 0.7 – 1.4% F^- ion, 150 – 300 MΩ with 2.3 – 4.5% F^- ion, and 700 – 1500 MΩ with 6.5% F^- ion. However, during leaching the resistance of the electrodes dropped to 15 – 50 MΩ. A sharp drop of the resistance of the electrodes after the electrodes were immersed in a solution is attributed to deep penetration of water into the bulk of the membrane. But in any case the introduction of fluorides into silicate glasses also is limited, since for fluorine mass content above 4 – 5% glasses are opacified because of the limited solubility of fluorides in the silicate melt and the separation of fluorides and silicon-fluorides in the crystalline state.

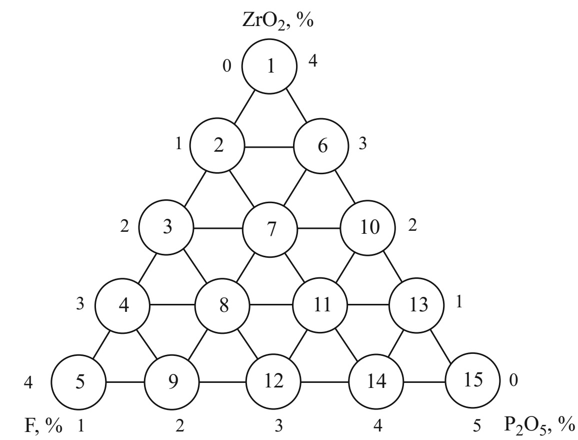

Fig. 1. Molar content of additions, %, in synthesized glasses (1 – 15) with molar composition $SiO_2 + La_2O_3 + Li_2O, K_2O\ (Cs_2O) = 95\%$.

Therefore the methods for acting on the resistance of silicate glasses to fluorine-containing media are very limited. The present work studies the effect of ZrO_2, P_2O_5, and F^- ion introduced together and increasing the resistance of electrode glasses to solutions of HF and fluorides; the behavior of experimental glasses in fluorine-containing media is also studied. The following requirements were taken into account: the glasses must be solderable to vessel glass with CLTE $98 \times 10^{-7}\ K^{-1}$, their electric resistance must be < 1000 MΩ at 25°C for membrane thickness 0.3 mm, and they must not crystallize when worked on a gas burner.

The glass with total molar content of La_2O_3, Li_2O, K_2O (Cs_2O) equal to 95%, into which 5% additions were made — ZrO_2, P_2O_5, and F^- ion in different ratios — was used as the base variant.

The compound LiF was used as the raw material for introducing the F^- ion, keeping the total content of Li_2O in the glass constant. The compositions of the synthesized glasses are presented in Fig. 1. The glasses were synthesized in corundum crucibles in a gas-flame furnace at 1300°C with soaking at the maximum temperature for 2 h. Under these conditions all glasses were well made and fined, the exception being the glass with composition No. 5 containing 5% P_2O_5, which was partially opacified.

The investigation of the crystallization power of the glasses in a temperature gradient 500 – 1000°C showed that all glasses investigated have a narrow interval of crystalliza-

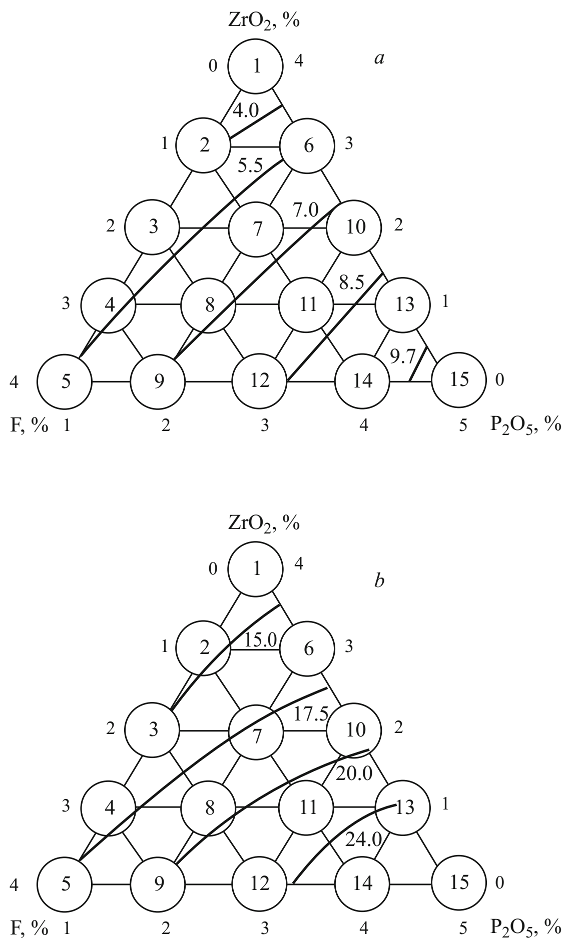

Fig. 2. Glass mass losses, mg/dm^2, with glasses held in an HF solution for 1 day (*a*) and 28 days (*b*), molar composition of the glass base $SiO_2 + La_2O_3 + Li_2O$, K_2O = 95%.

tion in the temperature range 850 – 950°C, above which the glasses completely spread without any indications of crystallization. The data obtained make it possible to work the glasses on a gas burner, blowing a bead out of the melted glass and soldering the bead to the vessel glass.

The linear thermal expansion coefficient of the glasses (α_{300}) varies in the range (100 – 110) × 10^{-7} K^{-1}, which also permits welding the experimental glasses with the vessel glass. The compound P_2O_5 gives the maximum increase of CLTE, which limits any subsequent increase in its content in the glasses, especially considering its tendency to opacify the glasses.

Samples in the form of plates or rods with the measured surface area of the samples were made to study the behavior of the experimental glasses in fluorine-containing media. The rods were first weighed and placed in a HF solution with concentration 1000 mg/liter. The mass losses (in % and mg/dm^2) of the glasses were measured after soaking in an HF solution of the prescribed concentration for 1, 3, 7, 14, 21, and 28 days using a freshly prepared HF solution after each measurement.

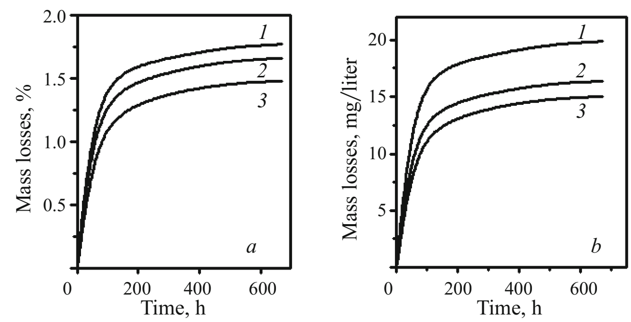

Fig. 3. Time dependence of the mass losses of the glass samples in % (*a*) and mg/dm^2 (*b*) with soaking in an HF solution with concentration 1000 mg/liter: glasses No. 3 (curve *1*), No. 7 (curve *2*), and No. 10 (curve *3*), containing 2% ZrO_2 (molar fraction).

Figure 2 shows the data on the mass losses after soaking for 1 (*a*) and 28 (*b*) days. All glasses showed high resistance to HF, even with very long exposure to the reagent. The most stable glasses lie in the region of minimum molar content of P_2O_5 (not exceeding 2%) and with molar content of SrO_2 from 2 to 4%. The comparatively stable mass loss indices with increasing F^- ion content are interesting. For P_2O_5 content 1 – 2%, replacing ZrO_2 with the F^- ion results in inconsequential change of the chemical stability of the glasses. Conversely, introducing P_2O_5 for ZrO_2 and for F^- ion substantially increases the mass loss. For this reason, if the F^- ion content can be varied over a wide range, from 0 to 4%, then P_2O_5 must be limited to 2 – 2.5%.

The curves of the time dependence of the mass losses of the glasses in fluorine-containing media showed a distinct behavior of the glasses in time (Fig. 3).

An almost proportional increase of the mass losses in time is observed during the first 7 days. This corresponds to the predicted behavior of the glasses in group-II reagents. Then, the breakdown of the glasses begins to slow down markedly, and the etch rate not only actively decreases but etching stops completely.

The retardation of the breakdown of the experimental glasses by a HF solution in time can be explained by several superposed processes, which together gradually form a protective layer, impeding further breakdown of the glass, on the surface of the glass samples. In the first place, according to the data presented in [1], the breakdown of silicate glass by HF occurs according to the following scheme:

$$(-\,Si - O - Si\,-)_\infty - O - Si - + HF \rightarrow$$
$$SiF_4 + (-\,Si - O - Si\,-)_\infty OH,$$

i.e., hydrosilicate forms in addition to silicon fluoride and gradually transforms into a “siliceous” film.

In the second place, in the case of electrode glass containing a substantial amount of Li_2O this process is accompanied by an additional interaction of HF with lithium oxide with formation of lithium fluoride LiF. The latter is insoluble in water and separates in the form of a precipitate during the early stages of exposure to HF. It can be supposed that at subsequent stages of the interaction of HF with glass not only is a layer of hydrolyzed silicate (“siliceous” film) formed but layers which are partially depleted of lithium oxide, similarly to leach layers in the case of exposure to water and acids on silicate glasses, are also gradually formed. Third, one other process can occur — interaction of La_2O_3 with fluorine ions and formation of the structural groups [$LaO_{3/2}F$], which are strongly acidic [9], which likewise will weaken the interaction of the glass with HF solutions.

In summary, the data presented confirm that the glass compositions developed with molar content 2 – 3% ZrO_2 and 2 – 2.5% P_2O_5 can be used as electrode glasses which resist HF solutions. However, when working with glass electrodes whose active part is made of the experimental glasses it is recommended that the electrodes be pre-soaked for 3 – 7 days in a HF solution with concentration to 1000 mg/liter.

REFERENCES

1. N. M. Pavlushkin (ed.), *Chemical Technology of Glass and Sitals* [in Russian], Stroiizdat, Moscow(1983).
2. B. P. Nikol’skii and A. A. Belyustin, “Glass electrodes — new aspects of theory, development, applications,” *Zh. Anal. Khim.*, **35**, 2206 – 2222 (1980).
3. G. Perley, *Anal. Chem.*, **21**, 394 (1949).
4. I. I. Kitaigorodskii and S. I. Sil’vestrovich (eds.), *Handbook of Glass Production* [in Russian], Moscow (1963), Vol. 2.
5. A. I. Parfenov and L. P. Filina, “Electrode properties of glasses in the systems, $Na_2O – Al_2O_3 – ZrO_2 – SiO_2$, $Na_2O – Al_2O_3 – SnO_2 – SiO_2$, $Na_2O – ZrO_2 – SnO_2 – SiO_2$,” *Fiz. Khim. Stekla*, **3**(2), 161 – 167 (1977).
6. É. L. Demskaya, T. I. Prokhorova, and A. G. Sokolova, “Chemical stability of glasses in the systems $P_2O_5 – SiO_2$ and $B_2O_3 – SiO_2$,” *Fiz. Khim. Stekla*, **16**(1), 145 – 147 (1990).
7. S. V. Mulivanova and V. Z. Bliskovskii, “Structure and chemical stability of glasses in the systems $SiO_2 – Al_2O_3 – Fe_2O_3 – RO – R_2O_3 – P_2O_5$,” *Zh. Prikl. Khim.*, **60**(6), 1391 – 1394 (1987).
8. A. A. Kiprianov and N. G. Karpukhina, “Oxyhalide silicate glasses,” *Fiz. Khim. Stekla*, **42**(1), 3 – 40 (2006).
9. A. A. Kiprianov and N. G. Karpukhina, “Effect of fluoride additions on the electric characteristics of alkali-silicate glasses,” *Fiz. Khim. Stekla*, **7**(1), 108 – 115 (2001).
10. N. G. Karpukhina and A. A. Kiprianov. “Electrode properties of certain fluorine containing alkali-halide glasses,” *Fiz. Khim. Stekla*, **27**(1), 101 – 107 (2001).