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One of the characteristic features of "normal" glass electrodes for the measurement of pH, pNa, and other characteristics is their lack of sensitivity of the presence of oxidation-reduction systems in the solution. As already reported [1-3], we have produced a new type of glass electrode possessing an electronic function, i.e., recording the oxidation potential of a solution in accordance with the equation

$$\varphi = \varphi^0 + RT / (nF) \cdot \ln(a_{\text{Ox}} / a_{\text{Red}}). \quad (1)$$

The present paper gives the results from an investigation into the production, and into certain characteristics, of this type of glass electrode. We established the electronic function in solutions of redox systems with high buffer capacity — ferri-ferro, ferri-ferrocyanides, quinone-hydroquinone, triiodide-iodide, bromine-bromide, chlorine-chloride. The oxidation potential of the solutions varied between 0 and 1100 mV (against the normal calomel electrode) and the pH between 0.5 and 9. The emfs* of the following electrolytic cells were measured:

- I. Pt | redox system solutions || normal calomel electrode (E_I)
- II. Pt | internal solution of redox system | glass | solution of redox system || normal calomel electrode (E_{II})
- III. Pt | internal solution of redox system | glass solution of redox system | Pt (E_{III})

It has been long known that platinum electrodes act reversibly in the above-mentioned systems even at low concentrations (down to 10^{-4} M) [4, 5]. From Fig. 1 it is seen that for various redox systems with the oxidized and reduced forms in various proportions $E_{\text{III}} = 0^\dagger$ and $\Delta E_{\text{I}} = \Delta E_{\text{II}}$. This result can be regarded as strong evidence for the presence of an electronic function in the glass electrode.

Glass electrodes with the electronic function were produced from iron-silicate glasses [2, 6]. The introduction of considerable quantities of Fe_2O_3 (an oxide of an element with variable valency) into the composition of the glass led to a change in the nature of conduction in the glass — from ionic to nonionic. The results of an investigation into the temperature dependence of the conductivity and transport numbers for certain glass compositions also enabled their assignment to the electron-conducting type [7]. We have also considered the work in [8], where for glasses with compositions close to those which we have investigated it was concluded from the sign of the thermomf that they are semiconductors with electron conduction. The very existence of the electronic function in the glass electrodes can be regarded as evidence for this theory. We also mention here that when the glass electrodes were used as cathodes in the electrolysis of silver salt or acid solutions, separation of metallic silver or gaseous hydrogen respectively was observed on the glass electrode.

Conversely electron conduction in a glass does not always signify that a glass electrode made from this glass will possess the electronic function. We found that these properties coincided when the activation energy of conduction $E_a^\ddagger$ was between 0.2 and 0.6 eV and the resistance of the glass electrode was between several kilohms and

*The emf of a cell signifies the potential difference between the left and right electrodes.

† In some cases (Fig. 1, dotted curves) $E_{\text{III}} = \text{const} \neq 0$, which is due to the asymmetrical potential of the glass electrode.

$^\ddagger E_a = 2k \ln(R_1/R_2) (T_2 - T_1) / T_1 T_2$, where R_1 and R_2 are the resistances of the glass electrode at temperatures T_1 and T_2 respectively; k is the Boltzmann constant.

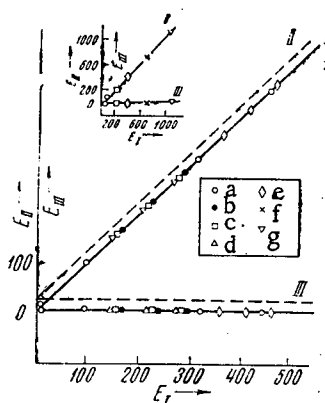


Fig. 1. Electronic function of glass electrodes. a) Quinhydrone (saturated), $0 \leq \text{pH} \leq 7.5$; b) potassium ferricyanide - ferrocyanide, pH 7; c) potassium ferricyanide - ferrocyanide, pH 4; d) potassium ferricyanide - ferrocyanide, pH 9; e) ferri-ferro, pH 1; f) bromine - bromide, pH 1; g) chlorine - chloride, pH 0.5.

several megohms in value. Glass electrodes made from glasses with electron conduction but not possessing the electronic function had a resistance of several tens of megohms or more, and E_a exceeded 0.8 eV. We note that the resistance of "normal" glass electrodes, with the H and M function and made from ion-conducting glasses of similar composition, is usually 10-10,000 MΩ, and $E_a > 1.5$ eV [7].

The emf of cells with high-resistance electron-conducting glass electrodes is extremely unstable and cannot be precisely balanced in any of the solutions which we have used. In the best case there is only a similarity of slope between the variations of the glass electrode potential and variation of the oxidation potential of the solution. As a rule the Fe_2O_3 content of these glasses was at the lowest oxide proportion at which electron conductivity and the electronic function appeared. They can be regarded as having low buffering properties with respect to the electricity carriers. This normally leads [9] to extremely low exchange currents, as a result of which the interphase potential depends on such factors as adsorption, incidental charging of the phase, and so on. In this case even the activity of the electrons in the glass can vary somewhat with change in the potential at the glass-solution boundary, which leads to nonfulfillment of Eq. (1). It must be stated that, with the same $\text{Fe}^{II}/(\text{Fe}^{III} + \text{Fe}^{II})$ concentration ratio (8-12% according to chemical analysis and Mössbauer spectra [10]), it is possible to obtain glasses both with high and with low electronic conduction and even with ionic conduction. It can therefore be supposed that the appearance of electronic conduction is related rather to specific structural characteristics of the respective iron-containing glasses, than simply to the above-mentioned ratio. This relationship will not be discussed here (see [2, 3, 6]).

To obtain more detailed characteristics of the glass electrodes as indicators for redox systems we used the following procedure. The emf of cell III was determined with the buffer capacity in the above-mentioned redox systems gradually reduced, both by reducing the over-all concentration of the system and by varying the proportions of the oxidized and reduced forms between 100:1 and 1:100 for each overall concentration level. In this way it was found that the limits of the electronic function depended substantially on the composition of the glass, the surface condition of the glass electrode, the nature of the redox system, and the pH of the solution.

Removal of the visibly nonuniform layer from the surface of the glass electrode (by means of hydrofluoric acid solution) usually shifted the limits of the electronic function considerably towards lower redox buffer values. Thus, after etching in hydrofluoric acid, the electronic function of the best glass electrodes in neutral solutions of the ferro-ferricyanide and quinone-hydroquinone systems was retained right down to a concentration of 10^{-5} M for one of the forms. At lower concentrations, there is no assurance of accuracy in the readings of the platinum electrode. It can, however, be considered established that the glass electrode can successfully compete with the platinum electrode as an indicator of the oxidation potential of a solution down to low concentrations in weakly acid, neutral, and weakly alkaline solutions (pH 4-9).

In acid medium the electronic function of the glass electrode is limited, and more limited the lower the pH. Figure 2 shows the emf of cell III as a function of the solution composition in the ferro-ferri and triiodide-iodide systems. It shows that E_{III} increases with decrease in the concentration of the oxidized form and with decrease in the pH (Fig. 2c and a) and does not change (in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system), or changes little (in the I_3^-/I^- system), when the redox system (Fig. 2b) becomes dilute with respect to the reduce form. The E_{III} values are readily reproducible, and in most cases do not depend on the degree of agitation in the solution. We note that the E_{III} value is positive in all cases. The dependence of E_{III} both on the composition of the solution and on the type of glass can be explained if it is remembered that the reason for deviations from the electronic function of glass electrodes in acid solutions is a specific cathode reaction involving hydrogen ions (electrochemical corrosion of the glass). If account is taken of the fact that the glass electrodes do not disintegrate appreciably even on prolonged standing in aqueous solutions, to explain the effect of the electrochemical corrosion of the glass on its electrode characteristics, it must be assumed that the exchange currents on the glass electrode in solutions of the investigated redox systems are small. The difference in the characteristics of glass electrodes of various compositions must be determined largely by the magnitude of the ratio between the corrosion current and the exchange current at a given solution composition.

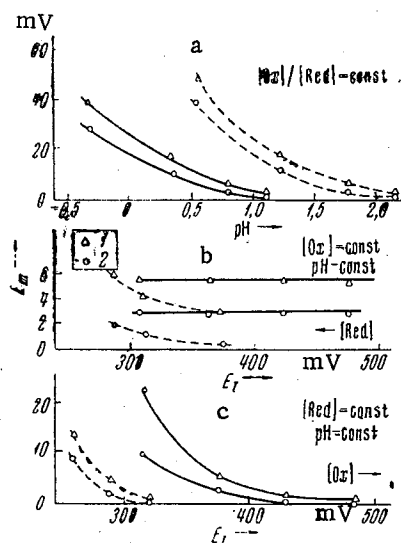


Fig. 2. Dependence of emf of cell III on composition of solution with low pH values. The continuous lines represent the ferri-ferro system and the dotted lines the triiodide-iodide system. 1) and 2) Glasses with various Fe_2O_3 contents: a) $[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = 10^{-3} \text{ N}/10^{-2} \text{ N}$; $[\text{I}_3^-]/[\text{I}^-] = 10^{-2} \text{ M}/10^{-1} \text{ M}$; b) $[\text{Fe}^{3+}] = 10^{-3} \text{ N}$, pH 0.8, $10^{-1} \text{ N} \geq [\text{Fe}^{2+}] \geq 10^{-4} \text{ N}$; $[\text{I}_3^-] = 10^{-3} \text{ M}$, pH 2.1, $5 \times 10^{-1} \text{ M} \geq [\text{I}^-] \geq 5 \times 10^{-2} \text{ M}$; c) $[\text{Fe}^{2+}] = 10^{-2} \text{ N}$, pH 0.8, $10^{-4} \text{ N} \leq [\text{Fe}^{3+}] \leq 10^{-1} \text{ N}$; $[\text{I}^-] = 1 \text{ M}$, pH 2.1, $10^{-3} \text{ M} \leq [\text{I}_3^-] \leq 10^{-1} \text{ M}$.

By recording polarization curves at constant current near and remote from the equilibrium potential (the experimental procedures will be dealt with separately), we established that the controlling stage is the electron transfer and that the exchange currents at the semiconducting glass-solution boundary are three to five orders of magnitude lower than on the platinum electrode (per unit of visible electrode surface). However, the exchange current values on the glass electrode vary in the same order as on the platinum electrode; the exchange current in the ferro-ferricyanide system > ferro-ferri system > triiodide-iodide system [5, 11].

We found that the overvoltage for oxygen evolution in acid solutions at a polarizing current density of 10^{-6} A/cm^2 amounted to more than 600 mV, and extrapolation to zero overvoltage gave an exchange current approximately equal to 10^{-18} A/cm^2 , which is in accordance with the observed absence of any effect of the gaseous oxygen on the potential of the glass electrode. It was also found that the glass electrode with the electronic function was insensitive to so-called catalyst poisons, H_2S for example. As known, noble-metal electrodes are "poisoned" by even brief contact with these substances, and the exchange current at the metal-solution boundary of a redox system is reduced by several orders of magnitude [12].

All that has been said above shows that the glass electrode with the electronic function, owing to its characteristic differences from the platinum electrode, is capable of giving additional information on the properties of various redox systems and is useful for solving various practical problems in redox investigations. In addition, by their investigation, it is possible to obtain new characteristics for glasses containing transition-metal oxides.

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