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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Temperature Dependence of the Electrical Conductivity of Orthophosphoric Acid in Porous Glass

M. V. Lyubavin, T. M. Burkat, and V. N. Pak

Herzen Russian State Pedagogical University, St. Petersburg, Russia

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Abstract—Temperature dependence of the proton conductivity of a 85 wt % solution of orthophosphoric acid in a set of porous glasses with predominant channel radii of 4.5, 9, 19, and 74 nm was studied. A method for saturating a wide-pore glass with a dehydrated acid is suggested. This method provides a conductivity on the order of 10^{-4}–10^{-3} ohm^{-1} cm^{-1} in the temperature range 373–473 K.

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A clear understanding of the need to raise the working temperature of low-temperature fuel cells to above 373 K arises on the background of a rapidly increasing number of studies concerned with their development [1–7]. It was necessary not only to make fuel oxidation faster and more complete, but also to raise the resistance of platinum and its alloys (contained in catalytically active electrodes) to poisoning in use of fuels alternative to hydrogen, methanol and hydrocarbons.

The possibility of raising the temperature to and above these values is primarily restricted by properties of proton-conducting materials serving as solid electrolytes in fuel cells. For example, the best studied Nafion perfluorosulfonic membranes (the U. S.) and their domestic analog MF-4SK, silently used as reference samples with high proton conductivity (10^{-1}–10^{-2} ohm^{-1} cm^{-1}) [1, 2, 4], retain it to temperatures of 363–373 K, above which their structure irreversibly changes. Therefore, studies of recent years have been aimed to create complex proton-conducting composites with enhanced thermal stability and to develop the so-called hybrid membranes with inorganic acids or salts incorporated into a polymeric base [2–8]. As encouraging examples of numerous studies in this area can serve modification of polyimidazoles with phosphoric acid [7] and copolymerization of multicomponent systems via formation of mutually penetrating polymeric networks [8].

It has been shown previously [9] that porous glasses (PGs) saturated with sulfuric acid solutions have a room-temperature conductivity $\sigma = 0.15$–0.25 ohm^{-1} cm^{-1}, which is rather high because of the large share of noncoducting silica skeleton. As, however, humidity and(or) temperature decrease, the resistivity substantially increases because of the dehydration of the systems. To further develop the previously employed approach and provide a protonic conductivity at 373–473 K, we fabricated and examined PG membranes with encapsulated orthophosphoric acid with an expectation to take advantage of the enhanced stability of the acid against thermal dehydration.

EXPERIMENTAL

As in [8], we used porous glasses in the form of 1-mm-thick plates with structural parameters listed in the table. The impregnation of PGs with a viscous 85 wt % solution of orthophosphoric acid could be performed most completely and reliably in an evacuated (to a residual pressure of ~10 Pa) desiccator via the capillary rise of the fluid in through channels of PGs, with the solution imbibed through a plane-parallel PG plate, which provided displacement of air from the pore space. To diminish the contact resistance, we deposited a ~1-mm-thick layer of a graphite powder with an average particle size of 10–20 μm onto the surface of the impregnated PGs. The samples were mounted between planar polished graphite pressure electrodes (with a constant load of 200 g cm^{-2}).

Structural parameters of porous glasses[a]

r_p, nm	V_p, $cm^3\ g^{-1}$	ε, %	γ	σ, $ohm^{-1}\ cm^{-1}$	σ*, $ohm^{-1}\ cm^{-1}$
4.5	0.260	33.1	0.86	0.022	0.077
9	0.531	53.4	0.86	0.034	0.074
19	0.423	46.3	0.87	0.028	0.070
74	0.348	42.1	0.89	0.027	0.072

[a] r_p, pore radius; V_p, pore volume; ε, porosity; γ, degree of filling of the internal space of porous glasses with a 85 wt% solution of orthophosphoric acid; σ and σ*, electrical conductivities of impregnated glasses and solution saturating the glasses.

The electrical resistance was measured in the temperature range 293–473 K in the ac mode at a frequency of 1 kHz with an E7-11 multimeter. The thus recorded resistance was recalculated to conductivity on the basis of the real dimensions of the PG plates.

The content Q of the encapsulated electrolyte, reduced to the mass of PGs preliminarily dehydrated at 393 K, is related to the pore volume V_p and density ρ of the impregnating solution by

$$Q = \rho V_p \gamma, \quad (1)$$

where γ is the coefficient that reflects the degree of pore filling.

A comparison of the experimentally measured values of Q with those predicted by (1) demonstrated that the close values $\gamma < 1$ are reached for all the PGs (see table). The inaccessibility of 11–14% of the internal space of the supports may be due both to the viscosity of the acid solution and to presence of nonthrough (dead) pores in the membranes.

Despite minor differences, values of the room-temperature electrical conductivity σ of impregnated glasses steadily increase as the support porosity ε becomes higher (see table). Because the parameters ε and γ reflect the share of nonconducting part of the systems, the experimentally measured σ can be represented as

$$\sigma = \sigma^* \varepsilon \gamma, \quad (2)$$

where σ* is the conductivity of the impregnating solution in the case when it would occupy a volume equal to the total (geometrical) volume of PGs.

Values of σ*, calculated for four systems and listed in the table, are close and almost coincide with the value of 0.078 $ohm^{-1}\ cm^{-1}$ for the bulk 85 wt % solution of H_3PO_4. This result indicates that the radius of silica channels does not affect the states of the encapsulated solution and the contribution of the surface conductivity to the recorded values of σ is insignificant.

Figure 1 shows how the equilibrium mass of PGs saturated with an H_3PO_4 solution decreases as temperature is elevated from room temperature to 473 K. It can be well seen that removal of water from the encapsulated solution is hindered in small-radius pores; nevertheless, on reaching a temperature of 473 K, the relative mass losses by the samples are equalized and approach a value of 15%, which corresponds to the total dehydration of the acid. The results of weight measurements are in agreement with the temperature dependence of equilibrium values of σ of the systems under study (Fig. 2). The rise in the electrical conductivity at lower temperatures (T = 293–363 K) is determined by the preservation of the main part of water as a proton-transport medium; the weakness of the activation of σ, observed in this case, is presumably due to the progressive thermal disintegration of the conduction channels, chains of hydrogen bonds. Further increase in temperature, which causes gradual dehydration of the solution, may lead to a change in

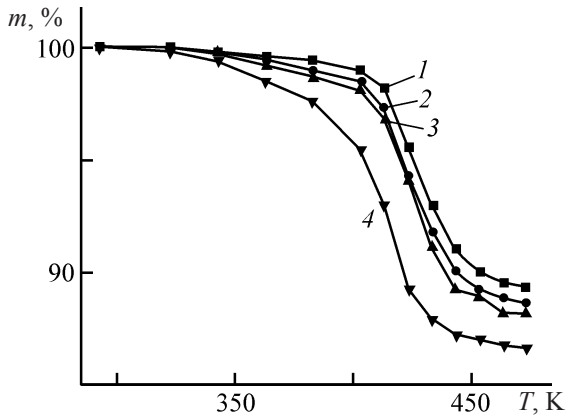

Fig. 1. Decrease in the mass m of a 85 wt % solution of orthophosphoric acid in porous glasses upon an increase in temperature T. Pore radius (nm): (*1*) 4.5, (*2*) 9, (*3*) 19, and (*4*) 74; the same for Fig. 2.

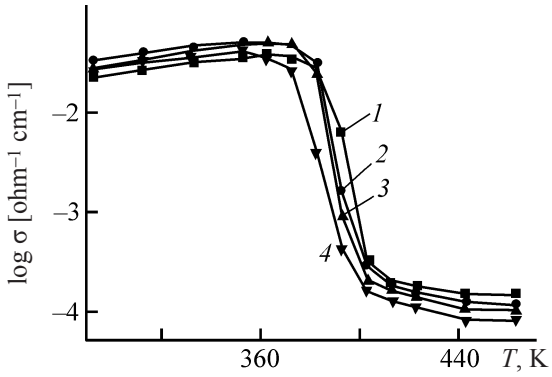

Fig. 2. Electrical conductivity σ of porous glasses saturated with a 85 wt % solution of orthophosphoric acid vs. temperature *T*.

the run of the σ–*T* dependence to the opposite, and just this is experimentally observed (Fig. 2). Here, there is reason to believe that a rather high conductivity level is preserved via its activation by the mechanism involving an exchange proton transfer between the pairs $H_4PO_4^+$/H_3PO_4 and H_3PO_4/$H_2PO_4^-$ [4]. However, at $T > 373$ K, σ unexpectedly sharply decreases (Fig. 2), which is in all probability due to disruption of the contact of electrodes with the pore solution: the contraction of this volume in the course of water removal is not compensated for by thermal expansion.

A possible method for obtaining impregnated PGs without a rise in their contact resistance upon an increase in temperature is that by encapsulation of orthophosphoric acid dehydrated at 473 K. In this case, we saturated glass plates with a 85 wt % solution of H_3PO_4, and then, without removing the plates from the solution, we raised its temperature to 473 K. The experiments demonstrated that a sufficiently high degree of pore space filling, $\gamma = 0.80$, is reached under these conditions only for the wide-pore glass with $r_p = 74$ nm. Measurements of the electrical conductivity of the sample obtained demonstrated its exponential rise in the temperature range 373–473 K (Fig. 3), with an activation energy of 35.5kJ mol^{-1}. The dependence is steadily reproduced in multiple cycling, with temperature raised and lowered. The values of σ, obtained in this case, are comparable with those known for composite proton-conducting materials in the temperature range under study [2–8]. Reverting to the results of weight measurements (Fig. 1), we emphasize once again that the process of thermal dehydration of the H_3PO_4 solution within PG channels is hindered. Therefore, conversion of encapsulated orthophosphoric acid to pyrophosphoric acid

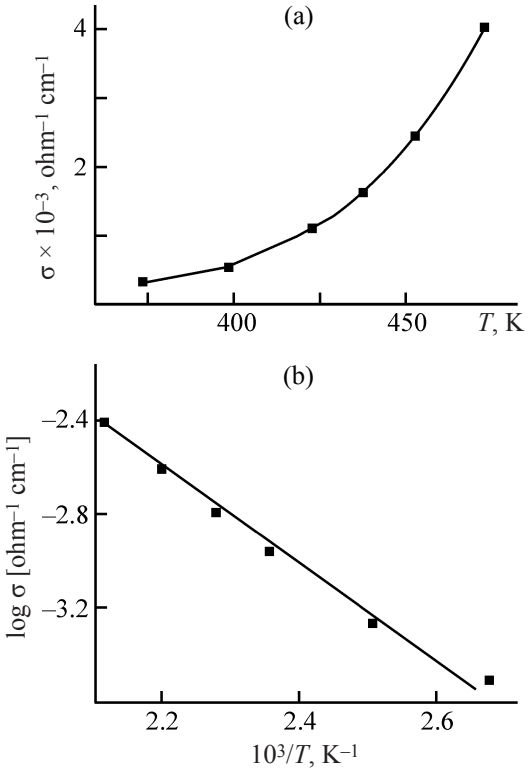

Fig. 3. (a) Dependence of the electrical conductivity σ of dehydrated orthophosphoric acid in a wide-pore glass (r_p = 74 nm) on temperature *T* and (b) its logarithmic anamorphosis.

$$2H_3PO_4 \rightarrow H_4P_2O_7 + H_2O \quad (3)$$

on raising temperature to 473 K seems to be unlikely because the loss of mass would be 23% in this case, which markedly exceeds the experimental results. Thus, there is reason to believe that the electrical conductivity of the sample in the temperature range 373–473 K (Fig. 3) is mostly provided by dehydrated orthophosphoric acid that fills the PG channels.

CONCLUSIONS

The proton electrical conductivity of porous glasses saturated with a solution of orthophosphoric acid is proportional to the volume porosity of the supports. Saturation of a wide-pore glass with a 85 wt % solution of H_3PO_4 in the mode in which the temperature is gradually raised to 473 K provides filling of through channels in the porous glass with a dehydrated acid, with the electrical conductivity of the resulting plates in the temperature range 373–473 K being on the order of 10^{-4}–10^{-3} ohm^{-1} cm^{-1}.

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