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O. A. ESIN, A. I. SOTNIKOV, Yu. P. NIKITIN

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Abstract

Full Text

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TEMPERATURE DEPENDENCE OF THE DOUBLE-LAYER CAPACITANCE IN MOLTEN OXIDES

(Presented by Academician A. N. Frumkin, 11 V 1964)

If in aqueous solutions the capacitance (C) of the double layer usually decreases with increasing temperature ([1]), then in molten salts it increases ([2]). Silicates, in their structure, are close to ionic liquids, but unlike the latter they contain silicic-oxygen groupings with a considerable share of covalency in the internal bonds ([3,4]). The polyatomic character of such groupings and their small effective charge apparently make them similar to solvent molecules. A study of the temperature dependence of the capacitance C could to some extent help to elucidate the structure of molten silicates.

In this connection we measured C at the interface of liquid iron, saturated with carbon, with molten calcium aluminosilicates and aluminates in the range 1300—1600°C.

The method of polarization by alternating current ([5]) was used, with active resistances in the constant arms of the bridge and with series connection in the compensation arm. The direct-current source was connected to the zero diagonal ([6]). The alternating-current density was $\sim$ 10 ma/cm^2, which is apparently acceptable in our case, where the exchange currents are rather large ([7]). In the cell (Fig. 1) two identical electrodes were polarized simultaneously.

Fig. 1. Cell diagram: 1 —graphite vessel; 2 —oxide melt; 3 —liquid metallic electrodes; 4 —rods of spectrally pure graphite; 5 —alumina capillaries; 6 — tungsten current leads.

The dispersion of capacitance with frequency observed by us is evidently caused not by penetration of the electrolyte between the columns of metal and the wall of the alumina capillary ([8]), but by electrochemical processes, since decreas-

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

ing the electrode surface from 0.25 to 0.02 cm^2 did not change the electrode capacitance (C_e) within $\sim$ 10%. In this connection we considered it possible, at sufficiently high frequencies, to model the interface between the metal and the electrolyte by the double-layer capacitance and the reaction resistance (R_p). Then

$$C_e = C + \frac{1}{\omega^2}\frac{1}{CR^2}, \tag{1}$$

where ω is the angular frequency.

Extrapolation of the straight line $C_e - 1/\omega^2$ to zero argument makes it possible to estimate the value of C.

Figure 2 gives the values of C at potentials close to equilibrium. It is characteristic that at temperatures (1300—1400°), not far from the liquidus line of the electrolyte, the capacitances are small. They increase with increasing temperature, just as in molten chlorides ([2]). These facts may

can be explained on the basis of the hypothesis of the multilayer character of the "double" layer in melts ([3],[2]), which increases its effective thickness.

The amount of excess charge in the first ionic layer of the melt from the electrode is determined by the charge of the metallic surface and by specific adsorption, but already for the second layer interionic forces may become determining. This causes, in the second layer, the appearance of an excess of charges opposite in sign to the charge of the first layer. The interaction of the third layer with the second is analogous. The thermal motion of the particles leads to a decrease in the density of excess charges with distance from the electrode surface.

Fig. 2. Temperature dependences of the capacitance of a liquid iron-carbon electrode in melts:
1 –40% CaO; 40% SiO_2; 20% Al_2O_3.
2 –52% CaO; 41% Al_2O_3; 7% SiO_2.
3 –47% CaO; 53% Al_2O_3.

Fig. 3. Temperature dependences of the capacitance of an iron-carbon electrode with additions of sulfur:
1 –0%; 2 –0.5%; 3 –0.8%; electrolyte –40% CaO, 40% SiO_2, 20% Al_2O_3.

According to ([9],[10]), this decay is described by a damped periodic function. Thus,

a multilayer ionic atmosphere arises, decreasing with increasing temperature. In this respect it is analogous to short-range order in liquids ([11]).

In solid electrolytes, the crystal lattice prevents the occurrence of such an effect. It is possible that this explains the usual values of capacitance obtained in ([13]).

The temperature dependence of the capacitance makes it possible to regard a silicate melt as an ionic liquid. However, the presence of covalent bonds with oxygen may exert a substantial influence on the structure of the double layer. The addition of silicon dioxide to calcium aluminate (Fig. 2, 2 and 3) leads to a sharp decrease in capacitance, apparently due to the appearance of structured aluminosilicate-oxygen "icebergs"([4]), which increase the thickness of the "double" layer.

Sulfur additions act in the opposite manner (Fig. 3), since sulfur is capable of being adsorbed at the phase boundary. Distributing itself between the metal and the electrolyte, sulfur replaces oxygen ions, but, unlike the latter, does not form large complexes with silicon ([12]) and destructures the "double" layer, increasing its capacitance.

We also attempted to determine the influence of potential on the capacitance of the "double" layer. Measurements were carried out with a melt of 40% CaO; 40% SiO_2; 20% Al_2O_3 at $t = 1390^\circ$ in a cell in which one of the electrodes had a surface approximately 100 times larger than the other. It turned out that, with a small deviation from equilibrium, the capacitance increases approximately

by 10%, while upon further polarization by 300 mV in the cathodic direction and by 500 mV in the anodic direction it practically does not change. This may indicate a small influence of the potential on the structure of the "double" layer.

Ural Polytechnic Institute
named after S. M. Kirov

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Note: Figure translations are in progress. See original paper for figures.