A. T. FILYAEV, S. V. KARPACHEV, S. F. PAL’GUEV

1963

SovietRxiv

Fig. 1. Curves of the dependence of capacitance and resistance on frequency. I —capacitance, II —resistance

Figure 1: Fig. 1. Curves of the dependence of capacitance and resistance on frequency. I —capacitance, II —resistance

Abstract

Full Text

A. T. FILYAEV, S. V. KARPACHEV, S. F. PAL’ GUEV

CAPACITANCE OF THE DOUBLE ELECTRIC LAYER IN SOLID ELECTROLYTES

(Presented by Academician A. N. Frumkin on 17 XII 1962)

The present article is a preliminary report on the results of measurements of the capacitance of the double electric layer on a platinum electrode in a solid solution of ZrO_2—CaO (85 mol.% ZrO_2 and 15 mol.% CaO).

The sample for measurement was a cylinder 10 mm in diameter and 6 mm thick, pressed from the indicated solid electrolyte. A platinum electrode was applied to the outer lateral surface of the cylinder; platinum powder was used for this purpose. The preparation of such pellets and the application of a platinum electrode to their surface were described in our previous works (^{1}-^{3}). The electrode under test was a platinum wire 0.1 mm in diameter, which was pressed at one end into the electrolyte pellet and was arranged along the axis of the cylinder. Its free end served as the current lead. The outer platinum electrode was the auxiliary electrode and the reference electrode. The surface of this electrode was 100 times larger than the surface of the electrode under test. In this connection, as a first approximation we neglected the polarization of the auxiliary electrode and its capacitive resistance in comparison with the polarization and capacitive resistance of the electrode under test.

Fig. 1. Curves of the dependence of capacitance and resistance on frequency. *I* —capacitance, *II* —resistance

The measurements were carried out in an atmosphere of argon that had been purified of oxygen by passing it at a temperature of 650° over metallic calcium. Polarization of the electrode under test by direct current was carried out from batteries. Measurements of capacitance and resistance were made at a temperature of 1020 ± 2° with the aid of an impedance bridge at various frequencies. The bridge circuit was analogous to that used by Leikis and Kabanov in work (^{4}), subsequently employed for measuring the capacitance of the double electric layer in molten salts (^{5}).

Fig. 2. Dependence of the capacitance of the double layer on the electrode potential. The curves are given for four different samples

Figure 2: Fig. 2. Dependence of the capacitance of the double layer on the electrode potential. The curves are given for four different samples

Measurements at different frequencies, carried out on an unpolarized electrode, show a very appreciable dispersion of capacitance and resistance. This phenomenon is well known in aqueous solutions and in molten salts (4–7) and, probably, can be explained in the present case in approximately the same way. The dependence of the capacitance and resistance on the frequency of the alternating current is presented in Fig. 1. Their appreciable decrease occurs with increasing frequency up to several thousand hertz. In view of the fact that already at 10 kHz the capacitance and resistance become practically constant, all measurements were carried out at this frequency.

Experimental curves of the dependence of capacitance on potential can be seen in Fig. 2.

The capacitance values obtained by measurement were recalculated per square centimeter of the visible surface of the electrode under study, which was determined from its geometric dimensions. All the capacitance curves (Fig. 2), at a potential of the electrode under study 0.1–0.15 V more positive than the equilibrium potential, have a clearly expressed minimum. In aqueous solutions, as was established in the works of A. N. Frumkin, B. V. Ershler, and T. I. Borisova (8,9), the capacitance minimum corresponds to the point of zero charge in connection with the diffuse structure of the electrical double layer at this point.

Fig. 2. Dependence of the capacitance of the double layer on the electrode potential. The curves are given for four different samples.

In the work of Ukshe, Bukun, and Leikis (7) an analogous phenomenon was found in molten salts. These authors showed that, in the case of molten electrolytes, the potential of the minimum on the capacitance curve corresponds to the potential of the point of zero charge. The authors rightly point out that such a coincidence in molten electrolytes is due to different circumstances than in aqueous solutions, namely the polarization of ions in the double layer and the compacting of the structure of the molten salt. Such an explanation appears plausible also in solid electrolytes. Thus, it is very probable that in solid electrolytes as well the capacitance minimum lies at the potential of the point of zero charge.

It is of considerable interest that the magnitude of the capacitance of the electrical double layer at the minimum is about 25 μF/cm^2. In not very dilute aqueous solutions and in molten salts, close values are obtained. This indicates that, in the case investigated by us, the structure of the double layer does not differ in any essential features.

In conclusion, we express our gratitude to Academician A. N. Frumkin for advice in discussing the present work.

Institute of Electrochemistry, Ural Branch
Academy of Sciences of the USSR

Received
22 IX 1962

CITED LITERATURE

1. A. D. Neuimin, S. V. Karpachev, S. F. Pal’ guev, DAN, **141**, No. 2, 402 (1961).
2. A. T. Filyaev, S. F. Pal’ guev, S. V. Karpachev, Tr. Inst. elektrokhim., Ural Branch, Academy of Sciences of the USSR, issue 2, 199 (1961).
3. S. F. Pal’ guev, A. D. Neuimin, Tr. Inst. elektrokhim., Ural Branch, Academy of Sciences of the USSR, issue 1, 111 (1960).
4. D. I. Leikis, B. N. Kabanov, Tr. Inst. fiz.-khim. AS USSR, issue 6, 5 (1957).
5. E. A. Ukshe, N. G. Bukun, D. I. Leikis, Tr. All-Union Conf. on the Physical Chemistry of Molten Salts and Slags, Moscow, 1962.
6. E. O. Ayayan, DAN, **100**, No. 3, 473 (1955).
7. B. N. Kabanov, I. G. Kiseleva, D. I. Leikis, DAN, **99**, No. 5, 805 (1954).
8. T. I. Borisova, B. V. Ershler, A. N. Frumkin, ZhFKh, **22**, 925 (1948).
9. T. I. Borisova, B. V. Ershler, ZhFKh, **24**, issue 3, 337 (1950).

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