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Abstract

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ON THE IMPEDANCE OF THE ELECTRICAL DOUBLE LAYER IN MELTS

The total impedance of an electrolytic cell consists of capacitive and active components, which can be measured by the usual methods used for studying RC circuits in electrical engineering ([1]). In this case, however, the obtained values of the separate components give no idea of the actual capacitance of the electrical double layer (e.d.l.). In fact, the resistance and capacitance of the circuit may be connected in series (Fig. 1, *a*) or in parallel (Fig. 1, *b*) in such a way that the total impedance, the total active resistance, and the reactance in both circuits will be equal, although $X \neq x_0$ and $R \neq a$. Thus, determination of the capacitance depends on the choice of the equivalent circuit of the cell. The circuit in Fig. 1, *a* will be applicable if the Faradaic current in the cell is neglected. For this it is necessary to use a strongly polarizable electrode ([2]) and the smallest possible amplitude of alternating current ([3],[4]). The circuit in Fig. 1, *b* is applicable if the active resistance of the electrolyte is neglected ([5]). Various variants of equivalent circuits were considered in detail by B. V. Ershler ([3]). The general case is represented in Fig. 1, *v*. The current expended on recharging the e.d.l. passes through the capacitive resistance X and the electrolyte resistance ρ. The current expended on electrolysis passes through the leakage resistance R ([6]) and the electrolyte resistance ρ. For this circuit, from impedance measurements the quantities X, R, and ρ generally cannot be calculated, since an infinite number of combinations of X, R, and ρ can be composed for which the impedance and its components will be correspondingly equal.

For molten electrolytes, the use of simple circuits (Fig. 1, *a*, *b*) is associated with known errors. The presence of large exchange currents requires taking into account the resistance R (Fig. 1, *v*). On the other hand, although the electrical conductivity of melts is greater than the conductivity of aqueous solutions, the resistance ρ still cannot be neglected. To eliminate the errors of simple circuits, we investigated the possibility of calculating the circuit in Fig. 1, *v* upon introducing an additional variable.

Although the resistance ρ cannot be directly determined from impedance measurements, it can be varied in a quite definite way, for example by changing the distance between the electrodes by a factor of n. The general circuit (Fig. 1, *v*)

Fig. 1. Equivalent circuits of cells

Figure 1: Fig. 1. Equivalent circuits of cells

is replaced by an equivalent one (Fig. 1, g). Impedance measurements give the quantities x and $A = r + \rho$. For two distances l_1 and l_2 between the electrodes we have

$$\frac{l_1}{l_2} = \frac{\rho_1}{\rho_2} = n \tag{1}$$

and

$$A_1 = r + \rho_2 n, \tag{2}$$

$$A_2 = r + \rho_2. \tag{3}$$

Then

$$r = \frac{A_1 - nA_2}{1 - n}. \tag{4}$$

From the condition of equivalence of the circuits in Fig. 1 , , we obtain

$$R = \frac{x^2 + r^2}{r}, \tag{5}$$

$$X = \frac{x^2 + r^2}{x}, \tag{6}$$

where X is the quantity of interest to us: the resistance of the actual capacitance of the EDL.

In our measurements we used a U-shaped glass tube 5 mm in diameter, filled with melt. Electrodes made of platinum wire 0.5 mm in diameter, sealed into glass, were lowered into this tube. The length of the free end was 10 mm. The distance between the electrodes was varied within the range from 70 to 220 mm.

Fig. 1. Equivalent circuits of cells

Impedance measurements were carried out by the previously described methods ([7]) at a frequency of 500 Hz and an effective voltage of 150 mV. The melt KNO_3 at 420° and the molten eutectic KNO_3—$NaNO_3$ at 280° were studied. The results of the measurements and calculations are given in Table 1.

Here the quantities x, X, r, R are given for the entire cell; C is the capacitance of the EDL for each electrode; C_d is the specific capacitance of each electrode, calculated for the apparent surface area 0.159 cm^2; R_d is the specific leakage resistance at each electrode.

The results of the measurements performed (the independence of the quantities x and r from the distance between the electrodes) indicate the possibility of calculating the actual capacitance of the EDL by the method described.

Table 1

Calculation of the actual capacitance of the EDL

Melt	x, ohm	ρl, ohm/cm	r, ohm	R, ohm	R_d, ohm/cm^2	X, ohm	C, μF	C_d, $\mu F/cm^2$
KNO_3—$NaNO_3$	116.3	4.54	40.7	372	1160	130.4	4.88	30.69
KNO_3	118.3	2.76	47.9	339	1062	137.6	4.66	29.30

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