ELECTRIC DOUBLE LAYER ON PLATINUM IN MOLTEN SALTS

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The platinum electrode was studied in the molten chlorides of alkali metals at temperatures from 450-700° by measuring the electrode/electrolyte interface impedance. It was shown that in the potential range from +0.5 to −0.1 V (against a lead reference electrode) the complex interface impedance is determined by the double layer capacitance shunted by a faradaic impedance. The latter comprises components due to diffusion and adsorption. At more negative potentials the discharge of alkali metal ions becomes important. The potential dependence of the double-layer capacitance of platinum has a clear maximum at −0.15 to +0.20 V corresponding to the point of zero charge.

In the first attempts at studying the electric double layer of platinum in a KCl−LiCl melt at 450°C by the impedance method, it could only be established that there is a noticeable dispersion of capacitance and resistance at frequencies from 100 to 3000 Hz [1, 2]. Subsequent measurements using potential steps lasting a few microseconds [3, 4] and the impedance method with extrapolation of the $C_s-\omega^{1/2}$ plot to infinite frequencies [5] allowed two sections on the $C_d-\varphi$ curve to be revealed within which the capacitance varied little with potential. At potentials in the range +0.8 to + 0.3 V* the capacitance was 108-115 $\mu F/cm^2$. The high capacities were ascribed to specific Cl^- ion adsorption, the low values to that of Li^+ ions. Therefore, the region where the capacitance decreased was considered as that near the potential of zero charge which, hence, must have a value of +0.20 ± 0.1 V. Recently Graves and Inman [6, 7], using a galvanostatic-pulse method with currents lasting up to 0.2 μsec, obtained $C_d-\varphi$ curves with a minimum near +0.28 V which they took for the null point of platinum. They ascribed the drop in capacitance at potentials more negative than −0.1 V to the discharge of alkali metal ions; the sharp rise and the plateau on the anodic branch ($\simeq$ 110 $\mu F/cm^2$) they attributed to oxygen chemisorption.

Considering the importance of the problem and the degree of controversy in the available data we undertook a more detailed study of platinum in the melt of chlorides by the impedance method.

Our measurements were done according to a series-RC network using an R-568 ac bridge [8] over the frequency range 1-50 kHz. The amplitude of the potential was 0.5 mV. The inductance of the leads and current leads was measured while short-circuiting the electrodes, and the corresponding correction was applied to the measured capacities. The polarizing and potentiometric parts of the apparatus were separated from the cell by a choking coil and a 10-kΩ resistor. The cell was a tall quartz beaker covered by a stopper with teflon shield. The lower part of the beaker was placed into a massive steel block which had been in a crucible furnace. The electrodes and a thermocouple were introduced into the cell through the stopper and were hermetically sealed by sections from a vacuum tube with spring clamps.

"Chemically pure" salts were recrystallized (LiCl was additionally purified from iron impurities). Sodium and potassium chloride were then heated to 600° for 6-8 h. Lithium chloride was dehydrated by drying for 48 h in a mixture with NH_4Cl under a vacuum of 0.1 mm Hg at 240°, and was then remelted while bubbling argon through it.

Prior to the measurements the salt mixture was smelted under a vacuum of 0.01 mm Hg, and the cell was filled with argon. The argon was dried over columns with $MgClO_4$ and P_2O_5 and was passed through a tube with spongy titanium which was heated to 700°.

*Here and below all potentials are referred to the lead reference electrode: Pb/2.5 mole % $PbCl_2$ + electrolyte.

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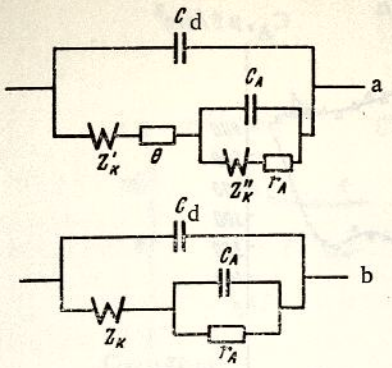


Fig. 1. Equivalent circuit for a platinum electrode in the melt. C_d is the double-layer capacitance, $Z_k = (1-j)A/\sqrt{\omega}$ is the concentrational impedance (the indices ' and " refer to the nonadsorbed and adsorbed forms of the electroactive material), θ is the reaction resistance, and C_A and r_A are the adsorption capacitance and resistance.

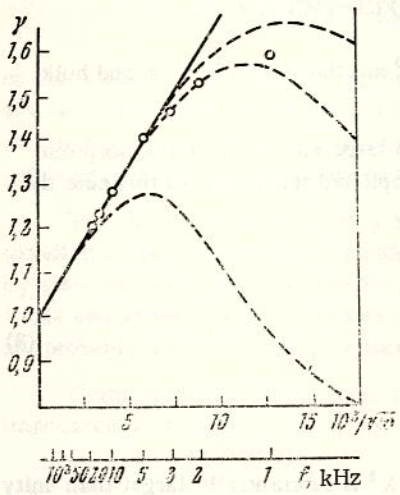


Fig. 2. The plot of γ against $\omega^{-1/2}$; $C_A = 70$ $\mu F/cm^2$; $A = 200\ \Omega \cdot cm^2 \cdot sec^{-1/2}$; 1) $r_A = 2\ \Omega \cdot cm^2$; 2) $r_A = 10\ \Omega \cdot cm^2$; 3) $r_A = 15\ \Omega \cdot cm^2$. The points are experimental data for Pt/KCl–LiCl, at 450° and +0.30 V.

The test electrode was a platinum wire (d = 0.5 mm, h ≅ 4 mm) fused into pyrex. Prior to the measurements the electrode was polished with a paste of chromium oxide and chalk, and then washed with water and alcohol. The auxiliary electrode was a coaxial graphite cylinder; the electrode for polarizing with dc was a graphite rod, and the reference electrode was lead in the melt containing 2.5% $PbCl_2$.

The residual current in KCl–LiCl at 450° and −1.0 V did not exceed 0.35-0.40 mA/cm², which corresponds to a fully dehydrated melt [9, 10]. In KCl–NaCl at 700° and −0.7 V the residual current was 1.1 mA/cm². At potentials between +0.45 and −0.15 V, the anodic polarizing current was not higher than 0.03 mA/cm², the cathodic 0.05 to 0.10 mA/cm². The potential of the platinum electrode became positive at first when it was immersed in the melt (+0.7 to +0.8 V). However, it very quickly and spontaneously shifted to the negative side and stabilized between +0.15 and +0.30 V. A similar phenomenon was observed also by Graves and co-workers [7].

The capacity values could rather well be reproduced when the electrode was not polarized too strongly to the cathodic side. Therefore, a large part of the measurements was made between +0.45 V (anodic current) and −0.15 V (cathodic current). At more cathodic potentials the capacity changed substantially with time, and the electrode surface became rough.

The measured capacities and resistances depended substantially on frequency. This dispersion changed with potential and could, hence, not be attributed to surface roughness as proposed by Laitinen and Gaur [2]. The presence of a stable, albeit very small, residual current gives rise to the idea that the dispersion of the impedance measured is caused by faradaic processes. The equivalent circuit of the electrode was unraveled in the following way.

The functional plot $1/\omega C_s$ against R was extrapolated to determine the resistance of electrolyte and leads [11]. The intercept R_e on the ohmic axis was practically potential-independent and was close to the estimated ohmic cell resistance. After its determination, R_e was subtracted from the measured resistance R, and the resulting components of the series-RC network, R_s and C_s, were transformed to the parallel network:

$$R_p = \frac{1+\alpha^2}{\alpha^2} \cdot R_s;\quad C_p = \frac{1}{1+\alpha^2} \cdot C_s;\quad \alpha = \omega C_s R_s, \qquad (1)$$

The functional plot C_p against $1/\omega R_p$ was extrapolated curvilinearly to infinite frequency to determine the double-layer capacity [11]. Such an extrapolation can, of course, only give a very rough value of C_d. For a more accurate calculation one must know the equivalent circuit of the faradaic impedance shunting the double layer.

Attempts to describe the data for platinum by the simplest circuit, where the faradaic impedance is considered, either as a purely concentrational [12] or as a concentrational impedance in series with the ohmic charge transfer resistance, were not successful. The frequency dependences of R_s, C_s, and $\tan \Phi = 1/\omega C_s R_s$ indicated that there is an additional capacitative element in the faradaic impedance network. We have, therefore, tried to use an equivalent circuit which takes into account the adsorption of species participating in the electrochemical reaction in order to describe the systems studied [13]. In the deduction it was assumed that one of the forms (the oxidized or the reduced) of the electroactive material can become adsorbed on the electrode. Then,

$$r_A = c_i^0 RT / n^2F^2(\partial \Pi_i / \partial c_i^0) \qquad (2)$$

$$C_A = c_i^0 n^2F^2(\partial \Gamma_i / \partial c_i^0) / RT,$$

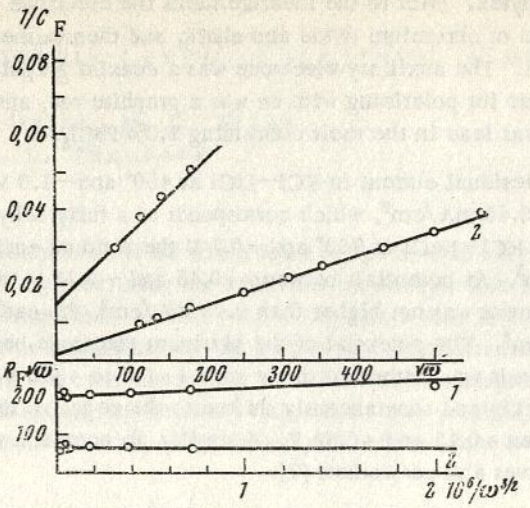


Fig. 3

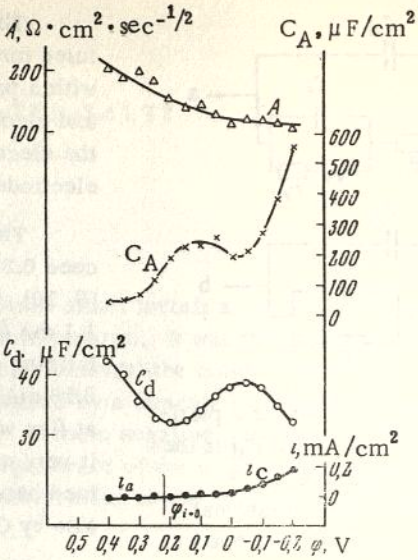


Fig. 4

Fig. 3. Applicability of Eq. (4) to the experimental data for the faradaic impedance of platinum: 1) KCl–LiCl, 450°, + 0.3 V; C_A = 70 μF/cm²; r_A = 10 Ω · cm²; A = 200; 2) KCl–NaCl, 700°, +0.1 V; C_A = 715 μF/cm²; $r_A \geq$ 10 Ω · cm²; A = 67.

Fig. 4. Potential dependence of the double-layer capacitance C_d, the adsorption capacitance C_A, the constant A, and the current density i for Pt/KCl–LiCl at 450°.

where Π_i is the mass flow of substance i to the electrode surface, and Γ_i and c_i^0 are the surface excess and bulk concentrations of the material.

Since r_A and C_A do not depend on frequency then $|Z_k''| \ll r_A$ at not too large adsorption and desorption rates and at sufficiently high frequencies (cf. Fig. 1a), and the circuit can be simplified (Fig. 1b). In this case the series components of the faradaic impedance are:

$$R_F = \frac{A}{\sqrt{\omega}} + \frac{r_A}{1+\lambda^2}$$
$$1/C_F = A\sqrt{\omega} + \frac{1}{C_A}\cdot\frac{\lambda^2}{1+\lambda^2}, \quad (3)$$
$$\lambda = \omega r_A C_A,$$

and since by convention the frequency ω, is not too small, one can assume that λ^2 is substantially larger than unity and

$$R_F\sqrt{\omega} = A + \frac{1}{C_A^2 r_A \omega^{3/2}} \quad (4)$$

$$1/C_F = 1/C_A + A\sqrt{\omega}. \quad (5)$$

We denote

$$\omega (C_p - C_d) R_p = (\omega C_F R_F)^{-1} = \gamma.$$

Assuming as before that $\lambda^2 \gg 1$ one can reckon that in the expression for $R_F\sqrt{\omega}$, the second term is small as compared to A. Then,

$$\gamma = 1 + \frac{1}{AC_A\sqrt{\omega}}. \quad (6)$$

In other words, with increasing frequency the $\gamma - \omega^{1/2}$ relation must become a straight line with an intercept of unity

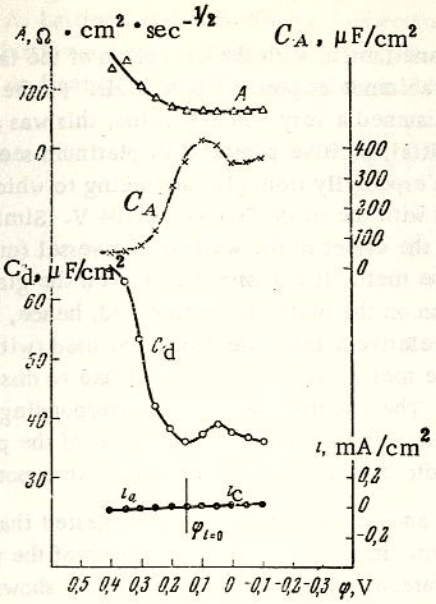


Fig. 5. Potential dependence of C_d, C_A, A, and i for Pt/KCl–LiCl at 600°.

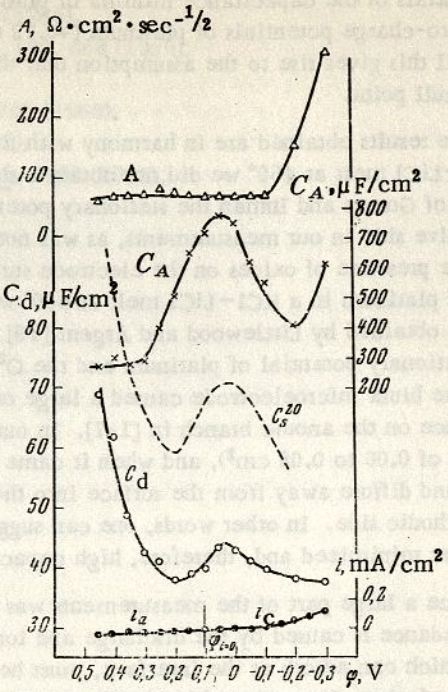


Fig. 6. Potential dependence of C_d, C_A, A, and i for Pt/KCl–NaCl at 700°.

on the ordinate. With decreasing frequency this function must deviate from the straight line in the direction of the abscissa. The slope of the straight line is $1/C_A A$. With condition (6) one can correct the values for C_d found by curvilinear extrapolation and determine the double-layer capacity with high accuracy. It is evident that this requires having at least two points in the high-frequency range which satisfy the condition (6).

The shape of the function γ for the circuit of Fig. 1b is illustrated for different r_A in Fig. 2 where the corresponding curves are obtained by calculation from Eqs. (3) and (5) while the points are experimental data. It is readily seen that the approximation discussed is successfully realized for systems of the type Pt/MCl at frequencies of 1 kHz and above. In certain cases (small C_A) deviations from Eqs. (3) were observed at lower frequencies, which are probably due to increasing concentrational impedance of the adsorbed particles.

Corrected values of C_d were calculated from C_p, and the capacitative and ohmic components of the faradaic impedance were determined:

$$1/C_F = \frac{\gamma^2}{1+\gamma^2}\cdot\frac{1}{C_p - C_d}, \qquad R_F = \frac{R_p}{1+\gamma^2}. \tag{7}$$

The correctness of the circuit and the C_d values obtained was further tested by constructing plots of the functions $1/C_F$ and $R_F\sqrt{\omega}$. It is seen from Fig. 3 that the relations (4) are quite satisfactorily fulfilled. The values of the constant A as determined from the slope of the straight line $1/C_F$ against $\sqrt{\omega}$ and from the intercept on the ordinate of the straight line $R_F\sqrt{\omega}$ against $\omega^{-3/2}$ coincided to within 3-5%. The value of C_A was calculated from the intercept on the ordinate of the straight line $1/C_F$ against $\sqrt{\omega}$. The resistance r_A could only be determined roughly and not too high C_A, which follows from Eq. (4). The equivalent circuit Fig. 1b described well the experimental data for practically all the systems investigated in the frequency range 1 to 50 kHz and at potentials between +0.6 and −0.20 V. Typical results are shown in Figs. 4-6.

A characteristic feature of the capacitance curves C_d against φ is the presence of a clear minimum at potentials between +0.15 and −0.20 V. This minimum is still present on the plots C_s against φ for finite frequencies (see e.g., Fig. 6). With increasing temperature the $C_d - \varphi$ curve becomes "sharper," and the value of the capacitance in the minimum increases. The same properties distinguish the $C - \varphi$ curves for liquid metals. The difference between

the potentials of the capacitance minima of platinum and lead [14] is 0.75 to 0.85 V, i.e., is close to the difference in the zero-charge potentials of platinum (+0.12 to +0.20 V: [15, 16]) and of lead (−0.64 V: [17]) in aqueous solutions. All this gives rise to the assumption that the minimum in the double-layer capacitance on platinum coincides with its null point.

The results obtained are in harmony with the work of Graves and Inman, with the exception of the fact that in the KCl−LiCl melt at 450° we did not obtain a sharp rise in the capacitance at positive potentials. Further, while in the work of Graves and Inman the stationary potential of platinum assumed a very positive value, this was shifted to the negative side in our measurements, as was noted above. The initial, positive potential of platinum seems to be due to the presence of oxides on the electrode surface. This follows especially from [18] according to which the potential of platinum in a KCl−LiCl melt at 450° which was saturated with the oxide PtO was +0.94 V. Similar results were also obtained by Littlewood and Argent [19] who demonstrated the effect of the walls of the vessel (quartz, glass) on the stationary potential of platinum and the O^{2-} ion content in the melt. It is possible that even the glass at the seal of the blunt microelectrode caused a large oxygen concentration on the platinum surface and, hence, a large capacitance on the anodic branch in [1-7]. In our measurements a relatively large electrode was used (with a surface area of 0.06 to 0.08 cm^2), and when it came in contact with the melt, the platinum oxides had to dissolve in the melt and diffuse away from the surface into the electrolyte [18]. The electrode potential correspondingly drifted to the cathodic side. In other words, one can suggest that under our conditions, the oxygen content of the platinum surface was minimized and, therefore, high capacitances on the anodic branch of the $C_d-\varphi$ curve were not attained.

Since a large part of the measurements was made applying an anodic current, it can be suggested that the faradaic impedance is caused by the discharge and ionization of platinum. In this case complex anions of the type $PtCl_4^{2-}$, which can adsorb at the interface, must be the result of the faradaic reaction. It was recently shown [20] that the accumulation of complex chloroplatinates leads to anodic passivity of platinum in chloride melts. This agrees with the conclusion that the adsorbed particles are slowly removed from the electrode surface (very large r_A) and explains the great polarizability of platinum in such melts as compared to other metals. The over-all reaction responsible for the faradaic impedance can thus be written as

$$Pt - 2e + 4Cl^- \rightleftarrows PtCl_4^{2-}.$$

In view of the large polarizability the reaction proceeds essentially as not in equilibrium, and the character of the potential dependence of the faradaic impedance components is difficult to elucidate at present.

When passing through the capacitance maximum at potentials between 0 and −0.1 V, the discharge of alkali metal ions begins to play an essential part; it can proceed, either under formation of solutions in the molten salt: $2Li^+ + e \rightarrow (Li-Li)^+$, or under intrusion into the platinum and the formation of intermetallic compounds: $Li^+ + e + xPt \rightarrow LiPt_x$. The destruction of the surface layer of platinum during cathodic polarization speaks in favor of the latter mechanism. In this respect there exists some similarity with the silver electrode [12] where the discharge of alkali metals leads to the appearance of steps on the cathodic branch of the $C_d-\varphi$ curve.

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