ELECTRODE POLARIZATION IN NaCl CRYSTALS

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The possibilities of interpreting the polarization effects, arising in ionic crystals in contact with metal electrodes, as electrode polarization are discussed. This is a consequence of the incomplete blocking of charge carriers at the interfaces. It has been demonstrated experimentally that the polarization in the system Pt|NaCl|Pt is electrode-related. The conductance of interfaces has been found to be non-linear and it can be interpreted by electrochemical kinetics.

I. INTRODUCTION

The great polarization effects occurring e.g. in sodium chloride crystals [1] are usually attributed to a build-up of space-charge in the vicinity of electrodes [2]. The attempts to treat the problem theoretically [3—11] are complicated by the nonlinearity of the differential equations describing the motion of free charges in the crystal. Therefore the existing solutions are restricted to simple cases only, like the steady state or the action of small a.c. signals. Although no universal solution of the transport equations at present exists and the results of theories [3—11] do not always coincide, they demonstrate the chances of the space-charge (SC) polarization model. The efforts to confirm theories experimentally were only partly successful. Disagreement was found in predicted and experimentally observed magnitudes of the capacities [4], [12—14], in the frequency dependence of the capacity and conductivity [9], [12], [14] and in the dependence of the capacity on temperature [15]. As a rule, the nonlinearities found in measurements using higher voltages were smaller than expected or even absent [16, 17]. Doubt was thrown on the adequacy of the employed boundary conditions [18] and the results were interpreted as interfacial polarization [16, 19, 20]. Some causes of the failure of experimental verification were elucidated, as well as some further possibilities of interpretation were shown in paper [21].

A very probable reason for doubts about the origin of the polarization is

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the fact that most of the employed experimental methods do not allow to distinguish between bulk and electrode-related effects. To do this, the possibility to investigate the area near the contact of the sample with the electrode is necessary. Measuring the potential distribution along the sample can be used in this way. More measurements of this kind are known [7] but in many cases their confrontation with other methods, supplying data about the polarization, is missing. The rate of the build-up of SC was investigated in [7], [22, 23]. The rate of the potential redistribution in the sample, following the application of a voltage step, was compared with the decay of charging currents in papers [24, 25].

The present paper deals with the consequences of incomplete blocking of charges at the interface. The possibilities of application of some ideas common in the electrochemistry of liquid solutions to solid systems are discussed. The demonstration of the electrodic origin of the polarization in NaCl in contact with Pt electrodes has been attempted. It appears to be possible to interpret the results as consequences of incomplete blocking at the electrodes.

II. THEORY

1. The incompletely blocking electrode

The usual simplifications introduced in theories of SC polarization may be summed up as follows: a. Charges of both signs are blocked at the interface, or charges of one sign are blocked while those of the opposite sign can freely pass the interface. b. Contact potentials are neglected. There is no SC without externally applied voltage. c. In some papers the discharge of a part of the excess charges without any further consequences is supposed [4], [9]. d. The ensemble of discrete charges is replaced by continuous charge density. e. The adsorption is neglected. It is partly a result of items b—d.

In the following we shall consider points a to c.

a. The behaviour corresponding to totally blocking conditions is usually observed in some liquid electrolytes. It seems to have been observed also in solid AgBr in contact with platinum [26] and in the system solid Ag|graphite [27]. However, the flow of a stationary current across the interface solid electrolyte|electrode even at small voltages is observed more frequently.

b. The charge on a totally blocking electrode is a function of the potential alone. In the case of incomplete blocking the equilibrium may be decisively influenced by a reaction at the electrode, leading to a transfer of electrons across the interface. The generally non-zero contact potential influences the concentrations of ions near the electrodes and gives rise to SC even without an externally applied voltage.

c. If ions from the electrolyte are discharged at an electrode which does not contain a great supply of these ions, the concentration of the products of the discharge reaction changes. The further "fate" of the products is not unimportant, unless the probability of the backward reaction is negligibly small.

If the interface is not entirely blocking, electrons cross it after the contact has been brought about and until the resulting potential difference does not stop further discharging. This process is generally accompanied by a change in the valence of ions from the electrolyte or the electrode and it can be considered a redox reaction. The transfer of electrons is reversible, its probabilities in both directions depend on the difference of the electrochemical potentials of ions in reduced and oxidized states. In equilibrium the reduction and oxidation current densities have the same magnitudes and no external current flows through the electrode. Changing the potential of the electrode with respect to the bulk of the sample to $\Phi = \Phi_0 + \eta$ causes a flow of a current of the density [28]

$$i = ne\{k_r a_r \exp(\alpha nen/kT) - k_0 a_0 \exp[-(1-\alpha)nen/kT]\} =$$
$$= i_0\{\exp(\alpha nen/kT) - \exp[-(1-\alpha)nen/kT]\}, \quad (1)$$

where η is the overvoltage, k_r, k_0 are rate constants and a_r, a_0 activities related to a scale of potentials in which $\Phi_0 = 0$, i.e. to the equilibrium potential, α — the symmetry factor of the potential barrier at the interface, k — the Boltzmann constant and T — temperature. Relation (1) presents the VA-characteristic of the interface at the activities a_r, a_0 and at a change in valence by n.

The flow of Faradaic current across the interface produces changes of the concentration and the activity of reaction products, provided the neutralized ions are of a different kind from those of the electrode, e.g. in case of the contact NaCl|Pt. Thus the probability of a backward reaction as well as the overvoltage must grow. A steady state is reached if the rates of production of the neutral species and of their transport from the interface are the same. In solid systems the most likely transport mechanism of neutral products e.g. Na°, Cl°, Cl₂, at moderate current densities is diffusion. The charge transfer itself may be fast in comparison with the transport of products. If the diffusion is linear across a layer of finite thickness such as an evaporated metal film, or in the case of two or three dimensional diffusion, the overvoltage may attain a stationary value

$$\eta = kT/(ne) \ln(1 - i/i_D) \quad (2)$$

[28]. i_D is the limiting diffusion current density. With a suitable polarity of the overvoltage the current-voltage characteristic resembles relation (1), with the opposite polarity the maximum of the current density is i_D.

2. The mixed potential

We have presumed hitherto the existence of a single electrochemical reaction, e.g.

$$Na^+ + e \rightleftarrows Na^0, \quad or \quad Cl^- \rightleftarrows Cl^0 + e$$

at the interface. However, the equilibrium may be ensured by more parallel reactions. This can lead to significant difficulties in the interpretation of the overvoltage, for different processes may predominate at different polarities of the applied voltage and the saturation of the current due to the slow diffusion of some component (2) may not arise at all.

We shall write (1) in the form

$$i = i_0[\exp(\alpha_1 en/kT) - \exp(-\alpha_2 en/kT)]. \quad (3)$$

Both polarities of VA-characteristics (1) are bound by the relation

$$\alpha_1 + \alpha_2 = n, \quad n = 1, 2, \ldots \quad (4)$$

In case of a mixed potential the resulting characteristics can be approximately of the form (3) but the condition (4) need not hold. On the other hand, both polarities of the current-voltage characteristic may be handled separately, as results of different processes.

3. Charging of the interface

The overvoltage according to (1) cannot appear immediately after switching on a current step. It is caused by charging the electrical double layer at the interface, i.e. by the build-up of a vacancy space-charge. Similarly the stationary diffusion and the corresponding overvoltage (2) are reached after a certain time [28]. This behaviour may be described in both cases as the charging of a capacitor. A suitable equivalent circuit for a symmetrical cell containing two incompletely blocking electrodes is in Fig. 1. The geometrical capacity of the sample has been neglected. The circuit is considerably simplified, a network consisting of elements with a simple or no time (or frequency) dependence would be more complicated.

Using the known theories including their limitations only an approximate

Fig. 1. Simple equivalent circuit of the crystal in contact with electrodes: R — resistance of the interface, C — capacity of the interface, R_b — resistance of the bulk of the sample. The geometrical capacity was neglected.
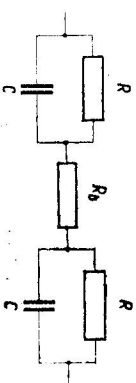
idea can be formed about the properties of the space-charge arising at the electrodes. However, in case of incompletely blocking electrodes effects appearing as capacities, exceeding the SC capacity, may be expected. Departures from the equilibrium concentrations produce changes of the electrode potential. After switching the cell short a depolarization current will flow until the original concentrations are re-established. In this way significant charges can be accumulated at the electrodes.

We shall assume a simple case of equilibrium ensured by one sort of ions reacting fast enough to allow considering the discharging quasistatic. The deviation from equilibrium can be expressed by means of the Nernst relation

$$\eta = kT/(ne)\ln[c(t)/\bar{c}].$$ (5)

$\bar{c}$ is the equilibrium surface concentration of the discharged ions at the interface and $c(t)$ is their concentration at the time t. The concentration of ions entering into the reaction is assumed to be constant, i. e. the transport through the sample to be faster than across the interface, which is a condition of at least partial blocking. If at $t = 0$ the current $i = $ const. is switched on and the products of the reaction cannot diffuse or escape by other mechanism, the concentration vs. time dependence is

$$c(t) = \bar{c} + \xi \int_0^t i \, dt = \bar{c} + \xi i t$$ (6)

with

$$\xi = (ne)^{-1}.$$

In case of diffusion, e.g. into the electrode, the increase of concentration must be slower. If we restrict the solution to linear diffusion and short enough times, it is possible to apply the Sand's result for the semiinfinite space [28], leading to

$$c(t) = \bar{c} + \xi i' \sqrt{t},$$ (7)

with

$$\xi' = 2/(ne \sqrt{\pi D}).$$

D is the diffusion coefficient. The overvoltage vs. time dependence may be interpreted as the charging of a capacitor with the differential capacity

$$C_d = dq/d\eta = i \, dt/d\eta = \frac{i}{d\eta/dt}, \qquad i = \text{const.}$$ (8)

We obtain the following relations for the differential capacity:

without diffusion and

$$C_d = ne(\bar{c}\sqrt{t}/\xi + it)/kT$$ (9)

$$C_d = ne \exp(ne\eta/kT)/\xi kT$$

with diffusion.

$$C_d = 2ne(\bar{c}\sqrt{t}/\xi' + it)/kT$$ (10)

$$C_d = 2nec^2 \exp(ne\eta/kT) [\exp(ne\eta/kT) - 1]/(kT\xi'^2)$$

If the surface of the electrode is fully covered by the reaction products ($\Theta \doteq 1$), the concentration attains its maximum. By further deposition the quantity of the products grows but not the concentration. Thus the overvoltage should attain a constant value.

Expression (6) is fully valid under the presupposition that the products do not come beyond the reach of the interface. If this is not true, irreversible changes at the interface should be expected. As diffusion itself is an irreversible process, a part of the discharged ions is lost for the backward reaction. The resistances R in the equivalent circuit correspond to the part of the current replacing these ions.

Relations (9) and (10) were derived under the supposition that the discharging was quasistatic. Some deviations from the relation (5) may occur in accordance with (1), if this condition has not been fulfilled. In addition a part of the overvoltage falls to the SC region in the crystal, and it can influence the slope of the dependence $\eta = f(\ln|i|)$ [28].

III. EXPERIMENTAL

In the present paper the charging of the interface NaCl crystal Pt electrode, following the application of a current step, was investigated. The measurements were compared with the voltage dependence of the charging currents.

The employed apparatus was described elsewhere [29]. It was completed by supplementary circuits for measurements of charging and discharging currents or by a source of constant current. Probe measurements were performed by means of a probe of a modified design, enabling to use forces pressing the Pt point to the sample in the range of 10^{-4} -- 10^{-2} N. At temperatures near 400 °C the force of 10^{-3} N was used. The time dependence of currents and of the probe potential was recorded by line recorders. Their response time was approximately 0.5 s. For all measurements an argon atmosphere was used. Samples of NaCl of a high purity as well as samples doped with 10^{-2} mol%

of Ca²⁺ ions were used. The crystals were grown by the Stocklarger method from analytically pure material repurified by means of ion exchangers and were free of OH⁻ impurities. The pure crystals were cleared of the residual Ca²⁺ impurity by selective extraction [30] and contained less than 10^{-5} mol% of Ca²⁺ ions. The specimens were cleaved to thickness of 0.7—1.5 mm. Any mechanical or chemical treatment was given up in order to avoid destruction and contamination of the surface. The crystals were just heated to about 100 °C before cleaving and were kept during the whole preparation at a raised temperature to reduce adsorption of humidity. Electrodes were applied to the opposite faces of the samples by cathode-sputtering of platinum. The fresh platinum was black but during a short anneal (1 hour at 600 °C) a bright metallic surface was obtained. Some measurements made using both sputtered and massive electrodes indicated that the actual surface was still about 3 to 5 times greater than the geometrical area of the electrodes. The samples were placed in the furnace between Pt holders under a light stress of about 10 $\mathrm{Ncm^{-2}}$. The measurements were performed in the temperature range of 300—600 °C.
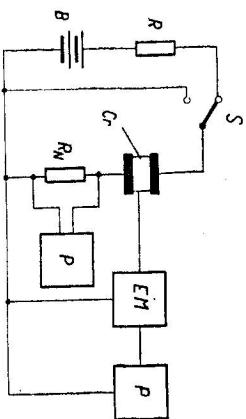

Fig. 2. Block diagram of the measuring circuit: Cr — sample, R_N — resistance box, EM — vibrating reed electrometer, P — line recorder, S — switching device, B — potential source, R — series resistor.

In the used arrangement (Fig. 2) the polarization of the counterelectrode has no influence on the potential of the probe. Measuring at various distances from the working electrode is a good check as to whether the investigated process is not a bulk property. The only difference between the results was in the magnitude of the Ohmic potential drop in the part of the sample between the electrode and the probe. The typical distance from the electrode was 20 µm. The influence of polarization of the probe was tested by changing the input resistance of the electrometer. Switching over from $10^{15}\,\Omega$ to $10^{11}\,\Omega$ changed the measured potential by a few percent, thus it could be assumed that with $10^{15}\,\Omega$ the polarization of the probe was negligible.

In order to achieve reproducible conditions for each measurement, the current was switched on for the shortest possible time (1—20 min), then a current reversal for the same time interval and at last short-circuiting followed. The sample could be depolarized in a relatively short time after a polari-

zation with lower current densities but hours of short-circuiting were needed to attain a state similar to the initial one after polarizing with greater currents.

IV. RESULTS AND DISCUSSION

Plots of overvoltage vs. time dependences, measured at 490 °C are shown in Fig. 3. The dependences are markedly nonlinear functions of the current density. Consequently the charging current density as well as the rate at which the steady state is reached should depend on the polarizing voltage. The obtained results are shown in Fig. 4. They demonstrate that though
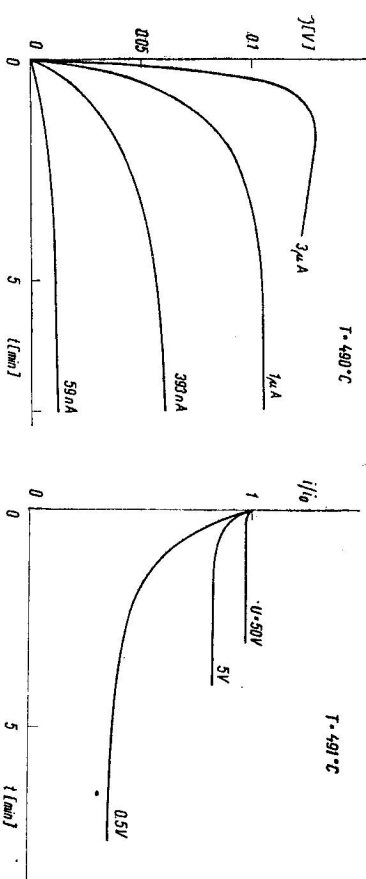

Fig. 3. Anodic polarization curves measured in pure NaCl. $S = 0.4$ cm².

Fig. 4. Charging currents measured with potential steps of different magnitudes in pure NaCl. $S = 0.4$ cm².

the potential is measured near the surface, it represents the whole cross-section of the specimen. A more detailed series of probe potential measurements at 419 °C is shown in Figures 5—7.

Attention has been paid to the question, whether the electrodes are entirely blocking at small polarizing voltages or not. With tens of mV a steady current flowed across the studied cell Pt|NaCl|Pt. Even after polarizing for days the current was stationary. Thus the electrodes could not be considered completely blocking.

Comparison of the depolarizing currents with the decaying part of the charging currents, measured with a potential difference of 50 mV, showed that the superposition principle was not valid even at small voltages. After polarizing with greater potentials, the depolarization became rather slow.
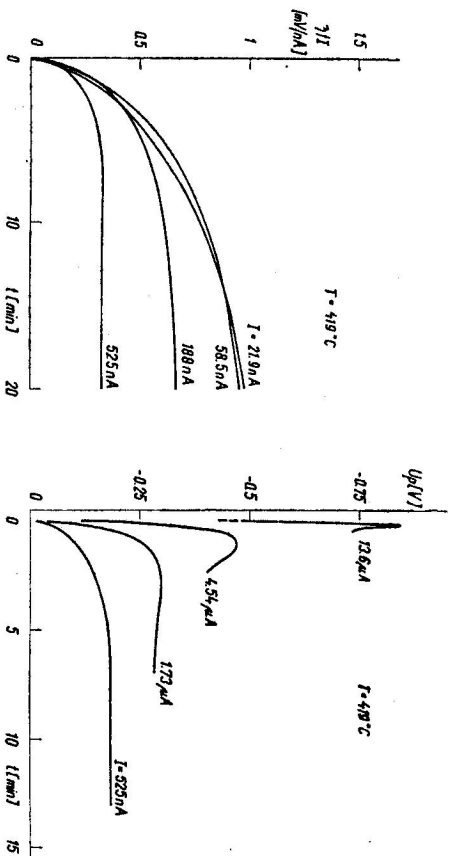
Fig. 5. Anodic polarization curves, corrected for Ohmic potential drop, measured in pure NaCl, referred to the current 1 μA.

Fig. 8 shows that the charge per unit area released during depolarization is greater than
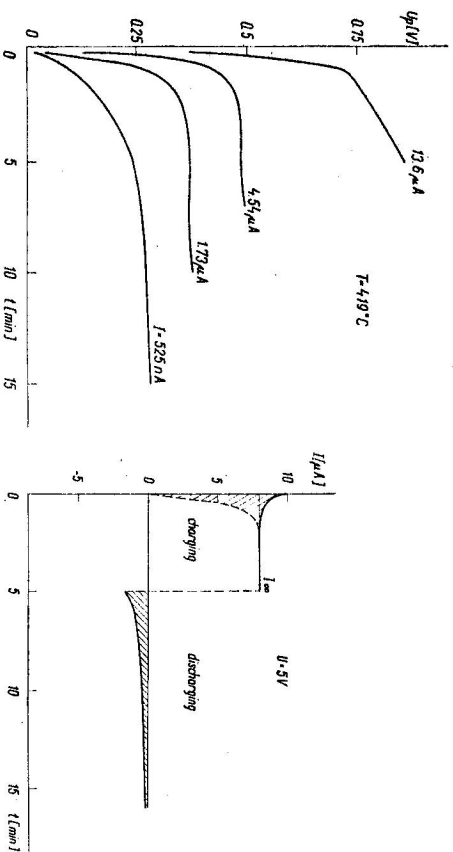
$$q = \int_0^\infty [i(t) - i_\infty]\, dt.$$

Fig. 6. Anodic polarization curves at higher current densities (pure NaCl), $S = 0.4$ cm².

Fig. 7. Cathodic polarization curves (pure NaCl), $S = 0.4$ cm².

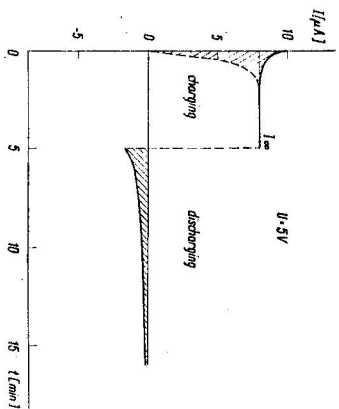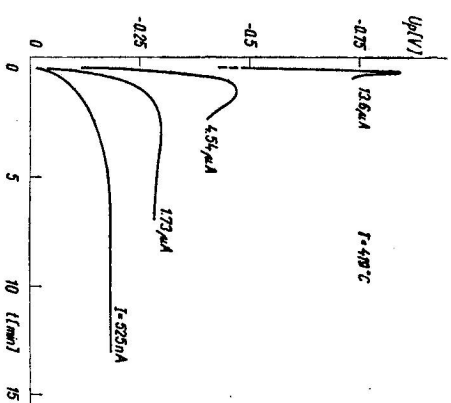Fig. 8. Polarization and the following depolarization current in pure NaCl.

Consequently the charging current is not the sum of the constant current i_∞ and of the polarizing current $i(t) - i_\infty$, but at the moment $t = 0$ the whole current is used up for charging the interface. The steady current is Faradaic and it reaches its maximum only after a certain time. It could hardly be considered electronic, because of its magnitude even at small voltages.

Plots of overvoltage vs. $\log|i|$, obtained from Figs. 5—7 by extrapolation of "steady" values to the time $t = 0$ and corrected for the Ohmic potential drop [28], are given in Fig. 9. The steady values of anodic overpotential are
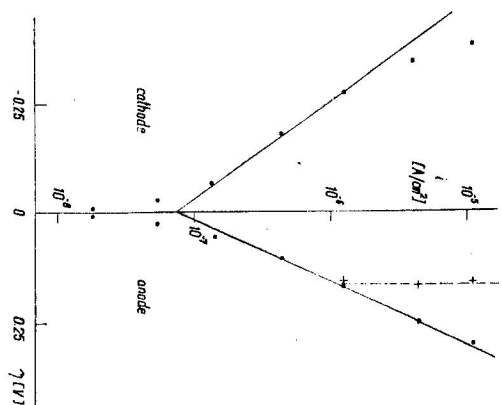
shown too. The result may be expressed in form (3) with the following values of constants

$$i_0 = 7.5 \times 10^{-8}\ \text{Acm}^{-2}, \qquad \alpha_1 = 0.94, \qquad \alpha_2 = 0.60.$$

Further information about the possible mechanism, determining the behaviour of the interface can be obtained from the analysis of the whole $\eta(t)|_{t=const.}$ dependence. Assuming the slow step of the overall electrode reaction to be the charge transfer and equation (1) in form (3) to be valid, then the current-voltage characteristic is no explicit function of time. The $\eta = \eta(t)|_{t=const.}$ are then the charging curves of a parallel RC circuit (Fig. 1) with a conductance of unit area

$$G(\eta) = R^{-1} = i_0[\exp(\alpha_1 e\eta/kT) - \exp(-\alpha_2 e\eta/kT)]/\eta.$$

The surface density of the charge, accumulated in a run between the start and

Fig. 9. The current = voltage characteristic of NaClPt interface at 419 °C. The points + are the steady state values of anodic overvoltage.

the moment of reaching either the maximum or the steady state overvoltage, is given by

$$q = \int_0^{t_m} \{i - i_0[exp(\alpha_1 e\eta/kT) - exp(-\alpha_2 e\eta/kT)]\}\, dt. \quad (11)$$

The graph calculated from anodic curves using (11) is shown in Fig. 10.

The interpretation of the VA-characteristic of the interface by slow discharging is equivalent to the concept of a sodium electrode with the reaction

$$Na^+ + e \rightleftharpoons Na^0.$$
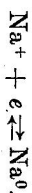
The initial steep increase of the overpotential would correspond to the charging of a great nonlinear double layer capacity [31]. However, some facts do not support this view:

a) experimentally found $\alpha_1 + \alpha_2 \neq 1$;

b) the charge accumulated at the interface corresponds to approximately one monolayer of ions. The corresponding double layer capacity is not realistic;

c) charging the interface must cause a significant change in concentration resulting in further decrease of the sum $\alpha_1 + \alpha_2$;

d) a completely blocking behaviour should appear in some range of potentials after the supply of sodium is used up at the anode. This has not been observed.

The existence of a mixed potential ensured by parallel reactions of the type

I. $Na^+ + e \rightleftharpoons Na^0$

II. $Cl^- \rightleftharpoons Cl^0 + e$

appears to be more realistic. However, the participation of platinum in the overall electrode reaction cannot be ruled out. In this case we do not expect complete blocking, nor $\alpha_1 + \alpha_2$ equal to an integer. The capacity of interfaces is given by concentrations of adsorbed atoms in accordance with relations of the type (8) and (9). The determination of the capacity is complicated by the possible explicit time dependence of the conductivity. The accumulated charge might be somewhat greater than in Fig. 10 but the shape of the dependence will be similar.

The value b of the Tafel slope [28]

$$\eta = a + b \ln|i|$$

of the anodic branch of the VA-characteristic is close to kT/e. This value and the nearly constant steady state values of overpotential at higher current densities suggest that at anodic potentials the one-electron step $Cl^- \rightleftharpoons Cl^0(ads.) + e$ of the overall electrode reaction $2Cl^- \rightleftharpoons Cl_2(g) + 2e$ with a small

charge transfer overvoltage might be dominant. After reaching the monolayer coverage $\Theta = 1$, the overvoltage remains nearly constant. The one-electron reaction

$$Cl^- + Cl^0(ads.) \rightleftharpoons Cl_2(g) + e$$

would lead to an increase of the slope b at $\Theta = 1$ [32].

The capacity of the interface near the equilibrium potential, calculated from the curves in Fig. 5 using (8), is $C_d \doteq 360 \ \mu Fcm^{-2}$. It corresponds to an equilibrium concentration of adsorbed atoms per cm^2 of the geometrical area $c = 1.37 \times 10^{14} \ cm^{-2}$. The maximum of the steady state anodic overvoltage $\eta = (0.17 \pm 0.01)$ V gives the maximum surface concentration in the polarized state $(1.97 - 2.75) \times 10^{15} \ cm^{-2}$. This value is in good agreement with the result in Fig. 10.

The anodic polarization curves measured with greater current densities exhibited an overshot. Its origin is not clear at present.

Comparing the pure and doped crystals gave no significant differences in the conductances of interfaces. The charging curves in Fig. 11 measured with a small applied voltage on equally thick samples show a small dependence
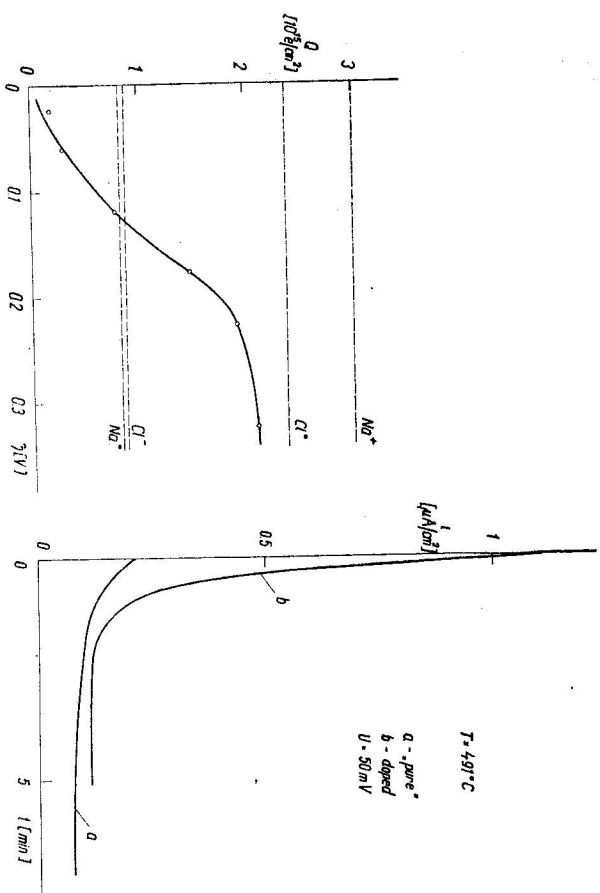
Fig. 10. The charge accumulated on the anode vs. maximum of overvoltage, derived from the anodic polarization curves.
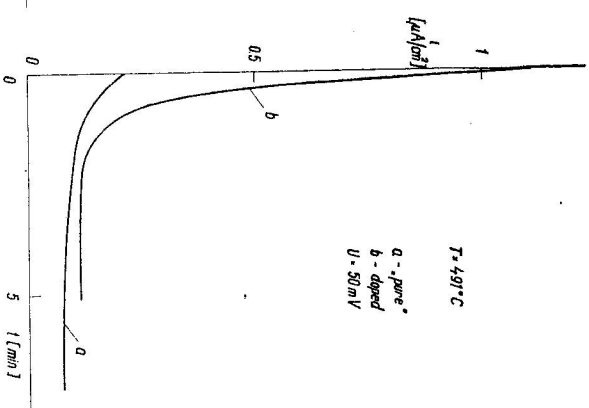
Fig. 11. Comparison of charging transients obtained in pure and doped NaCl.

of i_∞ on doping, whereas the initial value of the current transient is markedly influenced by the Ca²⁺ impurity present. The differences on i_∞ are merely a result of differing potential drops in the bulk. The interface conductances are within 10 % in both cases the same.

The charge transport in NaCl crystals is properly described as a motion of vacancies [33]. This model is less suitable in handling the transport across the crystal-electrode interface, it is then better to keep the reacting ions in view. Doping the crystal by divalent cations increases the concentration of cation vacancies and thus the bulk conductivity too. Adding some 100—1000 ppm of impurities may significantly modify the concentration of vacancies without influencing appreciably the concentration of ions. This applies also to the lattice plane adjacent to the electrode and thus to ions which may participate in electrode reactions. Therefore we do not expect an influence of doping upon the conductivity of interfaces.

V. CONCLUSIONS

Great polarization effects may arise in ionic crystals not only by virtue of a charge blocking at the electrodes but also when ions different from those of the electrode are discharged relatively easily. In this case deviations from the equilibrium electrode potential arise, caused by changes in concentrations at the interface. This effect can be similar to the build-up of the space-charge, although the blocking arises rather due to the slow-transport of neutral products of the electrode reaction than due to the slow rate of discharging. Complicated consequences of this process such as a nonlinear conductance and nonlinear time-dependent capacity of interfaces are expected.

The charging of the interface NaCl|Pt was investigated. It revealed the nonlinear conductance of this contact. The experimentally observed great capacities are in good agreement with the discussed model. Both the conductances and the capacity can be explained by the existence of heterogeneous reactions combined with the transport (most likely diffusion) of neutral products out of the reach of the interface.

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