

# ANOMALOUS TRANSIENT CURRENTS IN NaCl SINGLE CRYSTALS

STEFAN LANYI\*, Bratislava

The current-voltage characteristic of the ionic crystal|electrode interface is discussed in the paper. The role of products of electrochemical reactions, ensuring the charge transfer, in establishing the equilibrium on the electrode, has been pointed out. Measurements on the cell graphite|NaCl|graphite have shown that nonequilibrium initial conditions result in an apparent increase of the interface conductivity and may be the cause of non-monotonous transient currents following the switching-on or the reversal of the applied voltage.

## АНОМАЛЬНЫЕ ПЕРЕХОДНЫЕ ТОКИ В МОНОКРИСТАЛЛАХ NaCl

В работе обсуждается вольт-амперная характеристика на разделье сред кониния кристалл-электрод. Показана роль продуктов электрохимических реакций, обеспечивающих перенос заряда при установлении равновесия на электроде. Измерения системы Графит-NaCl-графит показывают, что неравновесное первоначальное состояние является причиной кажущегося роста проводимости на границе и может вызывать немонотонное поведение зарядного и коммутационного токов.

### I. INTRODUCTION

In the last years difficulties with the interpretation of polarization phenomena, observed in many ionic solids, led to a detailed investigation of processes taking place at the contacts with electrodes, which are usually electronic conductors [1—7]. In spite of a partial success the agreement of experimental results and theoretical predictions is usually not satisfactory. One of the causes is the frequently poor reproducibility of the properties of the interfaces. In papers [8, 9] an effect of electrical history of the sample on the interface conductivity was observed. It consisted of an apparent increase of the conductivity if the sample had been previously polarized with voltages in excess of approximately 1 V and then completely depolarized. Freshly prepared electrodes had a similarly enhanced conductivity. Such a forming of contacts was reported also by other authors [10, 11].

\* Institute of Physics, Dúbravská cesta, CS-899 30 BRATISLAVA.

Measuring the time or voltage dependence of charging and discharging currents is one of the suitable methods of investigating the electrical properties of contacts<sup>1)</sup>. A poorly defined state of the electrodes may appreciably influence them. The aim of the present paper was to point out the possible effect of the non-equilibrium of the electrodes on the charging currents and the currents following the reversal of the applied voltage.

### II. THEORY

In papers [3, 12] a nonlinear conductivity of NaCl | Pt and in [8, 9] of NaCl | graphite interfaces was observed, which could be described by the relation

$$j = j_0 \left[ \exp \frac{\alpha_1 e \eta}{kT} - \exp \left( -\frac{\alpha_2 e \eta}{kT} \right) \right] \quad (1)$$

where  $j$  is the current density,  $j_0$  is the exchange current density,  $\alpha_1$ ,  $\alpha_2$  are symmetry factors of the potential barrier at the interface,  $\eta$  is the overvoltage and  $kT$  has the usual meaning.  $\alpha_1$  may be interpreted as the fraction of time of an elementary act of reaction, during which the reacting ion is charged, and thus the electric field contributes to its energy. The current-voltage characteristic (1) is the consequence of an incomplete blocking action of the electrode and it could result from the charge transfer ensured by one reversible reaction [13, 9].

In this case  $\alpha_1 + \alpha_2 = n$  is expected, where  $n$  is the change in the valency of reacting ions. However, to enable the flow of a dc current across a cell consisting of an ionic crystal and two nonpolar electrodes (i. e. of different ions as Na or Cl in case of NaCl) two reactions are needed. These may be the discharge of Na<sup>+</sup> ions on the cathode and the discharge of Cl<sup>-</sup> ions on the anode, or perhaps the dissolution of cations from the anode in the crystal. The current across the interface may be written in the form

$$j = \bar{j}_1 - \bar{j}_2 - (\bar{j}_1 - \bar{j}_2) \quad (2)$$

where  $\bar{j}_i$  designates the current due to the  $i$ -th forward reaction,  $\bar{j}_i$  in the backward direction. The equilibrium condition for one reaction  $\eta = 0$ ,  $j = 0$  is not sufficient in case of two reactions (2), there must hold further  $\bar{j}_1 - \bar{j}_2 = 0$ . Note that equilibrium may arise only if both reactions are reversible.

<sup>1)</sup> From the point of view of electrical properties the sample can be replaced by an equivalent circuit consisting of capacitors and conductances, for which the expected isothermal transient currents should decrease with time. Any different behaviour of the transients will be called anomalous throughout this paper.

The current flowing across the interface under some deviation from equilibrium will be

$$j = j_{o1} \left\{ \exp \left( \frac{\alpha_1 e \eta}{kT} \right) - \exp \left[ - \frac{(1 - \alpha_1) e \eta}{kT} \right] \right\} + j_{o2} \left\{ \exp \left( \frac{(1 - \alpha_2) e \eta}{kT} \right) - \exp \left( - \frac{\alpha_2 e \eta}{kT} \right) \right\}. \quad (3)$$

$j_{o1} = j_{o2}$  are the exchange current densities of the individual reactions. Positive values of  $\eta$  correspond to positive potentials of the sample with respect to the electrode. The exchange current densities may be written in the form

$$j_{o1} = e \bar{k}_1 a_{o,1} = e \bar{k}_1 a_1 \\ j_{o2} = e \bar{k}_2 a_{o,2} = e \bar{k}_2 a_2$$

$\bar{k}_1, \bar{k}_2$  are rate constants related to the bulk activities  $a_{o,1}, a_{o,2}$  of reactants,  $\bar{k}_1, \bar{k}_2$  to the activities of reaction products  $a_{r,1}, a_{r,2}$  on the surface of the electrode. The subscripts  $o$  and  $r$  indicate the oxidized and reduced states of respective ions.

The scale of the overvoltage  $\eta$  and the exchange current densities  $j_{o1}, j_{o2}$  are related to the equilibrium contact potential, which is expected to be more negative than there would be the equilibrium potential of oxidation of the anionic component of the crystal on an electrode with a standard, e. g. unit, activity of atomic halogen ( $\text{Cl}^-/\text{Cl}_2$ ), and more positive than the equilibrium potential of reduction of the metal component on an electrode from this metal ( $\text{Na}^+/\text{Na}$ ). Therefore, the equilibrium activities or concentrations of reaction products, as well as the product  $a_{r,1} \times a_{o,2}$  will be small. Consequently the charge transferred by backward reactions may be important only for some transitory time, otherwise the supply of respective ions would be exhausted. This would cause a greater deviation from equilibrium and a greater overvoltage to arise than a modest decrease of concentration of one neutral component and a coordinated increase of the concentration of the other component. Such deviation from equilibrium appears to be energetically more favourable. Therefore, in the steady state only the first and the fourth term in relation (3) will be significant. Thus the dc current-voltage characteristic (3) reduces to relation (1) with a modified interpretation of both its branches. The condition  $\alpha_1 + \alpha_2 = n$  need not hold (3).

The overvoltage  $\eta$  can be resolved into a component acting on the potential barrier on the interface, and into a component present in the diffuse part of the double layer [14—16] and causing deviations of activities of ions at the barrier from their equilibrium values. In ionic crystals like NaCl, representing an unsupported electrolyte, such changes of activities are not negligible [17]. The equilibrium

activities of anions  $a_{r,2}$  and of cations  $a_{o,1}$  in front of the barrier may be expressed in the form [13]

$$a_{o,1} = a_{o,1} \exp \left[ - \frac{e \xi}{kT} \right] \\ a_{r,2} = a_{r,2} \exp \left[ \frac{e \xi}{kT} \right]. \quad (4)$$

$\xi$  is the equilibrium potential difference in the diffuse double layer. As long as the electrode is at least partly blocking, the interface barrier is higher than the barriers in the bulk, therefore the changes of activities at the interface barrier must be fast compared to the processes on the electrode.

A part of the overvoltage  $\eta$  reduced by the difference  $\xi - \xi$ , where  $\xi$  is the non-equilibrium potential difference in the diffuse double layer, may be formally ascribed to changes of interface activities. Its magnitude is given by the Nernst relation

$$\eta_e = (kT/e) \ln [a_{o,1} a_{o,2} / a_{r,1} a_{r,2}] \quad (5)$$

if no charge transfer across the interface occurs. This overvoltage component is more or less fictitious, as it is not possible to modify the activities of ions at the interface barrier without breaking the individual reaction equilibria; nevertheless, it enables to deduce the influence of neutral components upon the equilibrium. In reality, the overvoltage must differ from  $\eta_e$  in accord with relations (1) and (3). Thus it becomes evident that although the direct contribution of neutral reaction products to the charge transfer across the interface is not significant, they affect the contact potential. Due to the possible slowness of heterogeneous electrochemical reactions, which may be complicated by diffusion or by further chemical steps, changes in concentrations of neutral products may influence the situation on the electrode for a long time.

The conductivity resulting from the current-voltage characteristic (1) has a minimum. Provided that the values of  $\alpha_1$  and  $\alpha_2$  are not very different, the minimum is near the equilibrium potential.

The enhanced interface conductivity, observed before equilibrium sets in, can be explained using relation (3). Immediately after the contact has been brought about, the concentrations of the reaction products are zero, therefore in (3) the second and third terms are missing and relation (3) is reduced to (1). Since the contact potential is scarcely equal to the equilibrium one, one of the remaining terms may be small compared to the other and we can write

$$j \approx j_{o1} \exp \left[ \frac{\alpha_1 e (\Phi - \phi)}{kT} \right] \quad \text{if } \Phi > \phi,$$

$$j \approx -j_{o2} \exp \left[ \frac{-\alpha_2 e (\Phi - \phi)}{kT} \right] \quad \text{if } \Phi < \phi,$$

or

where the deviation from the equilibrium potential is now designated by  $\Phi - \Phi_0$ . Then the differential conductivity, which is effective in small signal measurements, will be

$$\frac{dI}{d\eta} = \frac{dI}{d\Phi} = \frac{\alpha e}{kT} i_0 \exp\left(\frac{\alpha e}{kT} |\Phi - \Phi_0|\right)$$

Unless the potentials of both electrodes are equal at any instant, a current of accidental direction and magnitude will flow in the external circuit until the equilibrium sets in.

Nonequilibrium of the electrodes may lead to the reversal of the polarity of one of the electrodes during short-circuiting. With a sufficiently great initial departure from equilibrium (representing at least tenths of a volt), owing to the asymmetry of the current-voltage characteristic and/or of the potential dependence of the capacity, after shorting one of the electrodes may be depolarized faster. Then the current flowing from the slowly depolarizing electrode will enforce upon the second electrode a potential slightly smaller than the instantaneous overvoltage of the first electrode, and thus an opposite one to that of the polarity of the second electrode at the start of short-circuiting. This will result in reducing the short-circuit current to a small value, which may be erroneously considered to be zero or negligible. In such a situation the increased differential conductivity of the interface is increased again. As the return to equilibrium, subsequent to polarization by high voltages, is rather slow [3, 12], the enhanced conductivity may appear to be steady<sup>2)</sup>.

In the case of a voltage of at least a few volts being applied to electrodes polarized equally with respect to the sample, the enforced current must gradually change the polarity of the overvoltage of the improperly polarized electrode. During the polarity reversal the contact potential passes through the value at which the conductivity attains its minimum and a temporary fall and rise, of simply a monotonous rise of the current may result. As long as the potential of the conductivity minimum is not the equilibrium one, with a suitable polarity and magnitude of the applied voltage even two minima may appear. The passing of interface conductivities through their minimum should lead to current minima also if the polarity of voltage of a proper magnitude is reversed after some time.

<sup>2)</sup> The term low voltage represents voltages at which the potential drops near the electrodes are small compared to  $kT/e$ . Since the potential drop in the bulk depends on the conductance of the sample, the range of low voltages cannot be simply defined. In case of doped NaCl it was up to 100 mV [8]. Similarly high voltages may represent  $> (10 \div 100)$  V.

### III. EXPERIMENTS

Experiments have been performed with the following aims:

- i) to find out the difference in the behaviour of the electrodes with regard to the magnitude of the accumulated charge and the rate of their depolarization,
- ii) to demonstrate the effect of the nonequilibrium state of the electrodes on the charging currents,
- iii) to demonstrate the existence of non-monotonous transients following the switching-on and reversal of the applied voltage.

Measurements were carried out on single crystals of NaCl doped with 100 ppm and 200 ppm of  $\text{Ca}^{2+}$ , grown by the Stockbarger method. Samples were cleaved to a small thickness, in order to achieve an advantageous ratio of the interface and bulk impedances. Their size was usually 3 mm  $\times$  3 mm  $\times$  (0.3  $\div$  0.5) mm. The samples were etched for 15 min. in a 90% methylalcohol, 9% ethylalcohol and 1% water mixture at room temperature, then rinsed in isobutylalcohol. Electrodes were deposited on the opposite faces of the samples using graphite dispersion, and dried. The measurements were performed in air, some in an argon atmosphere, at temperatures about 220 °C and 285 °C.

In the experiments i) discharge currents were compared, flowing if the sample was shorted immediately after switching-off the voltage; if it was shorted 20 min. after switching-off; if it had been removed for 20 min. from the oven and then shorted and if the electrodes had been washed down and newly prepared and then shorted. The last procedure lasted 20 min. again. In a further series of measurements one of the electrodes consisted of an aluminium foil pressed to the sample. The Al-foil was replaced by a new one during the discharging. For comparison also both Al-foil electrodes were used. The polarization time was 3 min., the applied voltage 50 V.

### IV. RESULTS

i) The discharging currents flowing from the cell graphite | NaCl | graphite after immediate short-circuiting, after shorting the cell removed for 20 min. from the furnace and in the cell Al | NaCl | Al after immediate shorting are shown in Fig. 1. If the electrodes were washed and newly prepared, the sample behaved as a previously not polarized one. This suggests that the charge was accumulated on the interface or in a thin surface layer unintentionally removed with the electrodes. The thickness of this layer was estimated to be less than 1  $\mu\text{m}$ .

Measurements on the cell graphite | NaCl | Al revealed a large and slowly decaying charge accumulated on the graphite anode and a much smaller and faster decaying one on the graphite cathode (Fig. 2). This conclusion is supported by the fact that exchanging the Al-foil had little effect on the current and the Al-foil

electrodes alone gave small discharge currents (Fig. 1.). Owing to the different contact potentials of the graphite | NaCl and Al | NaCl interfaces, the short circuit current in case of the Al anode and the graphite cathode had the same direction as the charging current. However, the discharge transient had the correct polarity. The slow decrease of the current results from balancing of contact potentials. Some results of experiments ii) are shown in Figs. 3 and 4. The currents flowing from the samples with fresh electrodes reached magnitudes corresponding to difference in the deviation of both electrodes from equilibrium, the order of magnitude change of the contact potentials with respect to the potential of the free surface to the bulk could be estimated to be 1 V. The effect of imperfect equilibrium on the charging currents or else on the interface conductivity is seen in Fig. 4. The influence of previous polarization and incomplete depolarization was similar, but the increase of conductivity was frequently at least one order of magnitude greater.

iii) Some of the non-monotonously decreasing charging currents are shown in Figs. 5—7 and non-monotonous transients following the polarity reversal of the applied voltage are in Figs. 8 and 9.

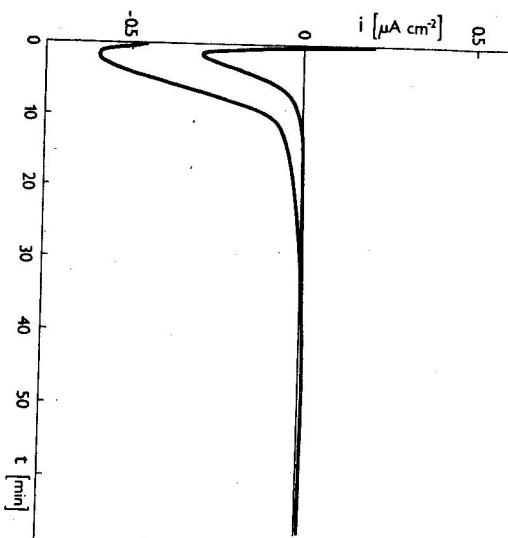


Fig. 3. Currents flowing in NaCl : 200 ppm  $\text{Ca}^{2+}$  from fresh graphite electrodes,  $T = 288^\circ\text{C}$ .

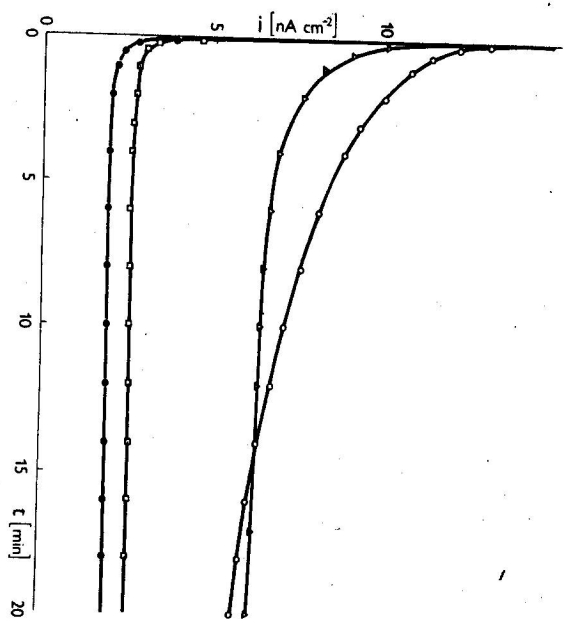


Fig. 4. Charging currents in the cell C | NaCl | C: ( $\Delta$ ) 70 min. from preparation of electrodes,  $T = 289^\circ\text{C}$ , ( $\bullet$ ) after 16 hours in short-circuit,  $T = 283^\circ\text{C}$ , ( $\circ$ ) 45 min. from preparation of electrodes,  $T = 287^\circ\text{C}$ , ( $\square$ ) after 16 hours in short-circuit,  $T = 289^\circ\text{C}$ , NaCl : 200 ppm  $\text{Ca}^{2+}$ .

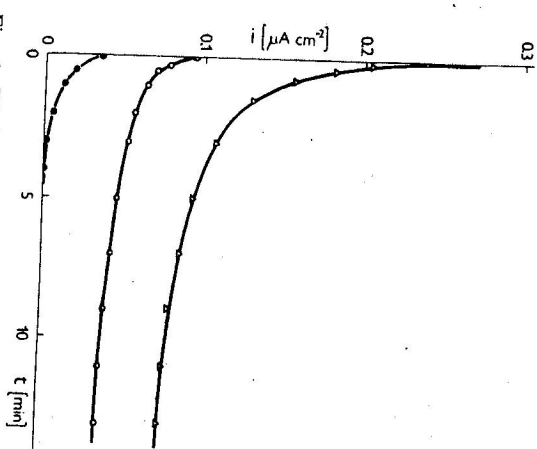


Fig. 1. Discharging current in NaCl : 100 ppm  $\text{Ca}^{2+}$ : ( $\Delta$ ) graphite electrodes, immediate short-circuit, ( $\circ$ ) graphite electrodes, sample 20 min. outside the furnace, ( $\bullet$ ) aluminium electrodes.  $T = 220^\circ\text{C}$ .

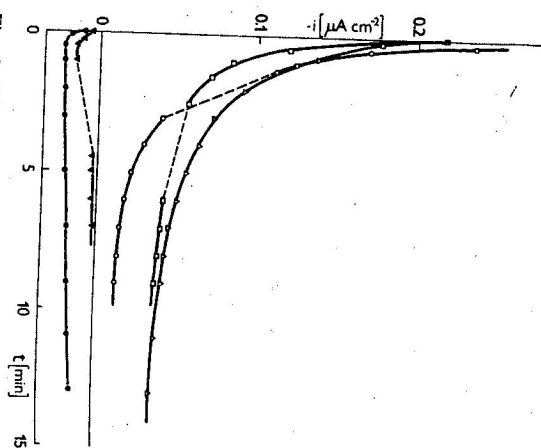


Fig. 2. Discharging current in NaCl : 100 ppm  $\text{Ca}^{2+}$ : ( $\bullet$ ) Al anode, graphite cathode, ( $\Delta$ ) Al cathode, graphite anode, ( $\square$ ) Al anode, Al cathode exchanged during discharge, ( $\nabla$ ) graphite cathode, Al anode exchanged during discharge.  $T = 220^\circ\text{C}$ .

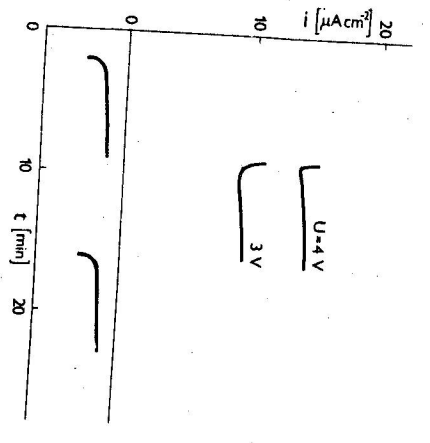


Fig. 5. Charging currents in the cell C | NaCl | C. Sample repeatedly polarized and short-circuited.  $T = 287^\circ\text{C}$ , NaCl : 100 ppm  $\text{Ca}^{2+}$ .

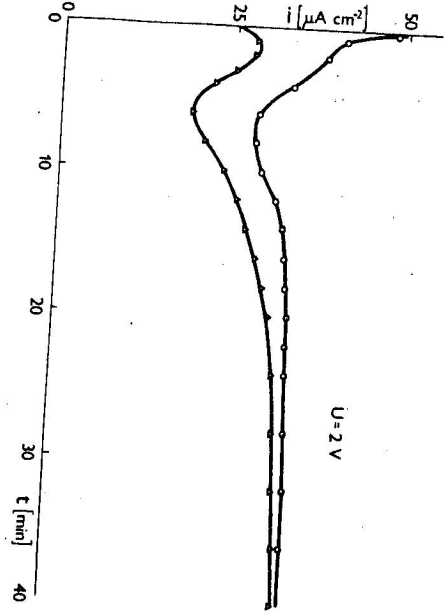


Fig. 6. Charging currents flowing after preceding polarization by 3 V and 60 min. short-circuit ( $\Delta$ ), and 110 min. short-circuit ( $\circ$ ).  $T = 288^\circ\text{C}$ , NaCl : 200 ppm  $\text{Ca}^{2+}$ , graphite electrodes.

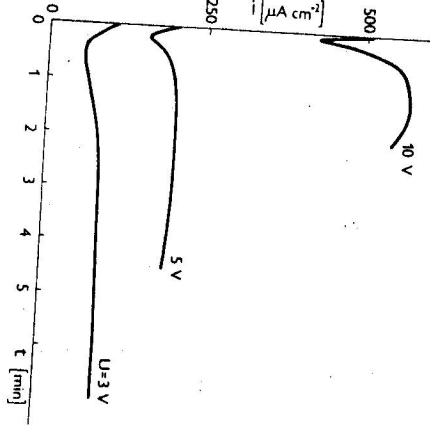


Fig. 7. Charging currents flowing at 3 V after 24 min. polarization by 1.5 V and 52 min. short-circuit, at 5 V after 100 min. short-circuiting and at 10 V after 24 min. short-circuiting.  $T = 289^\circ\text{C}$ , NaCl : 200 ppm  $\text{Ca}^{2+}$ , graphite electrodes.

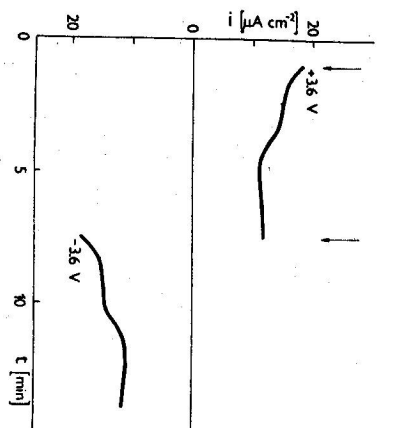


Fig. 8. Current flowing after repeated reversal of voltage.  $T = 284^\circ\text{C}$ , NaCl : 100 ppm  $\text{Ca}^{2+}$ , graphite electrodes.

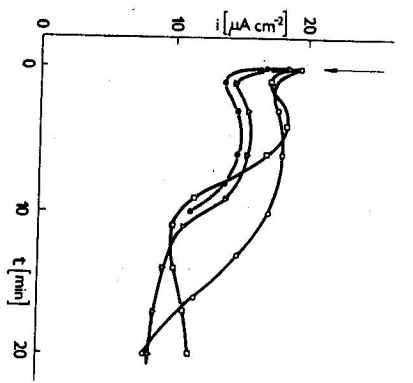


Fig. 9. Current flowing after repeated reversal of applied voltage 2.5 V, ( $\square$ ) reversed every 10 min., ( $\circ$ ) repeated reversal of +2.5 V, 20 min., -2.5 V, 10 min. the first time -2.5 V, 20 min.  $T = 284^\circ\text{C}$ , NaCl : 100 ppm  $\text{Ca}^{2+}$ , graphite electrodes.

### V. DISCUSSION

The observed consequences of the non-equilibrium state of electrodes are qualitatively in accord with the conclusions of the theoretical section of the present paper. As the diffusion of reaction products, which markedly complicate the picture [3], have not been considered, it is not possible to analyze the degree of the quantitative agreement.

Anomalous, i. e. non-monotonous transients result from both the nonlinearity of the properties of the interface and the non-equilibrium initial conditions, therefore they must differ from the results of simplified computations in papers [12, 18]. Currents increasing in time are frequently observed at high voltages in crystals in contact with metal electrodes. They result from the injection of electrons into the bulk of the sample. However, they are improbable in case of graphite electrodes and at polarization times used in this work. Moreover, a part of the bulk is affected by the injection and its consequences cannot be removed by a mere change of the electrodes.

The appearance of two minima in some transients following the voltage reversal (Fig. 9) and their indication in some charging currents (Fig. 6) is obviously in relation to different depolarization rates of the two electrodes (Fig. 2). The dependence of the voltage reversal transients on the polarization time (Fig. 9), and thus on the amount of the transferred charge makes it possible to ascribe the second minimum, which corresponds to the minima of the charging currents, to the



reversal of the polarity of the anode. It should take place when the excess atomic chlorine at the interface is used up. The different rates of depolarization of both electrodes indicate a smaller surface concentration of sodium and a significant concentration of chlorine on graphite electrodes. Sodium may rapidly oxidize in the employed atmosphere, thus its surface concentration is small and the possibility of its return to the crystal is limited.

The slower decay of the charging transients with fresh electrodes indicates that the electrical history and the nonequilibrium of the electrodes affect also the interface capacity. However, its properties are beyond the scope of the present paper.

Anomalous charging currents have to be expected also if the charging is interrupted for some time, allowing partial return to equilibrium. Currents resembling those from Fig. 7 were observed after the interruption of charging also in samples with platinum electrodes.

## VI. CONCLUSIONS

The current-voltage characteristic of the ionic crystal | electrode interface, across which a charge is transferred by means of at least two electrochemical reactions, discussed in the theoretical section, renders it possible to elucidate the role of the neutral reaction products in coming into existence of equilibrium and in return to equilibrium after preceding polarization. A well defined and as far as possible an equilibrium initial state is a necessary condition of reproducibility and of the possibility of a relatively simple interpretation of charging, discharging and voltage reversal transient currents.

The rise of equilibrium on freshly prepared electrodes may be a lengthy process, the case of the system graphite | NaCl | graphite at room temperature lasts perhaps thousands of hours. Therefore at lower temperatures measurements in equilibrium may be hard to realize. In some cases the effect of preceding polarization can be entirely eliminated by exchange of electrodes or by removal of thin surface layer from the sample. A necessary but non sufficient evidence of equilibrium is the absence of short-circuit current.

## REFERENCES

- Raleigh D. O., J. Phys. Chem. Solids 29 (1968), 261.  
Raleigh D. O., Phys. Stat. Sol. (a) 4 (1971), 215.  
Lányi Š., Acta Phys. Slov. 24 (1974), 80.  
Lányi Š., J. Phys. Chem. Solids 36 (1975), 775.  
Michel R., Maitrot M., Madru L., J. Phys. Chem. Solids 34 (1973), 1939.  
Mitroff S. P., Charles R. J., J. Appl. Phys. 43 (1972), 927.

- [7] Macdonald J. R., Jacobs P. W. M., J. Phys. Chem. Solids 37 (1976), 1117.  
[8] Lányi Š., Proc. of the 4<sup>th</sup> conf. of Czech. Physicists. Academia, Prague 1976.  
[9] Lányi Š., (to be published)  
[10] Cochrane G., Fletcher N. H., J. Phys. Chem. Sol. 32 (1971), 2557.  
[11] Benci S., Manfredi M., Paracchini C., Schianchi G., Sol. St. Comm. 17 (1975), 779.  
[12] Lányi Š., Harašta V., Czech. J. Phys. B 23 (1973), 1084.  
[13] Vetter K. J., Elektrochemische Kinetik. Springer Verlag, Berlin 1961.  
[14] Lehovec K., J. Chem. Phys. 21 (1953), 1123.  
[15] Kliever K. L., Koehler J. S., Phys. Rev. 140 (1965), A 1226.  
[16] Macdonald J. R., J. Chem. Phys. 29 (1958), 1346.  
[17] Lányi Š., Harašta V., Czech. J. Phys. B 25 (1975), 1409.  
[18] Harašta V., Acta Phys. Slov. 26 (1976), 118.

Received April 18<sup>th</sup>, 1977