ELECTRICAL CONDUCTIVITY OF NaCl|GRAPHITE INTERFACE

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It was observed that a steady d. c. current flows through the cell graphite | NaCl | graphite even at voltages very small compared to the decomposition potential difference. The activation enthalpy of the small signal conductance (1.20 ± 0.05) eV differs from the enthalpy of the bulk conductivity. The interface conductance is neither in simple relation to the conductivity of the crystal, nor to the partial conductivities of anions and cations. The nonlinearity of the cell and the independence of interface conductance from some properties of the bulk can be explained by the finite rate of electrochemical reactions, ensuring the charge transfer across the interfaces.

1. INTRODUCTION

As it has been shown recently [1, 2] great contributions to the capacity of ionic crystal | electrode interface may arise as a consequence of incomplete blocking of charge carriers. It is usually assumed that no steady d.c. current can flow at small applied voltages through the cell electrode | ionic crystal | electrode, if the electrodes do not consist of the same metal which is a component of the crystal, because of the change in transport mechanism at the interface (ionic in the sample and electronic in the external circuit). It is expected, that charge transfer due to decomposition of the crystal takes place only at voltages at least comparable with the decomposition potential difference usually representing a few volts [3, 4]. However, total blocking of charge carriers is usually not observed. In some papers the residual current was thought to be electronic [5]. The degree of blocking is interesting from the point of view of interpretation of various experimental results. Moreover, quantitative data may be useful for computations of cell parameters made possible by the present advanced state of theories [6, 7].

This paper presents results of measurements on the system graphite | NaCl | graphite, carried out with the aim to find out, whether complete charge blocking is possible. It was attempted to reveal relations between the rate of charge transfer across the interface and the properties of the crystal.

2. EXPERIMENTAL PROCEDURE

The voltage dependence of charging currents was measured on samples of NaCl in the range 25 mV – 5 V in order to obtain the static current-voltage characteristic. A long-term time dependence of the current was measured at 50 mV to prove the

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incomplete charge blocking at the electrodes. These measurements were carried out at 285 °C. Since the long term measurements showed, that the small signal conductance is constant after some time, its temperature dependence was investigated in the range from 130 to 460 °C with applied voltage 25 mV.

Single crystals of "pure" NaCl and of NaCl doped with 100 and 200 ppm of Ca$^{2+}$ and with 4-4 ppm of Ba$^{2+}$ were used. They were grown by the Stockbarger method, the pure ones from analytical grade raw material repurified by means of ion exchangers and cleaned of OH$^-$ ions. The residual divalent impurities were removed by selective extraction [8]. Samples were cleaved to thickness 0.25 − 0.5 mm, etched for 15 min. at room temperature in 90% methanol, 9% ethanol and 1% water mixture and then rinsed in isobuthylalcohol. Electrodes were painted to opposite faces using graphite dispersion in ethylalcohol (Dag 580) and dried. The crossection of the samples was 0.1 − 0.3 cm$^2$.

The measurements were performed on apparatus [9] completed by necessary supply and registration circuitry and by a capacitance bridge, used to measure a.c. conductivity at angular frequency $\omega = 10^4$ s$^{-1}$. The measurements were carried out in air. Before each measurement of a charging transient the cell was short-circuited for a few hours and the series of transients were measured with increasing voltages, thus the results were not affected by preceding polarization.

3. RESULTS

The temperature dependence of the conductivity of employed crystals is shown in Fig. 1. The measurement of the current flowing through the cell graphite | NaCl | graphite at 50 mV, lasting 218 hours, revealed that the current attained within $30 \div 60$ min. a constant small but nonzero value. Thus the electrodes were not completely blocking.

The voltage dependence of transients was similar as in the cell Pt | NaCl | Pt [1]. Results obtained on a sample with 200 ppm of Ca$^{2+}$ are in Fig. 2. The currents are related to their initial value calculated using the a.c. conductivity at $\omega = 10^4$ s$^{-1}$. A steady value was reached within tens of minutes, at voltages > 2 V usually within minutes. Fig. 3 shows the voltage dependence of the steady conductance of the cell. Results obtained on different samples of comparable thickness and on a sample, from which the electrodes were washed down and newly prepared, agreed within ±20%. This may be considered a sign of good reproducibility of properties of the contacts.

Measurements of temperature dependence of small signal conductance were carried out on samples with 100 and 200 ppm of Ca$^{2+}$. Due to their high conductivity the voltage drop in the bulk was typically below 1%, thus the current was contact limited and the interface conductance could be conveniently estimated without measuring the potential distribution [1, 10]. The results obtained on samples with low conductivity (pure and Ba$^{2+}$ doped ones) were corrected for the bulk voltage