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CHARGING AND DISCHARGING OF SPACE CHARGE CAPACITY SHUNTED BY NONLINEAR RESISTANCE

VLADIMÍR HARAŠTA*, Bratislava

The charging and discharging of the space charge capacity of the diffuse double layer connected in parallel with the nonlinear resistance of Me/MeX interface are numerically calculated. The transients have a nolinear behaviour and are significantly influenced by the contact potential between an electrode and a sample.

I. INTRODUCTION

Let us consider a material containing free charge carriers of a not too high concentration, e.g. a solid electrolyte placed between ideally blocking (polarized) electrodes. After applying the dc voltage, a region of a negative space charge (SC) arises at the anode and a region of a positive SC at the cathode. With respect to the opposite polarity of the SC against the corresponding lectrode, these two regions represent two SC capacities. For the static magnitue of such a capacity defined by $C = Aq/\Delta\varphi$, where q is the density of surface harge on the electrode of the area A and $\Delta\varphi$ the potential difference across he SC region, there follows relation [1]

$$C = C_0 \sinh(\alpha\Delta\varphi)/\alpha\Delta\varphi. \tag{1}$$

he constant $C_0 = \varepsilon A/L_D$, $\alpha = e/2kT$, where ε is the permitivity, L_D the Debye ngth, e the electronic charge, k the Boltzmann constant and T the tempe- ure.

The charging and discharging of the SC capacity through a great linear istance had been solved by Brachman and Macdonald [2]. The requirent of the great external resistance follows from the need of sufficiently slow tage changes on the SC capacity, so that deviations from the equilibrium SC ribution corresponding to an instantaneous magnitude of voltage may be ligible, or, in other words, so that the SC distribution may change quasista- lly in dependence on the voltage. An analysis has shown that the requirement of the magnitude of external resistance is not too restrictive — a resistance comparable to the resistance of the sample is sufficient.

Fyzikálny ústav SAV, Dúbravská cesta, 899 30 BRATISLAVA, Czechoslovakia.

In practice we meet the ideally blocking electrode rarely and usually we observe an appreciable current flow in the steady state too. Therefore, it is reasonable to consider a system, where a SC capacity is connected in parallel with a generally nonlinear resistance. Its magnitude and voltage dependence will be determined by conditions at the interface between the sample and the electrode, i. e. by the quality of the investigated sample and the electrode.

II. THEORY

The current flowing through an interface may be in many cases interpreted as a charge transfer current. This situation arises especially if the material (metal) of the electrode is a component of the investigated sample too, e. g. an ionic crystal of the MeX type with ionic conductivity and Me electrode. Then, at the electrode a reaction takes place:

$$Me^+ \text{ (in the crystal)} + e \rightleftarrows Me \text{ (on the electrode)}.$$

The system comes into the equilibrium state when the difference of the electrochemical potential of an ion on the sample and at the electrode is zero.

$$\Delta\tilde{\mu}_{Me^+} - \Delta\mu_{Me^+} - e\Delta\varphi_{eq} = 0,$$

$\Delta\mu_{Me^+}$ denotes the difference of the chemical potential of the Me^+ ion in the sample and on the electrode and $\Delta\varphi_{eq}$ is the equilibrium potential difference across the interface which arises owing to the charge transfer. If the voltage $\Delta\varphi$ is not the equilibrium one $\Delta\varphi \neq \Delta\varphi_{eq}$, then through the interface the charge transfer current is flowing [3]

$$I(\eta) = Ai_0\{\exp[(1-\beta)e\eta/kT] - \exp[-\beta e\eta/kT]\}, \tag{2}$$

i_0 is the exhange current density, β the symmetry factor of the energy barrier for the charge transfer from crystal to electrode and $\eta \equiv \Delta\varphi - \Delta\varphi_{eq}$ is the overvoltage. Consequently, the interface behaves as a nonlinear SC capacity shunted by the nonlinear resistance

$$R(\eta) = \frac{\eta}{I(\eta)} = \frac{\eta}{Ai_0\{\exp[(1-\beta)e\eta/kT] - \exp[-\beta e\eta/kT]\}}. \tag{3}$$

In agrrement with that, we can replace the considered system by an equivalent cicruit according to Fig. 1. The resistance R_0 is the sum of the sample resistance and of an external resistance. The potential distribution, after an external voltage has been applied, is schematically in Fig. 2.

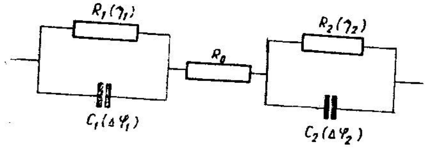

Fig. 1. Equivalent circuit of the system Me/MeX/Me. $C_{1,2}$ — SC capacities of the interfaces 1, 2; $R_{1,2}$ — resistance of the interfaces 1, 2; R_0 — sum of the bulk reistance of the sample and the external resistance.

We note that from the total voltage across the interface $\Delta\varphi_{eq} + \eta$, only its part η produces the charge transfer current.

Differential equations describing the charging and discharging of the system in Fig. 1 are rather complicated and we have restricted ourselves to the solution of the simplified circuit with one polarized electrode — Fig. 3.

We can realize such a case experimentally, if we chose the area of one of the electrodes much greater than the other. If we apply the dc voltage V_a in the circuit from Fig. 3, there follows for the current

$$I = \frac{d(VC)}{dt} + \frac{V}{R(V)} = \frac{V_a - V}{R_0},$$

where $V = \eta$ denotes the voltage on the nonlinear resistance $R(V)$ shunting SC capacity of the interface. After some rearrangement we have for the voltage V the relat·on

$$\frac{dV}{dt} = \frac{V_a/R_0 - V(1/R + 1/R_0)}{C + V\,dC/dV} \tag{4}$$

with condition $V = V_0$ at $t = 0$ and the current is given by $I = (V_a - V)/R$. Similarly for discharging follows the relation

$$\frac{dV}{dt} = \frac{V(1/R + 1/R_0)}{C + V\,dC/dV} \tag{5}$$

with the condition $V = V_0$ at $t = 0$ and $I = V/R_0$ for the current.

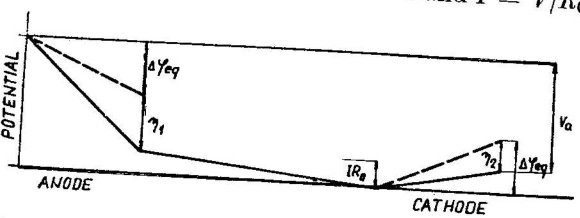

Fig. 2. Potential distribution on the circuit in Fig. 1. with m applied external voltage.

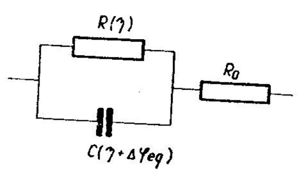

Fig. 3. Simplified equivalent circuit with one polarized electrode.

If we substitute for C and R in (4,5) the relations (1) and (3), and restrict ourselves to the case of a symmetrical energy barrier $\beta = 1/2$, we obtain

$$\frac{dV}{dt} = \frac{(V_a - V)/R_0 - 2i_0A \sinh(\alpha V)}{C_0 \cosh[\alpha(V + \Delta\varphi_0)]}. \tag{6}$$

The differential Eqs. (6) and (7) have not a solution in the closed form, therefore we have solved them numerically with adequate initial conditions. The results for some different parameters α, $\Delta\varphi_{eq}$, and V_a are plotted in Figs. 4—8.

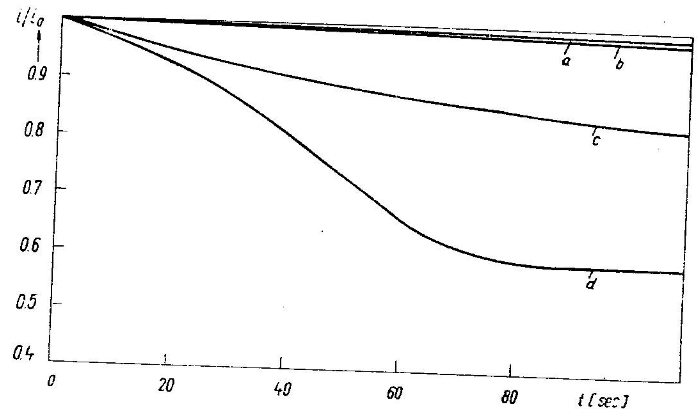

Fig. 4. Charging currents of the circuit in Fig. 3, calculated from [6] and normalized to the initial value. $V_a = 1$ V, $R_0 = 10^6\ \Omega$, $2i_0A = 10^{-7}$ A, $C_0 = 30\ \mu$F. *a)* $\alpha = 12\ V^{-1}$, $\Delta\varphi_{eq} = 0.5$ V; *b)* $\alpha = 12\ V^{-1}$, $\Delta\varphi_{eq} = -0.5$ V; *c)* $\alpha = 6\ V^{-1}$, $\Delta\varphi_{eq} = 0.5$ V; *d)* $\alpha = 6\ V^{-1}$, $\Delta\varphi_{eq} = -0.5$ V.

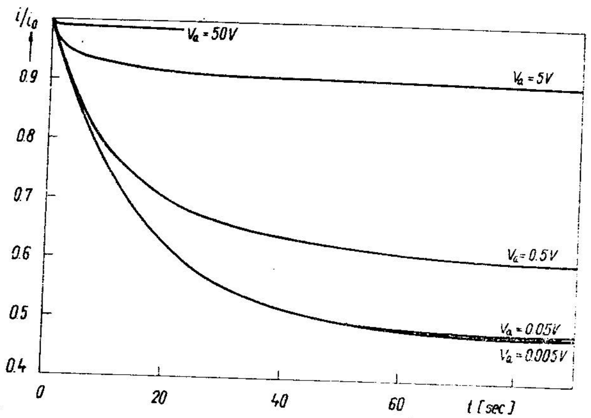

Fig. 5. Charging currents like in Fig 4. for different polarizing voltages V_a. $\alpha = 9\ V^{-1}$, $\Delta\varphi_{eq} = 0$, $R_0 = 10^6$, $2i_0A = 10^{-7}$ A, $C_0 = 30\ \mu$F.

III. DISCUSSION

The charging current of the circuit in Fig. 3 is at the moment of applying the voltage given by R_0, i.e. by the resistance of a sample and an external resistance. The current decay is initially linear, with the slope $dI/dt_{t-0} = -V_a/R_0^2C_0 \cosh(\alpha\Delta\varphi_{eq})$. For greater values of $\alpha\Delta\varphi_{eq}$ the decay may be rather slow (Fig. 4). The steady current can be determined from the relation $(V_a - V)/R_0 = 2i_0 \sinh(\alpha V)$. We can see that it is a nonlinear function of the applied voltage (Fig. 5) and of the factor α (Fig. 6). The decay rate increases with the

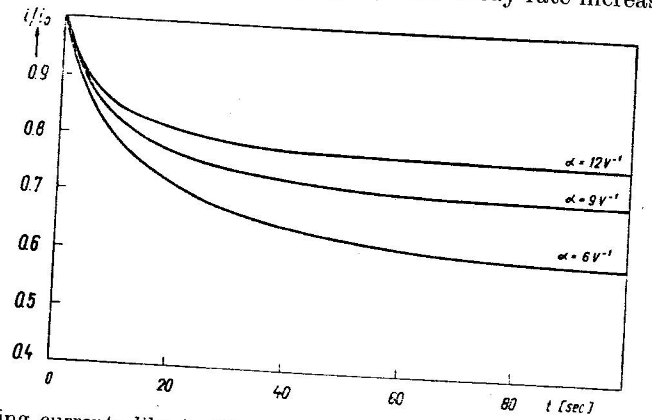

Fig. 6. Charging currents like in Fig. 4 for different values of α. $V_a = 1$ V, the other parameters are the same as in Fig. 5.

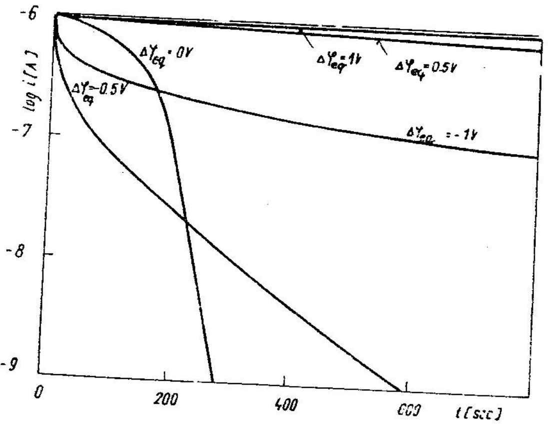

Fig. 7. Discharging currents of the circuit in Fig. 3 calculated from [7] for different values of $\Delta\varphi_{eq}$. $V_0 = 1$ V, $R_0 = 10^6$, $2i_0A = 10^{-7}$ A, $\alpha = 6$ V^{-1}, $C_0 = 30\ \mu$F.

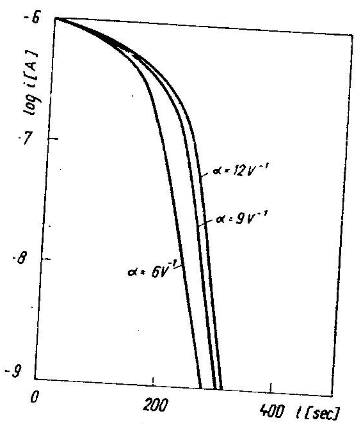

Fig. 8. Discharging currents like in Fig. 7 for different values of $\Delta\varphi_{eq} = 0$, the other parameters as in Fig. 7.

applied voltage. The contact potential causes an increase of the SC capacity and hence the following decrease of the rate of the charging current decay, which is more distinct in the case of an equal polarity of the polarizing voltage and the contact potential (Fig. 4). The discharging process is based on the discharging of the *SC* capacity $C(V)$ through the nonlinear resistance $R(V)$ in parallel with the constant resistance R_0. The decay rate depends again on the polarity of the contact potential (Fig. 7) and the value of Fig. 8. While for a higher voltage across the *SC* capacity the discharge current is a complicated function of time, for a low voltage $V \ll \alpha^{-1}$ it decreases exponentially with the time constant $\tau = C_0 \cosh(\alpha\Delta\varphi_{eq}) : (1/R_0 + Ai_0\alpha)$.

Some curves of transient currents have been calculated for the value of the contact potential $\Delta\varphi_{eq} = 0$. They can be interpreted as a limiting case of very small contact potentials, but the other possibility is to consider the existence of a nonlinear capacity at the electrode which depends exponentially roughly only on the overvoltage. The capacity of considered properties has been observed experimentally [4] and discussed theoretically by Lányi [5].

The contact potentials on systems like Ag/AgBr are of the order of some tenths of volts [6]. Their influence on the *SC* capacity causes in our model an anomalous behaviour of transient currents, which, however, as far as we know, have not been observed yet. This fact suggests the possibility that the transient phenomena on such systems are probably caused by a capacity that is independent on the contact potentials as it has been mentioned above. More definite conclusions are at present not possible. This is caused on the one hand by the approximative character of the considered model and the lack of experimental data on the other hand.

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