PASSIVATION OF ZINC IN KOH SOLUTIONS SUPERSATURATED WITH ZINCATE

IMPEDANCE DETERMINATION

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From the dependence of the impedance components on ac frequency, and allowing for the other electrochemical characteristics of the electrode, one can determine the parameters of a selected electrical equivalent circuit which quantitatively characterize the kinetics of the electrode reactions occurring during anodic metal dissolution [1]. This method has been used in studying the anodic behavior of zinc in alkaline solutions [2, 3].

In [3, 4] it has been shown that during anodic polarization of zinc in alkaline solutions at potentials between 0.2 and 1.0 V (nhe), which correspond to a state of deep passivity of the electrode, the rate of anodic dissolution is found to be potential-independent, and for solutions supersaturated with respect to zincate, that it is also independent of solution composition. It is hypothesized that under these conditions the greater part of the anodic current corresponds to direct electrochemical dissolution, which does not go through a stage of zinc oxide formation and which occurs without participation of hydroxyl ions:

$$\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2e^- \qquad (1)$$

Parallel with reaction (1) there is oxide film formation. On prolonged potentiostatic passivation, 7% of the total current passing the electrode are spent on film formation at −1.0 V, and 15-20% at deeper passivation, while the remaining 80-90% go into direct electrochemical dissolution of metallic zinc according to reaction (1). The lack of potential dependence of the rate of anodic zinc dissolution between 0.2 and 1.0 V in supersaturated solutions has permitted us to suggest that under these conditions the electrochemical reaction rate is determined by diffusion of zinc through the oxide film [3, 4]. Preliminary experiments involving ac measurements [3] have shown that on a zinc electrode subjected to prolonged anodic polarization in alkaline solutions supersaturated with zincate, at a potential of 0.2 V (deep passivation) there is indeed a limitation in the rate of anodic oxidation by the rate of diffusion of zinc atoms in the oxide layer.

It was the aim of the present work to investigate on the example of zinc the kinetics and mechanism of anodic metal dissolution in the passive state with the aid of electrode impedance measurements. The experiments were carried out in alkaline solutions supersaturated with zincate in order to exclude chemical dissolution of the film.

The test electrode was a TsO-band zinc wire of 0.5 mm diameter pressed into a teflon holder. The surface area of the electrode was 0.05 cm^2. The cell was connected according to the circuit outlined in [5]. A TsLA-5611 potentiostat and an R-568 ac bridge were used. The KOH starting solutions were purified by prolonged polarization. "Chemically pure" zinc oxide and "specially pure" KOH were used for the preparation of the solutions. Alkaline solutions supersaturated with zincate were used (see Table 1). The potential of the zinc electrode was measured relative to a mercury oxide electrode in alkali of the same molality, and converted to the normal hydrogen scale. The experiments were carried out in an atmosphere of purified argon.

The test electrode was anodically polarized for 1 h at every given constant potential from −1.3 V to 1.0 V in intervals of 0.1-0.2 V. Under these conditions, oxide layers of up to 10^{-5}-10^{-4} cm thickness form on the zinc.

TABLE 1

Compositions of the solutions	N-solutions		
	1	2	3
ZnO, moles/kg	0.66	1.25	4.39
KOH (free), moles/kg	1.69	2.86	5.36

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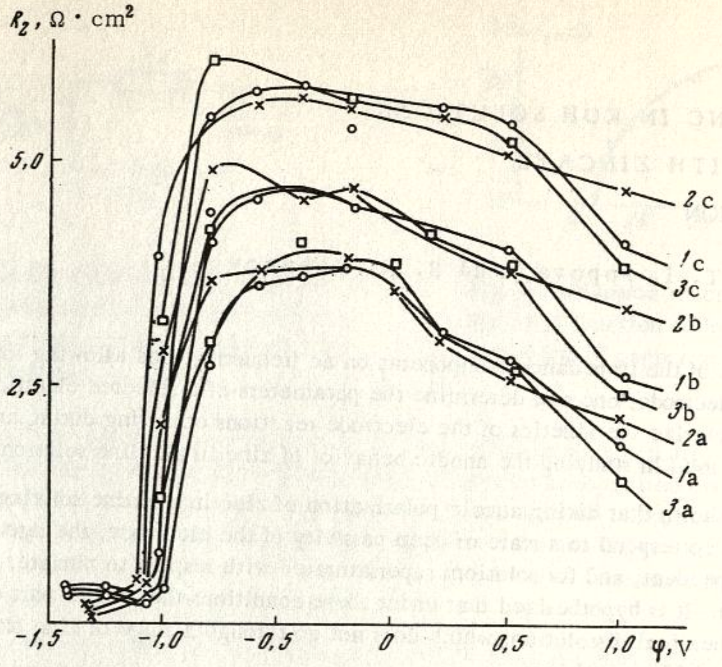

Fig. 1. Dependence of the ohmic impedance component R_2 on potential of anodic polarization in the solutions 1, 2, and 3 of Table 1. The indices a, b, and c refer to frequencies of 20, 10, and 5 kHz.

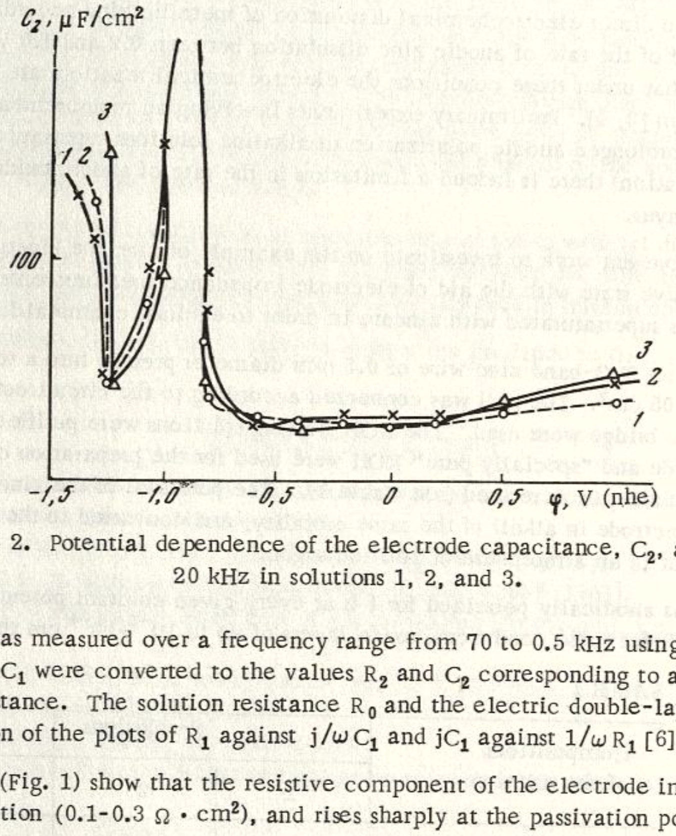

Fig. 2. Potential dependence of the electrode capacitance, C_2, at 20 kHz in solutions 1, 2, and 3.

After this the impedance was measured over a frequency range from 70 to 0.5 kHz using a series combination. The measured values of R_1 and C_1 were converted to the values R_2 and C_2 corresponding to a parallel combination after deducting the solution resistance. The solution resistance R_0 and the electric double-layer capacitance C_{dl} were determined by extrapolation of the plots of R_1 against $j/\omega C_1$ and jC_1 against $1/\omega R_1$ [6].

The results obtained (Fig. 1) show that the resistive component of the electrode impedance, R_2, is small in the region of active dissolution (0.1-0.3 Ω · cm²), and rises sharply at the passivation potential (2-4 Ω · cm² at $\varphi = -1.0$ V).

When the potential reaches values more positive than −0.4 V, some drop in R_2 is observed. In general R_2 depends little on solution composition at potentials corresponding to passivation of the zinc (Fig. 1). The capacitative

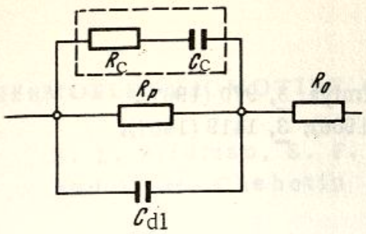

Fig. 3. Electrical model network for the system zinc/zinc oxide/ solution.

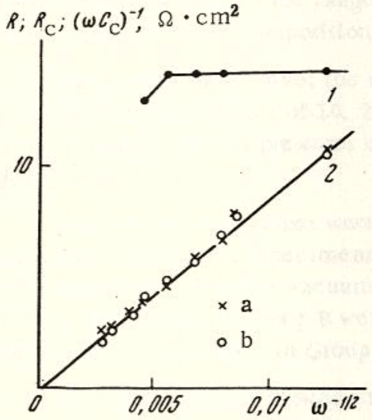

Fig. 4. Dependence of R_r (1), R_c (2a), and $1/\omega C_c$ (2b) on $\omega^{-1/2}$.

component of the impedance, C_2 (Fig. 2), is also practically independent of solution composition in the range of passive dissolution, and at 20 kHz seems to correspond to the capacity of the electric double layer.

When the frequency is raised further, C_2 does not continue to vary. The electric double-layer capacities calculated assuming a roughness factor of 2-3 are 1.5 times smaller than the double-layer capacity of metals. This means that the oxide layer has high electric conductivity and only to a small degree possesses semiconducting properties.

When considering the frequency dependence of the component R_2 of the electrode impedance we proposed that there were present a resistance R_r corresponding to the electrochemical reaction of formation of a passivating layer on the zinc,* and a diffusion impedance corresponding to the rate limitation of the anodic process by diffusion of zinc through the oxide film. When reaction (1) (limited by diffusion) occurs simultaneously with oxide film formation, one can represent the electrical equivalent circuit of the zinc/oxide /solution system in presence of the anodic process as diffusion impedance (elements R_c and C_c) and reaction resistance R_r combined in parallel (Fig. 3). If this scheme corresponds to the system studied, then the following must hold:

$$(C_2 - C_{dl}) = C_c / 2, \tag{2}$$

$$\omega C_c = \sqrt{\omega} / A, \tag{3}$$

$$R_c = 1 / (\omega C_c), \tag{4}$$

$$1 / R_2 = 1 / R_r + 1 / 2R_c. \tag{5}$$

The values of the capacitative component of the diffusion impedance as calculated from the curves and Eq. (2) do indeed fit relation (3) (Fig. 4, Curve 2). Values of R_c were then calculated from Eq. (4), and of R_r from Eq. (5). The resistance R_r, in agreement with the equivalent circuit (Fig. 3), has a constant value $R_{st} = 14\ \Omega\cdot cm^2$ at frequencies below 5 kHz (Fig. 4, Curve 1). The rate i of the electrochemical reaction obtained from R_{st} with the equation $R_{st} = b/(2.3i)$† agrees approximately with the results of potentiostatic measurements [3] at potentials between −0.8 and +0.5 V, and is 4-6 mA/cm² or 20% of the total current flowing through the electrode. The rate of this process is practically independent of electrode potential and composition of the solutions studied (Table 1).

The slope A calculated from Eq. (3) corresponds to the product of diffusion coefficient and square of the concentration of diffusing particles in the oxide layer, c^2D, and is $6\cdot 10^{-22}$. If the concentration of diffusing particles is taken as 10^{-3} moles/cm³, then the diffusion coefficient is $6\cdot 10^{-18}$ cm²/sec. This confirms the suggestion made earlier that the rate of anodic zinc dissolution is limited, under these conditions, by diffusion in the solid phase [3].

On the basis of the present experiments one can say that the rate of anodic dissolution of passive zinc at potentials between −0.8 and +1.0 V in alkaline solutions supersaturated with zincate is determined by the rates of two parallel processes: 1) direct electrochemical dissolution of zinc, controlled by diffusion of zinc atoms in the solid oxide layer, to the extent of 80% of the total current flowing through the electrode, and 2) the electrochemical reaction of formation of a passivating oxide due to penetration of superstoichiometric oxygen into the zinc oxide, to the extent of 20% of the total current. Both processes occur simultaneously, their rates do not depend on electrode potential in the limits indicated, nor on solution composition.

The electrical model in Fig. 3 corresponds to such a combination of processes. The reaction rates do not depend on solution composition and agree approximately with the values obtained by other methods, confirming the conclusions drawn previously [3]. In conclusion we express our gratitude to É. S. Sevast'yanov and to D. I. Leikis for their participation in the discussion of the results of this work.

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* In the preliminary measurements [3], the component R_r was not taken into account.

† The coefficient b = 0.2 V is taken from the nonstationary $i-\varphi$ curves for dissolution of passive zinc [4].

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