INVESTIGATION OF THE MECHANISM OF THE LIBERATION OF HYDROGEN AND THE INSERTION OF POTASSIUM INTO A ZINC ELECTRODE IN ALKALINE SOLUTIONS DURING CATHODIC POLARIZATION

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The principles of the processes of insertion of potassium and liberation of hydrogen from solutions of KOH with concentrations 0.125-3 M at potentials 0.05-0.27 V more negative than the equilibrium potential of the Zn-electrode were studied by the method of measurement of the impedance in conjunction with static polarization measurements. The exchange current of the insertion process exceeds 10^{-2} A/cm^2; a weak specific adsorption of K^+ ions on the electrode was detected, while the limiting step of the summary process of insertion under the experimental conditions is solid-phase diffusion of potassium ions in zinc (which have an estimated affinity coefficient of the order of 10^{-26} at a potential of −1.4 V relative to the normal hydrogen electrode) with the product $\sqrt{D} \cong 3 \cdot 10^{-10}$ mole · cm^{-2} · sec$^{-1/2}$. It was shown that the process of cathodic liberation of H_2 at the indicated potentials obeys electrochemical, and not chemical kinetics and proceeds through the addition of an electron to a water molecule.

The most widely studied cathodic processes, occurring on a solid zinc electrode in alkaline electrolytes of chemical current sources are the processes of deposition of zinc and liberation of hydrogen; the mechanism of the latter, as a rule, is considered electrochemical [1, 2]. On the other hand, it has been shown in a number of studies that in the polarization of zinc in alkali, as well as at the static potential, a process of insertion of an alkali metal occurs on it [3-7]. In [8, 9] in the study of the corrosion of zinc in alkaline solutions, it was concluded that the process of liberation of hydrogen at potentials more negative than −1.6 V* proceeds according to a chemical mechanism and the rate of the process is controlled by the step of discharging of the alkali cation. A knowledge of the principles of these processes is important for improving the characteristics of alkaline chemical current sources with zinc anodes.

In the present work the principles of the insertion of an alkali metal into a zinc electrode during cathodic polarization (−1.30 to −1.53 V) were studied by the method of measuring the impedance in conjunction with static polarization measurements. In the development of [5], we studied the dependence of the impedance of a zinc electrode on the alkali concentration (0.125-3 M) and the electrode potential (0.05-0.27 V more negative than the equilibrium value). The potential was measured against a mercuric oxide electrode in an alkali solution of the same concentration as the solution of the investigated system. In contrast to the measurements in [5], wire electrodes pressed into a teflon holder were used. The degree of purity of zinc, KOH, as well as the preparation of the electrode surface were the same as in [6, 7]. Measurements of the capacitance (C_1) and ohmic (R_1) components of the impedance were performed according to a successive scheme of substitution at the frequencies 0.06-30 kHz with a P-5021 bridge after 15-30-min exposure of the electrode at the set value of the cathodic potential. During the measurement of the frequency dependence, the change in C_1 and R_1 at the control frequency (10 kHz) did not exceed 5%. The dependence of the impedance of the electrode on the potential of cathodic polarization at a constant alkali concentration was studied on the same electrode. After a change to an alkali solution of a different concentration, the electrode either was polished again and reduced or was replaced by a new one.

*Here and henceforth the values of the electrode potential are cited relative to the normal hydrogen electrode.

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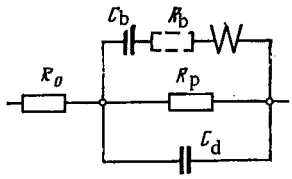

Fig. 1. Electrical circuit equivalent to the electrochemical processes occurring on a zinc electrode during cathodic polarization in 0.125-3 M alkali solutions.

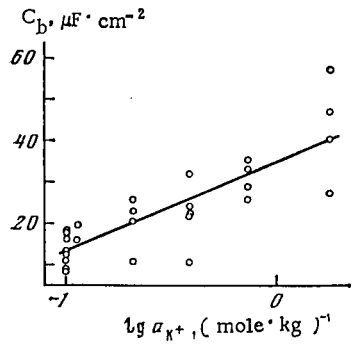

Fig. 2

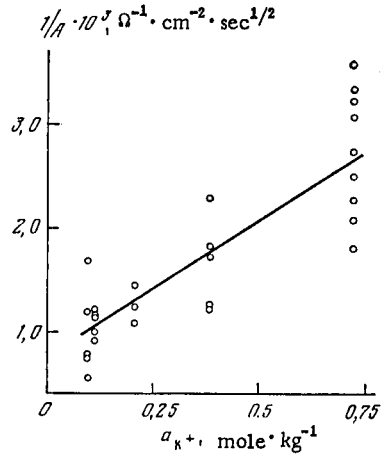

Fig. 3

Fig. 2. Dependence of the value of the capacitance element (C_b) on the activity of potassium ions in solution (a_{K^+}) at a constant potential (E) of cathodic polarization of the electrode. The points represent the experimental values of C_b; the straight line represents calculation of the linear dependence of C_b on log a_{K^+} according to the method of least squares, E = −1.40 V.

Fig. 3. Dependence of the value of 1/A on the activity of potassium ions in solution (a_{K^+}), proportional to the activity of potassium on the electrode, at the potential E = −1.40 V. The points represents the experimental values of 1/A; the straight line represents calculation of the linear dependence of 1/A on a_{K^+} according to the method of least squares.

The graphical analyses method used in the treatment of the results of the impedance measurements using an electronic computer made it possible (in agreement with the conclusions of [5] but with greater accuracy) to determine the parameters of an electrical circuit equivalent to the Zn−KOH solution system under the investigated conditions. Calculation of the parameters of several electrical circuits probably under the given conditions was performed according to pairs of frequencies by the Gauss−Seidel method, analogously to what was done in [10]. The circuit was selected according to independence of definite parameters of the circuit from the frequency and according to the minimum deviation of the calculated frequency dependence of the components of the impedance $1/\omega C_{2(p)}$ and $R_{2(p)}$ on the experimentally obtained frequency dependence of $1/\omega C_{2(e)}$ and $R_{2(e)}$. The values of C_2 and R_2 corresponding to a circuit with parallel connection were obtained by recalculation of the measured values of C_1 and R_1 after deduction of the resistance of the solution. The resistance of the solution R_0 was determined by extrapolation to an infinitely great frequency.

It was shown that within the region of electrode potentials and alkali concentrations studied, the system Zn−KOH solution at the frequencies 0.12-2 kHz is modeled by the electrical circuit cited in Fig. 1. Here W is the Warburg concentration impedance; C_b is the capacitance element; R_b is the resistance of the first reac-

TABLE 1. Dependence of the Parameters of the Electrical Circuit (Fig. 1) Equivalent to the System Zn–KOH Solution on the Alkali Concentration and on the Potential of Cathodic Polarization of the Zinc Electrode

c_{KOH}, M	$-E$, V	C_d, $\mu F \cdot cm^{-2}$	R_0, $\Omega \cdot cm^2$	$\Omega \cdot cm^2 \cdot sec^{-1/2}$	C_b, $\mu F \cdot cm^{-2}$	R_p, $\Omega \cdot cm^2$	R_H, $\Omega \cdot cm^2$
1	2	3	4	5	6	7	8
0,15	1,30	32,0	2,07	900	20,4	400	400
	1,35	32,0	2,12	980	15,0	200	220
	1,40	31,3	2,19	880	16,0	83	77
1,20	1,30*	37,0	2,21	700	23,0	250	300
	1,35	43,0	0,31	640	33,4	100	160
	1,40	34,7	0,35	480	33,5	80	75
	1,435	30,1	0,39	410	34,2	50	40

*After exposure of the electrode at E = −1.40 V.

tion; R_p is the resistance of the second reaction; C_d is the double-layer capacitance; R_0 is the resistance of the solution.

In [5-7] it was shown that the Warburg impedance under analogous conditions characterizes the process of insertion of potassium into zinc. The Warburg constant, determined from impedance measurements and characterizing the impedance W, is related to the concentration (c) and diffusion coefficient (D) of the atoms of the inserted metal in the layer of the cathode near the surface by the function

$$A = \frac{RT}{\sqrt{2}(nF)^2 c\sqrt{D}}, \quad (1)$$

when n = 1. The values of the product $c\sqrt{D}$ calculated from the values of A that we determined experimentally according to Eq. (1) in this work, in the entire region of potentials and concentrations of the solution used, coincide in order of magnitude with the values of the product $c\sqrt{D}$ obtained in [5] for 3 M KOH according to a simpler scheme and agree with the data of [11] on the study of the diffusion of alkali metals in the solid phase at room temperature by other methods. Thus, it can be concluded that the element W under our experimental conditions models the process of diffusion of the inserted potassium in the solid phase of the zinc electrode.

As can be seen from the scheme (Fig. 1), the summary impedance of the insertion process in our case includes not only W, but also the capacitance element C_b and the resistance R_b. The value of the capacitance element C_b is low; it is less than C_d and increases a little with the potential, while at a constant potential, when the activity of K^+ ions in solution is increased tenfold, it increases by approximately 20 $\mu F/cm^2$ (Fig. 2).* On the basis of the small value of the capacitance element C_b of the circuit and its dependence on the activity of K^+ ion, it can be assumed that the insertion process proceeds through a step of formation of a weakly specifically adsorbed cation K^+_{ads}, and not through a step of a chemically sorbed ion or adsorbed atom. The rate of discharging of an adsorbed cation with the formation of an introduced potassium ion (i.e., not only discharged, but also entirely reacted chemically with the electrode metal), characterized by the quantity R_b in the scheme of Fig. 1, is so great even in a dilute KOH solution (0.125 M), that R_b is not measured under our conditions. From the experimental data we can estimate only the lower limit of the exchange current of this step. According to this estimate, the exchange current of the insertion process exceeds 10^{-2} A/cm^2, and consequently, the slower step of this process is diffusion of the inserted potassium into the cathode.†

As shown in [5], the element R_p of the scheme (Fig. 1) characterizes the liberation of hydrogen on zinc from solutions of KOH free of zincate. Actually, in the entire region of hydrogen overvoltages, the value of R_p coincides in order of magnitude with the resistance of the reaction R_H ($R_H = b/2.3 \cdot i$), calculated from the polarization curve (Table 1, columns 7, 8), the slope of which (b) was determined as equal to 1.12 ± 0.03 V. This indicates that the one-electron electrochemical step is slowest in the liberation of hydrogen. As is well known,

*The dispersion of the values of C_b, as well as 1/A (Figs. 2 and 3), is probably the result of uncontrollable differences in the submicrostructure of the surface of the electrodes used in different experiments, which has a strong influence on the insertion process.

†Measurements of the frequency dependence of the impedance were performed a minimum of 10 min after the beginning of insertion, i.e., under conditions when the formation of several monolayers of the product of the interaction of potassium with zinc in the surface layer of the electrode has already been completed.

the liberation of hydrogen in alkaline solutions can occur either directly after the addition of an electron to H_2O or through the intermediate electrochemical step of insertion, followed by chemical interaction of the insertion product obtained with water. Since the exchange current of insertion is at least an order of magnitude greater than the rate of liberation of hydrogen at potentials more positive than −1.5 V (Table 1), and, consequently, insertion cannot be the slow step of the liberation of hydrogen, two consequences are obtained: In the first place, the slope of the semilogarithmic curve of the liberation of hydrogen, equal to ~ 0.12 V, indicates that the liberation of hydrogen at the potentials of our experiments proceeds according to a mechanism of direct addition of an electron to a water molecule, while the liberation of hydrogen according to a chemical mechanism occurs substantially more slowly; in the second place, in the region of potentials on the electrode used in our experiments, equilibrium between the atoms of the inserted metal in the layer near the surface and its ions in solution is preserved. At potentials more negative than −1.6 V, this equilibrium may probably be disrupted on account of the more rapid occurrence of chemical interaction of water with the product of insertion of potassium into zinc that was formed [9]. The fact that hydrogen on zinc at potentials more positive than −1.5 V is liberated according to an electrochemical mechanism of addition of an electron to a water molecule provides a basis for considering the observed dependence of its overvoltage on the activity of alkali (a_{OH^-}), namely, the decrease in the overvoltage by approximately 0.06 V in the presence of a tenfold increase in a_{OH^-}, as a consequence of the negligible value of the Ψ_1-potential. By analogy with a lead electrode [12], it seems quite possible that the formation of a solid solution of potassium in zinc on the surface of the electrode causes a small shift in the zero charge potential of the zinc electrode in KOH solutions in the negative direction in comparison with its value in weakly acid solutions [13]. As a result of this, the value of the negative charge of the surface and, consequently, also the value of the Ψ_1-potential should decrease and may even change sign.

Since, as was shown above, the electrode potential under our conditions is the equilibrium potential with respect to atoms and ions of the alkali metal, at the same potential the dependence of the activity of the metal inserted into the metal of the cathode on the activity of its ions in the electrolyte solution is directly proportional. On the basis of the data of the impedance measurements, the relationship between the product of the concentration of inserted potassium (c) by $D^{1/2}$, i.e., a quantity proportional to 1/A [Eq. (1)], and the activity of potassium ions in solution (a_{K^+}) can be established (Fig. 3). From Fig. 3 it is evident that the relationship between these quantities is described by the linear equation

$$(1/A)\cdot 10^3 = 0.75 + 2.6 a_{K^+}. \qquad (2)$$

If we take the standard potential of the system $K^+ - K$ as the standard value of the potential of the system $K^+ - K(Zn)$ and assume that the diffusion coefficient of the inserted potassium D in the region of activities used does not depend on the activity of potassium in its compound with zinc and is equal to approximately 10^{-14} $cm^2 \cdot sec^{-1}$, then from Eqs. (1) and (2) and the Nernst equation it can be calculated that the activity coefficient of potassium in the product of its interaction with zinc is equal in order of magnitude to 10^{-26}. Calculation also shows that a 5% increase in the potassium concentration in the solid phase of the electrode leads to a more substantial increase in its activity coefficient (by 10%) in the region of low values of a_{K^+} (0.1 mole/kg) in comparison with its change (by 4%) at larger values of the activity of K^+ ions in the electrolyte (0.75 mole/kg), which agrees with the concept of the mechanism of insertion [14]. In accordance with the literature data [15], in this case we should also take into account the increase in the diffusion coefficient of inserted potassium even in the presence of a relatively small change in its concentration in the solid solutions with strong chemical interaction of the components.

It should be noted that at a constant concentration of potassium ions in solution not exceeding 0.6 M, a shift of the potential in the cathodic direction causes practically no change in the value of the product $c\sqrt{D}$, proportional to 1/A (Table 1, column 5). In more concentrated KOH solutions, the rate of the diffusion process is greater (the value of the diffusion impedance is lower, Table 1, column 5), and its dependence on the electrode potential is more pronounced.

The influence of differences in the microstructure of the electrode surface on the insertion process, which was indicated above, is illustrated by a phenomenon analogous to the "development" of the surface as a result of anodic injection of vacancies [16]. This phenomenon consists in the fact that in each change of the potential in the positive direction on the electrode there is a partial removal of K from the product of the interaction of potassium with zinc, formed during prolonged exposure of the electrode at more negative potentials. As a result of this, the surface concentration of vacancies is increased, and, consequently, the diffusion coefficient D should also increase, as is evidenced by the decrease in the value of the Warburg constant A (compare lines 1 and 4 of Table 1). It should be noted that such "development" of the electrode accelerates not only the insertion process, but also the parallel process of liberation of hydrogen (Table 1). Evidently this phenomenon

can be explained by an increase in the energy of adsorption of hydrogen atoms on the defective electrode surface.

Thus, in a wide region of potentials, quantitative data were obtained on the insertion of potassium into zinc, permitting an elucidation of the relationship of the rates of the steps of this process. It was also shown that the liberation of hydrogen from KOH solutions with concentration 0.125-1.2 M, occurring simultaneously at low current densities (potentials more positive than −1.5 V), obeys the principles of electrochemical kinetics of the reaction of the water molecule with the electron.

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LITERATURE CITED

1. J. McBreen and E. J. Cairns, "The zinc electrode," in: Advances in Electrochemistry and Electrochemical Engineering, Vol. 11 (1978), p. 273.
2. R. J. Brodl and V. E. Leger, "Zinc," in: Encyclopedia of Electrochemistry of the Elements, Vol. 5, A. J. Bard, ed., Marcel Dekker, New York (1976).
3. B. N. Kabanov, D. I. Leikis, I. G. Kiseleva, and I. I. Astakhov, "Cathodic insertion of alkali metals into electrodes in aqueous solutions," Dokl. Akad. Nauk SSSR, 114, 1085 (1962).
4. D. P. Aleksandrova, I. G. Kisleva, and B. N. Kabanov, "Influence of insertion of alkali metals into electrodes on the hydrogen overvoltage," Zh. Fiz. Khim., 38, 1493 (1964).
5. L. A. Reznikova, B. N. Kabanov, T. I. Popova, and D. P. Aleksandrova, "Investigation of cathodic processes on zinc in alkaline solutions by the impedance method," Élektrokhimiya, 9, No. 6, 877 (1973).
6. L. A. Reznikova, D.P. Aleksandrova, and B. N. Kabanov, "Investigation by the impedance method of the processes occurring on a zinc electrode at its static potential in alkaline solutions," Élektrokhimiya, 16, 576 (1980).
7. L. A. Reznikova and I. I. Astakhov, "Microanalytic investigation of the process of insertion of potassium into zinc," Élektrokhimiya, 16, No. 5, 718 (1980).
8. V. S. Muralidharan and R. S. Rajagopalan, "Kinetics and mechanism of corrosion of zinc in sodium hydroxide solutions by steady-state and transient methods," J. Electroanal. Chem., 94, No. 1, 21 (1978).
9. L. Z. Vorkapic, D. M. Drazic, and A. R. Despic, "Corrosion of pure and amalgamated zinc in concentrated alkali hydroxide solutions," J. Electrochem. Soc., 121, No. 11, 1385 (1974).
10. M. Ya. Kats, R. A. Slivka, D. P. Aleksandrova, and D. I. Leikis, "The use of an electronic computer to interpret impedance measurements in the investigation of multistep processes," in: The Use of Microprocessors and Minicomputers in the Automation of Corrosion-Electrochemical Investigations [in Russian], Zinatne, Riga (1979), p. 43.
11. N. N. Tomashova, I. G. Kiseleva, I. I. Astakhov, and B. N. Kabanov, "Activation energy of the process of cathodic insertion of an alkali metal," Élektrokhimiya, 4, 471 (1968); I. I. Astakhov and B. N. Kabanov, "Diffusion of potassium through zinc membranes," Élektrokhimiya, 5, 749 (1969); G. L. Teplitskaya and I. I. Astakhov, "The formation of solid solutions in the cathodic insertion of sodium into lead," Élektrokhimiya, 6, 379 (1970); G. L. Teplitskaya and I. I. Astakhov, "Investigation of cathodic insertion by means of chemical analysis," Élektrokhimiya, 8, 1199 (1972).
12. I. G. Kiseleva, D. I. Leikis, and B. N. Kabanov, "Zero charge potentials of an alloy of lead with sodium," Élektrokhimiya, 8, 250 (1972).
13. Yu. P. Ipatov and V. V. Batrakov, "Estimation of the zero charge potential of the basic faces of a single crystalline zinc electrode," Élektrokhimiya, 12, 1174 (1976).
14. I. I. Astakhov, "Diffusion kinetics of electrochemical insertion," Élektrokhimiya, 9, 521 (1973).
15. I. I. Astakhov and G. L. Teplitskaya, "Investigation of the kinetics of cathodic insertion occurring with the formation of solid solutions," Élektrokhimiya, 15, 1363 (1979).
16. B. N. Kabanov, I. G. Kiseleva, I. I. Astakhov, and N. N. Tomashova, "Overvoltage and mechanism of cathodic insertion of alkaline metals into solid electrodes," Élektrokhimiya, 1, 1023 (1965); H. W. Pickering and C. Wagner, "Electrolytic dissolution of binary alloys containing a noble metal," J. Electrochem. Soc., 14, No. 7, 698 (1967).