DOUBLE-LAYER CAPACITANCE OF POLYCRYSTALLINE SILVER

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The dependence of the double-layer capacitance of a polycrystalline silver electrode on its potential in sodium fluoride solutions with a concentration of 0.005 to 0.5 M has been measured over a range from 0.0 to −1.2 V (S.H.E.). Comparison of the measured capacitance values with those calculated by Grahame's method shows that the structure of the electric double layer in this system is close to the Gouy−Chapman−Stern−Grahame model only in dilute (0.005, 0.01 M) solutions. The differences are greatest in relatively concentrated (of the order of 0.1 M) NaF solutions. It is suggested that the observed behavior of the double-layer capacitance can only be explained on the basis of a specific structure of the dense part of the double layer, and not simply on the basis of the crystallographic nonuniformity of the metal surface.

In [1, 2], attention is drawn to the fact that a quantitative interpretation of double-layer capacitance (C) measurements for polycrystalline silver in sodium fluoride solutions on the basis of the Gouy−Chapman−Stern−Grahame model encounters some difficulties, and it is suggested that these difficulties are connected with the crystallographic nonuniformity of the electrode surface.

Bearing in mind that the results of capacitance measurements on solid electrodes frequently depend on the method of surface preparation, it seemed advisable to study the double-layer capacitance of silver in sodium fluoride solutions using a technique different from that used in [1, 2], i.e., using a renewable silver electrode, which is known to give sufficiently good reproducibility [3, 4]. In addition, to obtain a complete picture of the double-layer capacitance in this system, it seemed profitable to perform the measurements over a wider range of sodium fluoride concentrations than was done before.

The experiments were performed using grade "os.ch." ["ultrapure"] sodium fluoride, which was calcined at 600°C for 1 h. The solutions were prepared using water doubly distilled from an alkaline potassium permanganate solution. The pH of the solution was maintained at 4 by adding appropriate amounts of hydrofluoric acid. Oxygen was removed by passing electrolytic oxygen through the solution until the residual currents in the potential range corresponding to "ideal polarizability" of silver were reduced to less than 10 $\mu A/cm^2$. We measured C using a rapid-response impedometer [5] at a fixed frequency with linear scanning of the potential (φ) from −1.0 V in the positive and negative direction at a rate of 0.8 V/min. The frequency dispersion of the measured capacitance was insignificant under these conditions (Fig. 1). The potentials are given relative to S.H.E.

Figure 2 shows the dependences of the double-layer capacitance of a polycrystalline silver electrode, as measured by the indicated method, on its potential and the electrolyte concentration. It can be seen that a clearly defined single capacitance minimum develops in the C, φ curves as the NaF concentration is reduced from 0.5 to 0.005 M. The potential corresponding to the minimum is in the vicinity of −0.7 V and varies insignificantly with varying concentration.* An analogous minimum has been observed several times [1, 2, 6] in this pH range and, on the whole, its behavior leaves no doubt that it is connected with the diffuseness of the electric double layer on polycrystalline silver.

At the same time, it is not difficult to see from Fig. 2 that the diffuse capacitance minimum extends to unusually high concentrations in the system being studied. Thus, it appears clearly in solutions with a concen-

*When the measurements are made under potentiostatic conditions (single points), the potential of the minimum shifts from −0.74 V in a 0.005 M solution to −0.76 V in a 0.1 M solution.

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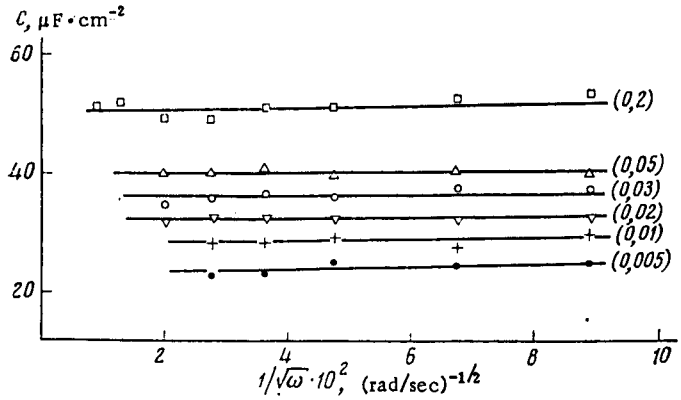

Fig. 1. Plots of measured capacitance versus frequency at $\varphi = -0.7$ V. The numbers in brackets are the NaF concentrations (M).

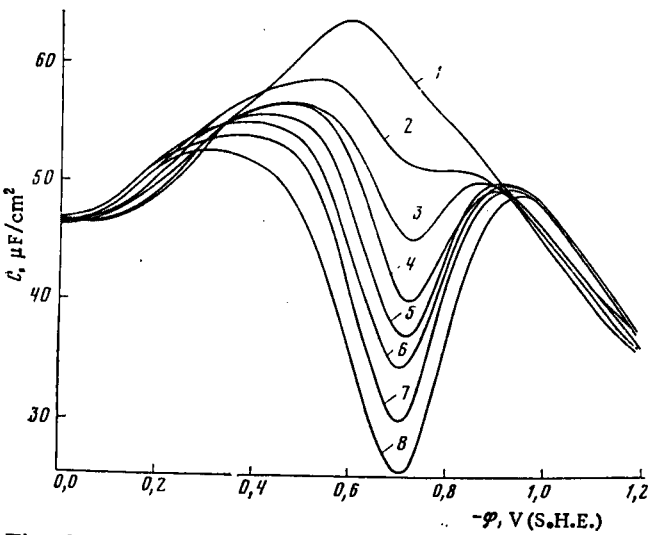

Fig. 2. Measured plots of specific double-layer capacitance versus potential for a silver electrode, based on the geometric surface area, at 25 ± 1°C in NaF solutions with concentrations of: 1) 0.5; 2) 0.2; 3) 0.1; 4) 0.05; 5) 0.03; 6) 0.02; 7) 0.01; 8) 0.005 M.

tration of the order of 0.1 M; this is not the case in known experiments on a mercury electrode [7]. Formally, this may indicate that the electric double layer on polycrystalline silver is more diffuse than that on mercury. Consequently, it would be profitable to analyze the data obtained to check their concordance with the Gouy–Chapman–Stern–Grahame model of the double layer.

If we assume that the zero-charge potential in the present system is determined by the position of the minimum in the C, φ curve, then, using this value as an integration constant, we can calculate the dependence of the measured C values on the electrode charge (q). The results of these calculations, in which we took into account the roughness factor (f) obtained from the slope of a Parsons–Zobel plot (Fig. 3), are given in Fig. 4a, which also shows (dotted line) the dependences of C on q calculated in accordance with [7] using the formulas:

$$1/C = 1/C_{dn} + 1/C_{df} \quad C_{df} = 19.46\sqrt{137.8a + q^2}; \quad C_{dn} \neq C_{dn}(a), \tag{1}$$

where C_{dn} and C_{df} are the capacitances of the dense and diffuse parts of the double layer, and a is the NaF concentration. The dependence of C_{dn} on q required for the calculations was obtained from measurements in 0.5 M NaF with allowance for f.

TABLE 1. Values of f Calculated for q = 0 by Simultaneous Solution of Pairs of Equations $1/C_1 = 1/C_{dn1} + 1/fC_{df_1}$ and $1/C_2 = 1/C_{dn2} + 1/fC_{df_2}$ with the Condition That $C_{dn1} = C_{dn2}$

α_2	α_1							
	0,500	0,200	0,100	0,050	0,030	0,200	0,010	0,005
0,500	--	1,31	1,34	$1,65_5$	1,78	1,88	2,13	2,28
0,200	1,31	—	1,37	$1,82_2$	1,94	2,03	2,28	2,44
0,100	1,34	1,37	—	$2,37_7$	2,28	2,29	2,51	2,61
0,050	1,65	1,82	2,37	—	2,19	2,25	2,54	2,65
0,030	1,78	1,94	2,28	$2,19_9$	--	2,32	2,67	2,73
0,020	1,88	2,03	2,29	$2,25_5$	2,32	—	2,87	2,83
0,010	2,13	2,28	2,51	$2,54_4$	2,67	2,87	--	2,80
0,005	2,28	2,44	2,61	$2,65_5$	2,73	2,83	2,80	--

*The subscripts 1 and 2 denote values corresponding to solutions with two different concentrations.

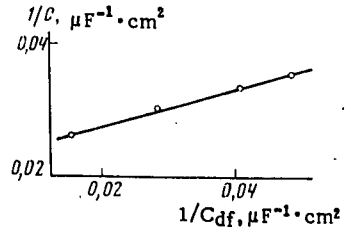

Fig. 3. Approximation of the dependence of 1/C on $1/C_{df}$ by the straight line $1/C = l/C_{df} + m$, where l and m are calculated by the method of least squares: $l = 0.368 \pm 0.009$ (2.6%); $m = 0.0183 \pm 0.0003$ (1.9%); $f = 1/l = 2.72$.

It can be seen from Fig. 4a that the aforementioned peculiarity in the capacitance behavior of polycrystalline silver also applies to the dependence of C on the electrode charge. An appreciable difference between measured capacitance values and those calculated from (1) is observed at relatively high concentrations. It might be supposed that this is due to inaccuracies in the determination of f from the data in Fig. 3, but the results of the calculations shown in Table 1 show that this is not so: Good agreement between the curves in Fig. 4a cannot be achieved by selecting any single value of f. Consequently, the relation between C and C_{df} in the present case cannot be described by the relation $1/C = 1/C_{dn} + 1/C_{df} \cdot f$ with values of f and C_{dn} which are both independent of the electrolyte concentration. We must assume, therefore, that, in contrast to mercury and a number of other metals, the properties of the electric double layer of polycrystalline silver in the vicinity of the minimum-capacitance potential are not the same as the properties characterized by the Gouy–Chapman–Stern–Grahame model at the zero-charge point.

An analogous conclusion is indicated by the dependences of C_{dn} on q if these are calculated on the basis of (1) from C values measured in solutions with different concentrations. Indeed, it can be seen from Fig. 4b that the C_{dn}, q curves in this case are nonmonotonic and differ substantially from one another. The shape of the curves in Fig. 4b (with extreme C_{dn} values localized in the vicinity of −0.7 V) and its variation with concentration are very similar to what was observed in [1]. This indicates that our experimental data are in qualitative agreement with the results in [1, 2] and rules out the idea of possible experimental errors.

To explain the peculiarities in the double-layer capacitance behavior in the present system, it was postulated in [1] that they are connected with the nonuniformity of charge distribution over the surface of the polycrystalline electrode, and a model was proposed to describe the effect of the crystallographic nonuniformity of the metal surface on the measured double-layer capacitance of such an electrode. Analysis of the properties of this model [8-10] has shown that they are largely analogous to those observed in the present system.

While not denying the possibility that polycrystallinity effects have a certain influence on the measurements, we should like to draw attention to the results of later works [11, 12] concerning the capacitance of the double layer on individual dislocation-free planes of a silver single crystal. The experimental data in these works indicate that the peculiarities in the double-layer structure of polycrystalline silver observed in the present measurements may also occur on the (100) plane. Thus, the diffuse capacitance minimum observed

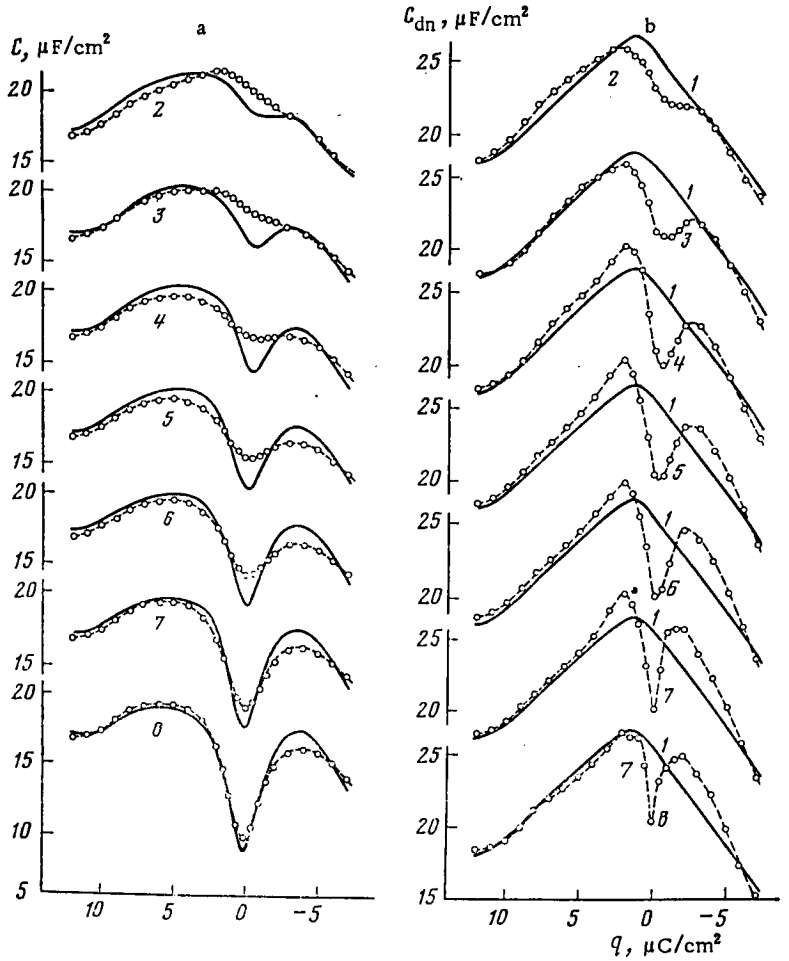

Fig. 4. Plots of measured (continuous line) and theoretical (dotted line) values of specific capacitance versus electrode charge (a), and plots of C_{dn} versus q calculated from measurements in solutions with different concentrations (b). The symbols are the same as in Fig. 2.

in 0.1 M NaF solution is just as pronounced on this plane as on the polycrystalline electrode. It is possible, therefore, that the concept of a specific structure in the dense part of the double layer must be brought in to explain the capacitance measurements in this system, as was done in [13] in the case of gallium. It seems that the formation of surface structures of solvent molecules is highly probable in the case of silver too.

LITERATURE CITED

1. G. Valette, C. R. Acad. Sci (ser. C), 275, 176 (1972); G. Valette and A. Hamelin, J. Electroanalyt. Chem., 45, 301 (1973).
2. É. S. Sevast'yanov, The Double Layer and Adsorption on Solid Electrodes [in Russian], Vol. 4, Izd. Tartusk. Univ. (1975), p. 281.
3. R. Yu. Bek and T. A. Lavrova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, 14, No. 6, 102 (1971).
4. A. G. Zelinskii, R. Yu. Bek, and A. I. Maslii, Élektrokhimiya, 9, 1515 (1973).
5. S. P. Novitskii, I. I. Burenkov, V. I. Kenzin, A. G. Zelinskii, and D. I. Leikis, Élektrokhimiya, 14, 270 (1978).
6. I. G. Dagaeva, D. I. Leikis, and É. S. Sevast'yanov, Élektrokhimiya, 2, 820 (1966).
7. D. C. Grahame, J. Amer. Chem. Soc., 76, 4819 (1954).
8. N. B. Grigor'ev, Dokl. Akad. Nauk SSSR, 229, 647 (1976).
9. U. V. Pal'm, M. P. Pyarnoya, and N. B. Grigor'ev, Élektrokhimiya, 13, 1074 (1977).
10. R. Yu. Bek and A. G. Zelinskii, Élektrokhimiya, 14, 632 (1978).
11. T. Vitanov and A. Popov, Trans. SAEST, 10, No. 1, 5 (1975).

12. T. Vitanov, A. Popov, and É. S. Sevast'yanov, Élektrokhimiya, 12, 582 (1976).
13. A. N. Frumkin, N. B. Grigor'ev, and I. A. Bagotskaya, Élektrokhimiya, 2, 239 (1966); A. N. Frumkin and N. B. Grigor'ev, Élektrokhimiya, 4, 533 (1968).

FORMATION OF ADSORPTION LAYERS AND MULTILAYER FILMS DURING THE ANODIC OXIDATION OF CADMIUM IN ALKALI SOLUTIONS

KINETICS OF IRREVERSIBLE OXIDE ADSORPTION

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Relaxation methods (voltamperometry and chronoamperometry) have been used to determine the conditions under which the kinetics of irreversible adsorption of passivating oxide predominate over anodic dissolution in 1-0.1 N KOH solutions. Regions of monolayer and multilayer surface coverage are distinguished. The kinetics of monolayer oxide growth are interpreted on the basis of Temkin–Zel'dovich-type equations for irreversible adsorption. Means of refining the kinetic equation for better agreement with experiment are discussed.

To elucidate the mechanism of the active dissolution and passivation of a smooth cadmium electrode in alkali, it is necessary to investigate the kinetics of the adsorption steps, the formation of adsorption layers and multilayer films of oxides, and also the role of the latter in retarding metal dissolution. The most well-founded experimental evidence for the formation of thin multilayer films of cadmium oxide during the passivation of cadmium in dilute alkali solutions has been given in [1]. Indirect evidence for the formation of an oxide film is also given in [2, 3], but this was neither detected nor discussed in [4, 5]. In the present work we have attempted to establish that adsorption layers and multilayer films are formed on a cadmium electrode during oxidation in dilute KOH solutions on the basis of an interpretation of data obtained by potential-monitoring techniques.

We have studied the general characteristics of the dissolution and passivation of a cadmium electrode in alkali by linear potential scanning at scanning speeds of 0.0002-200 V/sec (Fig. 1), and also by a modified chronoamperometric method involving linear potential scanning interrupted at different levels of electrode polarization. The investigations were performed on a KD-0 cadmium end-face electrode with an area of 0.2 cm^2 in 0.1-13.4 M KOH at 20°C and in 5.0 and 8.1 M KOH at temperatures from −50 to +60°C. The technique is described in [6]. The potentials are given relative to a mercury oxide reference electrode in the same solution.

On examining the general characteristics of the i, φ curves for KOH solutions with different concentrations, we found that when the process is in its least steady state (0.1-200 V/sec) it is possible to distinguish the conditions under which active dissolution and passivation change over to kinetics of adsorption and multilayer oxide film growth. Indeed, in the case of low potential-scanning speeds ($v \leq 0.1$ V/sec) and 1-13.4 N KOH solutions the quantity of electricity passed in the region of maximum active-dissolution current, counting from the start of scanning, corresponds to the dissolution of tens and hundreds of cadmium-hydroxide-forming metal monolayers,* whereas in the case of high potential-scanning speeds ($v > 0.1$ V/sec) and 0.1-2

*From 0.3 and 0.4 mC/cm^2 is required for the dissolution of a monolayer of cadmium atoms or the formation of a monolayer of adsorbed oxide on the various planes of a cadmium single crystal, and also for the formation of CdO and β-$Cd(OH)_2$ monolayers with the same lattice parameters, as in the case of the corresponding phase oxides [7]. If we assume (by analogy with [8]) that the surface roughness factor is three, then the formation of one monolayer of adsorbed oxide corresponds on average to 1.1 mC/cm^2.

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