Thus the chemical bonding of the inhibitor of thermooxidative destruction to the polyalkylmethacrylate chains increases its effectiveness by more than a factor of ten, and this is in agreement with the data presented in [11], and relating to the use of chemically bonded amine type inhibitor to prevent oxidative destruction of cellulose acetate. The high stabilizing effect [11] was observed at concentrations which were lower by almost a factor of ten, as compared with concentrations of mechanically incorporated stabilizer.

The rather unusual possibility of using polyarylenealkylene hydroperoxides both as polymerization initiators and inhibitors of thermooxidative destruction of polymers, provides a wide scope for their practical use in stabilization and modification of polymers.

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RELATIONSHIP BETWEEN THE CHARACTERISTICS OF THE ELECTRIC DOUBLE LAYER OF A POLYCRYSTALLINE ELECTRODE AND THE INDIVIDUAL FACES OF A SINGLE CRYSTAL IN ELECTROLYTE SOLUTIONS

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The suggestion that certain features of the structure of the solid metal/electrolyte interface can be related with the emergence of faces with different values of the zero charge potential on the surface was first set forth in A. N. Frumkin's work [1]. It is obvious that studies in the individual faces of metals would give new, important information about the effect of the nature of the metal on the regularity of the structure of the electric double layer and the adsorption of the solution's components. Essential conclusions can be made on the basis of [2] in which the structure of the electric double layer was studied on the individual faces of a silver single crystal – the (111), (100), and (110) faces – and also on polycrystalline silver.

In this communication an attempt is made to find the relationship, by means of model concepts, between the parameters of the electric double layer for the individual faces of a metal single crystal and the corresponding polycrystalline electrode, whose surface consists of sections with faces of the same orientation. For simplicity we assume that the surface of the solid electrode consists of two types of crystallites with different zero charge potentials φ_1^0 and φ_2^0 (φ_2^0 is more negative than φ_1^0). The size of the crystallites is assumed to be large enough so that the free energy of the surface does not depend on the area of the surface element being considered (the boundary sections were not taken into consideration). Both orientations are thermodynamical equilibrium orientations.

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Upon contact of the given metal electrode with the electrolyte solution the structure of the electric double layer will be different on the sections of the surface with different values of the zero charge potential for a fixed electrode potential, measured with respect to a constant comparison electrode, because of the equipotential nature of the surface of the metal. The total value of the charge, however, is equal to:

$$q=q_1\theta+q_2(1-\theta), \tag{1}*$$

where q_1 and q_2 are the charge density at the given potential on the sections of the surface with zero charge potentials of φ_1^0 and φ_2^0 and θ and $(1-\theta)$ are the fraction of the sections with respect to the total surface of the electrode. It follows directly from (1) that the condition $q=0$ corresponds to the equation:

$$q_1\theta=-q_2(1-\theta), \tag{2}$$

i.e., the overall charge for the surface is equal to zero when the partial values of the charge, which differ in sign, are equal. For a potential φ_1^0 the total charge on the electrode is equal to

$$q=q_2^{\varphi_1^0}(1-\theta), \tag{3}$$

and for a potential φ_2^0, accordingly, it is equal to

$$q=q_1^{\varphi_2^0}\theta, \tag{4}$$

from which it follows directly that the total charge on the electrode for φ_1^0 and φ_2^0 is the greater, the greater the difference in the zero charge potentials of the different sections of the surface.

In the given case Eq. (2) formally only indicates the absence of a charge on the surface of the electrode in spite of the fact that the total charge q is equal to zero. In practice, however, in adsorption and kinetic phenomena, the values have partial values of the charge on different sections of the surface and therefore the idea of a "zero charge potential" which is rigorously valid for a liquid metallic electrode and for individual faces of a single crystals, can only be applied to a polycrystalline electrode with some degree of approximation. By differentiating (1) with respect to the potential, we get an expression for the differential capacitance of the given electrode

$$C=C_1\theta+C_2(1-\theta). \tag{5}$$

Assuming that Stern's theory is applicable to the given system, in the absence of specific adsorption of ions, Eq. (5) can be written in the following form:

$$C=\theta\frac{C_{g1}C_{d1}}{C_{g1}+C_{d1}}+(1-\theta)\frac{C_{g2}C_{d2}}{C_{g2}+C_{d2}}, \tag{6}$$

where C_{g1} and C_{d1}, C_{g2} and C_{d2} are the capacitance of the dense and diffuse layers of sections θ and $(1-\theta)$, respectively. The expressions for the capacitance of the diffuse layer, which were calculated on the basis of the Gouy–Chapman theory for a 1–1 electrolyte, have the form

$$C_{d1}=F/2RT[2DRTc/\pi+\theta^2q^2]^{1/2};\quad C_{d2}=F/2RT[2DRTc/\pi+(1-\theta)^2q_2^2]^{1/2}, \tag{7}$$

where c is the electrolyte's concentration and D is the volumetric value of the dielectric permeability.

The analysis of Eq. (6) for the case of concentrated and dilute electrolyte solutions is of interest. For large electrolyte concentrations $c_{d1,2}\gg C_{g1,2}$ and therefore Eq. (6) at any electrode potential can be written in the form

$$C\approx C_{g1}\theta+C_{g2}(1-\theta). \tag{8}$$

As we know, the capacitance of the dense layer for a large number of metals with large and medium hydrogen overvoltages increases evenly in going from small negative to positive charges for the surface because of the intensification of the specific interaction of the water molecules, which are adsorbed by the negative (oxygen) end of the dipole, with the metal.

If it is assumed that the character of the change in the capacitance of the dense layer with the electrode potential (or charge) is the same on both sections of the surface, then the total capacitance for the zero point potential for the more negative face must be less than the capacitance of the dense layer on the single crystal at the zero charge potential. And, conversely, the total capacitance at the more positive zero point potential is greater than the capacitance of the dense layer of the single crystal at the zero charge potential.

*The given expression does not differ, in its meaning, from the analogous dependence for the total charge in the model of two parallel Frumkin condensers in his theory for the effect of the electrical field on the adsorption of neutral organic molecules.

At the zero charge potential for the most negative face (φ_2^0) the expression for the differential capacitance will have the following form:

$$C_{meas} = \theta C_{g1}^{\varphi_2^0} + (1-\theta)\frac{Ac'^{/2}C_{g2}}{Ac'^{/2}C_{g2}}, \quad (9)$$

where $A = (F^2D/2\pi RT)^{1/2}$. As follows from Eq. (6), for $c \to \infty$

$$C_{meas} \to \theta C_{g1}^{\varphi_2^0} + (1-\theta)C_{g2}^{\varphi_2^0}, \quad (10)$$

and for $c \to 0$

$$C_{meas} \to \theta C_{g1}^{\varphi_2^0}, \quad (11)$$

i.e., for a decrease in the concentration of the electrolyte the measured capacitance at φ_2^0 approaches not zero, as in the case of single crystal and liquid electrodes, but some constant value. The electrolyte concentration, at which such a transition should be observed, depends on the difference in the values φ_1^0 and φ_2^0, the character of the change in C_{g1} with potential, and the value of θ.

At a potential which corresponds to the value φ_1^0, the expression for the capacitance of the given polycrystalline electrode assumes the following form (ignoring the diffusivity of the electric double layer for the face with a zero charge potential φ_2^0):

$$C_{meas} = (1-\theta)C_{g2}^{\varphi_1^0} + \theta\frac{Ac'^{/2}C_{g1}}{Ac'^{/2}+C_{g1}}. \quad (12)$$

In this case for the value of the capacitance at a potential φ_1^0 the first term of Eq. (12) is greater than the second term in this equation because of the increase in the specific adsorption of the solvent in going to the positive charge for the surface. The minimum on the differential capacitance curve, which is due to the diffusivity of the electric double layer, is to a large extent masked by the large value of the capacitance of $(1 - C_{g2}^{\varphi_1^0})$ on the face with a zero charge potential of φ_1^0.

An experimental confirmation of the validity of the given model can be given by the results in [2, 3] in which the curves were measured for the differential capacitance of a silver single crystal and polycrystalline silver, and on individual faces of a gold single crystal and polycrystalline gold. On both polycrystalline silver and on gold a single minimum is observed on the curves for the differential capacitance in dilute electrolyte solutions at a potential which coincides, within several tenths of a millivolt, with the zero charge potential of the more negative face.

The given model for a polycrystalline electrode can also be applied to solid metal alloys which have a nonuniform surface, using the zero charge potential of the first component and the fraction of the surface occupied by it for φ_1^0 and θ and the zero charge potential and the fraction of the surface occupied by it for φ_2^0 and $(1 - \theta)$. The results of measuring the differential capacitance on binary solid cadmium–bismuth alloys are given in [4] for changes in the ratio of the components in the alloy over a wide range (for the given alloys the difference in the zero charge potentials of the individual components was 380 mV, $\varphi_{Cd}^0 = -0.75$ V and -0.39) for bismuth in (N7V7É). For changes in the bismuth concentration in the alloy from 0 to ~90%, the zero charge potential of the alloys did not depend on the bismuth concentration. It almost coincided with the zero charge potential of the component with the more negative φ^0, i.e., cadmium. This is in complete agreement with the experimental data on the differential capacitance for polycrystalline silver and gold. A detailed study of the structure of the electric double layer on alloys with a nonuniform surface might, in addition to its independent interest, be helpful in establishing the relationship between the electrochemical properties of the polycrystalline and single crystal metal electrodes.

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