

ELECTROREDUCTION OF PERSULFATE ANION AT A POLYCRYSTALLINE SILVER ELECTRODE AND AT THE SEPARATE FACES OF A MONOCRYSTAL OF SILVER AND OF BISMUTH

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An investigation was made on the dependence of the reduction rate of the persulfate anion on the potential, concentration, and nature of the supporting electrolyte, on electrodes of polycrystalline silver, and also on the faces of silver (111), (100), and bismuth (111). We determined the effective discharge of the anion from kinetic data and showed that the reduction of the persulfate anion at these electrodes proceeded by a retarded discharge mechanism. The differences in the discharge rates at the electrodes investigated, except for polycrystalline silver, were determined only by the differences in the structure of the double layer of these metals.

The anion $S_2O_8^{2-}$ was the first studied with the object of investigating the mechanism of the electroreduction of anions and establishing the reasons for the dependence of the rate of the electrochemical reaction on the nature of the electrode. The theory of the reduction of anions, which was mainly based on the assumption that the elementary act of the reaction proceeded with a finite velocity, led to the following relation between the potential E and the current density i_k :

$$i_k = Kc_A \exp \frac{\alpha F}{RT} \left(-E + \frac{n_1 + \alpha}{\alpha} \psi_1 \right), \quad (1)$$

where c_A and n_1 are the concentration and charge of the reacting particle in the volume of the solution respectively; α is the transfer coefficient; ψ_1 is the mean value of the potential in the plane in which are concentrated the charge centers of the reacting particles, in the transition state of the reaction [1-5].

This theory is based on the following assumptions: The reacting particle in the transition state of the reaction is in equilibrium with the particles in the bulk of the solution, in accordance with the Boltzmann equation, and the structure of the electric double layer can be represented with the aid of the Stern - Grahame theory; the non-Coulomb interaction of the reacting particles and of the reaction products, as with the electrode surface and as with the ions of the electric double layer, does not depend on the potential; the dependence of the velocity of the electrochemical reaction, in which an adsorbed particle participates, on the effective difference in potential, is described by the classical equation of Tafel, with a constant coefficient α ; no account is taken of the effects of discreteness of charge in the electric double layer.

It was shown in [6] that the preexponential coefficient K did not depend on the nature of the metal and, in this case, it followed from Eq. (1) that the dependence of the reaction velocity on the nature of the electrode was determined only by the structure of the electric double layer, i.e., by the value of the ψ_1 potential, the value and sign of which depended on the location of the zero charge potential. This view was confirmed by a study of the reduction of $S_2O_8^{2-}$, and $Fe(CN)_6^{3-}$, both at liquid and at solid polycrystalline electrodes, in aqueous and nonaqueous solutions [3 to 5, 7 to 13]. However, at the surface of polycrystalline electrodes there are crystallites, oriented about various crystallographic faces, which may have different zero charge potentials, which should lead to a difference in the adsorption and kinetic properties of the individual parts of the metal [14-16, 21]. In this connection it became necessary to investigate the kinetics of the reduction of anions at differing faces of monocrystalline electrodes.

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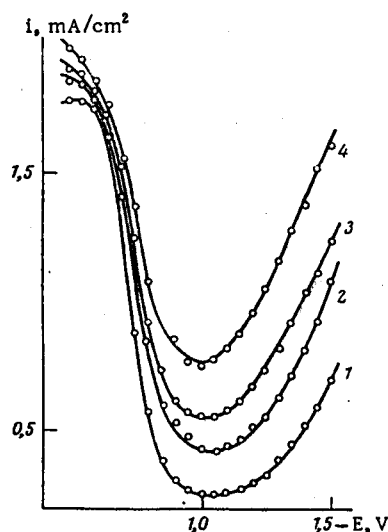


Fig. 1

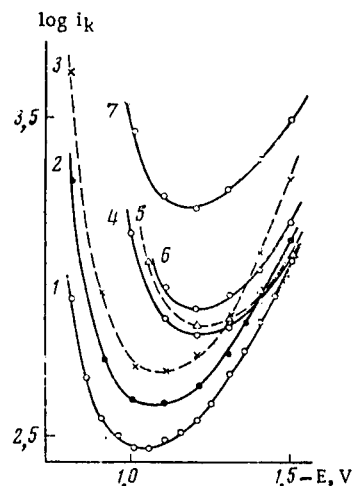


Fig. 2

Fig. 1. Polarization curves for the reduction of 10^{-3} N $K_2S_2O_8$ at a rotating electrode of Ag (111), in the presence of KF at various normalities: 1) $0.9 \cdot 10^{-2}$; 2) $1.4 \cdot 10^{-2}$; 3) $1.9 \cdot 10^{-2}$; 4) $2.4 \cdot 10^{-2}$. Rotation rate 10,000 rpm.

Fig. 2. Dependence of the reduction rate of 10^{-3} N $K_2S_2O_8 + 0.9 \cdot 10^{-3}$ M KF on the electrode potential, at various electrodes: 1) Ag(111), 2) Ag(100), 3) Ag, 4) Bi, 5) Bi(111), 6) Sn, and 7) Pb.

In the present work we carried out an investigation of the kinetics of reduction of the persulfate anion, at a polycrystalline silver electrode, and at the (111) and (100) faces of monocrystals of silver and bismuth (111). The choice of these electrodes was associated with the fact that, for the separate faces of silver, we observed the greatest differences in the zero charge potentials (z.c.p.), while the structure of the double layer, both for polycrystalline silver, and for the separate faces of silver, was investigated in detail [15, 16]. The method of operation was described in [10, 11]. The surface of the silver electrodes and of the bismuth electrodes was treated by the methods used for the preparation for measuring the capacities of the electric double layer [16]. The polarized i, E curves were adjusted for residual current. All the potential data are given in volts with reference to a standard calomel electrode.

The dependence of the reduction rate of $S_2O_8^{2-}$ on the electrode potential was the same at the polycrystalline silver electrode, and at the faces of a monocrystal of silver (111) and (100) and of bismuth (111). Reduction began at potentials corresponding to a positive charge on the surface of the metal; then the current achieved the value of the limiting diffusion current, corresponding to the experimental rate of rotation of disk electrodes, and a reduction in current was observed at potentials lying in the region of the z.c.p. of the electrodes. After passage of the current through a minimum, the reaction velocity increased again, with an increase in the negative value of the potential (Fig. 1). The reaction velocity for reduction of the $S_2O_8^{2-}$ anion at all the electrodes increased with increasing concentration of the supporting electrolyte (Fig. 1), and with increasing radius of the cation of supporting electrolyte, during which removal of the retardation of the reaction of anion reduction was observed at lower concentrations of supporting electrolyte, the more negative the zero charge potential of the metal.

From the data for the dependence of the reaction velocity on the concentration of the cation of the supporting electrolyte, we calculated the charge on the reacting particle n_1 , using the relationship:

$$\left(\frac{\partial \ln i_k}{\partial \ln c} \right)_{E - \frac{RT}{n_2 F} \ln c} = - \frac{n_1}{n_2}, \quad (2)$$

where c is the cation concentration and n_2 is the charge on the cation of the supporting electrolyte [3, 17]. For the calculation of n_1 , the experimental currents i were corrected for concentration polarization, in accordance with the theory of concentration polarization under stationary conditions. We determined n_1 in 10^{-3} N $Na_2S_2O_8$ and 10^{-3} N $K_2S_2O_8$, in the presence of various concentrations of NaF and KF respectively. By fulfillment of the

condition: $E - (RT \ln c)/n_2 F = \text{constant}$, for all the electrodes, we observed a linear relation between $\log i_k$ and $\log c$, and calculated, from the slopes of the straight lines, values of n_1 close to the theoretical value. The values of the charge for $S_2O_8^{2-}$, over the range of potential -0.9 to -1.2 , varied from -1.7 to -2.0 , i.e., closer to the theoretical value than the negative potential with which n_1 was determined.

Analysis of the data obtained showed that the rate of reduction of the persulfate anion, at the electrodes investigated, was determined by the slowness of the electron transfer stage (1). In this case the rate of discharge of the anion increased with the change from metals with a less negative value of the z.c.p. to metals with a more negative z.c.p. [3-5, 7-13]. The data presented in Fig. 2 confirmed this deduction: The reduction rate of $S_2O_8^{2-}$ increased at all potentials, with the transfer from Ag(111) to Ag(100) and polycrystalline Ag, the zero charge potentials for which were, respectively, -0.74 , -0.89 , and -0.96 [18].

If we compared the discharge rates of $S_2O_8^{2-}$ at silver electrodes, with the corresponding discharge rates for other electrodes, then, with negative surface charges, the rates of reduction of the persulfate anion on silver electrodes were less than would be expected from the position of the z.c.p. of these metals. Thus the zero charge potentials for Ag(111) and Sn, and for Ag(100) and Pb, practically coincided, while the discharge rates of $S_2O_8^{2-}$, at all potentials at silver electrodes, were considerably less. A similar relationship would be expected for the special features of the structure of the electric double layer on the faces of a silver monocrystal. The comparison, given in [19], of the capacity of the dense layer of the various faces of a silver monocrystal with analogous data for other solid metals showed the sharper dependence of the capacity of the dense layer on the electrode potential. The sharper dependence of the capacity of the dense layer on the potential for the faces of a silver monocrystal led to the result that in some region of negative surface charges the values of the ψ_0 potentials, for Ag(111) for example, became more negative than the ψ_0 potentials of tin and bismuth (Fig. 3). In this region of potentials the rate of discharge of $S_2O_8^{2-}$ on Ag(111) would naturally be less than on these electrodes. The values of the ψ_0 potentials were calculated in terms of the Stern-Grahame theory, and the surface charges, necessary for the calculation, were found by numerical integration of the experimental curves relating the capacity to the potential in the corresponding solutions using the data of [16, 19, 20].

Using the calculated values of the ψ_0 potentials, we obtained the corrected Tafel relations (c.t.r.) (Fig. 4). It is evident that the c.t.r., for the reaction of reduction of $S_2O_8^{2-}$, at all the electrodes except for polycrystalline silver, fell on one straight line with a value of $\alpha = 0.23 \pm 0.02$. The coincidence of the c.t.r., on the various faces of a silver monocrystal, and on polycrystalline electrodes of Bi, Sn, Pb, and other metals [4, 5], indicated that the differences for the rates of discharge, both for the faces Ag(100) and Ag(111), and for other polycrystalline electrodes, were associated only with the corresponding differences in the structure of the double layers of these electrodes.

The distinctive (as opposed to other electrodes) character of the behavior of the c.t.r. for polycrystalline silver could be explained on the basis of [21]. Here it was shown that, if the z.c.p. of the separate faces of

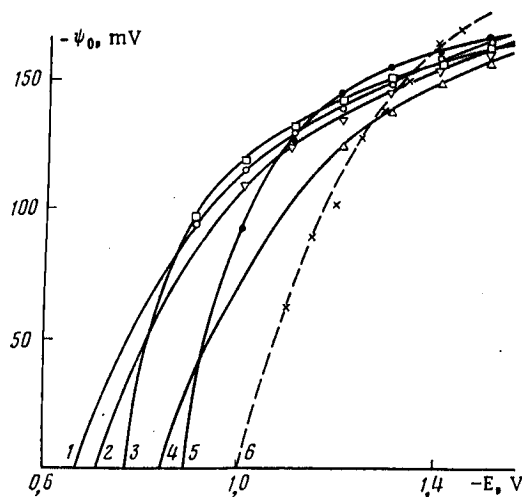


Fig. 3. Dependence of the ψ_0 potential on the electrode potential, in 10^{-2} N KF, at various electrodes: 1) Bi, 2) Sn, 3) Ag(111), 4) Pb, 5) Ag(100), and 6) Ag.

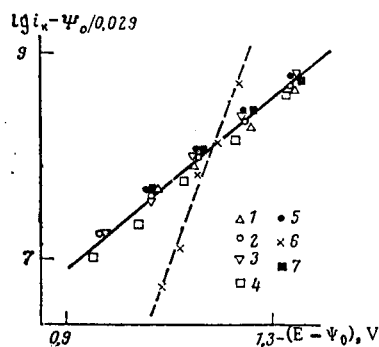


Fig. 4. Corrected Tafel dependences of the reduction of 10^{-3} N $K_2S_2O_8 + 9 \cdot 10^{-3}$ N KF electrodes: 1) Pb, 2) Bi, 3) Sn, 4) Ag(111), 5) Ag(100), 6) Ag, and 7) Bi(111).

a monocrystal of metal differed substantially between themselves, then the concept of "zero charge potential" for a polycrystalline electrode could be used for a fixed degree of approximation, although the capacity minimum on the C,E curves, in dilute solutions, did not correspond to zero surface charge. From this it followed that, for polycrystalline silver, it was impossible to calculate the charge, and hence the ψ_0 potential, from the curves relating differential capacity and potential. At the same time, for polycrystalline electrodes, for which the differences in the z.c.p. of the separate faces were small (bismuth, for example), the yield at the surface of the electrode face, with varying values of the zero charge potential, did not lead to the appearance of parts of the surface with sharply differing charge values, while the minimum, on the C,E curves of polycrystalline electrodes of this type, corresponded to the zero charge potential. In this case, the c.t.r. of the reaction of $S_2O_8^{2-}$ reduction, on polycrystalline bismuth and on monocrystals of bismuth (111), coincided.

The data obtained in this work were discussed with A. N. Frumkin, our teacher, in memory of whom this paper is dedicated.

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