

THE SELECTION OF ELECTRODE POTENTIAL DURING PREELECTROLYSIS AND THE SHAPE OF THE CALIBRATION CURVES IN THE STRIPPING VOLTAMMETRY OF METALS

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The appearance of double peaks on the anodic polarization curves of metals deposited onto an indifferent electrode and the shape of the calibration curves are governed by the conditions of metal deposition. When stripping voltammetry of metals is used in analysis, then the electrode potential during preelectrolysis must be set at a value sufficiently negative with respect to the minimum potential at which electrocrystallization of the metal is possible from a solution of given concentration.

The spread of work in the stripping voltammetry of metals has led to the discovery of a number of unexpected, delicate effects appearing on the anodic polarization curves in the form of multiple peaks of diverse shape [1, 2], and leading to a different character of the calibration curves [3-6]. Some authors [5] have concluded on this basis that solid electrodes, and in particular graphite electrodes, are limited in their use, or cannot be used in this area of electrochemical analysis. This is in contradiction with the huge amount of experimental data gathered up to now [3, 4, 7, 8].

The character of the polarization curves for the oxidation of metals deposited on the surface of a solid, indifferent electrode actually depends on the type of interaction existing between the metal and the support, and on the conditions of deposition [1, 2, 9]. For the latter reason one can use the polarograms of metal oxidation as a source of information about the initial stages of the electrocrystallization of metals on foreign supports [9]. An understand-

ing of these processes, and a reasoned choice of conditions for the electrochemical concentration of the metal on the electrode surface allow one to obtain the functional dependence of the metal's maximum oxidation current on the concentration of its ions in solution and on the duration of preelectrolysis of this solution.

We have demonstrated previously [9] that a correlation exists between the character of the anodic polarization curve and the dependence of the metal's critical deposition potential on the logarithm of concentration of its ions in solution (Fig. 1).

Polarization curves of the first type (electropositive peak) describe the electrooxidation of metal adatoms. Polarization curves of the third type (electronegative peak) are typical for the oxidation of the metal phase. The former we shall call adatom or adsorption peaks, the latter we shall call phase peaks. We shall introduce the idea of a phase potential (φ_{ph}), which is the minimum electrode potential at which metal ions can be discharged with attendant formation of the corresponding solid phase. Similarly to the critical potential [9], the phase potential is determined experimentally by extrapolating the plot of the quantity of metal corresponding to the phase peak against electrode potential in the deposition step.

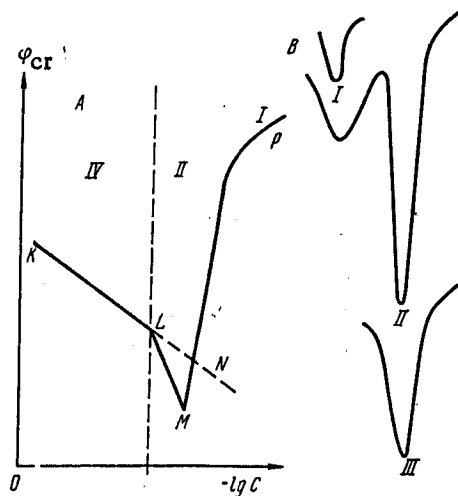


Fig. 1. Schematic presentation of the critical potential of the system: indifferent electrode-metal-metal ions in solution, as function of the logarithm of concentration of the metal ions in solution (A), and the corresponding polarization curves (B).

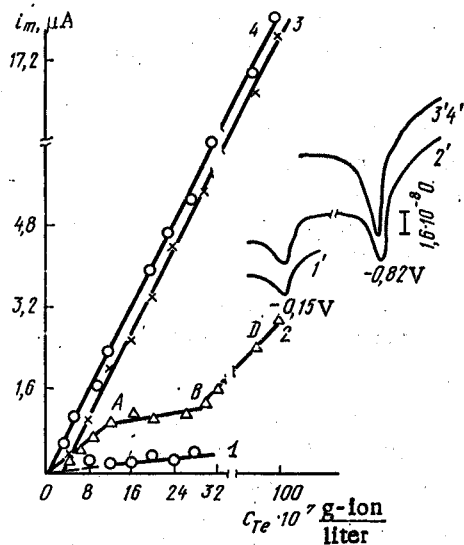


Fig. 2. The maximum oxidation current of thallium deposited on the surface of a graphite electrode, as function of the concentration of thallium ions on 0.05 N KNO_3 solution, and the corresponding polarization curves. 1) $\varphi_{\text{el}} = -0.76$ V; 2) $\Delta\varphi_{\text{ph}} = -0.04$ V; 3) $\Delta\varphi_{\text{ph}} \approx -0.05$ V, $\varphi_{\text{e}} = -1.086$ V; 4) $\Delta\varphi_{\text{ph}} \approx -0.25$ V, $\varphi_{\text{el}} = -1.28$ V.

Using as an example the system graphite electrode-thallium-thallium ions in solution, we shall discuss below the main features which are essential for analytical chemistry.

The investigations were performed on an OH-102 polarograph. The graphite working electrode was prepared by a 6-h vacuum impregnation with a 3:2 mixture of paraffin and polyethylene. The face of the electrode, which had an apparent surface area of 0.19 cm^2 , was cleaned with ground glass as an abrasive, and then brought to mirror-like smoothness with tracing cloth. After recording of the next polarization curve, the working surface of the electrode was cleaned by 3 min of anodic polarization at a potential of $+0.6$ V. A platinum electrode served as the auxiliary electrode and a calomel half-cell served as reference electrode. Stirring of the solution during electrolysis, and removal of dissolved oxygen from it were accomplished by a stream of type-A argon (pure).

All solutions were prepared with water that had been thrice distilled in quartz apparatus.

Polarization curves and the dependence of the maximum oxidation current of thallium on the concentration of its ions in 0.05 N potassium nitrate solution are reported in Fig. 2.

Electrolysis at potentials close to the critical (section NP of Fig. 1) is attended by the formation of adatoms. The polarization curves have the shape of curve 1', and the corresponding calibration curve is curve 1. A saturation region appears in some cases on this curve [9]. The oxidation current of the adatoms depends weakly on the metal ion concentration in solution, and even this only over a narrow range of concentrations; to use it in analytical chemistry can only be helpful in certain particular cases. Curve 2 describes the maximum electrodisolution current of thallium (the phase peak) as function of thallium ion concentration in solution. The solution was electrolyzed at a constant value of $\Delta\varphi_{\text{ph}} = \varphi_{\text{e}} - \varphi_{\text{ph}}$. Each solution concentration had its own electrolysis potential. Section AB of curve 2 corresponds to the polarization curve 2'. The phase peak practically does not grow over a certain concentration range, because a redistribution of currents takes place here. In one of the papers [5] this type of $I_{\text{m}}-C$ dependence has been explained by the metal being deposited in bulk states only, but this evidently does not correspond to reality. Under conditions which correspond to section BD of curve 1, a polarization curve with only the phase peak is observed. Its height is proportional to the thallium ion concentration in solution.

Polarization curves 3' correspond to the calibrating curve 3. They are obtained after electrolysis of the solution at an insufficiently large $\Delta\varphi_{\text{ph}} = \varphi_{\text{e}} - \varphi_{\text{ph}}$. Roizenblat et al. [6] have indicated that this type of $I_{\text{m}}-C$ dependence is more strongly developed when electrodes with a hydrophobic surface are used, rather than in the case where the electrodes have a hydrophilic surface (electrolysis being conducted at the same potential). This effect is

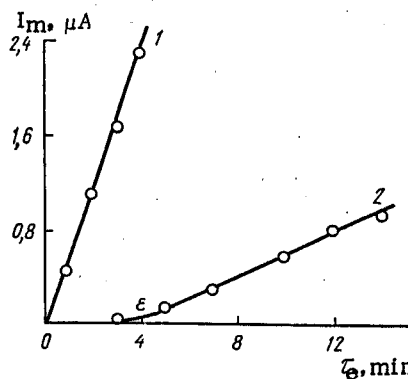


Fig. 3. The maximum oxidation current of thallium as a function of duration of the electrolysis in 0.5 N CH_3COOK solution; $\text{CTI}_+ = 1 \cdot 10^{-6}$ g-ion/liter; $\Delta\varphi_{\text{ph}} = -0.245$ V (1) or -0.045 V (2); and $\varphi_{\text{cr}} = -0.935$ V.

Along the section KLM, the phase potential coincides with the critical deposition potential of the metal, because only phase growth occurs in this case. Along the section MNP, the phase potential can be distinguished from the critical (it may be more negative), because the competing processes of adatom formation and phase growth are possible here.

readily explained by the higher crystallization overpotential on the hydrophobic surface. The value of φ_{ph} in this case is more negative than it is on the hydrophilic surface, and the corresponding $\Delta\varphi_{ph}$ value during electrolysis then is insufficient.

The calibrating curve 4 and the corresponding polarization curves 3' and 4' are observed when solution electrolysis is conducted at a sufficiently large value of $\Delta\varphi_{ph} = \varphi_e - \varphi_{ph}$, and under conditions of a diffusion-limited current of electroactive ions toward the electrode surface. Precisely these conditions must be selected when using the technique in analytical chemistry. Here one observes the theoretically predicted [3, 4], well-reproducible functional dependence of the maximum oxidation current on the concentration of solution ions being analyzed.

The method usually used in selecting the electrolysis potential according to the cathodic polarization curve is not always correct, because in this case the complex dependence of phase or critical potential of metal deposition on ion concentration in the solution is not taken into account.

The maximum oxidation current of metal (phase peak) is shown in Fig. 3 as function of the duration of solution electrolysis at large (curve 1) and small (curve 2) values of $\Delta\varphi_{ph}$. This corresponds to the calibration curves 4 and 2 of Fig. 2. Dependences similar to curve 2 of Fig. 3 have been observed by Perone and Kretlow [11] in the discharge-ionization of mercury, by Pnev et al. [10] in the discharge-ionization of copper, and by the present authors in the discharge-ionization of bismuth at the surface of graphite electrodes. It is shown here that the presence of a section OE on the $I_m - \tau_e$ curve, or the amount of metal that has been deposited on the electrode depending on the duration of electrolysis, is linked to the relaxation time of the crystalline nucleus.

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