

USE OF A COMPOSITE-PASTE ELECTRODE OF SMALL SURFACE AREA

(EXCHANGE OF EXPERIENCE)

Z. B. Rozhdestvenskaya, O. A. Songina,
I. Kh. Muldagalieva, and Ch. T. Mikheeva

In order to study the electrochemical behavior of metals and sulfides we previously [1-3] used a composite-paste electrode with a working surface of 0.3 cm^2 . Its anodic currents are several hundred micronampere. This can lead to deformation of the volt-ampere curves owing to the voltage drop over the ohmic resistance of the solution.

This report gives the results of experiments with a paste electrode of the same composition which has a considerably smaller surface: 0.03 cm^2 ("point" electrode). The electrode was tested with the anodic dissolution of copper and the cathodic reduction of cuprite as examples.

The volt-ampere curves were recorded on the polarograph LP-60. The potential scan rate was 0.2 V/min . All the potentials are given relative to the mercurous iodide reference electrode, $E = 0.029 \text{ V}$ (normal hydrogen electrode). A magnetic stirrer was used for mixing. The experiments were carried out at room temperature.

The paste was prepared by careful mixing of known quantities of the finely ground test materials and carbon; then α -bromonaphthalene was added, and the mixture was again carefully mixed in a weighing glass. Powdered carbon, calcined at 800°C and shifted on screens of -150 to $+250$ mesh, was used. The composition of the paste was: 1 g of carbon powder, a known quantity of the test material, and 0.5 ml α -bromonaphthalene.

Electrolytic copper of special purity (99.99) and monomineral cuprite, both powdered (-150 to $+250$ mesh), were used.

Figures 1 and 2 show the volt-ampere curves for the anodic dissolution of copper without and with thiourea in a base solution of sulfuric acid. The curves are well defined and have a steep slope in the section of active magnitude of the maximum current increases in proportion to the quantity of material in the paste, as when a conventional paste electrode is used under these conditions.

The curves lie in a narrower region of potentials than in the case where an electrode of larger surface is used. This guarantees the great selectivity of the method.

The point electrode can be especially useful in studying the anodic behavior of metals, since usually their oxidation currents are high. The paste electrode with a surface of 0.3 cm^2 is more promising in cases in which the oxidation currents of the test material are small, or the concentration of test material in the paste is low.

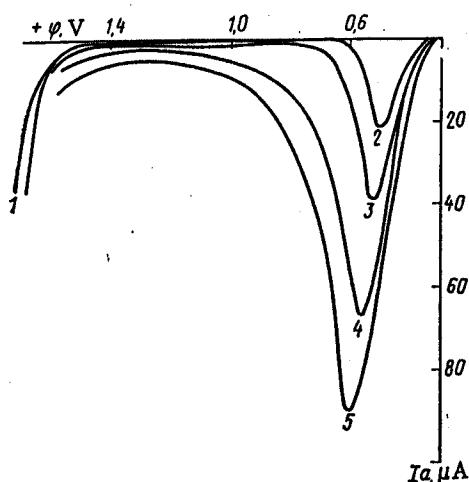


Fig. 1. Polarograms of the anodic dissolution of copper in a sulfuric acid medium. 1) Paste in a base solution of $1 \text{ H}_2\text{SO}_4$; copper content in the paste: 2) 5 mg; 3) 10 mg; 4) 15 mg; 5) 20 mg.

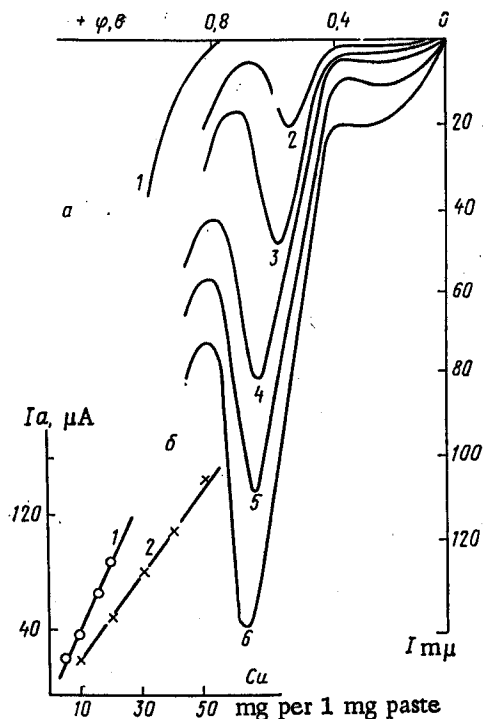


Fig. 2

Fig. 2. Polarograms for the anodic dissolution of copper in a sulfuric acid medium with $1 \cdot 10^{-2}$ M thiourea (a) [1] paste in a base solution of 1 M H_2SO_4 + $1 \cdot 10^{-2}$ M thiourea; copper content in the paste: 2) 10 mg; 3) 20 mg; 4) 30 mg; 5) 40 mg; 6) 50 mg], and the relationship between the maximum current and the quantity of copper in the paste in a sulfuric acid medium (b) [1] without thiourea; 2) with $1 \cdot 10^{-2}$ M thiourea].

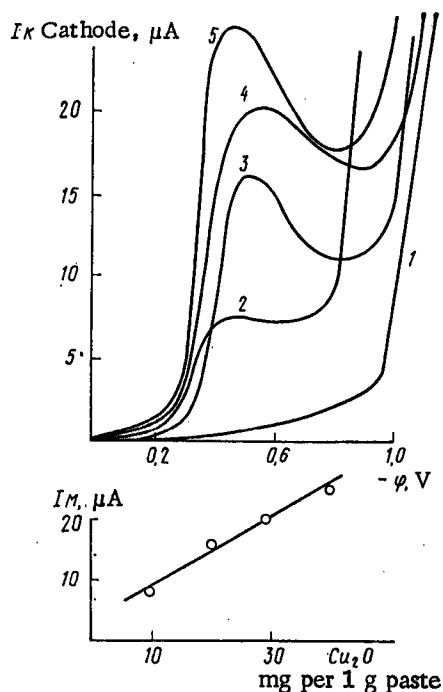


Fig. 3

Fig. 3. Polarograms for the cathodic reduction of cuprite in an ammonium chloride-ammonium medium, and the relationship between the limiting current and the cuprite content in the paste: 1) paste in a base solution of 1 M NH_4OH + NH_4Cl ; cuprite content in the paste: 2) 10 mg; 3) 20 mg; 4) 30 mg; 5) 40 mg.

Figure 3 shows the cathodic reduction of cuprite.

Well defined waves for the cathodic reduction of cuprite are obtained in a chloride-ammonia ammonium base solution. The limiting current is proportional to the quantity of cuprite in the paste.

Hence the electrode can also be used for cathodic processes.

By changing the solution composition with and without complex reagents, the electrode surface area and the cathodic and anodic polarization, it is evidently possible to come closer to a solution of the problem of separate electrochemical determination of free metals and their compounds with the carbon paste electrode.

LITERATURE CITED

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