PASTE ELECTRODE FOR THE DETERMINATION OF SILVER IN VARIOUS DEGREES OF OXIDATION

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Methods of electrochemical analysis in which polarization curves for electrochemical changes of metals or poorly soluble compounds localized at the electrode surface are used as a source of information are well known [1-3]. Ruby and Tremmel, and also Songina, Barikov, and Rozhdestvenskaya [4-6] proposed a new method for the introduction of the electrochemically active substance into the sphere of the electrode reaction. For this purpose they used a carbon paste electrode containing the investigated solid substance. It seems to us expedient to define this variant of electrochemical analysis as volume inversion voltamperometry.

The purpose of the present work was to investigate further the possibilities of using this method for the analysis of silver in various degrees of oxidation. The choice of subject for investigation was based on the use of silver oxides in current sources. The possibility in principle of determining compounds of various degrees of oxidation separately was investigated, and a procedure for work with the paste electrode was carefully worked out.

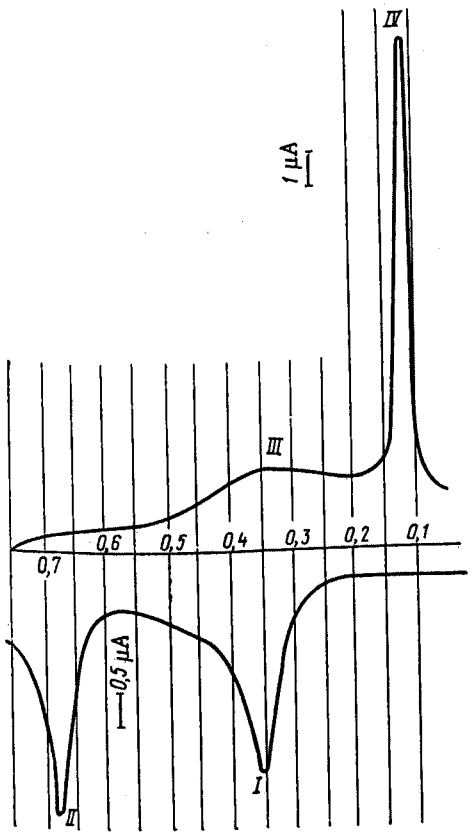

Fig. 1. Polarization curves for the oxidation and reduction of the metallic silver electrode.

A P-5827 potentiostat was used with a linear potential sweep, and the polarization curves were recorded by a low resistance KSP-4 potentiometer. The reference and auxiliary electrodes were silver chloride electrodes. The measurements were made in air, since a special cycle of measurements in a closed cell with prolonged saturation with pure argon gave the same results as measurements in an open cell. The electrolytes were 0.1 N and 1 N solutions of potassium hydroxide.

The oxidation of silver and the reduction of its oxides in 0.1 N potassium hydroxide solution of chemical purity were previously investigated by means of a metallic silver face electrode. The diameter of the electrode was 1 mm, and its sides were insulated with polyethylene. The curves were recorded from initial potentials of φ_0 = 0 V (oxidation) and φ_0 = +1 V (reduction) with a linear sweep rate of 0.2 V/min. Here and subsequently the potentials are referred to the silver chloride electrode.

In Fig. 1 peaks I-II correspond to the oxidation reactions $Ag \rightarrow Ag_2O$ and $Ag_2O \rightarrow AgO$, and the peaks III-IV clearly describe the reduction of the silver oxides $AgO \rightarrow Ag_2O$ and $Ag_2O \rightarrow Ag$. A large number of researches have been devoted to the mechanism of these processes, but opinions differ as to the composition and structure of the higher silver oxide [7, 8]. The formula AgO is used conditionally in the present work.

From Fig. 1 it is seen that the difference in the potentials for the oxidation $Ag_2O \rightarrow AgO$ and the reduction $AgO \rightarrow Ag_2O$ amounts to ~ 0.33 V. The difference in the potentials at which

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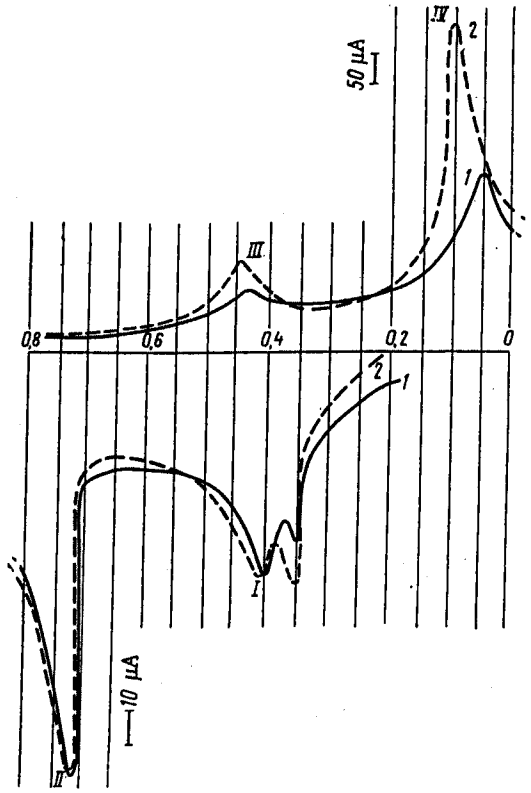

Fig. 2. Polarization curves for the oxidation and reduction of silver oxides on the paste electrode: 1) 0.1 g AgO, 0.9 g carbon, 0.3 ml dibutyl phthalate; 2) 0.1 g Ag_2O, 0.9 g carbon, 0.3 ml dibutyl phthalate.

TABLE 1. Effect of Grain Size on the Maximum Oxidation Current

Investigated process	d of grain, μ	I_{max}, μA
$Ag_2O \rightarrow AgO$	≤125	43
$Ag_2O \rightarrow AgO$	≤74	124

TABLE 2. Comparison of the Reproducibility of the Results as a Function of the Nature of the Mixing of the Components

Form of mixing	Electrode reaction	Mean current, μA	Number of determinations	Variation coefficient, %
Stirring for 30 min	$Ag \rightarrow Ag_2O$	29	11	45
Passing through sieve:	$Ag_2O \rightarrow Ag$			
10 times		333	12	46
15 times		235	12	41
20 times		325	10	27
Stirring in acetone	$Ag_2O \rightarrow AgO$	59	60	10
	$AgO \rightarrow Ag_2O$	125	70	14

the reductions $AgO \rightarrow Ag_2O$ and $Ag_2O \rightarrow Ag$ occur amounts to 0.23 V. Between the oxidation processes $Ag \rightarrow Ag_2O$ and $Ag_2O \rightarrow AgO$ there is a difference in potential of 0.32 V. Thus, all these processes are fairly well separated.

If the substances in the paste electrode behave similarly, the above reactions can be used to identify the respective silver oxides. To vetify this suggestion oxidation and reduction curves were recorded on a carbon paste electrode containing 10% of Ag_2O or AgO on the weight of powdered carbon. Reagent argentous oxide was used, and the argentic oxide was synthesized by the oxidation of freshly precipitated argentous oxide with potassium persulfate in alkaline medium. According to iodometric analysis it contained 99.9% of the principal compound.

The measurements were made under the same conditions as those on metallic silver. The results are presented in Fig. 2. Comparison shows that there is substantially no difference between Figs. 1 and 2. The data confirm that it is possible to determine the higher oxide AgO in the presence of Ag_2O by means of the reduction current of the higher oxide recorded at potentials between 0.40 and 0.55 V. Here the oxide Ag_2O does not participate in the electrode process, since the $Ag_2O \rightarrow AgO$ reaction takes place in the region of more positive potentials and the $Ag_2O \rightarrow Ag$ reaction is only possible at more negative potentials.

The lower oxide Ag_2O not containing silver with higher degrees of oxidation can be determined by means of the current for the reduction of Ag_2O to metal, which is observed at potentials between 0.15 and 0.02 V.

The lower oxide can be determined in the presence of the higher oxide by means of the current for the oxidation of Ag_2O, recorded at potentials between 0.65 and 0.80 V. Figure 3 shows the polarization curves for the oxidation of the paste. The oxidation of Ag_2O can be readily recorded both in the case of pure argentous oxide and in the presence of the higher silver oxide. The latter does not undergo electrochemical changes in the indicated range of potentials.

The method used for the preparation of the electrode has a significant effect on the reproducibility of the results. In the present work all the elements involved in the method were specially investigated.

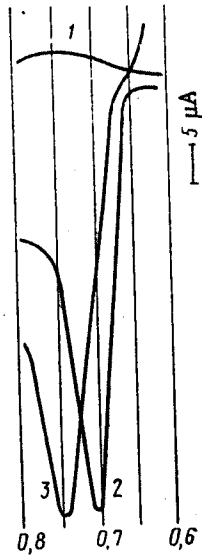

Fig. 3. Polarization curves for oxidation at the paste electrode (initial oxidation potential, 0.62 V): 1) and 2) the same as in Fig. 2; 3) 0.1 g AgO, 0.1 g Ag_2O, 0.8 g carbon, 0.3 ml dibutyl phthalate.

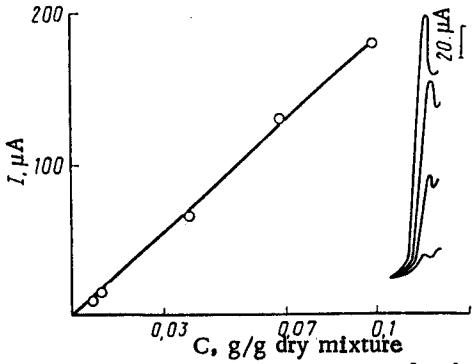

Fig. 4. The dependence of the currents for the reduction of AgO at the paste on the concentration (potential sweep rate, 4 V/min; initial reduction potential, 0.5 V).

TABLE 3. Reproducibility of the Results as a Function of Length of Storage of the Paste (Ag_2O → AgO electrode reaction)

Time from addition of liquid to paste, h	Current, μA	Number of tests	Variation coefficients, %
Immediately after addition of dibutyl phthalate	482	11	36
3	641	9	17
48	620	10	16

Spectroscopically pure graphite of grade V-3 was used for the preparation of the paste. An electrode of the design described in [5] but with a much smaller working surface (d = 1.5 mm) was used. This secured more rigid conditions for the assignment of the potential. An electrode from a new portion of paste was used for the measurement.

The effect of the particle size of the paste components on the magnitude of the current is illustrated by the data in Table 1. The concentration of the oxides in the paste amounted to 0.1 g per gram of dry mixture. The particle size fractions were obtained by sieving through one sieve of the indicated size. The oxidation current increases with decrease in the grain size.

The dependence of the reproducibility of the results on the conditions used for mixing the components of the paste is seen from Table 2. Three methods of mixing were employed: 1) The usual mechanical stirring of the dry powders for 30 min; 2) repeated sieving of the mixed powders through a sieve; 3) mechanical stirring of a suspension of the powders in special-purity acetone, followed by drying. The reproducibility of the results obtained with one batch of paste was compared.

Stirring the suspension in the liquid phase gave a significant and consistent gain in the reproducibility of the results. In addition to those described in the literature α-bromonaphthalene, decalin, and dibutyl phthalate were used as binding liquids. Dibutyl phthalate was the most inert in respect of the investigated silver compounds and the least volatile. The oxidation and reduction currents of the silver oxides were clearly defined in the presence of dibutyl phthalate. The optimum amount of the liquid was 0.3-0.5 ml per gram of powder. In the presence of a large quantity of organic substance the electrical conductivity of the paste decreased and the sensitivity of the determination was lower. A deficiency of the liquid made the paste friable. Small fluctuations in the amount of liquid in the paste led to poorer reproducibility.

The effect of the storage of the paste on the reproducibility is shown in Table 3. It is clear that, after the addition of the dibutyl phthalate to the paste, some time is required for the establishment of equilibrium between the liquid and the powder. The sample was stored in a weighing bottle with a ground-glass stopper.

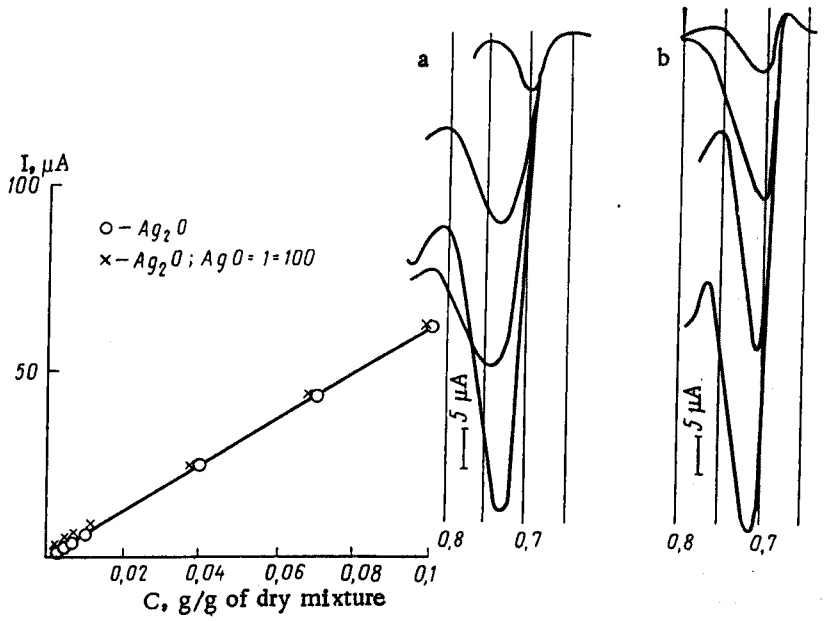

Fig. 5. Dependence of the currents for oxidation of Ag_2O at the paste on concentration (potential sweep rate, 0.2 V/min; initial oxidation potential, 0.62 V): a) Ag_2O; b) Ag_2O + AgO.

The following procedure was selected on the basis of the investigation. The graphite and silver oxides are sieved separately through a sieve with openings of 74 μ. The materials are stored and used in this form. To prepare the paste, weighed quantities of the components are stirred mechanically in acetone, and the mixture is dried until the acetone has completely evaporated. A 0.3-0.5-ml portion of dibutyl phthalate is added to the dry mass for each gram of the dry mixture, and the mixture is stirred. The obtained paste is placed in the electrode 3 h after preparation. This method ensured sufficiently high sensitivity and reproducibility in the polarization measurements.

The polarization curves for the reduction of the oxide AgO and the corresponding calibration curve are presented in Fig. 4. A proportional relationship is observed between the maximum cathodic current and the concentration of oxide in the paste. The reproducibility is entirely satisfactory. The variation coefficient amounts to 14.8% for n = 70.

Figure 5 shows the anodic polarization curves for Ag_2O and the calibration curves obtained for pure argentous oxide and Ag_2O + AgO mixtures containing various amounts of the lower oxide. The oxidation currents are clearly defined, and the calibration curves are linear and agree. The reproducibility of the determinations is satisfactory. The variation coefficient amounts to 11.3% for n = 40. Thus, the method makes it possible to determine both the individual silver oxides and their mixtures in the solid phase without dissolving the sample.

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