ULTRAMICROSCOPIC INVESTIGATION OF THE ELECTROLYSIS OF SOLUTIONS OF SILVER NITRATE

M. N. Polukarpov

Physical Chemistry Laboratory of the Molotov State University

Considerable attention has been devoted to the problem of the electrocrystallization of metals in electrochemical literature; this may be explained by the fact that the reason for the obtaining of one quality of metal or another is usually considered to be the electrolysis conditions, on which the final stage of the cathode process largely depends -- the crystallization of the metal from its atoms formed as the ions are discharged.

In particular, many of the papers in this field deal with the electrocrystallization of silver during the electrolysis of solutions of its salts.

Among the earliest of such papers are the rather extensive researches of Kohlschutter [1]. In his papers, containing experimental confirmation, the author points out the feasibility of the formation of colloidal systems during electrolysis and, examining colloidal solutions of silver, considers them to be an intermediate phase of the separation of silver at the cathode.

The constitution of colloidal systems during the electrolysis of silver-nitrate solutions had also been observed by other researchers. Thus, Kosonogov [2], observing the electrolysis of N/100 solutions under the ultramicroscope, discovered the formation of numerous mobile particles in the layer of the electrolyte near the cathode. To judge from the author's description of what he had seen, it may be concluded that what he observed was the formation of colloidal systems during electrolysis, though the author himself came to no such conclusion.

Systems of this sort were likewise obtained by Vozvizhensky [3]during the electrolysis of silver nitrate solutions; he called them thin suspensions, though in another paper [4] reporting on observations of the electrolysis of these solutions under the ultramicroscope, he speaks of observing vigorous Brownian movement of the particles formed.

Pavlov [5]and Zaprometov [6] likewise speak of the formation of colloidal systems in the electrolysis of silver-nitrate solutions. Thus, there apparently can be no doubt of the formation of colloidal systems in the electrolysis of silver-nitrate solutions. But it must be remembered that the problem of whether colloidal particles are formed at the cathode under all conditions of electrolysis or only under some conditions, andif so, under what conditions, is not entirely clear.

Another question, of fundamental importance but still moot, is the nature of the colloidal particles formed during electrolysis.

In his research, Vozdvizhensky endeavored to establish the nature of these particles experimentally, coming to the conclusion that in the electrolysis of silver-nitrate solutions what are formed are thin suspensions of silver hydroxide, rather than colloidal metal. The author based his conclusions upon the observed dissolution of the ''suspended matter'' when it came in contact with anode products and when more acid was added, as well as upon the ultramicroscopic picture observed by him in the electrolysis of acid solutions and the external analogy of the phenomena observed during electrolysis with what occurs when an alkaline solution is added to solutions of silver nitrate.

If the research methods employed by the author are borne in mind, the conclusions he drew on the basis of these three arguments is open to question.

The author performed his experiments under conditions that did not exclude the access of air and the liberation of oxygen at the platinum anodes; but it is known that silver is not stable under the action of acid solutions, including those of organic acids, when oxygen is allowed to have access to the metal [7]. All the more is this so in the case of colloidal silver, when it is in the state of a high degree of disintegration.

Some doubt is also aroused by the author's extremely brief periods of ultramicroscopic observation (1 to 20 seconds).

The analogy mentioned can hardly serve as an indication of the correctness of the conclusion made by the author.

What is of fundamental importance, but has not been elucidated experimentally in the literature, is the question of the fate of the colloidal particles formed during electrolysis, and more particularly, the question of whether the colloidal particles take a direct part in building up the cathode deposit.

We established the existence of such a phenomenon -- the participation of the colloidal particles formed during electrolysis in building up the deposit of metal on the cathode -- visually [8], in our investigations of the electrolysis of copper-sulfate solutions under the ultramicroscope.

The object of the researches listed below was to arrive at a solution of the indicated questions on the basis of the results of the research.

EXPERIMENTAL

The instrument used in our research was an ultramicroscope. The method of research was analogous to that employed by us earlier [8]. The electrodes were made of silver wire 1.0 mm in diameter.

The use of silver electrodes involved a considerable advantage over that of platinum ones, since it enabled us to carry out the electrolysis without liberating oxygen at the anode, afforded an adequate guarantee against changes in the composition of the electrolyte, and eliminated a cathode that was not identical with the metal separated at it. The electrodes were placed 5 mm apart in the electrolytic cell (chamber). The surface of the electrode traversed by the current was 25-30

sq. mm. All observations were carried out at a temperature of 18-20°. Silver nitrate solutions ranging from N/10,000 to N/10 were used in the experiments.

At first, the ultramicroscopic observations were made with solutions prepared in dark-red light in quartz vessels, using distilled water, which had been distilled in quartz apparatus and collected in a quartz receiver. Solutions prepared in this manner proved to be optically inactive media.

It was subsequently found that solutions made under electric light, in glass vessels, with ordinary, freshly distilled water that was not exposed to daylight, also proved to be adequately optically inactive media; under identical conditions, the observed results of the electrolysis of these solutions did not differ from the observed results of the electrolysis of solutions prepared with the precautions stated above. For that reason, many of the observations whose results are listed below were made with such solutions, which were employed in the experiments immediately after being prepared.

Two series of tests were made. One series was made with pure solutions of silver nitrate. In the other series of tests the same solutions were used with the addition of acids, chiefly nitric acid.

Test Results

The ultramicroscopic picture was sufficiently uniform in the electrolysis of neutral solutions of all the concentrations listed above, up to bath voltages of 0.9 - 1.1 volts.

The uninterrupted formation of colloidal particles about the cathode was established visually. They increased in quantity as the current rose and as the solution concentration diminished. Depending on these electrolysis conditions, the number of particles that made their appearance at the cathode per second ranged from $4 \cdot 10^3$ to $60 \cdot 10^3$ per sq mm of the colloid-producing zone.

The particles appearing in the cathode zone immediately left the point where they appeared, moving toward the anode, and just before they reached the latter's surface, they vanished from the field of sight. No movement of particles from the anode to the cathode was observed.

When the bath voltage reached 0.9 - 1.1 volts, the ultra-microscopic picture changed fundamentally. An extremely large number of particles, as high as six to seven hundred thousand per sq mm, is formed about the cathode, in the surrounding electrolyte zone.

In the electrolysis of the most dilute solutions N/10,000 - N/2500 the colloid particles in the form of a layer begin to move away from the cathode surface immediately after their formation, first from the section closest to the anode, but later from all the cathode surface. After moving away to a distance of approximately 0.08 - 0.02 mm, the layer of colloidal particles uniformly surrounds the cathode in a solid ring about 0.15 - 0.20 mm thick, which remains fairly constant during the further course of electrolysis. In the space between the cathode surface and the inner edge of the ring we did not observe the formation of any colloidal particles, and this space was an optically inactive medium, but in the layer itself new particles are formed rather intensively, although the increase in their number could not be observed owing to the fact that the particles bend around the cathode and

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make their way along its surface to the region that is closest to the anode. At this point the layer of colloidal particles is drawn out into a stream that interruptedly moves toward the anode.

Thus, all the particles formed at the cathode gradually leave the cathode area for the anode, where they vanish from the field of sight. No deposit on the cathode noticeable with the microscope was observed.

This ultramicroscopic picture is shown in Photo 1, in which the following items under illumination are shown: part of the cathode surface that faces the anode; underneath it a part of the colloid layer surrounding the cathode and flowing into the general stream of particles moving toward the anode. The photograph of the cathode area was made during the electrolysis of a 3N/10,000 solution of $AgNO_3$ at a voltage of 1.1 volt and a current of 0.04 ma two minutes after the appearance of the particle layer.

In the electrolysis of solutions of $AgNO_3$ in concentrations ranging from 0.0005 N to 0.002 N, the outstanding feature of the phenomenon observed under the ultramicroscope is the fact that the layer of colloidal particles does not leave the cathode surface at once but remains in its vicinity for some time. The length of time that the layer of particles remains in contact with the surface of the cathode depends on the concentration of the solution, increasing as the latter increases.

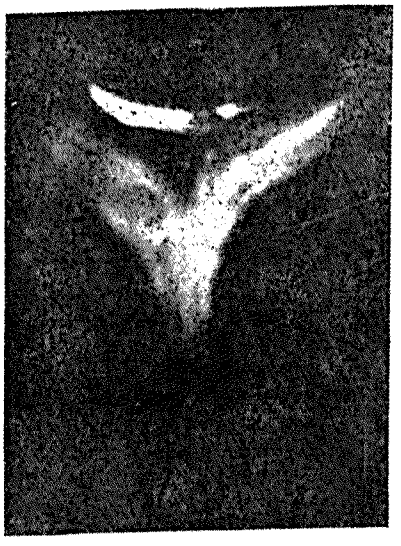

Photo 1.

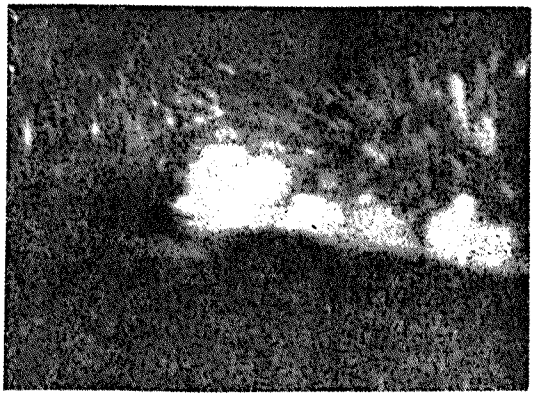

Photo 2

During the time that the layer is in direct contact with the cathode some of the colloidal particles that are closest to the cathode move toward it and are adsorbed at its surface, forming a deposit in the form of thin filaments. The higher the solution concentration, the larger the percentage of these latter colloidal particles. The rest of the particles moves toward the anode. Upon the expiration of the indicated time during which the particle layer is in direct contact with the cathode surface, the layer is observed to move away, and the nature of the phenomenon under observation becomes analogous to that taking place during the electrolysis of more dilute solutions. If the solution in the cell is agitated by moving the cathode, the picture observed under the microscope takes on its original character. The same thing happens if the circuit is broken after some time has elapsed, and then

electrolysis is resumed.

In the electrolysis of solutions containing 0.003 and more gram equivalents of $AgNO_3$ per liter, the layer of colloidal particles formed does not leave the cathode surface throughout the experiment, which usually lasted at least one hour. In this case, the clearly apparent change in the quality of the colloidal systems produced must be added to the distinctive features of the observed phenomenon that depend upon the concentration of the solution. In the electrolysis of 0.003 N solutions the layer of colloidal particles formed is easy to observe, owing to the thickness it attains, some 0.15 to 0.20 mm. The colloidal particles are easy to see, apparently being of fairly large dimensions. Aggregates are often present, in the form of short thin filaments, evidently consisting of a few individual particles. The particles exhibit low mobility. As the concentration of the solution is increased, the width of the layer diminishes. The size of the colloidal particles likewise decreases, as may be judged by the increasing difficulty of observing them. Their mobility increases. In 0.05 N solutions the particle layer formed is no more than 0.075 mm thick. In it the colloidal particles are quite mobile and rather hard to follow. In the electrolysis of 0.1 N solutions we succeeded in observing the extremely thin, scintillating layer of particles only after illuminating the object quite intensively and with a magnification of no less than 400.

Quite characteristic, and varying with the solution concentration, is the observed picture of the colloidal particles participating directly in building up the metal deposit on the cathode. The participation of the colloidal particles in building the deposit is observed extremely well in the electrolysis of 0.003 - 0.005 N solutions.

This building up of a deposit on the cathode begins with the adsorption of a certain quantity of colloidal particles on the latter's surface. These particles a are joined by new ones so that within a fairly short interval of time quite thin, rather long filaments are arranged on the cathode's surface and perpendicular to the latter. New colloidal particles, which are similarly growth centers for filaments in new directions, attach themselves to the sides of these filaments -- both those already formed as well as during their formation. Thus, at the beginning the deposit looks like a herringbone, with its base at the cathode surface. Subsequently, the lateral filaments felt together as they continue to grow, forming all in all a quite flocculent layer of silver. As electrolysis continues, many new colloidal particles are formed, which constitute the material for further building up of the deposit, their filaments running in all directions.

Photo 2 shows the general nature of the phenomenon observed -- the flow of particles toward the cathode and their participation in constructing the deposit. The picture was obtained by photographing the tip of the electrode and the electrolyte zone in the vicinity of the cathode during the electrolysis of a 0.005 N solution of $AgNO_3$ with a 0.25 ma current, 3 minutes 20 seconds after the commencement of electrolysis. As the solution concentration is increased the velocity with which the particles travel to the cathode is observed to rise considerably. Owing to this latter circumstance it becomes more andmore difficult to make an accurate count of the total of the colloidal particles arising in the cathode area and to determine the percentage of particles moving toward the electrodes.

When 0.01 N solutions are electrolyzed, an approximate count is still feasible; it indicates that not less than 90% of the particles go to build up the deposit. At higher concentrations not even an approximate calculation is possible, as the time elapsing between the instant the particles appear and their deposition on the

cathode is measurable in fractions of a second. For the same reason, under such electrolysis conditions adsorption on the cathode's surface can be followed visually for only a few individual particles, despite the undoubted fact of a large aggregate total of colloidal particles formed in the colloid producing zone. As the solution concentration is increased, the density of packing of the particles in the silver deposit formed on the cathode increases, the thickness of the filaments increasing and their length diminishing. Thus, they begin to look like needles, growing shorter and shorter and finally taking on the appearance of crystals scattered over the surface of the cathode when 0.1 N solutions are electrolyzed.

As may be seen from the data listed in the table, the appearance of the layer of colloidal particles in the electrolyte zone adjacent to the cathode is observed at about the same voltage but at current values (densities) that increase as the solution concentration is increased. It may be noted that the voltage does not play as much of a role as the current density. By attaching to the cell an auxiliary vessel filled with the same solution as that in the cell, we were able to move the anode farther away while leaving the cathode in the cell, thus being able to raise the voltage across the whole electrolytic cell to 2-3 times its value. Observations showed that when this was done the layer of particles appeared at about the same current values (densities).

Concentration of $AgNO_3$	Cell voltage (volts)	current (ma)	Cathode current density (amp/cm^2)*	Time that particle layer remains at cathode (sec)	Particles moving to anode (%)	Brief summary of phenomena observed under microscope
0.0001	1.10	0.02	0.08	0	100	Formation of layer of colloidal particles in cathode zone of electrolyte, which immediately move away from cathode surface. All particles move to anode.
0.0002	1.10	0.03	0.12	0	100	
0.0003	1.05	0.04	0.16	0	100	
0.0005	1.05	0.06	0.24	0	100	
0.0005	1.00	0.08	0.32	5 – 8	100	Layer of colloidal particles formed remains at cathode surface for some time. During this time some of the particles participate in building up cathode deposit. Later, layer moves away from cathode, and all particles move toward anode. Percentage so doing shown at instant of departure of layer from cathode.
0.0007	1.00	0.12	0.48	10 – 15	100	
0.001	1.05	0.12	0.48	40 – 50	100	
0.002	1.00	0.14	0.56	120 – 140	100	
0.003	1.00	0.16	0.64	throughout experiment	20 –30	Particle layer formed is in contact with cathode throughout experiment. Large part of particles contribute to building cathode deposit.
0.005	1.00	0.20	0.80		20 – 25	
0.01	0.95	0.48	1.92		10	
0.025	1.00	1.2	4.80			
0.005	0.95	1.8	7.20			
0.1	0.90	3.4	13.60			

The principal features of our foregoing exposition have been listed in the table given above. The currents listed (for constant polarized cathode surface) are the minimum values and most favorable for observation of the foregoing phenomena. Increasing the current within moderate limits (2-3 times) after the layer of colloidal particles has been formed in the cathode zone of the electrolyte does not affect the general character of the phenomena described above, merely making them occur more intensively.

Investigation under the ultramicroscope of the electrolysis of $AgNO_3$ solutions to which nitric acid has been added established the fact that the general nature of the phenomena observed remained unchanged on the whole. The addition of HNO_3 chiefly produces an effect analogous to that caused by increasing the concentration of silver nitrate. Thus, when N/1000 solutions of $AgNO_3$ that are also N/1000 with respect to HNO_3 are electrolyzed, the picture seen under the microscope corresponds on the whole to that observed when pure N/500 solutions of $AgNO_3$ are electrolyzed.

The effect of adding nitric acid is somewhat greater when more highly concentrated solutions are electrolyzed. For instance, when solutions are electrolyzed that are N/100 with respect to both $AgNO_3$ and HNO_3, the nature of the phenomena observed resembles the electrolysis of N/20 solutions of $AgNO_3$ more than it does that of N/50 solutions.

The electrolysis of silver-nitrate solutions containing 0.2-0.3 g of silver per 150 ml with the addition of 1 - 2 ml of nitric acid (sp. gr. 1.4) and 5 ml of alcohol, i.e., the solutions recommended by Kuster and Steinwehr [9] as the compositions most suitable for gravimetric analysis, were also subjected to ultramicroscopic investigation. When these solutions were examined under the ultramicroscope, they did not constitute optically inactive media even when placed in the cell right after they had been prepared. Moreover, even before the circuit was closed we observed the intensive formation of colloidal particles, which moved chiefly toward the sides of the cell, from which the colloidal particles spread as dense clouds throughout the solution in the cell. When the circuit was closed, all the colloidal particles moved toward the anode. A considerable number of them, formed along the cell walls behind the cathode, moved toward the anode and in passing through cathode zone of the electrolyte turned to the cathode surface with considerable velocity; they were adsorbed at the latter's surface and contributed directly to building up the cathode deposit. This phenomenon is observed no matter what current value is used in electrolysis. At currents of 1.2 - 2 ma a layer is formed in the cathode zone of the electrolyte that consists of numerous colloidal particles as a result of the course of the cathode process itself. Almost all these particles serve as material for building up the cathode deposit.

Besides acid solutions, containing nitric acid, solutions containing sulfuric, acetic, and boric acids were also subjected to electrolysis under the ultramicroscope. The results of these tests indicated that the effect of sulfuric acid upon the general character of the phenomena observed was like that of nitric acid. Acetic acid had but little effect, whereas no effect at all was observed upon the addition of boric acid.

To eliminate all doubt concerning the absence of photochemical action of the light rays used for illumination (an electric arc with carbon electrodes), control tests were run in which pure solutions of $AgNO_3$ were illuminated for long periods in the cell with the circuit open. The absence of any observable formation of colloidal particles during these tests indicated the groundlessness of the doubts mentioned.

In conclusion, it may be stated that when all the conditions of electrolysis are held constant, all the phenomena described above are easily repeatable.

Evaluation of the Research results

In most of our experiments the carrying out of electrolysis at comparatively low current densities, without the evolution of gaseous products at the electrodes and with adequate isolation of the solution in the cell against the access of air made possible observation over prolonged periods of time and study of the phenomena attentively. Analysis of these phenomena enabled us to explain them and reach definite conclusions.

The identity of the ultramicroscopic pictures observed in the electrolysis of pure solutions of silver nitrate and of acid solutions of the same, even those containing alcohol (which is added, as we know, to the electrolyte, to prevent the possible formation of silver oxides), affords us sufficient justification for asserting that the colloidal systems, consisting of particles of colloidal silver, formed during electrolysis constitute a dispersed phase. The different directions taken by the individual particles moving toward the electrodes might give rise to some doubt as to the identical nature of the colloidal particles.

These doubts are likewise groundless. The modern theory of electrolyte solutions, and the doctrine of surface ion layers of colloidal particles based upon it make it possible to explain the phenomena observed under the ultramicroscope, at least qualitatively; this explanation also covers the differences in direction taken by the moving colloidal particles despite their identical nature.

The initial stage of the origin of colloidal silver particles is their formation as nuclei, which under favorable circumstances may assume the dimensions of ultramicrons.

In the electrolysis of highly diluted solutions of silver nitrate, the region of the electrolyte near the cathode is soon impoverished in silver ions, even at low current densities. The possibility that nuclei will be formed does not disappear, but the conditions for their growth are unfavorable. Under the ultramicroscope we see an optically empty space surrounding the cathode.

In principle, nuclei may be distinguished from the other colloidal particles solely by their dimensions; otherwise they possess the same properties, i.e., they bear a negative charge like the particles of colloidal silver. This charge forces them to move toward the anode, attaining the zone of the solution that is richer in positively charged ions and thus facilitates the aggregation of the nuclei to the dimensions of ultramicrons.

Under the ultramicroscope we observe a colloid-producing zone located at some distance from the cathode, in which visible colloidal particles continually appear. We observe the continuing process of the aggregation of a few colloidal particles to form larger ones. Fully formed, negatively charged, colloidal particles may be likened in principle to anions in the sense that, like the latter, they are surrounded by an ionic atmosphere, consisting mainly of positively charged ions. Owing to the adequate distance of the particles from the cathode and their low velocity, the ion atmosphere surrounding them suffers no serious deformation and hence does not deprive the particles of the possibility of moving toward the anode; this is observed under the ultramicroscope with regard to all the particles that make their appearance in colloid-producing zone. As the concentration of positively charged

ions is raised, their sparseness in the area about the cathode will not make itself felt so sharply, and, naturally, the colloid-producing zone must move ever closer to the cathode's surface. Under suitable conditons the layer of colloidal particles formed therein may be in almost direct contact with the cathode surface. In this case, the ionic atmosphere around the particles that are close to the cathode will suffer serious deformation of spherical symmetry, owing to the cathode's electrostatic attraction. This inevitably gives rise to vigorous action of relaxation and electrophoretic forces, drawing the colloidal particles to the cathode and constraining them to adsorb to it.

In this deformation, i.e., in the displacement of positive and negative charges in opposite directions, the entire complex constituted by the colloidal particle and its surrounding ionic atmosphere acquires polarity. The degree of polarity must grow as the ion concentration in the solution rises, and with it the action of the forces mentioned above likewise increases, compelling the colloidal particles to move toward the cathode more energetically. The correctness of this notion of the cause of differences in the particles' directions of motion toward the electrodes is confirmed by the entirely analogous ultramicroscopic picture observed when direct current is passed through a solution of colloidal sulfur or a solution of sulfuric acid (in which a solution of colloidal sulfur is likewise formed in the cathode area, and the concentration of hydrogen ions in these solutions is changed by the addition of sulfuric acid. The nature of the dispersed phase, its negative charge, and the impossibility of overcharge in the given case can arouse no doubt.

The observed ultramicroscopic picture of the direct participation of the colloidal particles in building up the deposit on the cathode is quite characteristic of the course of electrolysis of fairly dilute solutions. What has been set forth above, and the careful analysis of the research results justify the assumption that the phenomenon dealt with also exist in the electrolysis of more highly concentrated solutions. The absence of adequate visual confirmation of this is, apparently, due solely to the unfavorable observation conditions arising from the extremely short distance from the cathode of extremely small particles, which are polarized within brief intervals of time and are adsorbed at the cathode.

Nor are the current values (densities) listed in the table at which the ultramicroscope picture makes its appearance a necessary condition for the formation of colloidal particles, but merely a condition providing the optimum observation conditions, owing to the corresponding change in the ion concentration in the space about the cathode.

Evidently, the formation of colloidal particles can occur at any current densities at which the cathode process itself is feasible. The appearance of colloidal particles moving toward the anode is a signal of this. Though the ultramicroscopic picture of the participation of the colloidal particles in forming the deposit that is observed under the most favorable conditions gives the impression of the deposit being formed of colloidal particles, this is no reason to reject the possibility of even the partial construction of the deposit directly out of atoms produced as the result of the discharge of ions. Nevertheless the participation of colloidal particles is a not insignificant factor in the formation of metallic cathode deposits. As our research results indicate, [illegible] of the deposited metal and, in particular, its quantity, depend on the quality of the colloidal systems produced during electrolysis, since the departure of the colloidal particles for the anode entails a reduction in the yield per unit current.

SUMMARY

1. Investigation of the electrolysis of silver-nitrate solutions under the ultramicroscope confirmed the formation of colloidal systems as a result of the cathode process.

2. The direct participation of the colloidal particles formed during electrolysis in building up the silver deposit on the cathode was observed visually.

3. The identity of the phenomena observed in the electrolysis of pure solutions of silver nitrate and solutions to which acids had been added justifies the acknowledgment that the dispersed phase of the colloidal systems consist of silver particles.

4. Depending on the overall concentration of cations in the solution, the optimum conditions for observation of the ultramicroscopic picture are attained at definite current values.

5. The phenomena observed under the ultramicroscope are explained on the basis of the theory of electrolyte solutions.

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