THE FORMATION OF DENDRITES IN THE ELECTROLYSIS OF GLASSES

B. I. Markin

The formation of dendrites is of great practical and theoretical interest, both in the electrolysis of aqueous and nonaqueous solutions of certain salts and in the electrolysis of solid salts and glasses.

The present paper constitutes an endeavor to ascertain the mechanism involved and the nature of dendrite formation during the electrolysis of solid glasses.

1. The electrolytic nature of the conductivity of glasses was established a long time ago [1, 2, 3]. Those glasses that contain oxides of the alkali elements exhibit the highest conductance. When an electric field is impressed upon a glass, a current passes through it, due to the motion of the ions of the alkali metals. It was shown that when a glass containing sodium oxide is electrolyzed, sodium is deposited at the cathode, its quantity rigidly complying with Faraday's law. Normal electrolysis of glasses is effected, however, only when amalgams of the alkali metals or electrodes made of their molten salts, containing the same cations as are present in the glass, are utilized as electrodes. Under these conditions a glass can be electrolyzed as long as we wish, provided its chemical and physical properties remain unchanged.

When electrodes of platinum, mercury, or other metals, whose oxides are not present in the glass under test, are employed, the current drops off greatly as the electricity passes through the glass. This is due to the fact that the field causes the mobile ions of the alkali metals to leave the region around the anode, thus establishing a poorly conducting layer of glass.

When a metal or a metal amalgam whose oxide is not part of the glass composition is employed as the anode a large percentage of the foreign metal may be introduced into the volume of the glass. This produces a change in the chemical composition of the glass besides causing significant changes in its physical properties. When a substantial percentage of lithium is introduced into sodium glass, for example, the latter turns milky-white and brittle and is easily broken. When potassium is introduced into sodium glass, the glass decrepitates. This phenomenon is due to the different volumes of the alkali metal ions. The alkali metals in glass are replaced by silver fairly readily, the glass turning yellow or brown and becoming brittle. The ability of silver to replace the alkali metals when glasses are electrolyzed enabled researchers to make direct measurements of the cation transference number in fused borax [4, 5]. The transference number turned out to be one with an accuracy of 1 to 2%, which indicates the unipolar nature of conductance in glasses.

It is essential that the chemical composition and the physical properties of glasses be conserved during any investigation of their conductance. That is why the conductance of glasses must be measured by the use of active electrodes, such as amalgams of the metals whose oxides are constituents of the glasses tested. We used this method in investigating the conductance of various binary and ternary systems of borax glasses [6].

The electrolysis process proceeded normally during the prolonged electrolysis of all glasses belonging to the foregoing systems, no changes in chemical or physical properties being observed after electrolysis was over. A somewhat different state of affairs was found to prevail when we explored the conductance of borax glasses that contained silver [7]. When we measured the conductance of these latter glasses with electrodes of silver amalgam, we noticed that their conductance was highly unstable after even comparatively brief electrolysis. The electrometer thread fluctuated over a wide range, sometimes moving out of the field of vision entirely. The storage-battery voltage was also unstable during this period, fluctuating wildly. After the test was over, the sample of glass was dark and opaque. Dissemination of metal throughout the volume of the glass is visible with the naked eye. We found that metallic fibers—dendrites—grow from the cathode to the anode during electrolysis, short-circuiting the anode and the cathode. The instability of the electrometer thread and of the battery voltage is due to the

fact that the anode and the cathode are shorted by dendrites, which are then burned out as the result of the passage of a comparatively high electric current through them. Samples of these glasses had so many metallic threads running through them that we were able to pass currents of 0.5 to 0.7 amps through such glass. We also observed dendrites forming when we utilized electrodes made of silver or platinum plates.

The glass sample employed for the test using platinum electrodes exhibited the polarization that is customary for glasses, but after some time had elapsed metallic threads were seen to form within the glass. The thread of the electrometer quivered, and the resistance of the glass was unstable. It should be noted that the strongest and most rapid formation of dendrites occurred in borosilver glasses when they contained more than 40% of silver oxide. When borosilver-alkali glasses were electrolyzed, dendrites began to form when their percentage of silver oxide was lower, which is apparently due to a certain increase in the conductance of these glasses.

We observed an analogous formation of dendrites when we investigated the conductance of glasses that contained monovalent thallium. As the percentage of the metallic oxide in the glass was increased, the passage of the electric current again led to the formation of dendrites. It should be noted that dendrites are produced not only near the electrodes, but also at their periphery. In the latter instance they run mostly in the plane of the glass. The reason for this phenomenon is apparently the nonhomogeneity of the electric field at the edges of the electrodes.

Figure 1 (See plate page 1141) is a microphotograph of a thallium dendrite formed in the plane of the glass. Silver dendrites are of the same shape. The photograph clearly shows that the dendrites' structures differ greatly. In addition to the fine threads, there are areas where a substantial quantity of metal has been deposited. It is characteristic that on the side facing the cathode the base of the dendrite is a thin thread, starting from a point on the surface of the glass. As we travel to the anode, this thread branches out into a widely branched dendrite.

2. The formation of dendrites in glasses containing silver or thallium oxide that we have discovered is typical of salt crystals. Investigations have shown that the electrolysis of solid salts involves an ion transfer that rigidly obeys Faraday's law [1, 4, 8]. It was also noted that in the electrolysis of most salts the metal separating out at the cathode is not deposited uniformly upon the latter, in most instances penetrating into the salt as dendrites, which grow from the cathode to the anode as the current passes. When electrolysis is prolonged, the dendrites grow all the way to the anode, short-circuiting the anode and cathode. At the instance of short circuit a high current passes through the dendrites, burning them out and spraying them throughout the salt. It was noted that the salt was colored brown, red, or blue at these points.

The formation of dendrites during the electrolysis of solid salts constituted one of the most serious obstacles in determining the ion transference numbers in salts, since it is impossible to determine the percentage of the metal in atomized form or in dendrites. It was determined experimentally that dendrites grow extremely slowly during the electrolysis of crystals of silver iodide. This salt was therefore suggested for use as an intermediate salt between the cathode and the salt under test in order to prevent the formation of dendrites in the course of electrolysis [4]. At about the same time S. A. Shchukarev pointed out that silicate cover glasses could be utilized for this purpose [9].

It should be noted at this point that the formation of dendrites likewise interferes with the measurement of the conductance of silver glasses when they contain a high percentage of silver oxide. We used an intermediate sheet of fused borax in measuring conductance in this case to eliminate the formation of dendrites, inserting it between the cathode and the glass sample being tested. No dendrites were formed even when electrolysis was carried out for a long time.

In their study of a sample of rock salt in a constant field, Walther and Inge likewise observed dendrites forming[10]. The authors comment that the growth process of the dendrites can be readily observed in crystals of sodium chloride at temperatures above 350°, it being important to bear in mind that this involves the creation of nonuniformity of the field at the cathode at the start of electrolysis.

A needle, serving as a cathode, was impressed into a rock salt crystal in order to produce such a nonuniformity of the field. When a constant field with a voltage of 8-10 kv was applied, a violet cloud began to appear around the cathode after 10-15 minutes had elapsed, spreading out toward the anode, while reddish sparks were seen inside the crystal. When we examined the crystal after this test, using moderate magnification, thin violet threads were visible, representing the paths along which electrolysis occurred and metallic sodium was deposited. The sodium vaporized as the result of the high current density along this path, yielding a colloidal metal. For the most part these threads were aligned with the edges of the crystal cube. The dendrites within the crystal had the same shape as those we had observed in glasses (Fig. 1).

3. In preparing borax glasses containing silver and thallium oxides our attention was drawn to the fact that these glasses were colored yellow, in contrast to all the other glasses we had handled. The yellow color of silver and thallium glasses grows very much stronger as the percentage of the metal oxide is increased, becoming dark-brown in glasses containing approximately 60% of the oxide.

Glasses that contain silver oxide are coated with an extremely thin film of metallic silver after solidifying and cooling, no matter what their composition. In glasses with a high silver oxide content this film covers the samples with a dense, opaque metallic mirror. As we know, the color of glasses, such as those colored with gold salts, is due to the presence of colloidal particles of gold within the solid glass [11, 12]. The color of the glasses we tested was likewise due to their containing colloidal particles of silver and thallium. With a microscope fitted with a cardioid condenser we succeeded in detecting colloidal particles of metal in the glass. To do this we carefully polished glass samples that contained 70% thallium oxide. The glasses had the shape of thin plates about 1 mm thick. Glycerol was used as the immersion liquid. The microscope field showed the usual picture of colloidal particles, the sole difference being the absence of any Brownian movement. Figure 2 is a microphotograph of colloidal thallium particles observed in the glass plate (see plate page 1141). In the figure we clearly see the particles that lie at the microscope's focus, together with several blurry spots, due to particles above and below the layer in question. As we move the microscope's tube up and down by means of the focusing screw, we can easily see that the colloidal particles are distributed at random throughout the glass.

A much clearer picture is obtained if we use a thin film of glass instead of a plate. Figure 3 is a microphotograph of colloidal silver particles observed in a thin film of borosilver glass.

4. It was stated previously that in preparing glasses containing silver oxide we utilized silver nitrate, which decomposed during the melting of the glass, giving off nitrogen oxides and part of the metallic silver, which settled as drops on the bottom of the crucible. Part of this deposited silver dissolved in the molten glass. When it dissolves, this silver apparently does not yield molecular-disperse solutions in the glass, but dissolves as particles whose dimensions range from amicrons to colloidal particles. We have observed colloidal particles of the metal, both in hard glass and in annealed glass. The minute particles of metal may be aggregated to the dimensions of colloidal particles during the annealing of the glasses, like the particles of gold in the production of ruby glasses.

We found that the solubility of silver rises as the percentage of silver oxide in the glass is increased. The solubility of metallic silver is low in glasses containing up to 30% of silver oxide, and they contain few colloidal particles. This is indicated by the absence of color in these glasses. As the percentage of silver oxide is increased, the color turns from pale-yellow to bright-orange and dark-brown in glasses that contain 60% of silver oxide.

In preparing glasses that contain thallium oxide, we utilized reagents prepared by oxidizing finely pulverized metallic thallium in air at 80-90°. During melting we noticed an increase in the intensity of the glasses' color as the percentage of the metallic oxide was raised. Glasses that contain 60-70% of thallium oxide were identical in appearance, transparent, and dark-brown in color. It may be thought that not all the metal was oxidized during the process of preparing thallium oxide from the metal, but dissolved in the melt during the fusion of the glass, yielding colloidal particles that are responsible for the color of the glasses. To eliminate any introduction of unoxidized thallium into the composition of the glass, we prepared the oxide chemically by reacting a solution of thallium sulfate with barium hydroxide. The precipitated barium sulfate was filtered out, and the solution of thallium hydroxide was evaporated. The deposit of thallium hydroxide was converted into the oxide by heating it in air to 100° in a thermostat. In contrast to the initial glasses, the glasses prepared with this reagent, which contained 60-70% of thallium oxide, were pale-yellow rather than dark-brown, which indicates that in the former case the reagent contained an appreciable percentage of metallic thallium. The pale-yellow color of the glasses prepared from pure thallium oxide is apparently due to the fact that a small portion of the thallium oxide is reduced at high temperature to the metal, which is dissolved in the melt.

If we introduce pieces of metallic thallium into a molten mass of borothallium glass, bubbles of gas appear in the molten mass, which rise to the surface and produce green flashes. After the thallium dissolves in the molten mass, the latter turns dark-brown and much more viscous than before the metal had dissolved in it. When we examine these glasses under a microscope with a cardioid condenser, we see a large number of colloidal particles throughout the glass (Fig. 2).

5. It was pointed out somewhat earlier that we observed no formation of dendrites during electrolysis when we explored the conductance of glasses of widely varying composition. Only in the electrolysis of glasses that contain silver and thallium oxides is the formation of dendrites observed. As has been shown, there are colloidal

particles of silver and thallium throughout these glasses, which are responsible for their color.

It is natural to suppose that the presence of these colloidal metal particles in a solid glass is responsible for the formation of metallic threads and occlusions of dendrites within the glass.

6. Somewhat earlier we pointed out that no dendrites are formed in binary systems of alkali borax glasses no matter how long electrolysis is continued.

We were interested in checking the hypotheses we have just advanced by electrolyzing a borax alkali glass after having dissolved an alkali metal within it. The preparation of such glasses constituted a complicated job. We know that alkali metals react vigorously at high temperatures with boron oxide, displacing the boron, and with silica, displacing the silicon. Moreover, at high temperatures it is extremely hard to introduce an alkali metal into molten glass, as much of it burns up.

The experiments were begun with our preparing a borax sodium glass. This was done by melting borax and electrolyzing it in the molten state, graphite rods being used as electrodes. Electrolysis lasted 15-20 minutes. at a current of some 2 amps.

Some of the metallic sodium deposited at the cathode burned, rising to the surface of the molten mass, though part of it dissolved in the glass. There were minute bubbles throughout all the molten mass. The viscosity of the mass increased substantially, as was the case when silver and thallium were dissolved in glasses that contained oxides of these metals. We endeavored to introduce pieces of metallic sodium into the melt without electrolysis. The resulting picture was the same as when the sodium was introduced by electrolysis.

The melt was kept in the furnace until the glass was formed into sheets, in order to let some of the bubbles escape from the molten mass. Flashes were observed at the surface of the molten mass, due to the burning particles of sodium. Still, the formed and annealed glass contained some bubbles and was pale-yellow in color. The plate of glass was polished and then examined in a microscope equipped with a cardioid condenser. Colloidal particles were visible within the glass, but they were few in number and were hard to observe due to scattering of light by the bubbles left after the molten mass had solidified.

To secure a clearer picture, we prepared thin films of glass, in which the colloidal particles of metal were clearly visible. The overall picture was the same as in the photographs reporduced in Figs. 2 and 3. Our electrolysis of such a hard glass at a temperature of some 300°, using electrodes of sodium amalgam, showed that dendrites grow throughout the glass from the cathode to the anode. The behavior of the electrometer thread and of the battery voltage was the same as that described above. Metallic occlusions were visible within the glass with the naked eye. It should be noted that in this case the growth of dendrites required electrolysis for a much longer time than was needed for the production of silver and thallium dendrites.

Analogous tests were made with borolithium and boropotassium glass. The lithium glass contained 13% of lithium oxide, the potassium glass containing 40% of potassium oxide. The lithium was introduced into the molten glass by electrolysis as well as by adding it as pieces. The potassium was added only by electrolysis. In both instances the molten mass exhibited higher viscosity and a larger number of bubbles.

Dendrites were observed to form during electrolysis of these glasses, as in the case of the sodium glass. The resistance of the glasses and the battery voltage were highly unstable during the process of electrolysis, as was the case in the previous experiments.

A microphotograph of a sodium dendrite is shown in Fig 4 (see plate page 1141). It should be noted that its form differs greatly from that of thallium and silver dendrites. The sodium dendrites are big, dense lamellae. The top of the dendrite, extending toward the anode, is very uneven, consisting of thin, narrow lamellae of true form. The lithium dendrites, photographs of which are shown in Figs. 5 and 6, are of approximately the same shape. These photographs show the appearance of a fracture of a lithium glass sample after electrolysis. The difference between the forms of the dendrites of the alkali metals and those of the silver and thallium dendrites is apparently due to the circumstance that the alkali metals are deposited in the liquid state under the conditions of the experiment (electrolysis of the glass being carried out at approximately 300°), whereas the dendrites of silver and thallium were produced at temperatures below these metals' melting points.

7. We are inclined to attribute the formation of dendrites in the electrolysis of glasses that contain colloidal metal particles within them to the nonuniformity of the glasses' surface in contact with the electrodes, particularly with the cathode. Actually, if there are nonuniformities at the surface of the glass in

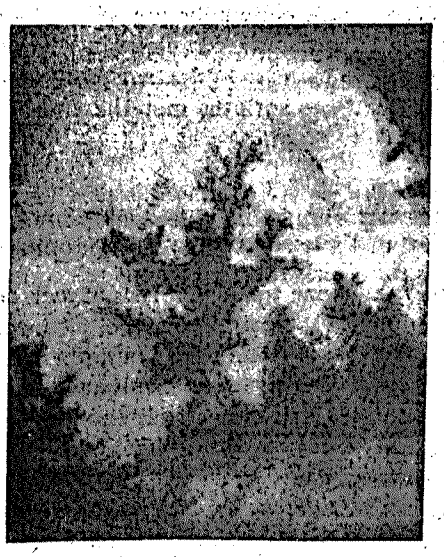

Fig. 1.

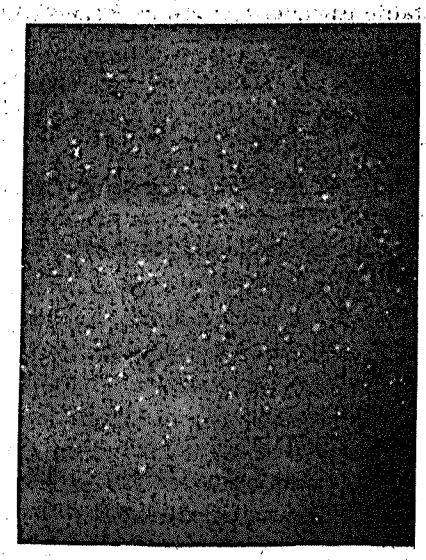

Fig. 2.

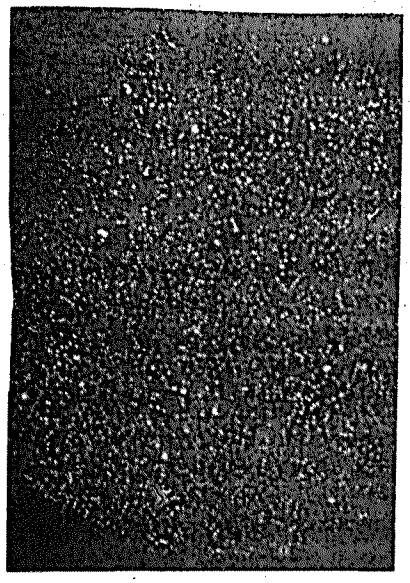

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

the shape of metallic particles that are in contact with the metallic cathode, the current density will rise in the vicinity of these particles. Thus, some of the ions are not directly discharged at the cathode during the process of electrolysis, but rather at these particles within the glass. This results in an increase in the number of particles emerging, leading to a growth of threads within the glass. This increase continues until the metallic thread reaches the anode.

What we have set forth is illustrated by the photographs in Figs. 1, 5, and 6. These photographs clearly show the spot at the surface of the glass in contact with the metallic cathode at which dendrites begin to build up within the glass.

From this point of view we can understand the formation of dendrites during the electrolysis of rock salt in the experiments by Walther and Inge described above. The nonuniformity of the cathode surface, produced artificially by the metallic needle pressed into the salt, results in the formation of dendrites. The formation of dendrites during the electrolysis of salt crystals is usually related to the uneven deposition of metal at the cathode. The unevenness of the crystal surface in contact with the surface of the cathode evidently also is a major factor. There are many fissures and recesses in the surfaces of salt crystals, as was pointed out by Academician A. F. Ioffe long ago. In the course of electrolysis of sheets of salts pressed between the electrodes the metal evolved (sometimes an alkali, liquid metal) fills up the fissures and hollows at the cathode, which then constitute metallic nonuniformities that penetrate into the interior of the salt, like the colloidal particles of metal in the glass discussed by us above. During electrolysis, the metal ions are discharged at these points, the nonuniformity progressing from the surface into the interior of the crystal, producing a dendrite, which reaches the anode as its growth progresses.

In conclusion I wish to express my thanks to Prof. S. I. Sklyarenko for his interest in this research.

SUMMARY

1. It has been shown that the formation of dendrites during the electrolysis of glasses is related to the presence of colloidal metal particles in the glasses.

2. Considerations are set forth concerning the mechanism involved in the formation of dendrites during the electrolysis of solid glasses.

LITERATURE CITED

[1] Warburg, Ann. Phys. Ch., 21, 622 (1884).

[2] Le Blanc and F. Kerschbann, Z. phys. Ch., 72, 168 (1910).

[3] Proc. Sessions of Russ. Phys. Chem. Soc., 32, 7, 10 (1926).

[4] C. Tubandt, Handbuch d Experimental Phys. B. XII, T. 1, Leipzig (1932).

[5] G. Ostroumov, J. Gen. Chem. 19, 3, 307 (1949).

[6] B. Markin, Jour. Tech. Phys. 10, 66 (1940).

[7] B. Markin, J. Gen. Chem. 11, 4, 2857 (1941).

[8] A. Ioffe. Physics of crystals (1929).

[9] P. I. Lukirsky, S. A. Shchukarev, and O. N. Trapeznikova, Jour. Russ. Phys. Chem. Soc. 56, 5, 6 (1924).

[10] Physics of dielectrics, ed. A. F. Walther (Russ. ed) (1933).

[11] V. Eitel. Physical chemistry of the silicates (Russ. ed) (1936).

[12] K. S. Evstropyev and N. A. Toropov. Chemistry of silicon and physical chemistry of the silicates, 97. Building Industry Press (1950).

Received November 19, 1950