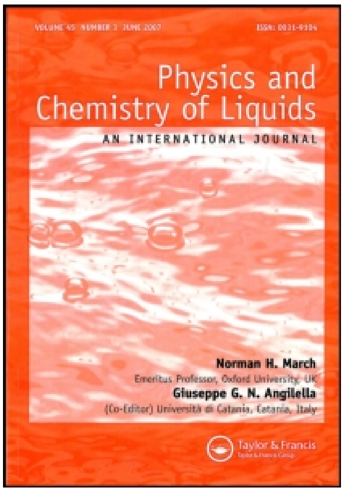

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Electrodeposition of Silver from Dense Gaseous Solutions of Silver Nitrate in Ammonia†

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Abstract—Silver was electrodeposited on platinum electrodes from solutions of $AgNO_3$ in NH_3 at temperatures from −70 °C. to 140 °C. The solutions were 0.036 molar in $AgNO_3$ at −78 °C. In the dense gaseous region, the concentrations of $AgNO_3$ and NH_3 were 0.018 and 22 moles/liter respectively.

The deposit was observed to become more and more crystalline in appearance as the temperature approached the critical temperature of NH_3(133 °C). All electrodeposits at temperatures above 133 °C were characterized by either dendritic or needle-like growths on sharp edges and corners. These were not observed at lower temperatures. Both three- and four-sided symmetries were observed, suggesting that the deposits were growing in the [111] and [100] directions, respectively.

1. Introduction

The process of electrodeposition out of a dense gaseous electrolyte is expected to have characteristics intermediate between comparable deposition processes out of the gaseous and liquid phases. This expectation is based on the continuous transformation of many properties, as gas densities are increased, from gaseous to liquid-like. Thus the dielectric constant of dense gaseous water exhibits a rapid increase with increasing density.(1) The solubility of NaCl in dense gaseous water at 750 °C increases with increasing solvent density until it exceeds the solubility in liquid water at room temperature.(2) However, ionic mobilities of dense gaseous electrolytes are expected to be higher than those of liquids. In addition, the dense gaseous medium is effectively without surface tension.‡ Because of the absence of surface tension, hydrogen produced during electrolysis in a gaseous electrolyte, when desorbed, is expected to diffuse away from the

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‡ However, Knapp and Sabersky have shown that, under large temperatures differentials, bubble-like flow can be produced in dense gaseous CO_2.(3)

cathode surface rather than being trapped there as bubbles. Such bubbles may interfere with the continuous growth of crystalline metallic deposits from a liquid electrolyte. In general, foreign material appears to inhibit continuity of crystalline growth out of both liquid and gaseous states. Traces of impurities have been shown to play an important role in determining relative growth rate in aqueous solutions.⁽⁴⁾ The use of a solvent which reacts with metal may produce a chemisorbed surface which may interfere with continuous crystal growth. For the present experiments ammonia was chosen as the solvent not only because of its convenient critical constants (132.9 °C, 112 atm), but because of its chemical inertness toward metals (e.g. Na at 190 °C in the absence of catalysts).† Silver nitrate was chosen as the salt because of its solubility in liquid ammonia as well as the insolubility of the electrodeposited metal in ammonia.

2. Experimental

The cells (Fig. 1) were made from 30 mm (O.D.) borosilicate glass tubing and were about 8 cm long, exclusive of the freeze valve. The internal volumes of the cells ranged between 35 cc and 40 cc. Three of the four electrodes were used as cathodes while the remaining one was used as the anode.

The anode was a platinum wire of either 0.4 or 0.5 mm dia. fused to a 0.75 mm dia. tungsten wire. The tungsten wire was brought into the cell through a uranium glass seal and the glass extended along the wire to completely cover the tungsten and part of the platinum wire. The glass-covered part extended 1 to 2 cm into the cell while the exposed platinum wire extended another 4 to 5 cm.

Several types of cathodes were tried but only two proved to be useful. The first of these was a platinum wire identical to the anode. The second was made by cutting the platinum wire flush with the feedthrough glass covering the tungsten and the lower portion of the platinum wire. The wire cutters used left the end of the wire in a wedge shape. Thus the exposed part of the cut off type cathode was wedge shaped, as was the end of the long wire type cathode.

Each cell was prepared as follows. Reagent grade silver nitrate was introduced into the cell which was then sealed onto the vacuum system.

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† Data to 165 °C have been reported,⁽⁵⁾ more recent unpublished data in this laboratory show the same inertness to 190 °C.

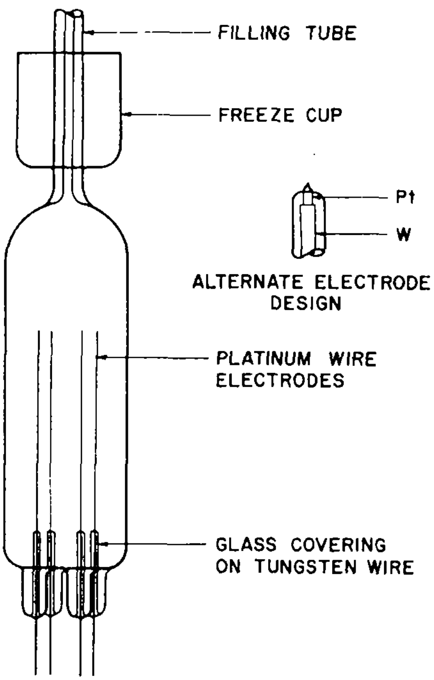

Figure 1. Cell for electrodeposition from dense gaseous ammonia solutions.

The system was then baked out under vacuo at 100 °C for an hour. Pumping continued while the ammonia was being prepared. Tank ammonia (Matheson, 99.99%) was passed through an activated charcoal trap and stored overnight as a liquid over metallic sodium.

In some cells two additional electrodes have been brought in through the top of the cell. In other cells ("alternative electrode design"), the cathodes have been cut off flush with the feedthrough glass. The filling tube is constructed of capillary both to simplify seal-off and to enable the freeze cup to operate effectively. The tungsten wire is welded to a 0.016 in. platinum wire, the glass sleeve covers all of the tungsten and the initial part of the platinum wire.

The ammonia was then condensed in the cell, which was maintained at −78 °C with a dry ice-alcohol bath. When the liquid level rose to a calibrated mark on the cell, the introduction of ammonia was discontinued. The fiducial mark was located at 50% of the sealed-off cell volume. At −78 °C, the filled cell contained 0.036 N $AgNO_3(NH_3)$. When heated into the dense gaseous state, the solution would be 0.018 molar in $AgNO_3$ and 22 molar in NH_3, assuming that all of the $AgNO_3$ remained in solution.†

The solution in the cell was maintained at −78 °C and liquid nitrogen poured into the freeze cup above the cell. In this way the electrodes were not subjected to thermal shock and strain. A solid ammonia plug formed in the capillary in the freeze valve. The plug was pumped to high vacuum and the cell sealed off.

The wires on the filled cell were soldered onto leads going through a head in a high pressure vessel and the cell placed therein. External nitrogen pressure inside the pressure vessel was used to keep the glass under compression thereby preventing the ammonia pressure within the cell from rupturing the glass cell. The external pressure was kept about 30 atm above the predicted internal pressure(6) during heating of the cell and deposition.

3. Results

The initial runs were done using the long cathodes at current densities of 1 to 2 ma/cm² for from 600 to 800 sec. Deposits made from the liquid showed increasingly crystalline appearance as the critical temperature was approached. At −70 °C the deposit appeared black, fluffy and non-metallic. At 15 °C the deposit was smooth and "silvery", giving spectral reflection. At 103 °C the deposit was "silvery" or metallic in appearance but somewhat sparkly, suggesting some crystallinity in the deposit.

At temperatures above the critical point of ammonia, the deposits were much more crystalline in character, as can be seen from Fig. 2. This shows the wedge shaped tip and some of the cylindrical body of a wire type cathode. Electrodeposition was carried out for 690 sec. at a current density of 1.6 ma/cm² and a voltage of 0.5 V. The deposit on the body appears to be made up of tiny crystals while at the tip are several projections which are presumably single crystals of silver. These are in the form of four-sided square cylinders with uniform cross section over most of their length but starting from a narrower base and ending in a pyramidal point.

Figures 3 and 4 show photographs of much larger needles and dendrites

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† It is probable that all or at least most of the $AgNO_3$ remained in solution in the dense gaseous phase. The overall conductance of the cell with the gaseous electrolyte was comparable to that of the liquid at room temperature. The situation is slightly complex because with increasing temperature the amount of the electrode exposed to the solution increases as the solution expands.

Figure 2. Photograph of electrodeposit made at 140 °C on long wire type cathode.

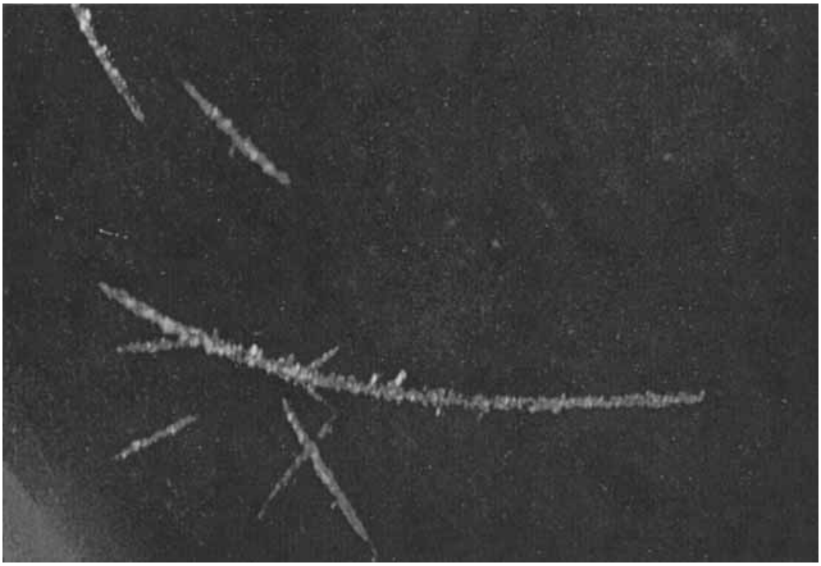

Figure 3. Needles deposited at 140 °C on cut-off type cathode. Longest needle appears to have grown in [111] direction.

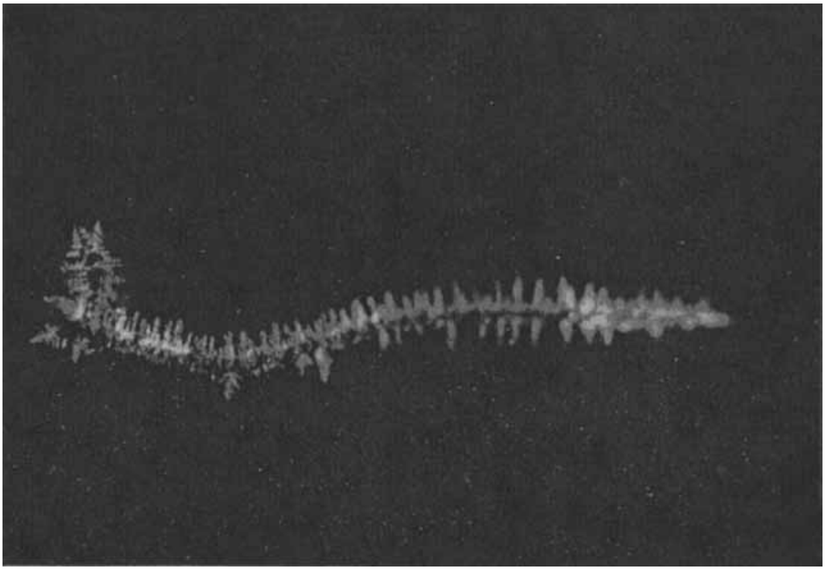

Figure 4. Dendrite obtained at 141 °C on cut-off type cathode, central stem appears to have grown in [100] directions.

grown on cut-off type cathodes. Because only the sharp, wedge shaped tip is exposed in these cathodes, the dendrites tend to cover the entire cathode and to rapidly increase the effective cathode size as they grow. Thus it was possible to grow much larger dendrites in a shorter time. In this case the electrodeposition was done at constant voltage rather than constant current, the current being allowed to increase as the deposit, and hence the effective electrode area, grew. The voltages used were 1.05 V and 0.85 V, respectively, while the total charges passed were 2.2 and 2.4 coulombs, respectively.

In Fig. 3 the needle-like growths are up to 6 mm in length. Examination of the longest growth with a low power microscope reveals that it consists of a three-sided central stem coming to a sharp point at one end and having the sides covered with short, stubby growths. These growths show both rectangular and hexagonal symmetries while there are also some longer, pointed branches, having three sides like the central stem. The dendrite shown in Fig. 4 is 7 mm long and has the central stem completely covered with branches growing perpendicular to the stem in two perpendicular planes. Although the branches tend to obscure the central stem, examination under a low power microscope suggests that it is four-sided with three-sided fern-like branches growing from the edges.

It should be noted that dendrites of the type shown in Fig. 4 occurred only in one run while the needle-like growths of Fig. 3 were obtained in several runs. The difference is believed to be due to the presence of impurities giving rise to the dendrites.

4. Discussion

The results indicate that there is a strong tendency for crystalline needles or dendrites to grow from sharp corners on the cathode in gaseous $AgNO_3$–NH_3 solution. The tendency for dendrites to grow on sharp corners was also found and explained by Arouete and Blurton in their studies of the electrodeposition of zinc in silver-zinc batteries.(7) A detailed account of the electrocrystallization process has been given by Bockris and Damjanovic.(8)

The observation of triangular and square symmetries suggests that the central stem and branches of the dendrites were growing by the propagation of screw dislocations in the [111] and [100] planes, respectively. Silver dendrites have been grown out of aqueous solution at room temperature by Wrangler(9) who observed only a flat form of dendrite which he deduced to be growing perpendicular to the [110] plane with branches in the [111] plane. With other metals (e.g. zinc) he also observed [100] dendrites of a similar form to that shown in Fig. 4. In these experiments a supporting electrolyte (e.g. NH_4NO_3) was added to the metal salt ($AgNO_3$), and the current density was found to be an important factor in dendritic growth. In the present experiments, no supporting electrolyte or precautions regarding current density were necessary, but needles or dendrites were obtained on sharp corners whenever electrodeposition was performed in the supercritical region of ammonia. The tendency for continuous crystal growth is probably strongly inhibited in the liquid, partially due to hydrogen bubble formation interrupting the growth on a single crystal face. It may also be that the mobility of adsorbed ions over the crystal surface is greater when the electrolyte is gaseous, thus allowing the ions to reach the sites of lowest activation energy so that the crystal structure is preserved as the deposit grows. It should be noted that as the critical region is approached the differences between liquid and gaseous fluids become small so that it is not surprising that as low as 100 °C the surface becomes sparkly due to small crystals.

The results are somewhat similar to those of vapor deposition in that with increasing temperature, vapor deposits tend to become more crystalline.

Finally, the ease with which fairly large crystalline electrodeposits are obtained in the supercritical region suggests that electrodeposition from dense gaseous ammonia might prove to be a useful process for growing whiskers or other desirable crystalline forms.

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