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Electrocrystallization in Microgravity

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ELECTROCRYSTALLIZATION IN MICROGRAVITY

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SUMMARY

Electrocrystallization under microgravity conditions is proposed as a potential method of crystallization that would be almost completely free of fluid convection. Such crystallization may result in purer, more perfect, and larger crystals than is possible under normal gravity conditions. Observations made and data collected during the crystallization process under convection-free conditions should add to our knowledge of the crystallization process. The proposed method would allow easy comparison of crystals grown in space with those grown under normal gravity conditions. Nine types of electrocrystallization are presented: an example of each is discussed. Electrocrystallization is compared with the compartmental crystallization method used by 3M Corporation in recent shuttle experiments.

INTRODUCTION

Crystals may be formed in basically three ways: from the melt, from the gas phase, and from solution. This report is concerned with only the last method. There are many techniques for the production of high purity and high quality crystals from solution (ref. 1). In general, the slower a crystal is grown, the purer, more perfect, and larger it will be. The slowest crystal growth rate is obtained by minimizing fluid convection and having the crystals form solely because of the diffusion of the molecular species. There are many well-known ways of minimizing convection, including the use of microgravity.

The purpose of this report is to propose a new general method for achieving nearly convectionless crystallization under microgravity conditions. The method is electrocrystallization which we define as any type of crystallization that is produced as a result of an electrochemical reaction. Electrophoresis and electroepitaxy are intentionally excluded from our definition. Reference 2 illustrates that crystallization of even organic compounds can be produced via electrochemistry. However, in the past, the word "electrocrystallization" (ref. 3) has been used almost exclusively in connection with the crystallization of metallic electrode materials.

In this report, we first discuss the techniques involved in minimizing convection during crystallization. Next, the overall concept of electrocrystallization under microgravity conditions is presented, followed by an enumeration and discussion of particular types and examples of electrocrystallization. The various types are then compared. Finally, the advantages of electrocrystallization over other microgravity methods of solution crystallization are discussed.

As in the case of all proposed microgravity space experiments, there must be justification. The prime purpose of the experiments is to add to our knowledge of the crystallization process. In turn, this may lead to better

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techniques for crystallization under microgravity as well as others under normal gravity. For crystallization to be practical as a space manufacturing technique, a small amount of crystallized material would have to be extremely valuable, such as a catalyst would be.

MINIMIZING CONVECTION DURING CRYSTALLIZATION

Via Temperature Gradient

There are many techniques for minimizing (not eliminating) fluid convection during crystallization. A dominant feature of methods used under normal gravity conditions involves keeping the more dense fluid at the bottom. A good example of this involves placing a solvent containing a solute to be crystallized into a vertical temperature gradient with the higher temperature on top. This example requires a greater solubility at the higher temperature. Excess undissolved solute is placed in the higher temperature region in contact with the solution. This solute will dissolve, diffuse downward to the cooler regions of the solution, and crystallize when this part of the solution exceeds saturation. If the temperature and the temperature gradient are kept constant, the different densities should not cause convection. However, the crystals formed will not have the same density as the solution from which they are crystallizing. Thus, if they form anywhere else than at the bottom, they could settle and induce convection within the fluid.

Via Changing Solvent

Another method of minimizing convection is depicted in figure 1. In this method, crystallization is achieved by changing solvents. Urea is soluble in methanol but less soluble in a mixture of methanol and toluene. A beaker containing a saturated solution of urea in methanol is placed in a larger container. Toluene is added to the outside container. Then methanol is added to cover both liquids. This is performed carefully so as to minimized convection. The density of the toluene is slightly greater than that of the solution of urea in methanol which is slightly greater than that of pure methanol. Some convection will occur when the liquids are first permitted to contact each other. But if no crystals are formed during this time, the convection may be ignored. More elegant designs for performing the experiment might prevent still more initial convection.

The important time to minimize convection is during the actual formation of crystals. After the initial convection takes place, the toluene and the methanol containing the urea interdiffuse. After the toluene diffuses into the methanol, the resulting liquid could acquire a density greater than that of the methanol containing the urea. This, in turn, could lead to some convection. Eventually, the mixing of the toluene and methanol (hopefully, only by diffusion) causes the crystallization of urea because of the lower solubility of the urea in the methanol-toluene mixture than in pure methanol. The urea crystals have a greater density than the liquid so that they will tend to settle. According to Stokes's equation (ref. 4) the larger the crystals, the faster they will settle. This settling, in turn, induces convection of the liquids. Calculations show that convection in any such system cannot completely be prevented (ref. 5).

Other Normal Gravity Methods

Crystallization can involve a chemical reaction as well as just a change in physical solubility. The method described above can be applied to methods involving such chemical reactions. An example would be the precipitation of barium sulfate by the interdiffusion of the barium ion of barium chloride in one aqueous solution and the sulfate ion from sodium sulfate in another aqueous solution. The product, barium sulfate, would have a higher density than the aqueous solution from which it would crystallize; thus, its formation will induce convection of the solvent.

Via Microgravity

It becomes obvious that an excellent way to overcome much of the troublesome convection during crystallization is to have crystallization occur under microgravity conditions. Experiments of this type have been performed in Spacelab-1 (refs. 6 to 8). The most publicized ones were performed in the middeck of the shuttle on a recent flight (ref. 9). In these experiments, crystals of three different compounds were formed. One of the compounds was urea; it was formed by the interdiffusion of toluene with a saturated solution of urea in methanol. The principal investigators of the shuttle experiment are from 3M Corporation.

A schematic diagram of the apparatus used to grow urea crystals on the shuttle is shown in figure 2. The three different compartments shown in this figure were separated by specially designed slit-type valves, so that one could prevent contact between the different liquids until microgravity conditions were established. When the apparatus was in orbit, its temperature was raised a little above ambient. About an hour after the system had reached this temperature, the sliding valves were opened to permit the liquids to interdiffuse. The system was maintained at this elevated isothermal temperature for the course of the experiment. The urea crystals formed under microgravity conditions were examined on earth; they appeared to be optically more clear than ones made in controlled experiments under normal gravity conditions. Complete analyses of the crystals have not yet been reported.

Indeed, when the crystals of urea formed under microgravity conditions, they should not have settled and thereby not have induced convection. However, there are factors occurring that could have produced some undersired convection. Although the opening of the valves was performed slowly, the opening could not have been completely free of convection effects near the valves. Moreover, a microgravity field does exist in the orbiting shuttle along with gravity jitter (bursts of gravity as high as one hundredth of a gravity unit). Fluid convection is also expected to have occurred during as well as after the shuttle landing. At these times, the methanol and toluene could have completely mixed due to convection, so that much of the urea remaining in solution would be precipitated. Such precipitation would be expected to be in the form of a powder or crystals of microscopic size. Precipitation of this type has not been reported to have occurred.

ELECTROCRYSTALLIZATION OVERVIEW

Electrocrystallization in microgravity would bypass some of the difficulties inherent in the 3M experiments. It is wise to give an overview of electrocrystallization before discussing specific types and examples. In such an overview, there are many factors to consider in addition to the nature of electrocrystallization itself.

Cell

Regardless of the reactions involved, the experimental cell would logically be cylindrical in shape. At one end, a metal plate would serve as the current collector of the anode, and at the other end, another metal plate would serve as the current collector for the cathode. The nature of the metals depends upon the nature of the electrode processes. The side walls would have to be constructed of an electrically insulating and nonporous material. The cell would be completely filled with a solution containing all the necessary components for the electrode reactions as well as the materials needed for the formation of the desired crystals. In some cases they contribute the necessary electrolyte properties to the solution. When the reactants are not ions, auxiliary noninterfering ions must be used. The dimensions of the cell are not critical; one could imagine the cell being about 10 cm long and 5 cm in diameter. In this type of cell, the diffusion which occurs would be one-dimensional in nature when convection is nil.

The Process Itself

Initially in electrocrystallization, the solution can and would be uniform in concentration. No reaction would occur until the current is turned on. When current is flowing, electrons are added to the cathode and removed from the anode. The crystallization may occur either near the cathode or the anode depending upon the nature of the crystallization. For clarity the electrode near which the crystallization occurs will be referred to as the "active electrode." The other is the counter electrode. In an ideal electrocrystallization process in microgravity, a chemical species is generated at the active electrode, diffuses into the bulk of solution, and contacts one or more other species, resulting in the formation of an insoluble crystalline product. The other species will be referred to as the precipitating agent(s). The diffusion of the generated species would always be in the direction perpendicular to the current collectors. When the current is shut off, this species is no longer generated; when that which was generated is used up by reaction with the other species, no further crystallization occurs. Thus, crystallization can be stopped by turning off the current.

A few additional comments concerning the reaction is in order. The nature of the final reaction may be either a chemical or physical process. Also initially, the reaction will occur close to the active electrode, but as the electrolyte is depleted of the precipitating agent(s), the species formed during the electrochemical reaction must diffuse further into the bulk of the electrolyte in order to contact the precipitating agents(s) which causes the crystallization. This, of course, is what is desired: crystallization caused exclusively by diffusion.

Separation of the Electrodes

In some cases, it will be advantageous to separate the active electrode region from the counter electrode region with an ion permeable membrane. With a membrane, crystals formed in the active electrode region can be isolated from solids which may be present in the counter electrode region, resulting in a potentially purer product. In addition, with a membrane, convection within the counter electrode region would not induce convection in the active electrode region. Convection at the counter electrode might be the result of gas formation or due to intentional stirring. Of course, in some cases a membrane may be unnecessary or even undesirable.

Rate-Controlling Factors

The maximum current is, of course, dependent on the size of the cell, as well as on the specific species and reactions. The current density may or may not be dependent on diffusion of a species to the electrode. If in a particular system the current "consumes" some ion in solution, then the current density will eventually be limited by the diffusion of that ion to the electode. In such a system, the concentration of the diffusing species at the surface of the electrode will decrease. When it drops to zero, no more current will flow.

Expected Yield

The amount of crystalline material expected to be grown during an experiment is dependent on the current and duration of the experiment. Thus, to calculate the expected yield of crystals, a mathematical model for electrocrystallization must be set up. Because we would generally desire the current to remain constant of the duration of the electrocystallization, we make this a provision in the model we use. Also, we assume that at least one species is consumed by the electric current, and that the current density is limited by the diffusion of one such species. The concentration of this species is assumed to be initially homogeneous throughout the solution. When the current is flowing, this species is not replaced. Also transport occurs exclusively by diffusion. With these assumptions, the concentration, C, of the diffusing species at the current collector surface is related to time as follows:

$$(C_0 - C)/F = (L/D) \left\{ D\ t/L^2 + 1/3 - (2/\Pi^2) \sum_{n=1}^{\infty} \{\exp\ (-D\ n^2\ \Pi^2\ t/L^2)/n^2\} \right\} \qquad (1)$$

where D is the diffusion coefficient (e.g., 5×10^{-6} cm^2/sec), L is the length of the active compartment (10 cm if no membrane is present, but 5 cm if one divides the cell in half), t is the time in seconds, F is the absolute value of the flow rate (equivalents/cm^2/sec), and C_0 is the initial concentration (e.g., 0.005 equivalents/cm^3). Equation (1) is easily derivable from equation (4.55) in reference 10.

When C in equation (1) becomes zero, current can no longer flow. Therefore, the t in equation (1) giving rise to $C = 0$ corresponds to the maximum time that a specified current can flow. Via equation (1), figure 3 was plotted giving the maximum time, t, for a specified total current and our assumed parameters. (The total current equals the F is equation (1) times the product of the cross-sectional area and the Faraday).

We define X as the maximum fraction of the original amount of diffusion species that can be consumed for a particular constant flow rate (current).

$$X = Ft'/C_0L' \qquad (2)$$

where L' is the length of the cell, 10 cm. By using both equations (1) and (2), one can now plot this maximum fraction as a function of the total current (fig. 4). To achieve X = 1, an infinitesimal current must be used. If an infinite current is used, no crystals are obtained. The extreme left scale of figure 4, grams of crystals, is based on the following assumptions: all reactions are stoichiometric; C_0 equals 0.005 equivalents/cm^3; and the equivalent weight of the crystals is 50. If one chooses to consume half of the diffusing species, figures 3 and 4 tell us that for a 10 cm long active compartment the maximum current is 7.4 mA, the time required is 1850 hrs, and about 25 grams of crystalline product are made. One, of course, could be limited by the length of the shuttle flight, e.g., 10 days; to obtain the maximum weight of crystals under this condition, the current would be set to 19 mA for the 240 hrs under microgravity, and about 10 g of crystals would be produced according to figures 3 and 4. Note that to keep a constant current, the applied voltage would have to be continuously increased because the concentration, C, at the current collector interface decreases with time.

Remember that figures 3 and 4 are dependent on the model used as well as the parameters. If a membrane were used to divide the electrocrystallization cell into two equal parts, the L in equation (1) is 5 cm. The total amount of diffusing species is still based on a 10 cm long cell. As expected the curves in figures 3 and 4 approach each other at high currents. At low currents,the value of X for the case with the membrane approaches one half because the equations used assume that the diffusing species is not transported through the membrane. At low currents with a membrane, the value of X would be greater for a model which would allow such transport of the diffusing species. The dependence of X on the current is also a function of the diffusion coefficient; the larger diffusion coefficient would result in a larger current for a specified yield. Nevertheless, the values given in figures 3 and 4 are good order of magnitude values for a cell of our selected size: 5 cm diameter and 10 cm length.

It is well to emphasize that equation (1) and figure 3 are applicable only under conditions for which convection is minimal (e.g., microgravity). If convection occurs, the transport rate of the species can be much greater so that to obtain the same yield, a higher current density can be used for a shorter time.

The Counter Electrode

If the active electrode is reversible along with all the accompanying reactions, the counter electrode can be the reverse of the active electrode. In the extreme case, impure crystals of the desired compound can be present in the counter electrode compartment and dissolve while their pure counterpart would crystallize slowly in the active compartment.

When the active electrode is not reversible, the selection of a noninterfering alternate electrode is required. Such an electrode should be dependable, noncurrent limiting, and noncontaminating to the active electrode compartment. The hydrogen and oxygen electrodes are good examples of this type and should be the first ones to be considered. If the counter electrode is the anode, and the oxygen electrode is used, oxygen gas would be formed. If a membrane is present to separate the two electrodes, convection caused by gas formation should not induce convection in the active compartment. The same sort of reasoning holds when the hydrogen cathode is used as the counter electrode. However, one might eliminate the formation of hydrogen gas by the use of a depolarizer such as manganese dioxide. Alternatives to the oxygen anode might be the sulfite-sulfate electrode or a metal-metal salt electrode which should produce no gas. The hydrogen electrode could be used as an anode, and the oxygen electrode could be used as a cathode, but this would entail a supply for these gases. Because this would complicate the system, this approach is not advisable.

Density Gradient

Initially it is possible to have no density gradient present in the electrocrystallization cell. However, as the current flows, a slight concentration (and associated density) gradient will develop. Under microgravity conditions, the effect of the density gradient is minor. Its effect can be still further reduced by placing the experimental cell in a vertical position below the center of mass of the spacecraft and with the denser part of the solution directed towards the earth. The experimental setup can be used in the same orientation under normal gravity conditions, and a comparison of results may be made between crystals formed under microgravity and those under normal gravity conditions.

Types of Solvents

The most obvious solvent is water. However, there are many organic solvents which may also serve as solvents for electrocrystallization at room temperature. At cryogenic temperatures, a condensed gas (e.g., liquid ammonia) might serve as a solvent. In all the above cases, a dissolved salt would be necessary for electrical conductivity. At elevated temperatures a molten salt could serve as the solvent; the salt itself would supply the ions required for conduction. Thus, electrocrystallization in microgravity is not restricted to water solutions and room temperature. However, the method is best illustrated by such a system, and therefore most of the examples given in this report involve the water solvent system.

PROPOSED TYPES

Table I presents nine types of electrochemical reactions that could lead to the crystallization of solids. The types listed are not intended to be all inclusive, and the classifications are somewhat arbitrary. Table I gives a potential example of each type. Each example is intended primarily as a starting point and as a means of explaining the details of the type. The examples are not expected to be the most useful for microgravity crystallization experiments. In fact at this stage of the concept, we cannot say that all the examples will actually work. Some examples are used to illustrate difficulties with the method.

Deposition of Metal

The best known type of electrocrystallization presented in Table I is the deposition of the metal (Type 1). Thus, this type is an ideal one to discuss first and for which to give specific details. In this method, metal ions are reduced to the free metal; the resultant metal crystals attach themselves directly onto the already present metal current collector because this is the locale of the reaction. Due to this attachment, the difference in density between the crystals and the solution would not give rise to convection; the crystals will not move. However, changes in density of the solution would produce density gradients and under normal gravity cause convection. Crystallization of a metal is certainly not the ideal type of reaction to perform in microgravity. We desire the crystals to be formed by the diffusion of ions or molecules into regions of low solubility. Nevertheless, the study of the crystallization of metals under microgravity conditions would be an interesting and informative study of the crystallization process and have application to battery research.

The reaction involved in the plating of a metal is generally reversible; thus, the anode can be the reverse of the cathode. There will be a slight density disturbance in the vicinity of each electrode; at the cathode the solution will become depleted of the metal ion and thus less dense. At the anode, the solution will become rich in the cation and thus more dense. The cations will diffuse from the anode to the cathode because of the concentration gradient. This diffusion of the metal ion will therefore eventually limit the current. In this type of system there is generally no reason to separate the anode compartment from the cathode compartment with a membrane. In the metal-metal ion system, the metal salt serves as the electrolyte, that is the ions of the metal salt will carry the current in solution: the metal ion will electrodiffuse toward the cathode, and its anion will electrodiffuse toward the anode. It is obvious in the metal-metal ion system that crystallization occurs only while the electric current is flowing. Moreover, the amount of metal crystallized is proportional to and can be calculated from the total number of coulombs that pass.

The anion chosen in dependent upon the metal used. For example, in the case of plating silver, the chloride ion would not be used because the chloride of silver is insoluble. If we used the example given in table I, copper, then the sulfate might be the best contender. Another thing to consider is the pH of the solution. This is particularly important for the proper plating of copper; the solution should be sightly acid.

McDonnell Douglas and the University of Alabama are planning a joint investigation of the plating of metals in space (ref. 11). Such a program appears to be directed toward smooth coatings as contrasted to single crystals which is the objective of this report.

Deposition of Nonmetallic Conductor

There exist certain organic compounds that are conductors. Recently, one of these (table I, Type 2) has been electrocrystallized (ref. 3). The compound is hydrogen bis (phthalocyaninato) neodymium(3). The factors involved in this electrocrystallization are for the most part identical to those for the plating of a metal. Obviously, the example given in table I is the first one to consider because the crystals have already been prepared under normal gravity conditions.

Inorganic Oxidation

Inorganic oxidation (table I, Type 3) has more of the characteristics that we desire to have in a microgravity electrocrystallization. A material (metal, lower valence cation, or higher valence anion) is oxidized to another valence. The oxidized species (e.g., ion) contacts another species (precipitating agent; e.g., ion) with which it forms an insoluble product (e.g., salt). This product should come out of solution in the form of crystals. The precipitating agent could be inorganic or organic, even an analytical reagent (ref. 12).

The concentration of the precipitating agent is decreased in the vicinity of the active electrode, and the oxidized species must diffuse out from the electrode to contact the precipitating agent(s) that remains. This is the type of crystallization that we desire: crystallization which is the result of diffusion. The crystallization roughly coincides wit the passage of the electric current; however, there is a slight delay. After the current is shut off, some oxidized ions will still exist in the vicinity of the active electrode, and only later will they react with the precipitating agent(s) to produce crystals. However, after they have reacted, the overall chemistry will be essentially stoichiometric: the number of crystals will be proportational to and calculable from the total number of coulombs passed. If the crystals are somewhat soluble, the stoichiometry between the amount of crystals and current can be preserved by initially saturating the solution with the reaction product (the crystals).

Many metals could be selected as the starting material, providing a suitable anion is available for the pair of ions to form an insoluble compound. The example given in table I (Type 3) illustrates a novel candidate of this type of electrocrystallization. Nickel dimethylglyoxime is a well-known compound in analytical chemistry; it is generally seen as a fine pink powder, and thus it would be interesting to prepare this material in large crystalline form. The precipitation of the insoluble compound is not expected to be immediate, because of the required diffusion and some sort of molecular rearrangement. This could increase the probability of forming large crystals. Also, the formation of the insoluble nickel salt is accompanied by very little change in density of the solution. As the nickel ion is formed at the anode, the local solution density would increase slightly, but the density will return quickly to almost normal as the nickel salt crystallizes. The crystallization of the nickel dimethylglyoxime salt requires a solution basic with ammonium hydroxide. This will serve as the necessary electrolyte.

One difficulty with this system is the lower solubility of the precipitating agent in ammonium hydroxide. A technique which bypasses this is the use of undissolved dimethylglyoxime in the counter electrode compartment. In a preliminary study, this method appears feasible (unpublished). Another difficult with the nickel dimethylglyoxime system might involve the counter electrode to the used; the reversible nickel electrode cannot be used as the counter electrode. If the nickel ion is present in the counter electrode compartment, it would be precipitated as its dimethylglyxime compound. A hydrogen cathode might be the best choice with a membrane preventing gas formation from causing convection in the active compartment. The hydrogen evolution might be prevented as stated earlier via the depolarizer, manganese dioxide. Perhaps one could use the reduction of copper as the counter electrode reaction; but the copper ion would tend to contaminate the nickel dimethylglyoxime.

Another example of electrocrystallization could be the formation of nickel oxalate. The cell would be very similar to that for the formation of nickel dimethylglyoxime. The differences would be: the use of a slightly acid solution rather than an ammoniacal one, and the presence of solid oxalic acid in the counter electrode compartment rather than solid dimethylglyoxime. In preliminary studies (unpublished), the oxalate rather than the nickel was oxidized at the anode. Still another example is the formation of silver chloride from the electrodissolution of silver into a chloride solution; this example is certainly a feasible one; the reaction is one occurring in the common silver-silver chloride electrode. Moreover, the counter electrode can be the reverse of the electrode under study. The oxidation of lead to form lead chromate, formerly used in paint manufacture, is another example of this type of electrocrystallization.

Inorganic Reduction

Electrocrystallization of Type 4 (inorganic reduction) is similar to the previously discussed one, except that the starting material is reduced. Thus, the starting material cannot be a free metal. It could be the higher valence cation whose lower valence salt is insoluble. It could also be a soluble nonmetal or a lower valence anion if the proper insoluble species of the other valence state existed. Most of the considerations are the same as those described for inorganic oxidation.

In table I, the crystallization of mercury chloride iodide is given as a novel example of Type 4. Iodine is reduced at the cathode to the iodide ion which diffuses and combines with the mercuric and chloride ions to form the insoluble mercuric chloride iodide. The diffusion of the iodine species would limit the current, while the diffusion of the iodide ion would control the crystallization rate. The mercuric chloride would initially serve as the eletrolyte, but another electrolyte such as sodium sulfate should be added to compensate for depletion of the mercuric ion as the experiment proceeds.

Again, one cannot use the reverse reaction for the counter electrode. The oxygen anode might suffice if a membrane is used between the electrode compartments. Another possible selection would be the a nickel-nickel ion electrode.

The depletion of the mercuric ion with time would cause the density in these regions to decrease. Because of the high density of the mercuric ion, the effect of the residual gravity would probably have a greater effect on this example than any of the others presented in table I. A possible difficulty with this example is that the mercuric ion may also be reduced. However, the iodine should reduce at a lower electrical potential.

The formation of insoluble mercurous chloride from the partially soluble mercuric chloride would serve as another example of this type of electrocrystallization.

Electro-organic Synthesis

Many organic compounds can be produced electrolytically (ref. 13). When the product is insoluble in the solvent being used, this type of process can be used as a method for electrocrystallization (table I, Type 5). The electrochemical reaction is usually a reduction. Generally, yields are low, and several products are made simultaneously. Side reactions can be permitted particularly if the side products are soluble. Because of possible side reactions, the desired reaction is not expected to be stoichiometric, and the yield will be less than predicted from the number of coulombs passed. Moreover, the reaction is likely to occur at the electrode with the immediate formation and crystallization of the product, perhaps with no diffusion involved. Some of the syntheses involve organic solvents; one would hope to find a system that would minimize the use of such solvents. Also, the systems used must be confined to those in which the starting organic compound is somewhat soluble in the solvent, and the desired crystalline product is less soluble. Moreover, the solution must generally contain an auxiliary electrolyte because the organic starting material is not likely to be ionic. The current collectors chosen should be inert because they should not partake in the reaction; they are merely the means of introducing or removing electrons. The electropotential must be carefully controlled to prevent electrolysis of the auxiliary electrolyte. The organic reaction will not be reversible so that provision must be made for a different counter electrode reaction.

The example given in table I (Type 5) involves the synthesis of insoluble naphthalene from the more soluble 2-iodonaphthalene by electrolytic reduction. This reaction is essentially free of byproducts. The electrolyte could be sodium sulfate. The current collectors could be platinum or palladium. The counter electrode might be the oxygen anode. An ion permeable membrane should then be used to separate the anode and cathode compartments.

Increasing pH

One can convert a soluble salt of an organic base into its insoluble form by increasing the pH of the solution. This is achieved at the cathode of most electrochemical cells regardless of the nature of the electrochemical reaction: plating out of a metal, dissolution of a nonmetal, or reduction in the valence of an ion. Of course, the presence of such ions could lead to the contamination of the desired crystals. The use of the hydrogen electrode as the cathode will eliminate this contamination. This method is illustrated in table I, Type 6. By this method, many organic bases may be crystallized in a pure form by electrocrystallization. When applying the method in microgravity, no gaseous molecular hydrogen should be allowed to form at the active electrode because this would induce convection. For this reason, the side of the palladium electrode facing the solution should be poisoned; poisoning prevents the hydrogen atoms from combining and forming gaseous hydrogen (ref. 14). In other words the following reaction cannot occur.

$$2H \rightleftharpoons H_2 \tag{3}$$

Instead, the atomic hydrogen diffuses into the palladium metal. As-received palladium foil appears to be poisoned (unpublished).

The ideal operation of the method is illustrated in figure 5; hydrogen atoms are generated at the palladium foil in the cathode compartment by the electric current. Because the hydrogen atoms cannot convert to gaseous hydrogen on the poisoned side, they diffuse through the palladium (in which hydrogen is very soluble) and eventually are liberated on the other side which is not poisoned. The counter electrode could involve the reverse reaction; the source of the hydrogen might be that generated at the cathode as indicated in figure 5. The chamber between the unpoisoned sides of the palladium foils would, of course, have to be charged with hydrogen before the experiment. If the hydrogen is not recirculated, then a constant supply of hydrogen would be necessary. Other alternatives for the counter electrode are the oxygen anode and the sulfite-surfate electrode.

As an electric current is passed though the solution, the anolyte becomes more acidic, and the catholyte becomes more basic. The acid will diffuse into the bulk, and as it contacts soluble ions of the organic base, the insoluble organic base will crystallize. To improve the general method, a membrane should be introduced (fig. 5) between the anode and the cathode compartments. Then, additional but poorly crystalline solid organic base can be present in the anolyte compartment. As a current flows, and the anolyte becomes more acid, the free base will dissolve. The net change will be the conversion of poorly crystallized insoluble organic base in the anolyte to the highly crystalline base in the catholyte. Only a slight concentration and density gradient will occur while current is flowing, and shortly after the current is turn off, the gradients will disappear. The final concentration and density will be identical to their respective initial values.

Amines are the most obvious organic bases to use. Preliminary ground-based experiments are necessary to make a judicious selection. Without such experiments, we have chosen for our example 2-naphthylamine. See table I, Type 6. The solution would thus consist of 2-naphthylamine sulfate in a slightly acid medium. Sodium sulfate should probably be added as an auxiliary electrolyte. The chloride ion should be avoided because of possible reactions with the palladium present in the system.

The urea-urea sulfate system is another example of Type 6 that deserves consideration. The urea crystals formed by this method could be compared with those formed in the 3M Corporation microgravity experiment. Unfortunately, urea itself is quite soluble in water so that the solution would have to be initially saturated with free urea. This would add complications to the system.

Decreasing pH

A similar type of electrocrystallization can be affected by decreasing pH. An insoluble (most probably organic) acid can be made to crystallize near the anode of a cell (table I, Type 7). The experimental apparatus could be essentially the same as that for the crystallization via increasing pH (fig. 5); hydrogen ions are converted to atoms at the cathode, and hydrogen atoms are converted to ions at the anode. The difference between the types involves the product and where it is produced. The solid product is an acid and is formed near the anode because the pH is lowered in this region. Again, one can improve the system by having the poorly crystallized material (the desired acid) present in the counter electrode compartment. In this compartment the pH will increase and the solid acid will be dissolved. The solubility of the acid is due to the formation of one of its ionized salts. Again, the net reaction is one of recrystallization of the acid, and very little disturbance of the density is expected to occur. Many of the general considerations which apply to electrocrystallization via increasing pH also apply here. For instance, the sulfite-sulfate anode might be substituted for the hydrogen anode in the active compartment.

The first acids to consider are the carboxylic acids. However, phenols, the oximes are possible choices. Proper selection requires preliminary earth experiments. The crystallization of benzoic acid (our example) appears to be a good compound with which to begin. See table I, Type 7. The starting solution would be sodium benzoate with perhaps sodium sulfate added as an electrolyte.

Changing an Inorganic Solvent

Passage of an electric current through a solution can remove, add, or change components of the solution and thus change its solvating properties. Decreasing the solvating power of a system is a standard method used for crystallization, as discussed earlier in this report. For such a concept to work in an electrochemical system, a proper solvent-solute combination would have to be found. Moreover, a discussion of the method can only take place in the context of an example.

Schweitzer's reagent is a solution of copper ions complexed in an aqueous ammoniacal solution; this solution will dissolve cellulose. If Schweitzer's reagent is depleted of copper, dissolved cellulose will precipitate. If the process is conducted slowly, crystals of cellulose might form. Copper ions, of course, can be removed from solution electrochemically (table I, Type 8). The crystallization would be controlled by the diffusion of ammoniacal copper ion to the active electrode. In basic solution, the copper would probably plate out as a copper (I) species. One would desire that the copper (I) species would attach itself to the current collector, and the cellulose would crystallize in the bulk of the solution so that the cellulose would not be contaminated by the copper. Because the solubility of cellulose is not necessarily proportional to the copper concentration, the amount of precipitated cellulose is not expected to be proportional to the number of coulombs passed.

One would likely begin by attempting to use the oxygen anode as the counter electrode. It would have to be separated from active compartment by a membrane. The sulfite-sulfate or other anode would change the nature of the Schweitzer's reagent so that the reagent would not act properly as solvent for cellulose.

Changing an Organic Solvent

In a previous section of this report, we discussed electro-organic synthesis (ref. 12). By this method one organic solvent can be converted to another organic solvent, and the solubilty of a solute can thereby be changed. It becomes obvious that this leads to another type of electrocrystallization (table I, Type 9). In such a method an auxiliary electrolyte is required to supply the conducting ions. The crystallization would be controlled by the diffusion of the old solvent to the active electrode and the new solvent away from it. Because the solubility of the desired product is not likely to be a linear function of the solvent composition, the crystallization is not expected to be linearly related to the number of coulombs passed. When the current is shut off, crystallization is expected to continue for some time until the composition of the solution is nearly uniform.

A possible system that one could try is a mixture of water and acetone. The acetone can be reduced electrochemically to isopropanol. The difficulty with the method is the selection of a compound that is soluble in an acetone-water solvent and is less soluble when the acetone is replaced by its reduction product. We refrain from the selection of an specific material in table I (Type 9) and refer to the compound by using the symbol Y.

COMPARISON OF THE TYPES

Evalution of the various types of electrocrystallization for experiments under microgravity conditions is at this time highly subjective. There are many reasons: table I is not complete. The examples given in table I are not necessarily the best ones. Some of the examples have not been tried even under normal gravity conditions. In spite of this, some comments may be made as to which method(s) might be preferable. To make a comparison, much repetition of concepts expressed in the previous sections are unavoidable.

For the most part, the types of electrocrystallization presented in table I are in decreasing order of our knowledge concerning the systems. This can be seen particularly clearly by comparing Types 1 and 9. There is much known about the deposition of metals from the fields of electroforming, battery research, and even quantitative chemical analysis. In contrast, the various aspects of Type 9 in table I are not well known; electro-organic synthesis is still in its childhood. In addition, the effect of changing the concentration of an organic component in water is largely unexplored. Because Type 9 is unexplored, we have not even suggested a candidate crystalline material for this method.

Comments can also be made concerning the troubles that might arise from each method. Obviously if one selects an electrochemical cell that has been tried many times on earth, the electrochemical behavior of such a cell should give us the least trouble under microgravity conditions. This is the general situation for Types 1, 3, and 4 which involve straightforward electrochemical cells. However, the examples chosen for Types 3 and 4 are not as trouble free as other examples that might have been given for these types. For Types 6 and 7, the precipitation reactions are speculative regardless of the example one might have chosen. Needless to say, Types 8 and 9 are the ultimate in speculation. Any reaction of Types 6 to 9 will require much research under normal gravity conditions before it could even be considered for a microgravity electrocrystallization experiment.

Types 1 and 2 are certainly the most direct method of producing crystals electrochemically; as soon as the electron is present at the surface of the metal, an ion is converted to the free metal. The same is likely true for Type 5. The other types, in general, are less direct because the crystallization is the result of a diffusion process.

The order of presentation used in table I also reflects somewhat a decreasing likelihood that the crystallization will be a stoichiometric function of the current. For Types 1 and 2, the number of equivalents of product will be equal to the equivalents of current used. In Type 3 and 4, this may not be precisely correct due to some solubility of the product. Type 5 may deviate even more from stoichiometric behavior because of possible side reactions. Types 6 and 7 can result in a temporary change in pH near the active electrode without immediate crystallization of the product because of a depletion of reactants near the electrode. Moreover, solubility of the product can also add to the deviation. Types 8 and 9 may be completely void of stoichiometry because solubility of the product is not likely to be a linear function of the composition of the solvent.

The initial difficulty with all the types is the selection of a good example. Here "good" means simple, one that is well understood, one with a minimum of side reactions, and one that would yield of product of interest. We cannot claim that any of our examples possess all the requirements of being "good." At present, the author believes that Type 3 has the greatest potential for success. If a few more specific details were known about the poisoned hydrogen electrode, Types 6 and 7 might head the list.

SUMMARY OF THE ADVANTAGES OF ELECTROCRYSTALLIZATION

Electrocrystallization in microgravity can be for the most part free of convection; crystallization occurs via diffusion of molecular of ionic species. This is the prime advantage of electrocrystallization in space.

The effect of the still present low gravity and gravity jitter would be minimal because the initial density of the liquid would be homogeneous, and the density gradient can be kept at a minimum during an experiment. Moreover, any slight gradient could be aligned parallel to the gravity field on earth with the greatest density at the bottom.

It follows that experiments to be performed under microgravity could be first performed under normal gravity in the same container; and a direct comparison of microgravity with unit gravity conditions can be made. The major difference would be the convection that should be produced on earth due to the difference in the density between the crystals and that of the electrolyte.

Let us now return to the reason for minimizing convection as presented in the Introduction. It is to slow down the crystallization process because it is the slow crystallization which produces pure and perfect crystals. When the electrocrystallization process is reexamined, one can see that the average rate of crystallization can be reduced to any desired rate merely by using a lower current (for the average rate of crystallization is a direct function of the current). This fact increases the usefulness of electrocrystallization but does not necessarily eliminate the need to reduce convection because without minimal convection the rate of crystallization may not be a well-behaved (monotonic) function of the time.

Comparison with Other Microgravity Methods

It is now useful to compare electrocrystallization with the 3M Corporation microgravity method for the crystallization of urea (ref. 9). In an electrocrystallization experiment, diffusion will not occur until the electrochemical potential is turned on; in the 3M experiment, diffusion does not occur until the valves are opened by a computer controlled motor. The turning on of the current in an electrocrystallization experiment should cause no convection; however, the opening of the values in the 3M experiment may cause some. Initially, no density gradient exists in the electrocrystallization system; thus no convection can occur due to the microgravity field or gravity jitter. However, in a 3M experiment, a large initial density difference (15 percent) does exist so that microgravity will induce at least some convection.

This density gradient in the 3M experiment continues to induce some slight convection during the entire experiment. There will also be a density gradient generated in the active compartment during an electrocrystallization experiment, but this gradient should be far less in magnitude than the one in the 3M experiment, and should cause less convection. Gradients, convection, and mechanical mixing are not permitted in the 3M experiment but are permitted in the counter electrode compartment in an electrocrystallization experiment. These will not induce convection in the active electrode compartment. In all microgravity experiments, the effects of microgravity can be reduced by proper orientation of any density gradient with respect to the microgravity field (parallel). Nevertheless, the greater the density difference, the greater will be the resulting fluid convection.

Previous to the landing in an electrocrystallization experiment, the electric current can be shut off, so that crystallization will be essentially stopped. In the 3M experiments, the valves could be closed before landing, although they were not in the shuttle experiment. Even if the valves were closed, some toluene would be in the compartment with the solution of urea in methanol. This would result in an ever increasing rate of convection of the toluene within the compartment as the shuttle goes through its landing procedure.

It is true that electrocrystallization is not completely free of convection effects in microgravity. But it should involve far less interference from convection than the simple three-compartment diffusion methods used in Spacelab-1 (refs. 6 to 8) and in the 3M shuttle experiments (ref. 9).

Lastly, note that not every crystalline material can be made by every method. Some crystals that can be made by the 3M compartmental diffusion method cannot be made via electrocrystallization, and vice versa. Thus, every type of crystallization technique may have an application in a particular situation.

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TABLE I. - TYPES OF ELECTROCRYSTALLIZATION

1. Deposition of a metal

$$Cu^{+2} + 2e^- \longrightarrow Cu\downarrow$$

2. Deposition of a conducting compound

$$\text{precursor of (a)} + 2e^- \longrightarrow (a)\downarrow$$

(a) = hydrogen bis(phthalocyaninato) neodymium(3)

3. Inorganic reduction

$$Ni \longrightarrow Ni^{+2} + 2e^-$$

$$Ni^{+2} + 2\ \text{dimethylglyoxime} \longrightarrow$$

$$2\ H^+ + \text{nickel dimethylglyoxime complex}\downarrow$$

4. Inorganic oxidation

$$I + 2e^- \longrightarrow 2I^-$$

$$HgCl_2 + I^- \longrightarrow Cl^- + HgClI\downarrow$$

5. Organic synthesis

$$2\ \text{2-iodonaphthalene} + H^+ + 2e^- \longrightarrow 2\ \text{naphthalene}\downarrow + I_2$$

6. Increasing pH

$$H^+ + e^- \longrightarrow H(Pd)$$

$$\text{2-naphthylamine cation}^+ \longrightarrow H^+ + \text{2-naphthylamine}\downarrow$$

7. Decreasing pH

$$H(Pd) \longrightarrow e^- + H^+$$

$$\text{benzoate ion}^- + H^+ \longrightarrow \text{benzoic acid}\downarrow$$

8. Changing inorganic solvent

$$Cu(NH_3)_4^{+2} + e^- + H_2O \longrightarrow CuOH\downarrow + 3NH_3 + NH_4^+$$

$$\text{cellulose (dissolved)} \longrightarrow \text{cellulose crystals}\downarrow$$

9. Changing organic solvent

$$\text{acetone} + 2H^+ + 2e^- \longrightarrow \text{isopropyl alcohol}$$

$$Y\ \text{(dissolved)} \longrightarrow \text{crystals of } Y\downarrow$$

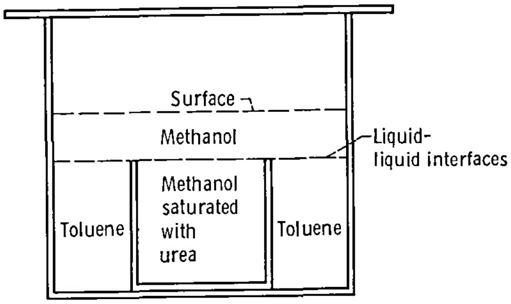

Figure 1. - Schematic for the crystallization of urea under normal gravity.

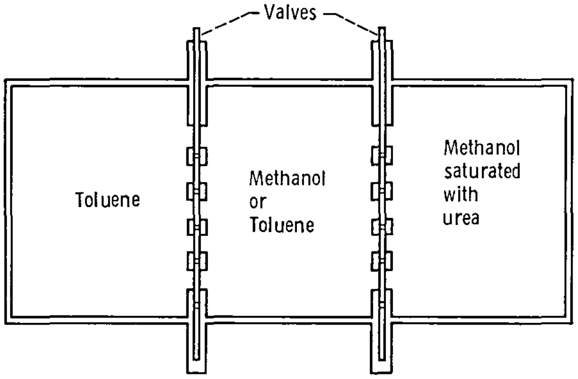

Figure 2. - Schematic of 3 M's setup for crystallization of urea in microgravity.

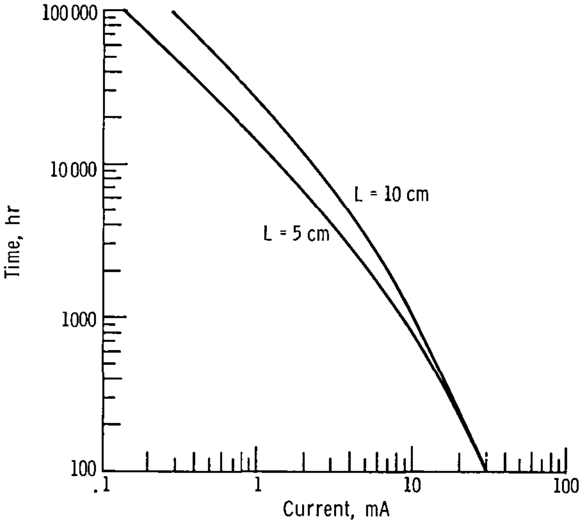

Figure 3. - Maximum time at specified current. Cell diameter = 5 cm; L = compartment length; concentration of diffusing species = 5 N; diffusion coefficient = 5×10^{-6} cm^2/sec; equivalent weight of product = 50.

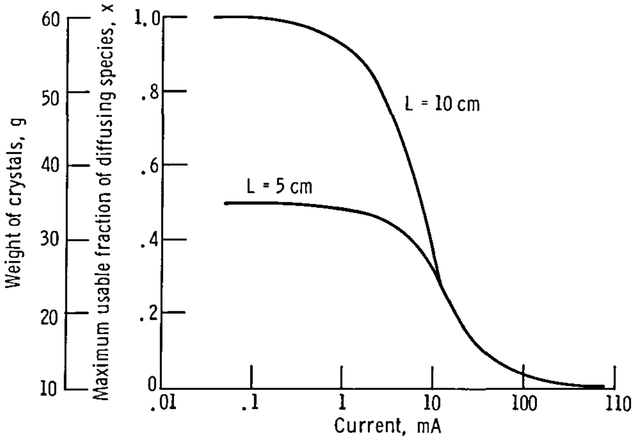

Figure 4. - Maximum yield of crystals as function of current. (Cell diameter = 5 cm; L = compartment length; concentration of diffusing species = 5 N; diffusion coefficient = 5×10^{-6} cm^2/sec; equivalent weight of product = 50.)

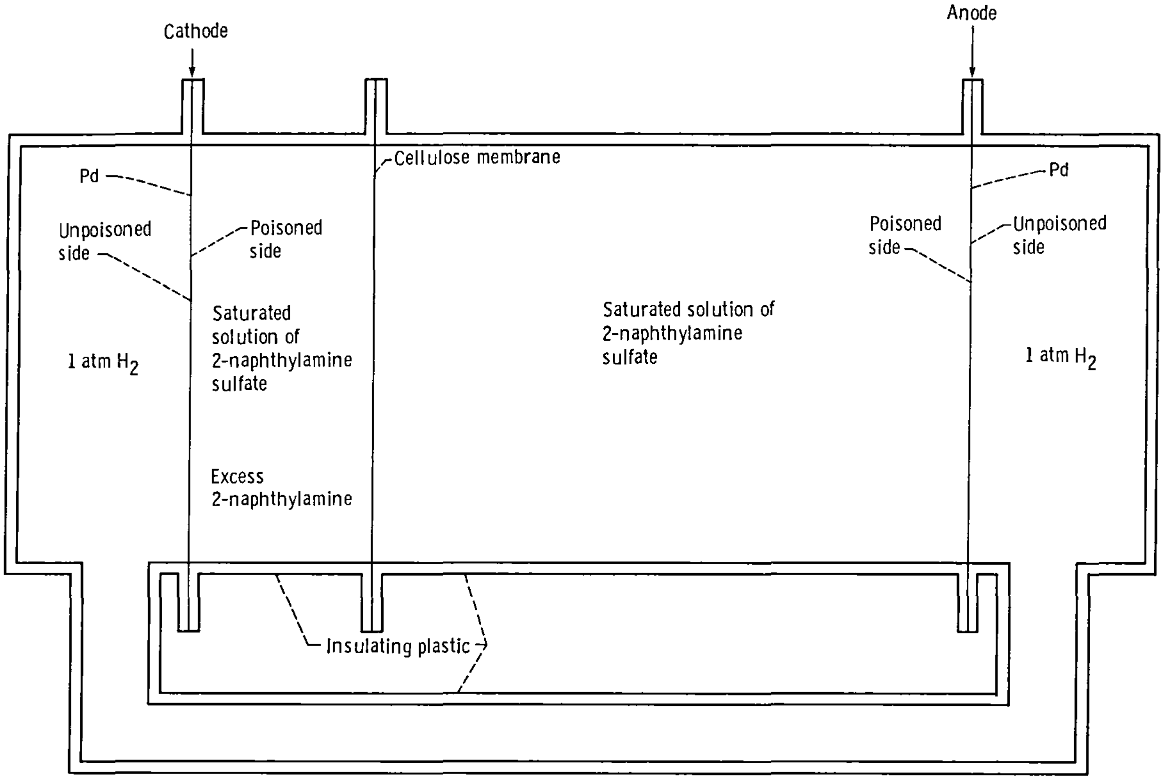

Figure 5. - Schematic for crystallization of 2-naphthylamine in microgravity (compartments are clamped together).

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16. Abstract

Electrocrystallization under microgravity conditions is proposed as a potential method of crystallization that would be almost completely free of fluid convection. Such crystallization may result in purer, more perfect, and larger crystals than is possible under normal gravity conditions. Observations made and data collected during the crystallization process under convection-free conditions should add to our knowledge of the crystallization process. The proposed method would allow easy comparison of crystals grown in space with those grown under normal gravity conditions. Nine types of electrocrystallization are presented: an example of each is discussed. Electrocrystallization is compared with the compartmental crystallization method used by 3M Corporation in recent shuttle experiments.

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