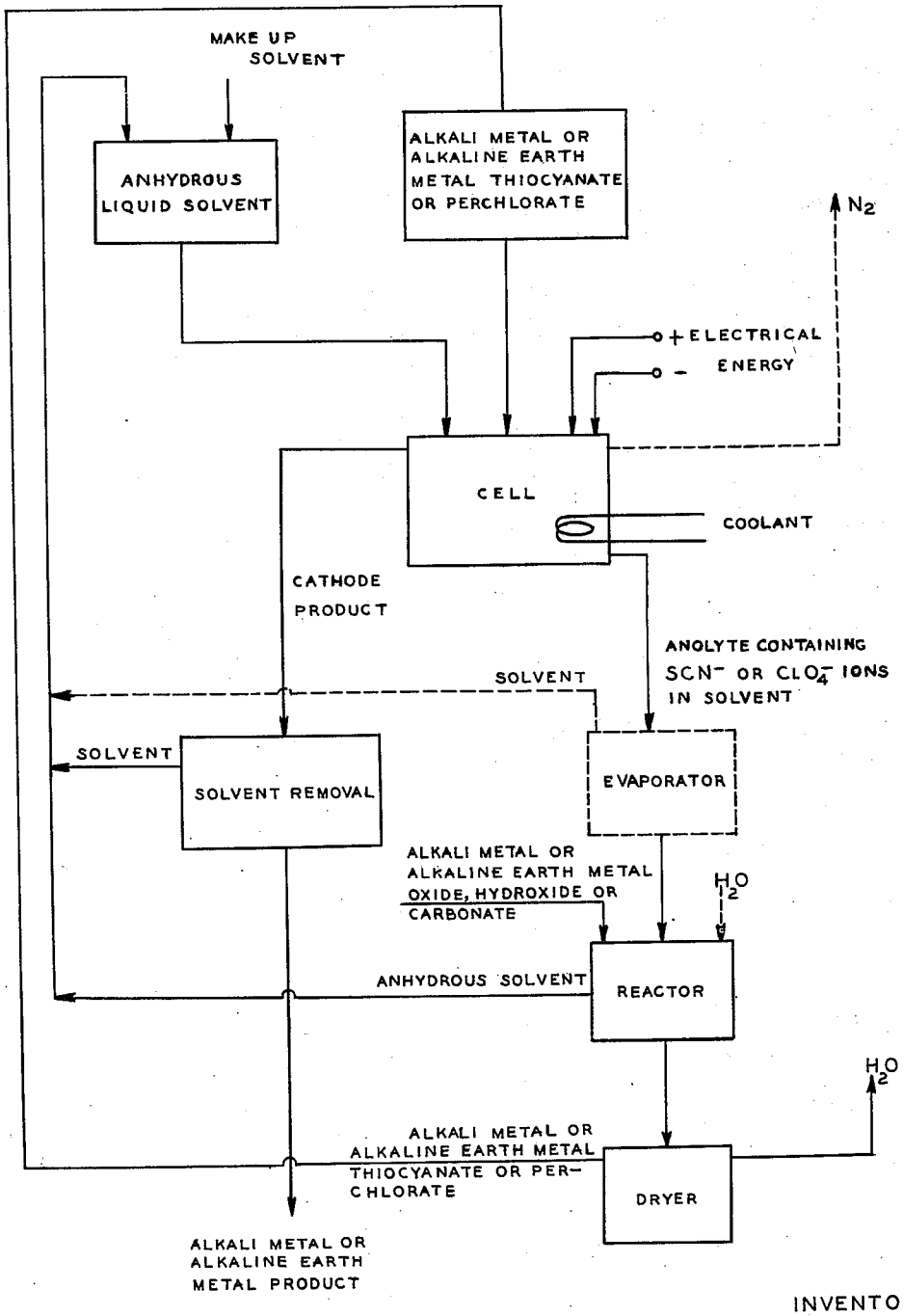
Oct. 28, 1952 L. J. MINNICK ET AL 2,615,838

ELECTROLYTIC PROCESS OF PRODUCING ALKALI AND ALKALINE EARTH METALS

Filed May 27, 1946



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Patented Oct. 28, 1952

2,615,838

UNITED STATES PATENT OFFICE

2,615,838

ELECTROLYTIC PROCESS OF PRODUCING ALKALI AND ALKALINE EARTH METALS

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Application May 27, 1946, Serial No. 672,704

8 Claims. (Cl. 204—59)

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The present invention relates to a process for the production of alkali and alkaline earth metals, and more particularly it relates to a process by which alkali and alkaline earth metals may be economically prepared by the electrolysis of a non-aqueous liquid comprising anhydrous liquid ammonia, methylamine, ethylamine, or pyridine combined with a salt of the metal.

The processes at present available for the preparation of alkali and alkaline earth metals are generally divisible into two types—first, the methods involving chemical reactions and, second, those employing the use of an electric current. The former type of method involves reduction reactions conducted in retorts under special atmospheres or high vacuum, and many problems are involved in the commercial operation of this type of process. The latter type of method involves, so far as commercial practice is concerned, chiefly the electrolysis, in the molten state, of an anhydrous salt of the metal.

Other methods for producing alkali and alkaline earth metals by electrolysis in both aqueous and non-aqueous solvents have been suggested. Usually, the use of an aqueous solution is impractical since there is a strong tendency for hydrogen to be evolved at the cathode, and the release of hydrogen is accompanied by decomposition of the solvent and the conversion of the metal into the hydroxide. Several ideas have also been described in which a co-deposit of hydrogen and the alkali metal is formed at the cathode during the electrolysis of an alkali metal salt dissolved in a non-aqueous solvent, such as propyl or other higher alcohol. In such cases, high voltage, with consequent high power consumption, is required and the co-plating of the hydrogen with the metal is also undesirable.

One object of the present invention is to provide an economical process for the production of alkali and alkaline earth metals by the electrolysis of a non-aqueous liquid comprising anhydrous liquid ammonia, methylamine, propylamine, or pyridine combined with a salt of the metal.

A further object of the invention is to provide an electrolytic process for the preparation of alkali and alkaline earth metals which may be conducted at relatively high current densities and with relatively low power consumption to produce a cathode product substantially free from contamination by unelectrolyzed salt.

Another object of the invention is to provide a method for producing alkali and alkaline earth metals as the cathode product, in conjunction with the production of an anode product that may readily be employed to prepare an alkali or alkaline earth metal salt available for recycling in the process.

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Another object of the invention is to provide a method for the production of alkali and alkaline earth metals from salts of the metal that can be prepared without difficulty from inexpensive raw materials.

A still further object of the invention is to make available a process for the electrolytic production of alkali and alkaline earth metals from salts thereof even when the salts are not anhydrous.

Still another object of the invention is to provide a process by which a substantially pure solution or paste, comprising the alkali or alkaline earth metal and the solvent of the electrolyte, may be prepared, which solution or paste may be used in the industries or may be readily converted into an alkali or alkaline earth metal of a high state of purity, merely by evaporation of the solvent.

Other objects, including the provision of a cyclic chemical and electrochemical process for the preparation of alkali and alkaline earth metals, will be apparent from a consideration of this specification and the claims.

The process of the present invention is applicable for use in the production of any of the various alkali or alkaline earth metals, namely, lithium, sodium, potassium, caesium, rubidium, calcium, strontium, and barium, and of alloys or mixtures thereof.

In accordance with the invention, a cathode product comprising an alkali or alkaline earth metal substantially uncontaminated by unelectrolyzed salt is prepared by the electrolysis of an electrolyte to form a cathode and an anode product. The electrolyte is a non-aqueous liquid comprising an anhydrous liquid selected from the group consisting of ammonia, methylamine, ethylamine, and pyridine combined with a salt of the metal selected from the group consisting of the perchlorate and thiocyanate, and in such an electrolyte the concentration of salt therein provides a solution in which the cathode product is substantially insoluble. The cathode product, as will be further discussed, may be a bronze liquid, a paste, or the metal itself. Since the liquid or paste is substantially insoluble in, and has a lower specific gravity than, the electrolyte, it floats thereon and, therefore, the product, substantially free from unelectrolyzed salt, may be easily separated from the electro-

lyte. The anode product comprising the anhydrous liquid, the anion of the metal salt and its associated solvated proton is separated from the cell, and the anion and its associated solvated proton are reacted with the oxide, hydroxide or carbonate of the desired metal to form the corresponding metal salt. This salt, in substantially anhydrous form, is then used as source material in the process.

The process of the present invention will be more clearly understood from a consideration of the drawing which illustrates the process by means of a flow sheet diagram.

Referring to the drawing, there is shown an electrolytic cell, the cathode and anode of which are connected to a source of electrical energy. The cell is equipped with cooling means. The anhydrous liquid solvent of the type described herein is fed to the cell, and the alkali metal or alkaline earth metal thiocyanate or perchlorate obtained as described herein is also fed to the cell. During electrolysis there is formed a cathode product comprising the desired metal, and anode product. Nitrogen may also be formed when ammonia is present. The cathode product is removed from the cell and the metal separated from adhering solvent. The solvent may be recycled to the cell as shown. The anode product comprises solvent and the thiocyanate or perchlorate anion, and the anion is converted to the alkali metal or alkaline earth metal salt by reaction between the anion and the oxide, hydroxide or carbonate of the desired alkali metal or alkaline earth metal. This reaction may take place in the cell itself as more fully discussed hereinafter, or may take place outside the cell as shown in the drawing and as also more fully discussed hereinafter. If this reaction takes place outside the cell, the reaction medium may comprise the entire anode product to which water may be added, or excess solvent may first be removed, as in an evaporator, and recycled, following which the remaining anode product is mixed with water which serves as the reaction medium. Any of the anhydrous solvent remaining after the reaction may be recycled for re-use in the process. In any event, the anion is converted to the alkali metal or alkaline earth metal salt which is dried and reused in the process. In view of the fact that some of the solvent may be destroyed during the electrolysis, make-up solvent may be added as needed. The process generally described above will be described more in detail hereinafter.

In place of using a single anhydrous liquid, a mixture of two or more liquids may be employed, for example, liquid ammonia containing an alkylamine having less than 8 carbon atoms, or pyridine. The solubility of the metal formed as the result of the electrolysis in such mixed liquids is usually less than it is in the case of liquid ammonia alone, and the paste, hereinafter described, forms more readily. Other materials which will not interfere with the desired electrolytic action may be added to the solvent, if desired, provided that they do not decrease the amount of the salt in combination with the anhydrous liquid to such an extent that the desired concentration of the salt cannot be obtained.

The use of an anhydrous liquid of the type described increases the advantages of the use of a non-aqueous medium for the electrolysis of alkali and alkaline earth metal salts and overcomes the objections that have been encountered in prior methods. Solubility of many of the metal salts is extremely high in this type of liquid and, as will be discussed, concentrations can be reached in excess of any requirements needed for the economic production of the metal. Furthermore, by employing the method described herein, the presence of water does not prevent the production of the metal and the process eliminates the water from the non-aqueous liquid, as will be further discussed. While the elimination of the water consumes a small amount of electrical energy, the cost is nominal and the effect on the operation of the cell is slight. Furthermore, the cost of a liquid, such as anhydrous liquid ammonia, is low and the material is available in large quantities.

For convenience hereinafter, the process will be described in connection with the use of anhydrous liquid ammonia since this is the cheapest of the non-aqueous liquids available for use in the present process, and for this and other reasons, it is used in the preferred embodiment of the invention. Furthermore, while, if desired, alloys or mixtures of two or more of the alkali or alkaline earth metals may be prepared from a solution of two or more of the salts of the desired metals in the anhydrous liquid, the invention will be discussed from the standpoint of the preparation of a single alkali or alkaline earth metal.

As stated, the concentration of salt in the anhydrous liquid is an important factor and in the process of the invention, the concentration of salt in the electrolyte provides a medium in which the cathode product is substantially insoluble. This permits the production of a cathode product which is substantially free from contamination by unelectrolyzed salt, and the cathode product removed from the cell in the process of the present invention is to be contrasted with the impure cathod product which would result if a low concentration of salt in the liquid ammonia solvent were to be used. Such impure solutions are blue in color and comprise a small amount of metal, unelectrolyzed salt, and solvent. As will hereinafter be discussed, the desired concentration is preferably obtained by the use of the alkali or alkaline metal salt alone, but if desired, the required concentration may be obtained by the use of another salt in conjunction with the alkali or alkaline earth metal salt.

The cathode product separated from the unelectrolyzed portion of the electrolyte may be in the form of a liquid or a paste or may be the metal itself, depending on the concentration of the electrolyte in contact with the cathode product and the operating conditions of the cell. The liquid is believed to be a blend or solvated compound between the anhydrous ammonia and the metal, and an excess of ammonia may be present. In higher concentrations, some of the metal may be in suspension or in colloidal solution in the compound, and these liquids may contain up to about 90% of the metal, the balance being ammonia. When the concentration is still higher, the paste is formed and in this case, it is believed that metal resulting from the evaporation of the ammonia from the metal-ammonia blend or compound is associated with that compound, and the concentration of the metal in the paste usually exceeds about 90% and may be as high as 99%. When the concentration of salt in the electrolyte in contact with the cathode product is still higher, the metal itself will plate out on the cathode.

Regardless of the physical state or the color of cathode product removed from the cell, it will be substantially free from contamination by unelectrolyzed salt. In the usual and preferred practice of the invention, the cathode product removed from the cell possesses a metallic lustre and will usually be of a yellow or bronze color although in some instances it may possess reddish characteristics. The term "bronze", is used herein to designate such coloration and to distinguish it from a liquid possessing a blue coloration. The paste when obtained may be colored reddish brown, dark brown, or even black, and the metal will possess the characteristic metallic lustre.

Both the liquid and paste cathode products are insoluble in and of lower specific gravity than the electrolyte and, therefore, float on the electrolyte and may be easily separated therefrom. In the case of the liquid, it may easily be separated from the electrolyte by siphoning, or decanting, or by the application of ammonia gas pressure, or by any other suitable procedure. It is to be understood that in order to insure the substantially complete removal of the bronze liquid, a portion of any blue underlying liquid may also be removed from the cell. The bronze liquid may then be separated from the blue liquid during which an additional amount of the bronze may be formed as the result of the evaporation of the anhydrous liquid. The paste forms as a scum on the surface of the electrolyte and may be removed by mechanical means from the electrolyte. The metal, when formed, will adhere to the cathode and may be removed by scraping or other expedient and, if desired, the cathode may be made removable to facilitate this step. If desired, a small amount of liquid ammonia or like solvent may be added to the cathode compartment of the cell to convert the metal to the paste or bronze liquid or the paste into the bronze liquid to expedite the removal of the cathode product from the cell.

The paste may be formed by the use of a concentration of the electrolyte substantially higher than that required to produce the bronze liquid or by the evaporation in the cell of a portion of the solvent from the bronze cathode product. Likewise, the metal may be formed by the use of an electrolyte of a higher concentration than that required to form the paste, or it may be formed by the evaporation in the cell of the solvent from the paste or bronze liquid. The metal or paste is more difficult to remove from the cell than the bronze liquid, but the use of a concentration of salt sufficient to provide a metal or paste has the advantage that the cell can be operated at substantially higher temperature, since the higher concentrations of salt in the solvent causes a corresponding raising of the boiling point of the electrolyte.

In any event, as stated, the concentration of salt in ammonia is sufficient so that the cathode product removed from the cell is substantially insoluble in the electrolyte and is, therefore, substantially free from contamination by unelectrolyzed alkali or alkaline earth metal salt. To meet these requirements, the concentration of salt in the liquid will provide a cathode product in the form of a bronze liquid or a paste or a metal.

Referring further to the concentration of salt in the ammonia, the molar concentration will be where the cathode product is collected prior to removal, that is, where the electrolyte is in contact with the cathode product, in general, at least about 2 molar (2 mols of salt in a litre of ammonia) and preferably will exceed about 3 molar concentration. In specific instances, the concentration may be about 4 molar or even higher. When the concentration is above about 4 molar, for example, 4.2 molar when sodium perchlorate is the salt employed, the metal is usually formed. The concentration may, in fact, by any value up to the saturation point of the salt in the ammonia, and even if the salt is used in an amount in excess of the saturation point, the electrolysis will proceed satisfactorily since in this case the excess salt merely sinks to the bottom of the cell. As the concentration is increased, the concentration of the metal in the cathode product increases, as may be noted by an increase in the viscosity of the bronze liquid, until, in fact, the product obtained is in paste or metallic form as has been described. While the concentrations given are generally applicable for the salts of the various metals, the compounds of higher molecular weight can be generally used in lower concentrations than the compounds of lower molecular weight.

It has been indicated above that the freedom of the cathode product from contamination by non-electrolyzed salt is dependent upon the concentration of salt in the ammonia at the point where the cathode product is collected. Preferably, the entire electrolyte is of a concentration required to obtain a salt-free cathode product. However, so long as the concentration at the point where the cathode product is collected is sufficient so that the cathode product which accumulates is a bronze liquid, a paste, or a metal, the concentration of the salt in the ammonia in the remainder of the cell may be somewhat lower; for example, this is possible when evaporation of ammonia is taking place at that portion of the cell where the cathode product is collected. Furthermore, a portion of the electrolysis may be conducted in one cell and the electrolyte may then be delivered to a second cell, with or without further adjustment of the concentration. In this case, it is the concentration of salt in the electrolyte of the second cell which determines the operation and it is the electrolysis in the second cell, therefore, which embodies the process of the present invention.

As stated, the required concentration of the salt is preferably provided by a salt of the alkali or alkaline earth metal to be obtained as the result of the electrolysis. If desired, however, this salt may be supplemented by the addition of another salt so that the concentration is the result of the presence of both salts. Since, however, the yield of the metal that is desired is directly proportional to its concentration, no advantage is obtained by the introduction of a second salt and unless the salt is an ammonium or other non-metallic salt, there will be co-plating of two metals so that the cathode product, except when an alloy is desired, will be contaminated by a second metal. When liquid ammonia is used, the addition of an ammonium salt, particularly to the cathode compartment, is usually not desirable since such salt increases the acidity in the cell and, among other things, decomposes the cathode product. An exception, however, is ammonium thiocyanate and other salts which do not react in this way.

As stated previously, the electrolyte comprises an anhydrous liquid, such as ammonia, combined with a salt of the metal to be formed. The liq-

uid is to be distinguished from a simple solution in which a low concentration of salt is dissolved in liquid ammonia. These differences between the two types of liquids may be noted, for example, if an alkali or alkaline earth metal is added thereto. In the case of liquid of the type used in the present invention, a bronze liquid will be formed upon the surface of the liquid by a reaction between a small amount of the ammonia in the liquid and the metal, such bronze liquid being immiscible in the liquid. When, however, an alkali or alkaline earth metal is added to a simple solution in which a low concentration of salt is dissolved in ammonia, the metal will dissolve in and be distributed throughout the liquid, providing a blue coloration thereof.

The salt employed in producing the electrolyte is selected from the group consisting of the perchlorates and the thiocyanates. These salts are stable and easy to prepare and may be obtained in an anhydrous state, if desired, by simple drying procedures. Furthermore, the ammonium perchlorate or thiocyanate formed at the anode may be readily reconverted into the alkali or alkaline earth metal perchlorate or thiocyanate by reaction with the oxide, hydroxide or carbonate of the alkali or alkaline earth metal. This reconversion may take place in the cell by adding the oxide, hydroxide or carbonate to the anolyte and the formation of the alkali or alkaline earth perchlorate or thiocyanate then proceeds simultaneously with the electrolysis of the salt in the same solution. However, since some water is formed by the reaction which requires additional electric current to dissociate it into its constituent parts, it will usually be desirable to treat the anolyte with the alkali or alkaline earth metal compound in a separate step. The halides do not possess the requisite solubility in ammonia or other solvent to permit their use as the primary source of alkali or alkaline earth metal.

In the preferred embodiment of the invention, an anhydrous or substantially anhydrous salt is employed. However, limited amounts of water may be associated with the salt, if desired, without seriously affecting the reactions that take place in the electrolysis of the salt, due to the fact that, as an initial step and before the metal plates out, the cell will purge itself of water. In purging itself of water, electric current is required and a sludge of the hydroxide of the metal will be formed. Because of the loss of materials and energy and the introduction of foreign solids in the cell which eventually require removal, the use of a salt containing as little water as practicable is recommended. However, since the amount of current is small, and an extended period may elapse before the sludge must be removed, it may, in some cases, be less expensive to use a salt with which a small amount of water is associated and to remove the water electrolytically in the cell, than it is to prepare a substantially anhydrous salt. The type of salt employed and the ease with which it may be dried are obviously the governing factors. The water content of the salt should be kept lower in the case of alkaline earth metal salts than in the case of alkali metal salts due to the fact that there is a greater tendency for the alkali earth metal to react with the solvent to form amides or the like, the reaction being catalyzed by the presence of the hydroxide formed when the cell purges itself of water. The important point to be noted in connection with the water is that, in the present invention, a reasonable amount of water can be present in a non-aqueous electrolyte and not interfere with the preparation of metals that are higher than hydrogen in the electromotive series. This is unique and is to be compared with the attempts that have been made heretofore to produce metals of this type in such solvents as acetone, acetonitrile and phosphorous oxychloride.

In general, the introduction of an alkali metal salt containing more than 5% of water is not recommended and if water is associated with the salt, it is advantageously below 1%. In the case of the alkaline earth metal salts, the use of a salt containing less than about 1% of water is desirable and, the salt advantageously contains less than about 0.5%. The alkali and alkaline earth metal salts, if they contain an excessive amount of water or if the use of an anhydrous salt is desired, may be dried by any suitable method, for example, by the methods described hereinafter in conjunction with the treatment of the salt obtained from the anolyte prior to its re-use in the cell.

The cell may be of any suitable design but is sealed by a lid or cover and is provided with a vent which permits the solvent vapor, the nitrogen generated at the anode and any other non-condensable gas to pass out of, but will not permit moisture to enter, the cell; for example, a mercury trap or a trap containing a moisture-absorbing material inert to ammonia may be used. The cell may be constructed of a wide variety of relatively cheap and available materials, for example, iron or steel, glass or enamelled material, rubber or synthetic rubber-like materials, and ceramics. This advantage itself makes the process of the present invention highly desirable as compared to other methods in use for the production of alkali and alkaline earth metals.

For most operations, it will be desirable to maintain a temperature below the boiling point of liquid ammonia at atmospheric pressure (—33.35° C.) and, therefore, the cell will usually be provided with refrigeration means, for instance, refrigeration coils around the cell, or in the electrolyte, or within the electrodes, the last named being preferred as the heat is then removed at the point of its chief source. If desired, the cell may be a pressure cell, in which event refrigeration is not required, or the cell may be operated under conditions where the conversion of the liquid ammonia into the gaseous phase is relied upon to provide self-refrigeration of the cell. While in most operations, the temperature of the cell, as stated, will be maintained by refrigeration means below the boiling point of liquid ammonia, the electrolysis can be conducted at much higher temperatures, for instance, where a very high concentration of the alkali or alkaline earth salt is employed so that the cathode product will be formed as a paste or a metal, temperatures as high as 30° C. or higher may be used. Thus, a solution of sodium perchlorate of relatively high concentration, for example 4.2 molar has been employed with the result that bright metallic sodium metal has been plated out on and adhered to the cathode.

The use of relatively low temperatures of operation, as contrasted with those required in the processes employing a bath of molten salt, possesses several advantages in addition to the saving of the energy required to maintain the bath in a fused state. For example, in the processes of the present invention, there is no difficulty

encountered due to sublimation or vaporization of the metal from the cell and there is no danger of losing metal by burning which is a hazard in the production of metals from molten baths. Furthermore, the use of relatively low temperatures permits the cell to operate substantially uniformly and without local electrode resistance, and the uniformity of operation is enhanced by operating at a low temperature, for example, below the boiling point of liquid ammonia.

The cell may, except as noted, be a conventional electrolysis cell with a cathode and an anode, and the electrodes may be of any shape desired, such as flat sheets, rods, cylinders, or the like. Since in most instances, the anode product will be reactive with the cathode product, a permeable diaphragm, such as a porous ceramic sheet, will usually be employed to divide the cell into cathode and anode compartments. In the case of the thiocyanates, however, where there is little or no tendency for reaction with the cathode product, the use of a diaphragm is not required.

The cathode may be any conductor, for example, platinum, iron, silver, copper, carbon, and the like. The anode is preferably made of a material which is substantially non-reactive toward the anode liquor such as platinum, electrolytic carbon, boron, zirconium, or tantalum. Of this group, carbon is the preferred material. The anode, however, may, if desired, be of the type that is reactive with the anolyte, for example, an iron, nickel, copper, zinc, or aluminum anode may be used. This second type has not only the disadvantage that it is consumed relatively rapidly, but also that, when it is employed, the anolyte containing the ammonium salt will be contaminated by a second salt which must be removed in an additional step before the values present in the anolyte may be used as the cell feed.

Referring to the electrical operating characteristics of the cell, while the current density is immaterial so far as operability is concerned and the cell may be operated at any current density desired, it has been found that the current densities are lower than required in aqueous systems. This is important from the standpoint of economy of operation and the dimensions of the cell. In a typical case, it is entirely feasible to operate cells in the commercial production of the metal at about 10 to 100 amperes per square decimeter. Likewise, the voltage may be varied as desired, but since the amount of voltage is a factor of the power cost, it is advantageously kept as low as feasible and it has been found that the voltage may be about half of that required in other types of processes making the same metals. In a typical case using current densities with the range mentioned, the voltage may be as low as 4 volts.

As stated, the cathode product may be readily separated therefrom, either periodically when a sufficient amount has been produced or continuously. The cathode product if a bronze liquid or a paste may be readily processed to obtain the free substantially pure metal, merely by removing the ammonia associated therein by evaporation. In the case of metals of low melting point such as sodium, lithium, or potassium, this is readily accomplished by evaporation at a temperature sufficient to produce the metal in liquid state. It may also be accomplished by evaporating the ammonia at a low temperature which results in a spongy solid mass of metal. This can be melted to form a homogeneous mass by the application of heat. The metals which possess high melting points, for example calcium, strontium, and barium, may generally be most readily recovered from the bronze liquid or paste by evaporation in a vacuum still operating at a temperature sufficiently high so that the metal can sublime and be recovered on a cooled condenser in a section of the still. The recovery in this fashion overcomes the difficulty of producing the metal in a pyrophoric state which is usually the case when metals of high melting point are recovered by ordinary evaporation procedure.

A further method that may be employed for the separation of the metal from the liquid product is to precipitate the material out chemically. This, in general, requires that the precipitating agent be miscible with the solvent present in the liquid, although this is not required in all cases. If a paste is obtained as the cathode product or if the bronze solution is too viscous for this purpose, additional amounts of solvent may be used to convert the product into a thin bronze or even a blue solution. Thus, for example, a solution of calcium in liquid ammonia in the form of a blue solution due to the addition of liquid ammonia to a calcium bronze liquid or paste may be treated with toluene to precipitate the calcium from the solution in the form of a spongy mass. A second example of this type of procedure is the precipitation of lithium in finely divided form from a lithium bronze solution in liquid ammonia by the addition of an amine, such as propylamine, in which the metal is substantially insoluble.

It is to be understood that no limitation is to be placed on the method of recovering the metal from the bronze liquid or paste and generally the method employed will be determined by the economics and the use for which the metal is produced. In some instances, for example, a highly pyrophoric finely divided metal may be desired, and in this case, a method of producing the metal is employed which results in a physical state corresponding to the desired form.

Furthermore, the liquid or pasty cathode product, especially in liquid form, may be used in the production of alloys in a chemical reaction. In the production of alloys, for example in the preparation of lithium plumbide, lead may be reacted with the lithium bronze solution in liquid ammonia, and the ammonia subsequently evaporated. Alloys of various alkali and/or alkaline earth metals may also be prepared merely by mixing solutions of the desired metals followed by evaporation of the ammonia. The liquid or pasty cathode product also possesses a high degree of reactivity and may, therefore, be used directly in chemical reactions, for example, as a powerful reducing agent.

The liquid or pasty cathode product may be handled without difficulty and the conditions of its storage will depend on the particular metal. For example, the product may be stored in glass or enamelled containers, a simple form of stopper, such as cork or ground glass, being employed, or in iron containers, such as cast iron retorts, steel cylinders, and the like. The product is relatively stable and in some instances, for example, a lithium product, can be kept at ordinary temperatures. In other instances, for example, for a sodium product, where there is a tendency for ammonia to be released from a liquid bronze solution if the temperature is raised appreciably, for example 5° to 10° C., which sometimes occurs

when the material is stored for long periods of time in a room, a refrigerated or water-cooled container or compartment may be employed to store the material. The product may be stored in pressure containers, if desired. By the use of cooled containers or pressure vessels, the ammonia or other solvent content of the product may be increased, for example, the use of such containers or vessels is recommended when a blue solution is prepared from the bronze liquid or the paste.

Referring to the formation of the anolyte, the anions of the alkali or alkaline earth metal salt during the electrolysis move toward the anode and when the electron charges of the anions are given up, the anions, in the case an inert anode is used, react with ammonia to form the ammonium salt with the concurrent release of nitrogen gas. This may be represented by the following equation where A^- is the anion of the metal salt:

$$6A^- + 8NH_3 \rightarrow 6NH_4A + N_2 \quad \text{(minus 6 electrons)}$$

Thus, it is evident that during the electrolysis a portion of the solvent is decomposed, and since the solvent must be made up by adding additional solvent, the use of ammonia is recommended due to its cheapness and availability.

The ammonium salt formed at the anode dissolves in the ammonia and thus an anode product is produced which can readily be re-processed to prepare additional cell feed. To illustrate this, the following well-known designation of acid, representing the dissociation of a strong acid in any solvent, must be employed:

$$HA + S \rightarrow SH^+ + A^-$$

where HA represents the acid of any anion A, where S represents any solvent, where SH^+ represents the solvated proton, and where A^- represents the acid anion. In the case of ammonia, the equation may be written as follows:

$$HA + NH_3 \rightarrow NH_4^+ + A^-$$

Therefore, it is evident that the addition or the formation of any ammonium salt to or in liquid ammonia forms precisely the same compound in solution that is formed when free acid is added. Thus, for example, when ammonium perchlorate is dissolved in liquid ammonia, it dissociates into ammonium ions and perchlorate ions and thus is precisely the same thing that happens when pure anhydrous perchloric acid is added to liquid ammonia.

As stated, it is usually advantageous to place a porous diaphragm around the anode so that, as the ammonium salt forms, it may be kept isolated from the remainder of the cell and either periodically or continuously drawn off. The anode material removed from the cell is a highly concentrated solution of the ammonium salt in the presence of some of the unelectrolyzed alkali or alkaline earth metal salt and is ideally suited for use in converting alkali or alkaline earth metal carbonate, oxide or hydroxide to the metal salt for re-use as a cell feed. This treatment of the anolyte will be further discussed hereinafter.

The anolyte removed from the cell possesses a boiling point considerably higher than that of an anhydrous liquid ammonia solvent and, in fact, in most instances possesses a boiling point considerably above room temperature. This is a further illustration of the different properties of the electrolyte used in the present invention as compared to an electrolyte in which a low concentration of salt is employed in liquid ammonia solvent.

When, however, instead of an inert anode, an anode, such as iron, copper, or nickel, which is attacked by acid, is employed, no free acid is produced but rather the metal salt of the acid. In the case of the use of an iron anode, for example, the solution quickly develops a dark red coloration, due to the formation of an iron salt, immediately adjacent the anode. While the use of an inert anode is preferred, the use of an anode such as an iron anode may be deemed to possess certain advantages, for example, the condition of the anolyte can be visually observed and there is no solvent waste due to the formation of nitrogen gas. However, as pointed out, an additional recovery step is required to separate the contaminating metal from the other materials, as will also be further discussed hereinafter.

In making up the original electrolyte, the alkali or alkaline earth metal salt, either anhydrous or containing a small amount of water as has been described, obtained from any suitable source, may be dissolved in the anhydrous liquid to provide the requisite concentration. One convenient method of obtaining a lithium salt, such as lithium perchlorate, is to react calcium perchlorate and dilithium calcium phosphate (obtained, for example, by reacting dilithium sodium phosphate in an autoclave under pressure with lime in the presence of water) forming lithium perchlorate and insoluble tricalcium phosphate. The lithium perchlorate solution is separated from the insoluble phosphate and the lithium salt is recovered from the solution and dried. This method of obtaining a lithium salt is not claimed herein but is the subject-matter of copending application Serial No. 666,187, filed April 30, 1946, now Patent No. 2,548,037.

Various methods may be employed in the treatment of the anolyte to prepare it for re-use in the cell. For example, when an inert anode has been used, the anolyte may be rendered suitable for re-use merely by the addition of the desired amount of alkali or alkaline earth carbonate, oxide or hydroxide thereto. In general, however, it will be desirable to employ a series of steps including a reaction in the aqueous phase between the ammonium perchlorate and the alkali or alkaline earth metal carbonate, oxide or hydroxide. In such a procedure, the ammonia is removed from the anolyte, by heating if necessary, and the residue is dissolved in water and reacted with the carbonate, oxide, or hydroxide of the desired alkali or alkaline earth metal. In the case a carbonate is employed, ammonium carbonate is obtained as a by-product. The solution containing the alkali or alkaline earth metal salt is then evaporated, advantageously after the addition of a small amount of the acid of the anion to make sure that all the ammonia has been removed and to serve as a make-up for any small loss of the anion. The salt recovered may be further dried if desired by any of the methods hereinafter discussed and is then mixed with anhydrous liquid ammonia to provide a cell feed containing the requisite amount of salt. The ammonia initially removed from the anolyte together with any other ammonia available from other portions of the process, for example, that which may be evaporated from the cell, is collected and condensed and is reused, with a small amount of make-up ammonia, to prepare the cell feed.

In the case the anode is not inert, the anolyte

after the removal of the ammonia therefrom is treated with water to precipitate a hydroxide of the metal introduced to the anolyte by the anode, for example, ferric hydroxide. The hydroxide is then removed from the solution and the solution is treated with the carbonate, oxide or hydroxide as described.

In a typical case, in the production of 10 pounds of lithium metal per hour, by a cyclic process, a cell having an iron cathode, a carbon anode, and operating with a current density of 20 amperes per square decimeter of electrode surface is employed. This cell requires 18,000 amperes and operates at 5 volts. The feed to the cell is a liquid comprising liquid ammonia with which is combined lithium perchlorate, the concentration being 2 mols of lithium perchlorate per litre of feed, and the rate of feed is such that the cell is supplied with 154 pounds of lithium perchlorate per hour. The cathode product is a bronze solution containing 12½% of lithium metal, balance liquid ammonia and floats on the electrolyte and is removed from the cell. The ammonia is evaporated from the bronze solution and delivered to the compressor. The anode product contains ammonia, ammonium perchlorate, and lithium perchlorate. The liquid ammonia is also evaporated from the product and is returned to the compressor. Water and lithium carbonate equivalent to the ammonium perchlorate is then added to the residue and ammonium carbonate is obtained as a by-product. Following evaporation of the solution and drying of the salt, substantially anhydrous lithium perchlorate is obtained. In this example, approximately 40% of the lithium perchlorate is recycled as the result of the presence of this salt in the anolyte as it is removed from the cell. The necessary make-up ammonia is added to the recovered liquid ammonia and the cell feed is prepared by mixing the required amount of lithium perchlorate and the ammonia to provide a cell feed of the stated concentration.

As has been stated, the process is operative when limited amounts of water are associated with the alkali or alkaline earth metal salt dissolved in the anhydrous liquid solvent to form the electrolyte, but, in the preferred embodiment of the invention an anhydrous or substantially anhydrous salt is employed. In the processing of the anolyte to convert it into a material for re-use as the cell feed, the alkali or alkaline earth metal salt is dried and this drying reduces the water content so that only a limited amount remains with the salt or it may remove the water substantially completely.

In the preparation of the salts from aqueous media, it has frequently been found desirable to crystallize, from a concentrated solution, a crop of hydrated crystals and then to subject them to dehydration, thus producing a product which is nearly free from impurities. The mother liquor from this separation can be further concentrated to produce more of the crystals and usually the mother liquor from several batches is accumulated into one large batch which is treated as stated. It is also possible to prepare anhydrous salts in a manner similar to that described, for example, by mixing solid lithium carbonates with solid ammonium perchlorate in the presence of water and applying heat until the water is removed.

The salts may be dried by any suitable method at atmospheric pressure or under a vacuum. The use of vacuum drying will result in the removal of moisture at temperatures lower than can be used at atmospheric pressure, and in the case of thermally sensitive salts, the use of vacuum drying may be found to be advantageous.

The particular method employed in the drying of the salt will depend on the extent of dryness desired and the characteristics of the particular salt. In the case of the perchlorates, it is usually only necessary to heat the material to a sufficient temperature to drive out all or substantially all of the water. Thus, in the preparation of lithium perchlorate, the wet salt may be heated to a temperature of about 300° C. and then cooled down to room temperature in which case the material frozen to a solid state can be broken up readily and dissolved in the solvent. In the case of the thiocyanates, which are subject to thermal decomposition, other methods are generally employed.

One of the methods which may be used in the production of a substantially anhydrous salt, where there is a tendency for the salt being treated to decompose, involves the step of ammoniating the partially dried salt at the same time that the residual water is removed. This is accomplished, for instance, by passing ammonia gas, for example, that which may be evolved as excess ammonia in the electrolysis step (usually mixed with nitrogen), over the partially dried salt which is maintained at an elevated temperature. Thus, in the preparation of lithium thiocyanate, for example, the partially dried salt is placed in a closed container maintained at a temperature in excess of about 150° C. and into which ammonia gas is passed. After a period of time sufficient to drive out the residual water, lowering of the temperature will result in a relatively hot solution of lithium thiocyanate in ammonia and, on cooling, this solution serves as a highly concentrated cell feed which can be added to the cell in the liquid state or can be further diluted before its addition to the cell. Alternatively, the material can be treated by crystallizing the ammoniated salt from the ammonia solution. This crystalline product may then be used as a cell feed either directly or in a dissolved condition. Furthermore, this salt may be de-ammoniated to form an anhydrous salt if that should be desired.

For salts highly sensitive to thermal decomposition, it is also possible to dry the salt from the frozen state at temperatures substantially lower than the freezing point. In such a case, the drying is conducted under conditions of high vacuum and the water sublimes from the solid mass.

Considerable modification is possible in the nature of the cathode product, as well as in the conditions of the process and the structure and operative characteristics of the cell, without departing from the essential features of the invention, and it is to be understood that such modifications and variations fall within the scope of the claims.

We claim:

1. A cyclic process for producing a metal selected from the group consisting of the alkali metals and the alkaline earth metals which comprises electrolyzing between substantially inert electrodes in a cell a solution of a salt of said metal selected from the group consisting of the perchlorate and thiocyanate in an anhydrous liquid selected from the group consisting of ammonia, methylamine, ethylamine and pyridine to produce a cathode product and an anode product, the concentration of salt in said anhydrous liquid

at least in contact with said cathode product being at least 2 mols of salt per litre of anhydrous liquid to provide a medium in which the cathode product is substantially insoluble; separating the cathode product from the electrolyte, whereby a cathode product comprising the metal substantially free from salt is obtained; separating the anode product comprising the anhydrous liquid, the anion of said metal salt and its associated solvated proton, SH^+, where S is said anhydrous liquid, from the cell; reacting the anion of said metal salt and its associated solvated proton with a compound of said metal selected from the group consisting of the oxide, hydroxide and carbonate to form the corresponding metal salt, and utilizing said metal salt, in substantially anhydrous form, as source material in the process.

2. The process of claim 1 wherein said anhydrous liquid is ammonia.

3. A cyclic process for producing a metal selected from the group consisting of the alkali metals and the alkaline earth metals which comprises electrolyzing between substantially inert electrodes in a cell a solution of a salt of said metal selected from the group consisting of the perchlorate and the thiocyanate in an anhydrous liquid selected from the group consisting of ammonia, methylamine, ethylamine and pyridine to produce a cathode product and an anode product, the concentration of salt in said anhydrous liquid at least in contact with said cathode product being at least 2 mols of salt per litre of anhydrous liquid to provide a medium in which the cathode product is substantially insoluble; separating the cathode product from the electrolyte, whereby a cathode product comprising the metal substantially free from salt is obtained; separating the anode product comprising the anhydrous liquid, the anion of said metal salt and its associated solvated proton, SH^+, where S is said anhydrous liquid, from the cell; reacting in an aqueous medium said anion and its associated

solvated proton with a compound of said metal selected from the group consisting of the oxide, hydroxide and carbonate to form the corresponding metal salt; removing water from said metal salt to render it substantially anhydrous; and utilizing said metal salt as source material in the process.

4. The process of claim 3, wherein said anhydrous liquid is ammonia.

5. The process of claim 3, wherein the metal produced is lithium, wherein the said metal salt is lithium perchlorate, and wherein the said anhydrous liquid is ammonia.

6. The process of claim 3, wherein the metal produced is lithium; wherein the said metal salt is lithium thiocyanate, and wherein the said anhydrous liquid is ammonia.

7. The process of claim 3, wherein the metal produced is calcium; wherein the said metal salt is calcium perchlorate, and wherein the said anhydrous liquid is ammonia.

8. The process of claim 3, wherein the metal produced is calcium; wherein the said metal salt is calcium thiocyanate, and wherein the said anhydrous liquid is ammonia.

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