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MANUFACTURE OF PERCHLORATES

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This invention relates to the manufacture of perchlorates and, more particularly, to a process for electrolytically oxidizing chloride ions to perchlorate ions in an electrolytic cell and recovering the resulting perchlorate from the electrolyte in the form of a perchlorate compound. The invention is based on the discovery that upon subjecting an aqueous electrolyte containing lithium chloride or lithium hypochlorite to electrolysis in an electrolytic cell, substantially all of the chloride and hypochlorite ions in the electrolyte can be electrolytically oxidized to perchlorate ions in a single oxidation stage at very high current efficiencies. The invention provides an improved process for manufacturing a perchlorate compound by electrolytically oxidizing lithium chloride to lithium perchlorate, which in turn may be used to form other perchlorate compounds, such as ammonium perchlorate, by metathesis.

It has long been commercial practice to manufacture alkali metal perchlorates by first oxidizing a chloride or hypochlorite to chlorate, and then, in a separate operation, oxidizing the chlorate to perchlorate. This two-stage oxidation system has been necessary because if it is attempted to oxidize the common alkali metal (sodium and potassium) chlorides or hypochlorites to perchlorates in a single operation, much of the perchlorate that is formed is reduced again to chlorate. To attain reasonably high current efficiency and a good perchlorate recovery, it has been necessary to form sodium or potassium chlorate from the chloride or hypochlorite in a first oxidation stage, and then to form the perchlorate from the chlorate in a second oxidation stage. We have found, however, that when an aqueous solution of lithium chloride in an electrolytic cell is subjected to electrolysis, substantially all of the chloride ions may be electrolytically oxidized in a single electrolytic operation and at very high current efficiencies to perchlorate.

Accordingly, the invention provides an improved process for manufacturing a perchlorate compound which comprises introducing an aqueous solution of lithium chloride (or lithium hypochlorite) into an electrolytic cell between an anode and a cathode, passing an electric current through the solution at a cell voltage in excess of the theoretical decomposition voltage required to form a perchlorate from a chloride, thereby electrolytically oxidizing the chloride in the solution to perchlorate, continuing electrolysis of the solution until substantially all of the chloride contained therein has been converted to perchlorate, and recovering the resulting perchlorate from the solution in the form of a perchlorate compound, either by crystallizing lithium perchlorate from the solution or by reacting the solution containing lithium perchlorate with a water-soluble metallic carbonate to form the corresponding metallic perchlorate by metathesis.

Although a solution of lithium chloride or of lithium hypochlorite alone may be used as the electrolyte, an aqueous solution containing both lithium chloride and lithium hypochlorite, prepared by chlorinating a solution of lithium carbonate or lithium hydroxide, is eminently satisfactory. Aqueous solutions containing the lithium chloride or hypochlorite may be electrolytically oxidized at any desired concentration, but the highest current efficiencies and most convenient operating conditions are obtained by using solutions containing from 100 to 300 grams per liter of lithium chloride or hypochlorite, or

mixtures of the two, and preferably about 150 grams per liter. At concentrations substantially above 300 grams per liter and approaching saturation (near 400 grams of lithium chloride per liter) current efficiency is generally lower than at the preferred concentrations.

A small quantity of a depolarizing agent, such as sodium fluoride, potassium fluoride, or lithium fluoride, in a concentration ranging up to about one gram per liter, may be added to the electrolyte to protect the anode and increase current efficiency during electrolysis.

To initiate the electrolysis, the aqueous solution is introduced into an electrolytic cell between an anode and a cathode. Although various types of oxidation-resistant anodes, such as platinum, graphite, or lead dioxide, may be employed in the cell, platinum has been found to yield the best results, especially when used in conjunction with stainless steel cathodes.

The electrolysis is generally carried out at a cell voltage in the range from 4.5 to 6 volts. The effective cell voltage, that is, the voltage available for effecting the electrolytic oxidation of the chloride ions in solution to perchlorate, must be in excess of the theoretical decomposition voltage required to form a perchlorate from a chloride. The voltage applied to the cell must in addition be sufficient to overcome the resistances at the interfaces of anode and cathode with the electrolyte, the electrolyte resistance, and the resistance of the anodes and cathodes themselves and of their contacts to the external circuit elements. To overcome all these various resistances and provide a sufficient excess to supply the required decomposition voltage for the electrolytic oxidation, the overall cell voltage should be at least 4.5. A voltage above 6.0 is generally undesirable because it results in a waste of power.

The anodic current density preferably is in the range from 15 to 25 amperes per square decimeter. Electrolysis is continued until substantially all of the chloride present in the cell electrolyte has been converted to perchlorate. Perchlorate yields from 90 to 95 percent of theory, at current efficiencies substantially in excess of 80 percent, may readily be attained.

Although the temperature at which the electrolysis takes place is not especially critical, it is preferable to maintain the electrolyte temperature between 30° C. and 40° C. At the higher temperatures the current efficiency decreases somewhat, but the conductivity of the electrolyte increases. Agitation of the bath, preferably by stirring or circulation of the electrolyte, is important to obtain maximum current efficiency and to minimize the evolution of gaseous products such as chlorine and oxygen at the anode. Theoretically no oxygen or chlorine is liberated, but nonetheless small quantities are always formed in side reactions.

Although the over-all cell reaction involves electrolytic oxidation of lithium chloride to lithium perchlorate, this over-all reaction evidently represents the sum of several individual oxidation reactions which take place during the electrolysis, with the formation of hypochlorite and chlorate ions in solution as intermediate reaction products. Neither of these intermediate products is isolated, however. The following equations illustrate several of the oxidation reactions which doubtless take place during the electrolysis:

$$LiCl+H_2O=LiClO+H_2$$
$$LiCl+3H_2O=LiClO_3+3H_2$$
$$LiClO+2H_2O=LiClO_3+2H_2$$
$$LiClO_3+H_2O=LiClO_4+H_2$$

In addition to these principal reactions, various side reactions which result in liberation of some chlorine and some oxygen also occur, as by decomposition of hydro-

chloric acid present on account of hydrolysis and by electrolytic decomposition of water.

It is a unique characteristic of the process of the invention that none of the reactions which take place in the cell seriously impairs the efficient oxidation of the chlorine-bearing ions to perchlorate. In this respect the behavior of the lithium salt electrolyte used in this process is quite different from that of other alkali metal chloride and hypochlorite solutions. The reason for this difference is not entirely clear, but it is another manifestation of the differences in the properties and behavior of lithium from the other members of the alkali metal group.

To attain the advantages which accrue from efficient oxidation of chloride and hypochlorite ions to perchlorate in a single electrolytic oxidation stage, the invention contemplates maintaining the electrolyte substantially free from all alkali metal ions except lithium (although very small concentrations of sodium or potassium ions, such as are introduced by the use of say 0.25 to 1.0 gram per liter of sodium or potassium fluoride as a depolarizer, are tolerated without substantial impairment of the efficiency of the oxidation process).

The electrolysis may be carried out either as a batch process or as a continuous process. In the former case a single charge of lithium chloride electrolyte may be oxidized to perchlorate, and the spent electrolyte may then be discharged from the cell and replaced by a fresh charge of electrolyte. In the latter case fresh lithium chloride or hypochlorite solution may be fed continuously to one or a series of electrolytic cells, and spent electrolyte may be continuously withdrawn for treatment to recover the perchlorate. In either case lithium perchlorate may be recovered by crystallization from the spent (oxidized) electrolyte after its withdrawal from the electrolytic cell.

Any conventional cell such as has been used heretofore in the electrolytic oxidation of chloride and chlorate solutions may be used in carrying out the process of the invention. A single cell tank containing a single anode and cathode will suffice for very small-scale operations. Preferably in the commercial manufacture of perchlorate, however, the cell comprises a tank containing a considerable number of anodes and cathodes arranged alternately and connected in parallel, or a series of such tanks disposed in a cascade arrangement may be employed.

An advantageous way of recovering the perchlorate is to treat the lithium perchlorate solution from the electrolytic cell with a water-soluble metal carbonate, such as ammonium carbonate, to form the corresponding metal perchlorate by metathesis and to precipitate lithium carbonate out of the solution. The precipitated lithium carbonate may be suspended in water and chlorinated to form an aqueous mixture of lithium chloride and lithium hypochlorite for recycling to the electrolytic cell. In this manner, ammonium perchlorate may be produced by a simple two-step process, in which an aqueous solution of lithium chloride is electrolytically oxidized to lithium perchlorate in a single oxidation operation, and the resulting solution of lithium perchlorate is reacted with ammonium carbonate to form an aqueous solution of ammonium perchlorate, from which the ammonium salt may be recovered by crystallization.

By a variation of this procedure, it is possible to upgrade lithium hydroxide to lithium carbonate as a by-product of ammonium perchlorate manufacture. To do so, lithium hydroxide is chlorinated to form the aqueous chloride-hypochlorite electrolyte which is electrolytically oxidized, and then the electrolyte is treated to precipitate lithium carbonate and form an ammonium perchlorate solution. Both these products in this case are recovered for commercial disposition, and the lithium is not recycled.

Following is an example of the process of the invention as it is applied to electrolytically oxidizing lithium chloride to lithium perchlorate in an electrolytic cell, and to forming ammonium perchlorate by metathesis of the lithium perchlorate thus produced.

An electrolyte containing 150 grams per liter of a mixture of lithium chloride and lithium hypochlorite in equimolar proportions is prepared by chlorinating an aqueous suspension of lithium hydroxide. Chlorination is conveniently effected by simply introducing gaseous chlorine into the aqueous solution, while agitating the solution, until all the lithium hydroxide has been converted to chloride or hypochlorite and has dissolved. About 0.5 gram per liter of lithium fluoride is added to the electrolyte as a depolarizing agent. The resulting electrolyte is introduced into an electrolytic cell comprising a rectangular tank containing an array of platinum anodes and stainless steel cathodes arranged alternately and spaced about two inches apart. The anodes all are connected to a single anode bus-bar, and the cathodes all are connected to a single cathode bus-bar. The electrolyte is kept agitated by circulating it continuously from the cell to a supply tank and then back to the cell. The temperature of the electrolyte in each cell is held constant between 30° C. and 40° C., preferably at about 35° C. The electrolysis is carried out at a cell voltage of 5 volts (measured from anode bus-bar to cathode bus-bar) and at an anode current density of about 20 amperes per square decimeter, until substantially all of the chloride ions contained in the circulating electrolyte are converted to perchlorate. The solution then contains approximately 300 grams per liter of lithium perchlorate, representing a yield of about 95 percent of theory. Current efficiency of the electrolysis is in excess of 80 percent.

Upon completion of the electrolytic oxidation, the electrolyte is withdrawn from the cell and mixed with a solution containing approximately a stoichiometrically equivalent quantity of ammonium carbonate. Lithium carbonate thereupon precipitates from the solution, leaving ammonium perchlorate in solution. The precipitate is filtered off and the clarified solution is evaporated to crystallize the ammonium perchlorate. The separated lithium carbonate may be disposed of as such, or it may be returned to the chlorination operation, where it may be used in place of fresh lithium hydroxide to prepare additional electrolyte for the oxidation cell.

It is clear from the foregoing that the new process provides a simple but efficient process for the production of perchlorates. Oxidation of the chloride or hypochlorite all the way to perchlorate in a single oxidation step, which is made possible by using substantially only lithium salts in the electrolyte, greatly simplifies the oxidation operation and reduces the amount of equipment required. Conversion of the perchlorate produced to any desired metal perchlorate, especially an alkali metal or ammonium perchlorate, by metathesis using an inexpensive carbonate reagent, is readily accomplished. Preparation of the electrolyte by direct chlorination of lithium carbonate or lithium hydroxide makes use of a relatively inexpensive reagent (chlorine) and at the same time produces a partially oxidized electrolyte (one containing hypochlorite as well as chloride) which requires less power for electrolytic oxidation than an all-chloride electrolyte. These and other advantages of the new process combine to make it an especially efficient and economical one for the production of perchlorates.

We claim:

1. A cyclic process for the manufacture of ammonium perchlorate which comprises introducing an aqueous solution of lithium chloride and lithium hypochlorite having a total concentration in the range between 100 and 400 grams per liter into an electrolytic cell between a cathode and an anode, passing an electric current through the solution from the anode to the cathode at a cell voltage from 4.5 to 6 volts and an anodic current density from 15 to 25 amperes per square decimeter, thereby electrolytically oxidizing the chloride and hypochlorite in the solution to lithium perchlorate, agitating the solution

undergoing electrolysis, continuing the electrolysis of the agitated solution until substantially all of the chloride and hypochlorite contained therein has been converted to perchlorate, then withdrawing the solution from the cell and reacting the lithium perchlorate therein with ammonium carbonate to form ammonium perchlorate by metathesis, thereby precipitating lithium carbonate while leaving an aqueous solution of ammonium perchlorate, recovering ammonium perchlorate from the resultant solution, chlorinating the precipitated lithium carbonate in an aqueous medium to form an aqueous solution of lithium chloride and lithium hypochlorite, and subjecting the solution thus formed to oxidation in the electrolytic cell.

2. A cyclic process for the manufacture of ammonium perchlorate which comprises chlorinating in an aqueous medium a lithium compound selected from the group consisting of lithium carbonate and lithium hydroxide with chlorine to form an aqueous electrolyte of lithium chloride and lithium hypochlorite having a total concentration in the range between 100 and 400 grams per liter, introducing the resulting electrolyte into an electrolytic cell between a stainless steel cathode and a platinum anode, passing an electric current through the electrolyte from the anode to the cathode at a cell voltage from 4.5 to 6 volts and an anodic current density from 15 to 25 amperes per square decimeter, thereby electrolytically oxidizing the chloride and hypochlorite in the electrolyte to perchlorate, agitating the electrolyte, continuing the electrolysis of the agitated electrolyte until substantially all of the chloride and hypochlorite contained therein has been converted to perchlorate, reacting the aqueous solution containing lithium perchlorate with ammonium carbonate to form ammonium perchlorate by metathesis, thereby precipitating lithium carbonate while leaving an aqueous solution of ammonium perchlorate, recycling the precipitated lithium carbonate to the chlorination step, and crystallizing ammonium perchlorate from the resultant solution.

3. A process for the manufacture of ammonium perchlorate and lithium carbonate which comprises reacting lithium hydroxide in an aqueous medium with chlorine to form an aqueous electrolyte of lithium chloride and lithium hypochlorite having a total concentration in the range between 100 and 400 grams per liter, introducing said electrolyte into an electrolytic cell between a cathode and an anode, passing an electric current through the electrolyte from the anode to the cathode at a cell voltage from 4.5 to 6 volts and an anodic current density from 15 to 25 amperes per square decimeter, thereby electrolytically oxidizing the chloride and hypochlorite in the solution to perchlorate, agitating the electrolyte, continuing the electrolysis of the agitated electrolyte until substantially all of the chloride and hypochlorite contained therein has been converted to perchlorate, reacting the aqueous solution containing lithium perchlorate with a stoichiometrically equivalent quantity of ammonium carbonate to form ammonium perchlorate by metathesis, thereby precipitating lithium carbonate while leaving an aqueous solution of ammonium perchlorate, and separately recovering the ammonium perchlorate and the lithium carbonate from the resultant solution.

4. A continuous process for the manufacture of ammonium perchlorate which comprises continuously introducing an aqueous solution of lithium chloride into an electrolytic cell between an anode and a cathode, passing an electric current through the solution from the anode to the cathode at an effective cell voltage in excess of the theoretical decomposition voltage required to form a perchlorate from a chloride, thereby electrolytically oxidizing the chloride in the solution to perchlorate, continuously withdrawing perchlorate-containing electrolyte from the cell, reacting the withdrawn electrolyte with ammonium carbonate, thereby precipitating lithium carbonate and forming a solution containing ammonium perchlorate, recovering the ammonium perchlorate from the solution, chlorinating the lithium carbonate to form lithium chloride, and returning the lithium chloride so formed to the electrolytic cell.

5. A continuous process for the manufacture of ammonium perchlorate which comprises continuously introducing an aqueous solution of lithium chloride having a concentration in the range between 100 and 400 grams per liter into an electrolytic cell between an anode and a cathode, passing an electric current through the solution from the anode to the cathode at a cell voltage from 4.5 to 6 volts and an anodic current density from 15 to 25 amperes per square decimeter, thereby electrolytically oxidizing the chloride in the solution to perchlorate, agitating the solution undergoing electrolysis, continuously withdrawing perchlorate-containing electrolyte from the cell, reacting the withdrawn electrolyte with ammonium carbonate, thereby precipitating lithium carbonate and forming a solution containing ammonium perchlorate, recovering the resulting ammonium perchlorate from the solution, chlorinating the precipitated lithium carbonate to form lithium chloride, and returning the lithium chloride so formed to the electrolytic cell.

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