

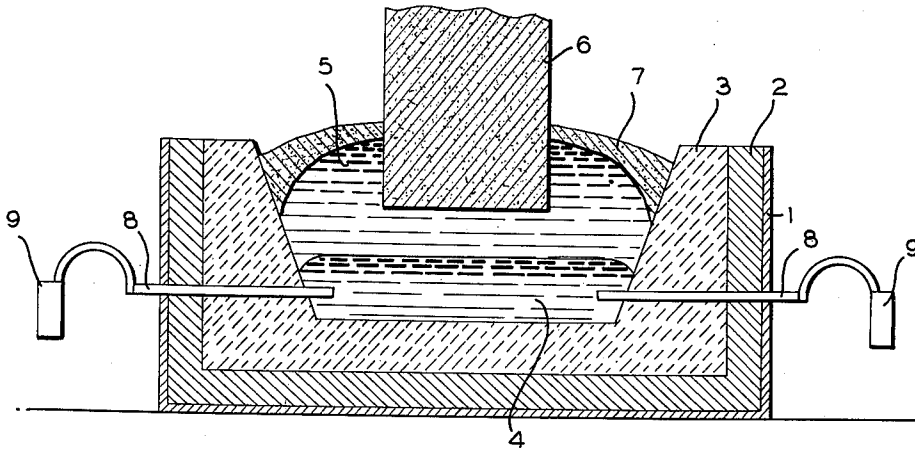
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ELECTROLYTIC PRODUCTION OF ALUMINUM

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ELECTROLYTIC PRODUCTION OF ALUMINUM
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This invention relates to the production of aluminum by electrolytic reduction of an aluminum-containing compound, e.g. alumina. More particularly, the invention relates to an improved method for the electrolytic production of aluminum.

The production of aluminum by electrolysis of an aluminum-containing compound, e.g. alumina, dissolved in a molten salt electrolyte, e.g. cryolite, and deposition at the cathode is a very old process. The alumina is broken down into its components; the oxygen is liberated at the anode and the aluminum is deposited at the cathode, which forms the bottom of the electrolytic cell. In practice, the pool of molten aluminum which is formed in the bottom portion of the cell in effect constitutes the cathode of the cell. Conventionally, use has been made of two types of electrolytic cells, namely, that commonly referred to as a "pre-bake" cell and that commonly referred to as a Soderberg cell. With either cell, the reduction process involves precisely the same chemical reactions. The principal difference between the two cells is one of structure. In the pre-bake cell the carbon anodes are pre-baked before being installed in the cell, while in the Soderberg cell or continuous anode cell the anode is baked in situ, that is, it is baked during operation of the electrolytic cell, thereby utilizing part of the heat generated by the reduction process.

Conventionally, the total voltage drop across the cell is about 4.5 to about 5 volts with a voltage drop between the anode and cathode of about 3.5 to about 4 volts. The voltage drop between the anode and cathode is composed of (1) the voltage required to overcome the ohmic resistance of the electrolyte and (2) the sum of the reversible decomposition voltage required for the cell reaction and the polarization voltages. The voltage required, e.g., in (1) above may be about 2 volts while the voltage of (2) may be about 1.7 volts. The remainder of the cell voltage is required to overcome the resistance of the lining, the external conductors and connections, the anode, anode effects, and various contact resistances. Power consumption per pound of aluminum produced generally falls within the range of from about 7.5 to 8.5 kilowatt-hours (kwh.).

Although the theory of the electrolysis of alumina in molten cryolite has not been fully developed, a considerable amount of knowledge has been gained over the past seventy years in regard to the electrochemical factors, such as voltage relationships and current efficiency, and the thermal aspects, such as heat generation and heat dissipation, of the process. The knowledge of these factors has been essential in the development of the electrolysis of alumina into a commercially feasible process. The thermal aspects, in particular, are of utmost importance for they determine the size, the design and the operational conditions of the reduction cell.

The current efficiency (or Faraday efficiency) of the aluminum reduction process is only about 80 to 88% of the theoretical. This relatively low efficiency is due to a number of causes, particularly the formation of a "metal fog" at the aluminum cathode and recombination of the anodic and cathodic products, which are brought together by stirring and diffusion. The formation and reoxidation of cathodic "metal fog" are more active the higher the temperature of the metal and the electrolyte, and the current efficiency thus becomes lower. Consequently, the

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highest efficiency is favored by the lowest possible temperature of the molten electrolyte consistent with other requirements, such as the solubility of alumina in the electrolyte and general workability of the cell. In order to maintain low electrolyte temperatures and prevent the excessive generation of heat, it is necessary to operate reduction cells employing conventional electrolytes at low current densities.

The minimum power required to produce aluminum metal may be calculated by the following equation:

$$(1) \quad P = \frac{2.04I \left(\frac{\%C.E.}{100} \right)}{1000}$$

where

P = the power in kw.

% C.E. = the percent current efficiency of the operation of the cell

2.04 = the voltage required to sustain the cell reaction

I = cell current in amperes

The voltage required to sustain the reaction is calculated, utilizing the heat of the overall cell reaction, by the following equation:

$$(2) \quad E = \frac{-\Delta H}{njF}$$

where

E = the voltage required to sustain the cell reaction

ΔH = the heat of reaction in calories

n = the valence change or number of chemical equivalents of substance reacting

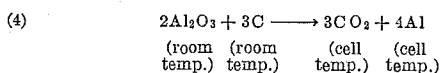
j = constant for changing joules to calories = 0.239

F = 96,500 coulombs of electricity passing through the cell for each chemical equivalent of substance.

Equation 2 may be expressed by

$$(3) \quad E = \frac{-\Delta H}{23,070n}$$

The overall cell reaction in the reduction of alumina is as follows:



The heat of reaction evolved in Equation 4 is expressed by:

$$(5) \quad \Delta H = 4\Delta H_{Al} + 3\Delta H_{CO_2} - 2\Delta H_{Al_2O_3} - 3\Delta H_C$$

Assuming a cell temperature of 975° C. and room temperature of 25° C.

$$\begin{aligned} \Delta H_{Al} &= \Delta H_{Al}^{\circ} + \text{sensible heat (room temp. to } 660^{\circ} \text{ C.)} \\ &\quad + \text{heat of fusion} + \text{sensible heat (} 660^{\circ} \text{ C. to cell temp.)} \\ &= 0 + \frac{(6.75)(660-25)}{1000} + 2.6 + \frac{(7.0)(975-660)}{1000} \\ &= 9.1 \text{ kcal./mole} \end{aligned}$$

$$\begin{aligned} \Delta H_{CO_2} &= \Delta H_{CO_2}^{\circ} + \text{sensible heat (room temp. to cell} \\ \text{temp.)} &= -94.05 + \frac{(11.9)(975-25)}{1000} = -82.75 \text{ kcal./mole} \end{aligned}$$

$$\Delta H_{Al_2O_3} = -389.49 \text{ kcal./mole}$$

$$\Delta H_C = 0$$

$$\Delta H = 4(9.1) + 3(-82.75) - (2)(-389.49)$$

$$\Delta H = +567.1 \text{ kcal./mole}$$

The voltage equivalent of the reaction then is:

$$E = -\frac{567,100}{12(23,070)} = -2.04 \text{ volts}$$

The power efficiency, that is, the percentage of the

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applied power used for the actual electrolysis, of a reduction cell is expressed by the equation:

$$(6) \text{ Power efficiency (\%)} = \frac{2.04I \left(\frac{\% \text{ C.E.}}{100} \right) \times 100}{IV} \text{ or } \frac{2.04 \left(\frac{\% \text{ C.E.}}{V} \right)}{V}$$

where

V = total voltage drop

IV = total power into the cell

In Equation 6, assuming a current efficiency of about 80 to 85% and a voltage drop across the cell of about 4.5 to 5 volts, which figures are representative for operation in the aluminum reduction industry, it is seen that the power efficiency is on the order of 30 to 35%. Consequently, the major part of the total power supplied to the cell is not utilized in producing aluminum.

In order to improve the power efficiency, a reduction of the heat losses caused by the various ohmic resistances in the cells is necessary. Consequently, many studies of the heat balance, that is, the heat generated and heat dissipated, of aluminum reduction cells have been made.

Much experimenting has been done in an effort to decrease the resistances (and hence improve the power efficiency) of the various elements of the cell, particularly the electrolyte which accounts for about two-thirds of the total heat generated. Only a portion of the heat generated in the electrolyte is essential in heating and maintaining the electrolyte at the operating temperature. The rest of the generated heat must be dissipated somehow in order to prevent the cell from running at too high a temperature which would reduce the current efficiency.

In an effort to reduce the heat generated in the electrolyte, prior work has been directed to lower operating temperatures of the electrolyte and increased electrolyte conductivity; the desired result being decreased cell voltages giving lower power consumption per pound of aluminum metal produced, as distinguished from increased productive capacity of the cell. A lower limit to operating temperature is fixed by the liquidus temperature of the cryolite electrolyte. The liquidus of cryolite is lowered by additions of sodium fluoride, aluminum fluoride, and alumina. Sodium fluoride additions are undesirable in that they promote the formation of cathodic "metal fog," and it is therefore usual practice to operate with electrolytes containing an analytical excess of aluminum fluoride. However, aluminum fluoride, due to its volatility, can be used only in restricted amounts, e.g. up to 10% in excess of the stoichiometric amount of aluminum fluoride in cryolite. Therefore, calcium fluoride has been used in amounts of up to 12.5% to further lower the liquidus which has been partly lowered by the addition of aluminum fluoride. The practical limit of solubility of alumina is about 8% and, also, the alumina content diminishes as the electrolysis proceeds. However, the addition of calcium fluoride as well as the additions of aluminum fluoride and alumina, undesirably reduce the conductivity of the electrolyte. Furthermore, calcium fluoride undesirably reduces the density differential between the electrolyte and the molten aluminum.

It was recognized in the prior art that some increase in current efficiency and decrease in carbon consumption should result if the operating temperatures could be lowered. Consequently, the prior art is replete with suggestions or proposals for modification of the basic electrolyte composition in order to accomplish this objective. In general, these proposals have been to add other alkali fluorides, cryolites, or chlorides as an equivalent or substitute for the sodium fluoride or sodium cryolite. It has been proposed to use sodium chloride as an additive or as a substitute for part of the sodium fluoride of the conventional electrolyte. Also, it has been proposed to use potassium fluoride or cryolite and lithium fluoride or cryolite as a substitute for the sodium fluoride or sodium

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cryolite constituent of the electrolyte or as an additive thereto. It should also be noted that in an attempt to reduce heat generation of the cell, in order to increase power efficiency, there has been a steady reduction in the industry in current density used in operation of electrolytic cells.

The usual electrolyte composition consists essentially of a mixture of the fluorides of sodium and aluminum in which alumina is dissolved. Generally speaking, it may be said that most electrolyte compositions consist essentially of cryolite and alumina and fall within the ranges, in percent by weight of electrolyte, of sodium cryolite (Na_3AlF_6)—80 to 90%, aluminum fluoride (AlF_3)—0 to 10%, calcium fluoride (CaF_2)—5 to 12.5%, and alumina (Al_2O_3)—2 to 6%. In operation, the electrolyte composition is generally restricted to a sodium fluoride to aluminum fluoride weight ratio in the range of between 1.20 to 1.50 and the calcium fluoride content restricted to an amount within the range of 7 to 9%.

The freezing point of electrolyte compositions in the ranges set forth above is on the order of about 950° C. to 960° C. In operation, the temperature of the electrolyte generally is maintained above about 965° C. to avoid operating difficulties due to excessive freezing and thickening of the electrolyte crust which forms over the molten electrolyte and the occurrence of ledges covering the interior sides and part of the bottom of the lining. Operating temperatures on the order of 965° C. to 975° C. are generally used in the industry today. Higher temperatures present difficulties due to reduced current efficiency resulting from two factors. One factor is the effect of temperature itself which reduces the current efficiency as temperature is increased. The other factor is the interaction of electrolyte and aluminum metal with the carbon side walls of the cell lining and stray currents to the side walls which result when the frozen electrolyte ledge covering the side walls melts off as the temperature increases. Consequently, practical considerations of maximum current efficiency dictate that reduction cells be operated with the electrolyte being at a temperature of not more than about 10 to 15° C. above the freezing point. This results in a rather thick crust forming over the top surface of the electrolyte and ledges forming over the sides and partially over the bottom of the cell lining, all of which tend to limit the heat dissipation from the cell itself. This in turn, limits the power input to the cell in order to prevent the operating temperatures from rising above the desired level. This means that there is a definite limit to the current density which can be used in practice for a given cell design which in turn limits the productive capacity of the cell in question.

The voltage drop in the electrolyte, caused by the ohmic resistance of the electrolyte and by which the corresponding resistance heat generation can be measured, is expressed by the equations:

$$(7) \quad V_e = IR_e$$

where R_e = the resistance of the electrolyte and

$$(8) \quad V_e = \frac{rl}{a} I = rld$$

where

r = the specific resistivity of the molten electrolyte

l = the anode-cathode distance

a = average cross-sectional area of electrolytic path over distance l

d = average current density in the electrolyte

In Equation 8 all of the factors are theoretically variable, but from a practical standpoint only d , current density, may be varied a considerable amount. The temperature cannot be increased for the purpose of reducing the specific resistivity because, as stated previously, an increase in temperature will result in lower current efficiency. The reduction of anode-cathode distance, l , would result in increased reoxidation of the cathodic metal. Consequently,

the current density becomes the basic characteristic of the cell, and a reduction of current density has been the means used for reducing the heat generated in the cell.

In view of the numerous and complex interrelated factors affecting the operation of an aluminum reduction cell, it is only natural that the philosophy of those engaged in the reduction field has been to limit the current density in order to reduce the heat generated in the cell, thereby improving the current efficiency and the power efficiency. This course of action, although it directly limits the productive capacity of the cell, has been deemed expedient and necessary in order to have economic harmony among the many interrelated factors of the cell. In order to increase the production of aluminum, cells of larger and larger dimensions are being built. With cells of these larger dimensions, the problem of power efficiency becomes greater. The rate of heat generation of a cell increases faster with increase in size than its ability to dissipate heat for the same electrolyte temperature. Consequently, under the prior mode of operation, further reductions in current density are mandatory in order not to generate excess heat in the electrolyte, even though this measure is at the expense of cell productivity.

Accordingly, it is the primary purpose and object of this invention to provide an improved method for operating an electrolytic cell for the production of aluminum which results in a substantial increase in the productive capacity or output of the cell.

A further object of this invention is to provide an improved method for the electrolytic production of aluminum metal wherein the electrolytic cell productive capacity is increased with little or no increase in power consumption per pound of aluminum metal produced and with a decrease in capital investment, maintenance, administration, and labor costs per pound of aluminum metal produced.

A further object of this invention is to provide an improved method for the electrolytic production of aluminum which results in better heat dissipation, greater current efficiency and lower carbon consumption per pound of aluminum produced.

Other objects and advantages of the present invention will be apparent from the following detailed description.

According to the present invention, it has been found that an electrolytic cell operating with a given voltage drop across the cell can be operated with significantly greater productive capacity or output and with better heat dissipation, greater current efficiency, and lower carbon consumption by carrying out the reduction of the aluminum-containing compound, e.g. alumina, by a method wherein a molten salt electrolyte consisting essentially of cryolite and alumina is modified by the presence of or containing a predetermined amount of a lithium-containing compound and wherein use is made of a substantially increased current or, in other words, where there is established a current flow so that the resultant voltage drop across the cell is maintained at least substantially as great as that existing in the cell devoid of the lithium addition to the electrolyte. The power consumption per pound of aluminum produced generally is substantially the same as that for conventional cells. However, the present invention also contemplates in some instances using a cell voltage and power consumption greater than that of conventional cells but wherein the extent of profit from increased production far exceeds the added cost of power.

An even greater increase in productive capacity of electrolytic reduction cells can be achieved by, in addition to the above features, passing electric current through such electrolyte from the anode to at least one cathodic current-conducting element exposed to the pool of molten aluminum at the base of the cell, which pool in effect constitutes the cathode, and wherein at least that portion of such element in contact with the molten aluminum consists essentially of a material possessing a low electrical resistivity, a low solubility in molten aluminum and molten

electrolyte under cell operating conditions, is wettable by molten aluminum under cell operating conditions, and has good stability under the conditions existing at the cathode of the cell. It has been found that the carbides and borides of titanium, zirconium, tantalum and niobium and mixtures thereof, exhibit all or substantially all of the properties hereinabove set forth. These compounds are referred to as refractory hard metals. If desired, the whole of the current-conducting element may consist essentially of one or more of such materials.

The expression "consists essentially," as used herein after in the specification and claims, means that the portion of the element made of one or more of the carbides and borides referred to above does not contain other substances in amounts sufficient materially to affect the desirable characteristics of the current-conducting element, although other substances may be present in minor amounts which do not materially affect such desirable characteristics, for example, small proportions of oxygen, iron, or nitrogen in titanium boride. It is preferred that the refractory materials in the current-conducting elements be essentially free from elements or compounds which would lead to undesirable contamination of the aluminum produced. Nevertheless, the current-conducting elements may contain initially, among others, certain compounds which dissolve out when the element is first put into use and which do not materially affect the element.

Desirably, that portion of the element consisting essentially of one or more of the above-mentioned refractory materials should be composed of at least 90% by weight of such materials. The elements have been found to possess a relatively high electrical conductivity (substantially better than that of carbon), a good resistance to attack by molten electrolyte, a very low solubility in molten aluminum at cell operating temperatures, are wet by molten aluminum under cell operating conditions, and have a resistance to oxidation considerably better than that of carbon. Such elements can be produced in suitable forms with good mechanical properties.

The modification of the electrolyte or bath by the presence of lithium can be accomplished by an addition or incorporation of a suitable lithium-containing material to the conventional molten electrolyte in the cell or as a substitute for calcium fluoride or sodium fluoride or both. Alternatively, the lithium-containing material may be incorporated by making up the electrolyte completely outside of the cell. By practice of the instant invention the calcium fluoride can be maintained at a minimum and in the preferred operation of the invention the electrolyte should not include intentionally added calcium fluoride.

According to the invention, lithium should be present in the electrolyte in an amount equal to that resulting from the addition of lithium fluoride in an amount from about 2% to 20% by weight of the molten electrolyte, preferably from about 3 to 8%. The lithium material may take the form of various compounds which are compatible with the other electrolyte constituents and do not introduce excessive amounts of impurities into the cell. For example, use can be made of lithium fluoride, lithium aluminum fluoride (lithium cryolite), lithium carbonate, lithium hydroxide, or lithium aluminate. In providing the necessary lithium content in the electrolyte, such compounds can be used singly or in combination. Regardless of the lithium compound used from the above list, the end result in the molten electrolyte, as far as composition is concerned, will be the same. Although various lithium-containing compounds are suitable for purposes of the present invention, from the standpoint of handling, moisture pick-up, gas evolution, etc., the presently preferred source materials are lithium fluoride, lithium cryolite, and lithium aluminate.

As discussed hereinbefore, the present invention involves the presence of lithium in the electrolyte in a predetermined amount coupled with maintenance of a voltage drop across the cell at least substantially equal to

that existing in the cell devoid of the lithium content in the electrolyte. Or, stated another way, the present invention utilizes a substantially increased current so that the resultant voltage drop is at least substantially as great as the first named voltage drop of the cell devoid of the lithium content. The current is maintained at greater than a 5% increase over normal operation, that is, operation of the cell devoid of the lithium content in the electrolyte. The anode current density used in the operation of the conventional "pre-bake" cells is in the range of from about 6.0 to 8.0 amperes per square inch and in the case of the conventional "Soderberg" cells, in the range of from about 4.5 to 6.5 amperes per square inch. The anode current density determinations cited herein are calculated by dividing the current supplied to the cell by the nominal bottom area of the anodes.

The ranges given above for current densities used in conventional cells are due to the size and heat balances of various cells. Smaller cells in general operate at higher current densities than do larger cells because of better heat dissipation. With the use of the lithium addition of the instant invention, the current density (and the current) for any given cell can be maintained at greater than a 5% increase in order to increase the productive capacity. It appears possible, through practice of the instant invention, that the increase in current density (and current) may be 25% or higher.

Practice of the invention has produced important and unexpected results in operation of aluminum electrolytic reduction cells, the most important being that of producing significant increases in production capacity of a conventional reduction cell, e.g. 12% increase in production per cell. Still greater increases in productive capacity have been found, according to the invention, when use is also made of cathodic current-conducting elements made of refractory hard metals, as discussed hereinbefore, e.g. 25% increase or greater, in productive capacity.

Moreover, the presence of lithium ion in the electrolyte results in little effect on the deposition efficiency for aluminum. Any adverse effect is more than off-set by the corresponding decrease in operating temperature made possible by the lower freezing point of the electrolyte resulting from the addition of lithium. Moreover, lithium shows no signs of increasing attack on the lining.

The significant increase in productive capacity of the reduction cell is believed primarily due to the lower electrolyte resistance and to an increase in heat dissipation of the cell. Moreover, it is believed that the increased heat dissipation of the cell is due to less bottom and side ledging and a thinner top crust.

It is to be noted that the initial freezing points of the lithium-containing electrolytes are substantially lower than those of the conventional electrolytes. The freezing point of an electrolyte containing 3% lithium fluoride is about 940° C., while an electrolyte containing 7% lithium fluoride has a freezing point of about 890° C. Therefore, with the lithium addition it is practical to use a lower operating temperature. It has been found that with an electrolyte consisting of 34% lithium cryolite (corresponding to about 16.5% lithium fluoride), 65% sodium cryolite and 1% alumina, operation of the cell could be carried out at 845° C. With an electrolyte containing 15% lithium cryolite (corresponding to about 7.5% of lithium fluoride), it was found that the freezing point was such that operation of the cell could be carried out at 910° C. At the lower temperatures possible with the higher lithium additions, the alumina solubility and solution rate is decreased; however, with the improvement of feeding techniques these higher additions will be of considerable value to the reduction operation. Utilizing a lithium addition corresponding to 3 to 8% lithium fluoride, the cell operating temperature may be from about 910° C. to 955° C.

The amount of super-heat (that is, the heat in excess

of that required for melting) in the electrolyte of the invention, while still maintaining a lower operating temperature, may be substantially greater than that existing in a conventional cell. This may account at least in part for less bottom ledging, lower cathode resistance and thinner top crust permitting better dissipation of heat. In addition, the lower operating temperature of reduction cells according to the present invention results in a lower net carbon consumption from anodes per pound of aluminum produced. It will be understood that the above discussion is in no way to be a limitation on the invention but is given merely as a possible explanation for the significant results achieved by the present invention.

It has been found also that because of the marked effect of lithium on the freezing point and electrical conductivity of the electrolyte, it is possible, by making relatively small changes in lithium content, to fully compensate for differences in heat dissipation with age of a given reduction cell in a cell line. This can be of substantial significance in reduction cell line operation in compensating for irregularities and poor current efficiency oftentimes encountered in individual cells in a given line of cells, particularly with regard to new cells placed in operation.

Also, the lithium additions to the electrolyte effect a greater density differential between the electrolyte and the aluminum metal. A greater density differential between the electrolyte and the aluminum metal reduces the tendency for metal to rise into the electrolyte under forces caused by electromagnetic fields, discharge of anode gases, and thermal convection. This not only allows for better separation of the metal from the electrolyte but also has a damping effect on the turbulence induced in the metal and the electrolyte by the magnetic fields resulting from the heavy electrical currents. Turbulence from electromagnetic forces, which becomes particularly acute in large size cells, results in reoxidation of the metal which will seriously impair the current efficiency. With the damping of the turbulence by the lithium-containing electrolyte, the working distance, that is, the anode-cathode distance, can be decreased.

For purposes of further understanding the invention, Table I below sets forth comparative, average operating data between two groups of nine conventional horizontal-stud Soderberg cells in a commercial operation, one group operating with and one group without the presence of lithium in the electrolyte or bath.

Table I

	Horizontal Stud Cells (No Li)	Horizontal Stud Cells (With Li)
55 No. of Cells.....	9	9
Period:		
Days.....	77	77
Pot Days.....	632	632
Total Production, Lbs.....	660,568	708,639
Production, Lbs. per cell day.....	1,035	1,212
Increase in Production, Percent.....		8.2
Lining Material.....	Carbon	Carbon
60 Current, Amperes.....	68,114	72,236
Current Increase, Percent.....		6
Voltage Drop Across Cell.....	5.06	5.03
Voltage Drop Between Anode and Cathode.....	3.70	3.64
Anode Current Density, Amps./sq. in.....	5.94	6.3
Bath Temperature, °C.....	970	951
Bath Ratio (NaF/AlF ₃).....	1.33	1.33
65 Bath Freezing Point, °C.....	957	930
Bath, Percent CaF ₂	6.5	13.9
Bath, Percent Al ₂ O ₃	5.5	5.5
Bath, Percent LiF (Source of LiF).....		4.35
		(Li ₂ CO ₃)
Anode-Cathode Distance, Inches.....	1.98	1.92
Lbs., C/Lb. Al.....	0.521	0.508
Current Efficiency, Percent.....	85.6	87.5
70 K.w.h. per Lb. Al.....	7.99	7.78
Cathode Voltage Drop, Volts.....	0.574	0.610
Bath Depth, Inches.....	5	5
Metal Depth, Inches.....	10	10

¹ CaF₂ not intentionally added—introduced into electrolyte as impurities from raw materials.

It will be apparent from the above table that the present invention, as applied to conventional electrolytic reduction cells for the production of aluminum, results in a very significant increase in the productive capacity of the cell and, also, a significant decrease in the consumption of carbon per pound of aluminum produced as well as other advantages.

Calculating the power efficiencies by use of Equation 6 above, the percent power efficiency of the Soderberg cells in Table I operating without the lithium electrolyte is 34.6% while those operating with the lithium bath is 36.2%, a substantial improvement.

Table II records data which shows a comparison between pre-bake cells, with and without the presence of lithium in the electrolyte.

Table II

	Pre-Bake Cell (No Li)	Pre-Bake Cell (With Li)
No. of Cells.....	1	1
Period, Days.....	252.6	251.4
Total Production, Lbs.....	37,450.8	41,742.8
Production, Lbs. per Cell Day.....	148.2	166.0
Increase in Production, Percent.....		12
Lining Material.....	Carbon	Carbon
Current, Amperes.....	9,716	10,783
Current Increase, Percent.....		11
Voltage Drop Across Cell.....	5.18	5.11
Voltage Drop Between Anode and Cathode.....	4.01	4.13
Anode Current Density, Amps./sq. in.....	7.64	8.48
Bath Temperature, °C.....	974	961
Bath Ratio, NaF/AlF ₃	1.39	1.42
Bath Freezing Point, °C.....	965	942
Bath, Percent CaF ₂	7.7	12.8
Bath, Percent Al ₂ O ₃ (Average).....	3.0	2.1
Bath, Percent LiF (Source of LiF)		4.93 (LiF, LiOH and LiCO ₃)
Anode-Cathode Distance, Inches.....	2.11	2.15
Lbs., C/Lb. Al.....	0.473	0.450
Current Efficiency, Percent.....	86.0	86.8
K.w.h. Per Lb. Al.....	8.15	7.96
Cathode Voltage Drop, Volts.....	0.68	0.457
Bath Depth, Inches.....	6.7	7.0
Metal Depth, Inches.....	5.5	5.1

¹ CaF₂ not intentionally added—introduced into electrolyte as impurities from raw materials.

From Table II it is seen that with the practice of the invention a substantial increase in productive capacity is realized. Also, a significant decrease in the consumption of carbon is realized. The power efficiencies (based on Equation 6 above) are 33.8% for the cell operating without lithium and 34.6% for the cell operating with lithium.

It is not the principal aim of the present invention, however, to improve the power efficiency of the reduction operation. There are instances in the practice of the invention wherein the power efficiency may be less than that of the conventional cell operation, but the sacrifice of power efficiency in these cases with the use of the present invention will be more than off-set by the increase in productive capacity.

As set forth hereinabove, it has also been found, according to the invention, that the use of the lithium-containing electrolyte combined with use of a cathodic current-conducting element or elements of the refractory hard metals, described above, results in still further significant increases in productive capacity of the aluminum reduction cell.

One embodiment of a reduction cell suitable for carrying out the method of this invention is shown schematically in the drawing. In this embodiment, 1 is a metal shell, generally steel, within which is disposed in the

usual manner an insulating layer 2 which can be any desired material, e.g. alumina, bauxite, clay, aluminum silicate brick, etc. Within the insulating layer 2 is disposed cell lining 3 which can be of any desired material, e.g., carbon, alumina, fused alumina, silicon carbide, silicon nitride bonded silicon carbide or other desired materials. Most commonly the lining is made up of a plurality of carbon blocks or is a rammed carbon mixture or a combination of a rammed carbon mixture for the bottom of the lining with side and end walls constructed of blocks of carbon. Alternatively, the side and end walls can be constructed of blocks of silicon carbide or other suitable refractory. The lining 3 defines a chamber which contains a pool of molten aluminum 4 and a body of molten electrolyte or bath 5, as described.

When carrying out the method of this invention and at the time when aluminum is being produced, electrolyte 5 and aluminum pool 4 are both in the molten state. Suspended from above the electrolyte, and partially immersed therein, is anode 6 of the conventional carbon type and which can be either of the "pre-bake" or "Soderberg" (self-baking) type known to the art. Molten electrolyte 5 is covered by a crust 7 which consists essentially of frozen electrolyte constituents and additional alumina.

As alumina is consumed in electrolyte 5, the frozen crust is broken and more alumina fed into the electrolyte. The anode is connected by suitable means (not shown) to the positive pole of a source of supply of electrolyzing current. For purposes of completing the electric circuit use is made of cathodic current-conducting elements 8. The elements 8 extend through suitable openings provided in the metal shell insulation layer and lining with the inner end thereof projecting into the pool of molten aluminum. The outer ends of such elements are connected by suitable means to negative bus-bars 9.

It will be understood that the drawing is but one of many apparatus embodiments using such cathodic current-conducting elements that can be used for carrying out the method of this invention. For example, other modifications involve the current-conducting elements projecting upwardly from the base of the cell lining with the upper end of such elements projecting into the molten aluminum pool or wherein the elements extend downwardly from above the cell through the electrolyte and with the lower end of the elements immersed in the pool of molten aluminum. In addition, it is not necessary that the elements project completely through the lining, insulating layer and metal shell of the cell structure. Instead, such elements may terminate short of the metal shell or insulation lining and suitable electrical connection means made between the outer end of the element and the negative bus bar. Moreover, as mentioned hereinbefore, such elements may be made up entirely of the refractory hard metal, as described, or only in part, it being essential that that portion of the surface of the end of the element which is in contact with the pool of molten aluminum and electrolyte consists essentially of such materials. Furthermore, the negative current-conducting elements can take the form of a sheet, plate, or other suitable shape and, also, where in effect it would function as the cathode of the electrolytic cell in place of the pool of molten aluminum.

Examples of practice of the present invention, and involving use of a reduction cell structure similar to that schematically shown in the drawings, are set forth in Table III below. In Table III data are given for two pre-bake cells (A and B) employing refractory hard metals as cathodic current-conducting elements and having lithium present in the electrolyte. For comparison, operating data are given for a prebake cell not employing refractory hard metal cathodic current-conducting elements and not involving a lithium-containing electrolyte.

Table III

	Prebake Cell (No Li)	A Prebake Cell Refractory Hard Metal Cathodic Elements ¹ (With Li)	B Prebake Cell Refractory Hard Metal Cathodic Elements ¹ (With Li)
No. of Cells.....	1	1	1
Period, Days.....	140.6	144.5	143
Total Production, Lbs.....	19,587	27,725.4	27,105.2
Production, Lbs./Cell Day.....	139.3	191.9	189.5
Increase in Production, Percent.....		37.8	36
Lining Material.....	Carbon	Bottom—Carbon Walls— SiC	Bottom—SiC Walls—SiC
Current, Amperes.....	9,366	11,895	11,806
Current Increase, Percent.....		27	26
Voltage Drop Across Cell, Volts.....	5.07	5.46	5.02
Voltage Drop Between Anode and Cathode, Volts.....	3.93	4.73	4.27
Anode Current Density, Amps./sq. in.....	7.37	9.35	9.30
Bath Temperature, °C.....	974	941	946
Bath Ratio, NaF/AlF ₃	1.49	1.32	1.32
Bath Freezing Point, °C.....	963	937	937
Bath, Percent CaF ₂	7.48	² 2.42	² 2.5
Bath, Percent Al ₂ O ₃ (Average).....	3.76	2.48	2.49
Bath, Percent LiF (Source of LiF).....		4.97 (LiF)	4.97 (LiF)
Anode-Cathode Distance, Inches.....	2.12	2.05	2.08
Lbs., C/Lb. Al.....	0.482	0.407	0.423
Current Efficiency, Percent.....	84.7	90.9	90.5
K.w.h. per Lb. Al.....	8.19	8.13	7.51
Cathode Voltage Drop, Volts.....	0.679	0.269	0.208
Bath Depth, Inches.....	6.8	6.5	6.5
Metal Depth, Inches.....	5.4	5.3	6.2

¹ A typical analysis of the refractory hard metal elements is as follows (in percent by weight): TiB₂—04.5%; TiC—2.5%; B₄C—1.5%; TiN—0.8%; Fe—0.25%; B₂O₃—0.25%; Free Carbon—0.20%.

² CaF₂ not intentionally added—introduced into electrolyte as impurities from raw materials.

It is thus seen from a comparison of the examples in Table III that the productive capacity of the cell is vastly increased, the carbon consumption per pound of aluminum produced is reduced, the current efficiency increased, and wherein the power per pound of aluminum produced is substantially the same as that resulting from operation of a conventional electrolytic reduction cell.

The power efficiencies of the examples in Table III are 34%, 34% and 36.8% for the prebake cell without refractory hard metal cathodic current-conducting elements, Cell A, and Cell B, respectively.

Although the invention is not so limited, it will be noted by way of the examples heretofore discussed that the cell voltage drops are within the range of about 4.5 to 5.5 volts.

It will be apparent from the above description that by practice of the present invention significant increases in productive capacity or output can be accomplished with existing conventional electrolytic reduction cells, e.g., "prebake" cells and Soderberg cells of either the horizontal stud or vertical stud type, wherein power consumption per pound of aluminum produced is substantially the same coupled with lower net carbon consumption per pound of aluminum and higher cell current and power efficiencies. Moreover, by modification of the cell structure to include the provision of cathodic current-conducting elements, as described, still further increases in productive capacity can be accomplished. In addition to conventional electrolytic cells, the invention is also applicable to other electrolytic cells, for example a multiple-cell aluminum reduction furnace having inclined bipolar electrodes as disclosed in French Patent 1,119,832 and a cell employing sloping cathode walls as disclosed in French Patent 1,119,821. Manifestly, from these significant increases in productive capacity or output stem important economic advantages. Capital investment in electrolytic furnaces per pound of aluminum produced will be decreased. Also, labor, maintenance, and administration costs per pound of aluminum produced will be substantially reduced.

It will be understood that various changes, modifications and alterations may be made in the instant inven-

tion without departing from the spirit and scope thereof and, as such, the invention is not to be limited except by the appended claims, wherein

What is claimed is:

1. The method of increasing the output of an electrolytic aluminum reduction cell, which cell comprises a carbon anode, a molten aluminum cathode and a molten salt electrolyte consisting essentially of cryolite and alumina, and in the operation of which current is passed from said anode through said electrolyte to said cathode with a given voltage drop across the cell, which method comprises incorporating lithium-containing material in said electrolyte in an amount to provide in said electrolyte a lithium content equal to that resulting from an addition of lithium fluoride in an amount from about 2 to 20 percent by weight of the electrolyte, and establishing a current flow so that the resultant voltage drop across the cell is at least substantially as great as said first named voltage drop, the temperature of the lithium-modified electrolyte being above about 845° C.
2. Method according to claim 1 wherein the lithium content of the lithium-containing material incorporated in the electrolyte is equal to that resulting from the addition of lithium fluoride in an amount from about 3 to 8% by weight of the electrolyte.
3. Method according to claim 1 wherein said lithium-containing material is at least one substance selected from the group consisting of lithium fluoride, lithium cryolite, lithium aluminate, lithium carbonate and lithium hydroxide.
4. The method of increasing the output of an electrolytic aluminum reduction cell which cell comprises a carbon anode, a solid cathodic current-conducting element wherein at least the operative surface thereof consists essentially of at least one of the materials selected from the group consisting of the borides and carbides of titanium, zirconium, tantalum and niobium, a pool of molten aluminum and a molten salt electrolyte consisting essentially of cryolite and alumina, and in the operation of which current is passed from said anode through said electrolyte to said element with a given voltage drop across the cell, which method comprises incorporating

lithium-containing material in said electrolyte in an amount to provide in said electrolyte a lithium content equal to that resulting from an addition of lithium fluoride in an amount from about 2 to 20% by weight of the electrolyte and establishing a current flow so that the voltage drop is at least substantially as great as said first named voltage drop, the temperature of the lithium-modified electrolyte being above about 845° C.

5. Method according to claim 4 wherein the lithium content of the lithium-containing material incorporated in the electrolyte is equal to that resulting from the addition of lithium fluoride in an amount from about 3 to 8% by weight of the electrolyte.

6. A method of increasing the output of an electrolytic aluminum reduction cell comprising the steps of passing a current from a carbon anode through a molten salt electrolyte consisting essentially of cryolite and alumina, and to a molten aluminum cathode, said electrolyte containing a lithium content equal to that resulting from the addition of lithium fluoride in an amount from about 2 to 20% by weight of the electrolyte, and increasing the current

flow so that the voltage drop across the cell is in the range of about 4.5 to 5.5 volts, the temperature of the electrolyte being above about 845° C.

7. Method according to claim 6 wherein said electrolyte contains a lithium content equal to that resulting from the addition of lithium fluoride in amount from about 3 to 8% by weight of the electrolyte.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,034,972

May 15, 1962

Robert A. Lewis

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 26, for "call" read -- cell --; column 8, line 29, for "electrolyle" read -- electrolyte --; line 35, for "electrolye" read -- electrolyte --; same column 8, Table I, first column, seventh item, for "Produstion" read -- Production --; column 9, Table II, column 3, line 19 thereof, for "LiCO₃" read -- Li₂CO₃ --.

Signed and sealed this 1st day of January 1963.

(SEAL)

Attest:

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