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APPARATUS FOR ELECTROLYTIC PRODUCTION OF A METAL PRODUCT FROM FUSED SALTS

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Fig. 1

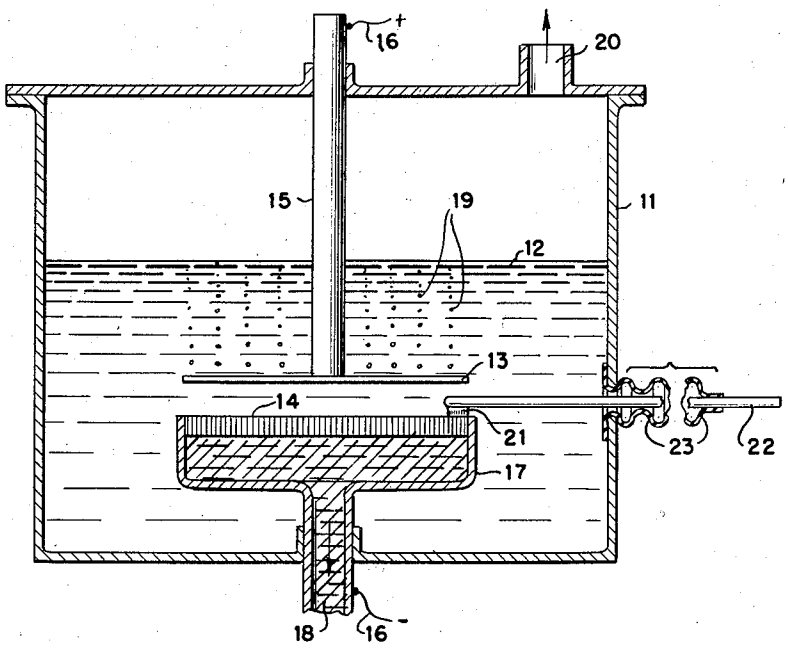
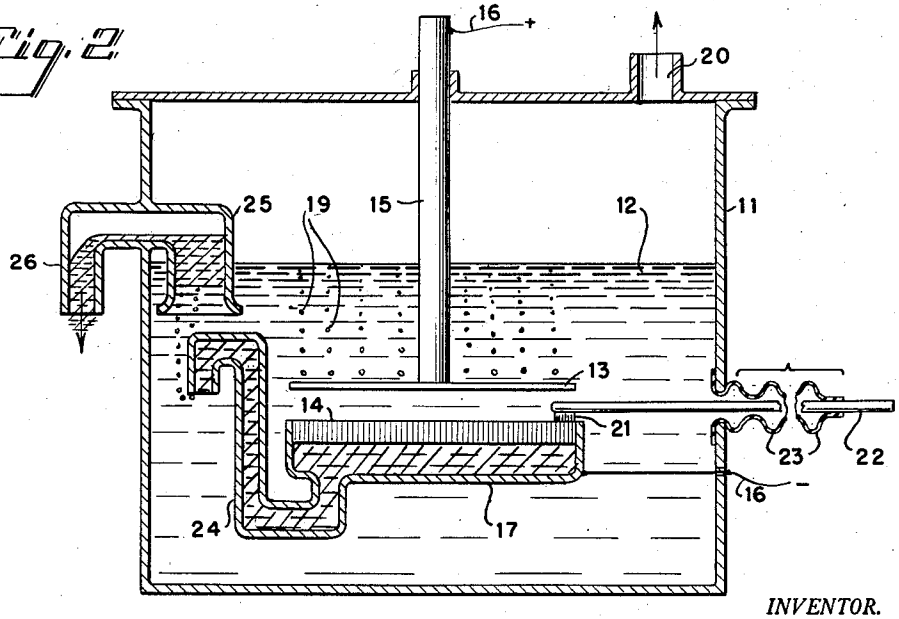


Fig. 2



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APPARATUS FOR ELECTROLYTIC PRODUCTION OF A METAL PRODUCT FROM FUSED SALTS

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3 Claims. (Cl. 204—227)

My invention relates to the electrolytic production of metals such as sodium, potassium, lithium, cesium, rubidium and magnesium including their alloys, from an electrolyte such as the respective halide or halides which has a greater density than the metal or alloys.

In the electrolysis of an electrolyte into a metal product and a halogen product, it is easier to operate an electrolytic cell when the metal product can be collected in the bottom of the cell rather than at the top of the cell where the halogen gas collects. When the metal product is less dense than the electrolyte, the advantage of collecting the metal product at the bottom of the cell has been achieved by collecting the metal product in a liquid metal cathode of greater density than the electrolyte. However, the use of a heavy liquid metal cathode such as molten lead necessitates subsequent separation of the collected metal product from the heavy liquid metal constituting the cathode.

The object of my present invention is to collect a metal product which is less dense than the electrolyte without the use of a heavy liquid metal cathode.

I achieve this object by using a porous cathode which is saturated with liquid metal product for the purpose of soaking up the metal product as fast as it is formed on the cathode surface. Excess liquid metal product collecting in the porous cathode is sucked out therefrom into a collector for said liquid metal product. The suction applied to draw the liquid metal product out of the porous cathode has to be so strong that the metal product is prevented from bubbling upward from the upper surface of the porous cathode, but not as strong as to suck electrolyte through the porous cathode.

The porous cathode is located under the anode so that as little as possible of the gaseous halogen being formed at the anode will contact it. The surface portion of the porous cathode from which metal product is being sucked may be any area on which metal product is not being formed.

The porous material comprising the porous cathode must be resistant to attack from both the metal product and the electrolyte at the operating temperature of the cell, and also must be able to be wetted thoroughly by the liquid metal product while being immersed in the electrolyte at the operating temperature of the cell. The porous cathode is comprised usually of sintered particles of a refractory metal such as iron, stainless steel, or molybdenum; however, other forms and other materials may be used.

The anode may be in any shape and position which allows the by-product gas forming on it to escape upward easily.

Suitable metal products to be formed and collected on the porous cathode are: sodium, potassium, lithium, cesium, rubidium and magnesium, or alloys of two or more such metal products. For example from a suitable electrolyte an alloy of sodium and potassium may be produced and collected on the porous cathode.

Any of the fused electrolyte compositions used in

electrolytic cells for producing the aforesaid metal products may be used in my new process providing the metal product is the only cathode product.

I prefer that the size of the pores in the porous cathode be as uniform as possible. I also prefer to operate the cell at such lowest temperature that will allow both the electrolyte and the metal product to be in liquid phase. I also prefer to have all portions of the porous cathode which contact the electrolyte to be on the same level. I further prefer that the anode be in the form of a screen or a grating in order that the halogen gas which forms on it can escape upward easily.

The said and other objects of my invention will be more fully understood from the following specification when read with the accompanying drawing in which two embodiments of an electrolytic cell for use in my new method are shown in a schematic sectional view in Figs. 1 and 2, respectively. In both figures the same reference numbers indicate the same or equivalent elements.

In the drawing, Fig. 1 shows an electrolytic cell **11** which contains a suitable molten halide electrolyte **12** such as a eutectic mixture of two or more alkali metal chlorides maintained in molten condition by not shown electric heaters or other suitable means arranged within the cell. The anode **13** held by support **15** and the cathode **14** are each connected to a suitable source of direct current by means of electric leads **16**. The anode **13** which may be made of graphite or a metal such as nickel has advantageously the form of a grid or screen of such design that the halogen gas may escape upward most easily and the total surface area of the anode grid **13** on which the halogen gas is formed is preferably considerably larger than the area of the cathode **14** on which the metal product is formed because a substantial portion of the area of the anode is covered by and electrically insulated from the electrolyte by the halogen gas forming on it. The porous cathode **14** may be fabricated from a suitable sintered refractory metal such as sintered stainless steel and is tightly placed in a box or similar member **17** which forms a suction chamber to prevent any electrolyte from leaking thereinto. The box **17** and its outlet conduit **18** are filled with liquid metal product prior to the starting of the operation and this liquid metal product is held therein by suitable closure means not shown in the drawing. When the cell is operating, liquid metal product is formed on the upper surface of the porous cathode **14**, passes through the porous cathode into cathode box **17**, and is withdrawn therefrom through conduit **18** by creating a pressure differential across the porous cathode such pressure differential being maintained within desirable limits by the application of a controlled suction on the metal product flowing out of conduit **18**, such suction being effected by a conventional apparatus (not shown) outside the cell.

The halogen gas **19** formed on the anode **13** bubbles up through the molten electrotype **12**, collects in the upper portion of the cell **11** and is vented from the cell through a suitable conduit **20**. Since, in all cases except when a highly purified electrotype is used, some sediment tends to collect on the upper surface of the cathode **14**, a wiper **21** may be provided to brush all sediment off the top of the anode into the lower portion of the cell. This wiper is usually made out of a non conductive material such as glass, vicor, quartz or the like and may be mechanically or manually actuated even while the cell is operating by a push pull motion imparted to rod **22**. The gland where rod **22** passes through the wall of the cell **11** is sealed by a metal bellows **23** or any other type or suitable gland seal. If desirable, means may be provided to raise or lower the anode **13** relative to the cathode **14** to facilitate the cleaning of the cathode surface and to permit to selectively distance the same from each other.

The modified embodiment illustrated in Fig. 2 comprises like the embodiment shown in Fig. 1 a cell **11**, an anode **13** held by support **15**, a cathode **14** and a wiper **21** actuated by the rod **22** which passes through the seal **23**. The cathode box **17** is provided with or attached to a syphon **24** located within the cell **11** and submerged in the electrotype **12**. This syphon **24** effects an automatic controlled suction on the liquid metal product in the box **17**, the suction force being proportional to the difference in level between the top surface of the porous cathode **14** and the level at which the liquid metal product escapes from syphon **24**. The thus escaping liquid metal product bubbles upward through the electrolyte **12** and enters a collector **25** wherein it accumulates above the depressed level of the electrolyte to leave the collector **25** through the overflow conduit **26**.

Example 1

In a cell of the type shown in Fig. 1 or Fig. 2 an electrolyte comprised of 60 atomic percent of potassium chloride and 40 atomic percent of lithium chloride is melted and maintained at about 375° C. The cell is a square stainless steel box 30 cm. by 30 cm. and 30 cm. deep. The porous anode is square and has an area of about 12 by 12 cm.^{2}. Its upper surface lies on a plane 5 cm. above the bottom of the cell, and it is comprised of 5 micron sintered stainless steel having a thickness of approximately 0.5 cm. The electrolyte covers the cathode to depth of 10 cm. The anode is formed by a grid of graphite perforated with ⅜ inch holes, having 60% open area and a thickness of about ¼ inch. The anode is suspended on each corner by a graphite rod, and has its lower surface of the cathode. No diaphragm is used, between the anode and the cathode. Before the operation of the cell is started, the molten electrolyte which fills the pores of the cathode, the cathode box **17** and either the outlet pipe **18** (Fig. 1) or the syphon **24** (Fig. 2) respectively, is displaced with molten sodium. The molten sodium saturates the porous cathode **14**. A 6-volt electric battery may be used to power the cell with about 6 volts at approximately 100 amperes. During the first part of each run the upper surface of the porous cathode tends to acquire a light deposit of impurities from the electrolyte which are easily brushed off. However, the further the run progresses the less is the tendency for impurities to settle on the cathode. The strong current of electrolyte flowing across the upper surface of the cathode is powered by the rising stream of chloride which is a great aid in keeping the upper portion of the cathode clean and allowing the sludge to settle at the bottom of the cell where the electrolyte currents are much weaker. As the run progresses the sodium in the cathode and the cathode box is replaced with molten potassium and lithium. At an average current of 100 amperes, about 110 grams of chlorine is produced in one hour. When 6 volts is used to power the cell, the amperage may be adjusted and held constant by raising or lowering the anode. If desired the cell can be operated on considerable less than 6 volts by decreasing the distance between the anode and the cathode and using lower amperage. Very high current efficiency is obtained if the anode is not brought so close to the cathode that chlorine washes the metal product forming on the cathode. However, the voltage required to operate the cell at a given amperage becomes less as the anode and cathode are brought closer together. The molten metal product being an alloy of potassium and lithium which assembles in the cathode box **17** is recovered therefrom by suction as described above either through the outlet conduit **18** shown in Fig. 1 or through the syphon **24** and collector **25** shown in Fig. 2.

Example 2

Sodium with a relatively small percent of calcium may be recovered in the manner above from an electrolyte composed of about 59% $CaCl_2$ and 41% NaCl at an operating temperature of 600° C.

Example 3

Sodium with a relatively small percent of cesium may be recovered in the manner described above from an electrolyte composed of a eutectic mixture of CeCl and and NaCl at an operating temperature of 500° C.

Example 4

Magnesium may be recovered in the manner described above from an electrolyte of MgCl having a possible addition of NaCl up to about 50% at a temperature of 675° C.

While specific embodiments of my invention have been shown and described in detail to illustrate the application of the principles of my invention, it will be well understood that the same may be otherwise embodied and performed without departing from such principles and without avoiding the scope of my appended claims.

What I claim as my invention is:

1. In an electrolytic cell for producing metal products which are less dense than the fused electrolyte the improvement comprising a substantially flat porous cathode adapted to be saturated with liquid metal product; an anode having the shape of a grid or screen permitting gaseous by-products formed on the anode to pass therethrough; said anode and said cathode extending in substantially horizontal planes immersed in the electrolyte, the anode being located over said cathode; a suction chamber tightly attached to the cathode in opposite relation to the anode, the cathode forming the top cover of said chamber; a suction piping attached to said suction chamber to suck liquid metal product deposited on and saturating the porous cathode into and from said chamber; means to create and to control the suction action; and receiving means collecting the sucked liquid metal product apart from the electrolyte and the gaseous halide products.

2. In an electrolytic cell for producing metal products which are less dense than the fused electrolyte the improvement comprising a substantially flat porous cathode adapted to be saturated with liquid metal product; an anode having the shape of a grid or screen permitting gaseous by-products formed on the anode to pass therethrough; said anode and said cathode extending in substantially horizontal planes immersed in the electrolyte, the anode being located over said cathode; a suction chamber tightly attached to the cathode in opposite relation to the anode, the cathode forming the top cover of said chamber; a syphon attached to said suction chamber to suck liquid metal product deposited on and saturating the porous cathode into and from said chamber; said syphon leading from said chamber to a level in the cell higher than the level of the surface of the cathode on which liquid metal product is deposited; a collector collecting the liquid metal product bubbling upward from the syphon through the electrolyte within the cell; and a receptacle receiving the liquid metal product from said collector.

3. An electrolytic cell according to claim 1 comprising a scraper for cleaning the surface portion of the cathode upon which the metal product is deposited and means to actuate said scraper from outside the cell.

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