

May 11, 1971

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3,578,580

ELECTROLYTIC CELL APPARATUS

Filed Oct. 17, 1967

2 Sheets-Sheet 1

Fig. 1.

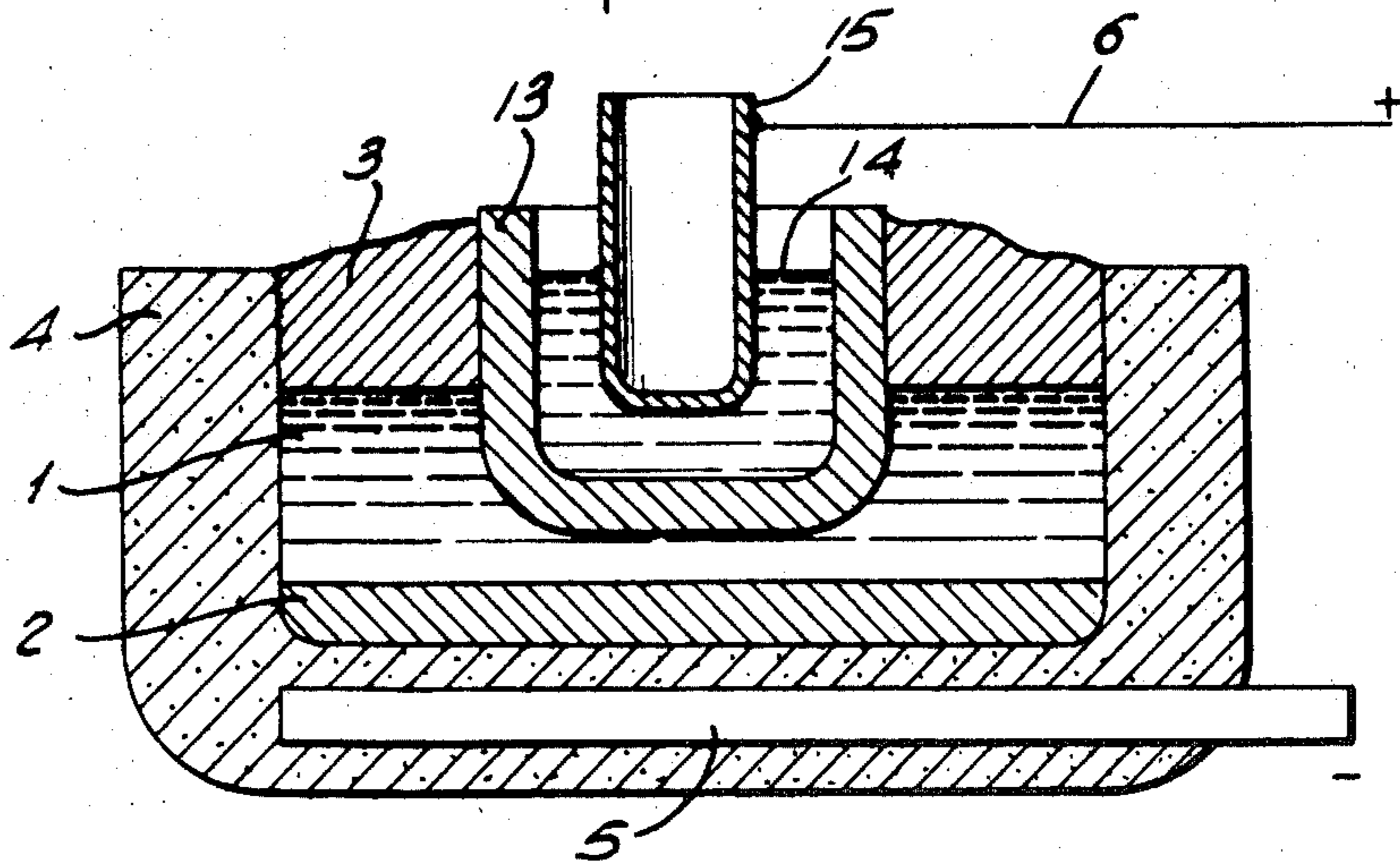
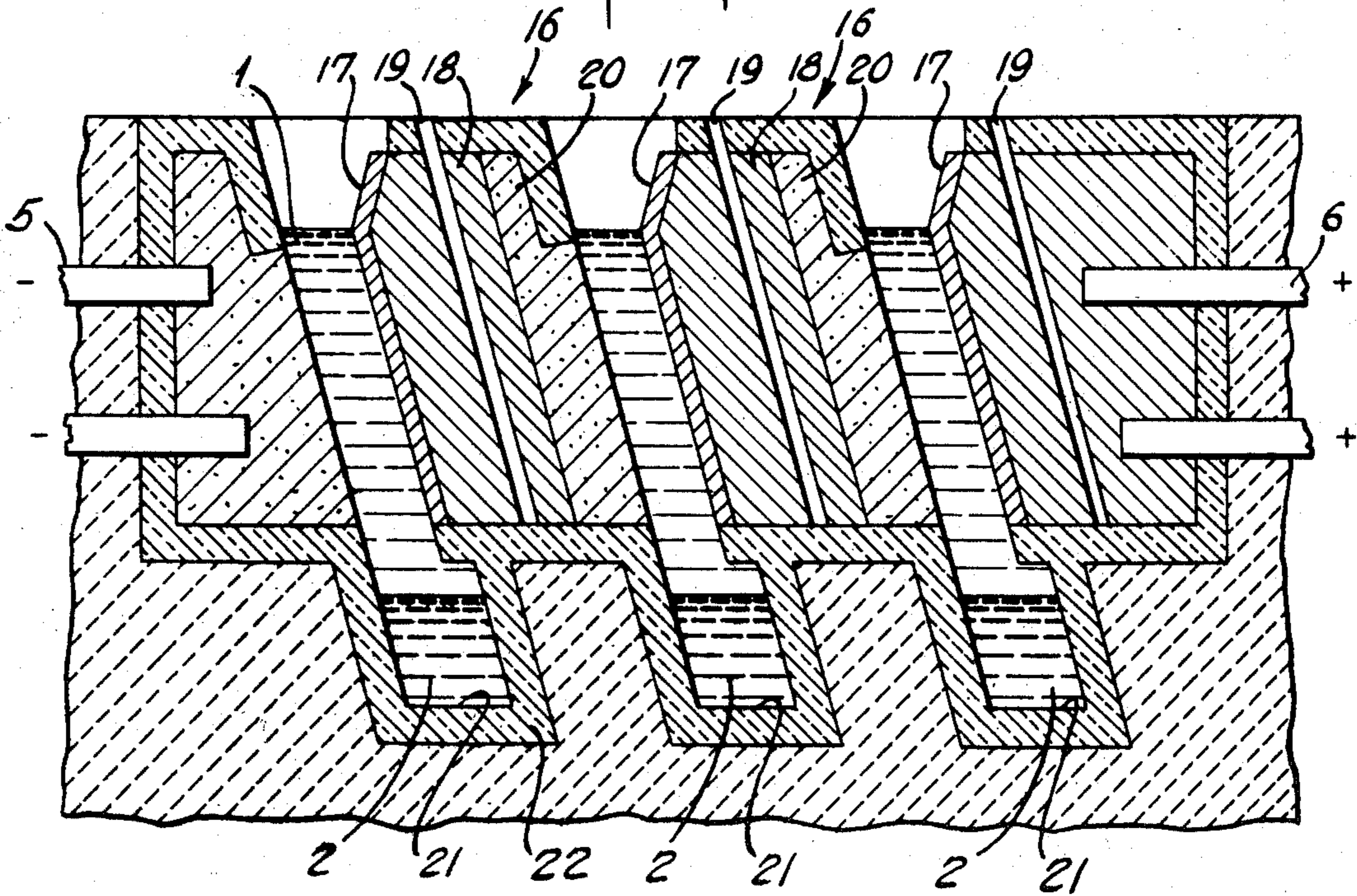


Fig. 2.



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Fig. 3.

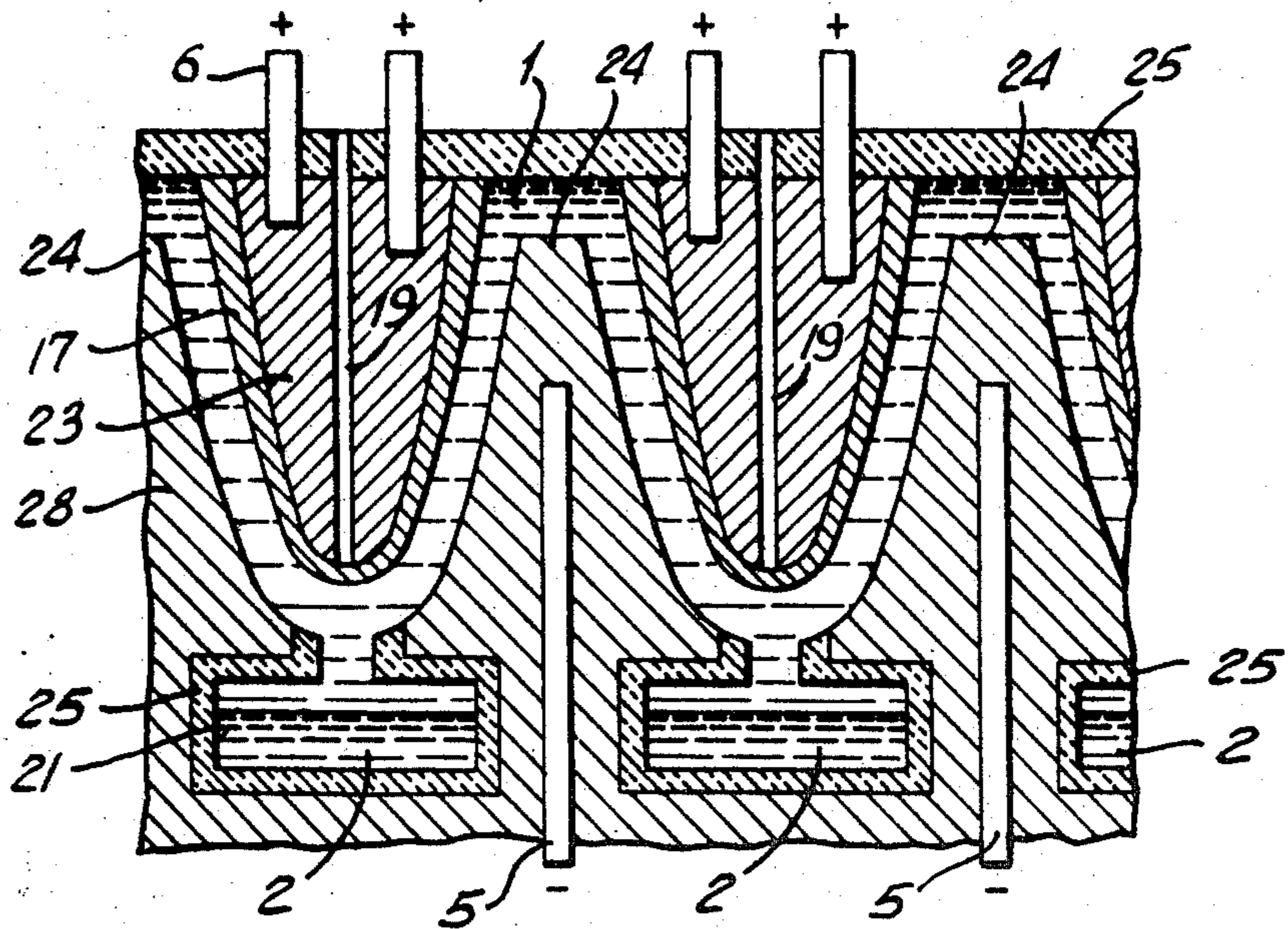
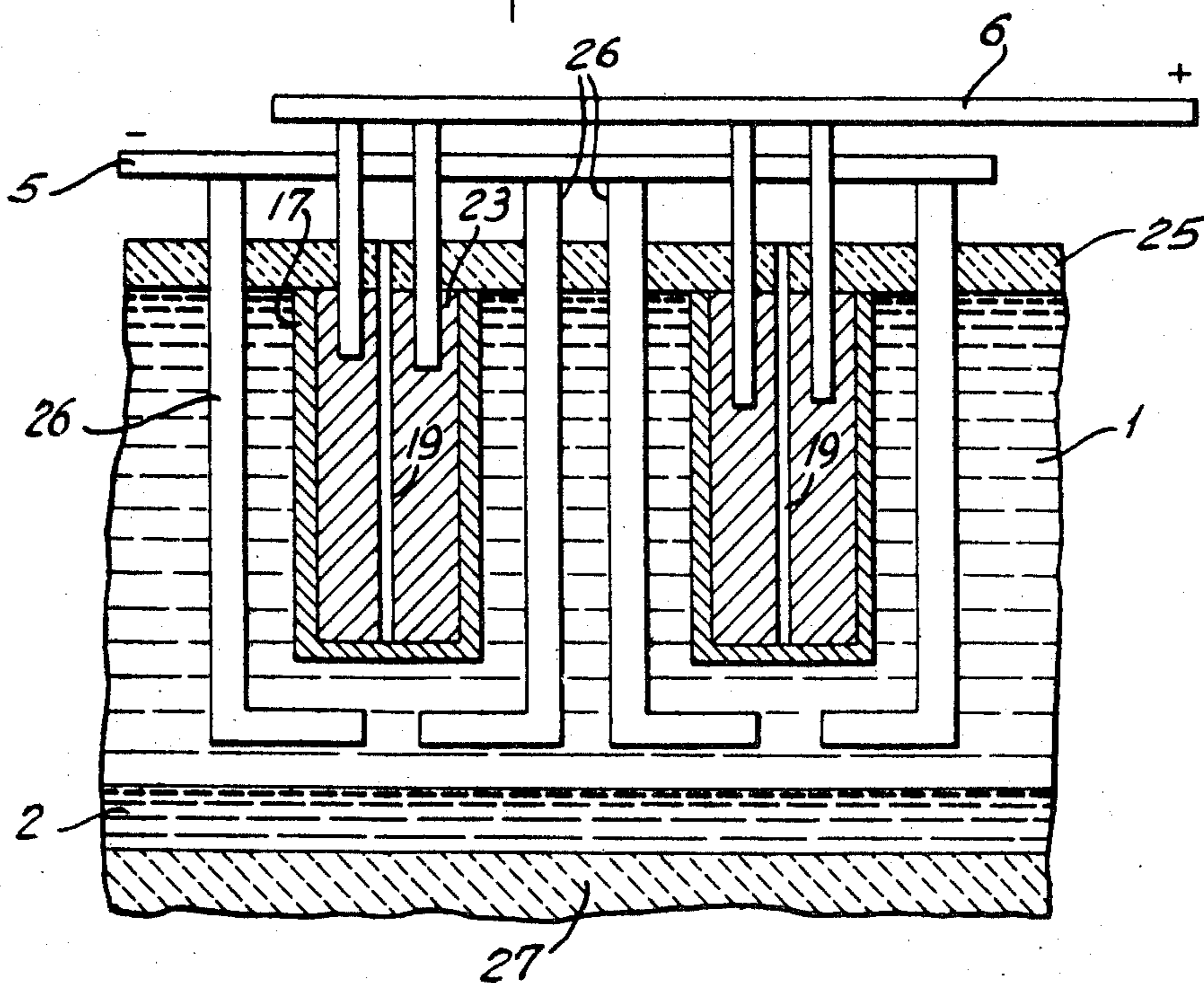


Fig. 4.



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**ELECTROLYTIC CELL APPARATUS**

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Filed Oct. 17, 1967, Ser. No. 675,881

Claims priority, application Switzerland, Apr. 28, 1967, 6,145/67

Int. Cl. C22d 1/02; B01k 3/04

U.S. Cl. 204—243

8 Claims

**ABSTRACT OF THE DISCLOSURE**

Apparatus for the electrolysis of molten oxides, especially of alumina, in which the anode is separated from the melt being electrolysed by a layer of oxygen-ion-conducting material, for example cerium oxide stabilised with calcium oxide or other oxides, which is resistant to the melt at the temperature of the electrolysis, and correlated inventions and discoveries appertaining thereto.

**BACKGROUND OF THE INVENTION**

The electrolysis of molten materials, for example of alumina, is carried out today with carbon anodes. In the case of alumina, the oxygen ions formed during the electrolysis react with the carbon of the anode at the process temperatures of 900 to 1000° C. and form carbon dioxide, which is partly reduced to carbon monoxide by the aluminium itself. Owing to the oxidation of the anode by the nascent oxygen, the carbon anode is consumed and, in fact, if only carbon dioxide were to be formed, 334 kg. of carbon per ton of aluminium produced would be consumed. In practice, about 400 to 450 kg. of anode carbon are consumed per ton of aluminium, which corresponds to about 8 to 10% of the cost of crude aluminium. It has only recently been possible to reduce the consumption of anode carbon even to this figure, and with the present method of working using carbon anodes, reduction of the consumption of anode carbon below the theoretically smallest amount, that is 334 kg. of carbon per ton of aluminium, is not possible.

It is possible to carry out the melt electrolysis of oxides without using carbon anodes, but using electrodes which are oxygen resistant without necessarily being resistant to attack by the melt being electrolysed, so that the oxygen can be obtained as a valuable by-product of the process. About 600 cu. m. of pure gaseous oxygen are formed per ton of aluminium; the value of the oxygen is about 3% of the cost of the crude aluminium. The oxygen which can be recovered in carrying out the process according to the invention into effect can be used for various oxidising processes, such as for example, steel production (by the oxygen blow method), the gasification of fuels (for producing synthetic gas) and the preparation of reducing gases for iron reduction.

We use an anode of any suitable conducting material, and we separate this anode from the melt being electrolysed by a layer of material which is oxygen-ion-conducting but non-permeable to and resistant to the melt at the temperature of the electrolysis, so that the oxygen ions diffuse through the layer and are then discharged at the anode with the formation of oxygen gas, and the anode itself is not subject to attack by the melt. The anode itself preferably consists of an electron-conducting material which does not react with oxygen or at least does not form with oxygen any compound impairing the conduction of electrons. Suitable materials include heat-resistant alloys, platinum or other noble metals, electron-conducting oxides, such as for example, wustite, certain materials with semi-conductor properties, and

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metals with a passivated surface. The thickness of the oxygen-ion-conducting layer may be very small so that the voltage drop across it is also small; this reduces losses of energy during the electrolysis.

Known stabilised forms of zirconium oxide are very suitable as the material which separates the anode from the melt. By stabilised, we mean zirconium oxide in which is incorporated proportions of other oxides such as calcium oxide, magnesium oxide and yttrium oxide, which serve firstly to stabilise the cubic (fluorite) lattice of the zirconium oxide, and secondly to confer on it the necessary oxygen-ion conductivity. By suitable choice of oxides and their proportions, a stabilised zirconium oxide can have a resistance as low as 10 ohms per cm. at 1000° C.

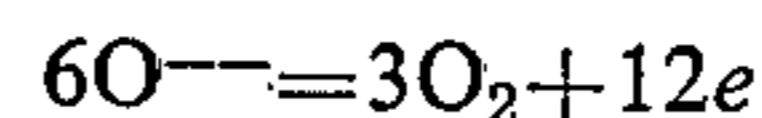
**SUMMARY**

We have found that other refractory oxides which have fluorite lattices can be used, such as for example, rare earth oxide-uranium oxide compositions, thorium oxide-uranium oxide compositions and cerium oxide suitably stabilised with calcium oxide or magnesium oxide. Substances which reduce the solubility of the oxygen-ion-conducting material may be added to the fused melt.

The invention will be described hereinafter with specific reference to the electrolysis of alumina for the production of aluminium. In such an electrolysis, the oxygen ions which are formed in accordance with the equation



diffuse through the oxygen-ion-conductive layer and are discharged at the anode in accordance with the equation



i.e. the oxygen ions combine to form oxygen gas and electrons are released in the process. These electrons are conducted away by the anode. Other oxides such as for instance, MgO, Na<sub>2</sub>O, CaO, Fe<sub>2</sub>O<sub>3</sub>, can also be electrolysed by the process according to the invention and similar equations can be formulated. In the electrolysis of alumina for example, cells according to the invention afford the following advantages, inter alia, in comparison with the present state of the art.

(1) There is no consumption, or only a very low rate of consumption, of anode material with the result that the rate of production of anode material can be substantially reduced.

(2) The formation of carbon scum in the bath results in a loss of operating efficiency, and this formation will not occur if the anodes are of material other than carbon.

(3) There is improvement of the quality of the aluminium metal produced, since no impurities, such as iron, silicon or vanadium are introduced from the anode material.

(4) There is less down-time of the cell, since the anodes do not have to be replaced.

(5) There is a reduction of the consumption of fluxing materials, since the cell can be sealed off more satisfactorily and this also gives an improvement in the shop atmosphere.

(6) Pure oxygen can be produced and collected as a by-product.

(7) There is no re-oxidation of the liquid aluminium by carbon dioxide and thus, there is increased output from the cell and a reduction in the energy required to produce a given weight of aluminium.

Cells according to the invention can readily be adapted for automation of operation with for example, continuous addition of alumina to the fused melt and maintenance of constant inter-electrode gap or cell voltage.

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Cells according to the invention may be constructed in two ways. In the first of these, the anode is coated with or is in contact with the layer of oxygen-ion-conducting material over at least that part of its surface which is immersed in the melt; the anode must then be in such a physical state that oxygen gas can pass through it.

The anode may be solid, in which case it must be porous, perforated or reticulated, or may be a liquid at the electrolysis temperature, so that the oxygen may bubble through it.

If the anode is solid, the layer of oxygen-ion-conducting material may be applied directly to it by pressing or casting with subsequent drying and sintering or by plasma spraying. Alternatively a body of the material may be preformed quite separately and put in contact with the anode, if the latter is, for example, a metal network. As a further possibility, a porous layer of platinum black may be applied to a preformed body of the material, and electrically connected to one terminal of the current supply. This last proposal is found to be very satisfactory, as platinum black is particularly suitable for the discharge of oxygen ions and the formation and removal of oxygen gas.

At the temperature of electrolysis the anode may be a liquid, for example molten silver. In this case, the oxygen-ion conducting layer is preformed in the shape of a cup, and dips into the fused melt, the anode of molten silver being contained in the cup. Oxygen ions diffusing through the ion-conducting layer are discharged at the silver anode. The silver is probably oxidised at the same time, but the silver oxide immediately decomposes again at the high temperatures and the oxygen escapes in the form of gas bubbles. These can be collected by means of a bell dipping into the liquid silver, the bell serving at the same time as a current lead to the anode and consisting for example of a chrome-nickel alloy.

In the second method of construction, the layer of oxygen-ion-conductive material is in the form of a cup-shaped preformed body and contains an auxiliary electrolyte which is liquid and dissociated at the temperature of electrolysis to yield oxygen ions; the anode itself dips into this auxiliary electrolyte. Obviously, the auxiliary electrolyte must be compatible with both the anode and the oxygen-ion conductive material, and should preferably have as low a vapour pressure as possible at the electrolysis temperature; we have found that lead oxide PbO is very suitable for use as the auxiliary electrolyte.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a transverse sectional view of one form of electrolytic cell embodying the invention;

FIG. 2 is a similar view of a modification;

FIG. 3 is a similar view showing a further modified form; and

FIG. 4 is a similar view of another modification.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention will now be described with reference to FIG. 1 of the accompanying drawings, which represents a section through an electrolytic cell for the electrolysis of fused alumina-cryolite mixtures. A carbon tank 4 contains the fused alumina-cryolite melt indicated as 1, and the liquid, electrolytically produced aluminium, which accumulates on the bottom of the cell and at the same time acts as a cathode in the arrangements according to FIG. 1 is shown as 2. The fused melt is covered by a layer 3 consisting of solidified melt and alumina. A bus bar 5 conducts the current from the tank.

The anode may consist of a gas-permeable, electron-conducting body which is covered with the oxygen-ion conductive material over at least the portion of its surface immersed in the fused melt. The oxygen-ion conductive material may be in the form of a hollow cup-shaped

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body, the inner surface of which is lined with a layer of platinum black as anode. The layer is electrically connected to a terminal which is itself connected to a source of direct current by means of a lead 6. During the electrolysis the oxygen ions of the electrolyte diffuse through the oxygen-ion conductive layer, are discharged at the surface of contact between the oxygen-ion conductive layer and the layer of platinum black and combine in the layer of platinum black to form gaseous oxygen which collects in a hollow space and escapes through a vent 11. The terminal forms the upper end of the hollow space and incorporates a gas vent. The electrons that are liberated flow off by way of the anode, the terminal and the lead 6. The oxygen gas evolved can escape under atmospheric pressure, be drawn off under reduced pressure or be collected under pressure in excess of atmospheric in the hollow space.

The oxygen-ion conductive material may be in the form of a plate which is in contact with a porous anode. The porous anode is connected to the source of direct current by means of the lead 6.

In FIG. 1, the oxygen-ion conductive material is in the form of a cup-shaped body 13 which dips into the melt 1 to be electrolysed. Within the cup-shaped body is an auxiliary electrolyte 14 consisting of lead oxide PbO. An anode 15 dips into the auxiliary electrolyte 14 and is connected to the lead 6. The anode consists of an electron-conducting material which is oxygen-resistant, for example platinum or a conductive oxide such as wustite.

In this arrangement, the oxygen ions from the cryolite-alumina melt diffuse through the oxygen-ion-conductive layer 13 under the effect of the applied direct current voltage. Oxygen ions are discharged at the anode 15, and the electrons are carried to the source of direct current by way of the current supply lead 6. The discharged oxygen ions from gaseous oxygen which escapes from the liquid auxiliary electrolyte or can be collected. At the boundary layer between the oxygen-ion conducting layer and the auxiliary electrolyte, precisely that number of oxygen ions in the auxiliary electrolyte which have been discharged at the anode is replaced by the oxygen ions which have diffused through the oxygen ion conducting layer 13, so that the auxiliary electrolyte is in a state of dynamic equilibrium and does not undergo permanent change.

The anode in the cell shown in FIG. 1 is not in direct contact with the oxygen-ion conducting layer 13 and therefore does not have to be porous. Difficulties which arise in the manufacture of an anode covered with oxygen-ion conducting material are thereby eliminated, as a direct electrical contact of large area between the oxygen-ion-conducting layer and a porous anode no longer has to be established. On the contrary, very favourable contact conditions in the electrical sense exist both at the boundary layer between the oxygen-ion-conducting layer and the auxiliary electrolyte and at the boundary layer between the auxiliary electrolyte and the anode, in that in both cases a liquid conductor and a solid conductor are in contact. The distance from the anode 15 to the oxygen ion-conducting layer 13 may be very small in order to keep the voltage drop in the auxiliary electrolyte small.

The invention may be used with advantage in multi-cell furnaces or in cells with bipolar electrodes, such as are described for example in German patent specifications 1,146,260 and 1,148,755. The electrolytic furnaces used today for alumina electrolysis have only two electrodes: an anode, which may consist of several separate anode blocks and a cathode, which is formed by the layer of deposited liquid aluminium on the bottom of the cell. The anodic current density is not very different from the cathodic current density, but is generally a little greater.

Customary values for the anodic current density are:

janode=0.6 to 1.4 A./sq. cm.

Since, for economic reasons, it is not desirable to increase the surface area of the anode to any great extent and as for satisfactory furnace control, the anodic current density also cannot be increased beyond certain limits, present day furnace currents are not higher than  $J=150$  kA.

The current yield is usually between 85 and 95%. If the number of pairs of electrodes (each anode and cathode form one pair of electrodes) in a furnace is referred to as  $n$ , the production in kg. of a furnace in any period of time can be represented as:

$$P=c \cdot n \cdot \eta \cdot J$$

$c$ =constant

$J$ =furnace current (amperes)

$n$ =number of pairs of electrodes.

$\eta$ =current yield (percent)

The constant  $c$  takes account of the time in hours and the electrochemical equivalent in kg. of aluminum per ampere-hour. If, the following calculations, the current yield is assumed constant, then the production of a furnace in a certain period of time is only dependent on the product  $n \cdot J$ , that is

$$P=C_1 \cdot n \cdot J$$

From this it can be deduced that the maximum furnace production in 24 hours which is possible is

$$P_{\max}=1100 \text{ to } 1200$$

$n$  being 1, and this requires the maximum practical furnace current of about 150 kA.

In carrying such high currents to the furnace away from the furnace, large bus bars must be used if high electrical losses are not to occur, and this is costly. With  $n=1$ , that is with one pair of electrodes per furnace, an unduly high proportion of the applied voltage is in fact lost in this way.

Known multi-cell furnaces, that is wherein  $n$  is greater than one, avoid these drawbacks which have been described—or at least reduce them. They have a disadvantage of another kind however, which has so far detracted from their practical value and this is that they have consumable anodes.

According to a further feature of the invention, a multi-cell furnace for the electrolysis of molten oxides includes one or more bipolar electrodes, the anode side of each bipolar electrode being porous to oxygen gas and covered with a layer of the oxygen-ion conducting material, the cathode side of each bipolar electrode being formed from a conducting material which is resistant to the melt at the temperature of the electrolysis, and the remaining sides of each bipolar electrode being protected from the fused melt by a layer of resistant electrically insulating material.

Bipolar electrodes, formed in this way, are shown incorporated in a multicell furnace in FIG. 2 of the accompanying drawings.

In the multicell furnace shown are mounted two bipolar electrodes 16, each of which is composed of an oxygen-ion conducting layer 17, a porous anode 18, the porosity of which is represented by a duct 19, and a cathode 20. The cathode consists for example of graphite or amorphous carbon in the form of calcined blocks or of some other electron conducting material which is resistant to the fused melt, such as titanium carbide, zirconium carbide, tantalum carbide or niobium carbide. The aluminium is separated at the cathodes and drops into collecting channels 21.

The cathode at the current outlet has embedded current collectors 5 and at the opposite end of the furnace, leads 6 are embedded in the anode. All those parts of the electrode blocks which are not active electrically, such as the narrow sides and end faces, are protected by an insulation 22, for example boron nitride.

If desired the anode part of each bipolar electrode may comprise a layer of the oxygen ion-conducting material,

an auxiliary electrolyte as before, and the anode itself, sealed at the narrow sides and end faces by an insulation.

In contrast to known multicell furnaces, the multicell furnace shown operated with an absolutely constant inter-electrode gap. This can be so calculated that exactly that amount of joulean heat is produced in the liquid electrolyte as is required during the electrolysis of the alumina and to cover the heat losses of the furnace.

In this construction, as is the case quite generally with all the arrangements according to the invention, as the oxygen discharged at the anode cannot come into contact with the fused melt the current yield is almost 100%. Accordingly, the optimum interelectrode gap can be determined by economic or other considerations. For the same reason, the inclination of the electrode blocks in the multicell furnace with respect to the vertical is no longer critical; the cathode and the oxygen-ion conducting layer can if desired, be arranged perpendicularly.

Other desirable features of known multicell furnaces such as, for example, making the electrolyte circulate through the cells, can be used in furnaces incorporating the invention.

In accordance with the formula

$$P=C_1 \cdot n \cdot J$$

the production of a cell can be increased when  $n$  is 1 by increasing the furnace current  $J$ . In this way, however, the surface areas of the cathodes and anodes must be so increased at the same rate as the furnace current, so that the optimum current density may be retained. This is achieved in known electrolytic furnaces by using conforming electrodes, that is to say, each anode dipping into the melt is disposed so that at its underside and at its lateral faces it is opposite a fixed cathode and as far as possible, the distance between the anode and cathode surfaces is constant, and corresponds to the optimum interelectrode gap. Such furnaces are described for example in German patent specifications Nos. 1,092,215 and 1,115,467.

The present invention can be applied with advantage to such furnaces, and two such furnaces are shown in FIGS. 3 and 4 of the accompanying drawings.

In FIG. 3, the furnace tank 28 forming the cathode is so designed that its surface is opposite both the underside and the side walls of the anode 23 which dips into the melt and is covered with the oxygen-ion conducting layer 17. Each anode is gas permeable and the anodes are connected in parallel. The surface of the furnace tank 28 forming the cathode is provided with elevated portions 24, so that not only the underside of the anode is opposite a face of the cathode as heretofore, but the side walls of the anode are also opposite such a face. The separated aluminium is received in the collecting channels 21 which are lined with an insulating layer 25, for example of boron nitride. A same layer 25 is used for covering the furnace.

The advantages of this type of construction reside in that larger active anode and cathode surface areas are available per unit of volume of anode and cathode. The relative proportion of lost energy to useful energy thereby becomes smaller. The type of construction which is usual today does not show this advantage to the same extent, since an increase in the active areas can only be achieved by increasing the base area of the furnaces, because of the liquid state of aggregation of the aluminium, which operates as cathode and cannot be extended upward like a solid cathode.

In an alternative construction, separate cathodes may be used instead of using the surface of the furnace tank lining as the cathodes. Such a construction is shown in FIG. 4 of the accompanying drawings, in which the cathodes are built up from conducting elements 26, electrically connected in parallel, with one pair of elements cooperating with each anode. The cathode elements may consist of any desired electron-conducting and cryolite-resistant materials.

The advantage of this arrangement is that the furnace lining 27 no longer has any kind of current-removing function. The furnace lining therefore no longer needs to be electrically conductive, but only cryolite-resistant. As a result, the thermal insulation of the furnace tank can be considerably increased and this leads to a considerable reduction in the power consumption per kg. of aluminium produced.

The arrangements shown in FIGS. 3 and 4 can naturally also be employed when the anode is not in direct contact with the oxygen-ion-conducting layer, but an auxiliary electrolyte is interposed between the anode and the oxygen ion conducting layer.

If the anodic and cathodic areas are increased in the manner described without increasing the number of pairs of electrodes or the current J, this means a reduction in the anodic and cathodic current density and this results in a fall in the power consumption per kg. of aluminium produced. These structural changes in the design of the cell, with the economic advantages associated therewith, can only be profitably used if non-consumed anodes are employed, and these are protected by oxygen ion-conducting materials, according to the invention.

We claim:

1. A multicell furnace for the electrolytic production of metals from metal oxides contained in a molten electrolytic bath and including one or more bipolar electrodes, the anode side of each bipolar electrode being porous to oxygen gas and resistant to the formation with oxygen of any compound impairing its conduction of electrons, a covering therefor in the form of a layer of material which is oxygen-ion-conducting but non-permeable to and resistant to an oxygen-producing melt at a temperature of the electrolysis, the cathode side of each bipolar electrode being formed from an electron conducting material which is resistant to such a melt at the temperature of the electrolysis and the remaining sides of each bipolar electrode being covered by a layer of resistant electrically-insulating material, and a source of direct current connected between said anode and said cathode to maintain said electrolysis, said current during said electrolysis effecting the diffusion of oxygen ions through the layer of oxygen-ion-conducting material to the anode and their discharge with the formation of oxygen gas.

2. A cell for the electrolytic production of metal from metal oxides contained in a molten electrolytic bath, comprising a container for a melt, a cathode, an anode the effective portion of which is covered with a layer of oxygen-ion-conducting cerium oxide stabilised by an oxide of the group consisting of calcium oxide, magnesium oxide and yttrium oxide, and arranged to separate the anode from a melt in said container.

3. A cell for the electrolytic production of metals from metal oxides contained in a molten electrolytic bath, comprising a container for the melt being electrolysed, a cathode for contact with the melt, a receptacle partially immersed in the said melt and made of oxygen-ion-conducting material but non-permeable to and resistant to the melt at the temperature of the electrolysis, said receptacle containing an anodic system including a substance which is adapted to be liquid at the temperature of the electrolysis, resistant to the formation with oxygen of any stable compounds impairing its conduction of electrons and capable of transforming oxygen from ionic into the molecular form during electrolysis, and said anodic system including also an electric conductor which is solid at the temperature of the electrolysis and having an end dipping into said substance, and a source of direct current connected between said cathode and said conductor of the anodic system to maintain said electrolysis, said current, during said electrolysis, effecting the diffusion of the oxygen ions of the electrolysed metal oxide

through the oxygen-ion-conducting wall of said receptacle and their discharge as gaseous oxygen from the said anodic system and the deposition of metal at the cathode.

4. A cell according to claim 3 in which the liquid substance included in said anodic system and contained in the said receptacle is silver.

5. A cell according to claim 3 in which the liquid substance included in said anodic system and contained in the said receptacle is an electrolyte able to transfer oxygen ions diffused through the oxygen-ions-conducting wall of the said receptacle to said solid conductor.

6. A cell, according to claim 5, in which said substance is lead oxide in the monoxide form.

7. A multicell furnace for the electrolytic production of metals from metal oxides contained in a molten electrolytic bath, comprising a container for the melt being electrolysed, a plurality of anodes resistant to formation with oxygen of any compound impairing their conduction of electrons and a covering for said anodes of a layer of material which is oxygen-ion-conducting but non-permeable to and resistant to an oxygen-producing melt at the temperature of the electrolysis and which separates said anode from said melt, said container having an electro-conductive lining comprising a cathode spaced from but corresponding in form with the form of said layer covering the anodes so as to ensure a substantially constant and regular interpolar gap between them, and a source of direct current connected between said anode and said cathode to maintain said electrolysis, said current during said electrolysis effecting the diffusion of oxygen ions through the layer and their discharge at the anodes with the formation of oxygen gas.

8. A multicell furnace for the electrolytic production of metals from metal oxides contained in a molten electrolytic bath, comprising a container for the melt being electrolysed, a plurality of anodes resistant to the formation with oxygen of any compound impairing their conduction of electrons and a covering for said anodes of a layer of material which is oxygen-ion-conducting but non-permeable to and resistant to an oxygen-producing melt at the temperature of the electrolyses and which separates said anode from said melt, a plurality of cathodes electrically independent of said container and including conducting elements electrically connected in parallel and spaced from said covering layer of the anode so as to ensure a substantially constant and regular interpolar gap between them, and a source of direct current connected between said anodes and said cathodes to maintain said electrolysis, said current during said electrolysis effecting the diffusion of oxygen ions through the layer and their discharge at the anodes with the formation of oxygen gas.

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U.S. Cl. X.R.

204—244, 247, 250, 284, 290