Title: ELECTROLYTE AND DIAPHRAGM FOR FUSED SALT ELECTROLYSIS

Abstract: An electrolytic cell for the production of chlorine and an alkali metal from a fused chloride electrolyte comprising at least one graphite rod anode, a concentric cylindrical cathode (14) surrounding each anode, a rigid cylindrical diaphragm (10) positioned between said anode and cathode, and self-aligning means (15) that align said diaphragm concentric with, and at a predetermined distance from, said anode and cathode.
ELECTROLYTE AND DIAPHRAGM FOR USED SALT ELECTROLYSIS

FIELD OF THE INVENTION

This invention relates to an electrolytic cell for the electrolysis of fused alkali chloride salts to produce alkali metals such as sodium and lithium.

DESCRIPTION OF THE RELATED ART

Electrolytic cells for the electrolysis of fused alkali chloride salts are used widely in industry to produce alkali metals, such as sodium and lithium, that are difficult to reduce to a metallic state. A major cost for operating these cells is the cost of electric power. Since the early 1970’s, the cost of electric power has increased sharply. Development of more energy-efficient electrolysis processes, therefore, has become increasingly important.

The electrolytic recovery of sodium metal is commercially carried out via non-aqueous molten chloride salt electrolysis. While the discussion below concentrates on sodium manufacture, the features relating to cell design and mechanical operation also apply to manufacture of lithium and other alkali metals.

Most industrial installations for molten salt electrolysis of sodium employ the Downs cell design to carry out the process, originally disclosed in U.S. Patent No. 1,501,756. A detailed description of this cell is given in Ullmann’s Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A24, VCH Verlagsgesellschaft, Germany, pp. 284-288 (1993). A typical industrial cell of this type is shown in Figure 1.

The electrolyte typically used is a mixture of sodium chloride with other salts to lower the melt temperature. A cell operating temperature of about 600 degrees C is ordinarily employed. Ullmann lists a suitable mixture as 28 wt% NaCl, 25 wt% CaCl2 and 47 t% BaCl2. US Patent No. 2,850,442 discloses a
mixture of about 26 wt% NaCl, 60 wt% SrCl₂, and 14 wt% BaCl₂. Adaev et al, Zh. Prikl. Khim. (Leningrad) (1973), Vol.46, No.1, pp 191-2 disclose the electrolysis of mixtures of 27 to 29 wt% NaCl, 64 to 67 wt% BaCl₂ and 9 to 4 wt% LiCl at temperatures above 650°C. The literature discloses numerous other ternary mixtures. The choice of mixture depends on such factors as the melting temperature of the mixture, its electrical conductivity, the desired purity of the resulting sodium, and the possible deposition of the salts at various points in the apparatus due to differences in solubility at the lower temperatures encountered in some parts of the sodium cell. These factors affect operability of the cell, how often the cell must be shut down for repairs, current efficiency and productivity of the cell, and in general what is referred to in the trade as the “health” of the cell.

A modern Downs cell typically contains four graphite carbon rods that serve as anodes. Each anode is surrounded by a concentric steel cylinder that serves as a cathode. In operation, sodium is deposited on the inside surface of the steel cathodes and chlorine gas is liberated at the graphite anodes. Typically, in a cell with four pairs of electrodes, the chlorine is collected in four shafts from the anodes while the sodium is collected in a single compartment covering all four cathodes.

A hydraulically permeable diaphragm is used to separate the cathode and anode compartments to prevent back-mixing and reaction of the sodium and chlorine. It typically is made of steel mesh, and has a relatively short life of about two months because it corrodes and plugs with debris. When the diaphragm develops any major holes, it must be replaced because the holes lead to back-mixing and reaction of the sodium and chlorine, in turn reducing current efficiency and energy efficiency. Replacement of the diaphragm is a labor-intensive and costly step.

Current diaphragm designs have a number of shortcomings. One shortcoming is that the diaphragms typically are rigidly attached to the sodium collector by a steel ring bolted to the collector. Attachment of the diaphragm to the sodium collector is accomplished by a laborious operation in a specially designed “pit.” Following the attachment step, the diaphragm is transported to the
cell and lowered into place. Because the bolted design is rigid, and because there are slight mechanical variations from cell-to-cell, this procedure rarely achieves perfect alignment between the new diaphragm and the electrodes in the cell along the entire cell length. Imperfect alignment causes partial shorting between anodes and cathodes, reducing current efficiency of the cell.

Improved current efficiency is a major area for potential power savings. While the efficiency of an electrolytic process theoretically could be above 99%, most commercial molten salt sodium cells operate at relatively low current efficiencies. Ullmann’s Encyclopedia, for example, lists a typical current efficiency of 80 to 90% (p. 287).

Another important area for power savings is to decrease the voltage drop across the cell. Typically the voltage drop across the electrolyte-filled space between the cathode and the anode accounts for about 40% of the electric energy required to run a sodium cell. Reduction of the electrical resistivity of the molten electrolyte would result in important energy savings for cell operation. However, to maintain smooth operation, any new electrolyte composition must not increase the melting temperature of the mixture or the tendency of associated metal salts to precipitate out of solution, and must produce a sodium metal of acceptable purity. Preferably, a new electrolyte composition also should improve the operability and “health” of the cell.

**SUMMARY OF THE INVENTION**

The present invention provides an electrolytic cell for the production of chlorine and an alkali metal from a fused chloride electrolyte having at least one graphite rod anode, a concentric cylindrical cathode surrounding each anode, a rigid cylindrical diaphragm positioned between said anode and cathode, and insulated aligning means that engage the diaphragm and the anode or cathode to concentrically align said diaphragm as it is placed in position (i.e., the diaphragm is self-aligning). In a preferred diaphragm the aligning means are sets of insulating rollers, conveniently mounted on the outer surface of the diaphragm to engage the inner surface of the cathode as the diaphragm is inserted into position.
In one embodiment, the self-aligning diaphragm has a buoyancy chamber that causes the diaphragm assembly to float in the electrolyte. In another embodiment, the self-aligning diaphragm mechanically locks into position by a locking mechanism mounted on top of the diaphragm that engages a sodium collector structure mounted above the cathode.

The invention also provides the following electrolytic compositions for the production of chlorine and sodium:

(a) about 20 to 40 wt% NaCl, 30 to 50 wt% BaCl₂, 15 to 30 wt% CaCl₂ and 0.2 to 13.0 wt% LiCl,

(b) about 20 to 40 wt% NaCl, 5 to 15 wt% BaCl₂, 50 to 70 wt% SrCl₂ and 1.0 to 13.0 wt% LiCl, and,

(c) about 20 to 40 wt% NaCl, 50 to 80 wt% SrCl₂ and 0.2 to 13.0 wt% LiCl.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1A and 1B are vertical and horizontal cross-sections, respectively, of a typical Downs cell having four sets of electrodes.

Figure 2 illustrates one embodiment of the self-aligning diaphragm of this invention.

Figure 3 illustrates a second embodiment of the self-aligning diaphragm of this invention.

**DETAILED DESCRIPTION OF THE INVENTION**

This invention provides several substantial improvements to the mechanical and electrolytic elements of an electrolytic cell for the production of molten alkali metal and gaseous chlorine by the electrolysis of fused chloride salts. While the mechanical and electrolytic improvements are discussed separately one or more of these improvements may be incorporated in a single design of an improved electrolysis cell. While the description is given in terms of
electrolyzing sodium chloride, the mechanical improvements of the improved cell may also be used for the electrolysis of lithium and other alkali metals.

**Downs Cell**

Figures 1A and 1B, respectively, illustrate vertical and horizontal cross-sections of a typical Downs-type cell having four sets of electrodes. The cell has a cylindrical brick-lined, steel casing 1. Cylindrical graphite anodes 2 project upwardly through the bottom of the steel casing. The cathodes 3 are steel cylinders having two diametrically opposed steel arms 4 that project outside the cell casing to serve as electric terminals. Cylindrical steel screen mesh 5 are suspended about midway in the annular space between the anodes and the cathodes. Annular collector ring 6 collects molten metal that rises in the fused electrolyte 7 from the cathodes. Outlet tube 8 carries the metal collected in the collector ring to the outside of the cell. Gas dome 9 carries gaseous anodic products formed by the electrolysis. Elements 5, 6, 8 and 9 are supported in the cell by means not shown, typically by rigid means such as conventional bolts, fasteners or welding.

A steel-mesh screen currently is employed as a diaphragm to separate the cathode and anode compartments. The diaphragm prevents back-mixing and reaction of the cathodically produced alkali metal and anodically produced chlorine. The relatively short life of the diaphragm, combined with the labor-intensive method of replacing and aligning them, is a major cost factor in the operation of the Downs cell. In addition, such diaphragms are of limited effectiveness, in part due to alignment deficiencies, with groups of cells typically only achieving overall current efficiencies in the range of 80% to 90%.

**Self-Aligning Diaphragm**

The diaphragm designs of the current invention overcome these limitations of the prior art by providing a self-aligning diaphragm. By “self-aligning” it is meant that the diaphragm aligns itself concentric with, and at a predetermined distance from, the cathode and anode as the diaphragm is inserted into place.

- 5 -
Figure 2 illustrates one embodiment of the self-aligning diaphragm provided by this invention. The diaphragm 10 is made of conventional screening or slotted materials such as disclosed in prior art, but has the following features that make it self-aligning. Instead of a rigid, bolted connection between the diaphragm and the sodium collector 11, the diaphragm floats in the electrolyte and rests against the bottom of the sodium collector, separated from it electrically by a number of mechanically rugged electrical insulator supports 12, such as a modified spark plug, fastened at intervals around the top of the diaphragm. These insulator supports are so fastened that their bottoms will rest on the cathode 14 when the floating diaphragm is in its lowest position. Also fastened to the top of the diaphragm is a buoyancy chamber 13, a hat-like device containing small bleed holes in the top. The volume of the buoyancy chamber is sized so that the diaphragm will rest against the sodium collector in normal operation, buoyed up by the upflowing chlorine gas collected in the chamber. When the electricity to the cell is reduced or shut off completely, chlorine slowly escapes through the bleed holes, causing the floating diaphragm to move downward or sink to the point that the insulator supports rest on the top surface of the cathode. This movable diaphragm has at least two sets of insulating roller-spacers 15, one near the bottom of the diaphragm and one set higher up on the diaphragm, to provide the self-aligning feature. Only the upper set is shown. The clearance between the roller-spacers and the cathode wall is sufficient to allow the diaphragm assembly to freely move up and down, but not so large as to allow mis-alignment that would unnecessary increase in the path for current flow, which would increase the cell voltage required for operation.

In operation, the buoyancy chamber fills with chlorine gas evolved at the anode, the remaining amount of chlorine bypassing the buoyancy chamber and going to the collection system. The chlorine in the buoyancy chamber floats the entire diaphragm assembly upwards until the upper part of the insulator supports rests against the sodium collector. Thus, need for a bolted or rigid connection to the collector is avoided, eliminating the costly “pit” operation required for repair and replacement by the conventional design.
When the cell current is turned off, chlorine evolution at the anode stops and the chlorine in the buoyancy chamber slowly escapes through the small bleed holes. The chamber gradually fills with molten electrolyte and loses its buoyancy, causing the diaphragm assembly to sink until the insulator supports rest on the top surface of the cathode. This up-and-down motion can be deliberately achieved by turning the cell current on and off. The up-and-down motion is very useful in breaking and shearing off calcium dendrites that often form during cell operation, causing partial shorts, arcing and loss of current efficiency. The sets of insulating roller-spacers keep the diaphragm centered and prevent it from shorting against the electrodes during this operation. Means other than insulated rollers may be employed to self-align the diaphragm, and the means may be mounted on the diaphragm, cathode, anode, or other structural element of the cell.

Figure 3 illustrates a second embodiment of the self-aligning diaphragm of this invention. As in the first embodiment, the diaphragm 20 is made of conventional screening or slotted materials. The diaphragm has a metal piece 21 rigidly fastened to its top portion that contains a number of L-shaped slots, of which slot 22 is shown in side view. Fitted into each slot is a rod, of which rod 23 is shown in end view. These rods are rigidly fastened to the sodium collector, but are not fastened to the diaphragm. The slots and rods are positioned such that the diaphragm assembly can be inserted from below the sodium collector, with the vertical portion of each slot in line with each matching rod, then moved upward and rotated (as if screwing a glass jar onto its lid) to the end of the slot’s travel. A small upward widening of the slot at its end locks the diaphragm in position within the cathode 24. The clearance between the widened slot locks and the rods is sufficient for a slight sideways free movement of the diaphragm. In order for this slightly moveable diaphragm to be self-aligning, it has at least two sets of insulating roller-spacers 25, one near the bottom of the diaphragm and one set higher up on the diaphragm to provide the self-aligning feature of this design. Only the upper set is shown in this Figure. The clearance between the roller-spacers and the cathode wall is sufficient to allow the diaphragm to be rotated into position, but not so large as to allow mis-alignment that would unnecessary increase the path for current flow, which would increase cell voltage required for
operation. Means other than insulated rollers may be employed to self-align the
diaphragm, and the means may be mounted on the diaphragm, cathode, anode, or
other structural element of the cell.

As in the previous diaphragm embodiment, there is no need for a bolted or
rigid connection between the diaphragm and the sodium collector, thus
eliminating the costly "pit" operation required for repair and replacement by the
conventional design.

The insulator supports and the insulating roller spacers for the above
diaphragms can be made of any insulating materials which have adequate strength
and mechanical properties at bath temperatures and are insoluble in the molten
electrolyte, such as silicon nitride (Si₃N₄), alumina (Al₂O₃) and other materials
known to those skilled in the art. The axles on the rollers can be any rigid
material which is suitable for the bath environment, preferably a metal such as
steel.

While the invention has been described in detail with respect to a preferred
embodiment wherein insulated rollers are employed as the aligning means, it will
be appreciated that equivalent means may be selected to space the diaphragm
concentrically with the anode and cathode. For example, rigid spacing means
could be mounted on the inner surface of the cathode. Likewise, means other than
the buoyancy chamber illustrated in Figure 2 may be employed to cause the
membrane to float in the electrolyte, and means other than the locking slots and
pins illustrated in Figure 3 may be employed to lock the membrane in position.

**Electrolyte Composition**

The electrolyte composition used in a sodium cell influences operability of
the cell in several ways. Not only is the melting temperature of the overall
composition important, but also the variation in melting temperature as the ratio of
ingredient changes. Due to poor cell circulation, both electrolyte composition and
temperature vary in different parts of the cell. Typically, the bottom of the cell is
cooler than the rest, creating problems due to deposition of electrolyte ingredients
and impurities. These depositions cause productivity and current efficiency of the cell to deteriorate, requiring the cell to be shut down for repair and/or replacement of the diaphragm. Other problems may occur, causing a phenomenon referred to in the trade as "smoking." The smoothness of operation of a cell, while maintaining good productivity, is referred to as the "health" of the cell. Correspondingly, cells with poor operability are referred to as "sick" cells. For the health of a cell, it is important that the electrolyte have a wide ratio of compositions that remain entirely molten over a wide range of temperatures. The ability of a substance to promote free movement of the fused electrolyte salts over a range of temperatures is referred to herein as its "fluxing" ability.

Another important character of the electrolyte is its conductivity. The voltage drop across the electrolyte-filled space between cathode and anode for a typical NaCl-CaCl₂-BaCl₂ electrolyte composition is almost 3 volts, accounting for about 40% of the electric energy required to run a sodium cell. Other typical electrolytes have similar voltage drops. Any reduction in the electrical resistivity of the molten electrolyte would result in important energy savings for cell operation. It is known that lithium chloride (LiCl) has substantially lower electrical resistivity than the ingredients in the above typical mixtures. Previous attempts to use lithium chloride as an electrolyte component were unacceptable, however, because of the high lithium content of the sodium produced or various other operating problems. These attempts did not include the specific combination of ingredients of this invention, in which small amounts of lithium chloride are added as an extra ingredient to existing commercially useful binary and ternary electrolyte mixtures, converting them to ternary and quaternary mixtures, respectively.

In accordance with the invention, it has been found that the presence less than 1%, and as little as 0.2%, of LiCl in the ternary and quaternary electrolyte mixtures is advantageous. Not only is current efficiency improved, but general health of the cell as well. The cell operates smoother, with less smoking and spurious electrolyte freeze-ups. In addition, the presence of even small quantities
of lithium chloride can result in 30% to 100% longer diaphragm useful life, reducing the amount of cell down-time for costly replacement of the diaphragm.

A series of experiments were conducted on the effect of LiCl addition on melting temperature of a typical calcium chloride-based electrolyte (26 wt% NaCl, 48 wt% BaCl2, 26 wt% CaCl2). The effect of small LiCl additions to the bath was studied. Addition of LiCl transforms this ternary system into a quaternary system for which no published data is available. These compositions were subjected to thermal analysis tests (DSC/Differential Scanning Calorimetry) to determine their melting temperatures, by which we mean the temperature at which all the material is molten. The results were as follows.

<table>
<thead>
<tr>
<th>Additions</th>
<th>Calc. Composition, wt%</th>
<th>Melting Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td>BaCl2</td>
</tr>
<tr>
<td>Control (no LiCl)</td>
<td>26.0</td>
<td>48.0</td>
</tr>
<tr>
<td>1% LiCl addition</td>
<td>25.7</td>
<td>47.5</td>
</tr>
<tr>
<td>2% LiCl addition</td>
<td>25.5</td>
<td>47.1</td>
</tr>
<tr>
<td>5% LiCl addition</td>
<td>24.7</td>
<td>45.7</td>
</tr>
<tr>
<td>10% LiCl addition</td>
<td>23.6</td>
<td>43.6</td>
</tr>
<tr>
<td>20% LiCl addition</td>
<td>21.7</td>
<td>40.0</td>
</tr>
<tr>
<td>40% LiCl addition</td>
<td>18.6</td>
<td>34.2</td>
</tr>
</tbody>
</table>

The experimental results obtained for this system showed that LiCl additions, even in quite small amounts, will significantly lower the melting temperature of electrolyte compositions and thereby improve operability of the sodium cells.

The strongest effect on lowering melting temperature is between 0.2% to 10% LiCl addition. The rise in temperature between 20% and 40% LiCl indicates the presence of a eutectic within this composition range for this quaternary mixture. A range of 0.2 to 15 wt% addition of LiCl is preferred for reasons of economy, corresponding to a composition of about 20 to 40 wt% NaCl; 30 to 50 wt% BaCl2; 15 to 30 wt% CaCl2; and 0.2 to 13.0 wt% LiCl.
A similar series of experiments addressed the effect of relatively small LiCl additions on the melting temperature of a ternary strontium chloride-based electrolyte for sodium manufacture (26 wt% NaCl, 12 wt% BaCl₂, 62 wt% SrCl₂). Addition of LiCl transforms this ternary system into a quaternary system for which no published data is available. Electrolyte compositions were prepared containing 5 wt% and 10 wt% of LiCl added to the above strontium-based bath. These compositions were subjected to thermal analysis tests as before to determine their melting temperatures. The results were as follows.

<table>
<thead>
<tr>
<th>Additions</th>
<th>Calc. Composition, wt%</th>
<th>Melting Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td>BaCl₂</td>
</tr>
<tr>
<td>Control (no LiCl)</td>
<td>26.0</td>
<td>12.0</td>
</tr>
<tr>
<td>5% LiCl addition</td>
<td>24.7</td>
<td>11.4</td>
</tr>
<tr>
<td>10% LiCl addition</td>
<td>23.6</td>
<td>10.9</td>
</tr>
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</table>

It is seen from the above data that even small additions of LiCl will significantly lower the melting temperature of the strontium bath, and thereby substantially broaden the operability of such a bath by preventing freeze-ups and similar problems. A range of 0.2 to 15 wt% addition of LiCl is preferred for reasons of economy, corresponding to a composition of about 20 to 40 wt% NaCl; 5 to 15 wt% BaCl₂; 50 to 70 wt% SrCl₂; and 0.2 to 13.0 wt% LiCl.

Similar experiments were conducted on the binary system of NaCl and SrCl₂. Published data show a eutectic composition of 30 wt% NaCl and 70 wt% SrCl₂ with a eutectic melting temperature of about 570°C. The melting temperature rises sharply with small changes in composition, allowing only a 15% wide range of compositions before the melting temperature would exceed a typical cell operating temperature of 600°C. By adding 11 wt% of LiCl to the above eutectic composition, the following results were obtained.
Table 3

<table>
<thead>
<tr>
<th>Additions</th>
<th>Calc. Composition, wt%</th>
<th>Melting Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaCl</td>
<td>SrCl2</td>
</tr>
<tr>
<td>Control (no LiCl)</td>
<td>30.0</td>
<td>70.0</td>
</tr>
<tr>
<td>11% LiCl addition</td>
<td>27.0</td>
<td>63.1</td>
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</table>

The above results show that even small additions of LiCl have a powerful fluxing effect on the NaCl/SrCl₂ binary system. That is, small additions of LiCl give a much broader range of melting temperatures, thereby improving operability at the typical 600°C operating temperature of the sodium cells. A range of 0.2 to 15 wt% addition of LiCl is preferred for reasons of economy, corresponding to a composition of about 20 to 40 wt% NaCl; 50 to 80 wt% SrCl₂; and 0.2 to 13.0 wt% LiCl₂.

To determine if relatively small percentages of lithium chloride would yield a sodium cell product with acceptable purity, laboratory experiments were designed and carried out to determine the degree of lithium pick-up by sodium metal in contact with lithium chloride-containing electrolyte at 600°C under non-equilibrium conditions (that is, with no stirring). The conditions chosen approximately various simulated conditions in the electrolytic cell and covered a wide range of exposure times, ranging from the few seconds time required for sodium droplets to rise through the electrolyte bath to the several hours when a thick layer of sodium metal inside the collector is in quiet contact with, and floats on, molten electrolyte. The electrolyte in these experiments contained (by weight) 4.8% LiCl; 24.7% NaCl; 24.7% CaCl₂; and 45.7% BaCl₂. Results of this preliminary study are shown in Table 4.
Table 4
Lithium Pick-up by Sodium Metal

<table>
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<tr>
<th>Exposure Time</th>
<th>Lithium Content of Sodium Metal</th>
</tr>
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<tr>
<td>1 minute</td>
<td>0.2 ppm</td>
</tr>
<tr>
<td>10 minutes</td>
<td>3.5 ppm</td>
</tr>
<tr>
<td>20 minutes</td>
<td>1.6 ppm</td>
</tr>
<tr>
<td>240 minutes (4 hours)</td>
<td>0.6 ppm</td>
</tr>
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</table>

These tests show that, although there is considerable scatter in these data, the absolute level of lithium pick-up by sodium metal under these conditions is minimal.

It is also important to know if Li will co-deposit with Na at the electrode. Such co-deposition would be highly undesirable and negate use of Li-containing electrolytes. In order to estimate the thermodynamic driving force for co-deposition of Li with Na for small LiCl additions, the EMF gaps at 600°C between Na and Li was calculated for the above strontium-based and calcium-based electrolyte compositions. The larger the EMF gap between the Na and the less noble Li, the less will be the tendency for the Li to co-deposit.

For a 5% addition of LiCl to the calcium-based electrolyte, the EMF gap increases from about 0.1 volts based on the standard EMFs between Na and Li at 600°C to about 0.2 volts. This is a big increase in the EMF gap, and means that at low LiCl concentrations the driving force is for Na deposition without Li deposition, a favorable result. Similar results were obtained for the strontium-based bath.

Using literature data on the electrical conductance for LiCl, NaCl, BaCl₂ and CaCl₂, it is estimated that the cell voltage change for a 10% LiCl-containing bath based on the above typical calcium chloride-based electrolyte would be about a 0.5 volts to 0.8 volts reduction, corresponding to about 7% to 11% power savings.
Plant tests confirmed the above preliminary information. Even at amounts of LiCl addition as low as 0.2 to 5 wt% resulted in noticeable increases in current efficiency. In the calcium chloride based electrolyte, a 0.2 to 3 wt% addition of LiCl showed about 2% higher current efficiency. In addition, a more uniform temperature distribution was noted throughout the cell, a 10°C variation from top to bottom versus about a 30°C variation without LiCl addition, and therefore more trouble-free operation of the cell, i.e., fewer upsets, "sickness" or "smoking" of the cell and less spurious freezeups near the bottom of the cell and in other locations. Over time, this will result in higher average energy efficiency and less maintenance and operating labor requirements. That is, the addition of LiCl to typical sodium electrolyte compositions surprisingly gives better cell operability.
WHAT IS CLAIMED IS:

1. An electrolytic cell for the production of chlorine and an alkali metal from a fused chloride electrolyte comprising at least one graphite rod anode, a concentric cylindrical cathode surrounding each anode, a rigid cylindrical diaphragm positioned between said anode and cathode, and self-aligning means that align said diaphragm concentric with, and at a predetermined distance from, said anode and cathode.

2. The electrolytic cell of claim 1 wherein said aligning means are insulated rollers.

3. The electrolytic cell of claim 2 wherein said insulated rollers are mounted on the outer surface of said diaphragm and engage the inner surface of said cathode.

4. The electrolytic cell of claim 1, 2 or 3 wherein a buoyancy chamber is present at the top of the diaphragm, said buoyancy chamber causing the diaphragm assembly to float in cell electrolyte while the cell is in operation.

5. The electrolytic cell of claim 4 wherein insulating separators are present on the top of said buoyancy chamber to electrically separate said buoyancy chamber from a sodium collector positioned above said chamber.

6. The electrolytic cell of claim 1, 2 or 3 wherein said diaphragm has a metal piece fastened to its top portion, said metal piece having a plurality of slots, and said electrolytic cell has a sodium collector mounted above said diaphragm and having a number of rods projecting therefrom that fit into said slots to position said diaphragm concentrically with the cell anode and cathode when said diaphragm is rotated to lock said rods in said slots.

7. An electrolyte composition for the production of chlorine and sodium from fused chloride electrolytes consisting essentially of about 20 to 40 wt% NaCl; 30 to 50 wt% BaCl₂; 15 to 30 wt% CaCl₂; and 0.2 to 13 wt% LiCl.
8. An electrolyte composition for the production of chlorine and sodium from fused chloride electrolytes consisting essentially of about 20 to 40 wt% NaCl; 5 to 15 wt% BaCl$_2$; 50 to 70 wt% SrCl$_2$; and 0.2 to 13.0 wt% LiCl.

9. An electrolyte composition for the production of chlorine and sodium from fused chloride electrolytes consisting essentially of about 20 to 40 wt% NaCl; 50 to 80 wt% SrCl$_2$; and 0.2 to 13.0 wt% LiCl.
FIG. 1A
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25C7/00 C25C3/02

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practical, search terms used)

WPI Data, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>X</td>
<td>WO 99 05343 A (E.I. DU PONT DE NEMOURS AND COMPANY) 4 February 1999 (1999-02-04)</td>
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<td>GB 1 151 654 A (E.I. DU PONT DE NEMOURS AND COMPANY) 14 May 1969 (1969-05-14)</td>
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X Further documents are listed in the continuation of box C.  
X Patent family members are listed in annex.

* Special categories of cited documents:

**A** document defining the general state of the art which is not considered to be of particular relevance.

**E** earlier document but published on or after the international filing date.

**L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified).

**O** document referring to an oral disclosure, use, exhibition or other means.

**P** document published prior to the international filing date but later than the priority date claimed.

**T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention.

**X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone.

**Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

**A** document member of the same patent family.

Date of the actual completion of the international search 21 March 2001

Date of mailing of the international search report 29.03.2001

Name and mailing address of the ISA European Patent Office, P.O. Box 5642 Patentlaan 2 NL - 2280 HJ Rijswijk

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Authorized officer

Groseiller, P.
<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>A</td>
<td>US 3 257 297 A (DAVID S. PATERSON) 21 June 1966 (1966-06-21) claims 1-4</td>
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<td>DE 11 62 575 B (ETHYL CORPORATION, NEW YORK) 6 February 1964 (1964-02-06) claims 1,2</td>
<td>9</td>
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<td>A</td>
<td>FR 1 259 880 A (SOLVAY &amp; CIE) 11 August 1961 (1961-08-11) résumé</td>
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Form PCT/ISA/02/10 (continuation of second sheet) (July 1982)
INTERNATIONAL SEARCH REPORT

Box I  Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.: because they relate to parts of the international Application that do not comply with the prescribed requirements to such an extent that no meaningful international Search can be carried out, specifically:

3. ☐ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II  Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☑ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.: 

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (1)) (July 1998)
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-6

   Electrolytic cell featuring a concentric cylindrical diaphragm positioned between a rod anode and a concentric cylindrical cathode. Self aligning means are provided for aligning the diaphragm concentric with and at a predetermined distance from the anode and the cathode.

2. Claims: 7-9

   Electrolyte composition
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<td></td>
<td></td>
<td>AU 8599398 A</td>
<td>16-02-1999</td>
</tr>
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<td>14-05-1969</td>
<td>CH 504895 A</td>
<td>31-03-1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 1558756 A</td>
<td>20-01-1972</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 3432421 A</td>
<td>11-03-1969</td>
</tr>
<tr>
<td>FR 2066836 A</td>
<td>13-08-1971</td>
<td>DE 1944712 A</td>
<td>22-04-1971</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 1288777 A</td>
<td>13-09-1972</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 3685121 A</td>
<td>22-08-1972</td>
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<tr>
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<td>DE 1162575 B</td>
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