Magnesium metal is produced by electrolysis of magnesium chloride employing a high surface area anode, for example, a porous anode to which hydrogen gas is fed. Hydrogen chloride is formed from the chloride ions at the anode, rather than chlorine gas; the process also has the advantage of operating at a lower voltage with a lower energy requirement than the conventional process in which chlorine gas is generated at the anode.
ELECTROLYTIC PRODUCTION OF MAGNESIUM
CROSS-REFERENCE TO RELATED APPLICATION

[0001] This Application is a Continuation of PCT/CA 00/00248, filed Mar. 9, 2000, in which the United States of America was designated and elected and which remains pending in the International Phase until Sep. 11, 2001.

TECHNICAL FIELD

[0002] This invention relates to production of magnesium by electrolysis.

BACKGROUND ART

[0003] Conventional electrolytic production of magnesium from magnesium chloride dissolved in a molten salt electrolyte in an electrolytic cell results in formation of magnesium at the cathode and chlorine gas at the cathode. The molten salt electrolyte typically comprises one or more alkali metal or alkaline earth metal chlorides in which the magnesium chloride is dissolved.

[0004] The production of chlorine as a by-product of the production of magnesium requires auxiliary equipment for recovery and storage of the by-product chlorine gas which typically is reacted with hydrogen gas to form hydrochloric acid. Electrolytic methods for producing magnesium are described in U.S. Pat. Nos. 4,073,703; 4,192,724; 5,089,094 and 5,665,220, the teachings of which are incorporated herein by reference.

SUMMARY OF THE INVENTION

[0005] This invention seeks to provide a new electrolytic process for the production of magnesium from magnesium chloride, in which hydrogen chloride is produced as the by-product.

[0006] This invention also seeks to provide a new electrolytic process for the production of magnesium from magnesium chloride at a lower energy requirement.

[0007] In accordance with one aspect of the invention there is provided in a process for the electrolytic production of magnesium from magnesium chloride in an electrolytic cell having an anode and a cathode, and in which magnesium is generated at the cathode, the improvement wherein hydrogen gas is fed to the anode and hydrogen chloride is formed in situ at the anode.

[0008] In accordance with another aspect of the invention there is provided a process for the electrolytic production of magnesium comprising: i) electrolyising magnesium chloride in a molten salt electrolyte in an electrolysis cell having a cathode and an anode, with formation of magnesium metal at said cathode, ii) feeding hydrogen gas to said anode and reacting chloride ions at said anode with the hydrogen gas to form hydrogen chloride, iii) recovering the magnesium metal from said cell, and iv) recovering the hydrogen chloride from said cell.

[0009] In accordance with still another aspect of the invention there is provided an electrolytic cell for production of magnesium metal from magnesium chloride comprising: a) a cell for housing magnesium chloride in a molten salt electrolyte, said cell having a cathode and an anode, b) means for feeding hydrogen gas to said anode, c) means for recovery from said cell of magnesium metal developed at said cathode, and d) means for recovery from said cell of hydrogen chloride developed at said anode.

DESCRIPTION OF PREFERRED EMBODIMENT

[0011] In particular the anode is a high surface area anode, for example, a porous anode in which case the hydrogen gas permeates the pores of the anode, such as by diffusion, or molten electrolyte containing the magnesium chloride permeates the pores of the anode, to provide the contact between the hydrogen gas and the chloride ions. The hydrogen gas may be fed along a non-porous tube or conduit to the porous anode. If this tube or conduit is in contact with the bath it should not be of a material which will function as an anode for the electrolysis.

[0012] As an alternative to a porous anode, any anode having a structure permitting delivery of hydrogen to the cell bath at the anode may be employed, for example, an anode having drilled channels for communication with a source of hydrogen gas. The requirement is that the anode structure delivers hydrogen gas to the cell bath at the anode, so that chloride ions at the anode react with the hydrogen gas to form hydrogen chloride, rather than discharging as chlorine gas.

[0013] By way of example, suitable anodes may be of graphite, silicon carbide or silicon nitride.

[0014] It has been found that introducing hydrogen at the anode in the electrolytic cell for magnesium metal production results in a lower energy requirement for the cell, and the cell can be operated at a cell voltage lower than the cell voltage of a corresponding cell having a conventional carbon or graphite anode, without hydrogen gas.

[0015] In addition it is found that hydrogen chloride is formed directly at the anode by the reaction:

$$2Cl^- + 2H_2(g) \rightarrow 2HCl(g) + 2e^-$$

[0016] where (g) indicates the gas phase.

[0017] Furthermore, the method has the advantage that this hydrogen chloride gas is produced with minimal, if any, production of chlorine gas.

[0018] In conventional cells in which chlorine gas is produced as the by-product, the anode is graphite, and at the high temperatures of operation some chlorinated hydrocarbons are produced by reaction between the chlorine gas and the carbon anode, and this presents environmental problems. Eliminating production of chlorine gas in the present invention can be expected to alleviate these problems.

[0019] Table I below shows how the decomposition voltage of the electrolysis decreases, with the process of the invention, as compared with the conventional process and how the minimum voltage required to maintain energy balance changes.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conventional</th>
<th>Invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>2.5 V</td>
<td>2.0 V</td>
</tr>
<tr>
<td>700</td>
<td>3.0 V</td>
<td>2.5 V</td>
</tr>
</tbody>
</table>
TABLE I

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^\circ$</th>
<th>$E_{\text{adiab.}}$</th>
<th>$E_{\text{adiab.}} - E^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MgCl}_2 \rightarrow \text{Mg} + \text{Cl}_2$</td>
<td>2.50</td>
<td>3.60</td>
<td>1.1</td>
</tr>
<tr>
<td>$\text{MgCl}_2 + \text{H}_2 \rightarrow \text{Mg} + \text{HCl}$</td>
<td>1.46</td>
<td>2.74</td>
<td>1.28</td>
</tr>
<tr>
<td>Difference</td>
<td>-1.04</td>
<td>-0.86</td>
<td>0.18</td>
</tr>
</tbody>
</table>

In Table I, $E_{\text{adiab.}}$ is the minimum voltage required to carry out the process, assuming 100% current efficiency and that the $\text{MgCl}_2$ and $\text{H}_2$ are fed at room temperature.

In particular, Table I shows the calculated decomposition voltage (1000 K) and adiabatic voltage required to cover the energy requirements of the process without heat losses.

Table I further shows that the decomposition voltage decreases by 1.04V and that the overall energy requirement decreases by 0.86V. This means that with HCl formation, another 0.18V per mole can be dissipated in the cell without causing overheating. The decrease of 0.86V translates to a reduction of about 25% less electricity consumption for magnesium production. With magnesium cells currently requiring an average of 12.5 MW-hr per tonne, and an average energy cost of 4 cents per KW-hrs, this translates to a savings of about $125 per tonne of magnesium produced in electrical consumption.

Another major cost saving comes from the fact that the cell is producing HCl rather than chlorine, requiring no HCl synthesis plant. Chlorine treatment and handling as well as HCl synthesis can provide for further cost savings.

Environmental problems associated with chlorine gas production are expected to be alleviated.

The hydrogen gas may be considered to form a hydrogen anode in the cell, for discharge of the chloride ions. In such case an anode structure is provided which, can be of any suitable material, for example, graphite, silicon carbide or silicon nitride.

1. A process for the electrolytic production of magnesium from magnesium chloride dissolved in a molten salt electrolyte in an electrolytic cell having an anode and a cathode, and in which magnesium is generated at the cathode, the improvement wherein hydrogen gas is fed to the anode and hydrogen chloride is formed in situ at the anode.
2. A process according to claim 1, wherein the anode is a high surface area anode.
3. A process according to claim 1, wherein the anode is a porous anode and the hydrogen gas permeates the pores of the anode.
4. A process according to claim 1, wherein said anode is a porous anode and the molten electrolyte permeates the pores of the porous anode.
5. A process according to claim 1, wherein the anode is of graphite, silicon carbide or silicon nitride.
6. A process, according to claim 1, for the electrolytic production of magnesium comprising:
   i) electrolysis of magnesium chloride in a molten salt electrolyte in an electrolysis cell having a cathode and an anode, with formation of magnesium metal at said cathode,
   ii) feeding hydrogen gas to said anode and reacting chloride ions at said anode with the hydrogen gas to form hydrogen chloride,
   iii) recovering the magnesium metal from said cell, and
   iv) recovering the hydrogen chloride from said cell.
7. A process according to claim 6, wherein said cell is operated at a cell voltage lower than the cell voltage of a corresponding cell having a carbon anode, without hydrogen gas, in which chlorine gas is developed at the anode.
8. A process according to claim 6, wherein said anode is a high surface area anode.
9. A process according to claim 6, wherein said anode is a porous anode and the hydrogen gas permeates from the pores of the anode into the cell.
10. A process according to claim 6, wherein said anode is a porous anode and the molten electrolyte permeates the pores of the porous anode.
11. A process according to claim 6, wherein said anode is of graphite, silicon carbide or silicon nitride.
12. An electrolytic cell for production of magnesium metal from magnesium chloride comprising:
   a) a cell for housing magnesium chloride in a molten salt electrolyte, said cell having a cathode and an anode,
   b) means for feeding hydrogen gas to said anode for production of hydrogen chloride at said anode,
   c) means for recovery from said cell of magnesium metal produced at said cathode, and
   d) means for recovery from said cell of hydrogen chloride developed at said anode.
13. A cell according to claim 12, further including a conduit for delivery of hydrogen gas to said anode.
14. A cell according to claim 12, wherein said anode is a high surface area anode.
15. A cell according to claim 12, wherein said anode is a porous anode.
16. A cell according to claim 12, wherein said anode is of graphite, silicon carbide or silicon nitride.
17. A cell according to claim 15, wherein said means for feeding hydrogen to said anode, feeds the hydrogen gas such that the hydrogen gas permeates from the pores of the porous anode into the cell.