

Chapter 6

MOLTEN SALT ELECTROLYSIS FOR SUSTAINABLE METALS EXTRACTION AND MATERIALS PROCESSING – A REVIEW

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ABSTRACT

The processing of material and their eventual recycling, with eliminated or minimized greenhouse gas emission, pose great technological challenges. This is particularly true for metals industry since most established high temperature extraction technologies use carbon as a reductant to reduce metal oxides and as a heat source by carbon combustion, causing CO₂ formation. Therefore, one must look at totally new strategies for metals extraction without using carbon as the reductant. Electricity, i.e., electrons, is one of most effective alternatives to the carbon reductant. Fused salt electrolysis has proved to be an attractive route and this technology would be further enhanced if the electricity were generated from renewable energy sources. As well as primary extraction, molten salt electrolysis also has enormous potential for materials processing. Considerable challenges facing fused salt electrolysis technology towards sustainable development lie within two key categories: (i) improvement of existing technologies and (ii) development of novel technologies, both having much less or zero environmental impacts. The latter can potentially lead to displacement of many conventional non-electrochemical technologies for metals extraction and materials processing. Unfortunately, the molten salt electrolysis technology for the above applications remains in many respects underexploited over the past 50 years. Only in the recent 15 years, it is undergoing a significant renaissance because of several innovative ideas being explored both in the laboratory and also at the pilot scale.

This article reviews molten salt electrolysis technologies and their advances for metals extraction and materials processing with special attention given to the

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sustainability in utilization of energy and chemical resources. It also presents some selected innovative molten salt electrolysis processes and describes the prospects for change. Examples are given for (i) development in the extraction, purification and recycling of aluminium, magnesium, titanium, silicon and related materials by fused salt electro-winning and electrorefining; (ii) novel electrolysis processes for processing advanced materials, including niobium-based superconductors, nonoxide ceramics, nanostructured materials and carbon nanotubes, which can find applications in energy generating and storage systems, such as solar cells, batteries and supercapacitors; and (iii) for treating waste materials. It is demonstrated that the next decade appears to be an exciting period for molten salt electrolysis technologies when many novel processes more efficient in their use of energy and reagents while at the same time reducing the greenhouse gas emissions, should find industrial applications. Finally, problematic issues, challenging, research trends and perspectives for molten salt electrolysis in the above applications are discussed.

1. INTRODUCTION

1.1. Electrolysis

Electrolysis is an electrochemical process in which an electric current is passed through an ionic substance using an electrolytic cell, resulting in non-spontaneous chemical reactions at electrode surfaces. It is commercially very important as a stage in the separation of elements from naturally occurring sources such as ores. The main components required to achieve electrolysis are (i) a liquid or solid containing mobile ions – an electrolyte, (ii) an applied voltage, (iii) an external source of direct current, and (iv) electronically conducting solids or liquids known as electrodes. The electrolytic cell typically consists of a pair of the electrodes (i.e., an anode and a cathode), both immersed in the electrolyte, and the electrolyte contained in a vessel or container, with an external electrical potential applied across the anode and cathode during electrolysis.

The mobile ions are the carriers of electrical current in the ionic electrolyte. The externally applied voltage supplies the energy necessary to create or discharge the ions at the electrodes in contact with the electrolyte, where the electric current is carried by electrons in the external circuit. Each electrode attracts ions that are of the opposite charge. Positively-charged ions (cations) move towards the electron-providing (negative) cathode, whereas negatively-charged ions (anions) move towards the positive anode. At the electrodes, electrons are absorbed or released by the atoms and ions. Those atoms that gain or lose electrons to become charged ions pass into the electrolyte whilst those ions that gain or lose electrons to become uncharged atoms and, usually, separate from the electrolyte. Ancillary practical components to achieve electrolysis include vessels to supply, contain, and remove the reactants and products and electrical circuitry.

The key process of electrolysis is the interchange of atoms and ions by the removal or addition of electrons from the external circuit, while products of electrolysis are in a different physical state from the electrolyte or electrode materials which can be usually removed by some physical manners. For example, in the electrolysis of Al_2O_3 dissolved in molten cryolite (Na_3AlF_6)-based fluoride electrolytes to produce primary aluminium metal in the Hall-Heroult (HH) process [1], the reduced metal is tapped out from the HH cells (HHC).

The mass of product formed is related quantitatively to the quantity of electric charge passed through the circuit by Faraday's laws of electrolysis [2].

1.2. Molten Salt Electrolysis

When an aqueous solution is used as an electrolyte, it is commonly termed aqueous electrolysis. This review will focus on another electrolysis process where the electrolyte used is a pure molten salt or a mixture of molten salts, known as molten salt electrolysis. Molten salt electrolysis is widely used for electrometallurgy, such as electrolytic reduction of metallic compounds to metals (electrowinning) and purification of impure metals to purer metals (molten salt electrorefining) [3]. For instance, molten NaOH can be electrolysed into sodium and oxygen, both of which have important chemical uses. Lithium is produced by electrolysis of a molten LiCl-KCl mixture. It also may cover a process for synthesis of various materials from compounds or a mixture of compounds and elements (fused salt electrosynthesis).

1.2.1. Characteristics of Molten Salt Electrolysis

A number of unique properties of molten salts affecting efficiency of electrolysis have been summarised by Fray [3] and Inman [4], The advantages mainly include:

- The most common solvent components are the alkali and alkaline earth halides and these all possess very negative Gibbs free energies of formation, i.e., high electrochemical decomposition potential windows.
- Overpotentials due to cathodic polarisation are often small in cathodic deposition, which is desirable from an energy efficiency point of view. However, mass transfer-controlled cathodic process generally create dendritic deposits, if the metals are deposited in the solid state, that are difficult to be separated from solidified salts after electrolysis.
- The high ionic conductivities ($2\text{-}9\ \Omega^{-1}\text{cm}^{-1}$) and diffusivities with low viscosities of molten alkali and alkaline earth metal salts and their mixtures are other desirable features both from the point of view of power losses and of temperature control by Joule heating.

There are some disadvantages associated with using molten salts:

- Molten salts are powerful solvents for inorganic materials. However, this can be a disadvantage, for instance in limiting the selection of cell materials for electrodes, linings, and containers. The corrosiveness of molten salts demands the use of expensive refractories for containment.
- The use of high temperatures and restricted environments must be considered a disadvantage. There are considerable problems associated with solidification of the electrolyte if the power supply fails or the cell has to be shut down.
- Apart from the problems mentioned above, extra energy cost must be incurred to keep the systems in a liquid state. The hydrolysis of many of the hygroscopic salts employed as solutes and solvents can cause difficulties when their use is required on

a large scale. Purification is often a prolonged process which necessitates considerable peripheral handling facilities.

- Other disadvantages arise from the high volatility of many of the high oxidation state certain metal halides (particularly chlorides), causing to fuming and loss of electrolyte.
- Specific disadvantages arise from anodic reactions where energy considerations are often in conflict with efforts to maintain cathode product purity.
- The corrosiveness of molten salts demands that use of expensive refractories for containment, and in many cases, inert atmospheres are required.
- Furthermore, with present cell designs the thermodynamic potential is usually insignificant compared to the resistive losses in the electrolyte which can be as high as several volts.

The most commonly used salts are chlorides, fluorides, and chloride-fluoride mixtures. Chlorides offer the advantages of a lower operating temperature and of a greater choice of electrode and container materials. As to disadvantages, chlorides react with moisture; some are hygroscopic, even deliquescent, while others decompose by hydrolysis. Hydrolysis prevents dehydration – simple heating will not result in the removal of the water of hydration from certain metal chlorides such as LiCl or NbCl₅. Fluorides, on the other hand, have the advantage of being less reactive with moisture and, additionally, can dissolve oxides directly, avoiding fluorination, which requires reaction with a fluorine containing compound. In principle, the use of an oxide-based cell feed simplifies the process flow sheet and reduces capital and operating costs. Unfortunately, the higher melting points and greater corrosion properties of the fluorides severely limit the choice of cell materials. Another disadvantage is the relatively low solubility of refractory metal oxides in molten fluorides.

Choice of suitable electrodes for molten salt electrolysis depends mainly on chemical reactivity of the electrodes towards an electrolyte and cost of manufacture of the electrode. There are advantages and disadvantages in producing solid metal or liquid metal, or metal dissolved in a metallic solvent as a liquid alloy [5]. When the solid metal is a cell product, it can be simply recovered by removing it from its cathode substrate. The disadvantage is that the solid metal deposited from molten salts is invariably dendritic and this results in salt entrainment with the need for some form of subsequent treatment for salt removal. The production of the liquid metal solves the morphological problem and facilitates the easy removal of the product from the cell by siphoning.

The majority of metals can be deposited from fused salt but as commercial production is restricted to the more reactive elements, it is worthwhile considering the advantages and disadvantages of fused salt electrolysis as compared to smelting and aqueous electrolysis

1.2.2. Comparison with Pyrometallurgical Processes

Compared to smelting, the advantages are generally perceived to be a higher purity product and, perhaps, intrinsically cleaner processes. However, as few metals are produced or refined using fused salt electrolysis, these advantages are normally outweighed by the disadvantages which include [3]:

- Pyrometallurgical processes are generally more energy efficient as reduction, using carbon, occurs directly rather than having to burn the carbon to generate heat which eventually is converted into electricity via the Carnot cycle,
- The higher operating temperatures, corrosive nature of the melts, and the tendency to fume, due to the high vapour pressures of molten salts, causing difficulties associated with containment and process control,
- For metals whose melting point exceeds the boiling point of the electrolyte, the metals are deposited in a solid, dendritic form for which, unless special precautions are taken, there may be difficulties in extracting the product, and
- The output of metal per unit volume and the metal production rate (space-time yield) are relatively low.

For many metals, the last point is, perhaps, the most significant and this is a result of the cell design which, in many cases, can be regarded as a two-dimensional reactor with large inter-electrode spacing. This can be contrasted with pyrometallurgical reactors where the reactions occur three-dimensionally, throughout the whole reactor, with very short diffusion distances and high surface areas. As well as a poor production rate per unit volume or floor surface area, the net result is a high energy consumption which is usually at least two or three times the theoretical minimum. Despite of these disadvantages, a few metals are produced commercially by molten salt electrolysis and these include the refractory metals, alkali metals such as lithium, sodium, and potassium and, more significantly magnesium and aluminium.

It is apparent that to make molten salt electrolysis processes more attractive, a “three-dimensional” reactor is required with substantially reduced inter-electrode spacing which would increase both the space-time yield and the energy efficiency. Some advances have already been made in this area [6-10].

1.2.3. Comparison with Aqueous Electrometallurgical Processes

The advantages over aqueous extraction are as follows:

- The much higher conductivities and diffusivities result in much lower iR losses and higher current densities can be achieved at modest voltages,
- The elevated temperatures of operation result in larger exchange currents which give rapid kinetics and lower activation polarisation for the electrode reactions,
- The absence of water as a solvent means that it is not necessary to consider the evolution of hydrogen as a competing cathodic reaction. Furthermore, alkali halide salts, often used as solvents in fused salt electrolytes, have high decomposition potentials, and
- Molten salts generally are mutually soluble and, therefore, concentration polarisation effects are minimised.

The disadvantages include:

- difficulties when operating at high temperatures,
- high volatility of electrolytes and corrosion of refractories, and
- when the product is a solid, it is difficult to separate the solid from the solidified electrolyte.

It is impossible to cover comprehensively a wide range of molten salt electrolysis which can electrodeposit most, if not all, of the metals of the periodic table. In this review, we will highlight the principles and focus attention on (i) development in the extraction, purification and recycling of metals and materials by fused salt electrowinning and electrorefining, (ii) novel electrolysis processes for processing advanced materials, and (iii) for treating waste materials.

2. CONVENTIONAL FUSED SALT ELECTROLYSIS

2.1. Fused Salt Electrowinning

The electrowinning of metals from their ores dissolved in an electrolyte is probably one of the oldest industrial electrolytic processes. The most basic type of electrowinning cell is schematically shown in figure 1. In fused salt electrowinning, the objective is to obtain the metal in a pure or semi-pure form by electrolytic extraction from a compound of metal dissolved in the molten salt electrolyte composed of solute and solvent. Any molten salt solvent to be used in an electrolytic operation should have the following attributes: (i) low vapour pressure and as low a melting point as possible, (ii) as high electrical conductivity, (iii) a low viscosity, (iv) a large decomposition voltage, (v) as non-corrosive as possible, (vi) readily purified, (vii) non-polluting, and (viii) inexpensive. The cell feed, containing the ions of the metal to be extracted, should be closely related to the original minerals. Ideally, it would be desirable to win the metals directly from their minerals – some partly-successful attempts to achieve this have been made [11] but, frequently, the minerals contain too many impurities to be used directly.

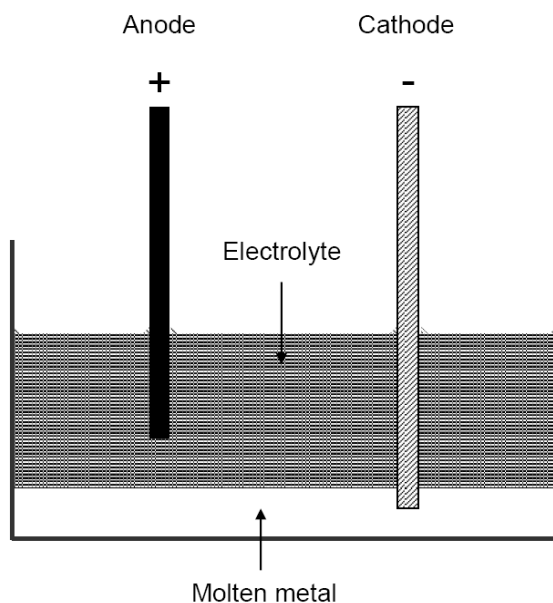


Figure 1. Basic electrolytic cell for fused salt electrowinning [3].

During electrolysis, the voltage required to drive the process is substantially higher than the reversible potential as calculated by the Nernst equation, which for metal halide (MX_n) in a multi-component molten salt solution and in equilibrium with pure metal (M) and pure gas (X_2) at atmospheric pressure can be expressed as the following:

$$E_{\text{MX}_n} = -\frac{\Delta G_{\text{MX}_n}^{\circ}}{nF} - \frac{RT}{nF} \ln a_{\text{MX}_n} \quad (1)$$

where $\Delta G_{\text{MX}_n}^{\circ}$ is the standard Gibbs free energy of formation of MX_n , F is the Faraday constant (9.64853×10^4 C), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature in Kelvins and a_{MX_n} is the activity of MX_n in the electrolyte solution. E_{MX_n} is the reversible potential or equilibrium decomposition potential of MX_n as a function of electrolyte composition and temperature. The difference between the equilibrium potential and the applied voltage is due to kinetic factors which increases the energy consumption of the electro-winning cell. The imposed cell voltage for the electrolytic decomposition of MX_n is given by the relationship below:

$$E_{\text{cell}} = E_{\text{MX}_n} + (\eta_a + \eta_c)_{\text{cathode}} + (\eta_a + \eta_c)_{\text{anode}} + \eta_{\text{electrodes}} + iR \quad (2)$$

where E_{cell} is the applied cell voltage, η_a and η_c are the activation and concentration overpotentials at the electrode, respectively, and are a function of electrolyte composition, current density and temperature; $\eta_{\text{electrodes}}$ is the voltage drops associated with the electrodes themselves, with the bus bars and the electrical contacts between them, i is the current, R is the cell resistance, and iR is the ohmic overpotential (or iR drop) and is due to the electrical resistance of the electrolyte and is proportional to current density and interelectrode distance and inversely proportional to the electrical conductivity of the electrolyte and to the electrode area. Therefore, cell voltages depend upon individual melt chemistry, electrode materials, and cell design. Existing industrial molten salt electrolysis cells, such as the HHC for aluminium and Dow cell for magnesium, operate at voltages three or five times the value of the Nernst potential.

The productivity of an electrolytic cell is expressed by several figures. Current efficiency is frequently defined as the ratio of the number of equivalents of metal product to the number of moles of electrical charge delivered to the cell by the power supply. As such, current efficiency is essentially a measure of compliance with Faraday's laws of electrolysis. In molten salt electro-winning, current densities of about 1 A/cm^2 are common and cathodic current efficiencies of 60-80 % are usual. These figures are well below those achieved for the HHC for electro-winning of aluminium, which typically attains current efficiencies exceeding 95 % [12]. Voltage efficiency is defined as the ratio of the reversible decomposition potential to the imposed cell voltage. It is an extent of the deviation from the Nernst equation and is a measure of inefficiency due to kinetic factors. For the electro-winning in molten fluoride electrolytes, voltage efficiencies are typically below 50 %, when using molten chloride electrolytes values of as low as 25 % or less have been reported.

2.2. Fused Salt Electrorefining

In an electrorefining cell, the anode consists of an impure form of the metal or alloy to be purified and the cathode is a purer metal, both immersed in an electrolyte containing ions of metal to be purified. A basic design of the electrorefining is schematically shown in figure 2. Electrorefining relies on the difference in the electrode potentials of the elements in the anode to separate metals from their accompanying impurities in just one step, saving time. It may be the least expensive way to purify metals because it is so selective in terms of what it produces, straightforward, and economical.

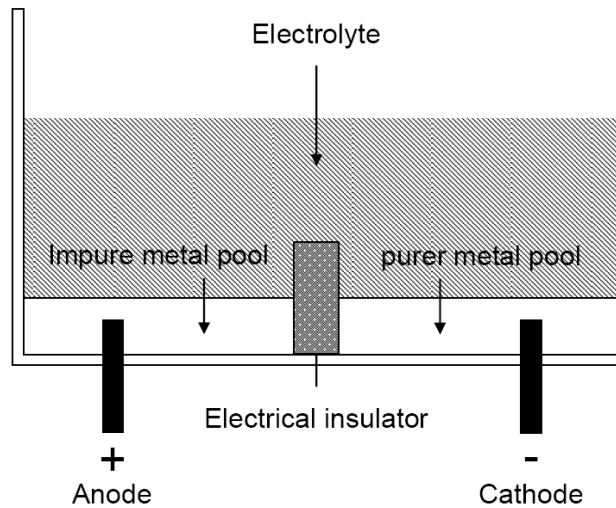


Figure 2. Simple fused salt electrorefining cell [3].

The metal is transferred by electrolysis from an impure anode to a pure cathode with impurities left in the anode residue as metals and dissolved in a molten salt electrolyte as ions. Fused salt electrorefining has considerable promise as a technique for metal refining, with possible advantages over pyrometallurgical and hydrometallurgical techniques. The thermodynamic potential for the electrochemical transfer of an element (X) at a low activity to a high activity is given by the Nernst equation:

$$E = -\frac{RT}{nF} \ln \frac{(a''_X)_{\text{anode}}}{(a'_X)_{\text{cathode}}} \quad (3)$$

where E is the theoretical potential of the cell, and a''_X and a'_X are the activities of X in the anode and cathode, respectively. It is assumed that the activity of the metal at the cathode is unity. In all systems there is going to be more than one element in the anode and the ease by which the elements dissolve is given by the position in the electrochemical series, and the relative position depends, to a certain extent, on the electrolyte system. Table 1 lists standard electrode potentials in a 0.48NaCl–0.52CaCl₂ melt at 727 °C against Cl₂/Cl⁻ reference electrode, taken from Winter and Strachan [13].

Table 1. Standard electrode potentials in 0.48NaCl-0.52CaCl₂ at 727 °C against chlorine reference electrode [13].

Electrode	Standard electrode potential (V)
Mg ²⁺ /Mg	-2.596
Mn ²⁺ /Mn	-2.001
Al ³⁺ /Al	-1.838
Zn ²⁺ /Zn	-1.582
Fe ²⁺ /Fe	-1.272
Pb ²⁺ /Pb	-1.112
Sn ²⁺ /Sn	-1.041
Cu ⁺ /Cu	-1.010
Sb ³⁺ /Sb	-0.821
Cl ₂ /Cl ⁻	0.000

Elements near the top of the table (more electropositive or less noble) will anodically ionize more easily than those near the bottom (more electronegative and noble) and will, therefore, dissolve into solution. As an example, aluminium dissolves more readily into the melt than copper. This calculated potential only applies when no current is flowing but as the activation polarization is generally low at high temperatures this voltage is unlikely to change dramatically.

Advantages of electrorefining are that a dross-free product is produced and, generally, much less atmospheric pollution is generated than for pyrometallurgical refining processes. For example, the chlorination of aluminium scrap to remove magnesium as the chloride produces a hygroscopic flux of low or negative commercial value with some unreacted chlorine escaping into the environment. However, designs of most existing fused salt electrorefining cells are inefficient, with large anode-cathode distances, causing excessive voltage drops and energy losses. The two dimensional nature of the cell designs leads to lower space-time yields and poor mass transfer compared to pyrometallurgical reactors, which are always three-dimensional in nature. This causes difficulties such as the depletion of the least noble element in the anode metal pool, allowing other elements in the anode to be anodically dissolved and transferred to the cathode. This depletion may be diminished by enhancing mass transfer in the anode pool or by stirring the liquid metal with a ceramic impeller. Secondly, the anodic current density may be reduced to balance the diffusion flux in the metal pool but this leads to economic penalties with conventional cells. The advantages of fused salt electrorefining over other metal refining techniques can be more obvious provided that efficient cell designs are devised [3, 9, 10].

In most cases the advantages are outweighed by the economic disadvantages, restricting electrochemical processes in molten salts to those metals which are most reactive and cannot be conveniently refined any other way. However, as pollution laws become more stringent and more complex alloys need to be recycled, these processes may become more economically feasible. Numerous laboratory studies have been made into the electrorefining of many metals and some demonstrated potential applications using fused salt electrolysis include the removal of magnesium from recycled aluminium cans and the refining of aluminium and metallurgical grade silicon [14-16]. It should be mentioned that some of metals, especially the rare earths and reactive metals, have multivalent states with little difference in the electrochemical stability between states; as a result, two or more separate

valence species may coexist in the electrolyte and this may cause problems during electrorefining, e.g., lowering cathodic current efficiency of the electro-deposition.

Thermodynamic potentials for electrowinning are much higher than for electrorefining yet the latter is only applied in limited cases. The fused salt electrowinning differs fundamentally from fused salt electrorefining in that gas is usually produced at the anode. Although the formation of coherent metal is less important in the fused salt electrowinning for metals extraction, it is nevertheless a desirable objective of research to improve the form of the electrowon deposits to avoid deleterious post-electrolysis separations.

In order to extend the application of fused salts in the electrowinning and electrorefining of metals, it is necessary to maximise the current density, minimise the voltage drop and greatly increase the area of electrode surface so as to compete with the space-time yield of pyrometallurgical reactions.

2.3. Combined Electrowinning and Electrorefining in Molten Salts

It might be possible to carry out carbochlorination of a metal oxide to produce a metal chloride that is soluble in a molten salt electrolyte within the anode part of an electrowinning cell. Unfortunately, carbon frequently introduces impurities in the electrolyte melt leading to an impure cathodic product. One way of alleviating this problem would be to deposit the cathodic metal in a metallic solvent and then refine the metal from the solvent. A design which allows both the electrowinning and electrorefining steps to be carried out in the same cell has been described by Slatin [17], as schematically shown in figure 3. The cell is divided into two compartments by an inert non-conducting barrier that extends from above the fused salt level until a seal is made with the bipolar, liquid metal pool in the bottom. Metal is electrowon into the metal pool on the top of membrane. This metal pool in contact with the electrolyte in the bottom compartment of the cell also acts as an anode and is electrorefined and collected on the bottom of the cell. Apparently, such a system is only possible for metals that are lighter than the electrolyte such as aluminium, magnesium, and lithium.

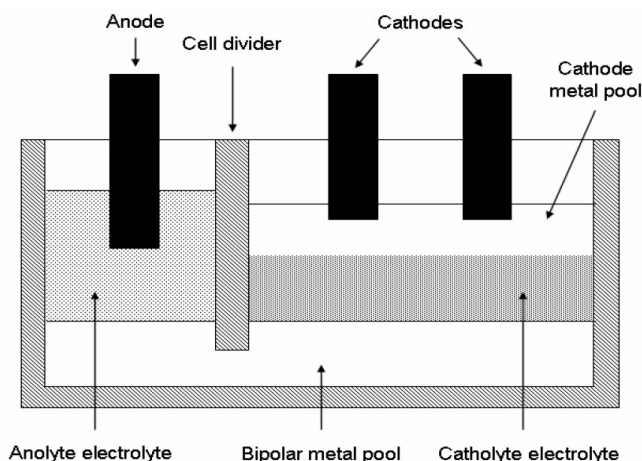


Figure 3. Schematic diagram of combined molten salt electrowinning-electrorefining cell [3, 17].

2.4. Applications of Conventional Molten Salt Electrolysis

There are many possible applications of fused salt electrowinning and electrorefining for metals extraction and materials processing. A number of typical examples for the applications to metals extraction and materials processing are given in this review.

2.4.1. Molten Salt Electrolysis for Aluminium Production

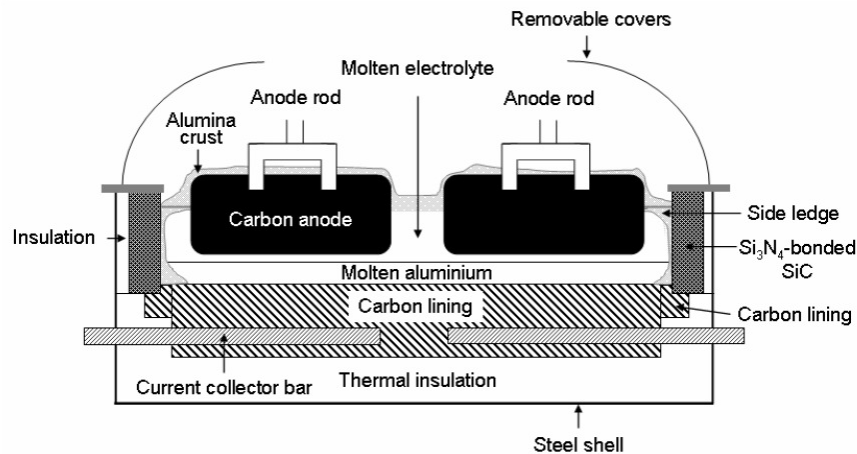
(1) The Hall-Heroult Process

All primary aluminium is worldwide extracted by electrolysis from Al_2O_3 dissolved in molten cryolite-based fluoride electrolytes, typically consisting of Na_3AlF_6 , AlF_3 , CaF_2 , and Al_2O_3 , in the HH process [1]. The HHC, as shown in figure 4, consists of a steel shell lined with refractory insulating bricks covered with Si_3N_4 -bonded SiC sidewall lining materials, a pool of molten aluminium on carbon blocks as the cathode at the bottom of the cell, and a carbon block immersed in the electrolyte from the top of the cell as the anode. Molten aluminium is produced at the cathode while the carbon anode is electrochemically oxidised and, thus, consumed during electrolysis to produce 70-90 % CO_2 , with the rest being CO . The overall cell reaction is given as follows:

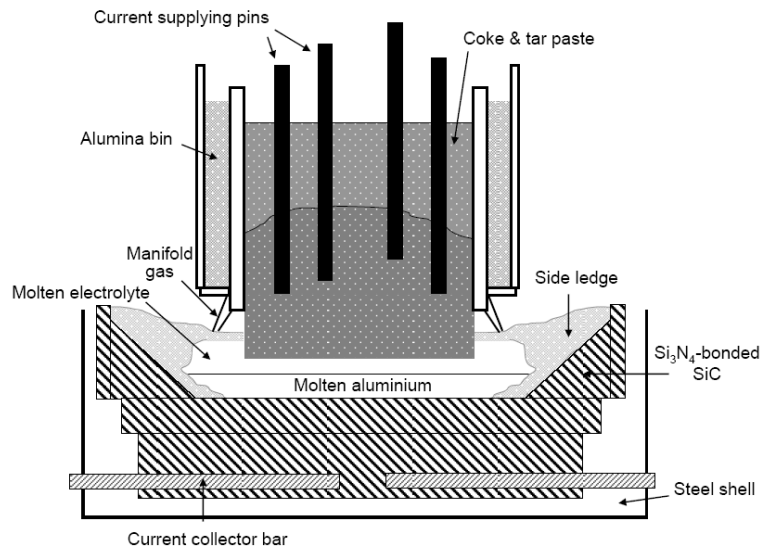


The reversible cell voltage is 1.19 V at a typical electrolysis temperature of 960 °C. To compensate for a sum of the resistances contributed by the electrolyte, the anode and cathode materials and their contact resistances, as well as the anodic overvoltage, HH cells operate at cell voltages of 4.0-4.6 V. There are two types of the carbon anodes, i.e., prebaked anodes (figure 4a) and Soderberg anodes (figure 4b) [1]. The prebaked anodes are large carbon blocks that must be replaced as they are consumed according to Reaction 4. The Soderberg anode is continuously formed by addition of a carbon/pitch paste to a mould held above the molten electrolyte in the cell with the paste being added at the rate of carbon consumption in the cell. The whole mass moves slowly down towards the melt and is baked *in situ* with the evolution of polluting gases. The density and electrical conductivity is also lower than that of the pre-baked anodes.

The three most characteristic features of the HHC are the consumable carbon anode, the liquid aluminium cathode, and the frozen bath lining. For the latter, heat must conduct through the cell sidewalls to stabilize the frozen bath on the sidewall linings. Thus, the heat produced in the cell and the heat losses must be balanced to maintain stable bath temperature and frozen bath lining. As a result, the energy consumption of the typical HHC is 12.9-13.5 kWh per kg Al and the energy efficiency is as low as 40-45 %, which means that a major part of the electrical energy input is released as heat and, essentially, wasted [12].



(a) Hall Heroult cell with prebaked anodes.



(b) Hall Heroult cell with Soderberg anodes.

Figure 4. The Hall-Heroult cell for electrowinning of aluminium: (a) HHC with prebaked anodes and (b) HHC with Soderberg anodes [18].

(2) Technological Improvements to the Hall-Heroult Process

Although significant optimization of process variables has taken place to cut production costs, reduce greenhouse gas emissions, and improve working conditions, the basic features of the HH process have remained essentially unchanged since the process was discovered.

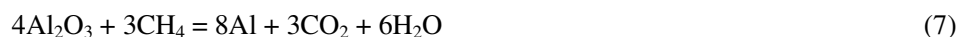
In the past 50 years, developments have taken place mainly in the areas of improved insulation, pot linings, and cathode and anode materials [1, 12]. The advances in the areas have been described in several review articles [3, 18-22]. For example, a compressible insulation has been developed to minimise the potlining heaving caused by sodium co-depositing with the aluminium and intercalating into the carbon lining. Subsequent increase in

pot life is to be expected when new carbon cathodes are slowly heated to 700 °C. Molten pools of cathodic aluminium have rippling surfaces which is the result of magneto-hydrodynamic effects which necessitates in large anode-to-cathode distances (high iR losses) to prevent contact of molten aluminium to the anodes. Aluminium cells with drained cathodes which are wet by molten aluminium allow smaller anode-to-cathode distance and lower cell voltages. Coatings of TiB₂ and TiC on carbon have been used in these cells. The development of oxygen-evolving inert anode materials for the HHC has met only with limited success so far. However, there have been other advances and innovations. For instance, automation and process control have been furthered by new sensor technologies allowing the bath chemistry to be characterised, to follow alumina feeding, and even to manage the electromagnetic fields in the cell. In mathematical modelling, thanks to improvements in computational capacity, it is now possible to model many physical properties of the electrolyte melts as well as transport phenomena in the HHC, including current distribution, thermal profile, and position of sidewall ledge.

Rapp evaluated the possibility of using modified solid oxide fuel cell (SOFC)-type anode for retrofit in the HHC [23-25]. With the SOFC-type anode, oxide ions dissolved in the cryolite-based electrolytes can transport through the dense oxide-ion-conducting membrane and then electrochemically oxidize the fuel inside the electrode according to anodic reactions below:



Using methane as a fuel, the net electrolytic reaction may be expressed as:



According to Reaction 7, less than half of the CO₂ gas would be evolved at the SOFC-type anode and no perfluorocarbons or volatile organic compounds (VOC) gases would be formed, either in the fabrication or in the use of this type of the anode. It is expected that application of such a non-consumable anode (NCA) retrofitted into the HHC can potentially increase the energy efficiency and reduce the cost of producing primary aluminium significantly compared to the best current and emerging anode replacement technologies. Rapp and Zhang, however, found that that a ZrO₂-based solid electrolyte membrane readily dissolved into any cryolite-based fluoride electrolytes containing dissolved Al₂O₃, from which aluminium could no longer be electrowon due to the resulting low Al₂O₃ solubility in the electrolytes [25].

(3) *Alternative Molten Salt Electrowinning of Aluminium*

Aluminium has been also produced industrially by electrolysis of AlCl₃ in molten NaCl-LiCl electrolytes at 700 °C [18]. The electrowinning cells developed by The Aluminium Company of America (Alcoa) utilised a bipolar multi-carbon electrodes unit so that chlorine is evolved on the bottom surface and molten Al is deposited on the top surface of each electrode, shown in figure 5. The overall electrolytic cell reaction is simply expressed as



The reversible cell voltage needed for the reduction reaction to occur at this temperature is 1.77 V at 700 °C and the cell voltage is about 3.3 V which can be compared with 4.5 V in the HHC, with the current density being 1.3 A/cm². Under these conditions, power consumption is 11.4 kWh per kg Al, which yields an energy efficiency of 60 %. This cell design improves significantly the space-time yield over that of the HHC and compares quite favourably with that of the typical HHC which is due to the higher electrical conductance of the chloride electrolyte and the smaller anode-cathode separation, hence the lower voltage drop across the electrodes, make the electrolysis of AlCl₃ more energy efficient than the HH process. This alternative chloride electrowinning technology promises to produce aluminium at around 4 kWh per 1b but requires a chemical plant to produce anhydrous AlCl₃. The electrolysis unit offers higher efficiency and probably also lower capital costs than the HHC of the same capacity. However, these advantages are outweighed by the cost of the extra process step, i.e., chlorination of alumina and the problem of removing dioxins, making the overall process less attractive economically (see also section 2.5.3). Yang and Fray simulated electrowinning cells with anodes of large surface areas for electrolysis of alumina dissolved in a chloride melt [26].

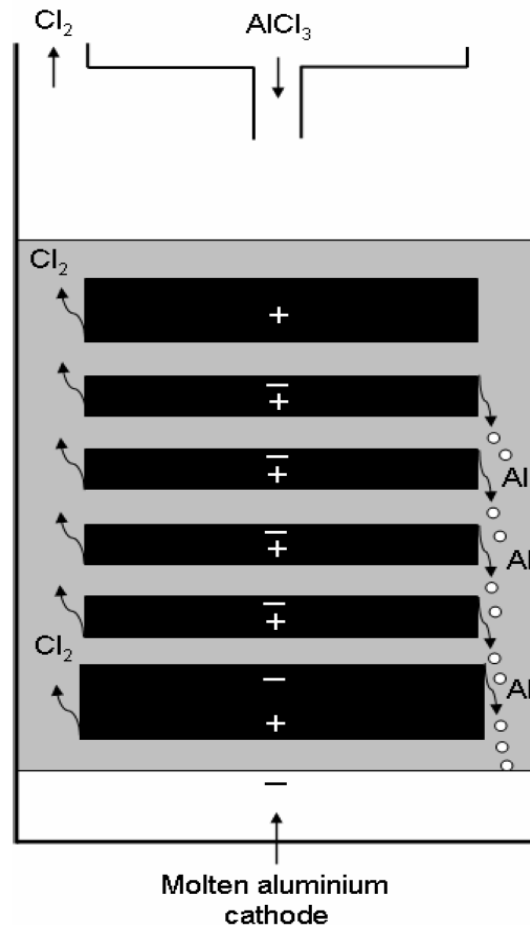


Figure 5. Schematic diagram of Alcoa's bipolar cell [3].

Recently, Rapp et al. investigated the possibility of using molten Na_2SO_4 as an alternative solvent for Al_2O_3 , with the SOFC-type anode, as they had found that the solubility of $\alpha\text{-Al}_2\text{O}_3$ to be 8 mol% and those for ZrO_2 and Y_2O_3 to be very much lower in a very basic Na_2SO_4 melt where NaAlO_2 was stable at 927 °C [27]. Very little information is available in the literature as to Al- Na_2SO_4 interactions and cathodic reactions in Na_2SO_4 -based electrolytes with dissolved with $\alpha\text{-Al}_2\text{O}_3$, at around 927 °C, although a better understanding of these behaviours is crucially important to Al electrowinning using these electrolytes.

More recently, Yan and Lanyon studied, in detail, the chemical and electrochemical reactions in the Al- Al_2O_3 - Na_2SO_4 system at 927 °C to evaluate this novel process using Na_2SO_4 as the alternate solvent for Al_2O_3 , incorporating with a SOFC-type anode, for electrowinning primary aluminium [28]. In their study, cathodic reactions at platinum, gold, and aluminium cathodes in the melts were also investigated using electrolytic cells with a graphite rod or SOFC-type anode. Their results indicated that both aluminium and sodium were co-deposited electrochemically from the Al_2O_3 - Na_2SO_4 melts in air at 927 and 960 °C, with low current and energy efficiencies. The observed phenomena were explained by the cathodic reduction of O_2^{2-} to O^{2-} as well as the back reactions of the aluminium and sodium at the cathode surface.

(4) Molten Salt Electrorefining of Aluminium

The basic design of fused salt electrorefining cells in figure 2 is unsatisfactory as it requires a large floor area and a long and irregular anode-cathode path which results in an excessive voltage drop in spite of the high conductivity of the electrolyte. In order to overcome these difficulties, a three layer refining cell was devised for refining aluminium [29, 30]. In the three-layer cell for aluminium, the density of the impure aluminium anode is increased by a 30 wt% copper addition, and the density of the molten cryolite electrolyte is increased by BaCl_2 or/and CaF_2 additions so that it falls between that of the high purity electrorefined aluminium and the Al-Cu alloy. However, as the density differences between three layers are small, the interfaces are relatively unstable, the electrolyte layer must be approximately 20 cm thick to prevent physical transfer of anode metal into the cathode layer. As a result, the voltage drop in the electrolyte is very large, around 7 V at 0.4 A cm^{-2} , which can be compared to a thermodynamic potential requirement for transfer of aluminium from Al-30 wt% Cu to pure aluminium of 7 mV. Tiwari and Sharma have used the three-layer approach to electrolytically remove magnesium from Al-Mg alloys [14]. Al-Mg alloys were used as an anode and a cathode was the purified magnesium, with the electrolyte being a molten mixture of CaCl_2 - MgCl_2 -KCl-NaCl. The current efficiency exceeded 85 % at the anodic current density of 1.1 A/cm^2 and cell voltages of 1.6-4.86 V.

2.4.2. Molten Salt Electrolysis for Magnesium Production

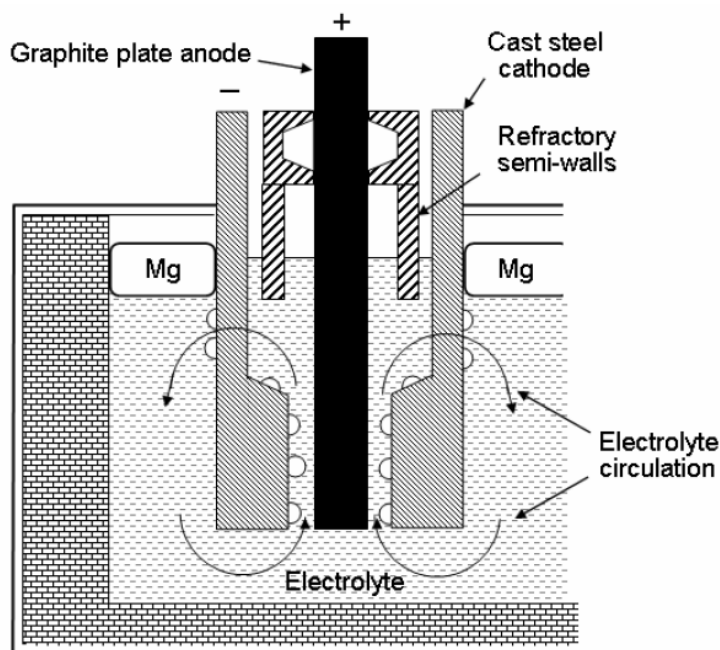
(1) Commercial Electrolytic Processes of Magnesium

At the present time, electrowinning of magnesium is also a major industrial process. There are two versions of industrial electrowinning processes for magnesium production [31, 32]. In one version, anhydrous MgCl_2 is used as the cell feed, this is practised by I.G. Farben Co., and is known as the I.G. Farben process. In the other version, the cell feed is partially dehydrated MgCl_2 ($\text{MgCl}_2 \cdot 1.5\text{-}1.7\text{H}_2\text{O}$) (a feed contains roughly 2 moles of water per mole of MgCl_2) and is used only by Dow Chemical Co. The raw material for magnesium

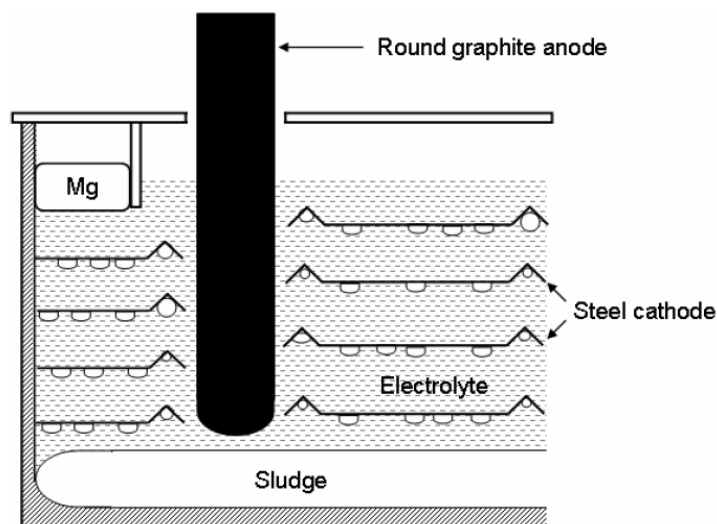
electrowinning is well brines or more commonly seawater, which contains about 0.13 wt% Mg. The Mg^{2+} ion is precipitated from seawater by addition of CaO (lime), produced by calcining (strong heating) of CaCO_3 (limestone or oyster shells). The insoluble Mg(OH)_2 is removed by filtration. Acidification of a slurry of this solid and an aqueous MgCl_2 solution with HCl converts the Mg(OH)_2 to soluble MgCl_2 , which is recovered as solid MgCl_2 by evaporation. This is dried to the hydrate $\text{MgCl}_2 \cdot 1.5\text{H}_2\text{O}$, which is the feedstock to an electrolytic cell in the Dow process. There is a tradeoff between complexity of dehydration operations and anode consumption rates in the Dow process. The cell electrolyte is a molten mixture containing about 25 % MgCl_2 -15 % CaCl_2 -60 % NaCl , and the cell is operated between 700 and 750 °C. Schematic diagrams of the conventional I.G. Farben cell and Dow Cell are shown in figures 6(a) and (b), respectively. The decomposition of molten MgCl_2 to produce liquid magnesium and Cl_2 gas is given by the reaction:



The reversible cell voltage for Reaction 8 is 2.52 V at 700 °C, in contrast to the typical operating voltage of 4.5-7.2 V at 0.4-0.7 A/cm^2 [32].



(a) I.G. Farben cell.



(b) Dow cell.

Figure 6. Electrowinning cells for commercial magnesium production: (a) I.G. Farben cell and (b) Dow cell [32].

In the Dow process, the graphite anodes are continuously consumed for the *in-situ* removal of water from the cell feed to produce hydrogen and oxygen; the latter reacting with the anode. This dehydration can be summarized by reaction below:



Due to the fact that the main anodic reaction is the evolution of chlorine, the reaction of the oxygen with the graphite does not lead to a decrease in the cell potential as in the HH cell for electrolytic reduction of Al_2O_3 where CO_2 is the predominant anodic reaction product. Gases of CO , HCl , and H_2 are detected in the anode gas, supporting the occurrence of Reaction 10. The Dow cell consumes about 0.1 kg of anode per kg Mg produced, a figure substantially higher than that of the I.G. Farben cells using anhydrous feed [33].

The power consumption for electrowinning of magnesium is 10.5-18 kWh per kg Mg. The current efficiency of the I.G. Farben cell exceeds 80 %, while that of the Dow cell is close to 80 %. The magnesium metal produced is about 99.9 % pure as it comes from the cell, since neither sodium nor calcium is reducible more easily than magnesium. The chlorine produced in the cell is converted to HCl for use in the acidification process by reaction with natural gas and steam or in a hydrogen/chlorine burner.

(2) Technological Improvements to Magnesium Electrowinning Processes

Research and development efforts have been directed towards fundamental studies of electrochemistry involved, improved cell designs, improved cathode conditions, and inert anodes for Dow process [3].

For example, Weert et al. explored the concept of producing HCl gas on the anode in molten salt electrowinning of magnesium to lower the cell voltage by 1 V compare to

chlorine gas evolution and to offer capital savings of the process [34]. Illustrated in figure 7 is the schematic of the magnesium electrowinning cell used in their work, where the anode consisted of a graphite rod of 25 % porosity, drilled out concentrically to direct the gases to the salt/anode interface. A variety of gas spargers attached to the bottom end of the graphite rod were tested. The cathode was either carbon or steel rod. The electrowinning experiments were conducted at 680-750 °C using a molten chloride electrolyte composed of 20.5 %MgCl₂, 39 %NaCl, 39 %CaCl₂, and 1.5 %KCl (in wt%). When hydrogen gas was introduced to the anode compartment, anodic and cathodic reactions and an overall cell reaction are given respectively by



The reversible cell voltage needed for Reaction 13 is 1.46 V at 727 °C as opposed to 2.50 V for Reaction 9. They found that the addition of hydrogen gas to the anode compartment decrease the anode depolarization and cell voltage and an increase in electrolysis temperature allowed further decrease in anode voltage. It was demonstrated that pure hydrogen gas added to the anode compartment lowered the anode voltage by about 1 V, confirming the concept proposed.

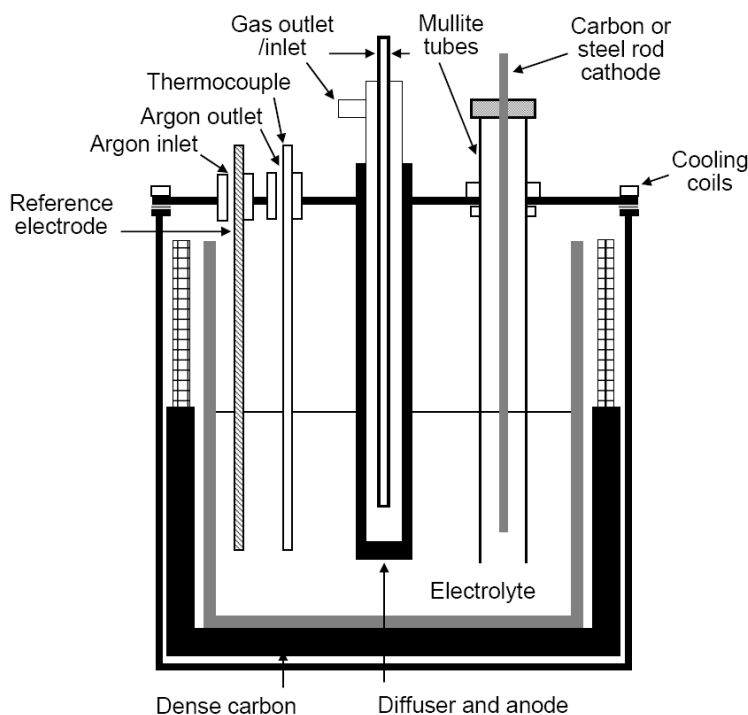


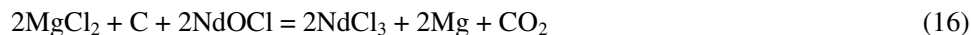
Figure 7. Magnesium electrowinning cell with HCl generation at the anode [34].

Yan et al. studied effects of the niobium doping level and the temperature, time, and atmosphere of sintering on microstructure and electrical conductivity of the synthesized polycrystalline niobium-doped TiO₂ (rutile) and also investigated the possibility of using the polycrystalline niobium-doped TiO₂ as the inert anodes for magnesium electrorefining [35, 36]. They found that the properties of niobium-doped TiO₂ anodes were greatly influenced by the factors studied and a niobium-doped TiO₂ anode with 3 mol% Nb₂O₃ doping level, sintered at 1300 °C under argon showed the most promising performance during electrolysis at the current densities of 0.75-1.25 A/cm², with the cell voltages of about 5-6 V. The results demonstrated that the polycrystalline niobium-doped TiO₂ was suitable for the use as an inert anode material in the industrial Dow cell for magnesium production.

Furthermore, Yan et al. measured liquidus temperatures of the molten MgCl₂-NaCl and BaCl₂-NaCl systems using the in-bath liquidus sensor with the aim to develop an on-line sensor for determining liquidus temperatures and superheats of magnesium electrowinning baths [37]. Such a sensor could be useful in better controlling cell operations and prolonging the cell life in fused salt magnesium electrowinning.

(3) Alternative Molten Salt Electrowinning of Magnesium

Sharma at General Motors has explored the electrolysis of MgO dissolved in a melt of NdCl₃, a process that exploits the fact that MgO will dissolve in neodymium chloride to form neodymium oxychloride and MgCl₂ [38, 39].



The NdCl₃ regenerated in Reaction 15 or 16 can react with further MgO due to Reaction 14, giving an overall process reaction below in the case of producing CO₂ only:



The reversible cell voltage for Reaction 17 to occur is 1.52 V at 750 °C, which can be compared with 2.50 V for MgCl₂ and 2.75 V for NdCl₃.

Recently, Lu et al. reported a similar technique of producing magnesium by direct electrolysis of MgO dissolved in molten LaCl₃-MgCl₂ electrolytes in a 5KA magnesium electrowinning cell with the steel cathode and the carbon anode at 700 °C [40]. In their process, the cathodic and anodic current densities were 0.81 and 0.539 A/cm², with the cell voltage of 4.6 V and, under these conditions, the cathode and anode products were electrolytic magnesium of 99 % purity and CO gas, respectively. The current efficiency achieved was 85 % higher than that in the Dow process (80 %), with the power consumption of 12 kWh per kg Mg. They indicated that this process has the advantages of less energy consumption, high energy efficiency and is environmentally sound. One of the disadvantages of both methods is the cost of the rare earth chlorides.

The above alternative magnesium electrowinning process obviates the need for carbochlorination of MgO in order to convert it into the chloride which is important as

oxychlorides are to be avoided in chloride electrolysis because of precipitation causing sludging. In this case, the oxychloride remains soluble in the electrolyte. The cathodic reaction is deposition of magnesium. At the anode, a number of reactions are proposed, but the one that seems dominant at industrial current densities is the oxidation of oxygen accompanied by anode consumption to form CO_2 . Reaction 17 is thus analogous to Reaction 4 in the HH process for primary aluminium production. The process has been tested on a laboratory scale and in pilot cells, but there are still many unanswered questions. Sometimes, chlorine evolution occurs at the anode and ore research is required to determine commercial viability.

Pal et al. developed the solid oxide membrane (SOM) process for green synthesis of metals, including magnesium, from oxides by molten salt electrolysis [41]. The electrolytic cell is shown in figure 8. The SOM process is an energy efficient alternative for oxide electrolysis using a solid-oxygen-ion-conducting stabilized ZrO_2 electrolyte (membrane) that separates the anode from the electrolyte melt containing the oxide of the metal to be reduced. If the membrane is chemically and electrochemically inert in contact with the melt, then it can be regarded as part of an inert anode structure. An inert cathode is placed in the melt. On application of cell voltage between the anode and the cathode greater than the dissociation potential of the oxide to be reduced but less than that of ZrO_2 and undesired oxides, the desired metal cations are reduced at the cathode, and the oxygen ions transfer through the membrane and are electrochemically oxidised at the anode.

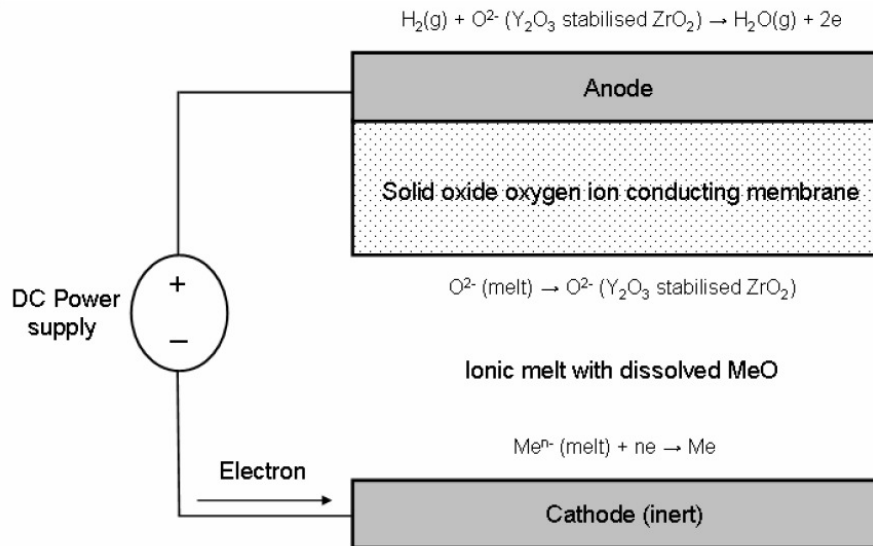


Figure 8. Schematic diagram of molten salt electrolytic cell with the solid oxide membrane (SOM) for magnesium production [41].

For magnesium synthesis from MgO , Krishnan et al. reported the recent success of the SOM process for magnesium production from MgO dissolved in molten (55.5 wt% MgF_2 - CaF_2)-10 wt% MgO electrolyte at 1150 °C and molten MgF_2 -10 wt% MgO at 1300 °C [42]. Extrapolation of the results showed that for a SOM cell with an output of 2 tonne per day, the electrolytic cell was operated at 1 A/cm^2 , with the cell voltage of 4.5-5.5 V and the power

consumption of 9-12 kWh per kg Mg, more efficient than the conventional industrial MgCl_2 electrolyzers. The magnesium would leave the cell as a vapour and be condensed as a high purity product.

2.4.3. Molten Salt Electrowinning of Titanium

The properties of titanium have long been recognised as a light, strong, and corrosion resistant metal, which has led to many different approaches over the past several decades to extract titanium from its ore. Most of the titanium produced worldwide is obtained by the Kroll process invented in the late 1930s and commercialised in the mid 1940s [43]. The Kroll process is basically a batch process that reduces gaseous titanium tetrachloride (TiCl_4) with molten magnesium inside a steel retort followed by vacuum evaporation or inert gas sweep to remove by-products at 1000 °C. Despite the many other methods investigated to produce titanium, the only method currently utilised commercially are the Kroll and Hunter processes. These processes utilise TiCl_4 which itself is produced from the carbo-chlorination of TiO_2 -rich feedstocks such as weathered ilmenite, natural and synthetic rutilites, and titanium slags or a refined TiO_2 according to the reaction:



In the Kroll process, TiCl_4 is reduced at around 800 °C under argon to produce titanium sponge:



The titanium sponge produced is then crushed, hand sorted, compacted into briquettes that are electron-beam welded into electrodes, the electrodes are then vacuum-arc-melted into a round ingots, which is finally machined into to remove the outer skin. The MgCl_2 is then separated and recycled electrolytically to produce magnesium as the reductant to further reduce the TiCl_4 and chlorine for the carbochlorination reaction. In the Hunter process, sodium is used as a reductant according to the reaction:



The titanium produced by either the Kroll or Hunter process must not only be separated from the reductant halide by vacuum distillation and/or leaching in acidified solution to free the titanium sponge for further processing to useful titanium forms, but also require the regeneration of the reductant by electrolysis of the molten magnesium chloride. This makes the entire process for preparing titanium highly labour and energy intensive. Because of these multiple steps, the resultant titanium is quite expensive which limits its use to cost insensitive applications. Alternative processes to the Kroll and Hunter processes have been investigated, including plasma techniques, molten chloride salt electrolytic processes, molten fluoride methods, the Goldschmidt process, and alkali metal-calcium techniques. Other processes investigated have included aluminium, magnesium, carbothermic and carbo-nitrothermic reduction of TiO_2 and plasma reduction of TiCl_4 , without measurable success.

Kroll predicted that titanium will be made competitively by fused salt electrolysis but, to date, this has not been realised. In the past 50 years, numerous attempts have been made to

produce titanium sponge continuously and more economically by electrochemical processes. Among major industrial developments, we can cite, the US Bureau of Mines in 1956 [44], Titanium Metal Corporation (TIMET) in the period 1970-1980s [45], Dow-Howmet in the 1980s [46], and RMI and Elettrochimica Marco Ginatta (EMG) in the late 1980s [47]. All these processes were finally aborted either due to engineering issues or for economical reasons.

As an example, high purity electrolytic titanium was produced continuously by the Dow-Howmet process developed by a joint venture of The Dow Chemical Company and Howmet Turbine Components Corporation [46]. It was based on a stable diaphragm type cell using a molten LiCl-KCl eutectic with TiCl_2 added by first reacting a stoichiometric amount of TiCl_4 as a cell feed with an amount of titanium sponge in a feed basket to produce lower valent titanium ionic species. The electrolytic cells operated at 520-600 °C under argon. The cathodes consisted of steel round bar stock, while the graphite rod was used as the anode. TiCl_4 was continuously fed into a pre-reduction cathode compartment where reduction to TiCl_2 occurred. Since titanium is multivalent, it has been shown that TiCl_4 could be reduced to lower valent ionic species of Ti^{3+} , Ti^{2+} , which do show some solubility in some molten salts [48]. However, because of secondary reversibility reactions, which lead to loss in current efficiency and poor quality of metal, no practical process has evolved for electrowinning titanium from a TiCl_4 feed. Investigations of separating the anolyte and catholyte to avoid alternating oxidation and reduction with low current efficiency have not proven successful on a commercial scale.

2.4.4. Molten Salt Electrowinning and Electrefining of Silicon

At the present time, carbothermic reduction of SiO_2 at around 2000 °C is the commercial process to produce metallurgical grade silicon (MG-Si) of 98-99 % purity. Molten salt electrolysis is an alternative to produce high purity silicon. Progress in molten salt electrowinning and electrefining of silicon and the possible applications of electrolytic silicon have been reviewed by a number of authors. Cohen discussed some prospective applications of silicon electro-deposition from molten fluorides to solar cell fabrication [49]. Elwell and Feigelson reviewed experimental data on the electrodeposition of silicon from molten salts and considered the potential of this method for photovoltaic applications [50]. Rao and Elwell briefly considered the prospects for economic electrowinning of silicon for more general applications [51]. General reviews of silicon electrowinning and refining were presented by Elwell and Rao [52], with particular emphasis on molten SiO_2 -and fluorosilicate-based electrolytes. These reviews concluded that the fused salt electrowinning could become the commercial process of producing silicon of significantly higher purity at a cost comparable with that of aluminium. The relative absence of carbon in the electrodeposited silicon should offer advantages for some high-grade metallurgical applications, and the electrowon silicon should be an attractive starting material for solar applications or as a feed material for the production of semiconductor or detector grade silicon. Olson and Carleton patented a molten salt process to upgrade MG-Si to SoG-Si by electrefining [53]. In their process, a semipermeable Cu_3Si -Si composite was prepared from copper of 99.999 % purity and MG-Si particles. The prepared composite was then used as the anode in their electrefining cell using a molten mixture of $\text{KF-LiF-K}_2\text{SiF}_6$ as the electrolyte. The electrefined silicon had greater than 99.999 % purity.

Most of the above studies were conducted in the 1980s. Recently, Pistorius and Fray reported their success in electrolytic production of silicon in molten CaCl_2 at 900 °C by electro-deoxidation of solid SiO_2 [54]. The work opened up a new opportunity to produce high purity silicon at lower costs, with less energy consumptions, and in a more environmentally friendly manner.

2.5. Novel Designs of Cell with Fused Salt Electrolytes

2.5.1. Diaphragm Cells

The anode-cathode distance can be reduced if a porous diaphragm saturated with molten salt were used to separate the liquid metal pools. A development of the diaphragm cell was patented by Alcoa for aluminium refining in which the diaphragm was a porous carbon membrane which was permeable to the molten alkali chloride- AlCl_3 electrolyte, but impervious to the molten metal [55]. As the carbon membrane was electronically conducting, it was also used as the anode feeder electrode. No chlorine evolution was detected as the potential for this reaction is much larger than the anodic dissolution of aluminium.

Schwarz and Wendt used the divided electrorefining cell in which the electrolyte contents of the diaphragm were continuously exchanged by gravity driven flow to improve purity of refined aluminium [56].

2.5.2. Bipolar Cells

As well as materials issues with existing cells, the other major problem with electrolysis cells is the low space-time yield due to the two dimensional nature of the electrode arrangements. The space-time yield can be increased if a bipolar cell, such as that shown in figure 5, is used [3]. With this arrangement, electronically conducting plates are inserted in the electrolyte between an anode and cathode so that during electrolysis, the intermediate plates become bipolar, with alternate anodic and cathodic surfaces down the stack. One of the advantages of this arrangement is that there is only one set of electrode contacts for many plates, thereby, reducing resistance losses. However, of greater significance, is the greater surface area per unit volume and hence output which increases the space-time yield. Overall, a lower energy consumption is possible with a bipolar cell because of the reduced overall resistance per pair of electrodes.

The most advanced industrial scale project involving a bipolar cell is Alcoa's aluminium chloride cell {section 2.41 (3)}, which, again, uses the evolved chlorine to improve circulation in the cell by sweeping the aluminium off the cathode surface and drawing in fresh electrolyte [18]. Coupled with the fact that graphite electrodes are effectively inert in the aluminium chloride based melt, the electrode gap could be reduced to 10 mm, as compared with approximately 50 mm in the case of the conventional HHC. This resulted in an energy consumption of less than 9.5 kWh per kg Al which is about 66 % of the value achieved in modern HHC [12, 29]. Unfortunately, although the bipolar cells operated successfully, problems associated with the preparation of the AlCl_3 feed to the cell have led to the curtailment of the project.

The Alcan process uses MgCl_2 from titanium production operations as cell feed using bipolar cells. Alcan has also developed a bipolar cell to extract magnesium from MgCl_2 which uses the evolved chlorine to improve circulation of the electrolyte [57]. In this case, the

magnesium is lighter than the electrolyte and the electrodes are arranged vertically with a weir system at the top to draw off the metal. Rapid circulation of the electrolyte is achieved by using small inter-electrode spacing and a high current density, which results in a lift rate generated by the large amount of chlorine produced. The cell has been run with gaps as small as 8 mm, compared to 50 mm or more in existing commercial cells, and a current efficiency of 70 %. However, no overall energy consumption is quoted and it may not be significantly more efficient than existing cell designs, as a result of the large amount of gas between the electrodes, leading to a relatively large resistance.

2.5.3. Cells Using Recessed Electrodes

It has been realized that anodic depletion, which causes co-dissolution of impurities in an impure anode and contaminating refined metal, is a major problem in fused salt electrorefining. The problem was overcome by using a flow-through electrochemical cell in which the anolyte was continuously removed, passed through a purification reactor and returned to the cathode side of the cell.

In order to address this problem, Fray patented cells using recessed electrodes which allowed molten metal to flow down the electrodes, separated by a ceramic fibre or blanket [58]. The great advantage of this cell compared to the other designs is that although the current density on the diaphragm can be very high, the current density on each individual droplet of metal, as it meanders down the cell, can be very low due to the large surface area of droplets in the cathode. This will obviously decrease the likelihood of surface depletion but, perhaps, more significantly the motion of the droplets in the bed ensures that the metal is continuously agitated, thereby, increasing mass transfer within the droplet. Furthermore, unlike other designs, the load of metal on the diaphragm will be virtually insignificant as droplets are on the order of a few mms in diameter.

Unlike electrowinning where there are many examples, it is perhaps instructive to consider areas in which fused salt electrorefining could find applications. Recently, Cox and Fray successfully removed 99 % of magnesium and 46 % manganese from beverage cans, an aluminium alloy based on AA5182 and AA3004, using the RCC in a molten $\text{MgCl}_2\text{-NaCl}$ electrolyte at 680-740 °C [59]. They reported that the magnesium formed at the cathode contained on average about 0.5 wt% Al, while the aluminium contained 0.0135-0.033 wt% Mg and 0.6485-1.079 wt% Mn. The electrical power consumption of the cell was only 2.7 kWh per kg Mg transferred, compared to 15 kWh per kg using a three-layer cell. They also indicated that such a cell has many economic and environmental advantages over conventional methods to remove magnesium from scrap alloy, least of which are a minimum of 80 % power savings based on chlorination and the three-layer cell, pollution-free operation, a very useful by-product, and the possibility of producing aluminium master alloys *in situ*.

2.5.4. Use of Rotating Electrodes

It is apparent that a further reduction in cell voltage can only be achieved if the anode-to-cathode distance can be decreased but, with existing technology, this would be at the expense of increased back reaction of the products and a lower current efficiency. Elimination of the back reaction can only be accomplished if the products of electrolysis can be removed more efficiently. One possible way of meeting this objective is to rotate the electrodes in order to apply a modest centrifugal field to encourage the separation of the products of electrolysis

and, thereby, allow the inter-electrode gap to be reduced [3, 60]. A centrifugal field acts on a mixture in the same manner as a gravitational field but the former can be varied by changes in rotational speed or the dimensions of the equipment with the result that a much better separation can be attained. In the particular case of molten salt electrolysis, there are three phases – liquid metal, molten salt and gas. According to centrifugal theory, the gas will flow inwards, whereas the denser fluids will be thrown outwards with the net result of a more rapid and efficient removal of the electrolytic products from the inter-electrode gap, improving the current efficiency at small electrode separations. Another possible advantage of the application of centrifugal fields is that the metallic electronically conducting phase will be ejected beyond the edge of the electrodes reducing the chances of the partial short circuiting the electrodes. This may be particularly important for bipolar electrodes.

3. NOVEL FUSED SALT ELECTROLYSIS

3.1. Molten Salt Electrolysis of Cathode Materials

The majority of electrolysis processes in molten salts produce liquid metals that deposit on an inert cathode. It is rare that a single salt is used as additions of other salts can raise the electrical conductivity and decrease the melting point of the electrolyte. The additions should, usually, have a higher decomposition potential than the salt to be electrolysed. As an example, magnesium chloride decomposes at a potential about 0.8 V lower than the other salts which may include NaCl, KCl, LiCl, CaCl₂ or BaCl₂. In most cases, the salt with the lowest decomposition potential electrolyses first even though the cell voltage may be greater than the decomposition potentials of the other salts. This is because the cell voltage (E_{cell}) is given by Equation 2.

It can be appreciated that the polarisation and iR losses can exceed the difference between the decomposition potential of magnesium chloride and the other salts. Provided there is no concentration polarisation, the salt with the lowest potential for decomposition will always decompose first, followed by the next least stable salt. In the case of electrowinning of sodium from a mixture of NaCl, CaCl₂, and BaCl₂, the decomposition potentials of NaCl and CaCl₂ are very similar so that both elements deposit and the calcium is removed by cooling the mixture.

Ono and Susuki have electrowon calcium from calcium oxide –calcium chloride mixtures and then used the calcium to reduce other metal oxides [61-64].

In the HHC, the deposition potential for sodium is only slightly less cathodic than the deposition potential for aluminium so that sodium always co-deposits at a low activity with the aluminium [1]. If the carbon cathode is exposed, sodium deposits in preference to aluminium as the sodium is able to intercalate into the graphite.

3.1.1. The FFC-Cambridge Process

In 2000, it was reported that it was possible to be able to electrochemically deoxidise a cathode preform made of TiO₂ in a molten CaCl₂ and this started a new era of intense research and development of producing a low cost titanium metal electrolytically from cost affordable oxides [65, 66].

The FFC Cambridge process, patented globally in 1998, is a novel electrolytic method for removing oxygen from a metal (or an alloy) dissolved with oxygen or reducing metal oxide to metal in a molten salt or salt mixture, such as CaCl_2 , that have appreciable solubilities for oxide ion (O^{2-}) [65]. Shown in figure 9 is the schematic representation of the FFC-Cambridge Process. Although originally developed for titanium, there are indications that the process is also able to produce other metals, alloys and intermetallic compounds in the form of powders or bulk materials at a fraction of the current costs [67, 78].

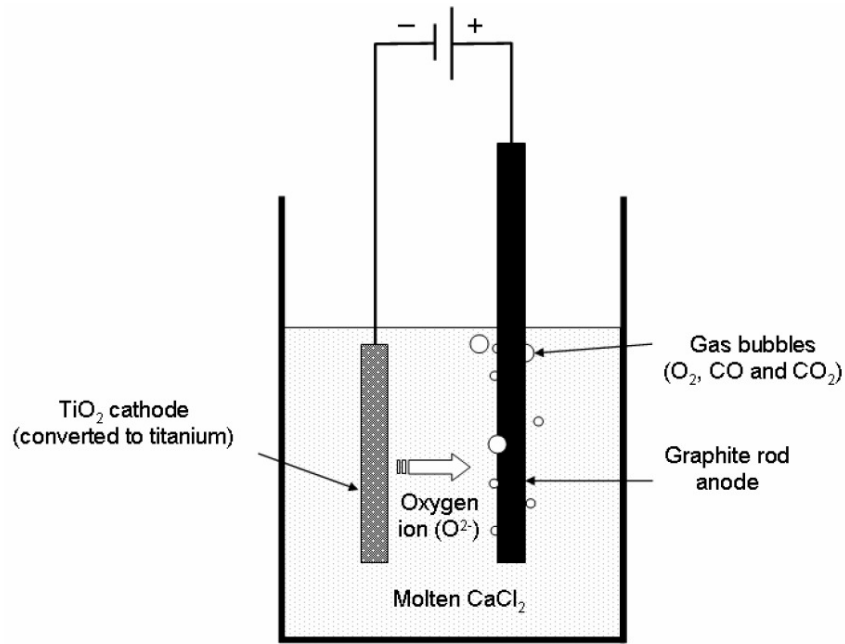
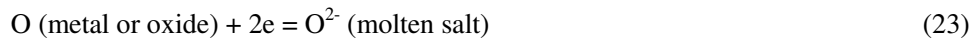


Figure 9. Schematic representation of the FFC-Cambridge Process [65, 66].

The FFC-Cambridge Process is based on the concept of cathodic ionisation. In this process, a metal or alloy dissolved with oxygen and metal or semi-metal oxides is immersed in molten salt bath and is acted as the cathode. On application of cathodic potentials more negative than oxygen ionisation potentials of the oxygen-containing cathode materials but less cathodic than cathodic depositions of cations from the electrolytes, the cathodic reaction is simply:



This novel cathodic process is termed electro-deoxidation [69]. The overall reaction is much more complicated as the metal oxide does not normally go directly to the metal but through a series of suboxides and compounds between the oxide and calcium oxide. The metal is left behind at the cathode. An alloy or intermetallic compound can form when cathode materials are an oxide mixtures or complex metal oxide. At the carbon anode, ionized O^{2-} ions are removed as CO or CO_2 gas:



The FFC-Cambridge Process is much simpler, in principle, in operation and uses less energy than many current industrial technologies, such as the Kroll process, and promises a great potential for cheap production of useful reactive metals such as titanium, niobium, and tantalum. Its other advantage is to produce various metal alloys directly from mixed metal oxide powders, including TiNb, TiNi and niobium aluminides. This will offer more savings in energy and operation cost. It is also scientifically interesting because the electrolysis can be carried out on an insulating oxide, such as alumina and silica where the electro-deoxidation reaction starts at the three phase boundary between the salt, the insulating oxide and the connecting lead. As the conducting reduced phase forms, the reaction is able to occur over the surface of the pellets and gradually penetrates inside the pellet.

Various oxides have been reduced by this technique and these include, amongst others, TiO₂ [66, 70], ZrO₂ [71], Ta₂O₅ [72], Nb₂O₅ [73-76], Cr₂O₃ [77], PuO₂ [78], and UO₂ [79]. It should be noted that the only species that are removed are the anionic species so there is no refining of the cationic species. However, this can be used to advantage as it means that it is possible to produce alloys from mixtures of metal oxides. The oxides need not be in solid solution but simply in intimate contact. These alloys include Nb-Ti and Nb-Sn, Ti-Mo, Ti-Ni, Ti-W, Fe-Ti, Al-Sc, Ce-Ni, zirconium alloys, and niobium aluminides [80-88].

As well as metallic alloys, it is also possible to produce carbides, borides and silicides [89-91]. The overall cathodic reactions are:



It is also possible to prepare coatings of metals, alloys and compounds by electro-deoxidising mixed layers of oxides or oxides and the metalloids on the surface of a substrate [91, 93].

3.1.2. Applications of the FFC-Cambridge Process

Fray has recently published several overview articles on novel molten salt electrochemical processes for sustainable production of metals and materials [93-96]. Apart from many of other metals, alloys, and intermetallics described above, the FFC-Cambridge Process has been applied to produce directly aluminium, magnesium, and silicon from Al₂O₃, MgO, and SiO₂, respectively [54, 97, 98]. CaCl₂-based electrolytes were used as the electrolytes and, thus, it would be much easier to incorporate O₂-evolving inert anodes into the electrolytic cells, potentially making these alternative reduction processes “greener processes” [72, 99].

3.2. Molten Salt Electrolysis of Anode Materials

3.2.1. The Composite Anodes Processes for Aluminium and Magnesium

Withers et al. reported fused salt electrolysis cells for the electrolytic deposition of aluminium or magnesium in which the anode consisting of a composite mixture of Al_2O_3 or MgO and carbon is the sole source of aluminium or magnesium in chloride or mixed chloride and fluoride electrolytes [100-103]. Their experiments with the composite anodes made of Al_2O_3 -carbon have been carried out in electrowinning cells at around 700 °C [102]. The overall reaction in the $\text{Al}_2\text{O}_3/\text{C}$ case is the same as in the HH process:



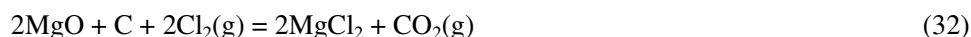
The main advantage of the composite anode is that the Al_2O_3 and carbon are mixed together in their stoichiometric ratio. A high solubility of Al_2O_3 in the electrolyte is not necessary and, perhaps, could be regarded as an advantage as this allows lower melting point electrolytes with higher conductivities to be used. Alumina powder is removed from the pot room giving a cleaner operation and the crust breaking procedure to feed alumina to the cells is eliminated. Furthermore, as there is always a supply of alumina, anode effects are no longer observed in the cell. The composite $\text{Al}_2\text{O}_3/\text{C}$ cell also offers the advantages of the lower electrolysis temperature and less corrosive property of the electrolytes over the HHC for primary Al production. For example, the new process utilising composite anodes also promises Al at 4 kWh/1b and design studies indicate that it can be retrofitted into existing the HH plants. However, these advantages are partially offset by the poor electronic conductivity of the composite anode which can only be overcome by inserting consumable aluminium conductors into the anode.

The incentive for the development of this technology to magnesium extraction is perhaps greater as the preparation of MgCl_2 feed to the cells consumes about 50 % of the cost and energy consumption for the production of magnesium. Withers and Loutfy utilized MgO-C anodes in mixed chloride-fluoride or all fluoride electrolytes and produced electrolytic magnesium at about 700 °C with only CO_2/CO as anode gases. The process has been demonstrated on a laboratory scale with the production of magnesium at less than 4 kWh per 1b. Again, there were problems with the conductivity of the composite anodes which were overcome by inserting rods of magnesium into the anodes [103].

Ratvik studied in more detail composite anodes for the electrolytic production of magnesium and aluminium in molten LiCl containing 10-20 mol% NaF at 700 °C [104]. They found that no anode effect was observed using nominal current densities up to 2 A/cm^2 and current efficiencies of as high as 90 % were achieved. The anodic gaseous products were found to be CO_2 and CO , with no halogens, HF , or HCl were detected. Balaraju et al. carried out detailed investigations into liquidus behaviour, Al_2O_3 solubility, electrical conductivity and decomposition potential of Al_2O_3 dissolved in various compositions of KCl-NaF melts to determine suitable electrolytes for electrolytic production of aluminium using $\text{Al}_2\text{O}_3/\text{C}$ composite anodes [105]. They concluded that the KCl-NaF system is a more suitable electrolyte than the LiCl-NaF system because of the higher cost of LiCl than KCl and operating problems associated with its hygroscopicity. However, both studies revealed that sludge formation and contamination of the electrolyte by fine carbon particles, causing

electronic conductivity are main problems with the composite anode reduction technology for production of aluminium and magnesium.

It may be possible to electrowin magnesium in a cell where MgO is actually reacted with carbon and chlorine in the anode section of the cell to form MgCl₂ [106]. The evolved chlorine from the anode reacts exothermically with MgO and carbon to give MgCl₂:



The U.S. Bureau of Mines reported on electrowinning magnesium into liquid lead and aluminium cathodes from melts containing a slurry of MgO and carbon particles [107]. They demonstrated that 98-99% of the chlorine reacted giving a gaseous product of 80-90 % CO₂, 8-15 % CO and a few percent chlorine. Cathode efficiencies were around 90 % but a major difficulty was found to be a build up of sludge consisting of MgO and Carbon, on top of the liquid metal cathode.

3.2.2. *The Composite Anode Process for Titanium*

More recently, in 2005, Withers and Loutfy patented thermal and electrochemical process for titanium metal production using partially reduced Ti_xO_y/C composite anodes, based on the same reduction technology for aluminium and magnesium as described above [108]. The process for producing titanium metal is recently called “MER process”, which is shown schematically in figure 10 [109]. It utilizes TiO₂ as a feed and essentially involves two steps: (i) carbothermic reduction of TiO₂ to suboxides of titanium which is used in a composite anode with stoichiometric carbon and (ii) anodic dissolution of titanium from the titanium suboxides/C composite anodes into a molten salt electrolyte to electrolytically produce titanium metal at 190-1000 °C, with anode gases of CO/CO₂. The electrolysis process can be performed on a continuous basis without opening the cell body. TiO₂ powders are mixed with carbonaceous material and binder, moulded into electrode form and thermally treated to form a composite anode at 1200-2100 °C. The composite anode contains a partially reduced TiO₂ compound as Ti_xO_y/C. Anodically ionised Ti³⁺ or Ti²⁺ ions are dissolved into the electrolyte and are cathodically deposited as solid titanium metal at the cathode. A gaseous mixture of CO and CO₂ is released at the anode. The deposited titanium metal can be in the form of powder, flake or a solid deposit, depending on electrolyte compositions and electrolysis operating conditions. While impurities are reported to be low, analytical confirmation is necessary. Processing cost as well as consistent production of any particular product form remains to be determined. Deposition of solid deposits with density, uniformity and configuration suitable for mill processing needs to be confirmed. The bench scale product has been produced with oxygen levels below 500 mass ppm. More recently, Maity et al. reported their studies on electro-deposition of titanium using TiO₂/C composite anode and molten aluminium cathode in an equimolar NaCl-KCl electrolyte at 800 °C [110]. The Faradic current efficiency of their process was 10-30 %.

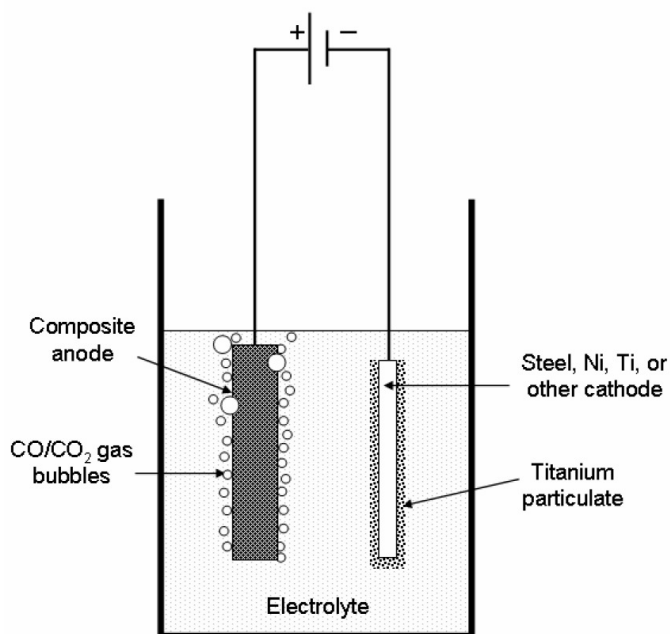


Figure 10. Schematic diagram of the MER process for titanium production [108].

Jiao and Zhu reported novel electrometallurgical process for titanium production by electrolysis of Ti_2CO solid solution anode in a NaCl-KCl melt at $800\text{ }^\circ\text{C}$ [111, 112]. In their process, titanium from the Ti_2CO anode dissolved into the melt as Ti^{2+} by potentiostatic electrolysis and the dissolved Ti^{2+} transported to the steel bar cathode where it cathodically deposited to produce highly pure titanium metal with less than 300 ppm oxygen, with a gas of CO being released from the anode. They found that the entire process resembles electrorefining since the cell voltages needed for the reduction to proceed were only 0.8 V, implying low energy consumptions of this electrolytic process. With this Ti_2CO anode material, problems associated with generation of residual carbon powder on the top of the electrolyte melt, as encountered with TiO_2/C composite anodes, could be resolved.

3.3. Molten Salt Electrolysis for Advanced Materials

3.3.1. Niobium-Based Superconductors

Niobium based superconductors, such as niobium titanium and niobium tin, are difficult to make due to the large difference in density and melting points of the constituent elements. Mixing the metallic powders together to form the intermetallics is also expensive. One way around this problem is to reduce the mixed oxides using the FFC-Cambridge Process. The oxides are sintered together and then made the cathode in a bath of a CaCl_2 containing melt. On the application of a cathodic potential, the oxides reduce and the individual elements alloy together to produce the superconductors [80, 113]. It should be noted that the oxide powders are significantly cheaper than the individual metals indicating that this might be a viable method to produce these interesting materials.

3.3.2. Nanostructured Materials and Carbon Nanotubes

During electro-deoxidation of metal oxides in calcium chloride using a carbon anode, it was noticed that a carbon sludge built up on the cathode. This was due to the carbon dioxide, evolving at the anode, either dissolving in the salt or reacting with the oxygen ions to form the carbonate ion. If the carbonate ion or dissolved carbon dioxide contacts the cathode the following reactions can occur:



or



The carbon product is in the form of carbon nanotubes and carbon nanoparticles [114].

Carbon nanoparticles can also be produced by a completely different route using graphite. If a graphite electrode is made the cathode in a bath of sodium or lithium chloride, the alkali atoms intercalate into the graphite and force nanotubes out from the surface of the graphite. It appears that this method produces far more carbon nanotubes than the decomposition of carbon dioxide or the carbonate ion. Although Faraday's laws will allow the amount of alkali deposited at the cathode, it is difficult to calculate the amount of stress caused by these intercalated atoms to form the nanotubes. The results show that about 80 % of the graphite ends up as nanotubes and, given that graphite is relatively cheap, this may be an inexpensive method of producing multiwalled carbon nanotubes [115]. Another interesting observation, is that if liquid metallic particles, such as tin, are deposited on the surface of the graphite, the carbon nanotubes are filled with tin. This product may find application as the anode in the lithium ion battery as tin can hold considerably more lithium than the graphite intercalation compound that is used at present. Preliminary results are very positive.

During electro-deoxidation of oxides, the final product size is, to a certain extent, dictated by the temperature of electro-deoxidation so that by working at lower temperatures, the reduced metal can be in the form of nanoparticles. TiC nanoparticles have been prepared by electro-deoxidation of the TiO₂/C pellets in molten CaCl₂-NaCl eutectic at 850 °C [91].

3.4. Molten Salt Electrolysis for Processing Wastes

Compared with pyrometallurgical methods, the products of fused salt electrorefining are frequently pure metals which are produced in a non-polluting manner. Pyrometallurgical processes frequently use toxic gases, such as chlorine, the processes are noisy, and although, a pure metal might be produced, the other products are usually drosses and slags which have a low or negative commercial value.

The very high energy input is necessary to produce primary aluminium. Industry will still require high grade aluminium for its products, a greater production of aluminium will have to be imported into certain countries and this aluminium will need to be recycled.

3.4.1. Electrolytic Removal of Magnesium from Scrap Aluminium

Tiwari and Sharma examined an experimental process designed to electrolytically remove magnesium from scrap charges in secondary aluminium industry using the three-layer cell configuration consisting of scrap Al-Mg as the anode on a bottom layer, 10 wt%MgCl₂-45 wt%CaCl₂-30 wt%NaCl-15 wt%KCl electrolyte as the middle layer, and deposited liquid magnesium on the top layer [14]. The graphite disk was used as the cathode for depositing the liquid magnesium. The refined aluminium contained 90 ppm Mg after the fused salt electrolysis at the current density of 0.1 A/cm² with the cell voltage of 0.8 V. Another example is the use of the packed bed cell to remove magnesium from aluminium to produce magnesium metal, as studied by Cleland and Fray [117]. Their laboratory results show that electrochemical separation gives the same aluminium product as chlorination but, at the same time, produces magnesium of commercial value. The process is also free from pollution. The second application is to upgrade low grade secondary aluminium to pure aluminium. Overall, electrorefining would give the necessary smelter access to the wrought aluminium market.

3.4.2. Processing of Dross

Yan recently studied a novel molten salt process, where Al as metal or contained in Al₂O₃ and AlN was recovered from Al from Al₂O₃ and AlN present in Al dross by electrolysis in molten salts [118]. Electrolysis experiments were carried out under argon at temperatures from 850-970 °C. In order to better understand the reduction behaviour, the as-received Al dross was simulated using simplified systems including pure Al₂O₃, pure AlN, an Al₂O₃/AlN binary mixture, and an Al₂O₃/AlN/Al ternary mixture. The reduction of the as-received dross was also studied experimentally. It was concluded that the value of aluminium was readily recovered from the Al₂O₃ present in the drosses during the electrolytic reduction processes. However, it was difficult to directly recover the aluminium from AlN in the dross. It was suggested to apply the AlN-to-Al₂O₃ conversion techniques to recover indirectly the aluminium value from the AlN. The reduction mechanisms are discussed based upon the present experimental observations. Flow sheets for recovering the metallic aluminium and the aluminium in the Al₂O₃ and AlN from aluminium dross are finally proposed.

3.4.3. Electrometallurgical Treatment of Spent Nuclear Fuels

Fresh metal oxide fuel rods for the generation of electricity from nuclear energy contain uranium dioxide. After use the uranium oxides have transmuted into a large number of other oxides and these need to be separated in order to reprocess the uranium. Oxides are very difficult to refine so that the oxides are usually reduced to the metals using calcium or lithium, with the calcium or lithium oxide dissolving in their respective chlorides which also need to be treated.

Electrometallurgical treatment of spent nuclear fuels using molten salts has been studied in several countries. These fuels exhibit a wide variety in their physical conditions, chemical stability, burnup, and environment, complicating their long-term storage and disposal. Such a molten salt process was initially developed by Argonne National Laboratory (ANL) suitable for conditioning U.S. Department of Energy (DOE) oxide spent fuel for long-term storage or disposal [119-122]. The ANL's process consists of an initial reduction of oxide compounds of the actinides to a metallic form. The actinide oxides are reduced using lithium dissolved in molten LiCl at 650 °C, yielding the corresponding metals and Li₂O. The metallic product from the reduction step becomes the feed material for the second stage of the process, known

as fused salt electrorefining. In the electrorefining step, the principal components of the fuel (uranium, cladding, and fission products) are electrochemically separated to become three products: pure uranium for storage and two stable high-level waste forms (one metal and the other ceramics) suitable for long-term disposal. Similar molten salt processes were reported by the Research Institute of Atomic Reactors in Russia and the Korea Atomic Energy Research Institute to process Irradiated mixed oxide fuels and to store PWR spent fuels, respectively [123, 124].

A more attractive route would be to use the FFC-Cambridge Process to reduce oxides to the metals [81]. The advantages of this process are that oxide ions do not accumulate in the melt allowing more of the actinide oxides to be reduced and allowing the salt to be used for far longer before disposal.

4. FUSED SALT ELECTROLYSIS COMBINED WITH OTHER PROCESSES

4.1. Electrolysis Combined with Chlorination Processes

It has been around 35 years since a major new technology for producing aluminium was installed: the Alcoa smelting process (bipolar electrolytic process). There can be no denying that the Alcoa smelting process was an engineering achievement with its bipolar electrode array, fluoride-free electrolyte and negligible carbon consumption rate. Yet the plant proved to be an economic failure and was ultimately closed, even though the electrolysis step was 30 % more efficient than the HHC.

4.2. Carbothermic Reduction Followed by Fused Salt Electrorefining

For the production of magnesium, there are basically two methods. Firstly, in the metallothermic processes, MgO is reacted with a reducing agent in an electric furnace under vacuum and, secondly, there are the electrolytic processes, described earlier in this article. The principal drawbacks of the bath thermic operation are the need to operate at greatly reduced pressure, a solid rather than a molten product is obtained, the purity of the product is low and the condensers are relatively inefficient. The main drawback of the electrolytic process is the high cost of feed preparation, which was mentioned earlier. There have been several attempts to use carbothermic reduction but in order to get the reaction:



to proceed, the temperature has to be around 2030 °C. However, on cooling the above reaction reverses producing MgO and carbon. Anderson and Parlee have suggested to conduct the reaction in a molten solvent, to reduce the activity of the reduced magnesium, driving the reaction to the right, and then removing the magnesium by distillation [125, 126]. As the overall reaction is endothermic, there is unlikely to be an excess of heat available, and this would appear to make distillation an expensive process. All the solvent metals suggested, tin,

bismuth, antimony or mixtures of these metals, are electrochemically more noble than magnesium indicating that fused salt electrorefining might be a suitable route for separation. In this case, the solvent metal, containing magnesium, is transferred to the electrorefining cell, where the magnesium is transferred to the cathode. It should be emphasised that the reduced activity of magnesium only has a small effect on the cell potential as the potential is related to logarithmically to the activity, as is shown in equation. The combination of carbothermic reduction in a metallic solvent followed by electrorefining could be applied to other metals such as aluminium.

The carbothermic reduction is also commercially used to produce silicon metal of 98-99 % purity (metallurgical grade silicon: MG-Si) from SiO_2 in an electric arc furnace at very high temperatures. The MG-Si metal produced must be purified to satisfy its high technology applications such as solar cells. Olson and Carleton reported their success in upgrading MG-Si to solar grade silicon (SoG-Si) by molten salt electrorefining [53, 127].

4.3. Electrolysis Combined with Calciothermic Reduction

Calciothermic reduction of TiO_2 in molten Ca- CaCl_2 has been investigated by Ono and Suzuki (the OS process) for producing titanium powders [61-63]. A schematic diagram of the electrolytic cell for the OS process is shown in figure 11. In the OS process, TiO_2 powder feed is charged into a molten bath of Ca- CaCl_2 melts, which subsequently reduced by calcium metal in a Ca- CaCl_2 melt according to the following reactions:



where Ca is the calcium metal dissolved in the melt or the calcium droplets present in the melt and is the reductant of Reaction 36, and (CaO) is the CaO dissolved in the melt and is a by-product from Reaction 36. Under the conditions used in the OS process, the dissolved CaO is electrochemically decomposed *in-situ* in the electrolyte to form CO/ CO_2 gases at the carbon and metallic calcium at the cathode, with an overall cell reaction being expressed as follows:



The reduced calcium metal dissolves immediately into the CaCl_2 melt and is used as the calcium reductant again for the reduction of TiO_2 . The OS process demonstrated the effectiveness of calcium metal dissolved in molten CaCl_2 in the reduction process. Although the Ca- CaCl_2 reaction medium is a powerful reductant, technical improvements have to be established before the process is scaled up for large-scale operations. This is because it is difficult to control the purity and quality of the reduced titanium metal.

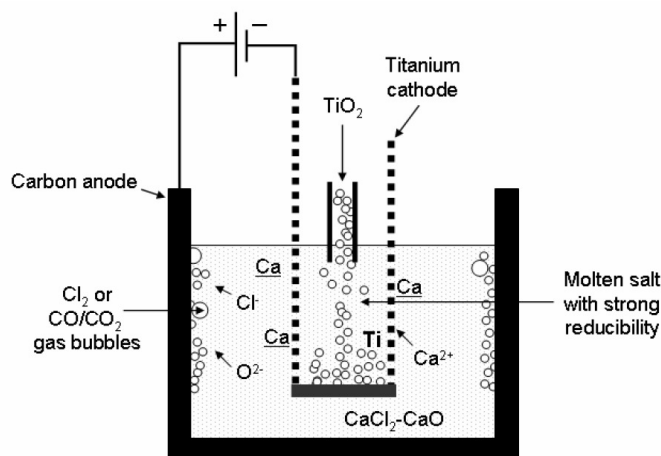


Figure 11. Schematic of the OS Process for titanium powder production [63].

5. PERSPECTIVES FOR MOLTEN SALT ELECTROLYSIS TECHNOLOGIES

5.1. Electrowinning and Electrorefining

5.1.1. Discussion of Electrowinning

Fused salt electrowinning cells have undergone considerable evolution since the cells of 100 years ago with the overall energy consumption falling to about $1/3^{\text{rd}}$. However, with existing materials, further improvements are only likely to be incremental in nature. The HHC, in particular, is in need of improved materials for refractories which are inert to cryolite, inert anode materials, and wetted cathode materials. Some progress has been made in this direction but none of the materials which have been developed are entirely satisfactory. Fortunately, there is considerable effort in materials technology and it is likely that novel and improved materials will be developed at an even increasing rate. However, even where inert materials are available, for example, in magnesium and lithium electrowinning, the energy efficiency is still quite low with large anode-to-cathode spacing.

The other major disadvantage of fused salt electrowinning cells is the two-dimensional nature of the electrodes which is partially overcome by the bipolar arrangement of electrodes but, even so, the output compared to the equivalent volume of a pyrometallurgical reactor is poor.

Much effort has been devoted to utilising the gas evolved at the anode to pump the electrolyte around the cell and, generally, to raise the mass transfer within the cells. However, more is needed in order to be able to reduce the inter-electrode spacing further and it may be necessary to apply other forces, besides gravity, to separate the products of electrolysis. Centrifugal forces are a possibility in that the magnitude of the force can be varied. It has been shown that with simple conical electrodes, the application of a modest centrifugal field permits a considerable reduction in the inter-electrode spacing whilst, at the same time, maintaining a high current efficiency. Some of the work was done using a size of electrodes which might find industrial application in the near future. With careful design, it may be also

be possible to apply the concept to more complicated electrode arrangements, thereby, approaching the output of pyrometallurgical reactors.

5.1.2. Discussion of Electrorefining

Although fused salt electrorefining is considerably less energy intensive than electrowinning, the only commercial application is in purifying aluminium from the HH cells and this is very energy inefficient. The limited application of fused salt electrorefining is due almost entirely to the present design of the cells which do not take advantage of the high electrical conductivity of fused salts and the very low thermodynamic potential required for electrorefining. Designs of cell have been suggested and evaluated on a laboratory scale which indicate that voltages as low as 0.2 V can be achieved at acceptable current densities. It appears that with an energy efficient cell, the possibilities for fused salt electrorefining are quite extensive, ranging from treatment of scrap, combination with carbothermic reduction and, lastly, in combination with electrowinning. It is perhaps in combination with carbothermic reduction that the greatest possibilities exist as carbothermic reduction, although energy efficient and rapid, generally gives a product which is impure and needs further treatment. Efficient fused salt electrorefining should give a very pure product at relatively low energy consumption. In addition, unlike purification using air or chlorine, all the metals remain in the metallic state and, therefore, retain their commercial value rather than appearing as a residue.

The electrolytic extraction processes of aluminium and magnesium must be improved to yield abundant quantities of metal at process competitive with ferrous alloys. There is also a growing need for refractory metals both as the primary constituents of structural components and as surface coatings on less expensive base-metal components. The potential of molten salt electrolysis to process the refractory metals remains largely untapped. Clearly, a broad new research initiative in fused salt electrometallurgy is in order.

Overall, environmental concerns will prompt a shift from thermochemical approaches to electrochemical approaches. We see evidence of this with the announced new magnesium smelters where ore bodies that historically were processed by metallothermic reduction are now being electrolysed. If we couple this trend to carbon-free generation of electricity, the results will be “greener” metallurgy. The second point is that the transitional technologies will play an uncertain role. This is largely due to the fact that the metals industry is very conservative due to the very high capital costs associated with technology. Whether we consider incremental changes in current technology or radical innovation, the future looks bright for molten salts.

Research specific to fused salt electrometallurgy: The HHC used to produce aluminium and fused salt cells for magnesium, titanium, etc., have problems not shared by other electrometallurgical operations. These problems provide worthwhile research opportunities, e.g.:

- Re-oxidation of metal product is a phenomenon that reduces productivity and wastes energy; the phenomenon is presently poorly understood.
- Transport phenomenon in aluminium cells, require further study.
- New materials are required to withstand the hostile high temperature, corrosive environment, e.g., materials for cathodes, anodes, containment, sensors and diaphragms.

5.1.3. Discussion of Electrowinning Combined with Electrorefining

It is concluded that by using recessed electrodes, separated by a diaphragm, the possibility of electrorefining with very low energy consumption can be achieved. Carbothermically produced metals are always cheaper than those produced by electrolysis but suffer from the disadvantage of low purity. It is proposed that fused salt electrorefining may offer an energy efficient way of upgrading the metal.

Fused salt electrowinning and electrorefining face different challenges in the next decade. Fused salt electrowinning is essentially a mature industry and, generally, one can only see incremental improvements in performance, without dramatic changes in cell design. These changes would be brought about by new materials for cell construction, anodes and cathodes, but it is difficult to foresee how the cells can be made competitive with pyrometallurgical reactors without a dramatic change in cell design and a substantial decrease in anode to cathode spacing. To a certain extent this can be achieved by modelling and careful control of the gas, evolved at the anode, to maximise mass transfer without increasing the recombination of the anodic and cathodic products. For a more striking change, one may need to consider other means to remove the products. It is suggested that centrifugal forces may find application in fused salt electrowinning. Using a modest centrifugal field, substantial decreases in the anode-to-cathode spacing have been achieved without any loss of current efficiency.

One interesting concept is to carbochlorinate in the anodic part of the cell, thereby, eliminating the high cost of chlorinating oxides, external to the cell. This would also have the effect of reducing the cell potential, but, perhaps, at the cost of a decrease in the purity of the cathodic product. In these cases, it may be necessary to combine electrowinning with electrorefining.

The development of electrorefining has been very much hindered by the lack of suitable cell designs to give energy efficient processing. Indications of possible design changes are given which make fused salt electrorefining more attractive. This opens up the opportunity for fused salt electrorefining to be applied to the treatment of scrap, combined with carbothermic reducing to give a high grade product and, lastly, combined with electrowinning.

Other areas may be as follows:

- Novel reactions and electrolytes.
- Innovative cells.

A properly balanced research effort from universities, government, and industry with sufficient resource base and directed toward gaining a better understanding and insight into the fundamentals involved in these processes is a very real need. The timing is right for the development of such a program and every possible effort should be made for its initiation.

5.2. The Challenges and Opportunities for Metals Extraction

For primary aluminium production, it seems reasonable to concentrate sustainable research and development efforts on the existing HH process and modification thereof because many improvements can still be made to cell design, electrode and cell lining

materials, and cell operations. Overall goals to be attained remain to be (i) lower energy consumption, (ii) lower production cost, and (iii) less emissions of greenhouse gases.

Overall, the major problems with the cell design and materials are as follows:

- Large heat losses in order to maintain a solidified layer of electrolyte to prevent failure of carbon lining.
- Deep unstable liquid aluminium pool.
- Relatively large anode to cathode distance.
- Consumable anodes.

Without a dramatic improvement in materials technology, it is difficult to envisage how these problems can be overcome. However, some success has been achieved in developing inert anode materials and cathode materials. Ideally, inert anode materials should have the following properties:

- Low reactivity with oxygen, fluorine and the electrolyte.
- Adequate mechanical strength and resistance to thermal shock.
- High electronic conductivity.
- Ability to be fabricated into large shapes.
- Relatively low cost.

These criteria are very demanding. Inert anodes would overcome the problem of each of the carbon anodes in a HHC being in a different state of consumption at any one time and, therefore, to ensure even distribution of the current, the anode to cathode distance are varied for each anode. Inert anodes would obviously result in much greater control over the inter-electrode spacing. Similar properties are demanded by inert cathode materials in conjunction with the proviso that the material be wetted by molten aluminium in order to eliminate the molten pool of aluminium from the cell. The most suitable materials are the borides and carbides of titanium and zirconium. The development of these materials is probably more advanced than that of the inert anode materials. An inert cathode would remove the necessity for a metal pool and allow a much smaller anode-to-cathode distance. Table 2 shows a comparison of the cell voltages in experimental industrial cells and the projected figures for inert electrodes and a reduced inter-electrode gap.

Table 2. Cell voltages for various cell designs [32].

Cell	Standard HH cell	Inert anode	Inert anode and wetted cathode
Inter-electrode gap / cm	4.45	4.45	1.90
Voltage / V	4.64	5.19	4.18

The increase in voltage for the inert anode is due to the fact that the fuel cell reaction of the carbon with oxygen does not take place and, therefore, the voltage of the cell increases. If both inert anode and a wetted cathode are used, there is an overall voltage savings in a reduction in electrical energy consumption of approximately 1.5 kWh per kg Al, down to 11.7kWh per kg for the most efficient industrial cells. However, with a theoretical minimum of 6.2 kWh per kg Al, this still leaves considerable possibilities for improvement.

All processes that involve the electro-reduction of oxides in molten salts could benefit from inert oxides as all existing processes emit carbon dioxide. An inert anode would allow the overall reaction to be:



totally eliminating the production of carbon dioxide, provided the electricity comes from a renewable source. The aluminium industry has led the research for an inert anode and has explored many oxides, including tin oxide, and has concluded that cermets, consisting of mixtures of metals and ferrites may be suitable.

In the FFC-Cambridge Process, there is an additional complication in using carbon anodes and that is carbon transfer from the anode to the cathode. Alternative anodes have been sought for this process. Tin oxide was shown to be unsuitable as an insulating layer of calcium stannate formed on the anode. By far the most promising was calcium titanate which is stable in the melt and, in order to increase its electronic conductivity, it was sintered with a small amount of calcium ruthenate to form a semi-conducting solid solution [128].

What are the challenges and opportunities for the future? One important area is new electrode materials enabling the use of inert anodes and drained cathodes. At the moment slightly less than ½ kg carbon per kg of Al produced is consumed. Eliminating carbon from the HH cells is by far the change that would have the greatest environmental impact. Installing cathodes made of a material that is wetted by molten aluminium and positioning such cathodes above the floor of the cell would eliminate the need to maintain a deep pool of liquid metal on the bottom of the cell. The materials showing the most promise is titanium diboride (TiB₂) which has graduated from laboratory testing to installation in industrial cells for long-term performance assessment. Novel refractories as a replacement for Si₃N₄-bonded SiC need to be developed for use as the HHC sidewall materials on which a frozen layer termed “side ledge” may be no longer required. With such a ledge-free sidewall, the heat within the HHC is kept rather than removed. This leads to a potentially 30 % saving in energy that would otherwise be lost through the sidewalls when operating the HHC with a side ledge. Furthermore, the cell capacity and productivity may be most increased with a ledge-free sidewall cell configuration. New electrolyte chemistry is also interest. In particular, there has been growing interest in so-called low-ratio baths, i.e., baths containing much greater amounts of AlF₃ (about 40 wt% in excess of cryolite stoichiometry) than is currently the practice (about 10 wt% in excess of cryolite stoichiometry). At such high levels of AlF₃ the liquidus temperature drops below 700 °C, almost 300 °C below the operating temperature of contemporary cells. The hope is that operation at lower temperatures will reduce the wear on cell components and perhaps even allow the sustained performance of inert anodes that have been found to be unworkable at 960 °C. Indeed, it may well be that if low-ratio bath is to be used at all, the cell will need to be free of carbon anodes. However, recent work by one of the authors suggests that at 800 °C electrolysis of low-ratio bath (B.R. = 0.56) on carbon anodes generates perfluorocarbons at normal operating voltages.

There is certainly a need for new electrode materials in the Dow cell where carbon consumption rates are very high; hence, an inert anode would constitute an improvement. There is also a need for a new process for preparing anhydrous MgCl₂ in a manner that is energy efficient and gives a product of high purity. As mentioned above, the development of O₂-evolving inert anodes for the FFC-Cambridge Process appears to be very significant for

improvements of electrolysis efficiency and product purities, as well as elimination of CO/CO₂ emissions.

5.3. The Challenges and Opportunities for Materials Processing

Much of this review has concentrated on using the molten salt electrolysis to extract metals from their oxides but, perhaps, the most exciting prospects lie in the field of high technology.

There are many thousand references to extraordinary properties of carbon nanotubes which describe the mechanical, thermal and electronic properties of these materials. With respect to the mechanical properties, there are very substantial businesses that could benefit from these materials such as reinforce polymers. However, at the present time (2009), the world production of carbon nanotubes was only a few hundred tonnes which is insufficient to meet any bulk demand. Carbon nanotubes are usually made a catalytic route whereby a hydrocarbon is cracked, in the presence of a catalyst, to form nanotubes. The rate of reaction is relatively slow and yield of carbon nanotubes from the hydrocarbon is low. On the other hand, the molten salt route, described earlier, is fast and highly efficient in that about 80 % of the starting graphite ends up as multiwalled carbon nanotubes. The price of multiwalled carbon nanotubes, produced catalytically, seems to vary from \$1000 to \$12000 per kg. The cost of graphite is around 1\$ per kg and the electrical energy for the production of the carbon nanotubes is \$1 per kg so that the cost of producing carbon nanotubes by the electrochemical route must be far less, perhaps by two orders of magnitude. Adoption of the molten salt route may lead to a wider usage of carbon nanotubes in materials.

The other opportunity offered by this route is to produce carbon nanotubes filled with metals. It is believed that carbon nanotubes filled with iron, cobalt or nickel could be used for data storage. However, these are not readily made by a molten salt route whereas tin and aluminium filled tubes are possible. These could find application as anode materials in lithium ion batteries where the capacities of the metals to combine with lithium are much greater than with the conventional graphite anodes. Preliminary results show that for tin filled anodes have a much larger capacity than the conventional anodes and this capacity is maintained over hundreds of charge-discharge cycles.

As well as bulk carbides and silicides, it is also possible to make nanosized particles and, in the case of tungsten carbide, these could find application as catalysts and in hard metals which are used as tool bits. The effectiveness of the tool bit is inversely proportional to the size of the carbide particles.

Overall, as well as improving existing processes, there are excellent possibilities for making a major contribution in the preparation of materials for high technology products.

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