CHAPTER 11.2

Molten Salt Electrolysis

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BACKGROUND

Electrochemistry Basics

Electrochemistry is a branch of chemistry that deals with the chemical changes accompanying the passage of an electric current. Perhaps the simplest definition may be to bring about a chemical reaction by using the potential energy gradient (electrode voltages), with the amount of reaction being dependent on the amount of electric charge transferred (current multiplied by time) to sustain that reaction.

Electrochemistry studies chemical reactions that take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and involve electron transfer between the electrodes and the electrolyte or species in solution. Electrochemical processes necessitate energy addition, when the introducing energy is not able to provide sufficient energy for the reaction to occur. Energy can be added electrochemically, provided the media used (electrolyte) is more stable. The overall process is split into two parts: one half reaction at anode potential and the other half reaction at cathode potential.

For some metallic elements, electrolysis is the only practical way of extracting the metal. This is done by enabling heterogeneous chemical reactions to occur that are energetically unfavorable. Consequently, energy has to be transferred into the materials, and simultaneously, recombination of the products must be prevented. Energy can only be transferred as *heat* (through a temperature gradient) or by doing *work* (mechanically or electrically).

Electrolytic Cells

Electrolytic cells are the focus of this chapter. Electrolytic cells do not have a favorable energy gradient to naturally proceed, and they require a voltage gradient to be imposed to enable it, plus they must have a favorable electrochemical reaction mechanism.

Based on this concept and in order to build an electrochemical cell, the following components need to be incorporated in the process:

- A reactor
- Electrodes—anode and cathode
- An electrolyte
- A completed electric circuit
- A process for melting and dissolution of the raw material
- Separation systems for the products in the reactor
- The impact of design and operations

The Reactor

For the context of this chapter, the reactor is a medium-to-high-temperature furnace that has a refractory lining. For the reactor a container is needed for the molten electrolyte and the liquid metal that is produced. Thus, the electrolyte and the metal are contained in a preformed carbon lining, which also has refractory and thermally insulating materials inside a steel shell. The container must be electronically conducting to enable electric energy to be brought to the reacting interfaces. The container should not be corroded by the metal or the electrolyte. The requirements for a cell lining material are that it lasts a long time and minimizes any metal contamination. Carbon comes closest to meet these requirements. Many types of cells use a carbonaceous-based lining for containing the metal and introducing the cathodic potential.

Preventing failure and obtaining a reasonable lifetime of the cathode lining are extremely important—some cells only last for several months before they begin operating inefficiently and consequently produce an unacceptable quality of metal. In the most serious case, they can also disintegrate and leak electrolyte and metal from the cell.

For aluminum electrolysis cells, the challenge is building a leak-proof container that holds the liquid metal and electrolyte with a large, flat, horizontal area and has a reasonable lifetime. The materials used are prebaked carbon cathode blocks, silicon carbide (SiC) sidewall bricks, and carbonaceous ramming paste. The containing carbonaceous lining material has embedded steel rods that are electronically conductive to introduce the current and thereby enable the energy to be brought to the reacting interface. The cathode blocks and sidewall materials are shaped and baked by manufacturers, while the ramming paste is formed directly in the cathode by ramming and is baked when the cathode is preheated and the cell is put into its early operation. For magnetic reasons, the

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container should not conduct current through the sidewalls. Frozen electrolyte (ledge) is used to seal and protect the sidewalls and conserve heat.

Electrodes—Anode and Cathode

Electrolysis involves at least three material phases—one must be a connecting ionic conductor (electrolyte), and the two others must be physically separated electronically conducting interfaces (electrodes). The electrodes can be inert and thereby do not contaminate the metal produced. The electronic conducting electrodes can also participate in the respective oxidation or reduction reaction (as the carbon anode does in aluminum electrolysis), or they can be passive (as is the aluminum metal pad cathode).

Aluminum production utilizes a consumable carbon anode that is horizontally orientated, and the carbon surface must be continuously replenished by gradually lowering the anodes. Anode change can cause a large operating disturbance, and it is a challenge to perform the anode replacement or replenishment without disturbing the continuous cell operation. The requirement for carbon anode design is that it will enable continuous electrolysis and minimize the disturbance that the anode replenishment introduces.

With consumable carbon anodes, the dominant electrochemical reaction is to form carbon dioxide by utilizing the oxide ions of the dissolved alumina. In industrial cells, these anodes have to be changed typically after about 25 days.

The Electrolyte

A solvent electrolyte (ionic) is used to dissolve the consumable (i.e., a metal oxide) adequately. This solvent must be electrochemically more stable than the metal oxide solute. The electrolyte can be a reactant or simply a solvent for the reactant.

Maintaining a density difference between the electrolyte and the metal is necessary to keep the two liquids apart. Direct common contact of the metal with the anode gas must be avoided. Different components of the electrolyte (such as those that are added to modify the melting point) could cause the density of the electrolyte to increase or decrease and thereby exceed or become less than that of the metal.

The main functions of the electrolyte are

- To pass electricity from the anode to the cathode;
- To be a solvent for the raw material to enable its electrolytic decomposition, forming metal at the cathode and a gas at the anode;
- To provide a physical separation between the cathodically produced metal and the anodically evolved gas to prevent back-reaction between them; and
- To act as a heat-generating resistor that allows the cell to be self-heating.

Optimizing cell performance and operations are important because all reactions have optimum conditions. To maintain the electrolyte at the optimum temperature and composition a control system and philosophy are needed to ensure that the electrolyte temperature and composition are within the control band.

Completed Electric Circuit

An electrolysis cell requires an adjustable power supply connecting the two electronic conductors. An electric energy supply is needed to enable an energy gradient to be established and then cause the electrochemical reactions. The direct current (DC) energy supply is at high voltage, because there is often a large number of industrial electrolysis cells (several hundred) connected in series. Electrochemical reactions are slow, so both high electric current and large electrode areas are needed.

Electrolysis is a continuous process, and a cell cannot be stopped and restarted easily. The requirement is a good and stable electricity supply. If the production is interrupted by a power outage for more than a few hours, the molten electrolyte in the cells will start to solidify. This results in a significantly higher electrical resistance and higher power line voltage, which then makes restarting cells almost impossible when the electrical power is restored. In aluminum electrolysis, the consumable carbon anodes lower the energy required and "complete the circuit."

Melting Process

With molten salt electrolysis there is a need for an energy control system to ensure that both reactions and temperature are maintained. Within material supply or removal limits, the rate of the electrochemical reaction is controlled by the imposed electric energy gradient at each of the reaction interfaces. An electric energy input is required to enable the reactions and must be at a rate that will control the reactions and simultaneously maintain the reacting temperature. Heat is generated by the cell ohmic resistance of the electrolyte and electrodes, and it is also generated by the electrode polarization. Heat is only supplied by the voltage between the anode assembly and the cathode. However, for small cells, external heating can be used to keep the cells hot.

Good cell operation also requires a method of replenishing the added raw material. It is a challenge to add the raw material in a manner that ensures that its dissolved concentration stays within the values that will enable the desired electrode reactions to occur without introducing contaminants to the metal product, and while not introducing cell operational disturbances through excessive amounts of undissolved material in the bottom of the cell.

The cell temperature is usually measured manually once a day using a thermocouple. Continuous temperature measurement is not easy because of the corrosive nature of most of the molten salt electrolytes. The easiest way to change the temperature is to vary the cell voltage, which implies an increase or decrease of the anode–cathode distance in the cell.

Separation Systems

Many molten metals are easily reoxidized, and it is therefore crucial to avoid having the anode and cathode products come in physical contact with each other in the cell. This is easiest when the metal has a higher density than the electrolyte, because then the metal moves downward and the gas upward. However, for example in magnesium electrolysis, the metal is lighter than the electrolyte and therefore moves upward and floats on top of the surface of the electrolyte. The anode gas, chlorine, also moves upward. This requires that the liquid magnesium is kept in a compartment in the cell where a chlorine atmosphere is not present.

The metal produced has to be removed from the cell periodically. Extraction of the molten metal is called tapping. This is a labor-intensive manual routine operation. The spout of a vacuum ladle or crucible is dipped into the metal pad in the cell, and the liquid metal is then siphoned into a ladle by suction from an air ejector system. Then the metal is analyzed, weighed, and transported to a furnace in the cast house. It is then an operational challenge to ensure that the metal has the required purity.

Impact of Design and Operations

Electrolysis is a continuous process with spatial batch operations. This results in conditions in the cell that are not uniform. The problems are aggravated by the limited number of measurements that can be made and the accuracy of the measurement because of the spatial and temporal variations. Development in the industry is clearly toward cells with higher amperage and at the same time attempting to reduce the electric energy consumption. The larger the cell and the lower the energy input, the worse it gets.

The chemical composition of solvent electrolytes would enable desired oxidation reactions to occur without introducing contaminants to the product. A major weakness of electrochemical reactors is that the potential gradient is not selective to the reaction. If it is too high, undesirable parallel reactions can occur (e.g., anode effect in aluminum electrolysis). This can seriously reduce the cell productivity.

Some manually interfaced work practices are unavoidable. A method is needed for replenishing the alumina that is continuously depleted. The alumina replenishment needs to be done in a measured manner so that the alumina concentration stays within a target band. The replenishment of the alumina should cover the full cross-sectional area of the cell to maintain uniform concentration distribution. Multiple volumetric feeders and "breakers" are required to ensure that the alumina goes into the electrolyte. Mixing and dissolving the alumina and distributing it uniformly are very important. Undissolved alumina getting beneath the metal pad is causing instability through changed current flow. Dense or clumped alumina can form sludge.

In aluminum electrolysis cells, a method is needed for introducing the consumable carbon anodes and replenishing them to a new target position. Multiple electrodes are used to minimize disturbance. Positioning of the anodes must be adjustable to maintain the cell voltage and anodic current distribution. Because the carbon anodes are hot, a technique is needed for protecting them from air oxidation and heat loss. Therefore the newly set anodes need to be re-covered and integrity maintained. The anode cover material must not introduce contamination; hence, a mixture of alumina and recycled solid electrolyte is used.

MOLTEN SALTS

Molten salts and their mixtures form a unique type of liquids, which are different from both aqueous solutions and organic liquids. In molten salts there is an array of electrostatically charged particles, negative anions and positive cations, which are in close contact. Because of the strong attractive forces of charges with an opposite sign and the strong repulsive forces between particles of the same sign, a cation will preferentially have anions as its nearest neighbors, and vice versa for anions. The structural units are either simple ions or associated groups such as paired ions and complex ions.

In the solid state, these ions are fixed in space, but when the material is molten, it is accompanied by an increase in volume, which is typically 20% for alkali halides. This expansion allows for ions to migrate without much restriction and it may be attributed to the presence of unoccupied positions in the molten salt.

Because of the ionic nature of the molten salts, they have been modeled after theories of gases and solid-state materials. In the molten salt, the vacancy model assumes that Schottky defects arise in the ionic crystal when the ions move out from their lattice positions. In the hole model, empty space is generated by thermal expansion of the cell when localized density changes. The cell model assumes that the ions in the molten salt will move within a defined cell space, which is considerably smaller than the volume it would have in the gas phase, and it defines the short-range order of the liquid. The liquid free-volume model states that the liquid has by itself a free volume and it is statistically distributed throughout the short-range cells (Bloom and Bockris 1964).

Using X-ray neutron diffraction, the interaction of ions has been modeled in what is known as radial distribution functions. This method determines a probability of finding two ions or atoms separated by a given distance. When an alkali halide material is molten, unlike ions are brought closer together while similar ions are separated from each other. At the same time, the long-range order is disrupted, while some short-range order remains. Because of the expansion of the volume, vacancies appear in the structure (Bloom 1967).

When the raw material for electrolysis, usually a metal oxide or a halide, goes into solution, it can form either ionic or molecular species. Ionic forms of the metal to be extracted are required for high extraction efficiency. If molecular (neutral) species of the dissolved raw material are formed, then the electrochemical reduction at the cathode is not possible. The electrolyte conductivity decreases because of the presence of neutral complex molecules. To avoid this, halide molten salts are usually used as electrolytes, because in general they are strong ionic solvents and tend to form single ionic species with the raw material. They have high electrical/ionic conductivity, high ionic mobility, and low viscosity and thus provide faster extraction kinetics. Some disadvantages of halide molten salts are their high vapor pressure and corrosiveness, and inert atmospheres are required in many cases.

During the electrolysis of molten salts, the metal produced has a tendency to be slightly soluble in the halide. In fact, all metals are soluble in their molten salts. In the case of alkali metals, the solubility increases with the atomic number, thus $Li < Na < K$. For alkaline earth metals, the tendency is the same: $Mg < Ca < Sr$. The solubility in either case is increased if a displacement reaction occurs, where the metal reduced reacts to form a different halide salt. Typically, in a mixture of salts, the salt of a less noble metal will reduce the solubility of the other metal compared to its pure salt. Also, the interfacial tension between the metal being deposited and the molten salt will dictate its solubility. Higher surface tensions lead to lower solubility (Corbett 1964; Bredig 1964).

The main characteristics that the electrolyte molten salt must have are low melting point; high thermal stability; low viscosity; low vapor pressure; good ionic conductivity; high solvent power of the raw material; high decomposition voltage; low corrosiveness with cathode, anode, and vessel; easy purification; proper density; and low cost (Minh 1985). Low melting points will allow the system to operate at lower temperatures, and thus the operating costs can decrease.

ELECTROLYSIS

The three types of electrolysis are based on the electrolyte temperature range stability: (1) aqueous solutions at low temperatures (<100°C), (2) ionic liquids at mid-temperatures (100°–300°C), and (3) molten salts at high temperatures (>300°C). These fluids, once in the liquid form, must form ions in single and complex forms. The more ionic strength, the more efficient the electrolysis is, because it is a measure of the ionic conductivity of the electrolyte and thus the mobility of the species dissolved.

Aqueous solutions electrolysis is less expensive, because of the lower temperatures, but many metals cannot be extracted in this medium because the required amount of electrical energy will decompose the electrolyte instead. When higher temperature electrolytes are required, the operating costs will increase because of the temperature requirement, so high efficiency must be met to have a cost-effective technology. The same fundamental concepts used for low-temperature electrolysis, to reduce metals from aqueous electrolytes, apply in molten salt electrolytic processes.

Electrochemistry Principles

The thermodynamic behavior of electrochemical reactions will be dependent on the activities of each component in the electrolyte and the temperature. This can be described by the use of the Nernst equation:

$$E(T) = E°(T) - (RT/nF) \ln K \qquad \textbf{(EQ 1)}$$

where E(T) is the reversible potential of the reaction at the specified activity and temperature; E°(T) is the standard electrode potential for unit activity of the species; R is the universal gas constant; T is absolute temperature; n is the number of electrons transferred; F is Faraday's constant; and K is the equilibrium constant for the electrochemical reaction.

Electrodes

The material and the stability of the electrodes are key aspects in any electrochemical process. Typically, they are categorized as working electrodes and reference electrodes. The materials of choice for the cathode and anode are of paramount importance. It must be relatively inert under the harsh environment of the molten salt. Platinum, nickel, molybdenum, and tungsten, among others, are common for fabricating the electrodes. In the case of fluoride systems, Inconel and nickel are typically used.

To obtain information about the electrochemical reactions (half-cell) occurring at the anode and cathode, it is necessary to determine the value of each single-electrode potential (E°). The use of reference electrodes is the only way to obtain the electrode potential based on a reference state. Then, equilibrium thermodynamic data can be obtained because

$$\Delta G° = -n\, F\, E° \qquad \textbf{(EQ 2)}$$

Here, ΔG° is the standard Gibbs energy for the electrochemical reaction. Varying the electrode potential (potentiodynamic scans) at a selected temperature and composition would allow for the determination of the electrode kinetics of the cathodic and anodic reactions.

In the case of aqueous solutions at 25°C, the standard hydrogen electrode (SHE) is employed as the conventional reference electrode in performing electrode potential measurements. Thus, the assigned potential for this (standard) reference electrode is zero. When using other reference electrodes, the measurement of a selected electrode potential yields a value that is offset from the tabulated values, because the potential of the other reference electrode is not the same as the SHE. The minimum cell voltage required in the electrolytic process (ε_{cell}) is the difference between the equilibrium electrode potentials of each half-cell reaction (anode and cathode) and is given by the following equation:

$$\varepsilon_{cell} = E_{cathode} - E_{anode} \qquad \textbf{(EQ 3)}$$

This value corresponds to the situation when no current is flowing in the circuit. The evaluation of the electrode kinetics is performed by the application of an overpotential to the electrolytic cell, thereby inducing an external current flow in the system.

A reference electrode must not influence the current and the potential changes occurring at the half-cell reaction. It must have basic requirements like stability, reversibility, good reproducibility, and simplicity of construction. Measurement of the electrode potential not only requires a suitable reference electrode but also a high impedance voltmeter (electrometer). In molten salts, the use of reference electrodes is very limited and rather troublesome. No universal electrode works in these electrolytes because of chemical interactions of different electrodes with different salts (i.e., corrosion of metal, reactivity of gases, etc.). The use of metals as reference electrodes in molten salts is well known. The use of silver as an electrode is very common (Ag/Ag^+) for chlorides, carbonates, nitrates, and sulfates. For fluorides, the use of Ni/Ni^{2+} is commonly used. Solid oxide electrodes are also employed as reference electrodes. In this case, the insoluble electrode forms a cell: $M/M_xO_y/O^{2-}$. Some of these solid oxide electrodes are chemically stable under high temperatures and highly corrosive environments. Gases, such as hydrogen, chlorine, and even oxygen, can be used as reference electrodes. For gas reference electrodes to work, they must have an inert support material like porous carbon.

Common anodes are made of graphite because of its high electrical conductivity, and it is chemically stable with the molten salt. The drawback of this material is that the anodic products, such as oxygen and chlorine, react with carbon and form carbon dioxide (CO_2) and toxic Cl-O compounds. To avoid these reactions, inert anodes are being considered and utilized. General guidance on the development of inert anodes, in particular metallic-based for molten chlorides, is provided elsewhere (Wang and Xiao 2013). Thermodynamic considerations and experimental evaluations in novel molten-salt electrolysis processes are reported.

The quality of the electrodeposited metal strongly depends on the temperature and cathodic current density (the amount of current per cathodic surface area unit). The larger the number of electrons available, the faster the deposition kinetics. If the metal atoms need to be reduced and deposited as a solid phase over the cathode, then its morphology (dense film, faceted phases, columnar morphology, and dendrites) will depend on the cathodic current density.

Electric Double Layer

When surfaces are charged electrically, excess charges will tend to accumulate on each side of the interface, and the electric double layer refers to the two parallel layers of charge surrounding the object. In the case of a cathode immersed in an ionic solution, the metal side of the interface will have

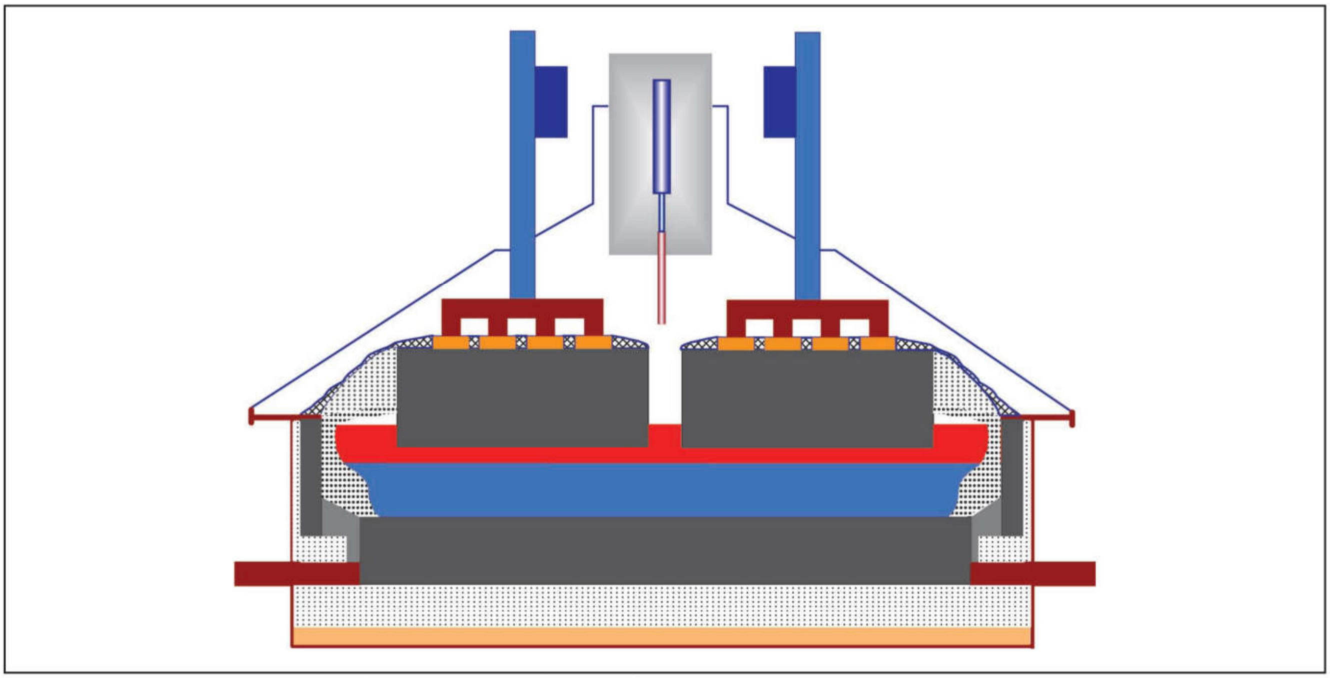

Figure 1 Hall–Héroult cell used in the industrial production of aluminum

electrons that are facing cations, which will accumulate on the electrolyte side. This effect was first suggested by Hermann von Helmholtz in 1879, after whom the "Helmholtz double layer" terminology was introduced, which refers to when a capacitance term is created at the interface. This first approximation of a double layer is very simplistic and does not take into account the effect of thermal motion of the liquid ions. In reality, the ions distribute themselves in a diffusive layer, and thus the potential drop across it decays exponentially.

Faraday's Laws

The mass of a material produced at an electrode during electrolysis is directly proportional to the quantity of electrical charge (the number of coulombs) transferred at that electrode. Also, the mass of the material formed at an electrode is directly proportional to the element's equivalent mass. The equivalent mass of a substance is the amount of an element that reacts, or is involved in reaction, with one mole of electrons. So, for each Faraday of electric charge (96,485 coulombs) one gram-equivalent of material will be produced or destroyed.

Faraday's laws assume a perfect system that does not include problems typically found in molten salt systems. One example of such deviations includes discharging of more than one type of ion simultaneously, for which the charge used will be consumed or given by more than one species. The formation of intermediate species near the cathode, which will then alter the effective charge used, also causes deviations. Electronic charges are also lost in some instances through conducting material in the electrolyte, or even by semiconductor types of transfers. Finally, the loss of deposited material at the cathode is the most common problem. Some materials deposited could redissolve partially in the electrolyte, or they could evaporate or simply be removed mechanically by fluid flow near the cathode. These deviations then reduce the effectiveness of the electrolysis process, thus reducing the amount of electrical current effectively used. The current efficiency of a cell is thus determined by obtaining the ratio of quantity of the substance effectively obtained to that predicted theoretically by Faraday's laws. One can say that the current efficiency in industrial processes is the percentage of the electricity that is used to produce the metal, while the rest of the current produces heat given off to the surroundings.

COMMERCIAL MOLTEN SALT ELECTROLYSIS

Several metals are currently being commercially extracted using molten salt electrolysis: aluminum (Hall–Héroult process), magnesium, sodium, calcium, and lithium.

Aluminum

Aluminum is second only to steel in annual production volume, and more aluminum is produced than all of the other nonferrous metals combined. The total world production of primary aluminum was 63 Mt (million metric tons) in 2017; in addition, around 20 Mt of aluminum were recycled (IAI 2018).

Aluminum is remarkable for its low density and ability to resist corrosion through the phenomenon of passivation. Aluminum and its alloys are vital to the aerospace industry and important in transportation and structures, such as building facades and window frames.

The process for electrowinning of aluminum revolves around the independent discoveries in 1886 and the subsequent patents of Hall and Héroult. The Hall–Héroult process is the electrolytic reduction of aluminum oxide (alumina) dissolved in a molten electrolyte of mainly cryolite (Na_3AlF_6) at a temperature of ~960°C (Figure 1).

Cryolite, a chemical compound composed of sodium, aluminum, and fluorine, constitutes about 80% of the electrolyte (the current-conducting medium) in the aluminum smelting operation. Naturally occurring cryolite was once mined in Greenland, but the compound is now produced synthetically for use in the production of aluminum. Aluminum fluoride is

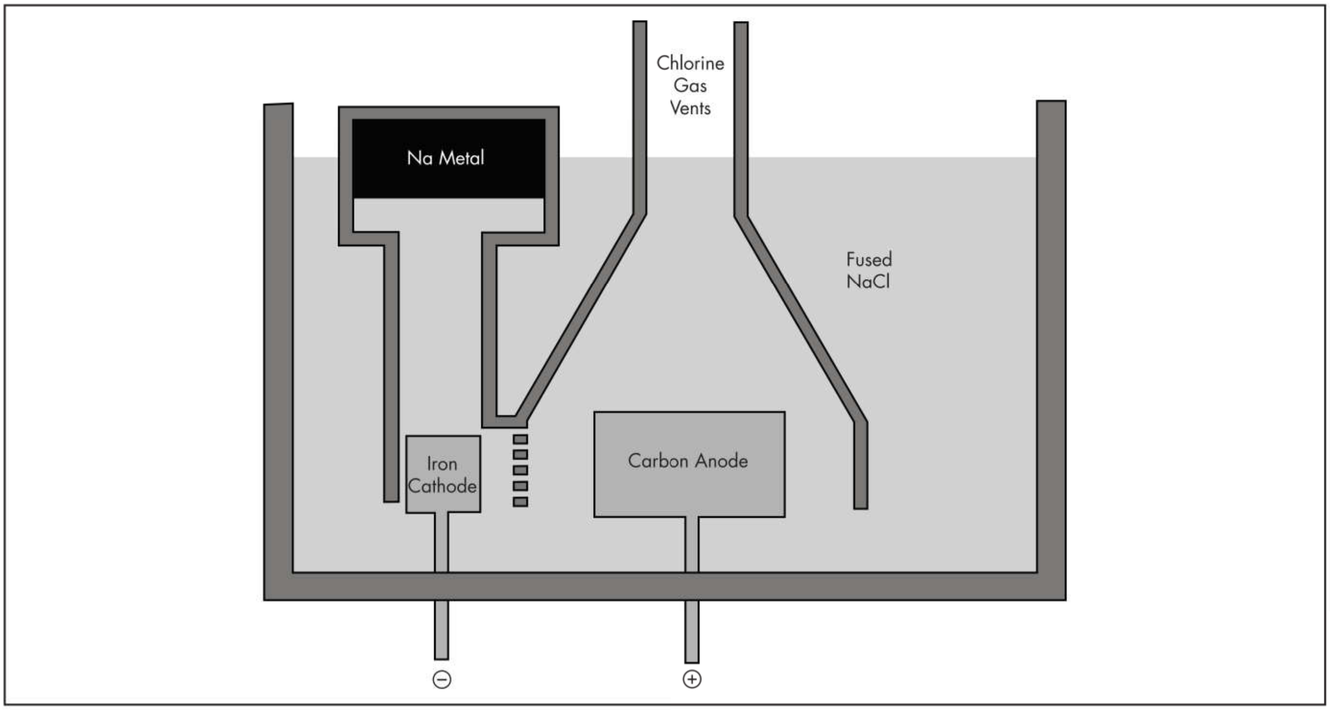

Figure 2 Downs cell used in the industrial production of sodium

added to lower the melting point of the electrolyte, but the main reason for addition of aluminum fluoride is to keep the electrolyte composition constant by neutralizing the sodium oxide impurity in the alumina feed. Modern cells typically have a target of 10 wt % aluminum fluoride in the electrolyte.

The anodes are made of carbon, prebaked or Soderberg, from a mixture of calcined petroleum coke and coal-tar pitch. The cathode is the molten Al (99%). The overall reaction is

$$Al_2O_3(\text{dissolved}) + 3/2C(s) \rightarrow 2Al(l) + 3/2CO_2(g) \qquad \textbf{(EQ 4)}$$

Thus, the other major ingredient used in the smelting operation is carbon. Carbon electrodes transmit the electric current through the electrolyte. During the smelting operation, some of the carbon is consumed as it combines with oxygen to form carbon dioxide. In fact, about 0.4 kg C is used for every kilogram of aluminum produced. Most of the carbon used as anodes in aluminum smelting is a petroleum coke, a by-product of oil refining, and additional carbon is obtained from coal-tar pitch.

Because alumina is a very stable compound and aluminum smelting involves passing an electric current through a molten electrolyte, it requires large amounts of electrical energy. As a global average, production of 1 kg Al requires 13.4 kW·h of electric energy. The cost of electricity represents about one-third of the cost of smelting aluminum.

Magnesium

Magnesium is the third most used metal in construction (after iron and aluminum). Nearly 70% of the world production of magnesium is used to make alloys, which have a very low density, comparatively high strength and excellent machinability. Other important uses are in the manufacture of titanium and high grade steel for construction.

The annual world production is now about 900,000 t. The industrial process involves two stages:

1. Production of pure magnesium chloride from sea water or brine
2. Electrolysis of molten magnesium chloride

The electrolyte composition in the cells varies considerably among the different magnesium producers. The so-called NaCl-KCl (sodium chloride–potassium chloride) type of electrolyte consists of 50 wt % NaCl, 35 wt % KCl, and 15 wt % $MgCl_2$ (magnesium chloride), which is kept at about 700°C. During electrolysis, magnesium and chlorine are produced. The molten metal is removed from the cell and cast into ingots. The high specific energy consumption (12–16 kW·h/kg) has been a motivation to improve the process with respect to energy and current efficiency. The cathodic process in dilute solutions of Mg(II) species, typically 0.1–10 wt % $MgC1_2$, is controlled by diffusion of the reactant (Børresen et al. 1997; Corrosion Doctors 2018).

Sodium

Sodium is the most important of the alkali metals, with annual world production of more than 200,000 t. It is used for manufacturing tetraethyl lead as an additive to gasoline ($[Pb(C_2H_5)_4]$, and also for metal reduction, particularly during titanium and tantalum production. Sodium is industrially produced by the Downs' process, in which molten NaCl is electrolyzed in a special apparatus called the Downs cell that uses a carbon anode and an iron cathode (Figure 2). Calcium chloride, $CaCl_2$, is added to lower the melting point of the electrolyte to below 600°C. The products (liquid sodium and chlorine) are kept from coming in contact to avoid NaCl reformation. Oxidation of elemental sodium is dangerous because it is explosive. To avoid oxidation, elemental sodium must therefore be prevented from contact with oxygen. Downs cells

Table 1 Cathode and anode materials and products, plus some cell operational data for production of aluminum and magnesium, and some alkali and alkaline earth metals

Cathode Product	Anode Product	Anode Material	Cathode Material	Amperage, kA	Voltage, V	Temperature, °C	Electrolyte Composition
Aluminum	CO_2	Carbon	Aluminum (carbon)	100–600	4.0–4.5	955–965	80% cryolite 10% AlF_3 5%–7% CaF_2 2%–4% Al_2O_3
Magnesium	Cl_2	Graphite	Steel	100–400	5	670–700	50% NaCl 30% KCl 20% $MgCl_2$
Sodium	Cl_2	Multi-electrode	Multi-electrode	40–80	6.5–7.0	590–600	46%–53% $BaCl_2$ 23%–26% $CaCl_2$ 24%–28% NaCl
Lithium	Cl_2	Graphite	Mild steel	12–40	6	400–460	40%–60% LiCl 60%–40% KCl
Calcium	Cl_2	Graphite	Liquid Ca–Cu alloy	20	7–10	650–715	80%–85% $CaCl_2$ 15%–20% KCl
Strontium	Cl_2	Graphite	"Contact-cathode"	—	8–12	680–800	84% $SrCl_2$ 16% KCl

operate at 25–40 kA and at potentials of 6.5–7.0 V. With a multi-electrode arrangement, modern Downs cells can have amperages up to 80 kA.

Lithium

All of the world's primary lithium is produced by molten salt electrolysis, with an annual world production of about 43,000 t. Lithium is the lightest of all metals and is used in a variety of applications, including the production of organolithium compounds, as an alloying addition to aluminum and magnesium, and as the anode in rechargeable lithium–ion batteries. The electrolysis cell has a central cathode of mild steel on which molten lithium is produced. Opposing graphite plates serve as the anodes, where chlorine is formed. A bell-shaped structure positioned above the cathode collects the rising liquid metal and prevents it from reacting with the rising chlorine gas. Anhydrous lithium chloride is the cell feed, and potassium chloride is the solvent. At 400°C the electrolyte composition is about 35–45 mole % KCl. The electric energy consumption is high, about 35 kW·h/kg Li (Kipouros and Sadoway 1998).

Operating Data for Industrial Electrolytic Processes

Table 1 summarizes data from industrial production of the so-called light metals aluminum and magnesium, and also for some alkali and alkaline earth metals. It is seen that graphite anodes and chlorine gas evolution is common for several of these metals, and chloride melts are then used as electrolytes at temperatures in the range from 450°C to 800°C. Amperage and voltage vary considerably between the various processes. Notably, aluminum production is unique, because it uses consumable carbon anodes and a fluoride-containing electrolyte.

PROPOSED PRODUCTION OF METALS IN MOLTEN SALTS

Boron

Many metals have been proposed to be produced by electrolysis in molten salts. Boron is one of the semi-metals and is primarily used in chemical compounds. About half of all boron produced globally is used as an additive in glass fibers of boron-containing fiberglass for insulation and structural materials. The next leading use is in polymers and ceramics in high-strength, lightweight structural and refractory materials. Elemental boron has been produced in molten MgF_2-NaF-LiF mixtures with B_2O_3 as the source of boron. The morphology of the product was agglomerated boron spheres with 0.5–5 μm of average particle size depending on the cell potential applied. The highest grade or purity of 88.4 wt % B was obtained at 700°C and 1.5 V, while the highest recovery of 91.7 wt % B was obtained for the experiment at 700°C, 2.0 V, and electrolyte premelted at 1,330°C (Zhang et al. 2007).

Ruthenium

Electrolysis of ruthenium (Ru) from LiCl–KCl molten salts using $RuCl_3$ as the raw material has been investigated. Effects of process parameters such as current density, time, and agitation of the electrolyte on the thickness and morphology of white/gray deposit of ruthenium layers were studied. The highest cathodic current efficiency (η) of 99.68% was achieved at a current density of 3 mA/cm^2 after 2 hours of electrodeposition time with rotating cathode speed of 50 rpm (Yan and Pang 2011).

Alloys of Lithium with Aluminum and Magnesium

Aluminum–lithium alloys are used in the aerospace industry because of the weight advantage they provide. The lithium content in the commercial alloys is low, only about 2.5%. The alloys can be produced by electrolysis of molten lithium chloride with a graphite anode and aluminum (or some aluminum alloys) as the consumable cathode.

Magnesium–lithium (Mg–Li) alloys with low lithium content (~25 wt % Li) for aerospace and aircraft applications were prepared at laboratory scale via electrolysis at low temperature in a molten salt electrolyte of LiCl:KCl = 1:1 (wt %). The optimum conditions, in which maximum current efficiency was obtained, were 480°C and cathode current density of 1.13 A/cm^2 (Sireli 2014).

Rare Earth Metals

Nowadays, rare-earth metals (REMs) are produced in the most convenient and economic way by molten salt electrolysis. Using fluoride–oxide molten salts is advantageous because they provide higher current efficiencies than the chloride melts (Zhu 2014). It is more difficult to study the REM electrode processes in fluoride–oxide systems than the aluminum ones. This is because REM electrolysis is carried out at higher temperatures and REM fluorides are more aggressive. Some researchers have reported the electrode reactions and anodic gases composition of neodymium electrolysis in LiF-NdF_3-Nd_2O_3 melts (Wang et al. 2007).

DIRECT OXIDE ELECTROCHEMICAL REDUCTION

Direct oxide electrochemical reduction (DOER) is the electro-deoxidation of a solid metal oxide in molten salts. Chen et al. (2000) first achieved the direct reduction of titanium dioxide (TiO_2) into titanium in a molten chloride salt composed of $CaCl_2$ from 800°C to 900°C with a cell potential of 3.0–3.1 V. This innovative method is now often referred as the FFC (Fray–Farthing–Chen) Cambridge process. A TiO_2 reduction pathway has been proposed (Schwandt and Fray 2005; Suzuki 2005; Nagesh and Ramachandran 2007) and several titanium sub-oxides (Ti_4O_7, Ti_3O_5, Ti_2O_3, and $CaTi_2O_4$) have been characterized

The overall reaction is the oxygen removal from a solid M_xO_y oxide at the cathode and the formation of $CO_2(g)$ at the carbon anode, according to the following reactions:

$$\text{Cathode: } M_xO_y(s) + 2y\ e- = x\ M(s) + y\ O^{2-} \qquad \textbf{(EQ 5)}$$

$$\text{Anode: } 2O^{2-} + C(s) = CO_2(g) + 4\ e- \qquad \textbf{(EQ 6)}$$

The FFC process in molten LiCl- or $CaCl_2$-containing salts has been intensively studied worldwide for reduction feasibility studies of

- High purity (solar grade) silicon (Yasuda et al. 2007),
- Reduction of rare earth oxides (Hirota et al. 1999; Song et al. 2015),
- Spent nuclear fuel (UO_2) (Sakamura et al. 2006; Choi et al. 2011),
- Triuranium octoxide (U_3O_8) (Jeong et al. 2006),
- Uranium dioxide-plutonium dioxide (UO_2-PuO_2) mixed oxides (Iizuka et al. 2007),
- Spent fuel (Herrmann and Li 2010), and
- Pure metals or alloys (reduction of Nb_2O_5, Fe_2O_3, NiO–TiO_2, and TiO_2-MnO_2) (Jeong et al. 2007; Wang et al. 2008; Zhu et al. 2006, 2015).

However, no process has yet reached the industrial scale. In some cases, this may be because of the purity of the product, which is usually contaminated with carbides produced as a by-product during the electrolysis.

The use of inert anodes has been proposed to avoid the carbide formation. Catalytic materials, such as gold, are required to allow the oxygen evolution electrochemical reaction:

$$2O^{2-} = O_2(g) + 4\ e^- \qquad \textbf{(EQ 7)}$$

However, this reaction is difficult to control in molten chloride salts because of the close potentials of $Cl_2(g)$ and $O_2(g)$ evolution. Molten fluorides have been proposed with the use of inert gold anodes to avoid the formation of anodic halide gases. Several eutectic compositions have been proposed, such as LiF–NaF (+2 wt % Li_2O) at 750°C for SnO_2 and Fe_3O_4, and LiF–CaF_2 (+2 wt % Li_2O) at 850°C for TiO_2, TiO (Gibilaro et al. 2011a), and UO_2 (Gibilaro et al. 2011b).

The process has been demonstrated for the electro-deoxidation of oxides of

- Titanium (Chen et al. 2000; Mohandas et al. 2011b),
- Tantalum (Jeong et al. 2007),
- Niobium (Vishnu et al. 2013; Song et al. 2012),
- Niobium carbide (Song et al. 2015),
- Zirconium (Mohandas and Fray 2009),
- Chromium (Chen et al. 2004),
- Chromium carbide (Dai et al. 2015),
- Iron (Li et al. 2009),
- Tungsten (Erdogan and Karakaya 2010),
- Aluminum (Yan and Fray 2009),
- Nickel (Descallar-Arriesgado et al. 2011),
- Silicon (Yasuda et al. 2007),
- Uranium (Gourishankar et al. 2002; Mohandas et al. 2011a; Sri Maha Vishnu et al. 2012), and so forth.

THE ANODE EFFECT

The anode effect (AE) can occur with carbon or inert anodes and in both molten salts and aqueous electrolytes. This is a characteristic and important phenomenon in molten salt electrolysis, and in particular in the primary production of aluminum by the Hall–Héroult process. There may be two causes of AEs: (1) the initiation of an AE is due to the formation of some intermediate compounds on the surface of the anode, or (2) the initiation of an anode effect is simply due to accumulation of gas bubbles on the anode. It is known that during the AE, other anodic reactions take place and the anodic gas composition changes because of the simultaneous discharge of oxygen and fluoride ions. It has been proposed that some events prior to the AE occur, such as the following (Zhuxian 1992; Qiu and Zhang 1987):

- A change in wettability of the electrolyte because of the electrolyte composition change. In this case, the anodic gas produced can accumulate at the anodic surface because the molten salt is not wetting the anode.
- A change in the anodic process because of the depletion of oxygen ions (e.g., low alumina concentration) so other ions such as fluorides can be oxidized at the anode and fluoride-containing gases are formed.
- An increase in the anodic overpotential because of the depletion in oxygen anions. The surface tension of the electrolytes thus increases and allows the formation of large bubbles at the surface, decreasing the electrical contact between the electrolyte and the anode.
- Electrostatic attraction of gases by the anode at high anodic potential.

During an AE in aluminum electrolysis cells, a gas film under the anodes is formed, which consists of perfluorocarbon gases (PFCs), mainly CF_4 and smaller amounts of C_2F_6 (Nissen and Sadoway 1997). These compounds are strong greenhouse gases with high global warming potentials, and they cause a much more serious effect on the environment than carbon dioxide. The U.S. Environmental Protection Agency and the primary aluminum producers in the United States have established the Voluntary Aluminum Industrial Partnership to substantially reduce the PFC emissions (Dolin 1999). There is a certain current density, called critical current density (CCD), in which the AE can be induced. The CCD depends on many factors such as type of electrode materials, anodic size and shape, electrolyte composition (in particular, the alumina concentration), and temperature, among others. Zhu and Sadoway (1999, 2000, 2001) suggested that PFC generation can be avoided completely in small laboratory cells by simply stepping down the cell current in small increments, because its formation kinetics is controlled by an interfacial step rather than by mass transfer.

Thus, an AE occurs when the electrolyte in the cell becomes depleted of alumina below a critical level, causing the cell voltage to fluctuate and increase several folds due to the presence of a gas film under the working surface of the anode. Previously it was believed that PFC gases were evolved only during AEs when the cell voltage was high (above 8 V). However, recently it has been discovered that large modern aluminum electrolysis cells can have PFC emissions also at much lower cell voltages. At high anodic current densities and for modern cell control strategies in high amperage cells, PFC emissions can start well below the normal cell voltage of 4.0–4.5 V. This may be due to poor dissolution and mixing of alumina in the electrolyte in these cells.

For several years now, there has been research and development work going on to reduce both the frequency and duration of AEs in industrial aluminum electrolysis cells. This reduces the total greenhouse gas emissions and also improves the cell operational stability. With modern cell control, AEs do not really have any useful purpose, and perhaps the future aluminum electrolysis cells can be operated without AEs. An excellent presentation of understanding AEs has recently been given by Dorreen et al. (2017).

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