Chapter 11
Molten Salt Electrowinning of Metals and Materials: Opportunities and Challenges

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Abstract Conventional metallurgical processes to produce metals involve carbothermal reduction of their compounds and suffer from massive carbon emissions. Electrowinning using aqueous electrolytes is a demonstrated approach to obtain many metals. However, aqueous electrolytes are not suitable to produce several classes of metals such as alkali, alkaline earth, refractory, rare earths, and actinides due to their high negative reduction potentials. Molten salt electrolysis is a commercially viable and feasible route for the production of these metals. The present chapter details on the molten salt electrowinning of alkali, alkaline earth, rare earths and refractory metals with a special focus on the efforts at CSIR CECRI in this niche area of science and technology.

Keywords Molten salt · Electrowinning · Pyrometallurgy · Light metals · Rare earths · High temperature

11.1 Introduction

The overall development of a country is directly related to the flow of materials, utilization of commodities, imports and exports. It is propelled by the population growth and rapid industrialization which further steers innovative technologies for the production of advanced materials. Mobilization of rural population to urban areas leads to higher utilization of lifestyle driven consumer products.

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In recent years, the consumption of minerals, metals and fossil fuels has steadily been increasing in our country which steers the development of improved ferrous and non-ferrous materials for sustainable growth in aviation, automotive, space, construction and heavy engineering sectors. As critical players, metallurgical industries have a compelling demand to maximize the production of metals and materials through improved process technologies. Traditional metallurgical processes involve carbothermal reduction of metal compounds to their respective metals which suffers from colossal carbon footprint (Springer and Hasanbeigi 2016). Electrowinning is a demonstrated approach to obtain metals by the passage of electrical charge into a molten solution containing the metal ion. Several classes of metals such as alkali, alkaline earth, refractory, rare earths and actinides cannot be produced in metallic form by electrolysis of their aqueous solutions due to the limited electrochemical stability of water (~1.23 V). These metals are characterized by their high negative reduction potentials that make their electrowinning into their metallic forms extremely difficult since their respective compounds are very stable. Molten salt electrolysis is the commercially viable and feasible route for the production of these metals. The present chapter dwells on the molten salt electrowinning of alkali, alkaline earth, rare earths and refractory metals with a special focus on the efforts at CSIR-CECRI in this niche area of science and technology.

11.2 Principles of Metal Extraction Processes and Electrometallurgy

The extraction of metals depends on the difference in chemical potentials which makes the separation of metal values from the compounds difficult. Metallurgical processes are classified into pyrometallurgical and hydrometallurgical processes. Pyrometallurgical processes generally involve beneficiation of minerals followed by the reduction of purified minerals such as metal oxides, sulphides and chlorides at high temperatures by using a reductant like carbon (C), hydrogen (H), carbon monoxide (CO) to produce the respective metals. The Ellingham diagram shows the relative thermodynamic stabilities of the various oxides as a function of temperature, thus enabling an understanding of the thermodynamics of the reduction process. In hydrometallurgical processes, the minerals are subjected to various ore processing steps like crushing, grinding, sieving, magnetic separation and calcining followed by dissolution in a suitable aqueous liquid from which the metals can be extracted.

In electrometallugical processes, the purified ore is leached with a suitable solvent and subsequently decomposed by applying an electrical potential, for example, in electrowinning of Cu, Ni, Zn, Cr etc. Mostly acids, alkalis and organic solvents are used to trap the metal values from the mineral particles. The process of leaching enables the dissolution of metal values in to the leached medium. The leached solution is then electrolyzed by applying a current to deposit metal at the cathode. Noble metals like copper, silver, gold etc. which exhibit reduction potentials more positive than hydrogen in the electrochemical series could be conveniently electrodeposited from aqueous solution (Vol'skii and Sergievskaia 1971). Even though certain metals such as manganese (Mn), zinc (Zn), chromium (Cr), iron (Fe), cadmium (Cd), cobalt (Co), nickel (Ni), tin (Sn) and lead (Pb) have negative reduction potentials, they could be electrowon from aqueous solutions taking the advantage of hydrogen over-voltage under appropriate conditions of electrolysis (Ray 1985).

In an electrolytic process, electrical current is passed through an ionic media resulting in non-spontaneous chemical reactions at the electrode surfaces. This concept is widely applied for the deposition and purification of a variety of metals from their primary and secondary resources.

The essential components required to carry out the electrodeposition process are,

1. An electrolyte either in liquid or solid form having mobile ions.
2. A power source, which provides energy through a voltage and current for the decomposition of soluble metal compound.
3. Electrodes are made of electronically conducting materials and current distribution system with control devices.
4. An electrolytic cell called the electrolyzer comprising of anodes and cathodes which are dipped into the electrolyte to complete the electrical circuit connected to a DC power source. The electrical energy supplied results in the discharge of the ions at the electrodes which are immersed in the electrolyte.

During electrolysis, the positively charged ions (cations) move towards the negative electrode called as cathode thereby depositing the respective metal, whereas the negatively charged ions, anions migrate towards the positively charged anode. At the electrode surface, the 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 whereas those ions that gain or lose electrons become uncharged atoms and usually separate from the electrolyte. Other components include electrolytic vessel to hold the reactants and products, electrical circuitry and control devices of the electrochemical reactor (Yan and Fray 2008).

Electrolytic processes may be subdivided into Electrowinning, Electrorefining, Electroplating and Electroforming.

1. In electrowinning process, the metal is deposited in a pure or partially impure form from a compound of the metal dissolved in the electrolyte.
2. In electrorefining, the pure metal is transferred from the impure anode to the cathode by the application of a suitable voltage. The impurities may reside at the anode itself or go in to the liquid electrolyte.
3. In electroplating, a thin uniform coating of the metal is formed on the surface of an inexpensive substrate to protect the substrate from corrosion or oxidation.
4. Electroforming is performed to produce an article on a disposable substrate through an electrolytic process (Mamantov and Marassi 2012).

During electrowinning of electropositive metals from aqueous solutions, electrolyte decomposition precedes metal reduction and the cathodic product is invariably H_2 and results in the formation of respective hydroxides or oxides of the metal.

Therefore, metals with more negative reduction potentials can be electrowon only from non-aqueous electrolytes. Among them, molten salt electrolysis is a feasible and scalable strategy for the electrowinning of alkali, alkaline earth, refractory, rare earths and actinide metals.

11.3 Molten Salt Electrolysis

Molten salt electrolysis involves passage of electric current into molten metal halides which act as the solvent and the electrolyte (hence termed as fused salt electrolysis) to enable efficient migration of the ions to the respective counter electrodes (Thonstad 1992). Majority of the molten salt systems comprise of alkali and alkaline earth halides such as chlorides and fluorides. They possess high negative Gibbs free energies of formation and therefore, they possess very high decomposition potentials at their operational temperature (Mamantov and Marassi 2012; Gale et al. 1983). The lowering of the decomposition voltage may be possible, when the activity of the deposited solvent metal is lowered either through interaction with the solvent cations or through interactions with the electrode surfaces or both. The energy necessary in terms of voltage and current may be small to deposit any metal from its compound and directly relates to the efficiency of the process. The molten alkali and alkaline earth salts and their mixtures have good ionic conductivities thereby the energy consumption can be reduced by lowering the temperature of the operation. Molten salt electrolysis reduces the number of preliminary steps and can be performed in compact electrolytic cells as compared to aqueous electrolysis. A very high current density can be applied in fused salt electrolysis for the deposition of various metals from their compounds (Thonstad 1992). Electrowinning of metals by fused salt electrolysis has been attempted to metals that cannot be directly electrodeposited from aqueous baths. Among them, the most important metals such as lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radium (Ra), aluminium (Al), tantalum (Ta), thorium (Th), tellurium (Tu), titanium (Ti), vanadium (V), zirconium (Zr) and many rare earth metals and alloys, are produced by fused salt electrolysis (Viswanathan 1985; Lovering 1982; Mouron 1997; Osaka et al. 1997; Sunshot 2016). In particular, aluminium and magnesium are the important metals produced in tonnages by fused salt electrolysis (Kannan et al. 1986).

11.3.1 Important Parameters in Designing Efficient Molten Salt Systems

11.3.1.1 Chemistry of Molten Salt Baths

An ideal molten salt bath should have low vapour pressure and melting point, high decomposition potential and ionic conductivity, non-corrosive, and constitutes environmental friendly and low-cost materials. Even though a wide range of molten salt mixtures are available, only some of the salts possess the above mentioned properties. Thus the possible range of molten salts is wide ranging from the low melting structurally complex and predominantly covalent system such as $KAlCl_4$ to the high melting structurally simple and ionic systems such as NaCl (Viswanathan 1985).

The fused baths can be classified as,

i. Chloride melts
ii. Fluoride or Fluoride-Chloride melts
iii. Oxides dissolved in Fluoride-Chloride melts

Chloride baths are generally chosen for alkali and alkaline earth metals, because their respective chloride salts can be easily purified from their raw materials. Chlorides are preferred electrolyte melts for the purpose of increasing the conductivity and lowering the melting point of the bath. The chloride mixtures could be chosen in such a way that they should have a melting point above that of the metal to be electrodeposited. Hence, the electrodeposited metal could be obtained in the molten form. Chloride salts are inexpensive, less corrosive and have lower melting points than fluoride salts. However most of the chloride salts are hygroscopic which requires dehydration and handling in inert atmosphere (Gale et al. 1983; Mishra and Olson 2005).

In case of refractory metals such as Zr, Nb, Mo Hf, Ta and W with high melting points and reactivity, the electrolysis is performed at temperatures below the melting point of the metal and the metal is obtained in the form of crystals. The refractory metal fluorides are stable compounds and are comparatively non-hygroscopic. Hence, the electrolyte baths chosen for the recovery of refractory metals are a mixture of double fluorides and alkali metal fluorides (Osarinmwian 2019). Refractory metal chlorides have high volatility and in some cases, they possess poor conductivity such as titanium chloride which becomes disadvantageous for easy electrolysis. This problem can be resolved either by complexing their chlorides with appropriate solvents such as BeCl–NaCl wherein the melting point of the chloride salts is lowered resulting in less volatility.

Whenever oxides are employed, they are generally dissolved in fluoride melts. Hall-Herault process for the electrowinning of aluminium is an outstanding example in this category (Choate and Green 2000). The application of similar procedures in other cases has considerable difficulties because of the poor solubility of oxides in fluoride or fluoride-chloride melts. Electrowinning of tantalum from its oxide dissolved in $KCl–KF–K_2TaF_6$ is an example, which is industrially practised. Some of the important factors affecting the deposition process are solutes, volatility of the feed, formation of cluster compounds, formation of insoluble oxides and oxy-halides and stable oxy-cations.

(a) **Solutes**

The solutes should have physical properties such as common anion which facilitate the dissolution and high degrees of miscibility of the mineral in the molten melt. For example, the appreciable solubility of alumina in cryolite melt is a critical factor for the successful electrowinning of aluminium (Choate and Green 2000). The strength of the interactions between the cations of the solute and the anions of the solvent and between the anions of the solute and the cations of the solvent are considered for the better solubility of the solute in the melt.

(b) **Fusibility**

Fusibility of mixtures of salts employed in molten salt electrolysis varies widely depending on the components of each system. Eutectic mixtures whose melting points are very low compared to individual components of the salts are used in molten salt electrolysis. For example, eutectic mixtures can have a melting point as low as 425 °C for the salt mixtures of $NaCl$–KCl–$MgCl_2$ whose individual melting points are 804, 790 and 712 °C, respectively. Practical molten salt baths necessarily do not employ a universal eutectic composition, as efficient electrolysis requires only a stable and clear molten melt and it may vary depending on the metal to be deposited (Vol'skii and Sergievskaia 1971).

(c) **Volatility of the Feed**

Fluoride solutes have less volatility in fluoride melts than in chloride melts. In some cases, a mixture of chlorides and fluorides is used in the electrowinning of refractory metals. In such conditions, the fluoride ions will complex with high oxidation state refractory metal ions more strongly than the chloride ions and are stabilized in the melt. For example, in the case of electrowinning of aluminium using aluminium chloride, its volatility can be reduced by the addition of fluoride in the melt which forms complexes such as AlF^{4-} and AlF^{6-} (Choate and Green 2000). In certain cases, this effect can be complicated by disproportionation reactions as observed during the addition of fluoride ions to stabilize Ta(IV) ions in LiCl–KCl eutectic melt; $5Ta^{4+} \rightarrow 4Ta^{5+} + Ta$ (Thonstad 1992). This reaction is possible due to higher valency of tantalum resulting in the formation of a stable complex. Further, the refractory metal ions can exist in different oxidation states; for example, tantalum can exist in oxidation states $+5$ to -1. As a result, tantalum chloride can undergo disproportionation reactions in the pure state at relatively low temperature and both homogeneous and heterogeneous disproportionation equilibrium are possible in chloride melts (Thonstad 1992).

$$2Ta^{4+} \rightarrow Ta^{5+} + Ta^{3+}$$

$$3\mathrm{Ta_6Cl_{18}^{4+}} + 16\mathrm{Cl^-} \rightarrow 4\mathrm{Ta} + 14\mathrm{TaCl_5^{2-}}$$

Similar reactions have been reported during titanium metal deposition in molten electrolytes in the presence of fluoride ions in the melt (Chamelot et al. 2000). While the disproportionation nature of the higher oxidation state of refractory compounds and their importance in electrolysis has been studied, refractory metal ions in lower oxidation states can occur as intermediates of the overall cathodic reduction process. The formation of such insoluble and soluble compounds with such diverse chemistries and their consequent disproportionation may or may not inhibit the overall reduction process.

(d) **Formation of Cluster Compounds**

Cluster compound formation is a particular feature of the lower oxidation states of the heavier refractory metals. While the cluster formation is thermodynamically favoured, it may be kinetically hindered. Tantalum can be produced from $\mathrm{TaCl_5}$ at positive electrode potentials with reasonably high current efficiency due to the anodic formation of clusters in the molten melts; $20\mathrm{MCl} + 16\mathrm{Ta} + 14\mathrm{TaCl_5} \rightarrow 5\mathrm{M_4Ta_6Cl_{18}}$ (Thonstad 1992; Chamelot et al. 2000; Sehra and Vijay 1998) where M = $\mathrm{Na^+}$, $\mathrm{K^+}$, $\mathrm{Li^+}$. On the other hand, niobium metal is produced with a low current efficiency because of the formation of clusters in the NaCl melt (Sehra and Vijay 1998).

(e) **Formation of Insoluble Oxides and Oxy-Halides and Stable Oxy Cations**

While the presence of alkali and alkaline earth metal oxides as impurities in the product is inevitable, they can have deleterious effect on the product formation. For example, oxypolynuclear anions or insoluble oxides may be formed as insoluble films on the electrode surfaces by the reactions between oxide ions and metal ions in a lower oxidation state (Jeong et al. 2008). On the other hand, the deposition of metal oxides from stable oxy-cations can be an inherent feature of molten salt electrolysis. For example, when $\mathrm{UO_2Cl_2}$ is dissolved in halide melt, the $\mathrm{UO_2^{2+}}$ cation is formed and the cathodic reduction produces $\mathrm{UO_2}$ (Dubrovskiy et al. 2018). On the other hand, there is an evidence for the formation of stable oxy anions during the aluminium electrowinning bath ($\mathrm{AlOF_5Cl^{4-}}$, $\mathrm{AlOF_3^{2-}}$) which are discharged at the anode (Sehra and Vijay 1998).

11.3.1.2 Electrochemical Aspects of Molten Salt Systems

(a) **Conductivity**

Molten salts are good conductors of electricity. Their conductivities are considerably greater than the conductivities of the same salts in their aqueous solution. For example, molten KCl at 800 °C has a specific conductance (K) of 2.24 mho/

cm, whereas for an aqueous solution of KCl at 20 °C, K is 0.1 mho/cm. Increase in temperature decreases the viscosity, and increases the conductivity in most of molten salt systems (Redkin et al. 2012). While an increase in temperature is expected to increase the conductivity linearly, fused salt mixtures do not usually follow such a trend but deviate from the law of mixtures.

(b) **Electrode and Decomposition potentials**

In the case of aqueous electrolysis of pure salt solutions, the potential (E_{cell}) of the cell depends upon the activity of the conducting ion, and the question of concentration or activity does not generally arise. Since, all the reactants are in pure state, they have unit activities and hence the electrode potentials are standard potentials. However, in the case of mixtures of salts, the deposition potential will depend on the concentration of the salt corresponding to the metal used as the electrodes (Castrillejo et al. 2002).

$$E_{deposition} = E_0 + RT/nF + \log A$$

wherein A is the activity of the conducting ions

(c) **Kinetic factors**

Kinetic limitations in the processes are minimal at high temperatures. Three main factors are considered with regard to the formation of metal deposition from soluble solution species.

- Solute mass transport
- Electron transfer
- Coupled chemical reactions and nucleation and growth

Electron transfer reaction of metal ions leading to metallization is generally rapid at interfaces in molten salt systems due to high exchange current densities. However, this may not be the case for many refractory metals. For example, the electron transfer reaction in the reduction of Mo(III) to Mo(0) in NaCl–KCl melt is characteristic of a slow charge transfer process as the overall rate is controlled by the rate of the preceding chemical reaction leading to the formation of Mo polynuclear complex ions and not by the electron transfer step (Andrew et al. 2020). Nucleation overpotential is another critical factor controlling the metal deposition process. In many cases, the deposit of metal is in dendritic form and is occluded with solidified melt which is subsequently removed by a leaching step. Powdery deposits can arise due to secondary processes like disproportionation reactions near the surface or the chemical reactions between the deposited alkali metal and metal ions as the alkali metals diffuse away from the electrodes (Inman and Lovering 1983; Redkin et al. 2012; Castrillejo et al. 2002; Gleb Mamanto 1987; Senderoff 1966; Inman and White 1978). Coherent metal deposition from fluoride melts may be partly attributed to the interfacial effects .

(d) Current Efficiencies and Critical Current Densities

The productivity of an electrolytic cell is expressed by current efficiency in terms of Faraday's laws of electrolysis. It is defined as the ratio of the number of equivalents of metal produced to the number of moles of electric charge passed into the cell from external power source. Current densities of about 1 A/cm^2 are common in molten salt electrolysis and the cathodic current efficiencies remain in the range 60–80% (Choate and Green 2000). In fused salt electrolysis, the deposition of the metal at the cathode is realized only at current densities above a critical value. When the current density is raised subsequently the rate of the cathode metal production is greater. The current efficiency may be zero at low current densities if the losses are greater or equal to the rate of the formation of electrode products. The maximum limit of the current density is set by heating effects, increase in IR drop, anode effects and metal formation. The factors which lead to lower current efficiencies during electrolysis are;

a. The mechanical losses occurring during the product formation are carried away in the slimes or entrapped in the cell lining.
b. Distillation, volatilisation or sublimation of the products may be controlled by adjusting the temperature of electrolysis.
c. Mixing up of the electrode products, such as the recombination of anodic chlorine and cathodic product may be minimized by employing a suitable diaphragm between anode and cathode.
d. Undesired reactions between the product of electrolysis and the materials of construction, or the reaction with gases at the vicinity of the electrodes.
e. The current efficiency may be reduced due to the formation of lower compounds at the cathode (e.g. $CaCl_2$ instead of Ca) or higher compounds at anodes (e.g. $SnCl_4$ instead of Cl_2).
f. The current efficiency may also be reduced by simultaneous deposition of several ions at the electrode surface, for example in the case of Mg extraction, the lower current efficiency may be due to the presence of moisture in the cell feed which leads to the decomposition of H_2 and O_2.
g. Dissolution of deposited metal in fused salt melts:

   There is a loss in current efficiency by the dissolution of the deposited metal in the fused salt itself. For example, in the case of Na metal extraction using fused sodium hydroxide, the metal may dissolve completely in the molten electrolyte if the temperature exceeds 350 °C. In some cases, the formation of sub-salts may lead to the dissolution of metal in the fused salts. The dissolved metal is totally dispersed in the bath which causes colour change in the melt and is termed as "metal fog". The solubility of metals is more in pure salt melts than in a mixture of salts, hence mixed salts are employed in many of the electrowinning processes.
h. Anode effect:

   The anode effect often occurs during the electrolysis of fused baths and is frequently seen in the production of aluminium by Hall-Heroult process (Haupin and Frank 1981), titanium and tantalum metals. The effect will abruptly increase the cell voltage wherein the cell current reduces to almost zero. Such a situation arises due to the formation of a gas film surrounding the anode surface offering high resistance during electrolysis. The anode effect will disappear when the surface of the anode is cooled or stirred. In addition, the current density can be minimized thereby the gas film collapses and the evolution of the gas reappears.

11.4 Extraction of Alkali and Alkaline Earth Metals Through Molten Salt Electrolysis

In general, the conventional metallurgical processes such as carbothermic reduction of metal salts to their respective metals are considered energy intensive and emit large amounts of greenhouse gases as by-product (Springer and Hasanbeigi 2016; WS 2008). Availability of electricity from renewable energy sources can change this scenario. Molten salt electrolysis is considered in the large scale production of alkali and alkaline earth metals such as lithium, sodium, magnesium and calcium. These metal salts exhibit extremely negative Gibbs free energies of formation, enabling high electrochemical decomposition potential to produce alkali and alkaline earth metals (WS 2008; Sohn and Geskin 1990). In molten salt electrolysis, steel and graphite are used as cathodes and anodes, respectively. The primary cathodic and anodic reactions are the reduction of metal and chloride evolution, respectively (Mishra and Olson 2005; WS 2008; Fray n.d.; Minh 1985). The annual production of lithium is 25,000 tonnes per year, while sodium accounts for 100,000 tonnes per annum. On the other hand, 20,000 tonnes of calcium is produced annually and owning to their structural applications in diverse technologies, magnesium accounts for the highest production of about 766,000 tonnes per year. China is one among the major producers of these reactive metals. This section will summarize the recent advancements in the chemistry and engineering aspects for the production of lithium, sodium, magnesium and calcium through molten salt electrolysis.

11.4.1 Electrowinning of Sodium Metal Through Molten Salt Electrolysis

Sodium (Na) is a highly reactive metal next to lithium and potassium and is well known that sodium metal reacts vigorously with water and tarnishes when exposed to the environment. Na is used as a reducing agent and as a coolant in heat exchangers in nuclear industries (De NoraPlacido et al.; Thayer 2008).

In 1888, Hamilton Castner introduced the production of sodium through Castner's cell which operates at a temperature of 330 °C to produce Na metal from sodium hydroxide. The Castner cell primarily consisted of anode and cathode either made of iron or nickel. Na metal is formed at the cathode and oxygen evolution occurs at the anode. The chemical reaction is given below,

$$4Na^+ + 4e^- \rightleftharpoons 4Na$$

$$4OH^- \rightleftharpoons O_2 + 2H_2O + 4e^-$$

The only side reaction at the cathode is hydrogen evolution due to the diffusion of water into the electrolyte resulting in the reduction of the cathodic efficiency of the process (De Nora et al.; Hine 1985; Gilbert 1952). In 1922, the Castner cell was replaced by Down's cell for the production of Na metal. Down's cell primarily consisted of four anodes and cathodes each with a steel or iron gauze diaphragm preventing the recombination of the products (Cl_2 gas and the metal). Unlike, Castner's process, the anodic reaction is Cl_2 evolution, since sodium chloride was used as the raw material. Graphite rods were used as anodes and steel plates were used as cathodes. The old-style Down's cell was operated at 50 KA in a molten melt of $CaCl_2$ and NaCl at a temperature of 600 °C. Modified Down's cell employed a molten salt electrolyte consisting of NaCl (28 wt%), $CaCl_2$ (25 wt%) and $BaCl_2$ (47 wt%) at a temperature of 600 °C. The cell was operated with an optimized current density of 1 A/cm^2 and a cell voltage of 7 V. The specific energy consumption was about 10 kWh/Kg of Na produced. The current efficiency of the process was as high as 90% (Ghareh Bagh et al. 2013; Kepler et al. 2001; Stewart and Michael 1961). The electrolyzer comprises of a metal collection chamber to collect the floating metal. The cell consists of electrolyte, electrodes and an absorption system, made of three packed columns containing NaOH solution, to collect the liberated chlorine gas. The main challenge for successful production of Na metal relies on preventing the recombination of Na metal and Cl_2 gas. Calcium chloride was used as the supporting electrolyte due to an increase in the conductivity of the electrolyte (Hine 1985; Thompson et al. 2002). In addition to the above, Ca can reduce the Na from NaCl electrolyte during electrolysis.

11.4.2 Electrowinning of Lithium Metal Through Molten Salt Electrolysis

Being one of the most anodic (or least noble) metals in the electromotive force series, lithium metal is the primary candidate as electrode material for the fabrication of new generation energy applications. Moreover, Li is also utilized in the production of organolithium compounds and also as an alloying addition to Al and Mg. Unlike Mg, Li is not a structural material but is widely employed as a chemical reagent in various chemical reactions. Li metal had many historical applications in the production of lithium greases in World War II and in the fabrication of nuclear weapons. In the modern days, the demand for Li metal is steadily increasing due to its applications in the energy sector. It is expected that Li metal will capture the market share similar to Mg metal widely employed in structural applications. Li is used to reduce the melting temperature of glass and aluminium oxide in the electrolytic production of aluminium. Australia, Chile and China are the major producers and exporters of lithium metal (USGS 2021). Due to its high reactivity, the metal does not exist in elemental form. It is disseminated in hard rocks and as brine in sea water. It is estimated that 230 billion tonnes of lithium content is available in sea water. Lithium aluminium silicate (Spodumene) is an example of a hard rock source of lithium (Dessemond et al. 2019). The silicate based material is transformed to carbonate form by alkali roasting and treating with acid, followed by calcination and carbonation (Margarido et al. 2014). The potassium lithium sulphate salt obtained from the brine of sea water is converted to carbonate after removal of K^+ ions. Finally, the obtained lithium carbonate is converted to chloride salt by treating with chlorinating agents such as HCl or Cl_2 gas (Yan et al. 2012). Similar to Na metal production, Lithium metal is extracted from the purified LiCl using the modified Down's cell. Here, the electrolyte employed comprises of LiCl and KCl eutectic melt with an operating temperature between 400 and 460 °C. Anhydrous LiCl is employed as the cell feed with high density graphite as the anode and mild steel as cathode. Chlorine (Cl_2) gas evolves at the anode and Li metal floats at the top of the melt. Due to low density of Li, the metal is collected in the bell shaped reaction chamber. The current density and energy consumption for ideal production of Li have been optimized to be 2 A/cm^2 and 35 KWh/Kg respectively. In order to reduce the melting point of LiCl (606 °C), KCl is employed as a supporting electrolyte. Li is generally stored in liquid petroleum, due to its recombination with chlorine. The current efficiency is generally between 50 and 60%. The other production processes employed, reduction of lithium oxide and hydroxide using carbon or iron carbides as the reductant has also been reported (Kipouros and Sadoway 1998). Metallothermic reduction of oxides and hydroxides under vacuum using Mg, Al, Ca and Si can be employed to obtain Li metal (Gourishankar and Karell 1999).

11.4.3 Calcium Metal Production Through Molten Salt Electrolysis

Calcium (Ca) metal is the fifth most abundant metal constituting 3.64% of the earth's crust. The most important source of the metal and its compounds are calcium carbonate, limestone, marble, calcite and aragonite. Like Mg, Ca is an effective reducing agent and its widely used for the reduction of other metals like Ti, V, Cr, Zr, Ta, W, Th and U. At elevated temperatures, it reacts with metallic oxides or halides to form its corresponding metal. It also combines with many metals forming a wide range of alloys and intermetallic compounds (Ca–Mg, Ca–Pb, Ca–Cu and Ca–Ni alloys). Calcium and its alloys find wide applications in a variety of processes including ferrous and non-ferrous metallurgy (Heilig 1994; Panigrahi et al. 2013; Ono et al. 2009). Demand for Ca is rising steadily, China is believed to be the world's largest producer and most important exporter. World production of Ca is estimated to be about 2500 tonnes per annum. The metallurgical applications account for about

90% of total Ca consumption. The steel industry uses Ca as a ladle addition to assist desulphurization and deoxidizer to produce killed steels. Total consumption in the steel industry is estimated to be about 650 tonnes per annum. The growing market of Ca metal accounts for 400 tonnes per annum.

Two major methods for the production of calcium metal are,

1. Thermal reduction of lime with Al under vacuum and
2. Electrolysis of fused calcium chloride.

Since nineteenth century, strenuous efforts have been made to produce calcium through molten salt electrolysis. The solubility of calcium in the melt seriously hampered the efficiency of the process. USA and Germany successfully conducted experiments to produce calcium ingots. The lower energy efficiency and impure product hindered the commercialization of the process. Zaikov et al. demonstrated an electrolytic process with the operational parameters to produce calcium with high current efficiency. The same group developed an improved version of the electrolyzer (0.5–3.0 A) to produce high purity calcium (Zaikov et al. 2014a, b).

An improved molten salt electrolytic process for the production of calcium metal was developed by CSIR-CECRI, using calcium chloride as the molten electrolyte. High purity Ca metal was produced in a single stage reactor with new cell design using commercially available raw materials. Anhydrous $CaCl_2$ with the addition of alkaline and alkaline earth salts was used for the efficient production of Ca metal. The electrolyte comprises of 85% $CaCl_2$, 15% NaCl, KCl and CaF_2. Mild steel cylindrical cell with fixed circular anode was used for the process. Cylindrical graphite with suitable arrangements was indented for the electrolysis (Lukasko and Murphy 1990). During electrolysis, calcium metal was deposited at the cathode and it was periodically collected and kept in high density diesel oil. The electrolyte level and the concentration were maintained with regular additions of $CaCl_2$. The metal obtained was purified by vacuum melting techniques depending on its application. An optimized electrolyte process was developed at CSIR-CECRI with different concentrations of electrolyte, current densities and cell voltage. The electrolytic cell was operated at 1000–1500 A capacity producing 10–12 kg/day (Berchmans 2003).

11.4.4 Production of Magnesium Metal Through Molten Salt Electrolysis

Magnesium metal because of its light weight, superior strength and its tendency to form alloys with many metals, finds several applications in defence, aerospace and nuclear sectors. Even though the resources for magnesium metal are widely distributed in nature, the cost of the metal is high due to high energy involved in its extraction. The world's production of magnesium has been growing steadily because of its demand both in domestic and industrial sectors. Over 50% of magnesium is consumed for alloying with aluminium to increase the strength and other properties for structural applications. Die cast magnesium alloys find applications in automotive and computer industries. Global magnesium metal market is expected to grow significantly owing to increasing demand in automotive sector and for the fabrication of Al–Mg alloys. The demand for Mg metal has steadily increased because of its applications including new batteries, light weight metal alloys, and wind turbines, capturing of CO_2, production of iron and steel, Ti and Zr metals. Mg scrap, wastes from metallurgical and agro-chemical industries are the sources of raw materials for the production of Mg metal.

Commercially, electrowinning of Mg metal is carried out by two processes namely, I.G. Farben and Dow's process. The primary difference in the processes lies in the Mg feed. I.G. Farben process employs anhydrous $MgCl_2$, whereas, Dow's process works with hydrated salts of $MgCl_2$ ($MgCl_2 \cdot 1.5–1.7H_2O$). The precursor for Mg is from brine which approximately comprises of 0.13 wt% of Mg. In general, Mg^{2+} ions are precipitated by the addition of calcium oxide (CaO). The precipitation of insoluble $Mg(OH)_2$ is acidified to yield $MgCl_2$. Dow's process employs 25%$MgCl_2$, 15%$CaCl_2$ and 60%NaCl, with the cell operating temperature of 700 °C. In Dow's process, the graphite anode is consumed by the reaction of graphitic carbon with water to form H_2 and CO_2. Electrowinning of Mg through I.G. Farben and Dow's process consumes ~10.5–18 Kwh/Kg of Mg with a purity of 99.9%. Technological improvements has been attempted to reduce the cell voltage, and in the development of alternate inert anodes as the replacement for conventional reactive carbon based anodes. The molten salt electrowinning experiments were performed at temperatures between 680 and 750 °C, using electrolyte melt comprising of $MgCl_2$ (20.5 wt%), NaCl (39 wt%), $CaCl_2$ (39 wt%) and KCl (1.5 wt%). During electrolysis, H_2 gas was purged into the anode compartment. The overall cell reaction of the modified Mg electrowinning cell is given below,

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

$$Mg^{2+} + 2e^- \rightleftharpoons Mg$$

$$MgCl_2 + H_2 \rightleftharpoons Mg + 2HCl(g)$$

Yen et al. developed inert niobium doped TiO_2 electrodes as a replacement for conventional reactive graphite anodes. The fabricated electrodes with 3 mol% of Nb_2O_3 sintered at 1300 °C were found to be more efficient for Mg electrolysis (Yan and Fray 2010). Sharma et al. investigated an electrowinning process, where MgO was dissolved in neodymium chloride to form $NdOCl_3$ and $MgCl_2$. The overall reaction of the process is the formation of metallic Mg and CO_2 (Sharma 1996). Lu et al. reported a process of dissolving MgO in $LaCl_3$–$MgCl_2$ electrolyte using steel and carbon as cathode and anode respectively (Lu et al. 2016). The main products were metallic Mg and CO_2 respectively with current efficiency of >85% and energy consumption of 12 kWh/kg of Mg. Cost of the rare earth salts is the primary and crucial disadvantage of the process. Pal et al. developed a synthetic route for the preparation of Mg and other metals using solid oxide membrane (Pal et al. 2001). In this process, solid-oxygen-ion-conducting stabilized ZrO_2 electrolyte separates the inert cathode and anode. The main products of this process are $H_2O_{(g)}$ and metallic Mg. Krishnan et al. reported the production of Mg using solid oxide membrane, from MgO dissolved in fluoride salts at 1300 °C. The cell was operated at a current density of 1 A/cm^2, with a cell voltage of 4.5 V and power consumption of 9–12 kWh/kg of Mg (Krishnan et al. 2005).

CSIR—Central Electrochemical Research Institute, Karaikudi (CECRI) has carried out significant work for more than two decades on the production of magnesium (Mg) metal using various raw materials like magnesite, sea bittern and anhydrous magnesium chloride.

1. Mg metal production from Low grade Magnesite ore as the primary source.
2. Sea bittern is a waste liquor produced from salt panes.
3. By-product Magnesium chloride ($MgCl_2$) from Titanium (Ti) and Zirconium (Zr) manufacturing plants.
4. Magnesium hydroxide $(MgOH)_2$ from chemical industries.

Pilot plant investigations were undertaken in all aspects of Mg metal production by molten salt electrolytic process.

1. Production of Mg Metal from Low Grade Magnesite Ore

CSIR-CECRI has tried for the production of magnesium metal from low grade Magnesite ore, which is extensively available in our country. In this process, finely ground magnesite ore was treated with HCl, resulting in the production of slurry and a clear solution of $MgCl_2$. This filtered solution was spray dried to produce fine powder of anhydrous magnesium chloride. The $MgCl_2$ powder was used as the cell feed for the electrolyzer. The molten electrolyte consisted of $MgCl_2$, NaCl and KCl salts. Electrolysis was performed by using mild steel cathode and graphite anode. Eutectic salt mixture was periodically fed into the electrolyzer and the molten magnesium metal was produced and casted in steel moulds.

2. Mg Metal Production Using Sea Bittern

Sea bittern a by-product from salt industries is considered a waste and disposed off into the sea. This solution was used as raw material for the production of Mg metal. Bittern solution consists of a fairly good concentration of magnesium chloride, obtained after the crystallization of common salt. The vast establishment of a number of salt farms around the coastal area is one of the major sources for the production of Mg metal. The solar heat available in plenty is used to concentrate the sea bittern.

CSIR-CECRI undertook the task of beneficiation of sea bittern to make it suitable for the production of magnesium metal. The concentration of the bitterns was identified as 36°Be. CSIR-CECRI has evolved a process for the removal of sulphate and boron which are considered as harmful impurities present in the concentrated brine. The process involved the separation of sulphates as calcium sulphate ($CaSO_4$) by treating with calcium chloride ($CaCl_2$) solution. The filtered solution has a concentration of $MgCl_2$ around 380 g/l, which is sufficient for the production of anhydrous magnesium chloride by spray drying process. Spray dryer was operated to produce anhydrous $MgCl_2$, having 85–90% $MgCl_2$ with 4–5% MgO and the rest being H_2O. The spray dried $MgCl_2$ was used as the raw material for the electrolytic cell. CSIR-CECRI also undertook the task of upgrading the electrolysers and developed the modular cells which brought down the energy consumption up to 16 kWh/kg.

Based on the CSIR-CECRI process, Tamil Nadu Magnesium and Marine Chemicals Ltd (TMML), Govt. of TamilNadu has put up a 600 TPA production plant at Valinokkam. The commercial plant started its operation in 1989. However, TMML could not be in operation after an year due to high humid and high wind velocities at their site. Due to high moisture content in the feed, large quantity of sludge was formed which lead to lower efficiency in metal production. These problems lead to passivation of cathodes which resulted in poor coalescence of the metal. Tiny magnesium metal globules recombined with anodic chlorine gas thereby the current efficiency was lowered. All these factors made the operation of plant difficult and due to these issues, TMML stopped its operations in 1993.

3. By-Product Magnesium Chloride ($MgCl_2$) from Titanium (Ti) and Zirconium (Zr) Manufacturing Plants

Magnesium is used as a reducing agent in Kroll's process for the manufacture of zirconium, titanium metals etc. $MgCl_2$ is produced as a by-product after the reduction of $TiCl_4$ and $ZrCl_4$. CSIR-CECRI and Nuclear Fuel complex (NFC), Hyderabad had developed a process for the production of Mg metal by using anhydrous magnesium chloride, which is a byproduct generated from the zirconium plant. Magnesium metal was produced with modular type, bipolar and multi-polar cells with active support from DMRL and NFC. DMRL-Hyderabad had set up a large scale Ti-sponge production unit for which, a captive Mg plant was jointly established by CSIR-CECRI and DMRL consisting of two 30 and 42 KA electrolytic cells at their site. Ti-sponge plant and the Mg plant had been operated for more than six years. The DMRL team had tried with different raw materials for the production of magnesium metal.

4. Magnesium Hydroxide $(MgOH)_2$ as Raw Material from Chemical Industries

Magnesium metal production was also tried using Magnesium hydroxide $(MgOH)_2$ as the raw material supplied from Birla Periclase. Concentrated $MgCl_2$ solution was prepared by dissolving magnesium hydroxide $(MgOH)_2$ in concentrated HCl solution. From this solution, anhydrous $MgCl_2$ was prepared by spray drying process. Then, it was used as the raw material for producing magnesium metal through molten salt electrolytic process.

Bipolar Technology Developed at CSIR-CECRI Karaikudi

There has been a tremendous interest in bipolar electrode configuration for the production of strategic metals like Aluminium (Al) and Magnesium (Mg). The advantages of the cell are compactness, high energy efficiency and flexibility in cell voltage and current. This bipolar cell allows with smaller bus bar without sacrificing the voltage. The production of Mg metal comprises of facing anode and cathode surfaces defining an inter-electrode space, through which the electrolyte is caused to flow. Chlorine is evolved at the anode surface molten metal is generated at the cathode surface and it is collected in a metal collection zone. If the metal and chlorine come into contact, they recombine and reduce the current efficiency. Recombination reaction can be reduced or prevented by separating the facing anode and cathode surfaces by introducing diaphragms. But the introduction of diaphragms increases the internal resistance of the cell.

A proto-type ALCAN tapered anode cell of the capacity of 80 KA (ALCAN Company) with small anode cathode distance could be used to advantage for the reduction of specific energy consumption. But the basic problem was the excessive heat generated at the electrodes. The most direct way to obviate the heat generated when operating at low specific energy consumption is by adopting a multi-polar cell design. Bipolar electrodes are valuable to increase the effective cathode area, where the metal formation can take place without either increasing the size of the cell or increasing the heat and power loss. Because of these bipolar electrodes, the productivity of the cell is nearly double. But in practise, a portion of the current bypasses the bipolar electrode and flows around it. The loss becomes one of the inherent factors, and can be minimized by inserting additional bipolar electrodes between anode and cathode to increase the cell productivity.

Dow had explored cell designs of this type in 1940's after that, the first ALCAN multi-polar cell of capacity 40 KA was installed in 1980 at Ocska Titanium company. Several configurations were tested before operating the cell at 80–140 KA capacity by the same company in 1982. The production of Magnesium 1000 MT/cell/year with a specific energy consumption of 9.5–10 KWh/Kg was tried. Comparative assessment of the tapered anode and multi-polar cell revealed that the later showed both capital and operating costs lowered by about 1/3.

The Ishizuka Research Institute Japan has developed a bipolar cell in 1983 and operated by Showa Titanium, Toyama. Five bipolar electrodes (Steel-Graphite) were used in the cell. The cell was operated at 670 °C and carried out 50 KA corresponding to 300 KA in a mono-polar cell. Current density was 5600 A/m^2 and the inter-polar gap of 4 cm. The power consumption was 11 KWh/Kg of Mg using molten $MgCl_2$ from Kroll's Titanium production. Ishizuka preferred electrolyte composition of 50% NaCl, 30% KCl and 20% $MgCl_2$. A European patent filed by Ishizuka Hiroshi described a method for electrolytically obtaining Mg metal. The electrolytic bath is composed of $MgCl_2$ and additional ingredients, with a bath density of 0.02–0.10 g/cm^3. The electrical conductivity of the bath was 2.4 Ω^{-1} cm^{-1}, holding magnesium metal at the surface of the electrolyte. Six intermediate bipolar electrodes were used. Each electrode consisted of an iron plate joined to a graphite slab with several bolts of iron implanted at one end in the graphite and welded to the iron at the other end.

In 1989, Hiroshi Matsunami et al. of Toho Titanium company filed a patent where, the electrolytic cell comprised of an anode, cathode and plurality of bipolar electrodes. A first partition wall is provided with partition openings situated beneath the level of the electrolyte. A second partition wall is comprised of an intermediate chamber between the first and the second partition walls for the removal of chlorine gas. A metal collection chamber was formed between the second partition wall and the front wall of the electrolytic cell and a control plate for preventing the deposition of sludge.

CSIR Central Electrochemical Research Institute (CECRI) Karaikudi, has undertaken the task of upgradation of the production of Mg metal by utilizing $MgCl_2$ (obtained from Zirconium and Titanium production) through adopting bipolar and multi-polar cell technology. Research activities had been focused on the development of stable heterogeneous bipolar electrodes, design and construction of different configurations of cells and the role of current density and energy efficiencies, etc. In CSIR-CECRI, bipolar cells of different capacities ranging from 0.5 to 6 KA were operated. These included graphite plates coated with electrodeposited or plasma sprayed iron on one side and snugfit type graphite-mild steel plates on the other side. Graphite-mild steel plates were connected with mild steel spacers in between the electrode configuration. Inter-polar gaps ranging from 1.5 to 3.5 cm and current densities ranging from 0.8 to 1.25 Acm^{-2} were tried. Electrolytes containing ternary $NaCl–KCl–MgCl_2$ and quaternary $NaCl–KCl–BaCl_2–MgCl_2$ systems were studied in bipolar electrolytic cells. Multi-polar cells with two and four modules were also designed and operated with varying capacities.

11.5 Molten Salt Electrowinning of Refractory Metals

The nine transition elements of Groups IVA, VA and VIA of the periodic table, comprising of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W, are known as the refractory metals because of their high melting points and the refractory nature of their compounds (Inman and White 1978; Konings et al. 2014). Refractory metals exhibit attractive mechanical, physical, corrosion resistance and nuclear properties. There has been a renewed interest in these metals in recent years (Tyrer and Gibbon 2012). Specifically, emerging applications in nuclear and aerospace industries under extreme conditions have increased the demand for titanium, niobium and zirconium. Many of these applications demand metal of very high quality whereas the extraction of refractory metals remains difficult due to their complex chemistries and ability to exist in multiple oxidation states (Industrial and Processes 2021; Sehra and Suri 1993).

Refractory compounds exhibit a fascinating array of properties (Liddell and Sadoway 1990). For example, the borides and nitrides are excellent electronic conductors; the electrical conductivities of TiB_2 and TiN exceed that of titanium metal itself (Liddell and Sadoway 1990). Due to their heat and erosion resistance, the carbides find usage in cutting tools. The silicides are used as heating elements in electrical resistance furnaces for service at elevated temperatures under oxidizing conditions. The compounds comprising the borides, carbides, nitrides and silicides of the refractory metals are also termed as ‘refractory hard metals’. Due to their unique properties suitable for specific critical applications, many of the refractory metals are considered strategically important.

The primary extraction of refractory metals can be accomplished in two ways; thermo-chemical and electrochemical methods (Inman and White 1978; Al-Jothery et al. 2020). The thermo-chemical extraction, practised especially with metals of Groups IV and V, involves metallothermic reduction of a refractory metal compound. The refractory compounds used are oxides, fluorides or chlorides; the reductant is primarily chosen from among aluminium, magnesium, sodium and calcium, although other reactive metals have also been used. For example, titanium metal is produced by the Kroll process which is based upon the reaction of titanium tetrachloride with magnesium.

Electrochemical extraction involves the electrolytic reduction of a refractory metal compound dissolved in an ionic medium. Aqueous solutions are unsuitable as electrolytes for the electro-reduction of the refractory metals, with the exception of chromium, because of the lower stability of water. Therefore, there is a need to use non-aqueous electrolytes, viz., organic solvents and molten salts. Due to their poor ionicity, low electrical conductivity, low flash points and violent reactivity with water, organic electrolytes are unsuitable for electrowinning of refractory metals (Huang et al. 2016). Therefore, molten salt eutectics are the only class of electrolytes suitable for the electrochemical extraction of refractory metals.

Because of high melting points and high densities of some of the refractory metals, preparing them in the liquid state involves high temperature operation above 1923 K and tapping at the bottom of the electrolytic cell, unlike light metals which are generally tapped at the top of the cell (Chenyao et al. n.d.). Therefore, the production of these metals in liquid state is not advisable; instead, the metal deposition is performed in solid state. Oxides, halides and double fluorides have been suggested as functional electrolytes for the electrodeposition of refractory metals (Chamelot et al. 2000). Oxides, except for MoO_3, have very high melting temperatures and cannot be electrolyzed directly. Suitable solvents, called carrier electrolytes, are required to dissolve them. The selection of a carrier electrolyte depends on the choice of the functional electrolyte. For example, if the oxides are functional electrolytes, the carrier electrolytes must possess high solubilities (Jeong et al. 2008).

The fused salt electrolytic process is a promising route for the preparation of refractory metals and offers the possibility of metals being produced continuously at a much lower cost than the metallothermic processes. During the electrowinning of the refractory metals, two kinds of reactions occur in the melts; homogeneous reactions of the type: $M^{(n+z)+} + \mathrm{ne}^- \rightarrow M^{z+}$ where $M^{(n+z)+}$ and M^{z+} are two oxidation states of the same metal ion; heterogeneous reactions leading to the metal deposition: $M^{n+} + \mathrm{ne}^- \rightarrow M^0$ (Dubrovskiy et al. 2018). The potentials corresponding to each of these reactions are linked to the Gibbs free energy of formation of salt solutions (Lantelme and Groult 2010). Table 11.1 compiles representative literature on molten salt eutectics and electrowinning parameters for obtaining high purity refractory metals (Sehra and Vijay 1998). In the electrolytic production of molybdenum (Mo) and tungsten (W), oxyionic baths are preferred than the chloride and fluoride based baths due to the volatile nature and they do not have the tendency to form stable complexes with alkali or alkaline earth metal chlorides (Lantelme and Groult 2010).

Table 11.1 Molten salt electrowinning of refractory metals: representative bath compositions and electrowinning parameters

Metal	Type of electrolyte	Operating temperature (K)	Molten eutectic system	Operating voltage (V)	Cathode current density (A/cm^2)
Ti	Chloride	1073	NaCl–KCl–$TiCl_4$	9.5–9.8	3
	Fluoride	1123–1223	NaCl–K_2TiF_6	5.7	0.95
Zr	Chloride	1073	NaCl–NaF–$ZrCl_4$	5.3	0.323
	Fluoride	1073–1123	NaCl–KCl–K_2ZrF_6	2.0–2.5	5
	Oxide	1273	NaF–ZrF_4–ZrO_2	2–3.8	2
Hf	Chloride	838	NaCl–KCl–$HfCl_4$	2.4–7	0.19–1.15
	Fluoride	1123	NaCl–K_2HfF_6		
Nb	Fluoride	1173	KF–K_2NbF_7		
	Oxide	1025	KCl–KF–K_2NbF_7–Nb_2O_5	2.5	
Ta	Fluoride	1023	NaCl–KCl–K_2TaF_7	2.7–3.4	0.75
	Oxide		K_2TaF_7–Ta_2O_5		0.17
Mo	Chloride	1323	$CaCl_2$–$CaMoO_4$		0.5–5
	Oxide	1273	$Na_2B_4O_7$–NaCl–NaF–MoO_3	8–12	0.38
W	Fluoride	1073	NaCl–NaF–$KAlF_4$–WO_3	5.0–7.5	3.5
Cr	Oxide	1173–1193	NaCl–Cr_2O_3–C	3.5–4.5	1.6–5.5

Recently, one of the authors (M.J.) reported electrodeposition of tantalum based superalloys using deep eutectic solvents (Andrew et al. 2020).

11.6 Rare Earth Metals

Rare Earth Elements (REEs) or Rare Earth Metals are the collection of 17 elements comprising of lanthanides (atomic numbers 57–71) along with scandium and yttrium (Lucas et al. 2015; Zhu 2014; Gupta and Krishnamurthy 1992; Jha et al. 2016; Haque et al. 2014). REEs are silver, silvery-white, or grey metals, characterized by high density, high melting point, high electrical and thermal conductivities, and readily oxidize in air. Due to their similar chemical properties, they are found together in minerals and it is difficult to separate or even distinguish one from another. REEs are classified into lighter REEs from atomic numbers 57 through 63 (La, Ce, Pr, Nd, Pm, Sm and Eu) and heavier REEs with atomic numbers from 64 through 71 (Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) (Ganguli and Cook 2018). Generally, lighter REEs are more common and more easily extracted than heavier REEs (Coey 2020).

The lanthanide ions are the first row of the f-block in the periodic table, often called the inner transition elements, due to their placement between the s- and the d-block. Owing to an increase in relativistic and non-relativistic nuclear attraction, atoms with heavy nuclei, starting with the third row of the periodic table, experience contraction of the s and p orbitals, while the d and f orbitals, already diffuse and less penetrating, further expand owing to increased shielding from the nucleus. This leads to an electronic configuration in which all 15 lanthanide elements share the xenon core, [Xe], corresponding to $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$. The 4f orbitals, while part of the valence configuration, are shielded from the coordination environment by the filled 5s and 5p orbitals, and that is the case for lanthanides in their atomic state as well as higher oxidation states and this phenomenon is called as 'lanthanide contraction' (Lucas et al. 2015). The remaining electrons, the valence electrons, are then placed in the 6s orbital and, with the exception of La, Ce, Gd, and Lu, in the 4f orbital, since the energy difference between the 4f and 5d orbitals is large. Rare earths are generally found with non-metals, usually in the 3+ oxidation state and there is little tendency to vary the valence, such as Eu^{2+} and Ce^{4+}.

REEs are considered key drivers of today's technologies. Their applications are spread across several areas such as catalysis in petroleum refining, automobile catalytic convertors (La, Ce), magnets (NdFeB, SmCo), polishing (CeO_2), batteries—NiMH (La), metallurgical additives and alloy preparation (Ce, La, Nd), lamp phosphors (Eu, T, Y), capacitors and ceramics (Bharadwaj et al. 2017). Emerging technologies include anodes of solid state fuel cells (Sc, Y), high temperature superconductors and lasers (Y) among others (Behrsing et al. 2014).

In India, monazite is the principal source of rare earths and is a prescribed substance as per the notification under the Atomic Energy Act, 1962. It occurs in association with other heavy minerals, such as ilmenite, rutile, zircon, etc. in concentrations ranging from 0.4 to 4.3% in beach sand and inland placer deposits of the country (Bharadwaj et al. 2017). It is estimated that 10.21 million tonnes of monazite are available in the beach and inland placer deposits (Vogel 2015) and India has almost 35% of the world's total beach sand mineral deposits rich in LREE (Krishnamoorthy and Guptha 2008). Generally, the processing of REE ores leads to the formation of pure REE or mixture of REEs, primarily in their oxide forms.

11.6.1 Electrochemistry of Rare Earths

Rare Earths are generally characterized by their high negative reduction potentials ($E^0(RE^{3+}/RE^0) = -1.99$ to -2.60 V vs. SHE) (Lide 2006) and are among the metals considered to be most difficult to produce in pure form. Therefore, electrowinning through molten salt electrolysis is the only viable route to obtain rare earths in metallic form. Electrochemistry and electrodeposition of REEs in chloride and fluoride molten salt eutectics using inert Ta, Mo and W electrodes have been studied by several research groups (Table 11.2, 82–93). Majority of the studies reported detailed reaction mechanism, nucleation phenomena, thermodynamic stability and transport properties. Most of the lanthanides undergo reduction reactions through a single-step, but sluggish three-electron charge-transfer, except, Nd(III), Sm(III),

Table 11.2 Electro-reduction of REEs in molten salt electrolytes

Element	Electrode	Reduction steps	Reference
La, Ce, Er	Mo and W	$RE^{3+} + 3e^- \rightarrow RE^0$	Vandarkuzhali et al. 2012; Kondo et al. 2012)
Pr, Gd, Tb, Dy, Ho, Sc	W		Castrillejo et al. 2005; Caravaca et al. 2007; Rayaprolu and Chidambaram 2014; Saïla et al. 2010; Han et al. 2017; Castrillejo et al. 2012)
Lu, Y	Mo		Bermejo et al. 2008; Li et al. 2011)
Nd, Eu	Mo and W	$RE^{3+} + e^- \rightarrow RE^{2+}$ $RE^{2+} + 2e^- \rightarrow RE^0$	Abbasalizadeh et al. 2015; Kuznetsov and Gaune-escard 2011)
Sm, Tm, Yb	W		Gao et al. 2016; Castrillejo et al. 2009; Castrillejo et al. 2011)

Eu(III), Tm(III), Yb(III) which exhibit a two-step reduction (Table 11.2). It was widely reported that the reduction and reoxidation of RE^{3+}/RE^{2+} redox couple is a reversible diffusion-controlled reaction.

11.6.2 Electrowinning of Rare Earths

Several processes have been developed for the production of rare earth metals of different purities. These include: (i) reduction of anhydrous chlorides or fluorides, (ii) reduction of rare earth oxides, and (iii) fused salt electrolysis of rare earth chlorides or oxide–fluoride mixtures. RE metals are highly reactive, particularly at the high temperatures required for their preparation.

The advantage in employing fused salt electrolysis is the avoidance of a number of preliminary steps normally involved in aqueous chloride electrolysis and in having very compact electrolytic cells as compared to aqueous electrolysis. REE extraction through molten salt electrolysis is strongly governed by key electrowinning parameters such as electrolysis temperature, concentration of the species, decomposition potential, current density and period of deposition (Naboychenko et al. n.d.). Fused-salt electrowinning of rare earths can be operated continuously, except for “tapping”. The first recorded attempt at the preparation of a RE metal is credited to C. G. Mosander (1827).

Lanthanum, Cerium, Praseodymium, and Neodymium have melting points that permit their recovery in the liquid state by electrolysis of relatively inexpensive chlorides at temperatures less than 1100 °C (Mishra and Olson 2005). Winning of rare earth elements in the liquid state facilitates slag (electrolyte) metal separation, minimizes contamination of the reduced metal, and enables continuous operation and high volume levels of production. The technical feasibility of preparing limited quantities of high melting rare earth metals such as Gadolinium, Dysprosium, and Yttrium in consolidated form has also been demonstrated by using fluoride electrolytes in place of chlorides (Han et al. 2016). The simplest type of rare earth metal electrowinning is through chloride electrowinning. The metal is denser than the electrolyte. It sinks to the bottom of the furnace where it is periodically syphoned out of the furnace via a vacuum pipe or drained out of the furnace through a submerged closable tap hole (Zhu 2014).

$$\mathrm{RE}^{3+} + 3e^{-}\underset{\longrightarrow}{\underline{\Delta(1050^{\circ C})}}\mathrm{RE}^{\circ}(\mathrm{liquid})$$

Industrial molten salt electrowinning is always designed to produce molten metal. A molten product is easily tapped, poured, or syphoned from the electrowinning furnace. It allows almost continuous electrowinning. Electrowon RE product is as pure as its rare earth chloride feed. Industrial chloride electrowinning started in the beginning of the twentieth century, mostly in China and Japan. Large (up to 50,000 amperes) electrolytic cells were used, producing several tonnes of metal or alloy per day (Gupta and Krishnamurthy 1992).

Molybdenum was recognized as a suitable cathode material after Guertler (1923) reported that molybdenum is insoluble in the REs at high temperatures (Inman and White 1978; Cao et al. 2011). Molybdenum was used as the cathode in the experiments for the preparation of high purity REs. A carbon crucible was used as the anode, and the cathode in the form of a spinning rod was employed for the electrolysis. However, the chloride process was subsequently replaced with oxide-fluoride electrolyte by many industries because of ease and safe handling. Rare earth metal preparation by electrolysis of a fluoride–oxide bath was first reported in 1907 (Gupta and Krishnamurthy 1992; Wang et al. 2013; Lee et al. 2015).

Electrolytic processes are inherently simpler and cheaper compared to complex metallothermic reduction procedures. The technical feasibility of preparing limited quantities of high melting rare earth metals such as gadolinium, dysprosium, and yttrium in addition to neodymium, praseodymium, and didymium (Nd + Pr) in a consolidated form has also been demonstrated by using the fluorides as electrolytes in place of chlorides (Yasuda et al. 2014). For cerium and lanthanum, cells have been designed and operated at U.S. Bureau of Mines for continuous production of these metals by oxide–fluoride electrolysis (Wang et al. 2013; Dysinger and Murphy 1994). Instead of pure metals, if the REs are recovered as binary alloys having melting points in the range of 600–1000 °C, the electrolytic process has been found applicable to all the rare earth metals with the added advantages of liquid metal recovery and low temperature operation (Takeda et al. 2014). By this process, all the REs, including those with stable divalency, could be recovered as alloys. If a relatively more volatile metal such as cadmium, zinc, or magnesium is used as the alloying component with a relatively less volatile high melting rare earth, e.g. neodymium, gadolinium, and yttrium, the alloy can be vacuum distilled to yield pure RE metal.

11.6.3 Electrowinning of Rare Earths at CSIR-CECRI

Molten Salt Metallurgy is a niche area of CSIR-CECRI not only among national laboratories, but among international research community as well, since its inception in 1953. Particularly, CSIR-CECRI has a seamless legacy of electrowinning of rare earths in metallic and alloy forms, and as compounds (Fig. 11.1). Molten salt electrowinning of lanthanum, cerium and neodymium has been successfully carried out. CECRI carried out a collaborative project on the electrowinning of cerium metal using ceria as raw material. Using chloride and fluoride baths, attempts were made to understand the electrochemical behavior of Ce(IV) using cyclic voltammetry. The team also developed various baths and optimized electrowinning parameters to obtain metallic cerium. Electrowinning of neodymium metal is currently being carried out under DAE-IREL sponsored project at CECRI.

Molten salt electrowinning of rare earth alloys such as $NdFe_x$ and $LaNi_y$ has been demonstrated at a scale of 100 g/batch. Continuous electrowinning of lanthanum-nickel alloy was carried out at 75 A capacity using chloride melt and soluble nickel cathode under CSIR sponsored project. Neodymium iron alloy was prepared from

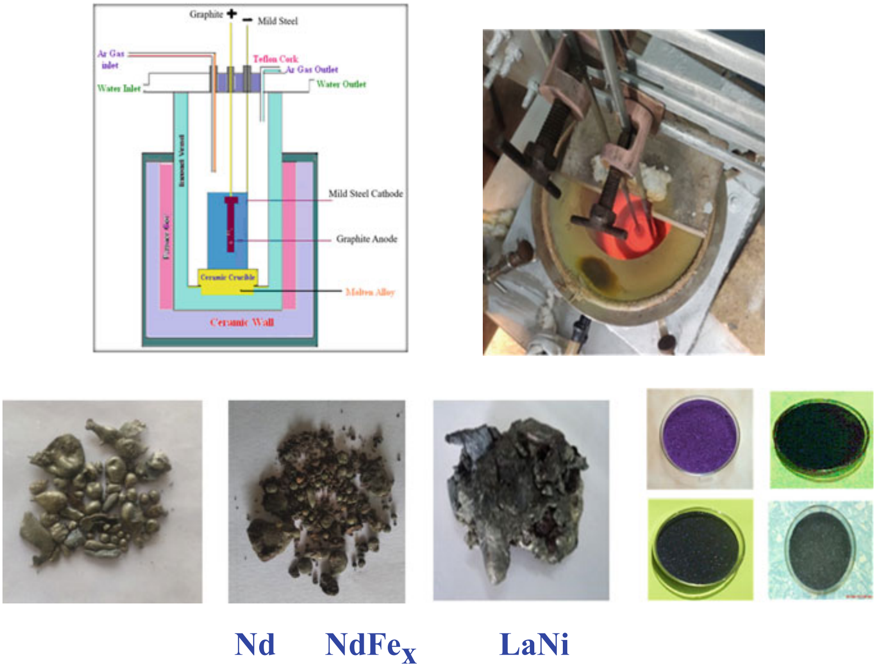

Fig. 11.1 **a** Schematic diagram of molten salt setup for electrowinning of rare earths **b** electrowinning cell with electrode assembly under operation (top open only for photograph) **c** Samples of neodymium, neodymium-iron, lanthanum-nickel and rare earth borides electrowon through molten salt electrolysis at CSIR-CECRI

chloride melts at various current capacities, 50–100 A. Among compounds, rare earth borides of the type, REB_6 (La, Ce, Nd, Sm, Eu) have been prepared at a scale of 250 g/batch. Further, CECRI has proven capability and strong interaction with strategic agencies such as DAE, BARC, IREL and IGCAR in producing strategic metals, particularly, rare earth metals, alloys and compounds. Recently, novel electrolyte systems based on Ionic Liquids and Deep Eutectic Solvents are also being developed at CECRI for studying the electrochemistry and electrodeposition of rare earths at near ambient temperatures (Andrew et al. 2021).

11.7 Challenges in Molten Salt Electrolysis

In addition to their merits, molten salt electrolytes have certain challenges as well. First, the melts have to be maintained in the liquid form at high temperatures throughout and the energy required is an added burden. The materials of construction should withstand the high temperature and have negligible or nil corrosion at the operational conditions. Fire, explosion, pyrophobicity, radioactivity (for nuclear materials) and toxicity are potential hazards when working with molten salts (Janz 1988). As most of the alkali and alkaline earth salts are hygroscopic, they are difficult to handle during the operations. Some of the salts are volatile at high temperatures. Prior to feeding into the electrolyzer, the salts must be purified for efficient melting and to form a uniform eutectic melt. Whenever there exists chance of the recombination of the cathode product with the anode gas, it is necessary to separate the anode and cathode by using high temperature ceramic diaphragms. The deposit at the cathode in the dendritic form is generally governed by mass controlled electrochemical process and such powdery deposits are difficult to separate from the frozen melt post-electrolysis (Fray 1988).

11.8 Scope for Molten Salt Metallurgy

Molten salt technology is a unique and potential area for the production of strategically important light metals, refractory and rare earth metals, and some of the transition metals like Al from their mineral and secondary resources. Even though significant amount of work has been carried out worldwide, many processes have not been commercialized to produce tonnage of metals to meet the requirements for various applications due to certain unresolved issues which mandate scalable and commercially viable solutions. In our country, only a few research groups are working in this important area of metallurgy. To meet the growing demand for speciality metals and alloys, indigenous technological approaches should be focused particularly in the production of special alloys in both ferrous and non-ferrous materials. While pilot scale production of metals such as lithium, magnesium and calcium metals have been established by CSIR Institutes like CSIR-CECRI, CSIR-NML and Defence

Laboratories like DMRL and DAE-BARC, due to various reasons their operations are not continuous to meet our requirements. Impetus research scope is there and it should be focused to evolve innovative technologies with automation and continuous production of these metals, alloys and materials. While India is blessed with abundant resources of rare earth minerals, bulk production of rare earth metals like La, Ce, Nd, Gd, etc. and their alloys using indigenous resources using molten salt technologies have not been taken up on a bigger scale.

There are several key areas of research that Indian research community can focus on in the field of molten salt technology. First, environment friendly technologies which can minimize the emission of toxic gases like CO_2 and NO_X from the metal production industries remain unsolved. Second, the development of conducting inert anodes to replace conventional carbon based materials, particularly, for the bulk molten salt production of aluminium metal is another key area. Some of the complex conducting oxides are to be developed and retrofit as inert anodes in the metal production technologies. Third is the development of bulk production technologies for refractory metals like Ti, Ta, Nb, Zr and V from their oxide raw materials by direct electrolysis. Fourth, molten salt electrodeposition of platinum group metals like Ir, Re, Rh and their alloys for the fabrication of complicated engineering devices like thrust chambers and exhaust lines for rocket nozzles is needed for strategic sectors. Considering the great demand for renewable energy sources, production of solar grade materials such as 6N Si (99.9999%), InAs and GaAs is another key area. Another important area of research is the development of strategies to recover critical metals such as lithium, cobalt, neodymium and samarium from end-of-life products such as permanent magnets, lithium ion batteries through molten salt processes. While this area has gained widespread interest from government and MSMEs in the country, the last-leg of the processing, i.e. getting the metallic products with high purity remains a coveted domain controlled by major foreign players. To thrust research in molten salt technologies, young researchers must be encouraged to work in this niche area along with domain experts and Centres of Excellence focused on R&D in molten salt technology need to be established under the sponsorship of government agencies and private partners involved in strategic metals production. To conclude, indigenous, commercially viable and sustainable processes using molten salt technologies are key cornerstones in India's march towards a responsible global power.

11.9 Author Contributions

M.J. and L.J.B. conceived the chapter and designed the plan. L.J.B. and M.J. contributed to Sect. 1 and 7. L.J.B. contributed to Sect. 2 (with R.S.P.) and Sect. 3. C.N.K., J.E. & N.M. contributed to Sect. 4. M.J. and R.S.P. contributed to Sect. 5 and Sect. 6 (with C.A.). M.J. and L.J.B. reviewed and supervised the overall manuscript.

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References

Abbasalizadeh, A., Teng, L., Sridhar, S., Seetharaman, S.: Trans. Inst. Miner. Metall. Sect. C Miner. Process. Extr. Metall. **124**, 191–198 (2015)

Al-Jothery, H.K.M., Albarody, T.M.B., Yusoff, P.S.M., Abdullah, M.A., Hussein, A.R.: IOP Conf. Ser. Mater. Sci. Eng. **863** (2020)

Andrew, C., Jayakumar, M., Chithambara Thanu, V.R.: Surf. Interfaces **19**, 100539 (2020)

Andrew, C., Dhivya, M., Jayakumar, M.: J. Electroanal. Chem. 115398 (2021)

Behrsing, T., Deacon, G.B., Junk, P.C.: The Chemistry of Rare Earth Metals, Compounds, and Corrosion Inhibitors. Woodhead Publishing Limited (2014)

Berchmans, L.J.: Improved Process with New Cell Design for the Production of Calcium Metal, 225/NF/2003 (2003)

Bermejo, M.R., Barrado, E., Martínez, A.M., Castrillejo, Y.: J. Electroanal. Chem. **617**, 85–100 (2008)

Bharadwaj, M.D., Kumar, P.: Natl. Conf. “Critical Strateg. Mater. Adv. Technol. (CSMAT-2017)” (2017)

Cao, P., Zhang, M., Han, W., Yan, Y., Wei, S., Zheng, T.: J. Rare Earths **29**, 763–767 (2011)

Caravaca, C., de Córdoba, G., Tomás, M.J., Rosado, M.: J. Nucl. Mater. **360**, 25–31 (2007)

Castrillejo, Y., Bermejo, M.R., Pardo, R., Martínez, A.M.: J. Electroanal. Chem. **522**, 124–140 (2002)

Castrillejo, Y., Fernández, P., Bermejo, M.R., Barrado, E., Martínez, A.M.: Electrochim. Acta **54**, 6212–6222 (2009)

Castrillejo, Y., Fernández, P., Medina, J., Vega, M., Barrado, E.: Electroanalysis **23**, 222–236 (2011)

Castrillejo, Y., Hernández, P., Rodriguez, J.A., Vega, M., Barrado, E.: Electrochim. Acta **71**, 166–172 (2012)

Castrillejo, Y., Bermejo, M.R., Díaz Arocas, P., Martínez, A.M., Barrado, E.: J. Electroanal. Chem. **575**, 61–74 (2005)

Chamelot, P., Taxil, P., Oquab, D., Serp, J., Lafage, B.: J. Electrochem. Soc. **147**, 4131–4137 (2000)

Chenyao, S., Che, Y., Li, J., Shu, Y., He, J., Song, J.: Integr. Med. Res. **9**, 9341–9347 (n.d.)

Choate, W.T., Green, J.A.S.: US, Department Energy Effic. Renew. Energy 12–24 (2000)

Coey, J.M.D.: Engineering **6**(2), 119–131 (2020)

De Nora, V., Spaziante, P.M., Nidola, A.: Molten salt electrolysis. US4187155A

Dessemond, C., Lajoie-Leroux, F., Soucy, G., Laroche, N., Magnan, J.F.: Minerals **9** (2019)

Dubrovskiy, A., Makarova, O., Kuznetsov, S.: Coatings **8**(12), 442 (2018)

Dysinger, D.K., Murphy, J.E.: 1–8 (1994)

Fray, D.: J. Miner. Metals Mater. **40**, 420 (1988)

D.J. Fray, October 60 (n.d.)

Gale, R.J., White, S.H., Lovering, D.G. (eds.): Molten Salt Technique. Plenum Press, New York (1983)

Ganguli, R., Cook, D.: Rare earths: a review of the landscape. MRS Energy Sustain. **5**, E9 (2018)

Gao, Y., Shi, Y., Liu, X., Huang, C., Li, B.: Electrochim. Acta **190**, 208–214 (2016)

Ghareh Bagh, F.S., Mjalli, F.S., Hashim, M.A., Hadj-Kali, M.K.O., Alnashef, I.M.: Ind. Eng. Chem. Res. **52**, 11488–11493 (2013)

Gilbert, H.N.: J. Electrochem. Soc. **99**, 305C (1952)

Gleb Mamanto, R.M.: Molten Salt Chemistry, An Introduction and Selected Applications. O. Reidal Publishing Company (1987)

Gourishankar, K.V., Karell, E.: Report in TMS Annual meeting, San Diego, California (1999)

Guertler, W.: Molybdenum as a constituent in alloys, Z. Metallkd. *15*, 151–154 (1923)

Gupta, G.K., Krishnamurthy, N.: Extr. Metall. Rare Earths (1992)

Han, W., Li, M., Zhang, M.L., De Yan, Y.: Rare Met. **35**, 811–825 (2016)

Han, W., Li, Z., Li, M., Hu, X., Yang, X., Zhang, M., Sun, Y.: J. Electrochem. Soc. **164**, D934–D943 (2017)

Haque, N., Hughes, A., Lim, S., Vernon, C.: Resources **3**, 614–635 (2014)

Haupin, W.E., Frank, W.B.: Compr. Treatise Electrochem. 301–325 (1981)

Heilig, M.L.: Personal communication 131–134 (1994)

Hine, F.: Fused salt electrolysis and electrothermics. In: Electrode Processes and Electrochemical Engineering. Plenum Press, New York (1985)

Huang, Z., Liu, J., Deng, X., Zhang, H., Lu, L., Hou, Z., Zhang, S.: Int. J. Refract. Metals Hard Mater. **54**, 315–321 (2016)

Petrovic, S.: Industrial electrochemical processes. In: Electrochemistry Crash Course for Engineers. Springer, Cham (2021)

Inman, D., Lovering, D.G.: Compr. Treatise Electrochem. 593–640 (1983)

Inman, D., White, S.H.: J. Appl. Electrochem. **8**, 375–390 (1978)

Janz, G.J.: Thermodynamic and Transport Properties for Molten Salts Correlation Equations for Critically Evaluated Density. American Chemical Society and the American Institute of Physics for the National Bureau of Standards, New York (1988)

Jeong, S.M., Yoo, H.Y., Hur, J., Seo, C.: J. Alloys Compd. **452**, 27–31 (2008)

Jha, M.K., Kumari, A., Panda, R., Rajesh Kumar, J., Yoo, K., Lee, J.Y.: Hydrometallurgy **165**, 2–26 (2016)

Kannan, G.N., Dandapani, K.S., Srinivasan, K.S., Srinivasan, L.K., Subramanian, P., Augustin, C.O., Selvin Devasakayam, T., Rajagopalan, N.: Report in Proc. Electrometallurgy Confs. India (1986)

Keppler, S., Messing, T., Proulx, K., Jain, D.: Molten salt electrolysis of alkali metals. US20010045365A1 (2001)

Kipouros, G.J., Sadoway, D.R.: Jom **50**, 24–33 (1998)

Kondo, M., Tanaka, T., Muroga, T., Tsujimura, H., Ito, Y.: Plasma Fusion Res. **7**, 7–9 (2012)

Konings, R.J.M., Beneš, O., Kovács, A., Manara, D., Sedmidubský, D., Gorokhov, L., Iorish, V.S., Yungman, V., Shenyavskaya, E., Osina, E.: J. Phys. Chem. Ref. Data **43** (2014)

Krishnamoorthy, N., Guptha, C.K.: Miner. Process. Extr. Metall. Rev. **22**, 477–507 (2008)

Krishnan, A., Lu, X.G., Pal, U.B.: Metall. Mater. Trans. B Process Metall. Mater. Process. Sci. **36**, 463–473 (2005)

Kuznetsov, S.A., Gaune-escard, M.: J. Nucl. Mater. **414**, 126–131 (2011)

Lantelme, F., Groult, H.: Trans. Inst. Miner. Metall. Sect. C Miner. Process. Extr. Metall. **119**, 82–87 (2010)

Lee, G.G., Jo, S.K., Lee, C.K., Ryu, H.Y., Lee, J.H.: TMS Annu. Meet., pp. 249–252. 15–19-March (2015)

Li, Y., Wang, F., Zhang, M., Han, W., Tian, Y.: J. Rare Earths **29**, 378–382 (2011)

Liddell, R.G.B., Sadoway, R.: Refractory metals extraction, processing and applications. Int. Nucl. Inf. Syst. (1990)

Lide, D.: Handbook of Chemistry and Physics, 87th edn. CRC Press, Boca Raton, FI (2006)

Lovering, D.G.: Molten Salt Technology. Springer, United States (1982)

Lu, H., Jia, W., Liao, C., Yuan, W.: Pilot experiments of magnesia direct electrolysis in a 5KA magnesium reduction cell. In: Essential Readings in Magnesium Technology, pp. 101–105. Springer, Cham (2016)

Lucas, J., Lucas, P., Rochelle, L., Davenport, W.: Rare Earths Rare Earths Production and Use. Elsevier Ltd., (2015)

Lukasko, J.J., Murphy, J.E.: Personal communication (1990)

Mamantov, G.E., Marassi, R.: Molten Salt Chemistry: An Introduction and Selected Applications. Springer Science & Business Media (2012)

Margarido, F., Vieceli, N., Durão, F., Guimarães, C., Nogueira, C.A.: Comun. Geológicas **101**, 795–798 (2014)

Minh, N.Q.: JOM **37**, 28–33 (1985)

Mishra, B., Olson, D.L.: J. Phys. Chem. Solids **66**, 396–401 (2005)

Mosander, C.G.: The preparation of cerium by reduction of CeCl with potassium, Pogg. Ann. **11**, 406–416 (1827)

Mouron, L.: Comput. Chem. **21**, 431–435 (1997)

Naboychenko, S.S., Murashova, I.B., State, U.: Production of Rare Metal Powders. Elsevier Ltd. (n.d.)

Ono, Y., Yamaguchi, M., Application, F., Data, P.: **1** (2009)

Osaka, T., Ito, Y., Aladjov, K., Stoyanova, A., Sefman, J.R., Lin, Y.P., Masuko, N. (eds.): Electrochemical Technology: Innovation and New Technologies. CRC Press (1997)

Osarinmwian, C.: ChemRxiv, **48** (2019)

Pal, U.B., Woolley, D.E., Kenney, G.B.: Jom **53**, 32–35 (2001)

Panigrahi, M., Iizuka, A., Shibata, E., Nakamura, T.: J. Alloys Compd. **550**, 545–552 (2013)

Ray, H.S., Sridhar, R.: Extraction of Nonferrous Metals. East-West Press Pvt Ltd (1985)

Rayaprolu, S., Chidambaram, D.: ECS Trans. **58**, 51–66 (2014)

Redkin, A.A., Nikolaeva, E.V., Dedyukhin, A.E., Zaikov, Y.P.: Ionics (kiel) **18**, 255–265 (2012)

Saïla, A., Gibilaro, M., Massot, L., Chamelot, P., Taxil, P., Affoune, A.M.: J. Electroanal. Chem. **642**, 150–156 (2010)

Sehra, J.C., Suri, A.K.: High Temp. Mater. Process. **11**, 255–292 (1993)

Sehra, J.C., Vijay, P.L.: Miner. Process. Extr. Metall. Rev. **19**, 523–556 (1998)

Senderoff, S.: Metall. Rev. **11**, 97–112 (1966)

Sharma, R.A.: Jom **48**, 39–43 (1996)

Sohn, H.Y., Geskin, E.S.: Jom **42**, 32–34 (1990)

Springer, C., Hasanbeigi, A.: Emerging Energy Efficiency and Carbon Dioxide Emissions-Reduction Technologies for Industrial Production of Aluminum, pp. 1–35 (2016)

Stewart, P.D., Michael, C.: Production of sodium. US3257297A (1961)

Sunshot: Molten Salt—Concept Definition & Capital Cost Estimate, Proj. No. 042839. (2016)

Takeda, O., Nakano, K., Sato, Y.: Mater. Trans. **55**, 334–341 (2014)

Thayer, A.M.: Having the mettle for sodium markets. Chem. Eng. News **86**(43), 20–21 (2008)

Thompson, J.S., Blank, H.M., Simmons, W.J., Bergmann, O.R.: Low temperature alkali metal electrolysis. US20020088719 (2002)

Thonstad, J.: Miner. Process. Extr. Metall. Rev. **10**(1), 41–55 (1992)

Tyrer, M., Gibbon, A.: Strat. Important Metals **69**, 12–13 (2012)

USGS: J. Chem. Inf. Model. 2020–2021 (2021)

Vandarkuzhali, S., Gogoi, N., Ghosh, S., Prabhakara Reddy, B., Nagarajan, K.: Electrochim. Acta **59**, 245–255 (2012)

Viswanathan, S.: Bull. Electrochem. **1**, 561–567 (1985)

Vogel, H.: Proceeding EMC, pp. 1–13 (2015)

Vol'skii, A.N., Sergievskaia, E.M.: Theory of Metallurgical Processes: Pyrometallurgical Processes, 2nd edn. MIR Publishers, Moscow (1971)

Wang, S.D., Li, Q., Ye, X.S., Sun, Q.G., Wu, Z.J.: Trans. Nonferrous Metals Soc. China (English Ed.) **23**, 3104–3111 (2013)

WS: Materials Performance Indices (2008)

Yan, X.Y., Fray, D.J.: Molten salt electrolysis for sustainable metals extraction and materials processing—a review. In Electrolysis: Theory, Types Appl., pp. 46–49. Nova Science Publishers (2008)

Yan, X.Y., Fray, D.J.: Molten salt electrolysis for sustainable metals extraction and materials processing—a review. In: Electrolysis: Theory, Types and Applications, pp. 255–301. Nova Science Publishers, Inc. (2010)

Yan, Q.X., Li, X.H., Wang, Z.X., Wang, J.X., Guo, H.J., Hu, Q.Y., Peng, W.J., Wu, X.F.: Trans. Nonferrous Metals Soc. China (English Ed.) **22**, 1753–1759 (2012)

Yasuda, K., Kondo, K., Nohira, T., Hagiwara, R.: J. Electrochem. Soc. **161**, D3097–D3104 (2014)

Zaikov, Y.P., Shurov, N.I., Batukhtin, V.P., Molostov, O.G.: Metall. Mater. Trans. B Process Metall. Mater. Process. Sci. **45**, 968–974 (2014a)

Zaikov, Y.P., Batukhtin, V.P., Shurov, N.I., Ivanovskii, L.E., Suzdaltsev, A.V.: Metall. Mater. Trans. B Process Metall. Mater. Process. Sci. **45**, 961–967 (2014b)

Zhu, H.: Rare earth metal production by molten salt electrolysis. In: Encyclopedia of Applied Electrochemistry. Springer, New York (2014)