SOME ASPECTS PERTAINING TO MOLTEN SALT ELECTROCHEMISTRY: RETROSPECTS AND PROSPECTS

S VISWANATHAN
Central Electrochemical Research Institute, Karaikudi - 623 006

ABSTRACT

An attempt is made to review and highlight the work on molten salt electrochemistry. The paper includes the broad development of the subject commencing with dilute aqueous solutions, the importance of such studies from both fundamental and applied viewpoints together with an indication of the future trends and possibilities.

Key words: Molten salt electrolysis, non-aqueous solvents, molten salt batteries

INTRODUCTION

The two extremes of the scale of concentrations are pure liquid water and anhydrous fused salt. The same is represented schematically in figure 1 where: 'a' denotes a very narrow region called infinite dilution region, 'b' indicates dilute aqueous electrolyte region < 0.01 M to which Debye-Huckel equation is applicable, 'c' depicts moderately concentrated aqueous electrolyte region ~ 1 M. This is the region which one normally comes across in the electrowinning of metals by aqueous salt electrolysis and 'd' concentrated aqueous electrolyte region. Finally, a region called 'anhydrous molten or fused salts' is reached.

![Fig. 1: Scales of concentration](image)

There are many inorganic substances which can be studied in the liquid state from below 0°C to temperature as high as 2000°C. For example, mixtures of NH₄NO₃ + N-methyl acetamide appear to form stable liquids melting below 0°C. Certain chlorocarbons are in the fused state even at room temperature. The melting point of Ca(NO₃)₂ . 4H₂O melt is around 40°C. The hydrate melts consist of fused hydrated salts such as Ca(NO₃)₂ . 4H₂O or MgCl₂ . 6H₂O, Zn(NO₃)₂ . 6H₂O etc, that behave in some respects like molten salts with large cations. Their concentrations are 9-14 mole of salts per kilogram of water. These systems need to be handled under precisely controlled water vapour pressures in order to maintain constant composition. The melting point of the other systems, for example, 60 mole % AlCl₃, 26 mole % NaCl and 14 mole % KCl is around 93°C whereas the melting point of the cryolite-alumina melt system i.e. Na₃AlF₆ + 2.6 w/o Al₂O₃ + (approx) 5 w/o excess CaF₂ + (approx) 5 w/o excess AlF₃ is about 930°C. Similarly if one considers the magnesium metal extraction (approx) 20 mole % (anhydrous) MgCl₂ and the rest 80 mole % constituted by a mixture of NaCl + KCl + BaCl₂ + (anhydrous) CaCl₂ + small quantity of CaF₂ or NaF are employed and the electrolysis is conducted around 700°C. In case of sodium metal extraction, the current trend is to use a ternary mixture consisting of NaCl + BaCl₂ + (anhydrous) CaCl₂ and the electrolysis is conducted around 500°C.

The utilization of such systems as solvents and reaction media has been the practice, especially in industries concerned with electrowinning, refining, plating and analysis. Scientific studies of a basic nature on these systems have been taken up in a big way recently. They form a large class of pure liquids in which positively and negatively charged particles co-exist, and which also exhibit electrolytic conductivity, i.e. the conduction of electricity is due to the movement of ions. The adherence to the Faraday's laws also proves that the process of conduction is ionic. Hence, logically they were classified as 'ionic melts' or fused salts or molten salts or molten electrolytes or liquid electrolytes. The term fused salt is generally used to refer to molten state of primary ionic compounds such as sodium chloride, the stable oxo-anion, such as carbonates, sulphates, nitrates etc. The fused salt may also contain other salts (i.e. solutes) added to lower the melting point, to decrease the metal solubility in the melt, thereby, increasing the current efficiency and to provide more favourable electrochemical conditions for economic operations. These changed conditions may be due to solvent-solute interactions, e.g. by formation of complex ions. Therefore, mixtures of molten salts often behave as if they contain new ionic species i.e. complex ions, formed by interaction between simple ions. In almost all industrial uses of fused salt electrolysis for the extraction of metals, complex (anhydrous) chloride baths are a common feature and are the rule rather than exception.

CLASSIFICATION

Molten salts may generally be classified into the following categories:

1. Simple ionic liquids, such as molten halides and cyanides
2. Simple oxy-anionic type, such as molten nitrates, carbonates, sulphates, hydroxides – tendency to glass forming especially in mixtures
3. The complex, highly polymerised oxy-anionic type, such as phosphates, borates, fluorides and silicides – typically glass forming, and
4. Nonionic and covalent melts – halides of Zn, Hg, Be, As, Sb and Al which are structurally complex. Their properties are susceptible to modifications by temperature, pressure and compositional factors.

Thus the possible range of molten salts is wide: right from the low melting, predominantly covalent and structurally simple system such as KAlCl₄ to the high melting structurally simple, ionic system, such as NaCl. Both the stems have good potentialities and vast commercial applications.

There is a growing interest in the utilization of above melts for a number of processes.
GENERAL PROPERTIES

Fused salts have been put to a variety of uses, owing to their high chemical, thermal and electrochemical stability, inertia, i.e. low vapour pressure, good electrical conductivity and diffusivity, low viscosity, high heat transfer coefficients, ability to dissolve many different materials, extremely wide useful temperature range and the very high temperatures which can be reached. These properties make them attractive for solar, geothermal and even photoelectrochemical energy conversion devices in addition to the well known applications in extractive metallurgy.

MOLTEN SALTS AS NON-AQUEOUS SOLVENTS OR REACTION MEDIA

A question may arise why use molten salts when water is less expensive and safer? For carrying out chemical reactions, molten salt systems possess a number of other advantages. Molten salts are often much better and more versatile solvents than water and other room temperature liquids. Fused salts dissolve diverse substances as water, organic matter, metals, metallic oxides, gases and the other salts such as sulphides, nitrates, carbides, hydrides and non-metallic elements. The range of stability in oxidation-reduction system is much greater than in aqueous solutions. For example, while aqueous solutions decompose at around (hydrogen bonding), even photoelectrochemical energy conversion devices in addition to the salts dissolve diverse substances as water, organic matter, metals, metallic reduction system is much greater than in aqueous solutions. For example, well known.

Molten salts have high electrical conductivity and its dependence on temperature and pressure

i) Structural Models

Molten salts are also of theoretical interest in relation to studies of the liquid state. Let the gas be represented by model ‘A’, solid by model ‘B’ i.e. lattice model and liquid by model ‘C’ (Figure 2).

Therefore, one finds that there are two types of models for pure liquid electrolytes, one being based on gas oriented and the other on lattice oriented models. Here liquids are in a state of aggregation intermediate between that of solids and of gases and their theoretical treatment combines all of the difficulties and none of the simplifications of the theories of gases or crystals. The semi-empirical descriptions can faithfully reproduce some of the equilibrium properties of these liquids. All of the semi-empirical models are Arrhenius in character i.e. they involve the concept of an activated jump, an activation controlled volume fluctuation or both, whereas in fact the observed activation energies (especially those at constant volume) are small and close to kT, the average thermal energy. The predominant view today is that the liquid is much nearer to the solid than the gaseous state. This view is supported by the comparisons of the heats of fusion of solids with the heats of vapourisation of the corresponding liquids. As a rule, the heat of fusion is small compared with entropy of vapourisation. In NaCl, for example, \( \Delta H_{\text{fusion}} \) is 6.69 kcal/mole and \( \Delta H_{\text{vap}} \) is 45.3 kcal/mole. Correspondingly, the molar volume change on melting, although appreciable (approximately 25%) is insignificant in comparison with the molar volume change on vapourisation. These data indicate that the disorder introduced on melting is much less than the disorder introduced by vapourisation.

At the onset of crystallisation, extensive preorientation occurs at the melt/crystals interface with the formation of ‘islands’ which are already subject to a certain ‘ordering’ opposing the thermal motion. Crystal growth from the melt can therefore be regarded as a special case of crystalline transitions.

Molten salts, however, are a simple class of liquids. Because of their ionic character, molten salts are thought to be subject to powerful intermolecular forces which are predominantly of coulombic origin and therefore easily described. The attractive forces between particles of opposite sign and repulsive forces between particles of the same sign are very strong. Therefore, the electrostatic forces have an orienting effect so that the negative ions have only positive ions as nearest neighbours and vice versa. The energy required to mix positive and negative ions randomly would be of the order of lattice energy of a crystal. Hence among liquids, molten salts would be expected to be mostly nearly like solids, since there is a short range order although certainly no long range order. Thus, quasi-lattice model of molten salt solutions has been rather successful in explaining many of the thermodynamics of molten salt solutions.

Molten salts are also of interest in connection with the theories of electrolyte solutions. From Figure 1 it is clear that molten salts represent the ultimate in ion concentration, and advances in the understanding of their behaviour should help in understanding other concentrated solutions. Although there has been a growth of interest in molten salts, the intermediate range of concentrations between molten salts and dilute aqueous salt solutions has been virtually unexplored. Therefore, another approach to the problem of concentrated aqueous electrolyte solutions is to consider the effect of water vapour of the equilibria in molten salt electrolytes.

Theoretical studies of this region may lead to better models for the understanding of salt solutions at ordinary concentrations and bridging the gap between theories of molten salts and dilute aqueous electrolyte.
The hydrate melts such as the molten hydrates of nitrates and halides of Ca, Mg, Cd, Zn, i.e. Ca(NO₃)₂, 4 H₂O, MgCl₂, 6 H₂O etc because of their stoichiometry and certain structural, transport and thermodynamic properties suggest that they might be considered as analogs of molten salts and as concentrated aqueous electrolyte solutions with extensive ion pairing. Such salts can be treated as molten salts with low field cations—the water molecules firmly bound to the calcium ions, i.e. anions and hydrated salts and dilute aqueous electrolyte solutions.

Thus, models of concentrated aqueous electrolyte solutions must reduce at the molten salt end of the concentration scale to one that recognises charge alternation because of electrostatic ordering, and at the water end of the concentration scale to a model in which the water dipoles permit random mixing of cations with anions. The models should not be considered 'real', but representations of the physical behaviour.

**Conductivity**

The physical property like conductivity of a molten salt is usually measured at a fixed temperature, keeping pressure as constant. The value obtained under such conditions includes the influence of density or in other words, the change in volume because of the fact that when a solid is melted, volume change is observed.

Alternatively, the above may be expressed as follows:

<table>
<thead>
<tr>
<th>Method</th>
<th>conductivity at a fixed temperature and pressure</th>
<th>density or volume change due to temperature change</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\Delta \sigma$</td>
<td>$\Delta \sigma / \Delta T$</td>
</tr>
<tr>
<td>II</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>+</td>
<td>$\Delta \sigma / \Delta V$</td>
</tr>
</tbody>
</table>

(* for molecular melt, volume increase should decrease the conductivity, and for ionic melt volume increase should increase the conductivity due to increased mobility).

Usually, the contribution by III is neglected and its experimental value also is not readily available. Hence, the interpretation based on the results obtained from I is erroneous.

Based on the experimental values obtained by methods I and II, if graphs are plotted between $\log \sigma$ vs $1/T$, one would get linear lines. But the slope of the lines obtained by method II (i.e. the method in which contribution by III is avoided) is lower than that of method I, the reason being that the energy change due to temperature is not appreciable in method II.

If method II is adopted, even conductivity of molecular melts increases linearly with temperature, and the system behaves just like ionic melt about which further details are given subsequently.

It is the density of the system which is most important and because this means that pressure is a more discriminating variable than temperature, much effort has gone into developing experimental technique for making measurements at high temperature (~1000°C) and pressures (~1000 atmospheres).

With increasing temperatures, conductances normally rise whereas with increasing pressure they usually fall because of reduction in free volume and the consequent decrease in ionic mobilities. This is true so far as the composition and degree of ionisation remain the same. However, this property 'ionisation' is independently affected by changes in pressure or density, the degree of ionisation invariably increasing with pressure. Thus the feebly ionised mercuroic iodide (or liquid containing complex ions) become markedly more ionic, even at a few kilobars, simply because the equilibrium

$$2 \text{Hgl} \Leftrightarrow \text{Hgl}^+ + \text{Hgl}^-$$

is increasingly displaced to the right hand side as the result of the substantial contraction in volume attending the ionisation reaction. In other words, one may expect that molecular Hgl quadrants may become ionic at sufficiently high densities and vice versa. Thus, ionic and molecular melts differ only in degree and not in kind. Furthermore, since in such compounds the cation is very much smaller than the anion, it seems natural to interpret this behaviour in terms of anion-anion contact. Compression of the melt would result in changes in anion-anion coordination, but would leave the anion-cation coordination relatively undisturbed.

**PROPERTIES OF MELTS**

**Non-electrolyte**

If the salt is heated to a high temperature in the vicinity of melting point, such a salt possesses a noticeable electrical conductance. The fusion of a salt is essentially the destruction of crystal lattice usually accompanied by the increase in volume. In other words, melting may be looked upon as a process of mixing the solid with some empty space so as to give a completely random mixing and these empty spaces or free volumes make room into which ions can migrate. At high temperatures in melts, thermal vacancies are large as compared with impurity vacancies. When a crystalline salt melts the ions formerly fixed in the rigid lattice not only become free to move but adopt, on the average, modified interparticle distances (Table I)

Also, x-ray and neutron diffraction studies indicate that on melting a solid,

i) the inter-ionic distance i.e. average distance between unlike ions decreases by up to 10%

ii) the coordination number i.e. the average number of ions immediately surrounding a given central ion, also decreases, and

iii) average distance between like ions increases than in the solid.

iv) an increase in volume of the solid occurs on melting and the local order extends only over a very short distance (few angstroms). It is as if the fused salt forgets how to continue the ordered arrangement of ions of the parent lattice.

**Table I**

<table>
<thead>
<tr>
<th>Salt</th>
<th>Cation-anion distance Å</th>
<th>Coordination number</th>
<th>Cation-anion distance Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>2.47</td>
<td>4.0</td>
<td>3.85</td>
</tr>
<tr>
<td>LiF</td>
<td>2.85</td>
<td>5.6</td>
<td>4.45</td>
</tr>
<tr>
<td>NaI</td>
<td>3.15</td>
<td>4.0</td>
<td>4.80</td>
</tr>
</tbody>
</table>

For alkali metal halides, melting causes an expansion of the order of 20%. This is shown in Table II.

**Table II**

<table>
<thead>
<tr>
<th>Salt</th>
<th>Volume increase (100 ΔV/V0) on melting for alkali metal halides</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Cl</td>
</tr>
<tr>
<td>Li</td>
<td>29.4</td>
</tr>
<tr>
<td>Na</td>
<td>27.4</td>
</tr>
<tr>
<td>K</td>
<td>17.2</td>
</tr>
<tr>
<td>Rb</td>
<td>—</td>
</tr>
<tr>
<td>Cs</td>
<td>—</td>
</tr>
</tbody>
</table>

In the crystalline solid phase for the salts at low temperatures, each ion is surrounded by a symmetrical collection of nearest neighbours, under whose confining influence the central ion undergoes harmonic vibrations about its lattice position. Structurally, the constituent particles, atoms, molecules or...
ions of a crystalline salt are arranged in an orderly repetitive pattern in three dimensions. This pattern is such that having observed the pattern in some small region of the crystal, it is possible to predict accurately the positions of particles in any region of the crystal, however far it may be removed from the region of observation. The crystal has long range orders.

The particles composing a liquid are not arranged in such a precise fashion. In a small region of a liquid, there may appear to be a pattern arrangement. However, if we observe a neighbouring region, the pattern will be somewhat different or if it is nearly the same, it may not be accurately joined to the first region. In terms of the arrangements of the particles, a liquid has 'short-range order' but lacks the long range order of the solid.

Further, on melting, the system also acquires the characteristic property of 'fluidity'. The changes cannot be explained by merely assuming that the lattice of the solid state undergoes an expansion. Firstly, the observed expansion is more than that corresponding to the elastic limit. Secondly, removed from the region of observation. The crystal has long range orders. The changes cannot be explained by merely assuming that the arrangement of 'fluidity'. The changes cannot be explained by merely assuming that the arrangement of ions of a crystalline solid are arranged in an orderly repetitive pattern in

...
fused bath gets fouled, the purification of the electrolyte is much more difficult and troublesome, as compared to aqueous bath. This is due to the fact that the electrolyte from the cell will have to be emptied, brought into the solution in water, purified, filtered, evaporated and then anhydrous chlorides prepared for feeding the fused chloride into the cells, whereas in aqueous electrolysis, purification and filtration are alone needed and washing of the cell is very easy.

Therefore, whenever metals could be produced by aqueous chloride or sulphate electrolysis in a very form they are preferred to other methods of production such as fused salt electrolysis or by thermal or electrothermval procedures. The fused salt electrolysis is mainly confined to the production of reactive metals. In addition, fused salt electroplating is preferred in order to avoid the influence of hydrogen embrittlement in the deposits of zinc and cadmium, and to avoid employment of cyanide bath for silver copper etc.

CAUSES FOR THE DEVIATION FROM THE THEORETICAL CURRENT EFFICIENCY

The low current efficiencies observed in fused salts may be divided into three types: those associated with side effects at the cathode, those at the anode and those in the body of the electrolyte.

The following factors are believed to cause current losses:

Evaporation or volatilisation of metals

For example, in the electrolysis of fused sodium chloride, sodium depositing at the cathode has a high vapour pressure which promotes the evaporation of metal. This could be reduced by temperature control.

Chemical side reactions

The material for making the electrolyser always reacts with the electrolysis at the anode, for example sodium at the cathode and chlorine at the anode in fused metal. This could be reduced by temperature control.

The formation of higher compounds at the anode

For example, in the electrolysis of stannous chloride, current is consumed in the formation of stannic chloride at the anode and not chlorine:

$$2SnCl_2 \rightarrow Sn + SnCl_4$$

The dissolution of the metal in the fused salt

As explained earlier, the dissolution of the metal in the molten electrolyte is the characteristic property of molten salts. In case of electrolysis of fused sodium hydroxide, sodium metal may dissolve completely in the electrolyte if the temperature exceeds 350°C or so, to form a true solution. In some cases, sodium may form due to the dissolution of metal in the fused bath. In the electrolysis of cadmium or bismuth chloride, because the metal is freely soluble in the melt, the net cathodic current efficiency is negligible.

The current yield is dependent on the composition of the melt. The electrolyte composition is of paramount importance in obtaining high current efficiency and purity of the metal. Addition of NaCl, CaCl_2 or BaCl_2 raises the current efficiency in the electrolysis of magnesium chloride, other cell conditions being the same. This explains the fact that solubility of magnesium in these foreign salts is high and falls sharply as the melt becomes increasingly rich in them. It is assumed that the energy levels of the quasi-lattice of the melt are raised by the foreign cation, so that the metal to be dissolved can no longer give up its valence electrons so easily to the energy bands of the whole system, i.e. its solubility is reduced. In addition, the melting point of the mixture of salts is low compared with pure substances, thereby facilitating the conduct of electrolysis at a lower temperature. The same is happening in all the other cases viz. sodium, lead etc.

The recombination of electrolysis product into original salt

The metal that is deposited at the cathode and the gas that is liberated at the anode, for example, sodium at the cathode and chlorine at the anode in fused sodium chloride electrolysis have a tendency to recombine to form the salt. If the apparatus is constructed using a diaphragm so that the products of electrolysis are not allowed to make direct contact with each other or with atmospheric oxygen (e.g. sodium burns in the air), approximately quantitative yields can be obtained. Moreover, diffusion, thermal convection and sintering evolved at the anode are to be minimised.

Simultaneous deposition of several ions

For example, in the electrolysis of fused MgCl_2 or Al_2O_3 containing a certain amount of moisture, the water is decomposed first and oxygen and hydrogen are evolved then magnesium chloride gradually decomposes. In the case of aluminium cell, both sodium and aluminium co-deposit. Data obtained from polarographic, e.m.f. studies etc. would help us in finding the electrochemical behaviour of the system.

Anode effect

Generally speaking, the anode reactions involve the expulsion of oxygen or hydrogen from fused salts. There may be side reactions involving the anode also with the formation of the halogen compounds or the oxygen compounds or mixtures of these. A phenomenon known as 'Anode effect' occurs under a combination of certain special and extreme conditions while conducting fused salt electrolysis. This is one of the practical difficulties associated in electrolysis of fused salts, especially in the production of aluminium, magnesium and tantalum. This results in an abrupt increase in cell voltage and a fall in cell current from the normal value to almost zero.

INDUSTRIAL PROCESSES

Aluminium

At present, the average energy consumption requirement for making aluminium in the Hall-Héroult cell is reported as (approx) 18 kWh/kg and in recent installations the value is brought down to 1.3 kWh/kg by reducing the inter-electrode gap and by lowering the cathode current density from 11,000 to 8000 A/m². The electrical energy wastage is minimised by this way. However, there are economical limits for reducing the power consumption by lowering the current density as capital-related costs are increasing at the same time.

The experts in the aluminium industry believe that the future belongs to the new Alcoa bipolar cell employing a mixture of chlorides of aluminium, sodium, lithium, potassium and magnesium. It is claimed that aluminium could be produced at less than 9.5 kWh/kg and well above the I 900 kg/day level.

Magnesium

In the case of electrolytic metal, a good conducting electrolyte bath with lower specific gravity viz anhydrous mixture of lithium chloride plus magnesium chloride has been chosen in order to reduce the energy consumption, instead of the usual anhydrous magnesium chloride in admixture with other alkali and alkaline earth metal chlorides, like NaCl, CaCl_2, BaCl_2, KCl. In the new composition developed, in addition to the lower cell voltage achieved viz half of the usual cell voltage of 9-10 V, the current efficiency is improved by taking advantage of the low density of the system, thereby making molten magnesium to sink to the bottom of the cell and chlorine gas to ascend up and escape at the top of the electrolyte, preventing, to a large extent, the recombination reaction between the liberated molten magnesium metal and chlorine.

Zinc

In the case of zinc, although work is in progress in developing suitable dimensionally stable anode or catalytic oxide-coated lead/lead alloy based anode with low oxygen overpotential, which would also permit reducing the inter-electrode gap and energy for cooling, it appears that fused salt electrolysis of zinc chloride in a bipolar cell is promising. An energy consumption of ~2.5 kWh/kg in a small pilot plant cell operating at 8000 A/m² and 500°C has been reported, whereas the customary aqueous zinc sulphate process consumes ~5.5 kWh/kg. The added benefits of such a process would be a high space-time yield, due to nearly 250 times higher cathode current density and production of molten zinc which can be cast directly. Zinc chloride or lead chloride is prepared from sulphide ore concentrate by ferric chloride leaching or chlorine/oxygen, avoiding sulhide or dioxide fumes, and simultaneously elemental sulphur is obtained as by product.
**Sodium**

Recent development of beta-alumina diaphragm suitable for use in molten saltds, like molten sodium chloride, gives rise to the expectation for the production of sodium and chlorine at a cheaper rate.

Instead of using NaCl of a high melting point (800.4°C), employment of a molten mixture of NaCl-AlCl₃ and beta alumina diaphragm leads to the preparation of chlorine and sodium metal at a lower temperature as 200°C. The cell operates at 200°C at 6 V instead of the conventional 7 V for Down's cells making sodium at 600°C. Again, average current efficiency is 100% compared with 85-92% for Down's cells. Power consumption of the process at the same productivity is 20-30% lower than for the Down's cell.

The electrolysis of molten ZnCl₂-NaCl or PbCl₂-NaCl electrolytes in the absence of such diaphragm leads to the deposition of zinc or lead metal and chlorine.

From the sodium metal, sodium hydroxide could also be produced by treating the liberated sodium with pyrochlore steam. Thus hydrogen also is produced as a byproduct. This method of production of sodium, chlorine and hydrogen could also compete with the production of sodium hydroxide, chlorine and hydrogen by electrolysis of sodium chloride solutions even in modern membrane cells fitted with long life, dimensionally stable anodes and diaphragms like 'Nafoon' (perfluorosulfonic acid cation exchange membranes) or perfluorocarboxylic acid or carboxylate membrane or bilayer membrane of sulfonic/carboxylic acids type.

It is also proposed that utilisation of beta-alumina diaphragm (similar to the one used in the sodium-sulfur battery) in the electrolysis of molten caustic soda containing about 3% water as catholyte and sodium chloro-zinc chloride in the ratio of 1:1 as anolyte at 330°C also leads to the production of caustic soda and dry chlorine with a lower direct electrical energy requirement. Sodium ions move from the anolyte to catholyte through the beta-alumina diaphragm. The reaction is similar to the electrolytic processes of membrane cells:

\[ \text{H}_2\text{O}(g) + \text{NaCl}(\text{NaCl-ZnCl}_2) \rightarrow 1/2 \text{H}_2(g) + \text{NaOH} + 1/2 \text{Cl}_2(g). \]

Here the beta-alumina diaphragm is in constant contact with molten caustic soda on one side and a highly corrosive molten medium on the other side. The success of the processes employing beta-alumina diaphragm depends much upon the performance and life of the diaphragm under the corrosive conditions at elevated temperatures.

**MOLLEN SALTS BATTERIES**

The good conductivity molten salts lend themselves for use as electrolytes in conjunction with highly reactive electrode materials that cannot be used with aqueous electrolytes. This permits (i) the development of batteries having very high specific energy (180 - 200 Whr/kg) (ii) employment of high current densities, thereby achieving high specific power (>100 W/kg) and (iii) long life with attendant advantages like high voltage, low equivalent weight materials, high utilisation of active material, rapid mass transport, low internal resistance etc.

Of the possible combinations of negative electrode reactants, electrolytes and positive electrode reactants, the ones that are under current investigation or hold promise for the future include:

- LiAl
- LiCl-KCl
- Na⁺ solid electrolyte | S
- Na⁺ | NaCl
- SbCl₅-Sb

**Application**

Because of the unique properties of molten salt batteries they raise the following interesting possibilities:

- i) High performance electric vehicles with a long range between recharge: an electric vehicle with a 200 Whr/kg battery occupying 40% of its weight can be expected to have an urban driving range of 400 km.
- ii) Stationary energy storage applications like off-peak energy in the electric utility systems or electrical energy generated by solar or wind-powered generators.

None of the molten salt batteries has reached the stage of development where costs can be estimated accurately.

In conclusion it may be stated that further work should produce results of interest to the entire field of fast reactions in molten salts. It is hoped that many workers will be stimulated to enter into this challenging but exciting field, in view of the progress in materials science together with demands for new and cleaner process.

**BIBLIOGRAPHY**

13. J Braunstein and HC Gaur, Lectures delivered at School of Thermodynamics and Electrochemistry of Molten Salts, University of Delhi (1971)
24. V Aravanathan and S Viswanathan, Inst Chemists (India), XXXIX, Pt II (1967) 72
ELECTROPYROMETALLURGY
Compiled by Miss Shanmugasigamani

ABSTRACTS

1. Extraction of metals by molten salt electrolysis Chemical fundamentals and design factors
Nguyen Quang Minh
(Alcan International Ltd., Bambury, Oxon, England)
and G Gheetham
J Metals, 11-1 (1985) 28
The chemical fundamentals of electrolyte, solute, and cell reactions in molten salt electrowinning and types of electrolysis cells used for this process are discussed. Emphasis is given to the basic physicochemical and electrochemical factors in the optimum design of electrowinning processes. Examples of practical and fundamental limitations encountered in molten salt electrowinning are given. Ways to avoid those limitations are also discussed.

2. Crust formation on the ends (transverse sides) of aluminium reduction cell cathode units
YU D Lozovei, VF Anosov, and VA Kungnetsov
Tsvet Metal, 25-4 (1984) 40
One of the operational drawbacks of high-powered electrolytic cells for aluminium production installed in a building at intervals sufficient to permit regular work on the cell ends is the difficulty of producing protective crusts on the transverse walls of the cathode. The absence of end crusts leads to accelerated breakdown of the cathode lining, reduced cell service life, losses of current, and poor technical and economic figures for the electrowinning process. Protecting the carbon lining on the ends of the cathode is the subject of constant attention: a cathode design has been introduced in which the height of the carbon blocks exceeds the depth of the portion, e.g. extra-high ends, machinery for working on the transverse sides of reduction cells is being developed, research is in progress on using various protective materials to increase the life of the end lining, etc.

3. Electrorefining of zirconium metal in alkali chloride and alkali fluoride fused electrolytes
G.J Kipouros (Dept. of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts)
S.N Flenigas (Dept. of Metallurgy and Materials Science, University of Toronto, Toronto, Ontario, Canada)
The electrorefining of zirconium metal in alkali halide melts has been investigated. Variables affecting the electrodeposition process such as composition of the electrolyte, current density, and the configuration of the electrodes were studied. Two types of electrolytes were used; the alkali chloride-rich and alkali-fluoride-rich electrolytes. The various electrolytes are considered in terms of their ability to complex the soluble zirconium ions, a property which is important for the electrodeposition of coherent metal deposits from these melts. Crystalline zirconium metal of good quality has been obtained from fluoride melts containing NaF, LiF, and either ZrF₄ or K₂ZrF₇ at about 750°C.

PATENTS

1. Cell for the electrolytic refining of aluminium
Sylvesture Vire (Swiss Aluminium Ltd)
Eur Pat 136969, Jul 27 (1984)
A thermally insulated cell is described. The cell consists of a tank with steel walls enclosed in a material resistant to the electrolyte and to the high temperature. Apparatus is provided for the removal of pure aluminium and for the separation of the melt. A conduit for the electrolyte material is also designed as gas outlet serves as the collector and outlet for Al. The cell is provided with bipolar electrode units parallel to the end electrodes. The electrode units consist of one or more open pore diaphragm plates wettable by the electrolyte but not by the Al. The anodes and cathodes are of graphite. The electrolytes are alkali metal chlorides.

2. Aluminium reduction cells
Ernest William Dewing, Adam Zan Gesing,
Thomas James Hudson, Louis John-Manfredo
Douglas Lames Wheeler, William Raymond Bennett and Thomas Merle Cleere
Eur Pat 145411, Jun 19 (1985)
The cathode collectors are embedded in the pot lining of this Al electrowinning cell. A section of the current collector comprises a major portion, by volume of discrete electric conducting Al-wettable bodies joined or surrounded by Al-containing metal which at least partially fluid when the cell is in operation. These Al-wettable bodies in the form of sheets or thin slabs are aligned with their major faces parallel to one another and to the axis of the collector section. The pot lining is Al₂O₃ and the collector bodies TiB₂.

3. Aluminium reduction cells
Ernest William Dewing, Adam Jan Gesing, David Nelson Nitchell and Aniket Pant (Alcan International Ltd)
Eur Pat 145412, Jun 19 (1985)
In this Al electrowinning cell, the cathode current collectors are embedded in the pot lining. In the floor of the cell are depressions wherein are placed the end of a current collector, the other end being connected to the external electric supply. The depressions are filled with metal-wettable bodies e.g. TiB₂ spheres with the interstices filled with molten Al. The spheres are of a size to prevent entry of electrolyte or sludge.