SOME ASPECTS PERTAINING TO MOLTEN SALT ELECTROCHEMISTRY: RETROSPECTS AND PROSPECTS

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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

T he 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 $\sim$ 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.
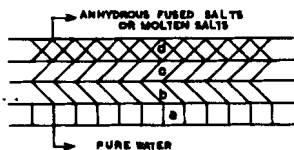

Fig. 1: Scales of concentration

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 NH_4NO_3 + N-methyl acetamide appear to form stable liquids melting below $0°$C. Certain chlorocuprates are in the fused state even at room temperature. The melting point of $Ca(NO_3)_2 . 4H_2O$ melt is around $40°$C. The hydrate melts consist of fused hydrated salts such as $Ca(NO_3)_2 . 4H_2O$ or $MgCl_2 . 6H_2O$, $Zn(NO_3)_2 . 6H_2O$ 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 % $AlCl_3$, 26 mole % $NaCl$ and 14 mole % KCl is around $93°$C whereas the melting point of the cryolite-alumina melt system i.e. Na_3AlF_6 + 2.6 w/o Al_2O_3 + (approx) 5 w/o excess CaF_2 + (approx) 5 w/o excess AlF_3 is about $930°$C. Similarly if one considers the magnesium metal extraction (approx) 20 mole % (anhydrous) $MgCl_2$ and the rest 80 mole % constituted by a mixture of $NaCl$ + KCl + $BaCl_2$ + (anhydrous) $CaCl_2$ + small quantity of CaF_2 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 $NaCl$ + $BaCl_2$ + (anhydrous) $CaCl_2$ 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 ionic liquids 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 oxyanion, 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 complex system such as $KAlCl_4$ to the high melting structurally simple, ionic system, such as NaCl. Both the systems 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, nitrides, 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 1.2 V, the range of stability (i.e. potential span for investigation) for example in LiCl-KCl eutectic or NaCl-KCl eutectic is up to 3.5 V at 700°C. In molten nitrates, approximately 5 V is available between the oxidation of nitrate and reduction of alkali metal in the fused sodium and potassium nitrates. Thus highly electronegative metals can be obtained by electrolysis of molten salts in the absence of water.

Different molten salt systems give rise to media of vastly different oxidising properties ranging from strong oxidising to strong reducing systems, and different acidities including basic molten Na_2S and acidic molten $ZnCl_2$ or aluminium chloride. This greatly influences the course of chemical or electrochemical reactions, which may proceed in different ways different molten salt solvents.

For example, $AlCl_3$ - NaCl systems form a special class of solvents in as much as they may be considered as acid-base systems in which the acid and base are Cl^- acceptors and donors respectively. It has been shown that as the ratio of alkali metal chloride to aluminium chloride is varied, the nature of aluminium-containing species changes. In basic melts, that is, the one in which excess alkali metal halide is present, the predominant species are $AlCl_4^-$, while in acid melts containing excess $AlCl_3$ the predominant species are $Al_2Cl_7^-$. The mechanism of deposition of aluminium in the acidic region is proposed as

$$4 Al_2Cl_7^- + 3 e \rightarrow Al + 7 AlCl_4^-$$
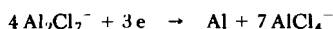
and that in basic melt as $AlCl_4^- + 3 e \rightarrow Al + 4 Cl^-$ and this has been observed experimentally using glassy carbon electrode, tungsten and platinum working electrodes.

The difference in the temperature range of stability between water and molten salt is due to the difference in the cohesive forces for the two classes of liquid. Electrical forces between Na^+ and Cl^- is stronger in NaCl even at 600°C as compared with those of water with its weaker dipolar forces (hydrogen bonding).

Moreover, the higher temperature of molten salt solvents causes a very marked increase of reaction rate, leading to reaction times of only a few seconds for both organic and inorganic reactions. This factor coupled with the very high yields achieved (often approximately 100%) makes molten salts ideal solvents for a large variety of chemical reactions. Because melts have high thermal capacities and conductivities, heats of reaction are efficiently dissipated.

STRUCTURE AND SOME PHYSICAL PROPERTY LIKE 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).
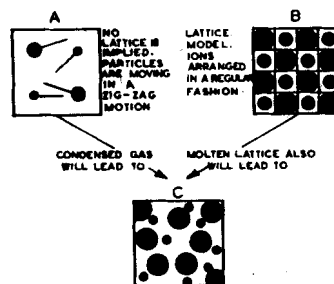

Fig. 2 : Models for gases, solids and liquids

Therefore, one finds that there are two types of models for pure lquid 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, $\Delta H_{(fusion)}$ is 6.69 kcal/mole and $\Delta H_{(vap)}$ 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 $+ \frac{-}{+} +$ 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 ionic 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. $Ca(NO_3)_2 . 4H_2O$, $MgCl_2 . 6H_2O$ 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:

I	II		III
λ Conductivity at a fixed temperature and pressure i.e. λC_p	= λ Conductivity measured at constant volume i.e. λC_v	+	λ Conductivity change due to density or volume change*

(* 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 λ 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 remian 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 mercuric iodide (or liquid containing complex ions) become markedly more ionic, even at a few kilobars, simply because the equilibrium

$$2 HgI_2 \rightleftharpoons HgI^+ + HgI_3$$
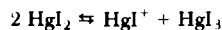
is increasingly displaced to the right hand side as the result of the substantial contraction in volume attending the ionisation reaction. In other words, one may expect that molecular liquids may become ionic at sufficiently high densities and vice versa. Thus, ionic and molecular melts differ only 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-electrolytic

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 [7] : Interionic distance and coordination number for some molten and solid salts

Salt	Liquid at melting point			Solid at m. pt.		
	Cation-anion distance Å	Coordination number (cation-anion)	Cation-cation or anion-anion distance Å	Cation-anion distance Å	Coordination number (cation-anion)	Cation-cation or anion anion distance Å
LiCl	2.47	4.0	3.85	2.66	6	3.76
LiI	2.85	5.6	4.45	3.12	6	4.41
NaI	3.15	4.0	4.80	3.35	6	4.74

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

Table II [7] : Percentage volume increase (100 ΔV/Vs) on melting for alkali metal halides

	F	Cl	Br	I
Li	29.4	26.2	24.3	–
Na	27.4	25.0	22.4	18.6
K	17.2	17.3	16.6	15.9
Rb	–	14.3	13.5	–
Cs	–	10.5	26.8	28.5

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 solid 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, even if one explains the volume expansion in terms of an expansion of the lattice, the property of free flow remains unaccounted for. It is now universally accepted that liquid state is formed from the solid state accompanied by the introduction of some 'empty space' into the lattice. The empty space is known as 'free volume' and can be present in 3 main ways:

i) 'Fluctuation volume' of approximately 2% which is the volume through which an ion can move in the 'cage' formed by its neighbours based on cell model

ii) 'hole volume' of approximately 10-20% which is the amount of empty space in the liquid present as individual units or holes that are on the average large enough to accommodate at least one of the ions. Hole volume may be considered as the total volume less the sum of the volumes of the individual molecules (or ions) calculated from their actual dimensions as determined by x-ray diffraction studies on solids and

iii) 'expansion volume' the difference between molar volume at a temperature T and the volume extrapolated to $0°K$.

Measurement of the velocity of ultrasonic vibrations in molten salts can be used to determine the fluctuation volume. Hence, as the total empty volume can be determined by the volume expansion on melting, the difference between empty volume and fluctuation may be regarded approximately as the holes introduced into the salt on melting. The empty volume in the melt provides a mechanism for transport properties such as electrical conductance, thermal conductivity, viscosity and diffusion. All theories of liquid state are based on different postualtes regarding the shape, size and distribution of this empty space.

It may be intellectually satisfying to think of solids as regular and coherent, liquids as irregular and coherent, and gases as irregular and incoherent.

Physical properties

In general, properties of ionic melts are similar to those of common fluids.

Table III represents some of the physical properties of molten salts compared with roc n temperature liquids.

Table III [10,23]: Comparison of the physical properties with some liquids

Property	NaCl	KCl	H$_2$O	Benzene	CCl$_4$
At temperature ($°C$)	850	800	25	25	25
Surface tension σ (dynes/cm)	111.8	96.8	72	28.2	27
Viscosity η (Millipoises)	12.5	11.0	8.95	6.14	10.38
Density d (gm/cc)	1.539	1.510	1.00	0.87	1.595
Refractive index n	1.408	1.385	1.332	1.501	

The physical properties are not very different. In fact, one can go further and say that molten salts look like water and near their melting points, have viscosities, density and surface tensions of the same orders of the magnitude as those of water.

In the above physical properties, ionic liquids are typical liquids, but in respect of freezing point and electrical conductivity, the two classes of liquids differ greatly, e.g. the specific conductivity of molten NaCl at 850°C is 3.74 ohm^{-1} cm^{-1} compared with 6.2 x 10^{-8} ohm^{-1} cm^{-1} for water at 25°C and the freezing point for NaCl is 801°C compared with 0°C for water. Again, for molten KCl at 800°C specific conductance K = 2.24 mho/cm compared with K = 0.1 mho/cm, for 1 N KCl solution at 20°C, i.e. 22 times greater than that of aqueous solution. In other words, electrical conductivity of molten salt is usually extremely high.

But the specific conductivities of molten electrolytes are much smaller as compared with metals, e.g. specific conductance of copper is 5.8 x 10^5 ohm^{-1} cm^{-1} and that of mercury is 1.1 x 10^4 ohm^{-1} cm^{-1} whereas as already pointed out, the specific conductivity of molten NaCl at 850°C is 3.74 ohm^{-1} cm^{-1}

COMPARISON BETWEEN AQUEOUS AND FUSED SALTS

In many cases, the electrolysis of fused salts is accompanied by the liberation at the electrodes, of the same substances as those which are discharged during the electrolysis of aqueous solutions. For example, lead chloride, iron chloride, copper chloride etc. form the corresponding metals at the cathode with the liberation of chlorine at the anode. The fused salt electrolysis is mainly confined to the production of aluminium, magnesium, sodium and such reactive metals, as these metals cannot be recovered economically by aqueous electrolysis. Over 80% of the total world production of magnesium and 100% of the world production of sodium are being carried out by fused chloride electrolysis. Over 95% of the world production of aluminium is made by electrolysing alumina dissolved in molten cryolite.

At the first glance it may appear that as far as the ions of the solvent are absent and ionic spaces are not hydrated in the molten salt, this medium is simpler than aqueous solution of the same salt. But in actual practice, the fused systems are highly complicated. High temperatures create great difficulties while conducting an experimental work, designing and fabricating suitable cells. However, the techniques in these operations are more an art than science, as the mechanism of the electrode reactions in the more complex electrolytes is not fully understood. The relatively high temperature of the electrolysis of melts accelerates all the processes considerably. If, for example, the dissolution of the metal depositing at the cathode can be generally disregarded in the electrolysis of aqueous solutions, the phenomenon of metal dissolution in the melt and the melt dissolution in the metal are often notable characteristics of the electrolysis of molten salts.

The advantage in employing fused salt electrolysis for obtaining these metals consists in the avoidance of a number of steps normally involved in aqueous chloride electrolysis and in having very compact electrolytic cells as compared with aqueous electrolysis. This is because of the fact that high current densities of the order of 0.7-1.0 A/cm^2 could be employed in fused salt electrolysis, whereas 0.01-0.04 A/cm^2 i.e. 100 times less are alone possible in aqueous electrolysis. In addition, remelting of the metal is not necessary. However, there are many operational difficulties.

Taking the typical case of extracting lead by fused salt electrolysis, it is claimed that lead sulphide concentrates could be directly fed into the anodic chamber, where mixtures of lead chloride with alkali and alkaline earth metal chlorides are electrolysed to get lead at the bottom and chlorine as anodic product. The chlorine could, no doubt, react with lead concentrates producing lead chloride and it is thought it could be so adjusted that the rate of depletion of lead chloride from the bath is equivalent to the rate of formation of lead chloride. Chlorine, sulphur, sulphur monochloride and mixtures of these could be produced as anode products. However, if unreactive lead sulphide or lead oxide is present, they get either distributed in the bath or at the bottom and hence the electrolysis could not be conducted smoothly.

The electrolyte in a fused bath very easily gets contaminated with oxides of metals which are formed as decomposition products of the anhydrous chlorides employed. In general, when once the electrolyte of a

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 electrothermal 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 voltilization 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 electrolysers always reacts with the electrolysis to some extent. This is sometimes seen in the formation of compounds resulting from the reactions of anod e gases e.g. oxygen evolved at the anode tends to react with it and the cell materials to form oxides of carbon as in aluminium cell.

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:

$$2SnCl_2 \rightarrow Sn + SnCl_4$$
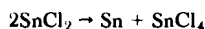
The dissolution of the metal in the fused salt

As explained already, 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 subsalts may be formed due to the dissolution of metal in the fused bath. In the electrolysis of fused cadmium chloride 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 KCl, NaCl, or $BaCl_2$ raises the current efficiency in the electrolysis of magnesium chloride, other cell conditions being the same. This finds explanation in the fact that solubility of magnesium in these foreign salts is small 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 stirring by gas 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 hydrogen and oxygen are evolved; then magnesium chloride gradually decomposes. In the case of aluminium cell, both sodium and aluminium codeposit. 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 halogen 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, titanium 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-Heroult cell is reported as (approx) 18 kWh/kg and in recent installations the value is brought down to 13 kWh/kg by reducing the inter-electrode gap and by lowering the cathode current density from 11,000 to 8000 A/m^2. 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 13000 kg/day level.

Magnesium

In the case of electrolytic magnesium metal, a good conducting electrolytic 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/m^2 and 500°C has been reported, whereas the customary aqueous zinc sulphate process consumes 3.5 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 sulphur dioxide fumes, and simultaneously elemental sulphur is obtained as byproduct.

Sodium

Recent development of beta-alumina diaphragm suitable for use in molten salts, 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 as low a 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 $ZnCl_2$-NaCl or $PbCl_2$-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 byproduct 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 'Nafion' (perfluorosulphonic acid cation exchange membranes) or perfluorocarboxylic acid or carboxylate membrane or bilayer membrane of sulphonic/carboxylic acids type.

It is also proposed that utilisation of beta-alumina diaphragm (similar to the one used in the sodium-sulphur battery) in the electrolysis of molten caustic soda containing about 5% water as catholyte and sodium chloride-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 requirements. Sodium ions move from the anolyte to catholyte through the beta-alumina diaphragm. The reaction is similar to the electrolytic processes of membrane cells :

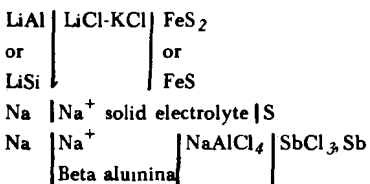$$H_2O\,(g) + NaCl\,(NaCl\text{-}ZnCl_2) \rightarrow 1/2\,H_2\,(g) + NaOH + 1/2\,Cl_2\,(g).$$
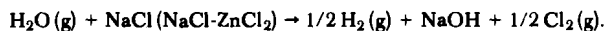
Here the beta-alumina diaphragm is in constant contact with molten caustic soda on one side and a highly corrosive molten medium on the other side. The success of the processes employing beta-alumina diaphragm depends much upon the performance and life of the diaphragm under the corrosive conditions at elevated temperatures.

MOLTEN SALT 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 cell 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 | FeS₂
or | | or
LiSi | | FeS

Na | Na⁺ solid electrolyte | S

Na | Na⁺ | NaAlCl₄ | SbCl₃, Sb
| Beta alumina | |

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 recharges - an electric vehicle with a 200 Whr/kg battery occupying 30% 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.

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