THERMAL BATTERY AS A POWER SOURCE IN GUIDED MISSILES

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The battery based on low melting eutectic salt mixture electrolyte is thermally activated by raising the temperature of the electrolyte to its melting point. The battery is capable of discharging at very high rates for short duration. The battery employs a combination of elements with low electronegativity and capable of giving higher electrode potentials such as Ca or Mg as anode, a wide variety of eutectic salt electrolytes and various oxides, sulphates, silicates, phosphates, chromates as cathode depolarizers. Only those thermally activated systems which find application as potential power source in guided missiles are reviewed.

Guided missiles require batteries with special features such as ruggedness, compactness, high reliability, prolonged storage stability, large amount of power per unit volume and weight; and very high discharge rates for a few minutes. Thermal battery is based on an electrolyte which is solid and non-conducting at the room temperature, and is activated by raising the temperature to the melting point of the electrolyte to render it in the conducting molten state. Therefore, it lends itself to easy miniaturization with exceptional ruggedness; and more electrical power per unit volume and weight of the system packed into it. The electrolyte being non-conducting at the room temperature prevents self-discharge and ensures exceptionally long extended storage life. Because of very high electrical conductivity of molten electrolyte the battery is capable of providing very high discharge rates. The conductivity of molten salts is from 10 to 100 times higher[1,2] than those of aqueous systems. Therefore molten salt cells should have low voltage losses due to IR drop. It is in this area of very high discharge rate ($\geqslant 1$ amp/in.) that the thermal battery finds most application. Batteries have been designed[3] to satisfy certain requirements upto 100 watt-min. Pulse current of 57 amperes (25 amp/in.) was measured[2] in $Ca/LiCl\text{-}KCl/CaCrO_4$ Ni sytstem. Another battery [4,5] could be discharged at 100 ampere without any significant polarization even after 6 minutes. Batteries with a capacity up to 50 amp-hr have been designed[6]. Batteries with comparatively short performance life have been designed for use in guided missiles [2, 4, 5, 7, 8, 9, 1 ', 11, 12 1 , 14, 15, 16 17, 18]. Attention has also been directed towards the development of long-life batteries with performance life of 3-6 days for space probe applications.

Very little open literature is available on these batteries, because of the classified [1, 2, 19] nature of the information. The older work which is now of only historical significance has been reviewed by Allamand & Ellingham [0], Cooper [1], and Vinal [9]. McKee[2] discussed the subject in rather too general and popular manner. His survey also contains comparatively older work and therefore is limited in scope. Another review of the subject[1] though quite recent is not as extensive, so far as short duration missile batteries are concerned and also lacks in significant details. We have made a thorough search of openly available literature upto the end of 1970 through Chemical Abstracts, NASA reports and all other open sources of information, exclusive of classified reports to which we had no access.

HISTORICAL DEVELOPMENT

Jablochkoff [1] constructed a cell with carbon (or iron) electrode in fused potassium or sodium nitrates. Fabingi & Farkas [3] used carbon and platinum as electrodes in the hydrate of sodium or potassium; to which external heating was applied. Carbon was the obvious fuel in these systems, but it did not ionize in electrolytes. Most of the cells involved gaseous reactions [24, 25, 26 27, 2]. Gyuris[29] used molten sodium and manganese dioxide. Hammer & Schrodt[30] investigated the cell system Mg/Molten electrolyte/MnO_2, C (acetylene black). Mg was chosen as anode because of its higher electrode potential. $NaOH$ was the molten
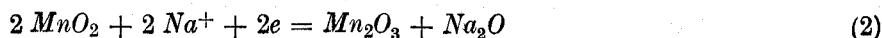
electrolyte. The open circuit voltage of the cell increased from zero at room temperature to about 1 volt, long before the m.p. of $NaOH$ was reached owing to the presence of residual moisture in the electrolyte followed by decrease upto 200°C and finally rose to a maximum of 2 V at 700°C. The cell maintained a closed circuit voltage of over $1 \cdot 1$ V while discharging through a 100 ohm load for a period of 12 hours.
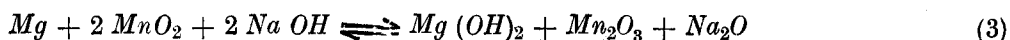
The cell reactions are represented as

At anode :

$$Mg + 2OH^- \rightleftharpoons Mg(OH)_2 + 2e \tag{1}$$

At the cathode :

$$2 MnO_2 + 2 Na^+ + 2e = Mn_2O_3 + Na_2O \tag{2}$$

The net cell reaction is :

$$Mg + 2 MnO_2 + 2 Na\,OH \rightleftharpoons Mg(OH)_2 + Mn_2O_3 + Na_2O \tag{3}$$

Goodrich & Evans[3] discussed various cell systems that had been developed till then. A $LiCl$-KCl eutectic was commonly employed as molten electrolyte. Negative electrodes (anode) were normally calcium or magnesium because of their high potential in fused salt electrolytes. The former giving about one volt more than magnesium. Potassium chromate incorporated in the electrolyte and tungstic oxide, molybdenum trioxide and similar oxidising agents applied as coating to the metal of the positive electrode (Ag, Cu, Ni, or iron) acted as cathode depolarizers. An integral heat source based upon a variety of exothermic chemical reactions (pyrotechnic compositions) provided sufficient heat to raise the cell temperature above the melting point of the electrolyte. Open circuit voltages as high as $3 \cdot 0$ V per cell were obtained with the working voltage being lowered as a function of the discharge rate. At current density $1 \cdot 6$ amp/dm² ($0 \cdot 1$ amp/in.²) this voltage dropped approximately 10 percent, increasing to 20 percent at a current density of $7 \cdot 8$ amp/dm² ($0 \cdot 5$ amp/in².). A cell comprising of calcium sheet anode, nickel cathode coated with 80 percent WO_3 and 20 percent lead chromate and $LiCl$-KCl eutectic mixture (45 percent-55 percent respectively) operated at 400°C and had an open circuit voltage of $2 \cdot 8$ V, working voltage of $1 \cdot 8$ V $\pm$ 10 percent, and useful life of 5 minute under $0 \cdot 18$ ohm load. The energy of the battery was $4 \cdot 89$ watt min/cm³ or $2 \cdot 37$ watt-min/g.

IMPORTANT CONSIDERATIONS IN THE DEVELOPMENT OF A THERMAL BATTERY

In order to derive higher output power from an electro-chemical cell system, it is important to choose right type of anode-cathode combination so as to obtain a very high output voltage in conformity with the discharge characteristics of the system. The characteristics that primarily affect the specific energy are electronegativity and equivalent weight. Elements having the lowest electronegativity are those of group IA and IIA of the periodic table, that is alkali and alkaline earth metals. Their low electronegativity makes them most suitable for use as anode materials because they surrender their electrons more easily than the other elements. Conversely the elements with the highest electronegativity are most suitable as cathode materials because they have greatest affinity for electrons. These elements are found in group VIA and VIIA, the chalcogens and the halogens. The large difference of electronegativity between anode and cathode materials provides a relatively large cell voltage (in the range of 2 to 4 volts). Selection of anode (Group VIA and VIIA) from elements of lower equivalent weights (those high up on the periodic table) yields the lightest weight combination of reactants corresponding to a high specific energy (more energy per unit weight). The standard electrode potentials of a large number of elements [1, 31, 32] have been measured in $LiCl$-KCl molten eutectic mixture at 450°C. Table 1 lists the electrode potentials when 10 percent K_2CrO_4 is incorporated in the fused electrolyte, (since $K_2Cr_2O_4$ is most frequently the main reactant at the cathode). $Ag/AgCl$ reference electrode[33] is more frequently employed in fused-salt potential measurements.

In missile batteries where relatively lower specific energy may be required (highest specific energy is available from Li-Cl_2 system) for short duration (of the order of few seconds) Ca or Mg as anode material and oxygen containing materials like oxides sulphates, chromate, nitrates as cathode depolarizer are the obvious choice.

TABLE 1

EMF SERIES[2] OF METALS IN $LiCl\text{-}KCl$ EUTECTIC $+ K_2CrO_4$

(incorporated in the electrolyte)

EMF in Volts

Metal	Referred to Pt (II)-Pt $10\% K_2CrO_4$ added to eutectic electrolyte	Metal	Referred to Pt (II)-Pt $10\% K_2CrO_4$ added to eutectic electrolyte
Mg	—2·19	Co	—0·70
Th	—1·95	Ge	—0·59
Ca	—	Tl	—0·58
Mn	—1·53	Cu	—0·47
Al	—1·20	Ta	—0·46
Zr	—1·03	Ag	—0·45
V	—0·95	Fe	—0·44
Zn	—0·91	Bi	—0·42
Tl	—0·86	Ni	—0·37
Ga	—0·82	W	—0·31
In	—0·81	Mo	—0·26
Cd	—0·81	Au	—0·24
Pb	—0·80	Pt	0·000
Sn	—0·80	Pd	+0·05

ELECTROLYTE

A low melting electrolyte facilitates easy operation and many designing problems are reduced. $LiCl\text{-}KCl$ eutectice mixture (m.p. 450-500°C)[4, 5, 13, 14, 17, 18, 32, 34, 35, 36] has been most widely used. Addition of 10 % $AgCl$ to the electrolyte in the cathode section was also made to achieve certain desired results. added[6] to $K_2CrO_4 LiCl\text{-}KCl$ eutectic in cathode section stabilises the Ca potential. $LiCl\text{-}KCl$ eutectic being hygroscopic is difficult to purify and is always contaminated with the traces of moisture. Moisture when present may lead to the self-discharge of the battery thereby seriously affecting the storage-life. Suitable procedures have been recommended for removing traces of moisture from the eutectic[34]. Another added advantage of fused $LiCl$ KCl eutectic is its very high conductivity (2·1 ohm—^{1} cm—^{1} at 500°C compared to 0·0391 ohm^{-1} cm^{-1} of 0·1 $NHCl$ solution). $KCl\text{-}LiNO_3\text{-}K_2CrO_4$ (27·8, 68·5, 3·7 parts by weight respectively) has also been used[37]. In system $Mg/LiNO_3\text{-}KCl/Ag$ the O.C.V. of 1·4-1·6 V was obtained at 300–500°C when KCl was greater than 20% KCl[18] has also found application in thermal battery.

THE ANODE

Calcium—Calcium has been used as anode in a number of batteries [2, 5, 7, 8, 13, 15, 16, 17, 18, 38] Lithium forms an alloy with calcium, which is partially liquid at temperatures above 231°C. The deposition of lithium metal on the calcium electrode is accompanied by the introduction of calcium ion in the electrolyte according to the reaction.

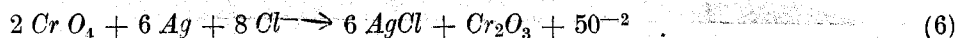$$Ca\ (s) + 2\ Li + (l) \rightleftharpoons Ca\ ++ (l) + 2\ Li\ (l) \tag{4}$$
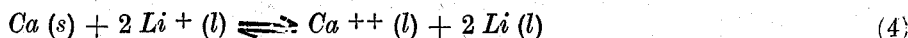
Lithium metal so formed develops a liquid alloy with calcium above 231°C. It is postulated that this fluid surface continuously renewed by convection flow would not be subject to the marked polarization. Indeed fast activation times and low polarization at high rates are observed. However, it is possible that the liquid negative material may migrate through the electrolyte compartment and discharge at the positive

plate resulting into electrical shorting. Apparently this effect can become pronounced at higher temperatures. There is also contained in these reactions a mechanism for thermal run away since both reactions the alloy formation and self-discharge reaction are exothermic. This reaction can limit shelf-life to 5-10 minute Electrical shorting due to $Ca-Li$ alloy formation has been overcome by forming a layer of $3 Ca(A_3O)_2$. $2 A_6OH$ on Ca anode surface prior to assembly in cells. An anode consisting of a Ni base 0·005 in thick and a Ca coating 0·01 in. thick, was immersed at ~27°C in a solution of ~25 volume percent glacial A_6OH in Me_2CO for ~120 seconds. It was removed and dried at 27°C until excess M_2CO was evaporated. Thereafter, it was heated from 200-325°C to produce a $Ca(A_2O)_2$ coating and finally assembled into cells with $LiCl-KCl$ eutectic electrolyte (45/55 wt ratio) and $CaC_2O_4 + K_2CrO_4$ mix cathode reactant and Fe cathode. The heat of activation decomposed anode layer to $CaCO_3$ ~0·002-0·003 in. thick.

Calcium electrode[39] is very reactive in $LiCl-KCl-K_2CrO_4$. It is characterised by high degree of passivation. In $BaCl_2-NaCl-CaCl_2$ at 500°C, the electrode is slow to activate due to the formation of a layer of calcium oxide and nitride on the surface during the cell assembly. Apparently dissolution of CaO is a slow process in this system. In $LiCl-KCl$ eutectic CaO is fairly soluble therefore activation is very fast.

Addition of chromate[2] (6·65 mole %) to the electrolyte gives very stable anodic potential and long discharge life. A somewhat insoluble and protective coating containing calcium and Cr_2O_3 develops on the discharged calcium electrode. Apparently this film is sufficient to suppress, but not completely inhibit, the lithium-alloy reaction. A cell employing this system was discharged for 11 minute at 1·50 A/cm². The system $Ca/KCl-LiCl$ $AgCl-K_2CrO_4/Ag$ has been investigated by Seils[5] et al. When the cell was discharged at 100 ampere, the positive electrode polarised by no more than 0·15 V even after 6 minute whereas 29·4 g of $AgCl$ included in 150 g of electrolyte is equivalent to only 3·30 minute at 100 ampere. This is a combined effect of $AgCl$ and K_2CrO_4 reduction and the following scheme has been suggested to explain the lower polarization in presence of $AgCl$

$$2 \ AgCl + 2e^- \rightarrow 2 \ Ag + 2 \ Cl^- \tag{5}$$

$$2 \ Cr \ O_4 + 6 \ Ag + 8 \ Cl^- \rightarrow 6 \ AgCl + Cr_2O_3 + 5O^{-2} \tag{6}$$

$AgCl$ is the part of the initial electrolyte, but is also formed by way of above reaction which replace silver ion used galvenically at the positive electrode. A battery[1] based on above system utilizes calcium anode, $LiCl-KCl$ eutectic electrolyte and cathodically active $AgCl$ and K chromate (5 to 7 mole%) incorporated in the electrolyte. A porous separator between anode and cathode sections, inhibits short-circuit. At least 10 mole percent $AgCl$ is preferably used in the electrolyte mix for highest power drains. Lesser molar proportion may cause drop in voltage while more than 20% causes calcium potential unstable despite the presence of chromate. The battery is operated below 550°C. Another battery [8,38] based on Ca anode and $LiCl-KCl$ eutectic electrolyte contained in a porous support employs as cathode Au impregnated with a mixture of cathodic reactants $Fe_2(SO)_3$, $CuCl_2 + CaCrO_4$, M_2O_3, WO_3 and 10% of the electrolyte. The battery with Ni or Au coated base metal cathode and $FeSO_4$ cathode reactant gives activation time of 0·2-0·3 second and useful life time ~20 Seconds. A mixture [15,16] of an aluminate, borate, carbonate, phosphate, silicate, sulphate, alumino silicate, $LiCl-KCl$ eutectic electrolyte and conducting grannulas of C or Cu is employed as cathode depolarizer mix in thermal batteries with Ca or Mg anodes. One such cell with Ca anode and a cathode depolarizer mixture containing 40% $Fe_2(SO_4)_3$, 14% graphite, 12% Cu powder and 34% $LiCl-KCl$ eutectic had an open circuit voltage of 2·52 V at 560°C and theoretical capacity of 330 W hr/lb of the active material. Yet another cell [17,18] utilises Ca anode and either of $LiCl-KCl$ or $CaCl_2-NaCl-KCl$ eutectic electrolyte and as cathode reactant a mixture of V_2O_5 (5-75%) and $LiCl-KCl$ eutectic coated on Ni/Al or steel wire. A thermoelectric generator[13] especially useful for projectiles and missiles may be composed of a series of miniature battery cells. The casing of each cell is formed into a rectangular cup-shaped container each consisting of two half-cell units, one of which has a lower calcium deposit as negative electrode, $LiCl-KCl$ eutectic electrolyte and the bottom face of conducting tab insulated from the walls of the container resting on the electrolyte forming the positive electrode and the other unit consists of upper face of the tab, the electrolyte and the calcium deposit in the upper part of the container. Each casing unit has a conducting tab for interlinking the cells and is also provided with a strip of heat paper pad composed preferably of a thermal mixture to generate large amount of heat for activating the battery. The cells may be arranged in series in linear fashion or in a spiral.
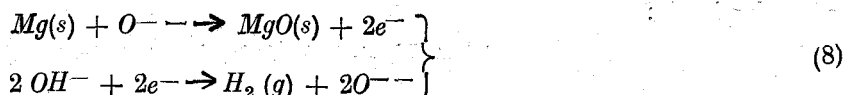
Goldsmith and Smith have evaluated the performance characteristics of thermal batteries with calcium anode $LiCl$-KCl eutectic electrolyte and a variety of polarizing agents such as CuO, $CaCrO_4$, WO_3, Fe_2O_3, V_2O_5. It is found that CuO and Fe_2O_3 give low voltage with CuO exhibiting longest performance life. V_2O_5, because of its tendency to react with melt to form Cl_2 and insoluble reduced V compounds such as Li_2O $2 V_2O_4 . 4 V_2O_5$; shows lowest performance life. $CaCrO_4$ gave best energy ouput.

Mg—The half cell potential[36] of Mg in $LiCl$-KCl eutectic is approximately $0.3 V$ less negative than a calcium electrode. At reasonable discharge rates the electrode efficiency[32] is generally greater than 91%. Half cell reaction is as follows :

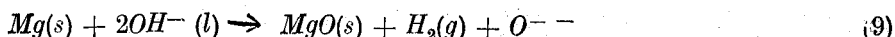$$Mg + 2 Cl^- \rightarrow Mg^{+2} + 2Cl^- + 2e^- \tag{7}$$

In the system[36] $Mg/LiCl$-KCl/Ni, if the electrolyte itself contains oxide ion or hydroxide ion (water) as impurity, significant amount of insoluble MgO may be formed. At lower temperatures $390°$-$40°C$ OH^- ion is cathodically reduced to hydrogen gas and oxide ion.

At the anode :

At cathode :

$$Mg(s) + O^{--} \rightarrow MgO(s) + 2e^- \left.\begin{array}{r}\\ \\ \end{array}\right\}$$
$$2 OH^- + 2e^- \rightarrow H_2 (g) + 2O^{--} \tag{8}$$

Net reaction is :

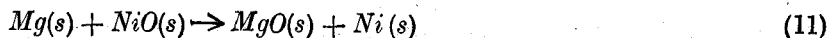$$Mg(s) + 2OH^- (l) \rightarrow MgO(s) + H_2(g) + O^{--} \tag{9}$$

At higher temperatures ($445°$-$535°C$) Ni (II) oxide formed by the action of hydroxide ion on Ni metal is the cathodically reduced species.
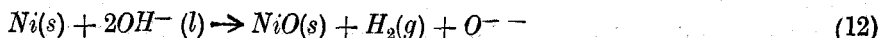
At cathode :

$$Ni O(s) + 2e^- \rightarrow Ni(s) + O^{--} \tag{10}$$

Net reaction :

$$Mg(s) + NiO(s) \rightarrow MgO(s) + Ni (s) \tag{11}$$

NiO is formed by the reaction :

$$Ni(s) + 2OH^- (l) \rightarrow NiO(s) + H_2(g) + O^{--} \tag{12}$$

In practical batteries a variety of cathode depolarizers have been used. It is indicated from the investigation[32] of slightly soluble iron oxides ($FeOx$) as cathode depolarizer in the above system, that for large voltage with greater energy output during short-time discharge γ-Fe_2O_3 should be the choice. α-Fe_2O_3 can be used for flat discharge curve when large voltage is not important. The voltage can be shifted up or down to some extent by incorporating small amount of TiO_2 and SiO_2. A high peak-voltage of short duration may be had by blending the iron oxide with conductive carbon. The cells are discharged at $420°C$. The fabrication of terminals for a magnesium anode thermal cell is described in a patent[10]. The electrode is made from a thin flat electrode plate and a terminal consisting of a metal tab bifurcated on one end to produce two legs placed over metal plate with the end of each leg folded over a free edge of the metal plate. Two slots are cut into a 0.015 in. thick Mg foil anode and terminal tab is made by folding over lengthwise on itself a Ni strip 0.05 in. wide giving a double strip of 0.25 in. width. The end of this double strip is split into legs with one placed over one side of the Mg electrode and the other over the other side. Both are then threaded through the slots with ends flapped over the edges of the slots. The entire electrode is pressed at $40,000$ p.s.i. and the two legs are then spot-welded to the Mg foil. The anode and cathode for use in multicell battery[17] may be fabricated by compressing powdered Mg and V_2O_5 respectively into opposite ends of the same metal screen bases of steel, Cu, or Ni wire. V_2O_5 is the cathodic reactant. Three larger pelletized[14] cells using Mg powder anode, $LiCl$-KCl eutectic electrolyte and V_2O_5 catholyte were studied. Varying the thickness of the layers and their relative ratios $KCl/LiCl$ ratio was fixed at 1.25. Cell performance was affected by the purity of materials and the presence of voids in the pellets. The catholyte mixture containing a mixture of V_2O_5 (5–75 wt $\%$) and $LiCl$-KCl eutectic may also be coated on Ni, Al, or steel wire and assembled with a thermal battery[18] with Mg anode and $LiCl$-KCl or $CaCl_2$ $NaCl$-KCl eutectic electrolyte.

In a different design for Mg anode thermal cell an anodic cone such as Mg drawn to a flexible wire or tube, a $LiCl$-KCl eutectic electrolyte layer surrounds the cone co axially and a cathodic layer such as Ag-Cl surrounds the eutectic layer co-axially. Cathode layer is surrounded by an electrically conducting casing such as one made of an Ag tube (12·7 mm diameter 0·5 mm wall thickness) inside with a 2·5 mm thick layer of $AgCl$. After insertion of a Mg rod (2 mm diameter the remaining space is filled with $LiCl$ KCl eutectic containing $\leqslant 50\%$ MgO and the diameter of the unit is reduced to 0·25 mm by mechanical drawing. The unit delivered 2 V at 350°.

The batteries mentioned so far have very short useful life of the order of few minutes. The attempts have also been directed towards the development of long life thermal batteries with performance life extending upto several days for space-probe applications[40]. Cu_2O-CuO as catholyte in batteries with Mg anode and $LiCl$-KCl eutectic extends performance life upto several days. These cells are discussed later.

Yet another system $Mg/LiNO_3$, KCl/Ag has been investigated by Jening[12] at temperature 300–500°C. With greater than 20 mole % KCl, open circuit voltage of 1·4–1·5 V was obtained. Cells were discharged at 4–100 mA/cm². The electrical output of cells with KCl less than 20 mole % was poor. The postulated mechanism is:

$$Li_2O + Mg + 2\,AgCl \rightarrow MgO + 2\,Ag + 2\,LiCl \qquad (13)$$
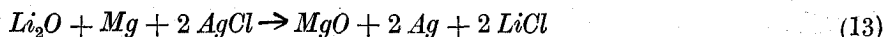
Li_2O is produced in the reduction of nitrate. A battery[37] based on this system consists of a low voltage section 'A' and high voltage section 'B' and an ignitable cylindrical block with thermally conductive metal heat rod. 'B' cells are fabricated by lining a Ag cup with chrysolite asbestos paper impregnated with a solution containing K chromate 3·7, KCl 27·8 and $LiNO_3$ 68·5 parts by weight. A discoid button type Mg electrode is placed on the electrolyte body and is covered with an insulating washer. After crimping the Ag side, 'B' cells are placed in a brass tube. 'A' cells are composed of Mg anode surrounded by 2 sheets of glass fibre cloth impregnated with K chromate, KCl, $NaCl$, anhydrous $CaCl_2$ 0·5 & $LiNO_3$ 5 part by weight and positive electrode of two thin sheets of Ag. 'A' cells can be stacked by crimping the edges of the outer sheet.

CATHODE

Oxygen containing compounds such as Sulfates[3,6,8,14] Oxides[15,17,18] Chromates[19,30,32,38,40,41,42,43] Phosphates[4,5,15,36,37] etc. have been used as cathode materials.

A large number of compounds[15] such as an Aluminate, Borate, Carbonate, Phosphate, Silicate, Sulfate, Alumino silicate, etc. were investigated as cathode depolarizers in thermal battery with either Ca or Mg anodes, Ni cathode and $LiClKCl$ eutectic electrolyte. A cell with a cathode depolarizing layer containing 40% $Fe\,(SO_4)_3$, 14% graphite, 12% Cu powder and 34% $LiCl$-KCl eutectic, Ca anode had an open circuit voltage of 2·52 V at 560°C and theoretical capacity of 330 W hr/lb. of active material. A small amount of F^- was added to the PO_3^- depolarizers to enhance the conductivity. Various sulfates, phosphates and other oxygenated anions and oxides of group IIIA to VIA are reported[16] to be effective depolarizers for thermal batteries operating at 500°C. In the case of sulfates the pyrosulfate ion is the active species at cathode and S is the probable end product of the reduction.

Iron Oxides[32]

The material has been used in thermal batteries. Discharge behaviour has been observed to vary with the particular oxide employed i.e. —Fe_3O_4, αFe_2O_3,γ- Fe_2O_3. The physical and chemical reasons for differences in behaviour have been discussed on the basis of two broad considerations. One of these is the amount of reducible iron. Thus a magnetite cell containing only 3·42 magnesium-ions of Fe (III) polarizes more rapidly than a Fe_2O_3 cell with 4·96 magnesium ions. The addition of conductive carbon enhances behaviour at the beginning of discharge, but voltage drop is very fast, presumably because of non-galvanic reduction of the iron oxide. The other general consideration is the specific resistance of the oxide. In each instance, discussed above, those effects which enhance conductance lead to higher cell voltage and those which increase resistance result in lower terminal voltages. Flatter curves result because of decreased discharge current. In this regard the performance of the magnetite and γ-Fe_2O_3 spinels is to be compared with that of α-Fe_2O_3 obtained as such or thermally prepared. Samples containing small amounts of Silica have higher resistivity than pure samples and this is reflected in cell performance. Small amounts of titanium ion decrease resistivity, and this is also reflected in cell performance. Unfortunately this
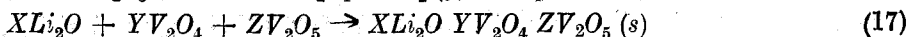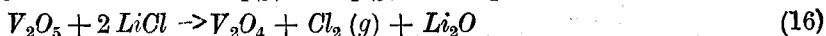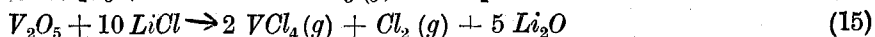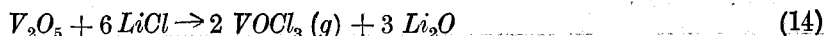
resistance parameter, which is of primary importance is difficult to measure directly. It is also affected by such factors as compacting pressure, particle size, and porosity.

One may select a cathode reactant to yield desired electrical characteristics. γ-Fe_2O_3 or magnetite when chosen may provide high voltage with greater output energy for short duration of discharge. α-Fe_2O_3 may provide flat discharge.

Fe (III)[8,16,38] ,Fe (O)—The soluble iron cathode is reversible and has high exchange current. $Fe_2(SO_4)_3$ has been used in the cell system[16] $Ca/LiCl$-KCl, $Fe_2(SO_4)_3/Fe$, C, $FeCl_3$ when used in cathode mixture of 1 mole $FeCl_3$ in $4\cdot5$ moles of $LiCl$-KCl eutectic showed a polarization of $0\cdot1$ V at 150 mA/cm^2 (450°C).

Sb_2O_3[16]—Cell of the type Ca/KCl, $LiCl$, MgO/Sb_2O_3 had open circuit voltages ranging from $2\cdot2$ to $2\cdot4$ V and energy of 110-120 W hr of active material. Cell performance was not particularly sensitive to Sb_2O_3 content over a wide range of cathode mix composition. However when Sb_2O_3 fell to 45% of the cathode cake a considerable reduction in output occurred. Additional graphite is needed in mixtures dilute in Sb_2O_3. The compound discharged at positive at 600°C and the solubility was $0\cdot5\%$ at this temperature. Half-cell reaction proceeds directly to the metal.

V_2O_5 [11,14,17,18]—This material because of its high solubility and tendency to react with $LiCl/KCl$ melt to form Cl_2 and insoluble reduce V compounds such as $Li_2O.$ 2 V_2O_4 4 V_2O_5, gives lowest performance life. Chemical analysis of the reaction products formed in mixtures of V_2O_5 and molten $LiCl$-KCl at 380-500°C over the concentration range 5-30 mole % V_2O_5 indicates decomposition reactions of the following type.

$$V_2O_5 + 6\,LiCl \rightarrow 2\,VOCl_3\,(g) + 3\,Li_2O \tag{14}$$

$$V_2O_5 + 10\,LiCl \rightarrow 2\,VCl_4\,(g) + Cl_2\,(g) + 5\,Li_2O \tag{15}$$

$$V_2O_5 + 2\,LiCl \rightarrow V_2O_4 + Cl_2\,(g) + Li_2O \tag{16}$$

$$XLi_2O + YV_2O_4 + ZV_2O_5 \rightarrow XLi_2O\,YV_2O_4\,ZV_2O_5\,(s) \tag{17}$$

In a $LiCl$-KCl eutectic melt at 450°C, V_2O_5 is electrochemically reduced to an insoluble mixed lithium vanadium oxide at a potential which is a function of V_2O_5 concentration, chemical analysis of Li, vanadium bronze formed in potential region $0\cdot00$-$0\cdot20$ V Vs Pt (II) $(1M)/Pt$ reference electrode gave a compound with stoichiometry $LiO_2\,V_2O_4\,4\,V_2O_5$.

V_2O_5 has been used in cells[17,18] of the type $Mg/LiCl$-$KCl V_2O_5/NiAl$, Cu or steel. V_2O_5 content varied from $0\cdot5$-$0\cdot75$ percent by weight. Cathodes[18] giving high potential were prepared by dipping Ni, Al, steel or Mg metal wire in a melt of $5\cdot35$ percent by weight B_2O_3 in V_2O_5 obtained by heating the mixture at 700-800°C for 2 hours. Alternately a coating of slurry ($0\cdot002$-$0\cdot006$ in. thick) of powdered V_2O_5 and B_2O_3 in non-aqueous solvent such as acetone was applied and fused by heating.

Chromates[4,5,7,36,37]

Chromates e.g. K_2CrO_4 have been used as soluble depolarizers in thermal batteries. It has been shown that K_2CrO_4 in $LiCl$-KCl is reduced electrochemically at platinum electrodes to give an insoluble lower oxide of chromium probably containing lithium ion and melts. However the situation is more complex[36]. Potential-time curves for the discharge of the cell $Mg/LiCl$-KCl-K_2CrO_4 through 2,000 ohm load at 440°C showed a series of discrete potential plateus corresponding to $1\cdot80$-$1\cdot81$, $1\cdot76$, $1\cdot70$, $1\cdot67$ V, which could be explained in terms of different reducible phases at the cathode. Chromate functions in oxidising Ni as indicated by the reaction.

$$2\,x\,CrO_4^{-}(1) + 3\,Ni(s) \rightarrow 2\,x\,O^{-}(1) + Cr_2O_3(s) + 3\,NiO\,(x)\,(s) \tag{18}$$
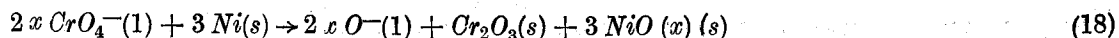
followed by the half cell raction NiO (x)

$$NiOx(s) + 2\,(x-y)\,e^{-} \rightarrow NiOy(s) + (x-y)\,O^{--}(1) \tag{19}$$
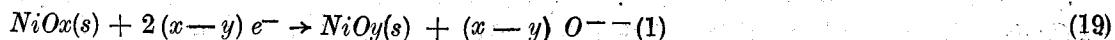
In another study the primary reduction product has been found to be CrO_4^{-5} which decomposed to yield CrO_3^{-3} and O^{--}. At sufficiently high concentrations of CrO_4^{-5} solid Li_2CrO_4 is deposited.

Other chromate[2] depolarizers which have been employed are calcium chromate, basic sodium zinc chromate and potassium dichromate. With most of these materials, the voltage drifts with time

TABLE 2

PEAK VOLTAGES OF THE SYSTEMS Ca OR $Mg/LiCl$ KCl/DEPOLARIZER/Ni AT A CURRENT d.o. 11 amp/in.²

System	Voltage	System	Voltage
$Ca/NaZnCrO_4$	3·28	$Ca/SrCrO_4$	2·62
$Ca/ZnCrO_4$	3·28	$Ca/BaCrO_4$	2·50
Ca/Basic $ZnCrO_4$	3·09	Ca/WO_3	2·48
$Ca/CaCrO_4\text{-}PbCrO_4$	3·05	$Mg/NaZnCrO_4$	2·46
$Ca/CaCrO_4\text{-}NaZnCrO_4$	2·95	$Mg/ZnCrO_4$	2·39
$Ca/CaCrO_4$	2·80	$Ca/PbSO_4$	2·30
Mg/Basic $ZnCrO_4$	2·23	$Mg/SrCrO_4$	1·84
$Mg/CaCrO_4\text{-}PbCrO_4$	2·20	Mg/WO_3	1·72
$Mg/CaCrO_4\text{-}NaZnCrO_4$	2·19	$Mg/PbSO_4$	1·57
Ca/Fe_2O_3	2·03	Mg/Bi_2O_3	1·50
$Mg/CaCrO_4$	1·96	Mg/Fe_2O_3	1·25

and so no stable equilibrium potential could be measured. The particular depolarizer used can have an influence on anode polarization. For example when $CaCrO_4$ is used, a magnesium anode polarizes much more than in a cell in which Fe_2O_3 is employed. This is due to the solubility of $CaCrO_4$, which in $LiCl\text{-}KCl$ is 7 percent by weight at 400°C, and 19 percent by weight at 600°C. Chromate depolarizers, and some oxides have been classified[2] according to the peak-voltages they produce in the cells of the type Mg or $Ca/LiCl\text{-}KCl$ eutectic, depolarizer/Ni. The voltage obtained at current density of 110 mA/in.² are shown in Table 2.

The systems give excellent peak voltages, but lives are relatively short. The system however permits very high current drains for short periods of time. In one experiment a direct short was applied across the terminals of a cell and a current of 57 amperes (25 amp/in.²) was measured. This was of course for only a pulse and the cell voltage dropped to about 0·1 V.

Nitrate

Nitrate ion serves as depolarizer[12] in the cell system $Mg/LiNO_3\text{-}KCl/Ag$. Best results were obtained with 50% KCl giving an open circuit voltage of 1·5 V. Platinum plates were superior to silver. It was originally assumed that silver was oxidised by $LiNO_3$ to give $AgCl$, Li_2O and oxides of nitrogen. The silver chloride would be discharged electrochemically. However, it has been shown, that molten nitrate does not react with silver or platinum, but discharges directly to oxide ion and oxides of nitrogen.

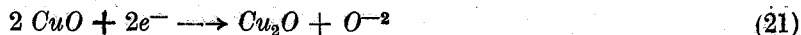COPPER OXIDES[6,40,41,42,43,44,45,46,47]

Copper (I) Oxide

The solubilities of Cu_2O, as determined from potential measurements and from a current—voltage curve, were $3·8 \times 10^{-2}$ and $5·8 \times 10^{-2}$ moles/litre respectively. A plot of log (0^{-2}) Vs. E gave a slope of 66·2 mv and an E° oxide value of −1·207 V corresponding to the electrode reaction $Cu_2O + 2e^- \rightleftharpoons 2Cu + O^{-2}$. The system $Cu/Cu_2O, O^{-2}$ acts as an electrode of the second kind.

Copper (II) Oxide

Ideally this material should discharge as follows

$$CuO + 2e^- \longrightarrow Cu + O^{-2} \tag{20}$$

However because of the existence of a stable intermediate oxide the reaction could be expected to proceed as follows—

$$2\ CuO + 2e^- \longrightarrow Cu_2O + O^{-2} \tag{21}$$

$$Cu_2O + 2e^- \longrightarrow 2\ Cu + O^{-2} \tag{22}$$

$$CuO + Cu \longrightarrow Cu_2O \tag{23}$$

Since Cu_2O/Cu couple is reversible to O^{-2} in $LiCl$-KCl electrolyte and its solubility being approximately 4×10^{-2} moles/liter it may complicate cell behaviour due to chemical short-circuiting.
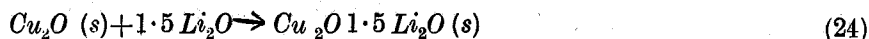
A number of test cells of the type $Ca/LiCl$-$KClMgO/CuO/C$ or Cu have been built[16]. The open circuit voltage was generally between 2·3 and 2·4 V. The peak load voltage was 1·45 V. The peak current was 188 mA/cm^2 and the energy density was reported as 177 W hr/lb of the active material.

The mixtures of CuO-Cu_2O have been employed as cathode mixture in a large number of cells with Mg anode and $LiCl$-KCl eutectic electrolyte. The cells utilizing this cathode material have extended life measured in days upto 3—6 days[40], and prime objective in their development has been their possible use in space exploration.
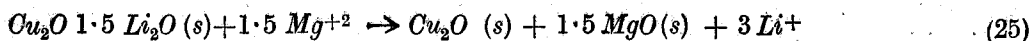
In an investigation[6] on this cell system five CuO/Cu_2O cathode compositions were tried. Needle type cathodes made of 100% CuO showed efficiencies between 67% and 89 % at 2 day and 75 to 78·2% at 6 day discharge rate. For 100% Cu_2O cathodes at 2- and 6-day discharge rates the efficiencies were between 78·5 and 88·8% and 71·4 and 82·7% respectively. Use of pure cupric oxide cathode is recommended in view of greater energy density and ease of fabrication. 5-cathode configurations were investigated and a design for 50-A hr cell is presented.

Thaller[40,42] has reported electrode efficiencies upto 73% for the cell discharged at 425–535°C over a period of six days, and 93% for a cell discharged over a period of one day. For non-optimized cell energy densities of 28 W hr/lb of total battery weight were obtained.

The cell design was found to effect[42] the discharge characteristics of the cell. The average rate of self-discharge taking place concurrently with electrochemical discharge at constant load varied from < 1 to 200 mA. As cell design was changed to decrease the rate of self-discharge (greater electrode spacing, higher Cds in the electrolyte and different electrolyte) the overall polarization increased. The equivalent internal resistance of the cell varied from ~0·2 to 2 ohms. The discharge is influenced by three factors affecting the mass transport inside the cell i.e. the rate of discharge, the electrode shape and spacings. The amount of electrolyte per unit of cell capacity had little effect. The cause of the end-of-life failure was found to be due to freezing of the electrolyte. During the latter stages of discharge (beyond ~50% depths of discharge) a large drop in open circuit voltage (~0·25 V) occurred due to the formation of a cuprous complex resulting into change in mass transport conditions during the latter stages of discharge which reduces the activity of cuprous ion by ~2 order of magnitude. Complex formation takes place according to the reaction

$$Cu_2O\ (s) + 1·5\ Li_2O \rightarrow Cu_2O\ 1·5\ Li_2O\ (s) \tag{24}$$

complex dissociation

$$Cu_2O\ 1·5\ Li_2O\ (s) + 1·5\ Mg^{+2} \rightarrow Cu_2O\ (s) + 1·5\ MgO(s) + 3\ Li^+ \tag{25}$$

Anolyte[46] studies of Mg anode in the cell indicated that Mg ions and oxide ions do not rapidly diffuse away from the electrodes producing $MgCl_2$ rich anolyte with accompanying decrease in cell voltage and increase in the electrolyte freezing point. For better current efficiency the $MgCl_2$ activity in the eutectic $LiCl$-KCl must be very low. Poor operating characteristics of Mg anode under certain conditions were explained in this way.

A cell [44] using $LiCl$-KCl eutectic electrolyte, a separator of porous layer of powdered fused MgO, ZrO_2 or Al_2O_3 impregnated with electrolyte placed below calcium or magnesium electrodes a cathode depolarizer mix cake (CuO 65·8, Cu 6·6, $LiCl$-KCl eutectic 28·6%, and a cathode current collector of Ni was operated at 600° and had open circuit voltage 2·43 V with theoretical energy density of 282 Whr/lb based on the reaction $Ca + CuO \rightarrow CaO + Cu$.

Cu (II), *Cu* (O)

Cu^{+2}/Cu° couple being reversible and having a high exchange current would be expected to discharge at high rates. The use of $CuCl_2$ was complicated because of highly oxidizing nature of this compound. For example gold substrates rapidly dissolved (10 min.) upon immersion in the molten $CuCl_2 + LiCl\text{-}KCl$. A tantalum wire, 50 mm in diameter completely dissolved within 15 hours in the melt at 525°C. A tungsten wire was partially dissolved (in 25 minutes). However pyrolytic graphite, "glossy carbon" and boron carbide were stable. The polarisation at 150 mA/cm² was only 0·53 V. $CuSO_4$ has also been used [16]. At temperatures of the order of 600°C, the sulfate ion is inert as a depolarizer and the half-cell reaction is essentially $Cu^{+2} + 2e \rightleftharpoons Cu^0$

Diffusion of SO_4^{-2} to the nagative would result in sulfide formation. Cells of the type Ca/KCl $LiCl$, $CuSO_4/Cu$, C are reported to give power outputs of 300 W hr/lb based on active material or 140 W hr/lb based on electrodes, grids electrolyte and spacers. Depolarizers such as $CuPO_3\text{-}LiPO_3$ produced up to 293 W hr/lb on an active material basis or 222 W hr/lb on total cell basis.

DESIGN CONSIDERATIONS

The design considerations of thermal battery for projectile applications[9] have received special attention. The entire cell stack and connectors are completely encapsulated except for a small fill channel in the encapsulating material, whereby the electrolyte may have access to the batttery cells. Battery cells are assembled by stacking the plates and separators in alternate order in a single stacking operation, after which an elastomer moulding compound is applied to and completely encloses the entire cell stack except for an ampoule cavity and a fill channel inter-connecting the various acting cell elements. The elastomer molding compound can be of a vinylite base or any other suitable compound. The battery utilizes annular shaped plates of electrically conducting material stacked at right angle to the unit axis. The first plate is coated with a *Ni* surface on the side abutting the cell support disc and with a *Pb* oxide coating on the other surface. The annular plates are stacked in such a manner as to place the *PbO* coating on the adjacent plate.

PYROTECHNIC COMPOSITION

The required heat for raising the temperature of the electrolyte to its melting point is provided by a pyrotechnic composition incorporated in the battery assembly. Several suitable compositions have been described. A pyrotechnic material[4] formed of about 26% by weight zirconium and the balance barium chromate can be used. A paste is applied as a wet surface coating and dried. An electric match is embedded in the coating to provide a means for igniting pyrotechnic material. A percussion primer or acceleration force can also be used for this purpose. The electrical match is connected to an electrical power source in series with a switch. Closing of the switch permits a flow of the current through the electric match igniting the match composition, which in turn ignites the pyrotechnic material. The ignition of the pyrotechnic material generates heat which fuses the electrolyte salts thereby activating the battery. These materials have been employed[38] in composition 38% Zr, 57% $BaCrO_4$, 5% glass or asbestos fibre. Another[38] gaseous fuse-delay composition containing powdered Zr 3·0–4·5, powdered Ni 15 – 31, $KClO_4$ 7 – 22 and $BaClO_4$ 75–42% gives burning time of 15 to 4·5 seconds. Powdered Ni used is prepared by evaporation of Hg from a Ni amalgam. $KClO_4$ may be replaed by chlorate or nitrite. $BaCrO_4$ may be replaced by $PbCrO_4$, MoO_2, PbO or Pb_3O_4. The burning time is accurately reproducible and is not affected by storage at high temperature and high humidity. The same materials can also be fabricated in a block[37] by ball milling $KClO_4$ 17·53, powdered Zr 4·07, Ba Chromate 12·05, Fe (by H) 66·35 with $EtoH$ (0·5 c.c./gm powder). After drying 47 parts by weight of the mixture and 52·75 parts Fe are mixed with 0·5 part of mold release agent (Ca stearate) and 0·02 part vapour phase inhibitor (dicyclo hexa ammonium nitrate) and pressed into a mold. Short circuiting of thermal batteries[48] by the combustion products of the rapidly combustible flammable material (pyrotechnic composition) used in the batteries; can be overcome by using a mixture of Pb_3O_4 (60 parts), Si (30 parts) and SiO_2 (10 parts) as the reactants, which form silicates of high resistance on combustion. Heat generated by the ignition of the pyrotechnic mixture can also be used to melt a material of high latent heat, which then maintains the battery temperature as it solidifies after the combustion is complete[49]. Cooling can be further delayed if the proportion of the reductant e.g. Si or Zr is increased to 25% and if space within the reactant mixture is filled with a mixture of BaO_2 and V_2O_5. Heat of combustion results in the reaction

$$BaO_2 + V_2O_5 \rightarrow Ba \ (VO_3)_2 + 1/2 \cdot O_2 \qquad (26)$$
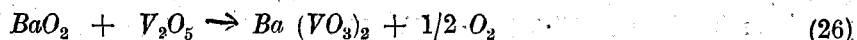
and *O* combines with unreacted Si thus generating further heat. Thus battery can be activated for 2·5 minute. A stoichiometric[50] mixture of powdered S and finally divided reactive Ni powder prepared by

the evaporation of Hg from Ni amalgam will burn with extreme, rapidity but without evolution of gaseous products of combustion when mixed with diatomaceous earth as a diluent and pressed into a suitable container. The composition is useful as a short-delay fuse element in military explosive devices.

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