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NEW PROCESSING TECHNIQUE FOR DEB POWDER FOR THERMAL BATTERIES

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The purpose of this paper is to explore how material processing influences thermal battery performance, and how battery performance can be improved by changes in processing. This discussion is confined to the class of thermal batteries designed by Sandia Laboratories and built under the supervision of General Electric in St. Petersburg, Florida. The electrochemical system employed is: $Ca/LiCl-KCl-CaCrO_4/Fe$. These batteries are primary reserve batteries which employ a pelletized cell design. Each cell consists of an electrolyte-depolarizer pellet sandwiched between an anode and a heat pellet. The anode employed may be one of two forms: sheet calcium disc, mechanically attached to an iron or steel backing; or a substrate disc of iron or steel on which 3-5 mils of calcium had been evaporated. The depolarizer-electrolyte, commonly referred to as DEB, is composed of $CaCrO_4$, LiCl-KCl eutectic and SiO_2 binder powder, which has been blended and pressed into pellets. The DEB pellet serves as electrolyte and as active cathode when the salt becomes molten upon battery activation. The heat pellet serves the dual purpose of providing the heat necessary to activate the battery and as the cathode current collector. The heat pellet is composed of iron powder and $KClO_4$. A battery is made up of one or more stacks of about 12 cells connected in series to produce a voltage of 28-32 volts. Since activated life requirements for batteries vary from seconds up to one hour, the battery must be well insulated to conserve the heat produced by the ignition of the heat pellets to maintain the electrolyte in a molten state. This insulation is also important to protect sensitive electronic components in contact with the battery case. Because the electrolyte, particularly LiCl, is hygroscopic, the batteries are hermetically sealed in stainless steel cans, and are manufactured in dryrooms maintained at 3% relative humidity or better.

A history of the development of these batteries and a description of all their components has been given earlier by Van Domelen and Wehrle.(1) Studies leading to the presently employed processing techniques were conducted over a fifteen year period by Sandia Laboratories. Don Bush was responsible for the pelletized DEB concept, and for the powder processing optimization.(2) He established that $CaCrO_4$ must be prebaked prior to processing with the electrolyte,(3) and that simple blending of these materials produce powders with poor pelletizing properties. Pellets with acceptable mechanical properties can be prepared from DEB powders which have been prefuzed.(4) Two sequences of powder processing are employed to produce DEB powder: a one step process in which electrolyte, binder and depolarizer are fuzed, ground, sieved and dried; and a two step process in which the electrolyte and binder are prefuzed, pulverized, blended with $CaCrO_4$

fuzed a second time, ground, sieved and dried. Bush established the optimum fuze times and temperatures to be 400°C and 16 hours for the former and 600°C for 4 hours followed by 400°C for 16 hours for the latter.(4) Blending was originally performed in ball mills, but more recently, a fluidized bed concept was adopted in which blending was performed in liquid freon.(5)

Recent changes in vendors for both calcium and calcium chromate resulted in a sharp reduction in battery performance for batteries built using established procedures. This clearly indicated a need to establish new powder processes and, in turn, has prompted a renewed effort to improve material understanding and powder processing. It is now recognized that no single combination of anode or DEB can be qualified as best, rather, optimum materials and processing will be designed for specific battery performance requirements i.e., pulse, power and long life batteries.

This paper will deal with the problem of DEB powder processing only, and how these influence battery operations. Other studies now in progress, dealing with anode characteristics and correlating those with performance, will be published in the future. Before proceeding to the discussion of DEB materials and processing, it is instructive to discuss in some detail the chemical and electrochemical reactions that take place upon battery or thermal cell activation.

The reduction of Cr(VI) in molten LiCl-KCl eutectic was the subject of much research by Laitinen and his students. They had shown that this process is complex, and is further complicated by the presence of impurities such as SiO_2, other oxides and moisture content. They demonstrated that the chromate reduction takes place in a series of steps involving a number of intermediate products and intermediate chromium oxidation states. There is some question as to how much of the Cr(VI) is actually reduced to CR(III). The final product was identified as having the approximate formula $Li_4Ca(CrO_3)_2$ which represents Cr(III).(6) Jennings(7) pointed out that these products are usually insoluble and form a film or layer on the cathode. This film, however, does not produce excessive polarization because these products apparently transmit charge.(7) Nissen(8) and Hlava and Headley(9) studied the reactions at the anode/electrolyte interface by single cell pulsing and microchemical analysis(8) and by electron microprobe and transmission electron microscope of the reaction zones in the discharged cells.(9) Immediately upon activation, calcium and $CaCrO_4$ begin to react chemically producing a layer of $Ca_2CrO_4Cl_2$ which is impervious to the chromate ion, but permits Ca^{+2} to migrate through it. This chemical reaction and its product at the anode is critically important for proper cell performance, for it forms a separator between the anode and active cathode. Normally, no separator needs to be incorporated in this system, but there are other designs which do employ an electrolyte separator layer. A second series of chemical reactions takes place between the anode and the electrolyte. Calcium ions displace lithium, forming a low melting alloy $CaLi_2$ and a double salt $KCaCl_3$; these are formed in conjunction with Ca_2CrO_4Cl. A total of six layers of different combinations of electrolyte and products have been identified by Hlava and Headley.(9) In the last two layers, those furthest from the anode, the binder SiO_2, was found incorporated in two reaction products. One product has been identified as $Ca_6Cr_4O_xSiCl_2$ in a matrix of mixed chlorides and the second was a Ca-Cr-Si-O compound which has not been identified.

The low melting point alloy (M.P. 220°C) $CaLi_2$, is actually the active anode for this system, and is required for satisfactory anode/electrolyte wetting. Excess alloy, however, is undesirable, as it is a cause of cell noise and/or shorting, as will be discussed below. Nissen(7) showed that initial anode polarization takes place during the first discharge stage, but no further polarization takes place until the end of cell life, at which time the reaction products begin to freeze out forming resistive layers. Ternary phase diagram of the system $CaCl_2$-LiCl-KCl shows that the melting point of some compounds in this system are 200°C or more, higher than normal battery operating temperature.(11) The initial polarization was shown to be time dependent, and thought to be activation polarization associated with the formation of the separator layers. The final polarization was shown to be mainly ohmic due to the formation of resistive precipitates at the anode. This rather oversimplified picture will serve to show how DEB processing can influence battery performance.

Thermal battery performance is rarely limited to depletion of active materials. Normal end of life is due to the increase in the internal resistance which is due to either the accumulation of high melting reaction products or cooling of the battery with the attendant freezing of the electrolyte. The former is the shutoff mechanism for batteries operating under high load; the latter is common for long life batteries. Thermal management of batteries is considered one of the central design considerations for new battery designs.

Normal internal operating temperatures of thermal batteries range from less than 500°C to more than 550°C in an ambient environmental temperature range of -55°C to 75°C. One of the problems in optimization of thermal battery design is that the ambient temperature range is greater than the operating temperature range. To minimize heat losses, a very efficient insulating material, Min-K*, is employed. To reduce the initial temperature spike (>750°C) during the ignition of the heat pellets and to flatten out the cooling curve, buffer pellets have been used in some designs. Buffer pellets are prepared from salts which melt exothermally at about 500°C. Buffer pellets are not currently in vogue in DOE thermal batteries. Battery cooling is, to some extent, balanced by heat generated by exothermic side reactions, particularly those involving the calcium-calcium chromate reactions described above. Successful thermal management, therefore, requires careful balance between the designed calorific output of the heat pellets and control of the exothermic side reactions. Thermal runaways are considered to be one of the major causes for thermal battery failures.

One of the consequences of thermal runaways is electrolyte leakage, which causes extensive corrosion of battery components and battery failure due to depletion of electrolyte. The battery operating temperature range, 500°-550°C, is 150° to 200°C higher than the eutectic melting point (352°C). However, the DEB pellet initially contains dissolved $CaCrO_4$ and binder, and as the discharge progresses, reaction products accumulate. In the ternary system $CaCrO_4$-LiCl-KCl, a ternary eutectic freezing point of 342°C exists for a composition 41 wt. % LiCl, 50 wt. % KCl, 9 wt. % $CaCrO_4$.(11) Of course, further increases in $CaCrO_4$ in the ternary increase the

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melting point rapidly. To prevent electrolyte leakage during initial battery activation, Cab-O-Sil** (SiO_2) binder is employed to immobilize the electrolyte. Cab-O-Sil is a finely divided silica with very high specific area (up to 400 m^2/g). Initially, it was considered that immobilization is a surface phenomena and good gelling results from the use of a porous material processing a high specific area that is wet by the electrolyte. More recent data(12) indicates that electrolyte immobilization is more complex and not yet fully understood. Electrolyte immobilization, like thermal management, must be carefully balanced. One of the consequences of excess immobilization is the absence of anode wetting and battery failure.

Another major failure mode for thermal batteries is shorting by excess alloy, which extrudes to the cell edges causing short circuits. Excess alloy is prevented by balancing alloy formation and alloy consumption. One method employed for controlling alloy formation is by increasing Ca concentration at the anode-electrolyte interface by the addition of $CaCl_2$ to the DEB. According to Nissen,(7) at the anode electrolyte interface, there is a continuous recycling of lithium in a sequence of chemical and electrochemical reactions involving calcium, the electrolyte and the alloy, as shown in reactions (1) and (2).

$$2Ca + 2LiCl + KCl \rightarrow Li_2Ca(l) + KCaCl_3 \qquad (1)$$

$$4Cl^- + Li_2Ca(l) \rightarrow CaCl_2 + 2LiCl + 4e^- \qquad (2)$$

Increasing $CaCl_2$ concentration in reaction (2) should result in a decrease in alloy. In practice, increasing the binder content in the DEB is more effective in reducing alloy formation. This is probably accomplished by immobilizing the electrolyte and minimizing contact between Ca and LiCl.

To control electrolyte leakage, eliminate pellet deformation and cracking, and to improve the cell's coulombic efficiency, a novel fabricating technique to form the catholyte layer was developed. Two new concepts are incorporated in this technique. One, to employ a DE powder in which the chromate was completely solubilized in the electrolyte while in the molten state followed by a rapid quench. The DE powder so produced is a homogeneous dispersion of fine chromate precipitate in the eutectic. Two, to employ DB powder, formed by sintering chromate and Cab-O-Sil together to form a porous matrix to hold the DE within its structure.

It has long been recognized that $CaCrO_4$ is the active cathode in this system.(13) The cathodic reaction takes place by an electron transfer step at the current collector-DEB interface. As chromate adjacent to the collector is reduced, fresh chromate must replenish it. Hence, the cathodic reaction is transport limited. Cathodic polarization will be reduced if the molten electrolyte with dissolved chromate can flow unimpeded to the current collector, and if the reaction layers formed are electronically conducting as claimed by Jennings.(7)

**Trademark of the Cabot Corporation

In conventional DEB processing, the ingredients are fuzed at 400°C for 16 hours in order to fuze the mass and produce a uniform dispersion of chromate and binder in an electrolyte phase. At 400°C a partial liquid state occurs which contains up to 12 weight percent $CaCrO_4$ in solution(10), the balance chromate and all the binder remain as solids. The new DE powder processing is prepared entirely in the liquid state. Starting with the ternary eutectic composition, the molten electrolyte is heated slowly and stirred while additional chromate is added, keeping the phase liquid at all times. The final composition is 12 weight percent $CaCrO_4$ and the melt temperature is 550°C, which is more than 100°C above its melting point. The melt is then rapidly quenched to prevent segragation of chromate, and to achieve a fine dispersion of the chromate in the electrolyte.

In conventional DEB formulation, immobilization of the electrolyte was accomplished by the binder and by undissolved chromate. It is assumed that the binder does not enter into chemical reactions with the other components, and that it does not change in its physical form i.e., specific area. In fact, SiO_2 does react with the other components as cited above. The specific area of the new compounds can be expected to change as does also the contact angle between the electrolyte and these products. The new technique relies on retention of the electrolyte by employing a porous structure to hold the electrolyte. This concept is based on porous "tiles" devised by Arendt and Curran(14) to prevent electrolyte leakage encountered in molten carbonate fuel cells. An electrolyte-free, structured DB powder is prepared by sintering $CaCrO_4$ and Cab-O-Sil. The resulting mass is granulated maintaining a narrow particle diameter range in the powder. Powders sintered at T 600°C can be pressed into pellets without pellet growth following its ejection from the die cavity. The DB and DE powders are blended together and fuzed at 425°C; at which temperature the DE should be a liquid. Following the final fuze, the DB and DE powders are granulated and pressed into pellets by conventional techniques. To prevent electrolyte flooding, the ratio of DB to DE must be adjusted so that the DE would impregnate all the pore structure without leaving empty pores or having excess electrolyte.

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