Journal of Power Sources, 3 (1978) 95 - 104

THE $LiAl/NaAlCl_4/MoCl_5$ THERMAL BATTERY*

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(Received September 10, 1977; in revised form April 17, 1978)

Summary

Recent U.S. Air Force experimental work on the development of a new thermal battery and electrochemical system utilizing aluminum or a lithium–aluminum alloy as its anode, a Cab-O-Sil/$NaAlCl_4$ mixture as anolyte and a mixture of anolyte, $MoCl_5$ and graphite as its cathode is presented. The results of 135 single cell tests, in some of which four cell variables were subjected to a factorial design analysis, are summarized. Two conventional heat source materials were investigated in batteries: $Zr/BaCrO_4$ and $Fe/KClO_4$. Both were found to be satisfactory. Thirty batteries were tested and results are presented. The total functionality of a thermal battery utilizing these cells was demonstrated by the performance of 28 V, 2 A batteries operating over the environmental range of −55 °C to +74 °C. These batteries have demonstrated a comparatively long life and high energy density capability. The optimum internal battery temperature is 200 °C and the skin temperature of the battery is ordinarily low enough so that it can be held in the hand. Batteries of this design present an excellent manufacturing potential via conventional thermal battery production processes and techniques; they appear to be cost-competitive with current technologies.

Introduction

The $LiAl/NaAlCl_4/MoCl_5$ thermally activated reserve battery (thermal battery) is fabricated from a three layer pelletized thermal cell of the type

*Paper presented at The International Symposium on Molten Electrolytes and High Temperature Batteries organized by the Electrochemistry Group of the Chemical Society, Brighton, Gt. Britain, September 22 - 23, 1977.

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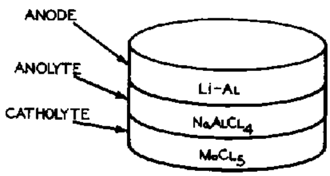


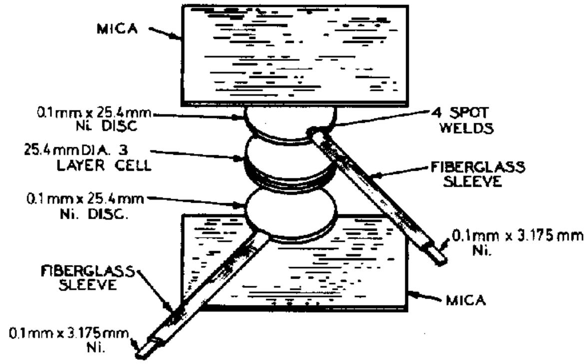


Fig. 1. $LiAl/NaAlCl_4/MoCl_5$ three layer cell.

Fig. 2. Single cell test assembly.

shown in Fig. 1. The anode, the top layer of the cell, is made of powdered Al–Li alloy. An alloy of 28 w/o lithium was found to be superior for this work. The cathode, the bottom layer of the cell, is mostly $MoCl_5$ mixed into a matrix of $NaAlCl_4$, Cab-O-Sil* and graphite. The center layer, the anolyte or separator layer, is 90 w/o $NaAlCl_4$ with 10 w/o Cab-O-Sil added to prevent flow when the battery is thermally activated. The basic cell electrochemistry is similar to that described by Nardi *et al.* [2] with individual component modifications as described below.

The basic cell electrochemistry and development was conducted, and is currently under investigation, by the U.S. Air Force [1 - 4]. Early in 1976 the U.S. Air Force initiated a program with the Eureka Company, Eureka Advance Science Division of Bloomington, Illinois, U.S.A. The program objective was to determine the feasibility of taking the fundamental cell technology and producing a practical thermal battery using conventional production techniques and facilities. If this preliminary program demonstrated that a battery could be fabricated and exhibited a potential for meeting U.S. Air Force requirements, then further engineering development would be conducted to develop a battery which would fulfill the requirements for a high-energy, low cost, practical thermal battery system.

Single Cell/Battery Development and Testing

Prior to battery construction a considerable number of single cells were tested. Figure 2 is an exploded view of one of the one hundred and thirty five (135) single cells in its test assembly just prior to insertion into the single cell tester. The data presented in Fig. 3 show a typical single cell

*A silica powder — Cab-O-Sil is a registered trademark of the Cabot Corp.

TABLE 1

Results for a typical series of single cell tests

Single cell No.	V_p (peak) (V)	Load res. (ohms)	Cell temp. (°C)	Current density at V_p (mA/cm^2)	Internal resistance (ohms at t s)	Lifetime (s to % V_p)	Energy density (Wh/kg to % V_p)	w/o $NaAlCl_4$ in anode
9A	1.86	25	200	14.7	7.05 at 2060	2407 to 50%	17.53 to 41%	5
10A	1.63	25	200	12.9	2.30 at 170	700 to 70%	6.62 to 70%	10
11A	1.63	25	200	12.9	7.51 at 300	1160 to 60%	11.02 to 70%	15
12A	1.87	25	200	14.8	1.16 at 120	1210 to 70%	9.94 to 70%	20
13A	3.05	25	200	24.1	1.94 at 60	1325 to 50%	24.57 to 50%	25

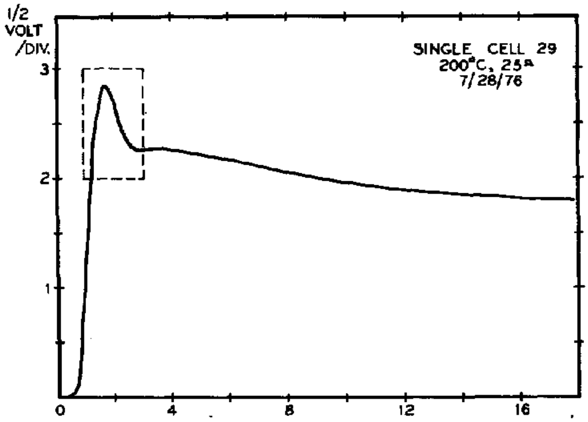


Fig. 3. A typical single cell discharge curve; cell No. 29, 2.54 cm diam., 200 °C, R_L = 25 ohms.

discharge voltage–time trace. As may be seen the discharge voltage is relatively flat except for the voltage "spike" which occurs within the first few minutes of discharge. This high voltage "spike" was observed in many of the single cell tests, and its characteristics are a function of cell conditioning, cell composition, and anode interaction with other cell components. The useful life of a thermal battery is usually measured from the time at which peak voltage occurs to some fraction of the peak voltage, such as 80% of peak voltage. When the peak was tall and narrow the life time to 80% of peak voltage would be very short. It can be seen (Fig. 3) that the rest of the discharge voltage–time trace is relatively flat and if the "spike" could be eliminated then a much longer useful life could be realized.

In the initial stages of single cell testing a series of cells was constructed with the composition of one component varying. Table 1 presents the results of one such series of experiments in which the amount of $NaAlCl_4$ in the anode mass was varied from 5 to 25 w/o. In these experiments the load resistance was 25 ohms and the cell temperature was 200 °C. The cell mass was 2.26 g. The catholyte mass was 0.833 g of 45.0 w/o $MoCl_5$, 14.5 w/o graphite and 40.5 w/o $NaAlCl_4$ (90/10 mix). The 90/10 mix $NaAlCl_4$ is 10 w/o Cab-O-Sil and 90 w/o $NaAlCl_4$. The anolyte was 0.675 g of $NaAlCl_4$ (90/10 mix). The anode mass was 0.750 g of LiAl alloy (20 w/o Li) and $NaAlCl_4$ (90/10 mix). No clear trend could be established in any of the data presented in Table 1. The inability to correlate component variables with test data was related to the seemingly random nature of the voltage peak; however, the flat region of the discharge curve was predictable.

With the above apparent limitations in mind a factorial design study was conducted on four cell variables. A factorial design study is a statistical method for processing the data for a large number of precisely varied experiments. For this study the four cell variables are defined as:

$$X_1 = \frac{\text{anode weight}}{\text{anolyte weight}} \qquad X_3 = \frac{MoCl_5 \text{ weight}}{NaAlCl_4 \text{ weight}}$$

$$X_2 = \frac{\text{catholyte weight}}{\text{anolyte weight}} \qquad X_4 = \frac{\text{graphite weight}}{NaAlCl_4 \text{ weight}}$$

After variable selection, upper and lower limit for each must be selected. For this study the limits were determined by the practicality of mechanically making a cell with these extreme limits. If a cell has four variables and each variable has two possible values then it is possible to construct sixteen (16) unique cells with the various high–low combinations. For example, one cell would have all four variables at the high limits (HHHH) or it could have the first three at the high limits and the fourth at the low limit (HHHL), etc.

After the sixteen cells were made and tested at 200 °C across a 15 ohm load, the data were "fitted" to a hyperplane in five-dimensional space. The general equation for such a surface is:

$$y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_5X_1X_2 + B_6X_1X_3 + B_7X_1X_4 +$$

$$+ B_8X_2X_3 + B_9X_2X_4 + B_{10}X_3X_4 + B_{11}X_1X_2X_3 + B_{12}X_1X_2X_4 +$$

$$+ B_{13}X_1X_3X_4 + B_{14}X_2X_3X_4 + B_{15}X_1X_2X_3X_4$$

where: y = any observable operational characteristic of the cell, *i.e.*, peak voltage, life time to % V_p and energy density; B_0, B_1, B_2, ... = constants determined by the factorial design experiment; X_1, X_2, X_3, X_4 = the four variables previously defined.

An example of the type of equation generated under this study is the equation for the peak voltage:

$$V_p = 2.43 + 0.11X_3 - 0.03X_4 - 0.04X_1X_2 - 0.04X_1X_3 + 0.07\, X_3X_4 -$$

$$-0.05X_1X_2X_3$$

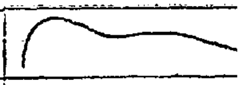
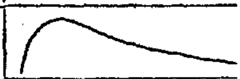
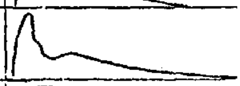
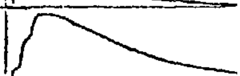
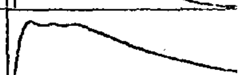
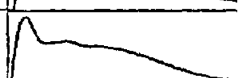
This equation was not very good for predicting peak voltage because it is based on the assumption that the relationship between the voltage peak and four defined variables is a linear one, and this is not necessarily true. However, it can be said that out of the sixteen possible terms in the general equation, only seven are significant for the V_p equation, and those are the seven terms that appear in the above equation. The equations for the life-time in seconds to 80% V_p (T_{80}) and energy density in Wh/lb to 80% V_p (ED_{80}) were:

$$T_{80} = 359.65 - 51.10X_1 + 48.02X_3 + 81.65X_1X_2 + 36.44X_1X_3 -$$

$$- 48.81X_2X_3 - 22.60X_2X_4 + 72.35X_1X_2X_3 + 29/54X_1X_2X_4$$

TABLE 2

Factorial design results

CELL TYPE	CELL #	V_p	T_{80}	ENERGY DENSITY	PEAK SHAPE
HHHH	1	2.43	483	8.62	
	17	2.43	516	9.21	
	33	2.44	504	9.07	
HHHL	2	2.38	556	9.52	
	18	2.46	429	7.85	
	34	2.44	468	8.43	
HHLH	3	2.34	282	4.67	
	19	2.28	272	4.28	
	35	2.28	350	5.50	
HHLL	4	2.47	191	3.52	
	20	2.43	266	4.75	
	36	2.42	299	5.30	
HLHH	5	2.51	360	6.86	
	21	2.57	321	6.41	
	37	2.63	239	5.00	
HLHL	6	2.58	300	6.04	
	22	2.39	333	5.75	
	38	2.68	207	4.50	
HLLH	7	2.13	161	2.21	
	23	2.30	221	3.54	
	39	2.14	117	1.62	
HLLL	8	2.48	161	2.99	
	24	2.43	205	3.66	
	40	2.48	164	3.05	
LHHH	9	2.85	38	0.93	
	25	2.71	166	3.69	
	41	2.86	80	1.98	
LHHL	10	2.58	390	7.85	
	26	2.63	255	5.33	
	42	2.61	355	7.31	
LHLH	11	2.24	380	5.77	
	27	2.23	315	4.74	
	43	2.18	523	7.52	
LHLL	12	2.38	414	7.09	
	28	2.35	468	7.82	
	44	2.35	499	8.33	
LLHH	13	2.40	545	10.14	
	29	2.43	656	11.62	
	45	2.64	724	15.26	
LLHL	14	2.51	494	9.41	
	30	2.42	665	11.78	
	46	2.37	700	11.09	
LLLH	15	2.20	425	6.22	
	31	2.20	353	5.17	
	47	2.12	462	6.26	
LLLL	16	2.42	329	5.83	
	32	2.36	276	4.65	
	48	2.41	346	6.08	

and

$$ED_{80} = 14.02 - 1.85X_1 + 2.93X_3 + 3.00X_1X_2 + 0.948X_1X_3 - 1.96X_2X_3 + 1.01X_2X_4 + 2.62X_1X_2X_3 + 1.21X_1X_2X_4$$

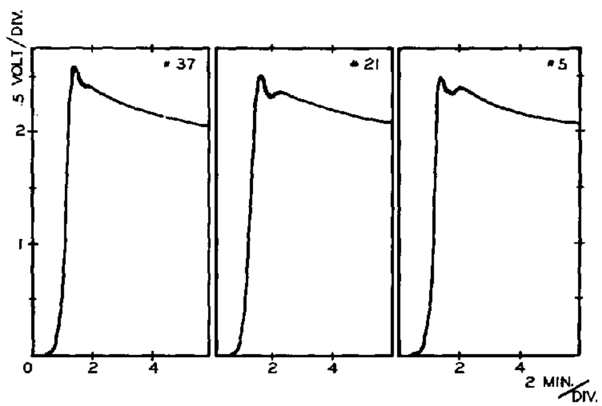


Fig. 4. Discharge curves (HLHH) single cells Nos. 5, 21 and 37; 2.54 cm diam., 200 °C and R_L = 15 ohms.

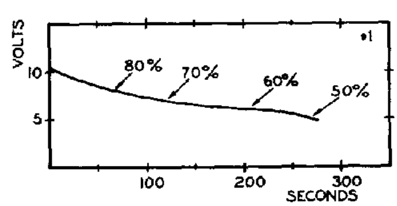


Fig. 5. Battery discharge curve, battery No. 1; 5 cells, 2.54 cm diam. cells and R_L = 15 ohms.

It was concluded from the factorial design study that: (a) the peak voltage was influenced primarily by the concentration of $MoCl_5$ and graphite in the catholyte; (b) the lifetime (T_{80}) depends upon the relative anode and cathode weights and is largely independent of the catholyte formula; (c) the energy density is influenced by the identical variables which affect the life to 80% V_p and therefore the best way to increase the energy density is to increase the useful life; and (d) the voltage peak is not a random phenomenon. Table 2 presents all the results from the factorial design study. The column on the right is a representation of the high voltage peak area of the discharge curve. It was observed that the sixteen cell types displayed sixteen unique high voltage peak characteristics, and this observation was confirmed by the repeatibility of these peaks. For example, Fig. 4 is a reproduction of three discharge curves for one of the variable combinations (HLHH), for the cells. The characteristics of these three voltage peaks are similar and reproducible. Therefore, the high voltage peak is not a random phenomenon but is, in fact, somewhat dependent upon the cell composition and formula of the catholyte. This fact became very important when battery construction began.

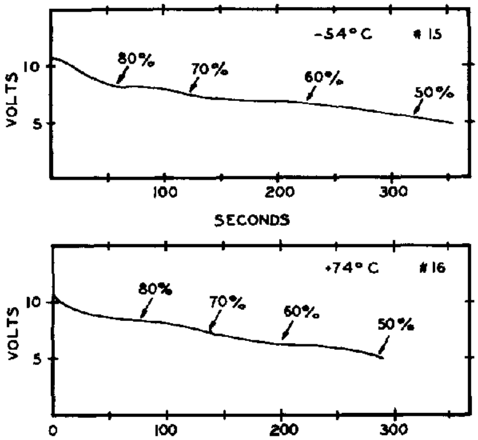


Fig. 6. Battery discharge curves, battery No. 15 and No. 16, 5 cells, 2.54 cm diam. cells and R_L = 15 ohms.

The discharge voltage–time trace for the first $LiAl/NaAlCl_4/MoCl_5$ battery test is presented in Fig. 5. This battery performed well, without venting, deforming, overheating or producing electrical noise. The above test proved that thermal cells similar to those developed by the U.S. Air Force could be used to construct a functional thermal battery, and it was now necessary to engineer the battery to prove the feasibility of producing a practical thermal battery using conventional production techniques and facilities.

The first step was to optimize the calorie content of the heat paper. The $Zr–BaCrO_4$ heat paper used in the first battery had 18.6 cal/cm^2 (120 cal/in^2). The plan was to try progressively hotter, larger heat content paper until the battery was too hot, then progressively cooler heat paper until the battery was too cold from a performance standpoint. From this study, using the $Zr–BaCrO_4$ heat paper, optimum battery performance was obtained using heat paper in the range of 17.1 cal/cm^2 (110 cal/in^2) to 21.7 cal/cm^2 (140 cal/in^2). For conventional thermal batteries this is a very large range of operational calorie values and this should contribute to the ease of manufacture and quality control.

One of the more difficult thermal battery specifications to meet is the operational environmental temperature range. This battery had to operate at —54 °C (—65 °F) to 74 °C (105 °F). Three batteries of identical construction were fabricated and tested. The room temperature and 74 °C tests were satisfactory, however the —54 °C test was not. Therefore, two additional batteries were constructed using slightly hotter heat paper. Figure 6 is a reproduction of the discharge voltage–time trace for these two batteries. Battery number 15 was tested in a —54 °C environment and battery number 16 in a 74 °C environment. These two tests demonstrated that the $LiAl/NaAlCl_4/MoCl_5$ thermal battery could function throughout the required temperature spectrum.

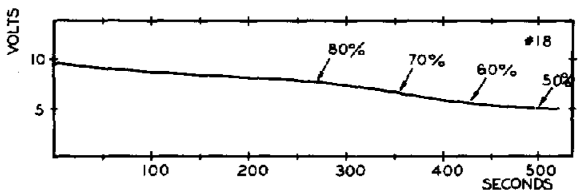


Fig. 7. Battery discharge curve (battery No. 18) using the Fe/$KClO_4$ heat disk; 5 cells, 2.54 cm diam. cells and R_L = 15 ohms.

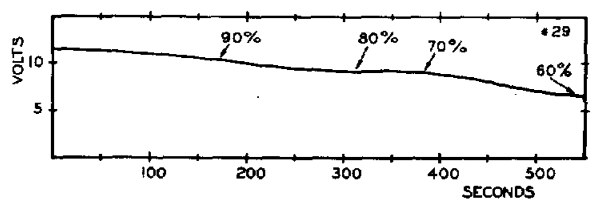


Fig. 8. Battery discharge curve (battery No. 29); 5 cells, 2.54 cm diam. cells and R_L = 15 ohms.

While it was clear that the new cell system and the Zr–$BaCrO_4$ heat paper were compatible, it was felt that a benefit could be gained, for long life operation, from the use of the Fe–$KClO_4$ heat disk system. Indeed the first battery tested using the Fe–$KClO_4$ heat disk system gave encouraging results, as shown in Fig. 7. However, later tests indicated that the Fe–$KClO_4$ heat disk system was not always compatible with the new cell system since battery overheating and venting occurred. Further experiments demonstrated that these problems could be overcome by placing a nickel buffer disk between the catholyte and heat source and a nickel separator between the heat source and anode. Different calorie contents were evaluated, different anolyte and catholyte compositions were examined, and finally kaolin clay was added as an additional antiflow agent. Kaolin clay was used because its antiflow properties were familiar due to 25 years of thermal battery production experience. From the above results and experiments battery number 29 was fabricated and tested. The discharge voltage–time trace is presented in Fig. 8.

Finally, battery number 30, the last battery, was constructed. This battery contained eleven 4.86 cm (1.914 in) diameter cells with 18.6 cal/cm^2 (120 cal/in^2) Fe–$KClO_4$ heat disks and when activated produced 28.8 V at a current density of 43.4 mA/cm^2. The 80% V_p life was 362 s and produced 22.9 Wh/kg based on the total weight of the cells (see Fig. 9). The voltage trace was clean showing no electrical noise above a level of 50 mV peak to peak, the limit of resolution of the equipment used. The activated battery was cool enough to be hand held, *e.g.* the case temperature measured at the center of the external surface of the cylindrical can reached only 51 °C, 15 min after activation.

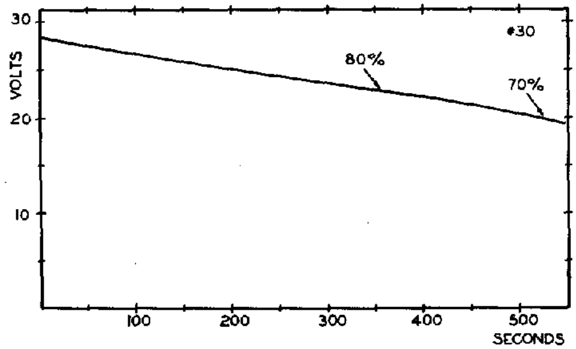


Fig. 9. Battery discharge curve (battery No. 30); 11 cells, 4.86 cm diam. cells and R_L = 35 ohms.

Conclusions

The LiAl/$NaAlCl_4$/$MoCl_5$ thermal battery has demonstrated the capability of providing the thermal battery industry with a new technology. While the battery system requires additional engineering development it has already demonstrated that it can perform across the entire (thermal battery) operational temperature spectrum. Although not optimized, it is evident at this time that the LiAl/$NaAlCl_4$/$MoCl_5$ thermal battery is capable of producing a high energy density, with an active life of several minutes, and the discharge voltage is clean and noise free. This new system will also be cost-competitive ($0.44/Wh *vs.* $3.42/Wh for the Mg/KCl·LiCl/V_2O_5 battery based on the cost of the materials) with existing battery systems and may be relatively easy to produce with a high degree of quality control.

This battery has been demonstrated to have the potential for development into a superior electrical source for service in present and future ordnance systems, notable in terms of operational lifetime and internal operational temperature.

Acknowledgements

This effort was sponsored by the Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright Patterson AFB, Ohio, under Contract F33615-76-C-2080 and is being continued under Contract F33615-77-C-3147.

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