A PRE-TESTABLE LOW TEMPERATURE LITHIUM THERMAL BATTERY

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Summary

The operating temperature of the LiAl/$NaAlCl_4$/$CuCl_2$ thermal battery is about 200 °C, and it can work in an ambient temperature range of —40 to +50 °C. When discharged through a constant resistance of 700 Ω at room temperature, it can operate effectively for 10 min. Prior to use, the battery can be pretested to see whether it is properly assembled and to ensure its performance and reliability. Batteries after pretesting can still be activated without substantially reduced performance.

Introduction

Thermal batteries presently in production use either LiCl–KCl or LiBr–KBr as electrolyte and operate at high temperatures (400 - 600 °C), which present great difficulties in extending battery life, reducing battery weight, and preventing overheating of adjacent electronic components. In recent years, several novel thermal batteries working at lower temperatures have been developed. This paper describes an LiAl/$NaAlCl_4$/$CuCl_2$ thermal battery system based upon the concept developed by the Seiler Research Laboratory. It works at about 200 °C, a temperature much lower than that for thermal batteries using conventional electrolytes, and it can be satisfactorily used at ambient temperatures of —40 to +50 °C.

Unlike secondary batteries, conventional primary batteries cannot be pretested prior to use, resulting in uncertainty about their reliability to users. Pretestable before use, the LiAl/$NaAlCl_4$/$CuCl_2$ thermal battery system has solved this problem. The melting point of $NaAlCl_4$ is only 152 °C [1], significantly lower than the flash point of the heat source Zr/$BaCrO_4$ (whose flash point is about 200 °C). The battery can be heated at temperatures lower than the flash point. When a particular temperature is reached, local melting of the electrolyte occurs, giving rise to a particular conductivity, voltage, and load-carrying ability. Using this method, the battery performance and the reliability of its assembly technology can be pretested. Batteries, after pretesting, can be still activated without substantially reduced performance.

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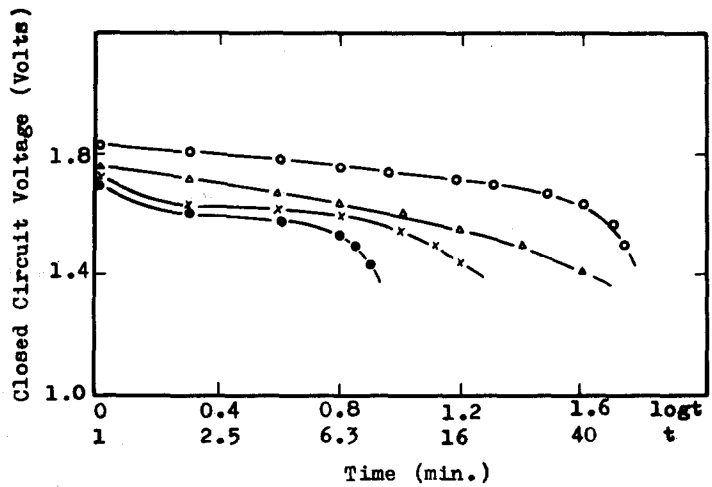


Fig. 1. Cell performance under different discharge conditions (200 °C). —○—○, 7 mA/cm^2; —△—△, 15 mA/cm^2; —×—×, 20 mA/cm^2; —●—●, 30 mA/cm^2.

Anode, cathode and electrolyte

Anode. LiAl alloy powder [2 - 5] was supplied by the Fushun Aluminum Plant. The particle size was <100 mesh. No additional treatment was necessary before use.

Electrolyte. 90 wt.% $NaAlCl_4$ + 10 wt.% SiO_2 were evenly mixed and ground into powder by a ball mill.

Preparation of $NaAlCl_4$ [2, 4]. 50.5 mol.% anhydrous NaCl + 49.5 mol.% anhydrous $AlCl_3$ were evenly mixed and heated at 178 °C in a special sealed container for 72 h. The synthetic product was pinkish and crystalline, and the powdered crystals were greyish in colour. X-ray analysis showed it to be $NaAlCl_4$. The hygroscopicity of $NaAlCl_4$ could be determined using differential thermal analysis [6].

Cathode [3]. $CuCl_2 \cdot 2H_2O$, after being dehydrated at 160 °C was brown and crystalline and its optimum particle size, after being ground, was 50 - 100 mesh. 58 wt.% $CuCl_2$ + 26 wt.% electrolyte + 16 wt.% graphite were evenly mixed to provide the required cathode material.

Single cells

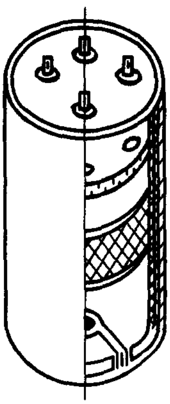
Single cells were of pressed-pellet construction. The optimum pressing pressure was 2.3 t/cm^2 (22.5 × 10^7 MPa). The electrode area was 3.8 cm^2.

The testing temperature range for single cells was 175 - 300 °C. The optimum operating temperature was 200 °C. The single cell performance behavior at various current densities and 200 °C is shown in Fig. 1. Its operating lifetime decreases sharply with increase in current density.

Battery

The external dimensions of the battery were 31 mm dia. and 51 mm height, as depicted in Fig. 2. It was composed of 15 single cells, with a 1.2 mm insulation layer around the stack. The battery was activated by an electric pulse. The highest internal temperature and the highest surface temperature were, respectively, 270 °C and 110 °C. The battery performance behavior at various discharge conditions and room temperature is shown in Fig. 3.

The operating performance at various ambient temperatures is shown in Fig. 4. The activation time was always less than one second.



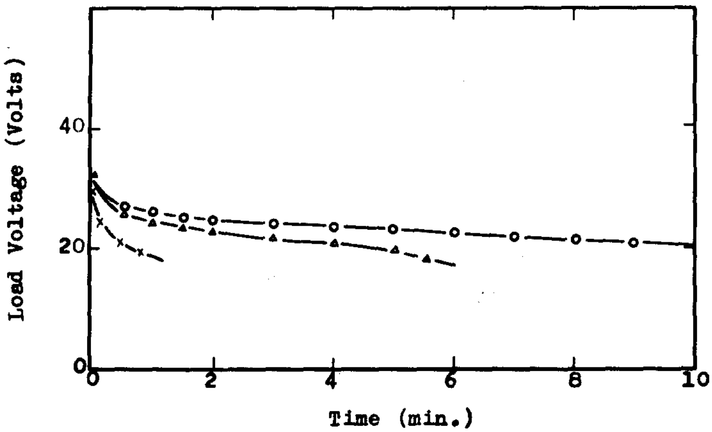


Fig. 2. Schematic view of the battery.

Fig. 3. Battery performance under different discharge conditions (room temperature). —o—o, 700 Ω; —△—△, 20 mA/cm^2; —x—x, 30 mA/cm^2.

Battery pretesting

A copper casing, with an internal diameter slightly larger than the external diameter of the battery was preheated in an oven for one hour. The battery was placed in the copper casing and the battery open circuit voltage was recorded at the same time. When the open circuit voltage reached its maximum, a 0.5 mA or 1 mA load was applied and the battery on-load voltage was noted. The battery was then removed from the casing and cooled in a water bath at a temperature below 10 °C. Tests were conducted at several pretesting temperatures and the data for several groups of batteries tested at 130 °C are given in Table 1.

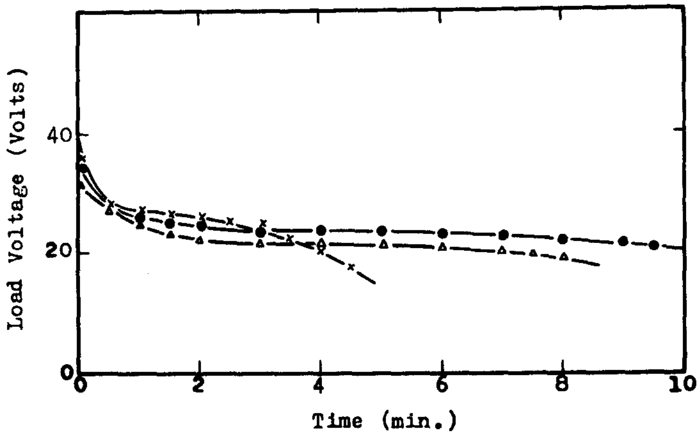


Fig. 4. Battery performance under different ambient temperatures (700 ohms). —●—●, 50 °C; —△—△, room temperature; —×—×, −40 °C.

TABLE 1

Battery pretesting data at 130 °C

Battery no.	Heating time (min)	Max. OC voltage (V)	Load voltage (V)	
			0.5 mA	1 mA
024	13	46.6	41.2	
025	11	42.6	37.0	
028	12	42.0	35.0	
A35	12	42.0	37.5	
A36	11	45.0	37.3	
A54	12	43.5		34.9
A55	14	47.0		38.1
A57	11	46.9		37.8

As shown in Table 1, the open circuit voltage reached a maximum of over 42 V 12 min after the battery was deposited in the oven, and it dropped to over 34 V when a 0.5 or 1 mA load was applied.

The pretested battery could still be activated for operation. The battery discharge performance at various ambient temperatures and a comparison with that of unpretested batteries are shown in Figs. 5, 6 and 7.

The pretested battery's performance proved to be nearly identical with that of the unpretested battery and their discharge curves almost coincided.

The battery, when pretested at 175 °C for 10 min, suffered a performance loss, and its operating lifetime was 20% shorter than that of the unpretested batteries.

If there were broken connections inside the battery, no open circuit voltage appeared in the course of pretesting; very low open circuit voltages

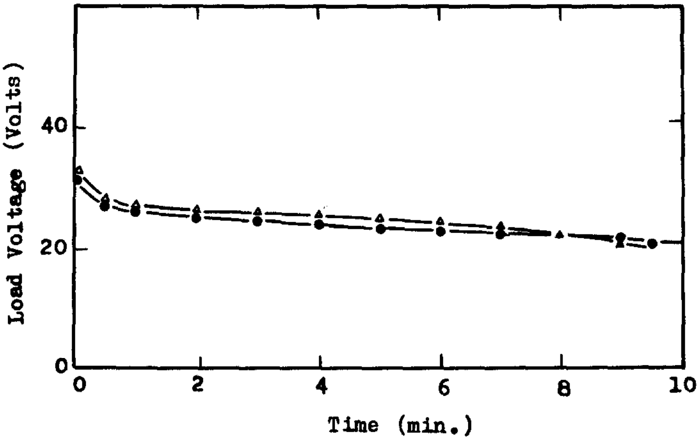


Fig. 5. Variations in performance between pretested and unpretested batteries (room temperature, 700 ohms). —●—●, pretested; —△—△, unpretested.

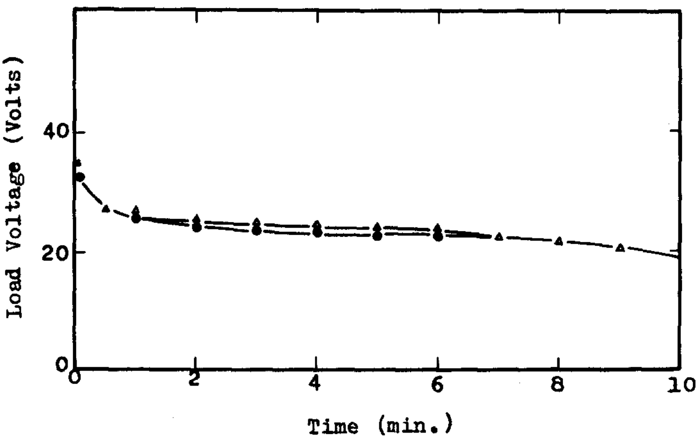


Fig. 6. Variations in performance between pretested and unpretested batteries (50 °C, 700 ohms). —●—●, pretested; —△—△, unpretested.

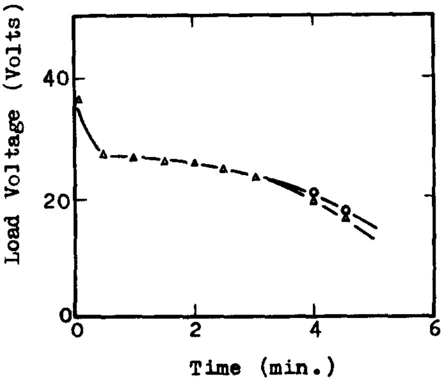


Fig. 7. Variations in performance between pretested and unpretested batteries (—40 °C, 700 ohms). —○—○, pretested; —△—△, unpretested.

TABLE 2

Pretesting data for two batteries (each with 1 cell with reversed polarity)

Battery no.	Heating time (min)	Max. OC voltage (V)	Load voltage at 0.5 mA (V)
029	15	25	1
034	15	25	1

resulted from micro-shortcircuits; and low open circuit voltages were obtained where single cells were connected with reversed polarity and the load voltage was below 1 V. Table 2 presents the pretesting data obtained at 130 °C for two batteries, each with a single cell connected with incorrect polarity.

Heat sources

Two types of heat source for battery use, *i.e.*, $Zr/BaCrO_4$ and $Fe/KClO_4$ were tested. The battery performance for each heat source with the same quantity of heat, and for the same battery lot is shown in Fig. 8.

The test results proved both heat sources to be applicable to the battery. The battery using $Fe/KClO_4$ had a longer life, but it required a longer activation time. The data listed in this paper were based on $Zr/BaCrO_4$.

Miscellaneous

Figure 9 presents the battery performance after storage for one year. No significant degradation was observed.

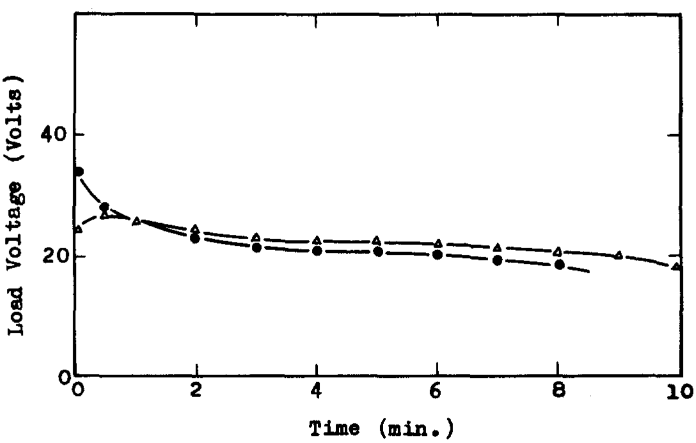


Fig. 8. Variations in performance of different heat sources (room temperature, 700 ohms). —●—●, $Zr/BaCrO_4$; —△—△, $Fe/KClO_4$.

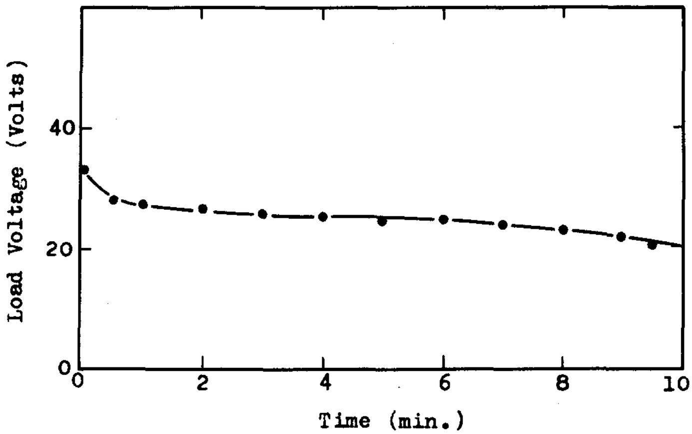


Fig. 9. Battery discharge curve after storage for one year (room temperature, 700 ohms).

TABLE 3

Operating life data for batteries from different batches

Battery no.	Pretested	Ambient temp. (°C)	Operating life (cutoff voltage, 20 V) (min)
A35	No	−40	4.0
A36			3.7
A53			3.3
A58			3.8
A33	Yes		4.0
A34			4.0
A57			4.3
A59			4.3
A48	No	Room temp.	7.2
A46			7.5
A55			7.7
A5	Yes		10.0
A6			6.8
A56			8.2
A27	No	50	7.7
A31			9.3
A50			8.8
A1	Yes		9.0
A2			10.2
A52			8.5

The operating lifetime data for batteries from different batches as listed in Table 3, show a favourable repeatability.

The sources of materials for construction of the $LiAl/NaAlCl_4/CuCl_2$ thermal battery are abundant, their prices are relatively low, and the electrode materials are harmless to health.

Discussion

(1) Considering the discharge mechanism of the $LiAl/NaAlCl_4/CuCl_2$ thermal battery [3], the anode reaction might be one of dissolution of the β, τ and δ phases of the LiAl alloy at a certain temperature to produce fresh lithium, which reacts with $NaAlCl_4$ in the electrolyte to displace fresh aluminum. Both fresh Al and fresh Li could start an anode reaction with NaCl. The Li anode potential is higher than the Al anode potential. The presence of the high voltage spike, as seen within a few seconds of the initial discharge period, was, presumably, due to the Li anode, which played a leading role in the initial discharge period. Afterwards, the Al anode played the leading role, resulting in a flat, low discharge voltage.

The cathode reaction could be divided into two steps [7]:

$$Cu^{2+} + e^- \longrightarrow Cu^{1+} \qquad (1)$$

$$Cu^{1+} + e^- \longrightarrow Cu^0 \qquad (2)$$

The two flat voltage plateaus in the single cell discharge curve suggested two steps in the cathode reaction. As seen in Fig. 10, the first step is at about 1.8 - 1.5 V, while the second step is at about 0.7 - 0.5 V. Reaction (2) could be inferred from the existence of a copper deposit on the nickel sheet of the cathode current collector.

(2) When the battery pretesting temperature was lower than 130 °C, the open circuit voltage was only a few volts, even after extended pretesting.

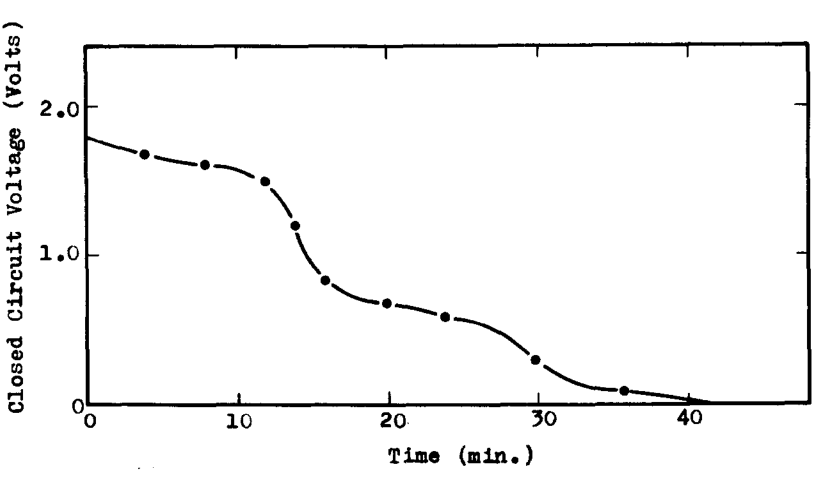


Fig. 10. Single cell discharge curve (200 °C, 200 mA/cm^2).

Only when the temperature exceeded 130 °C could the battery display an OC voltage of over 40 V and a particular load-carrying ability. The responsibility for this is due to the low eutectic point (123 °C) of the NaCl–LiCl binary salt system, at which temperature local melting of the electrolyte occurs giving rise to a particular conductivity.

Conclusion

The $LiAl/NaAlCl_4/CuCl_2$ thermal battery, with a low operating temperature, can be pretested before use for its reliability. It is suitable for applications in ambient temperatures of −40 to +50 °C. In addition, it is characterised by its longer operating life, fast activation, low cost, simple fabrication technology and the feasibility of utilizing a non-metal shell. Unfortunately, the battery does not give a good voltage characteristic, and a high voltage spike exists early in the discharge, for which no remedy has yet been found.

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