

Optimization of externally heated thermal battery

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Abstract

An externally heated thermal battery (EHTB) using an $\text{LiAl/Ag}_2\text{CrO}_4$ couple was developed to meet the unusual requirements of an open circuit stand of 8 h. The battery was designed to maximize the voltage output, to control cathode growth and corrosion of cell components, and to minimize passivation of pellets during wet stand. The final design of the EHTB consisted of three parallel strings of two cells for a total of six individual cells. The battery exhibited a stable OCV from 5.75–5.77 V throughout a slow temperature ramp at 3.3 °C/h from 120–149 °C and yielded currents in excess of 2.5 A when pulsed for 50 ms through a 1 Ω load.

Introduction

This study was directed at developing a suitable electrochemical cell and thermal battery that would respond to external environmental heat and that would, by definition, contain no self-contained pyrotechnic heat to melt the fused salt electrolyte. This concept was based on prior work [1–4] and the term EHTB was coined to denote an ‘externally heated thermal battery’. The EHTB would have to respond to an environmental temperature increase of 3.33 °C/h within a temperature window of 121–149 °C which was defined as a ‘slow cook-off’ test. The electrochemical investigation focussed on evaluating mixed nitrate salts for use as suitable low melting electrolytes, optimizing an $\text{LiAl/Ag}_2\text{CrO}_4$ couple in the various nitrate electrolytes, and developing a battery design that would minimize self-discharge resulting from 7 to 8 h open circuit on the ‘slow cook-off’ ramp before delivering a required electrical pulse of 2.5 A at 2.5 V.

Experimental

The preparation and selection of applicable electrolyte salts, through single cell screening experiments and optimization of electrolyte and cathode pellet formulations, were described previously [5]. All electrolyte compositions

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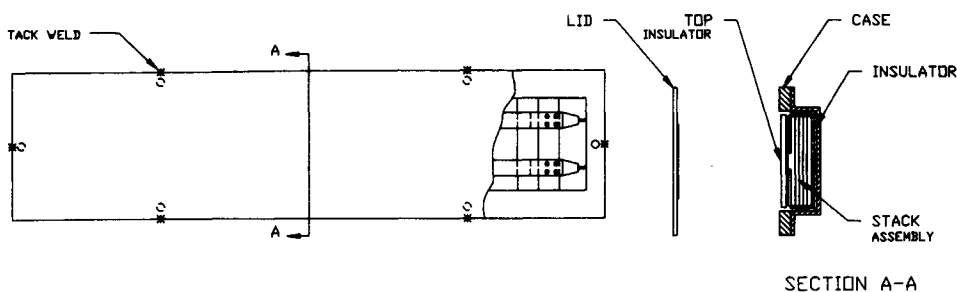


Fig. 1. Final battery assembly.

were expressed as mole percent. (mol.%) while pellet compositions used weight percent. (wt.%).

All batteries were built in a dry room with relative humidity of 2% or less, using stainless steel hardware designed to achieve reproducible stack pressure. A specially designed battery welding fixture/heat sink, equipped with circulating cooling fluid, was used to maintain the case temperature at 9 °C during welding, to eliminate the thermal effect of header/case welding on battery insulation and electrochemical components. The overall outer dimensions of the EHTB battery measured 119.94 l × 29.72 w × 6.99 t mm, Fig. 1.

The original battery design [5] employed four cells in series with anode and electrolyte pellet dimensions of 16.51 × 41.40 × 0.38 mm while the cathode pellets were 15.50 × 40.39 × 0.38 mm. The final electrical configuration was a six cell battery, designed with two cells in series per each of three parallel legs. The batteries were vacuum dried at 72 °C for 2 h and back-filled with argon gas before closure. Battery testing was conducted using a Thermoline model 30400 automatic programmable furnace at a temperature ramp of 3.33 °C per h starting at 121 °C and ending at 149 °C, whereupon the battery was pulsed through a 1 Ω load for 50 ms. The 50 ms pulse width was governed by an external timing circuit, and current and potential data were computer acquired.

Results and discussion

An extensive electrochemical research effort was directed to prepare and evaluate mixed nitrate salts, for use as suitable molten electrolytes, melting in a temperature window between 120 and 149 °C. In reality, only eutectic salts melting below about 135 °C could be used because the battery had to operate at a high current density at 149 °C, and this required a sufficiently conductive and fluidic electrolyte. The electrolyte evaluation and cathode optimization [5] resulted in the following cell composition:

Anode	LiAl
Electrolyte	LiNO ₃ :NaNO ₂ :LiCl (30:55:15 mol.%)
Cathode	Ag ₂ CrO ₄ , electrolyte, graphite (55:35:10 wt.%)

For a preliminary study, four-cell-series batteries were built. These batteries demonstrated fluctuation and decline of *OCV* after about 45 min of temperature ramping at 3.3 °C/h. Another observation of these single cell experiments was the degradation of pulse current/voltage at 1 Ω as a result of extended open circuit conditions at 149 °C. Post-mortem analysis of these prototypes revealed anode to cathode intercell shorting caused by cathode pellet expansion. Single cell experiments were conducted to elucidate the extent of cathode growth and it was found that the expansion along the length of the cathode pellet was about 2 mm.

One known method of alleviating cathode spreading is to use a side-crimped cell cover or 'cathode cup'. This approach was tried, but it became difficult to close the battery because it was necessary to fit the battery header with an applied stack pressure and this resulted in crushed pellets. This situation arose because the crimped sides of the cell covers created a stronger, inflexible edge area, while the cell cover center remained flexible. Therefore, this potential solution was abandoned in favor of a new technical approach.

A small quantity of MgO binder (10 wt.% based on the salt weight) was incorporated into the electrolyte portion of the cathode mixture to assist in immobilizing the liquid salt. The cathode pellets were further modified by trimming approximately 1 mm on all four sides. This allowed the cathode to expand by the amount observed in the single cell experiments. Concurrent with the cathode containment work, it was suggested that a thicker electrolyte layer should help with two problems: edge shorting and the observed loss or absorption of molten electrolyte into anode and cathode. However, no improvements were achieved with the thicker electrolyte, and a 0.38 mm thickness was used for the final battery tests. After these procedures were instituted, no degradation or loss of *OCV* was found in any of the batteries, and intercell shorting was successfully eliminated.

Battery hardware development was given equal attention. The final hardware design allowed the direct application of the closing pressure on the stack surface via appropriate layers of top insulation, achieving an optimum and reproducible pressure of about 34 kg/cm² (333×10^4 Newtons/m²). This design also physically moved the header case/case weld area away from the battery stack so that the low melting internal components would not be adversely affected by the heat of the weld.

Figure 2 shows the voltage/time plot of one of these batteries that was built with these provisions and tested through a slow ramped (3.3 °C/h) wet stand of about 5 h. The unit yielded 1.6 A at 1.2 V when pulsed for 50 ms through a 0.8 Ω load. No degradation or loss of *OCV* was observed over the entire 5 h period.

A post-mortem examination of the batteries containing four cells in series, suggested that there were definite oxidation processes occurring that increased the internal resistance. The surfaces of the LiAl and Ag₂CrO₄ pellets were noticeably different in color from their original appearance. These

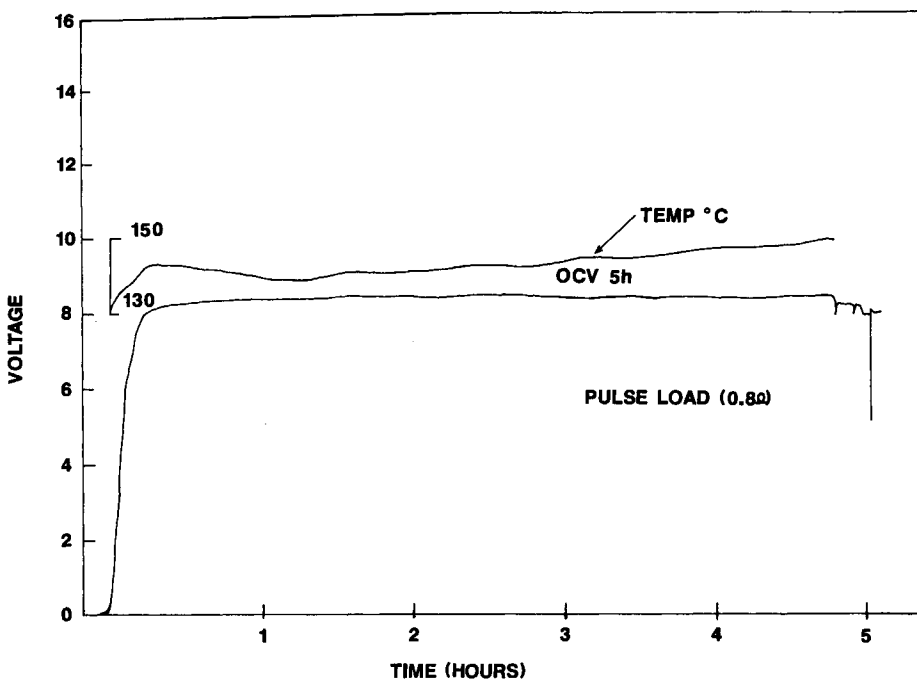


Fig. 2. Voltage vs. time curve of a four-cells-in-series battery, tested through a wet stand of 5 h slow ramp at 3.3 °C; pulsed for 50 ms through 0.8 Ω load.

observations suggested that chemical or electrochemical degradation reactions may occur during the extended open-circuit-stand ramp conditions.

There were actually two passivation problems: the chemical reactions occurring on interfacial LiAl and Ag_2CrO_4 pellet surfaces, and corrosion reactions between the stainless steel cell covers and the anode/cathode pellets. One approach to solve the cover/pellet corrosion problem included sealing the back surface of LiAl and Ag_2CrO_4 pellets with methyl cyanoacrylate. A small quantity of the monomer was dissolved in methyl isobutyl ketone and this solution was painted on exterior pellet surfaces. Unfortunately, the solution dried so rapidly that it was not possible to seal the anode/cathode pellets to their cell covers. Single cell tests on methyl cyanoacrylate-coated electrodes showed 50 ms pulse voltages at 1 Ω of 1.12 V after 2 min and 1.34 V after 5 min open circuit. This voltage 'delay' was attributed to the electrically insulating effect of the polymer which disappeared upon polymer thermal decomposition at the 149 °C test temperature. Silver powder was also used to coat the back of the electrodes to improve conductivity while allowing the cell processes to occur during wet stand. Unfortunately, both approaches gave no improvements in the 1 Ω pulse performance of either single cells or practical, sealed test batteries. To reduce the stainless steel cell cover corrosion by molten nitrate electrolytes, the material was changed to nickel.

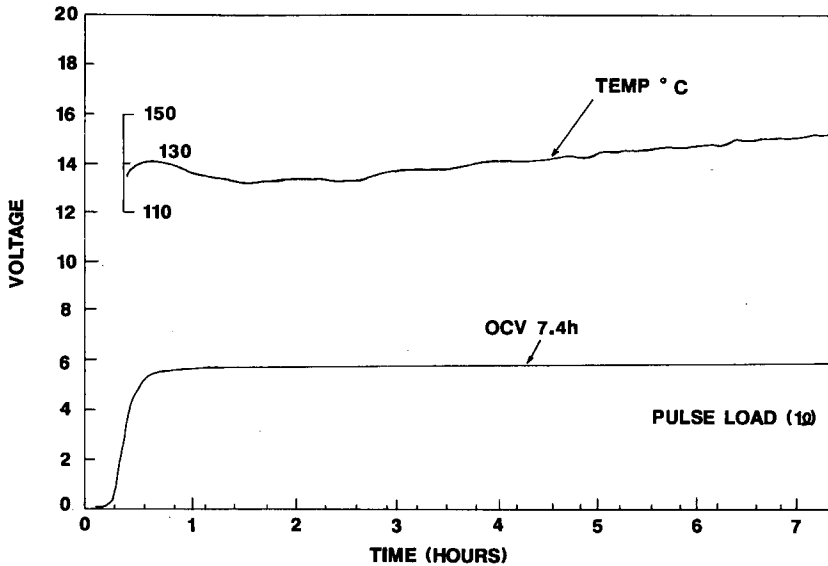


Fig. 4. Voltage and temperature vs. time curves of a three-parallel-stacks-with-two-cells-in-series EHTB battery tested through a slow cook-off period of 7.5 h to 149 °C at 3.3 °C/h slow ramp; pulsed for 50 ms through 1 Ω load.

$$[m/(6/m)](r) = 1 \text{ or} \quad (2)$$

$$m^2 = (6/r)$$

The internal resistance of a single cell was calculated as follows. A battery composed of six cells in series was built and tested through a slow cook-off period of 7.5 h to 149 °C, giving a stable *OCV* of 17.02 and an average of 1.43 A at 1.49 V on pulsing. Then, the internal resistance of the battery may be estimated as $r_t = E/I = (17.02 - 1.49)/1.43 = 10.86 \Omega$. Assuming the total external resistance to be equal to the sum of the internal cell resistances, that is, neglecting the contribution of external cell connections, one can say therefore

$$R = r_t = 6(r) \text{ or}$$

$$r = 1.81 \Omega \text{ per cell}$$

From eqn. (2)

$$m^2 = (6/1.81) \text{ or } m = 1.82$$

Assuming the nearest whole number gives a value of $m=2$, from this, it follows that $n=3$. The application of this design analysis to this battery therefore revised the stack configuration to three parallel stacks of two cells in series, assembled as shown in Fig. 3.

Batteries were built incorporating both the design change and the cell component improvements, and were then tested through the slow cook-off period of 7.5 h to 149 °C. The voltage versus time plot of one of these batteries is shown in Fig. 4. The battery gave a stable, noise-free, open-

circuit potential of 5.75–5.77 V over the entire 7.5 h period, and resulted in an average current of 3.0 A at 3.0 V on pulsing for 50 ms through a 0.8 Ω load. The improvement in current and voltage levels over earlier experiments may be attributed to the battery redesign, which minimizes internal impedance by virtue of operating at a lower electrode current density.

Conclusions

A look, in retrospect, at the effort to develop the EHTB shows that nearly equal time was spent on electrochemistry and on battery development. The research effort was comprehensive and focussed on preparing and evaluating mixed nitrate salts, for use as suitable molten electrolytes, melting in a temperature window between 120 and 149 °C. The outcome of this work was the selection of an $\text{LiNO}_3\text{:NaNO}_2\text{:LiCl}$ electrolyte salt. The final electrode pellets selected were electrolyte salt with MgO (binder), Ag_2CrO_4 cathode with graphite and electrolyte, and LiAl powder anode. These selections were successful in giving the correct operating temperature window, immobilizing the molten salt, decreasing the cell impedance and improving the load voltage and, finally, controlling the cathode physical expansion on wet stand.

A series of battery designs and tests led to an elucidation of the major issues that needed to be addressed when a cell stack of this type was utilized. Of importance is the long, elevated temperature, open-circuit stand required for this application that magnified thermal battery corrosion and internal resistance factors. Optimization of the component geometry and the battery stack design to three parallel stacks of two cells led to prototypes capable of sustaining a 7.5 h wet stand, and providing a minimum 2.5 A pulse at 2.5 V.

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