Some New Techniques to Improve Thermal Batteries with LCCM Battery as the Benchmark

Michael Ding, Frank Krieger, Rebecca Lennen, and Jeffrey Swank
US Army Research Laboratory
2800 Powder Mill Road, Adelphi, Maryland 20783

Karen Amabile, Richard Dratler, and Maria Allende
US Army Armament Research, Development and Engineering Center
Picatinny Arsenal, NJ 07806

Abstract

This report summarizes and discusses the experiments and results from our investigations into the effectiveness of some new techniques in prolonging the lifetime of molten salt thermal batteries, using our previous developed Low Cost Competent Munitions (LCCM) thermal battery as the benchmark. The new techniques included the control of operating gas atmosphere inside the battery case, optimal spatial distribution of heat source materials in the form of side- and end-wall heating, electrochemical rebalance of cathode and anode loadings, and deployment of newer and better thermal insulation materials. The techniques identified as effective for the LCCM thermal battery were expected to have the same benefits in other similar molten salt thermal batteries.

Introduction

Techniques to build thermal batteries with a longer lifetime or higher energy density are of paramount importance for the successful development and use of future smart munitions by the Army. It is therefore the aim of this work to investigate and develop some new ways of building a more energy-dense, longer running pellet-based thermal battery. For this, we chose as our benchmark the low cost competent munitions (LCCM) thermal battery that had previously been developed at ARL (1), and we focused our attention on the effects and control of operating gas atmosphere, optimal spatial distribution of heat source, electrochemical rebalance of the cathode and anode loadings, and deployment of newer and better thermal insulation materials.

The investigation of the effects and control of the operating gas atmosphere was aimed at prolonging the lifetime of thermal battery through reduction of heat loss by eliminating the hydrogen component in the gas. The investigation was carried out by evacuating a thermal battery during operation to demonstrate an extreme case of hydrogen elimination and by incorporating a gas getter in a battery for hydrogen reduction. Previous results of computer modeling and calculation for different gas compositions and pressures in LCCM were also used as a guide. The optimal spatial distribution of heat source materials was implemented by side- and end-wall heating with heat paper and heat pellets, respectively, although a preliminary study of some nano-layered bimetallic foils was also carried out with regard to their application as the alternative side-wall heating material. Electrochemical rebalance was done through constructing thermal cells and batteries with cathodes and anodes of variable loadings and testing them in a temperature-controlled furnace or as a complete thermal battery. The better thermal insulation was achieved by using thinner and more efficient Microtherm material in the place of Min-K in the benchmark battery.

Experimental

The thermal battery components were made in the dry room here at ARL from commercially purchased and in-house processed heat papers and cathode, anode, electrolyte, and pyrotechnic powders. The battery case of the benchmark LCCM thermal battery as well as the improved versions in this work measured 33.3 mm in diameter by 35.8 mm in height. The thermal cell active stack was 19 mm in diameter with no center hole. Ignition was accomplished by connecting a pre-charged capacitor with a piece of Nichrome wire buried in a heat paper pile which in turn was connected with a heat paper fuse strip. For laboratory testing of the batteries, a heavy, sealable, and reusable steel test fixture was used to insure that the case temperature would remain near ambient temperature and closely approximate worst case heat sink conditions. More experimental details can be found in (2).

As shown schematically in Figure 1, the testing system for the thermal batteries consisted of 1) a Tenney Jr. Environmental Chamber capable of providing an environment temperature between –70 and 200 °C; 2) a Maccor

4300 battery tester with 8 testing channels of 24 V 5A capability for applying the discharge load and recording the voltage and pressure (through A/D ports) profiles; 3) an Agilent 34970A Data Acquisition/Switch Unit for monitoring and recording temperatures on a thermal battery; 4) a manual switch unit for initiating the battery and providing zero-time mark for other instruments; and 5) a gas tubing manifold for monitoring gas pressure, collecting gas samples, and back-filling the battery with a selected gas when desired.

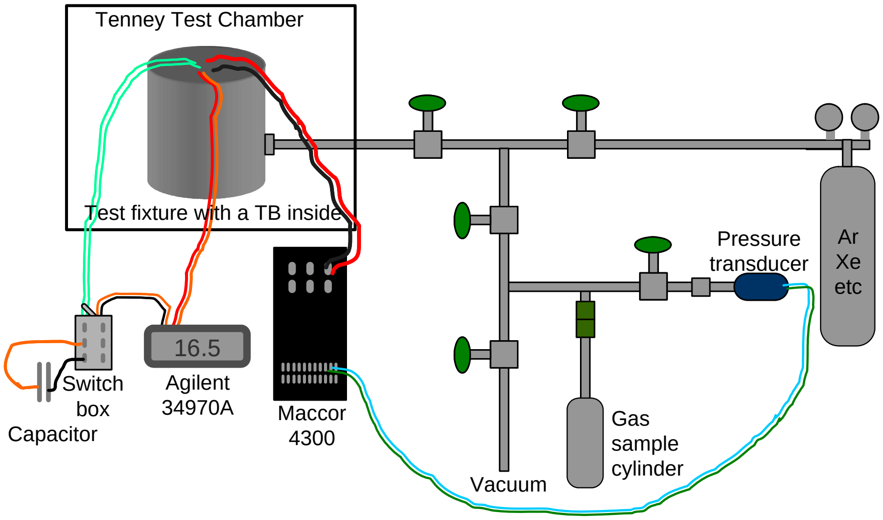

Figure 1. A schematic of the testing system for thermal batteries

The benchmark temperature for the battery testing was chosen at –40 °C, as this is the most demanding of the application temperatures in term of heat containment. The load profile for the test was made of a constant 1.5 A discharge current and a pulse current of 0.5 A of 10 ms duration every 10 seconds, as plotted in Figure 3 (a). The pulse was applied primarily to privide information on the internal resistance of the thermal battery. Such discharge currents is equivalent to a current density of 0.526 A/cm^2. Several K-type thermocouples were spot-welded in and around the thermal battery to be tested, typical on the stainless steel electrodes and on the fixture case. Gas samples were taken at specified times for offline analysis on an HP 5890 Series II Gas Chromatograph (GC).

Effects of Gas Atmosphere and Control

As a molten salt thermal battery operates at temperatures as high as 600 °C, prevention of rapid heat loss is the most critical in prolonging its operating lifetime. For this reason, an operating gas atmosphere rich in a light element such as hydrogen is always to be avoided. The situation is clearly demonstrated by our previous calculation results (3, 4) for LCCM thermal batteries with three different gas compositions, as shown in Figure 2. In going from a hydrogen rich gas through air to xenon, the calculated lifetime is steadily and considerably increased.

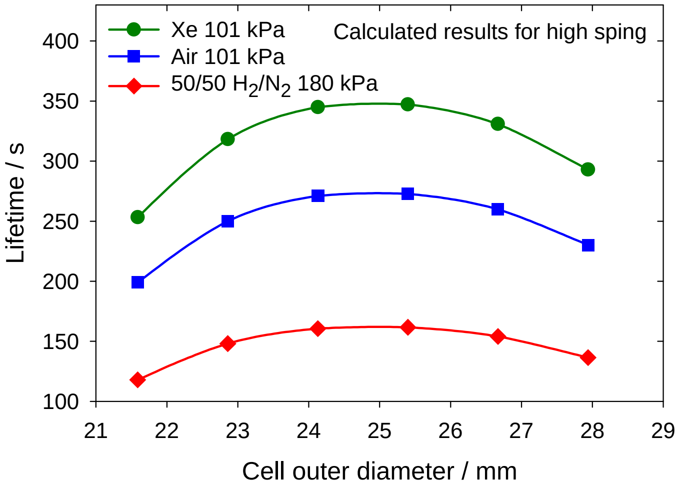

Figure 2. Calculted lifetimes for LCCM thermal batteries with different operating gas atmospheres

The experimental investigation of the effects of gas atmosphere in the lifetime of the LCCM battery was carried out by applying a vacuum of 7 Pa to a thermal battery during its operation and comparing the results with those of another battery without evacuation. The voltage profiles of the two, as shown in Figure 3 (b), demonstrate an increase in runtime (at cutoff voltage of 11 V) from 113 to 168 s, an improvement of almost 50%. Meanwhile, the internal resistance values, as plotted in Figure 3 (c), show that the application of evacuation had no effect on the internal resistances of the batteries. This is to be expected as the internal resistance measures the collective resistance to the passage of electrons and ions in the battery though only solid phases. These internal resistance values were calculated from the curve in (a) and those in (b) by the equation

$$R = \Delta V / \Delta I$$

where ΔI is the drop of current in a current pulse shown in (a), which in this case is 1 V, and ΔV is the corresponding jump in a voltage curve in (b).

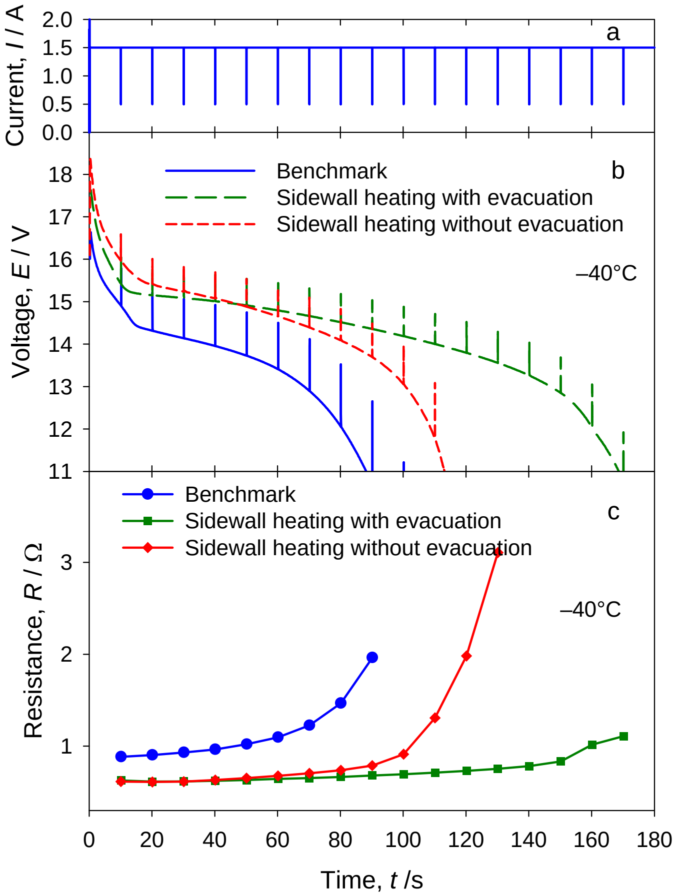

Figure 3. Voltage-time (b) and resistance-time (c) curves at a loading current (a) for different thermal batteries tested at –40 °C

To demonstrate that it is indeed the prevention of rapid heat loss by evacuation that prolonged the lifetime of the battery, we plotted the temperature profiles of the two batteries in Figure 4. It is seen that the temperature declines in the core of the battery without evacuation were much more rapid than those with evacuation.

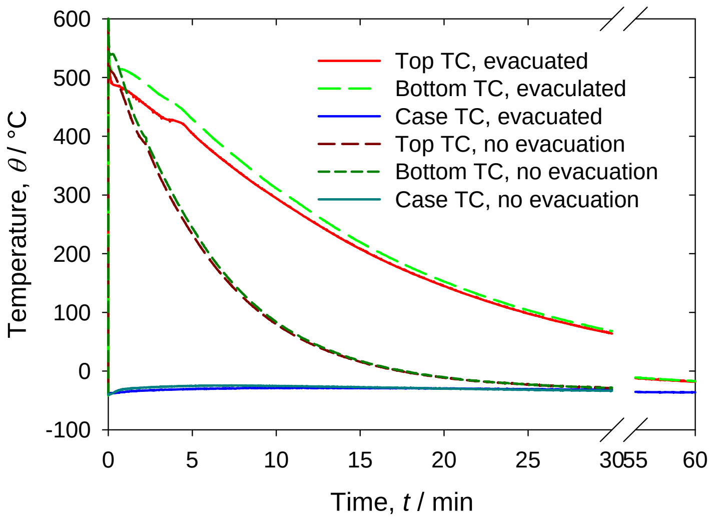

Figure 4. Temperature profiles of a battery with evacuation and another without

Although possible through careful engineering, evacuation of a thermal battery would add to the complexity and cost of its manufacturing. Furthermore, such an evacuation would have only a small part of the benefits due to the application of an active vacuum. In this regard, a better approach would be the use of an effective gas getter for the light component of the gas. For this, we have studied several gas gettering materials and found a zirconium-based metallic getter to be especially effective for absorbing hydrogen. Of particular interest is that the getter is active only at elevated temperatures. However, preliminary experiments of incorporating this getter into the LCCM battery have yielded no conclusive results. We are working on this approach and will report more conclusive results when available.

Effects of end- and side-wall heating

It is imperative that a sufficient amount of heat be provided in a thermal battery for its proper operation. It is equally important that this heat source be spatially distributed in such a way that the heat generated can efficiently create a sustained uniform high temperature zone in the core without local temperature spikes. In this sense, the traditional way of having pyrotechnic heat pellets stacked and interlaced with the thermal cells as the only source of heat supply is far from ideal. On one hand, it runs the risk of overheating the central core; on the other, it sets up very high temperature gradients both radially and axially causing rapid heat losses. We felt that one of the most effective and direct ways of remedying the situation would be to take some heat source from the central core and place it near the case, a measure commonly called side-wall heating. We also experimented with different numbers of end heat pellets to observe the effects and to obtain an optimal number.

Figure 5 shows the results of voltage profiles and resistance values for different numbers of end heat pellets. As shown in (b), the runtime of the batteries increases steadily with the increase in the number of heat pellets, up to four. The resistances change accordingly (c). A higher number of end heat pellets not only provides more heat for bringing the battery internals above the eutectic point of the electrolyte but also prevents rapid heat loss through the ends.

The case of side-wall heating is demonstrated in Figure 3, between the curves of the benchmark battery and those of the battery without evacuation but with its side-wall heated by a layer of heat paper and with Microtherm as the thermal insulation material. As shown, the combined effects of side-wall heating and improved thermal insulation resulted in an increase in the lifetime of the battery from 88 to 113 s, an improvement of 22%. Although we cannot tell from the experiments so far just how much of the 22% is due to the side-wall heating alone, we think it is significant. For this purpose of heating the side-wall, we recently have started to investigate and experiment with nano-layered bimetallic foils as the alternative materials, and found them to be very promising due to a unique and special set of properties. More details can be found in (5, 6).

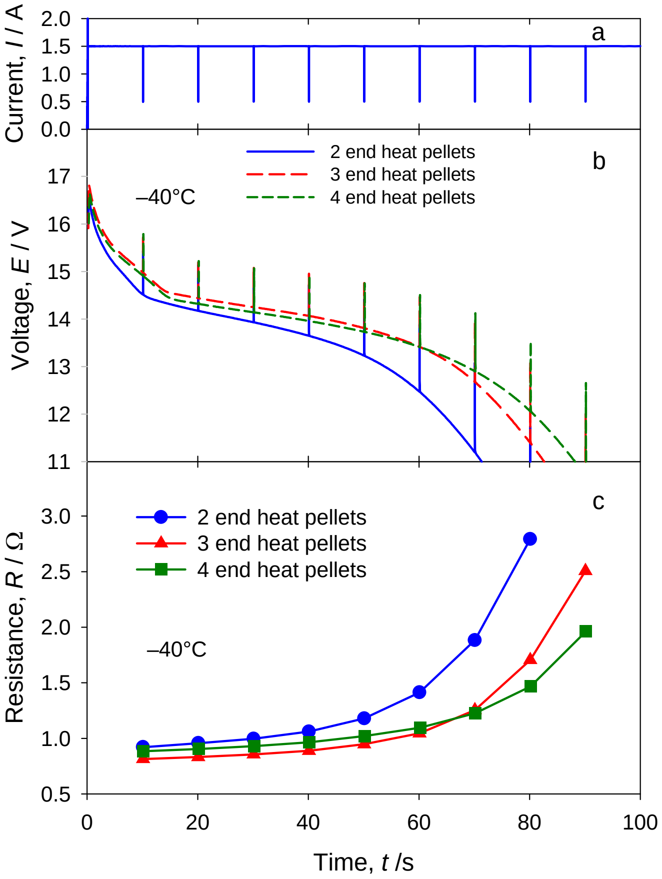

Figure 5. Voltage-time (b) and resistance-time (c) curves at a loading current (a) for thermal batteries with varying numbers of end heat pellets

Electrochemical Rebalance

During the course of this work, we have rebalanced the cathode and anode loadings in order to achieve the optimal ratio, which resulted in an increase in runtime by about 15%. This rebalance was carried out by either varying the loadings and observe the resulting batteries in the tests described above, or making thermal cells made of thinner cathode or anode pellets and testing them in a temperature-controlled tubular furnace. Figure 5 shows some selected results from the latter experiments. It can be seen that the results are quite consistent, in terms of both the voltage levels and the lifetimes of the different batteries. With the thermal cells made of regular cathode and anode pellets, the voltage (a) and resistance values (b) of the double-cell stack is precisely twice those of the single cell stack in the majority of the discharge time. When the thickness of cathode or anode pellet is changed, the runtime of the thermal cell changes in accordance with the amount of active material contained in the limiting component. It follows that variations in runtime we observe for a particular thermal battery are likely the results of variations in factors other than electrochemical loading factors, such as heat source material loading and distribution and thermal insulation.

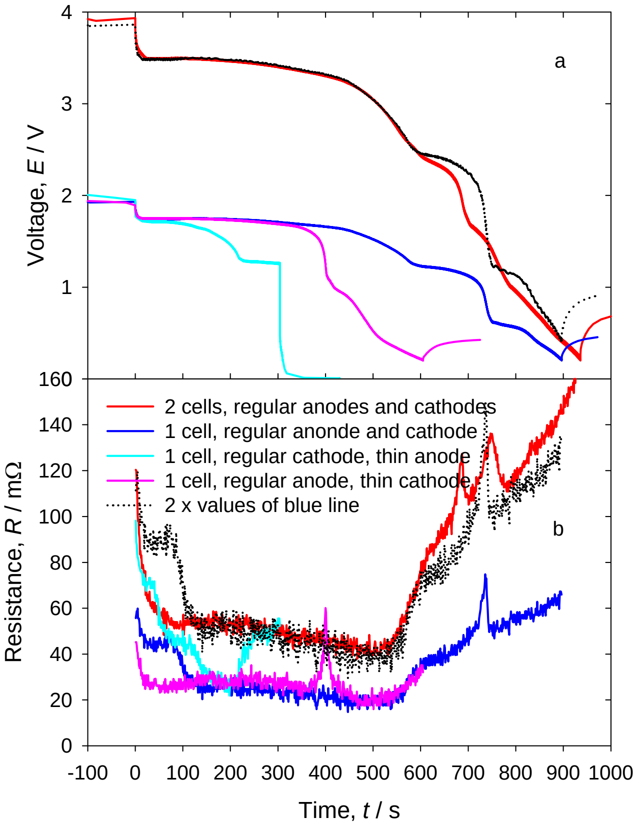

Figure 6. Voltage-time (a) and resistance-time (b) curves for thermal cells of different loadings tested in a temperature-controlled tubular furnace

Conclusions

Operating gas atmosphere has been found to have a strong impact to the lifetime of the LCCM-type thermal batteries. In the extreme case of evacuation, the lifetime can be prolonged by as much as 50%. Gas gettering is a promising technique for controlling the gas atmosphere but more work is needed for its successful implementation. Side-wall heating, having the right number of end heat pellets, and deploying more efficient thermal insulation materials are other ways of considerably increasing the lifetime of a thermal battery.

References

1. F. Krieger and R. Lennen Proc. 42nd Power Sources Conference (2006) 253
2. F. Krieger and M. Ding, 43rd Power Sources Conference (2008)
3. F. Krieger and A. Goldberg, Proc. 41st Power Sources Conference, (2004) 187
4. F. Krieger, Proc. Sensors and Electron Devices Symposium, College Park, MD (1997) 299
5. M. Ding, F. Krieger, et at., 43rd Power Sources Conference (2008)
6. M. Ding, F. Krieger, et al., 43rd Power Sources Conference (2008)