Thermal Characterization of Materials for Improved Modeling and Simulation of Thermal Batteries

Giuseppe L. Di Benedetto, Charles W. McMullan, Lauren A. Morris, Daniel P. Schmidt, Aaron M. Stern, Richard Dratler, Peggy A. Sanchez, and Lynne K. Rider
U.S. Army Combat Capabilities Development Command Armaments Center,
Picatinny Arsenal, NJ 07806, USA
Contact Author Email: giuseppe.l.dibenedetto.civ@army.mil / 1-973-724-1977

Abstract

Thermal batteries are the predominant power source for defense munitions systems due to their high-power performance and extreme ruggedness. U.S. Army Combat Capabilities Development Command Armaments Center (DEVCOM-AC) employs modeling and simulation to understand and optimize internal heat distribution to improve thermal battery performance. Sandia National Laboratory's Thermally Activated Battery Simulator (TABS) is a robust software tool set for simulating heat transfer throughout the entire lifetime of a thermal battery; its simulations rely on the use of physical and chemical material properties within the materials database.

In this study, anode, cathode, separator, and insulation materials were characterized experimentally using simultaneous thermal analysis (STA). Temperature-dependent heat capacity, melting temperature, enthalpy of melting, decomposition temperature, etc. were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) over the full range of operating temperatures for thermal batteries (25-600 °C). The experimentally determined thermal properties were uploaded into the TABS materials database and simulations attained with the updated material properties were compared to those generated using the legacy database. TABS simulations estimate internal cell stack temperatures for various configurations and heat balances that allow comparison of peak temperature and runtime.

Keywords

thermal properties; thermal battery; molten salt battery; modeling and simulation; thermal analysis

Introduction

Back in 1991, the Deputy Secretary of Defense approved a plan to strengthen the use of modeling and simulation (M&S) across the Department of Defense (DoD) to aid in research and development, test and evaluation, and operation and cost analysis [1]. The initiative has proven to be heavily successful, especially as computing technology has advanced allowing even desktop computers to design and model DoD products [2-3]. Over the years, as M&S tools were validated with test and evaluation, considerable M&S implementation has accelerated research and development and resulted in significant schedule and cost savings [2-3]. In recent years, M&S tools in the commercial sector shifted some focus to modeling power sources, especially with the potential to investigate new chemistries for batteries [4]. However, these M&S investigations focused on commercial battery applications, and, naturally, did not include niche battery applications such as missiles and munitions [4]. Focus on the M&S of missiles and munitions batteries, particularly thermal reserve batteries, also known as molten salt reserve batteries, would not occur until the DoD and Department of Energy (DOE) made considerable investments toward the development of advanced models [5-7].

Thermal reserve battery design and modeling are difficult as their performance is dependent on many intricate material and interfacial parameters [8]. The high operational temperatures with the vast range of environmental temperatures required, as well as the relatively small size of thermal battery cells make it incredibly problematic to accurately study and observe these thermal and electrochemical processes in isolation without high-end characterization equipment and specialized custom test fixtures [8-14]. To overcome these obstacles, multiple efforts have been progressing to develop competing thermal reserve battery design models. The Erigo Technologies led model was funded through several DoD SBIR programs and progressed to establish a code consisting of a 2-D or 3-D finite element thermal model coupled to a user-defined number of 1-D electrochemical models of individual battery cells [6,15]. The model has limitations but has improved through corrective fitting to experimental data [15]. The other major model is a multi-physics simulator called Thermally Activated Battery Simulator (TABS) [16]. TABS was developed and led by Sandia National Laboratories, and partially funded through the DoD/DOE Joint Munitions Program [16]. TABS started as only a thermal model but has progressed to include predictions of electrochemical performance and coupling of the thermal-electrochemical portions for single-cell and full battery simulations [16-17]. Both models allow customized materials databases through the inclusion of accurately measured material and thermal properties.

DEVCOM-AC has adopted TABS v5.1 to understand and optimize thermal reserve battery design and performance. To fully accomplish this adoption, DEVCOM-AC engineers have thermally characterized many thermal reserve battery materials including cathodes, electrolytes, separators, anodes, insulations, and other internal material

components, and established an advanced TABS Materials Database [14]. Utilizing the advanced TABS Materials Database, an investigation to model and improve the Low-Cost Competent Munition (LCCM) Battery performance was completed.

Material Characterization

Material Characterization Details: For all internal material research and development investigations, an extensive material characterization strategy is employed to monitor and understand effects of the investigation on the materials and thermal properties of the samples [14]. Complete thermal analysis was performed using a Netzsch STA 449F1 Jupiter 449C (Netzsch Instruments North America, Burlington, MA, USA) thermal analysis system: simultaneous TGA-DSC (thermogravimetric analysis-differential scanning calorimetry) was performed in a silicon carbide (SiC) furnace under Ar with a heating rate of 5 K min^{-1}; heat capacity (Cp) measurements were performed in a platinum (Pt) furnace under Ar with a heating rate of 20 K min^{-1} using sapphire as a reference standard. Data analysis was performed using Proteus Analysis software and Cp was calculated using ASTM 1269.

TABS Material Properties: In order to add new materials to the TABS Materials Database, key material and thermal properties must be accurately measured or retrieved from reliable sources. The key thermal properties are powder density (ρ), pellet density, solidus temperature, peak temperature, liquidus temperature, latent heat of fusion (ΔH_m), heat capacity (Cp), and thermal conductivity (k). The database has the ability to vary the properties based on temperature if information is available. Using the characterization capabilities described earlier, Cp and k were measured as a function of temperature as well as a function of powders or consolidated pellets. Characterization was also conducted for pure compounds and formulated mixtures. The TABS Materials Database has options for M&S with both sets of material and thermal properties. Figure 1 displays an example of measured thermal characterization results. In this case, the measured results are micron FeS_2 and nanostructured FeS_2. The DSC and TGA data were used to determine solidus temperature, peak temperature, and liquidus temperature, while the calculated Cp was recorded as a function of temperature and added accordingly to the TABS Materials Database.

Modeling & Simulation Parameters

Battery Design: The LCCM battery was chosen for the investigation due to its unique design, history, and Government owned technical data package. Figure 2 shows a cross-section of the test setup used by Krieger, et. al [19] when evaluating the performance of the LCCM battery. The large steel case and insulation layers made up the reusable test fixture (RTF). The battery chemistry was assumed to be 95% LiSi/5% electrolye-binder mix for the anode, 65% LiCl-KCl/35% binder for the separator, and 73.5%FeS_2/1.5% Li_2O/25% electrolyte-binder mix for the cathode.

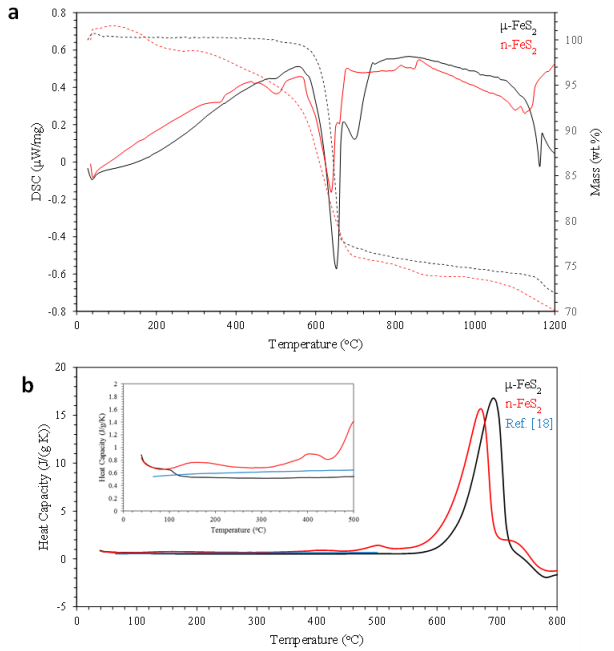

Figure 1: Example measured thermal property data: (a) DSC (solid) and TGA (dashed) of μ-FeS2 and milled n-FeS_2 powders in argon at 5 K min^{-1}, and (b) calculated heat capacity of μ-FeS_2 and n-FeS2 plotted against reference data [18] with inset showing heat capacity data for T < 500 °C (932 °F).

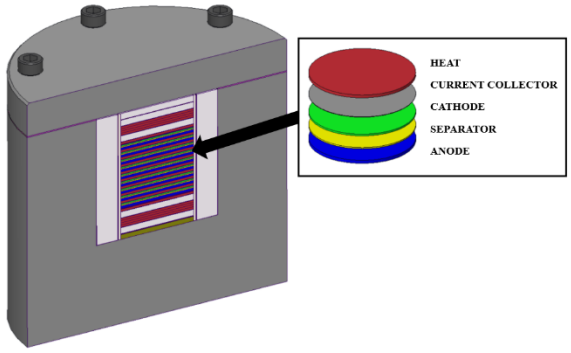

Figure 2: Cross-section drawing of LCCM in RTF assembly with cell component details.

Modeling Parameters: Full battery TABS models utilized radiative and convective boundary conditions for the top, side, and bottom of the battery can. The emissivity of the can material was assumed to be 0.25, and the environmental temperature for discharge was 20°C (68°F). The initial starting temperature of the battery and all of its components was set to either -40°C (-40°F) or +70°C

(+158°F) to evaluate the heat balance of the battery at hot and cold.

Single cell models used the output of the full battery model to define the thermal environment of the cell. There are 9 cells in the LCCM model [19-20], the single cell model used the thermal environment of cell number 5. The system load was assumed to have a load with a constant resistance of 1Ω. Single cell models were only investigated at cold since the model does not include the effects of overheating, so discharge at cold will be the factor limiting performance estimates. The multi-plateau mode for both the anode and cathode were used to improve accuracy.

Modeling & Simulation Results

Full Battery Thermal results: Three versions of the LCCM battery were modeled. V1 was the base configuration, V2 utilized a Fiberfrax based insulation blanket, and V3 used an advanced insulation material. Figure 3 shows the full battery thermal results using the temperature of all nodes of the separator at -40°C (-40°F) to evaluate the thermal lifetime of the battery. The thermal lifetime of this battery configuration is projected to be reduced with the V2 configuration and improved with the V3 configuration.

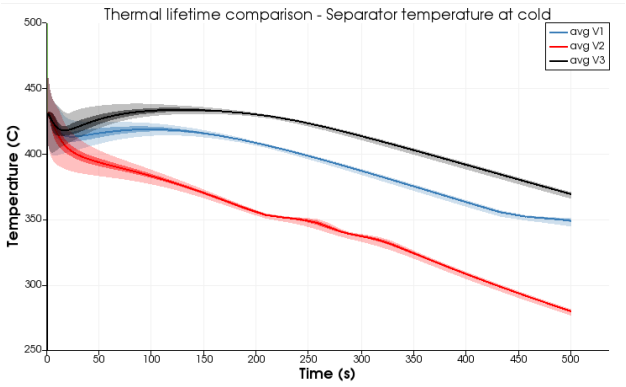

Figure 3: TABS simulations of all battery separator temperature nodes with starting temperature of -40°C (-40°F) to estimate thermal lifetime of the battery.

Figure 4 shows the temperature of all cathode nodes at +70°C (+158°F), which is when it would be most likely to decompose. While the model assumes this is not occurring, the cathode will start to decompose when exposed to these conditions in reality, as it will negatively affect battery performance. The cathode temperatures near activation are all very similar for these three battery configurations, which indicates that the change in configurations is not expected to reduce the performance of discharging the battery at hot with all other parameters held equal. It does not appear that a change in the heat balance of the cell stack is necessary.

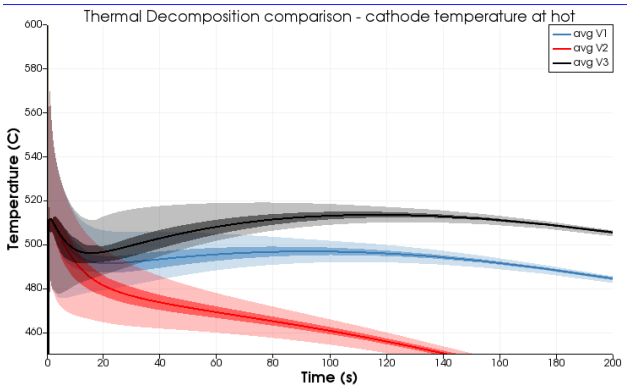

Figure 4: TABS simulations of all battery cathode temperature nodes with starting temperature of 70°C to estimate thermal decomposition.

Single cell modeling allows us to estimate the electrochemical output of a cell with these different thermal profiles. For this study we have multiplied the voltage prediction of the middle cell by the number of cells to estimate the overall performance of the battery. This is likely an optimistic estimation since the middle cell is probably the warmest cell. This is important to keep in mind when comparing to application specific requirements and margin projections, but the trend should still be the same regardless of which cells were utilized in the analysis.

Figure 5 shows these voltage predictions for each of the battery configurations. The runtime to 12V is 112s, 109s, and 137s for V1, V2, and V3 respectively. If you consider the baseline as the worst performer, the advanced insulation is projected to improve runtime by 30% with no additional changes.

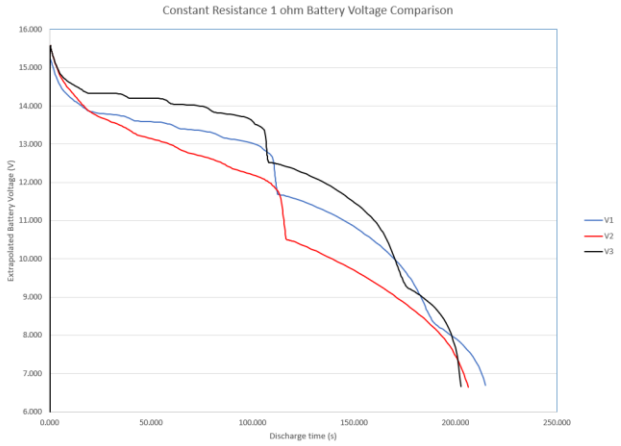

Figure 5: TABS single cell simulations extrapolated to battery performance by multiplying the result by the number of cells.

Conclusion

These simulations describe an approach to evaluating the expected performance of a thermal battery design with various insulation materials. The materials characterization work we have completed allows us to make these estimates of battery performance without even building a battery. While this is not a substitute for actual prototypes, it could be used to focus a more limited set of prototype builds on those designs that are expected to have the most impact.

Acknowledgements

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References

1. Piplani, Col. L. K., et. al., "Systems Acquisition Manager's Guide for the use of Models and Simulations," Report of the DSMC 1993-1994 Military Research Fellows, Defense Systems Management College Press, Ft. Belvoir, VA, September 1994.
2. Carter, III, J. R., "A Business Case for Modeling and Simulation," U.S. Army AMRDEC Special Report RD-AS-01-02, September 2001.
3. Oswalt, I., et. al., "Calculating return on investment for U.S. Department of Defense modeling and simulation," Defense A R Journal, vol. 18, no. 2, 2011.
4. Tamilselvi, S., et. al., "A Review of Battery Modeling Techniques," Sustainability, vol. 13, p. 10042, 2021.
5. Ingersoll, D., et. al., "Highly Instrumented Thermal Battery for Thermal Model Validation," Proceedings of the 43rd Power Sources Conference, Philadelphia, PA, 7-10 July, 2008.Grillet,
6. Kenton, M., et. al., "A Comprehensive, Physics-Based Model for Thermal Batteries," Proceedings of the 44th Power Sources Conference, Las Vegas, NV, 14-17 June, 2010.
7. Roberts, S. A., et. al., "Modeling Separator Deformation and Electrolyte Flow in Thermally-Activated Batteries," Proceedings of the 45th Power Sources Conference, pp. 603-606, 2012.
8. Guidotti, R. A., and P. J. Masset, "Thermally activated ("thermal") battery technology: Part I: An overview," Journal of Power Sources, vol. 161, no. 2, pp. 1443-1449, 2006.
9. Masset, P. J., and R. A. Guidotti, "Thermally activated ("thermal") battery technology: Part II. Molten salt electrolytes," Journal of Power Sources, vol. 162, pp. 397-414, 2007.
10. Masset, P. J., and R. A. Guidotti, "Thermally activated ("thermal") battery technology: Part IIIa: FeS_2 cathode material," Journal of Power Sources, vol. 177, pp. 595-609, 2008.
11. Masset, P. J., and R. A. Guidotti, "Thermally activated ("thermal") battery technology: Part IIIb. Sulfur and oxide-based cathode materials," Journal of Power Sources, vol. 178, pp. 456-466, 2008.
12. Guidotti, R. A., and P. J. Masset, "Thermally activated ("thermal") battery technology: Part IV. Anode materials," Journal of Power Sources, vol. 183, pp. 388-398, 2008.
13. A. M., et. al., "High temperature mechanical properties of thermal battery separators," Proceedings of the 44th Power Sources Conference, Las Vegas, NV, 14-17 June, 2010.
14. Di Benedetto, G. L., et. al., "Nanostructuring of Iron Disulfide Cathode Materials for Enhanced Thermal Batteries," J. Electrochem. Soc., vol. 168, no. 4, 046520, 2021.
15. Kenton, M., and D. Bhakta, "Improving Thermal Battery Performance through Model-Based Development and Improved Component Designs," Proceedings of the 48th Power Sources Conference, Denver, CO, 11-14 June, 2018.
16. Roberts, S. A., et. al., "TABS: A Thermal Battery Desktop Design Tool," Proceedings of the 48th Power Sources Conference, Denver, CO, 11-14 June, 2018.
17. Voskuilen, T. G., et. al., "Multi-fidelity electrochemical modeling of thermally activated battery cells," Journal of Power Sources, vol. 488, 229469, 2021.
18. Gronvold, F., and E. F. Westrum, "Heat Capacities of iron disulfides Thermodynamics of marcasite from 5 to 700 K, pyrite from 300 to 780 K, and the transformation of marcasite to pyrite," J. Chem. Thermodyanmics, vol. 8, p. 1039, 1976.
19. Krieger, F. C., and M. Ding, "Heat Transfer in the LCCM Thermal Reserve Battery," Tech. Rep. ARL-TR-4843, Army Research Laboratory, 2009.
20. Krieger, F. C., "Reducing Low Cost Competent Munition (LCCM) Thermal Battery Volumesby Factors of 2 to 3 and Extending LCCM Thermal Lifetimes by Factors of 10 to 20 or More: Part 1," Tech. Rep. ARL-TR-8822, Army Research Laboratory, 2019.
21. Ahrens, J., et. al. “ParaView: An End-User Tool for Large Data Visualization,” Tech. Rep. LA-UR-03-1560, Los Alamos National Laboratory, 2005.