Enhanced Performance in Thermal Batteries Containing Nanostructured Cathode Materials

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Abstract

The U.S. Army is developing advanced munitions systems that require higher power and larger current densities than what can be supplied by commercially available thermal batteries. Nanoscale materials have properties which differ significantly from their conventional counterparts due to their high specific surface area (SSA) and increased reaction rates. Incorporating nanomaterials into otherwise legacy power sources has the potential to provide the necessary performance improvements, such as higher voltages at increased current densities. Particle size reduction via high energy milling (HEM) is one way to shift the primary particle size of a material into the nanoscale. Brittle materials such as iron disulfide, FeS_2, mill quite readily and so very high SSA is attainable, and with very little contamination.

Previously, U.S. Army Combat Capabilities Development Command Armaments Center (DEVCOM-AC) and EnerSys Advanced Systems, Inc. jointly reported on an optimized, high SSA, nanostructured FeS_2 for thermal battery manufacturing synthesized via HEM. In that work, performance improvements were realized using nanostructured FeS_2 at the single cell level. In this study, full lithium primary reserve multi-cell batteries were built with nanostructured catholyte made from nanoscale FeS_2, as well as with standard catholyte, and blends thereof. The battery prototypes were built with different thermal balances and end-heating configurations and the electrochemical performance was characterized during discharge testing and polarization type scans. It was determined that full prototype batteries built with the nanostructured FeS_2 have higher voltage performance and higher current handling capacity than the legacy batteries. However, data from the electrochemical testing of the different end heat configurations indicates that a fully optimized thermal balance for the nanostructured cathode material has not yet been fully achieved.

Keywords

nanomaterials, thermal battery, molten salt battery, cathode, nanoscale, iron disulfide, polarization, milling

Introduction

The thermal battery is the chosen power source for many critical defense weapons systems due to its long shelf life and high power density. The defense industry continues to produce more sophisticated munitions and longer-range weapons systems, which has triggered a high demand signal for advanced thermal batteries that can provide higher voltages and longer run times as compared to the current commercial, off-the-shelf batteries.

New material solutions are being investigated to design and develop thermal batteries with superior performance that will meet future munition power requirements. One such solution is the use of nanostructured and nanoscale cathode materials as a direct replacement for conventional cathodes. Recently, the use of nanoscale iron disulfide (n-FeS_2) has been reported by many research groups. Improved performance and nanomaterial properties were reported including increased total power density, increased run time, and increased robustness of electrode pellets, all attributed to the ultra-small particle size (<100 nm) of the FeS_2 [1]. Additionally, single cell thermal battery (SCTB) testing demonstrated higher maximum cell voltages and longer run time using n-FeS_2 (< 100 nm) in place of standard micron-sized FeS_2 (μ-FeS_2) [2]. While n-FeS_2 has been synthesized by chemical hydrothermal synthesis [3,4], high energy ball milling [2,5,6] has been employed more recently. Previously, our group has reported scale up of high energy ball milling, fully characterized the chemical and physical properties of n-FeS_2 and demonstrated performance benefits of using n-FeS_2 in place of μ-FeS_2 in single cell thermal battery testing [2]. In this study, we explore the use of high energy milled n-FeS_2 as a replacement for standard μ-FeS_2 in full scale battery prototypes, using the commercial G3190B2 battery as a model system.

Experimental

Cathode Preparation and Characterization

High energy ball milling was used to synthesize n-FeS_2 from commercially available micron-sized powder using previously reported milling conditions [2]. All powders were stored in an inert argon environment with less than 10 ppm oxygen and water. Catholyte powders were produced using micron and nanoscale FeS_2 as previously reported [2,6]. The resultant micron and nanostructured catholyte powders were pressed into micron cathode (µ-cathode) and nano cathode (n-cathode) pellets, respectively. In this study we also investigated cathodes synthesized from blends of the micron and nano FeS_2. Synthesis of the blended cathode pellets was identical except that the micron and nano FeS_2 powders were blended using resonant acoustic mixing prior to being mixed with the electrolyte. The blends of micron:nano that were investigated were 100/0, 75/25, 50/50, 25/75, and 0/100 by weight and are referred to herein as Blends A, B, C, D, and E, respectively.

The synthesized nanoscale FeS_2 powder properties were characterized using a variety of techniques. X-ray diffraction (XRD) was performed using a Rigaku Ultima with Cu-Kα source with MDI Jade software. Chemical analysis was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and ASTM D1353 to determine Fe and S content by weight. The Barret-Emmet-Teller (B.E.T.) method for surface area analysis and particle size derivation was done using a Quantachrome Nova 4000e. Scanning Electron Microscopy (SEM) was performed using a Zeiss Supra V40 using in-lens and backscatter detectors at 15 kV. Particle size analysis was performed using a Horiba LA-950V2 to determine the d10, d50, and d90 on a volume basis.

Battery Design and Testing

Single cell thermal battery (SCTB) testing was performed as previously reported [2]. A constant 350 mAh discharge was applied to the cell for the entire discharge time with a 7 A by 500 ms pulse occurring every 60 seconds. Finally, full prototype batteries were built using micron and nano cathodes and blends thereof at EnerSys using their commercial thermal battery production line and standard methods. The anode and separator pellet chemistry, size, and compaction force were maintained consistent with the standard G3190B2 battery. Three different battery build groups and a total of 124 batteries were produced. Batteries were soaked to three temperatures: cold [-45 ºF (-42.8 ºC)], ambient, and hot [+160 ºF (+71.1 ºC)] and tested.

Results and Discussion

Cathode Preparation and Characterization

Six kilograms of high energy ball milled FeS_2 was synthesized from micron powder and analyzed; its properties were characteristic of those previously reported and are summarized in Table 1. The empirical formula was within the acceptable limit ($FeS_{2.129}$ – $FeS_{1.882}$); however, ICP analysis revealed an increase in the acid soluble iron (free iron) content in the milled powder as compared to the unmilled powder.

Table 1: Properties of micron and nano iron disulfide.

		µ-FeS_2	**n-FeS_2**
Empirical Formula		$FeS_{2.014}$	$FeS_{2.040}$
Acid Soluble (Fe_2O_3)	(%)	0.03	3.41
Specific Surface Area	(m^2/g)	0.512	19.561
BET Equivalent Diameter	(nm)	2493	65.0
Crystallite Size	(nm)	> 500	50.8

SEM images of cathode pellets synthesized from blends of micron and nano FeS_2 powders are shown in Figure 1 and illustrate that smaller length scales of mixing among the catholyte constituents exist with increased n-FeS_2 content.

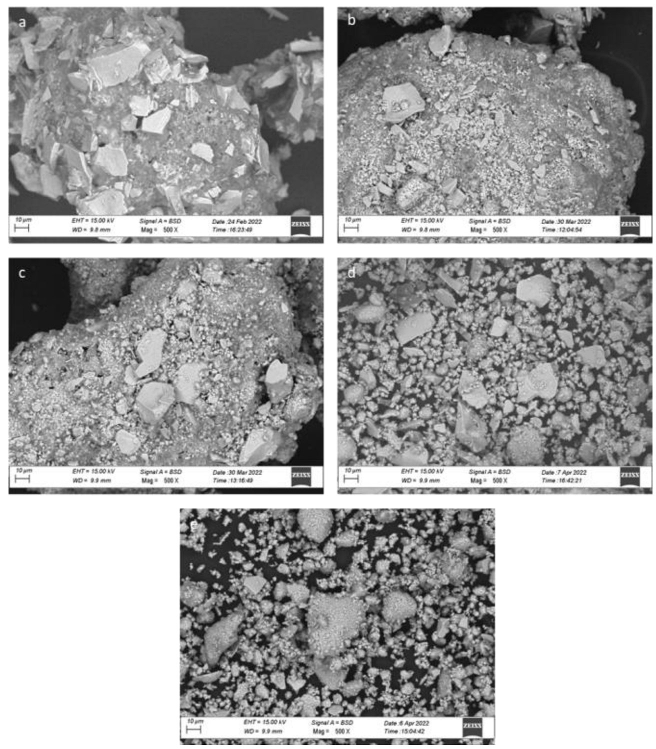

Figure 1: Backscattered scanning electron images of (a) Blend A/100% µ-FeS_2 catholyte, (b) Blend B, (c) Blend C, (d) Blend D, and (e) Blend E/100% n-FeS_2 catholyte powders.

Battery Design and Testing

Cathode, separator, and anode cells were prepared with Blends A-E cathodes and subjected to single cell capacity testing. The average cell voltage with respect to time is plotted in Figure 2. The Blend E/100% n-FeS_2 cell had the highest initial cell voltage, performed best under the pulse loads in the capacity test, and maintained the highest voltage under the background load for the first 6 minutes of discharge. Blends A and D performed best and second best, respectively, in the capacity tests under background load out to 14 minutes of discharge. Blends A, D, and E were therefore down selected for full battery builds in Battery Group 1.

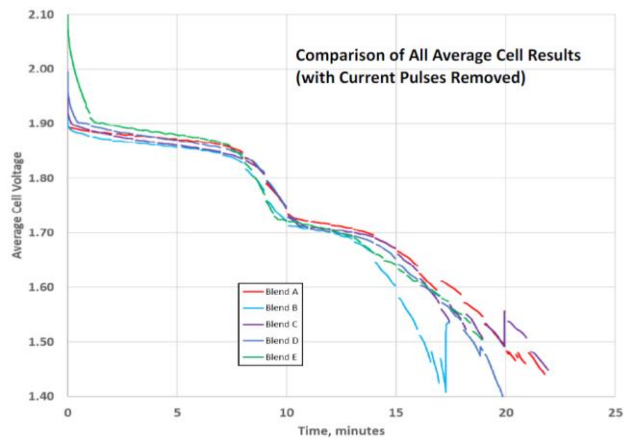

Figure 2: SCTB discharge testing of cells made of Blends A, B, C, D, and E with a 350 mAh background load current and a 500 ms 7A pulse every 60 seconds at 500 ºC platen temperature.

A total of 36 Group 1 batteries were built (12 each of Blends A, D, and E) with identical cell stack configuration and pellet weights. Group 1 batteries were tested using a combined constant current and pulse discharge profile until the battery dropped to 1.5 V or 10 pulse cycles were achieved. Battery testing revealed that the batteries made with Blend A performed best at ambient and hot temperatures, while Blend E batteries performed best at cold temperature. Blend E batteries also demonstrated slightly better power capability than Blend A and D batteries. Ambient battery test data from Group 1 batteries is shown in Figure 3. The performance advantages of the nanocathode demonstrated in SCTB testing were not realized at the full battery level in Group 1 batteries.

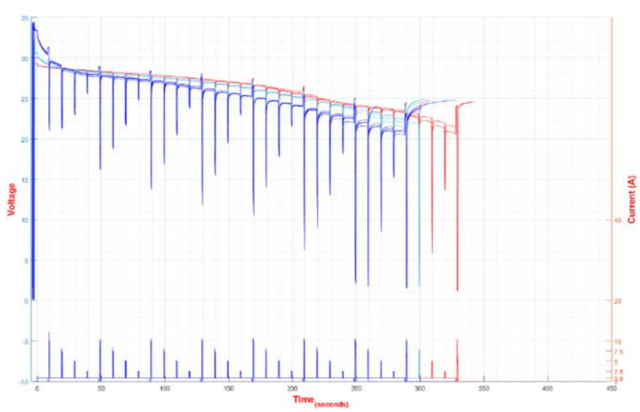

Figure 3: Voltage and current battery test data for batteries built with Blend A/100% µ-FeS_2 (red), Blend D (teal), and Blend E/100% n-FeS_2 (blue) cathodes.

It was hypothesized that the nanocathode may require design changes within the battery to maximize its capacity. A second group of batteries (Battery Group 2) was designed and built using only 100% nFeS_2. DEVCOM AC used a multi-physics simulator called Thermally Activated Battery Simulator (TABS) [7] to explore design changes and simulate predicted performance of batteries built with the nanocathode. Initial thermochemical simulations in TABS indicated that the nanocathode pellets may be overheating and so design options were explored which may lower the internal temperature of the molten nanocathode. A promising design, "Army V8" was identified which utilized an optimized end heat configuration that minimized local overheating of the ends of the cell stack. Simulations demonstrated that the optimized end heat configuration may protect the nanocathode pellets located near the end heat from instantaneous overheating when the battery is activated. A second potential design that was explored used a lower heat balance that was designed to run ten degrees lower (-10 ºC) than the standard design.

A total of four (4) battery designs (48 batteries) were tested in Battery Group 2, all containing 100% nanocatholyte: Group 2.1 was built using the standard design, same as Battery Group 1, Blend E (control); Group 2.2 was built using the Army V8 design; Group 2.3 was built using the standard design but with lower heat balance; and Group 2.4 was built using the Army V8 design and lower heat balance. Twelve of each battery design were made and tested at cold [-45 ºF (-42.8 ºC)], ambient, and hot [+160 ºF (+71.1 ºC)]. The batteries built with the higher heat balance (Groups 2.1 and 2.2) performed best overall in run time and pulse performance at all temperatures. Batteries built with the Army V8 design configuration resulted in more consistent discharge performance and significantly reduced battery to battery performance variations.

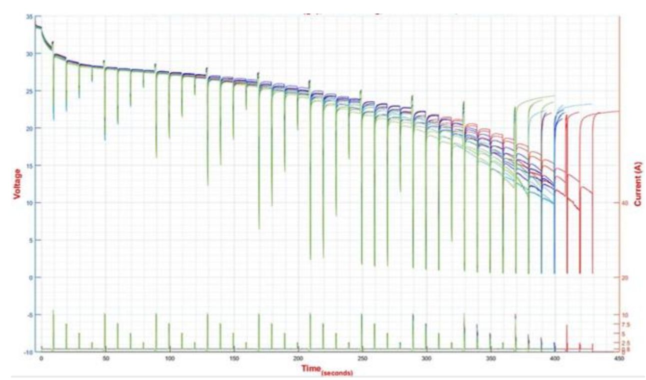

Figure 4: Voltage and current battery test data for batteries built with Group 2.1 (red), 2.2 (purple), 2.3 (cyan), and 2.4 (green) modified designs.

Finally, 40 batteries were built for Group 3 testing. Group 3.1 consisted of 24 batteries built with the Army V8 configuration and 100% nanocatholyte (same as Group 2.2) and Group 3.2 consisted of 12 batteries built with 100% micron catholyte and the Army V8 configuration. All batteries were tested with the same load profile at cold [-45 ºF (-42.8 ºC)], ambient, and hot [+160 ºF (+71.1 ºC) temperatures. Results from the battery testing indicated that the Army V8 design normalized the heating within the batteries in both Groups 3.1 and 3.2 and no evidence of overheating was observed. The Group 3.1 batteries performed best overall at the extreme cold temperature during background load and with high current pulses. The Group 3.1 (nanocatholyte) batteries consistently showed higher voltage response early in life at all temperatures as compared to the Group 3.2 (micron catholyte) batteries, but that response diminished 30-40 s into discharge. The Group 3.2 batteries outperformed the Group 3.1 batteries at ambient and hot temperatures for overall run time and voltage under the high current pulse load profile. The battery test results at ambient temperature are shown in Figure 5.

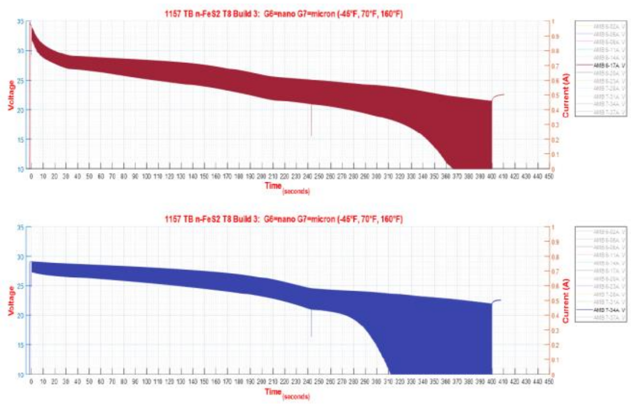

Figure 5: Voltage battery test data for Group 3.1 (top), and Group 3.2 (bottom) batteries built with the Army V8 configuration and 100% nano and 100% micron catholyte, respectively.

In all test cases explored here, batteries built with the nanocatholyte experienced higher initial cell voltage at the beginning of life. It remains unclear if this higher initial voltage is the result of the high specific surface area of the nanocathode material or if it is due to excess iron. Chemical analysis results shown in Table 1 reveal that high energy milling induces minor chemical changes in the FeS_2 cathode material, including an increased amount of excess acid soluble iron. If the high voltage is due to increased excess iron, then there would be a corresponding drop in cell/battery capacity as well, which is observed in many of the nano batteries tested in this effort (see Figures 3 and 5). Further optimization of the high energy milling process could minimize the formation of excess iron and should be explored in future studies.

Conclusion

The batteries built with 100 % n-FeS_2 perform better than the batteries built with 100 % µ-FeS_2 at cold temperature; however, at ambient and high temperature the batteries built with µ-FeS_2 perform best. There is no observed performance advantage in blending the n-FeS_2 and µ-FeS_2. An optimized cell stack design for the n-FeS_2 was necessary and was driven by M&S using TABS. No nano cathode decomposition was observed using the optimized Army V8 cell stack design which utilized an optimized end heat configuration. The nano batteries built with the Army V8 design performed better than the standard design and outperformed micron batteries built with the same configuration at extreme cold temperatures; but, the micron batteries performed better than the nano at ambient and extreme hot temperatures. The work discussed here comes closer to achieving performance improvements demonstrated for the n-FeS_2 previously in SCTB testing in full scale batteries and demonstrates a clear performance enhancement using n-FeS_2 for applications in extreme cold environments. However, more work should be done to further optimize cell stacking and n-FeS_2 chemistry to maximize nano cathode performance in a full battery.

Acknowledgements

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