SAND2016-3756C

Electrolyte-Binder Powder Processing to Improve Manufacturability of Thermal Battery Separator Pellets

Joseph Beck and Brian Perdue
Power Sources Technology Group
Sandia National Laboratories
PO Box 5800
Albuquerque, NM 87185-0613
Contact Author: jbeck@sandia.gov

Abstract: *Thermal battery electrolyte-binder powder processing was investigated with design-for-manufacturing considerations with attempt to improve separator pellet production. Low separator pellet yields increase manufacturing costs and waste valuable or expensive battery materials. Alternative powder blending and sizing processes are reviewed and their impact on powder flow and compaction characteristics discussed. Reprocessing scrapped separator pellets was demonstrated to be a viable process to reclaim scrapped materials through mechanical and electrochemical test results.*

Keywords: Thermal battery; molten salt battery; electrolyte-binder; powder; pellet; reprocessing; LiCl/KCl; MgO; design for manufacturing

Introduction

A molten salt thermal battery is a reserve power source containing a stack assembly comprised of electrochemical cells made of anode, separator, and cathode pellets along with heat pellets for a heat source. The purpose of the separator pellet is to isolate the anode and cathode and provide ion transport during battery function. Thermal battery pellets are fabricated by compacting powder materials under a static force. Automated pellet presses, where the powder flows from a hopper into the die cavity, are utilized by industry to achieve higher throughput but introduce challenges related to the flow and compaction properties of the specific powder.

Low pellet production yields increase manufacturing costs, create financial and schedule opportunity costs, and scrap highly valuable battery materials. This research investigates and characterizes LiCl/KCl/MgO electrolyte-binder powder with intent to improve the manufacturability of separator pellets. The motivation of this work was design-for-manufacturing thermal battery powders and pellets while maintaining performance characteristics. This work investigates optimizing final powder characteristics during powder processing for high yield pellet production and the effects of using scrapped material on pellet performance.

Experimental results

Powder Processing – Blending: Overview of the thermal battery powder and pellet production process is shown in Figure 1. Electrolyte-binder powder processing operations are blending, fusing, grinding, and sizing with the final product being pelletized and accepted/rejected based on inspection criteria. In order to contain the molten electrolyte during battery operation, the LiCl/KCl eutectic is mixed with MgO as a binder in ratios ranging from 65/35 to 60/40 weight percentages. Traditionally, powder constituents are mixed using blending equipment, such as a "V"-blender, with no additional materials added. This process is commonly known as dry blending. Good homogeneity is difficult to ensure in dry blending even when using multi-axis blenders, such as the Turbula blender, due to magnesium oxide's high angle of repose which impacts its flow characteristics. To overcome the challenges of homogeneity extended mix times were required for dry blending. Powder homogeneity is a critical parameter impacting flow characteristics and especially important in the use of automated pellet presses where the material is flowing to fill a die [1].

In response to dry blending challenges, Sandia developed a process that used Freon TF as a mixing medium together with a Waring-type blender [2]. In the early 1990s due to environmental awareness, the Department of Energy began restricting and eliminating several common halogenated organics including Freons. Guidotti led research to identify alternative blending media and concluded that liquid nitrogen was the best replacement [3]. However, the use of liquid nitrogen created other issues including maintaining temperatures along with local condensation of moisture in water sensitive materials. In the mid-2000s, Sandia again pioneered the use of electrolyte-binder blending agents this time led by Moya. Vertrel XF, a hydrofluorocarbon, was selected as suitable material due to its similar physical properties of Freon TF. In all instances the media was added during the blending step to enhance mixing, which was then forced evaporated out before fusing. This process is referred to as wet blending.

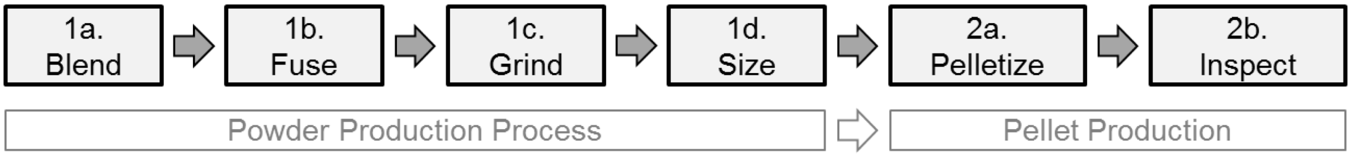

Figure 1: Thermal battery electrolyte-binder powder and pellet production process

The use of Vertrel XF decreased mixing time required for a homogenous blend compared to dry blending by almost two orders of magnitude, by acting as a fluidization aid decreasing inter-particle friction. While reducing mixing time is beneficial, an additional process step is required for wet blending to drive off the Vertrel XF prior to fusing. The implementation of wet blending was long accepted to improve pellet integrity. Experimental results from pressing dry and wet blended powders on automated pressing equipment exhibited no significant improvement in powder flow properties, as quantified by weight standard deviations, or pellet integrity. SEM/EDX was used to probe powder sample homogeneity and to ensure the Vertrel XF has been completely removed. Results indicate that both samples were equally homogeneous and the Vertrel XF had been completely removed.

Powder Processing – Sizing: After blending, the powder is fused at high temperatures to melt the electrolyte. The material is then ground using a relatively high energy mill through a 0.033” screen, before granulating and sieving through a #60 US Standard mesh (0.010”). The granulating and sieving operations are referred to collectively as the sizing operation. Granulating, widely adopted by the pharmaceutical industry, is the process of forming larger, multiparticle granules. Resulting granules typically have increased average particle size and are more isodiametric, both of which improve flow and compaction properties in an automated press [1]. Powder samples of both dry and wet blended powders were analyzed post-grinding, post-granulating, and post-sieving for particle size distribution. Samples were run in triplicate dry (not suspended in liquid medium) and measured using laser scattering.

The particle size distribution results for the wet blend are shown in Figure 2. As expected, the dry blended powder exhibited the same trends as the wet blended powder because powder homogeneity has no effect on grinding and sizing. After each sizing operation, the mean size and standard deviation decreased. Granulation of the electrolyte-binder resulted in high percentage of particles distributed around the mesh size. This was a result of both granulating the smaller particles and decreasing the size of the largest particles. The granulation equipment input enough energy to reduce the largest particles of the very soft electrolyte-binder. The material was then reduced in size again during the low-energy sieving operation but also the standard deviation decreased as well. The final powder exhibits a single peak whereas the post-grinding and post-granulating samples may exhibit a slight bimodal distribution or at least a wider particle size range. Further work is continuing on characterizing the impact on the final powder characteristics by the granulation step.

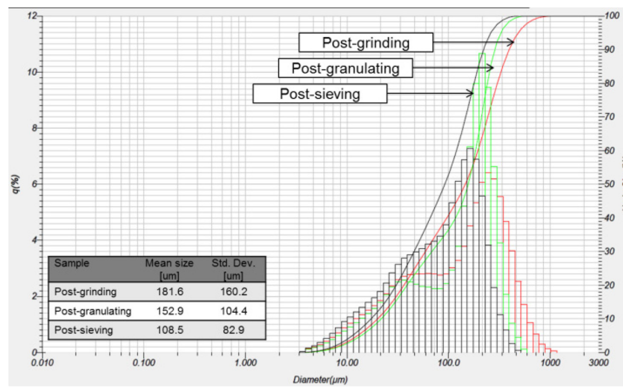

Figure 2: Particle size distribution of grinding and sizing

Pellet Reprocessing: Scrapped and rejected materials during the battery production process represent a significant portion of material losses. “Rejected” separator pellets were reprocessed using two different methods shown in Figure 3: fusing pellets before grinding (2b to 1b, “reprocess 1b”) or just grinding the pellets back into electrolyte-binder powder (2b to 1c, “reprocess 1c”). The reprocessing was completed three times on the same materials in attempt to exaggerate any effects the reprocessing would have with all pellets fabricated on manual pellet presses. Mechanical and electrochemical performance impacts were investigated by comparing the mechanical and electrochemical properties of the 3X reprocessed pellets to control pellets, virgin pellets with no reprocessing, as the baseline.

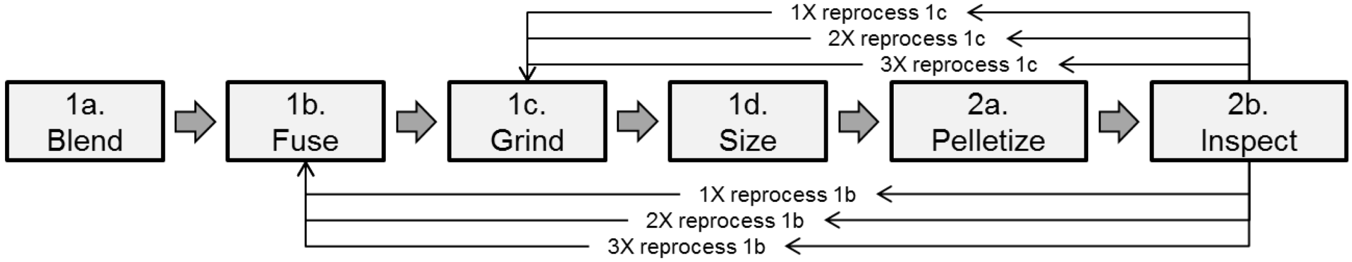

Figure 3: Separator pellet reprocessing processes

Firstly, acceptable pellets were fabricated using the reprocessed materials demonstrating that this process may be viable to reclaim scrapped materials. As the materials continued to be reprocessed, the pellet press operators qualitatively noted the powder was finer resulting in increased pellet defects of bad edges and soft spots. The reprocessed 1c powder without fusing exhibited a change in compaction properties requiring the forming force of the press to be reduced by almost 10% between the 1X and 2X reprocessing where it remained for the 3X pellets. The powder that was reprocessed 1b with fusing did not require any changes to the forming force, dwell time, or stripping force through the 3X pellets. Due to the pellets being pressed on manual presses where each charge is individually weighed and filled by hand, no data exists on its flow or compaction characteristics in automated pellet press.

Reprocessed materials were tested using Differential Scanning Calorimetry to identify bulk material property changes. Table 1 compiles the mean value of three replicates and one standard deviation for the various test results with the exception of surface area being a single measurement. Heat capacity at the lower temperature range when the eutectic is still in solid phase showed a minor decrease with reprocessing 1c but was only statistically significant using Student's t-test ($p<0.05$) at the reprocessed 2X and 3X pellets compared to the control. No data was statistically significant for the heat capacity at the higher temperature range when the electrolyte is molten. No change in melting point is estimated which is intuitive because no materials were added or removed from the eutectic salt formulation as part of either reprocessing. Finally, no change in the heat of fusion is estimated for any of the reprocessed pellets. BET surface area decreases with additional reprocessing. This is attributed to the additional grinding operations in both 1b and 1c reprocesses reducing the electrolyte particle size resulting in finer salts and a change in porosity.

Table 1: 3X reprocessed material properties

Material	Cp avg		Melting Point Onset [°C]	Heat of Fusion [J/g]	BET Surface Area [m^2/g]
	150-250 °C [J/g°C]	400-500 °C [J/g°C]			
Control	1.21 ± 0.06	1.42 ± 0.07	343.6 ± 0.6	127.8 ± 1.0	5.3
1X reprocess 1b	1.14 ± 0.08	1.31 ± 0.09	343.1 ± 0.5	127.9 ± 0.2	2.4
2X reprocess 1b	1.07 ± 0.04	1.39 ± 0.05	343.3 ± 0.6	130.8 ± 2.5	2.0
3X reprocess 1b	1.09 ± 0.07	1.52 ± 0.06	343.2 ± 0.2	130.3 ± 0.6	2.2
1X reprocess 1c	1.04 ± 0.10	1.43 ± 0.12	343.4 ± 1.0	126.2 ± 1.7	4.2
2X reprocess 1c	1.11 ± 0.02	1.36 ± 0.07	344.0 ± 0.6	125.5 ± 0.8	4.6
3X reprocess 1c	1.08 ± 0.02	1.42 ± 0.02	342.4 ± 0.7	124.9 ± 0.5	2.6

To determine the effects of pellet reprocessing, electrochemical impedance spectroscopy was performed. Control, 3X reprocessed 1b, and 3X reprocessed 1c pellets were tested under a load force equating to 7.5 psi at 375, 400, 475, 500 and 550C with impedance spectra taken at each temperature in triplicate. To evaluate the performance of the pellets, slopes of the impedance spectra were calculated utilizing the last 10 data points comprising the most linear portion of the spectra. Results from these tests can be found in Figure 4. Control pellets were run to establish a baseline which contained no reprocessed materials. These pellets had spectra taken while the heating up to 550C as well as cooling down to 375C. It was found that when the temperature reached 475C the impedance spectrum remained constant indicating that the pellet had reached equilibrium and no longer changed when cooling. The test procedure was then altered to only measure on heating allowing for faster data collection. The performance of all pellets were compared at 550C which is in the normal operating temperature range of the cell chemistry. The control pellets exhibited an average slope of -0.565 with a coefficient of variance (CV) of 3.6. A small CV demonstrates how little variance there is between pellets which is to be expected for the control pellets. The 3X reprocessed 1b pellets with fusing exhibited an average slope of -0.541 with a CV of 5.4. The reprocessed pellets performed very similar to the control pellets suggesting that recycling material has little to no measurable effect on pellet performance even when made from three-times reprocessed materials with fusing. The 3X reprocessed 1c pellets showed a slope of -0.641 and a CV of 10.9. This suggests that reprocessing without fusing has an adverse effect on performance and variability likely due to non-uniform wetting. Thus, reprocessing scrapped pellets is a viable option in salvaging valuable material. Mechanical slump data collected from these experiments show that on average the reprocessed samples exhibit less slump than the controls. This is consistent with reprocessed pellets containing being grinded additional times reducing the electrolyte particle size resulting in lower porosity than virgin material.

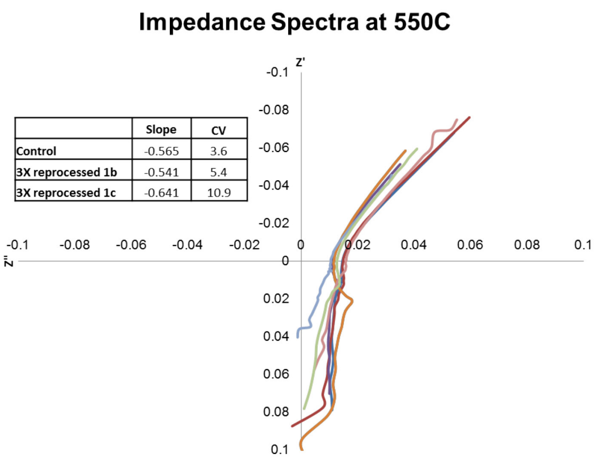

Figure 4: Reprocessed materials impedance spectra at 550C

Conclusion

The electrolyte-binder powder processing for thermal batteries was investigated and characterized in relation to separator pellet manufacturing and performance. Original hypotheses related to powder processing operations and their direct impact on pellet production did not hold fully true. Nonetheless, alternative powder blending and sizing processes are presented that each introduce both benefits and drawbacks. The use of a blending aid to improve mixing when using MgO significantly reduces the required mix time to achieve homogeneity but introduces additional processing steps. Granulation of the powder, while widely used in pharmaceutical industry to improve flow properties, may have influenced the final particle size distribution of the powder but experimental results did not show significant benefit on automated pellet press. Electrolyte-binder powder processing may be robust in that the process parameters evaluated as part of this research showed no significant impact on pellet production metrics evaluated.

While designing a powder process to result in improved pellet manufacturing was not immediately successful, reprocessing of scrapped separator pellets is a promising approach to reduce material waste. Separator pellets were reprocessed three times to exaggerate any effect using two different reprocessing methods. It was first demonstrated that reprocessed materials, both with and without fusing, can be fabricated into acceptable pellets requiring only minor adjustment in pellet press parameters attributed to a change in mechanical property of the reprocessed powders. 2X and 3X reprocessed pellets without fusing measured statistically significant changes in heat capacity over a temperature range when the electrolyte is still solid while all pellets behaved similarly in the molten phase. It is estimated that there is no change to melting point or heat of fusion for pellets using either reprocessing method. No change to the thermal properties of the reprocessed materials is important from the battery design perspective because it would not require a change to the heat balance if reprocessed materials were incorporated.

BET surface area showed a decreasing trend with reprocessing which is attributed to additional grinding reducing the electrolyte particle size and lowering the porosity. A reduction in porosity is supported by lower slump values for reprocessed pellets measured during impedance testing. At 550C and compared to control pellets, 3X reprocessed pellets with fusing exhibited similar impedance and coefficient of variance demonstrating that materials could likely be recycled. Reprocessed pellets that were not fused exhibited both higher impedance and coefficient of variance. Additional cell discharge data using reprocessed separators and cathodes is planned. It is recommended that reprocessed materials be fused to ensure good electrolyte wetting and then be mixed back in with virgin material at a defined maximum weight percentage.

Acknowledgements

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DEAC04-94AL85000. Approved for unlimited release, SANDxxxx-xxxx.

References

1. J. Prescott and R. Barnum, "On Powder Flowability," *Pharmaceutical Technology* (October 2000)
2. D. Nissen, "Processing Effects on Powders for Thermal Batteries," *SAND80-8024* (May 1980)
3. R. Guidotti, F. Reinhardt, and A. Andazola, "Blending Study of MgO-Based Separator Materials for Thermal Batteries," *SAND2002-1458* (June 2002)