SAND2016-5617C

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

Joseph Beck and Brian Perdue
Power Sources Technology Group
Sandia National Laboratories

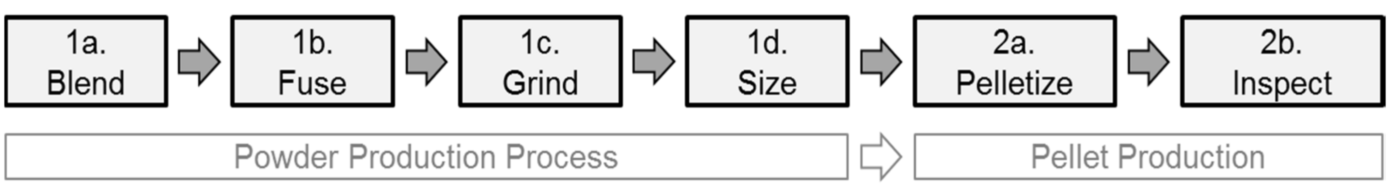
Sandia National Laboratories

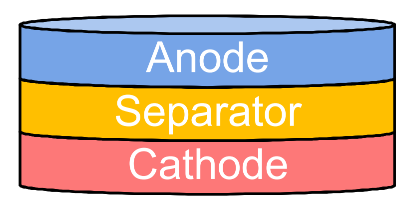
Exceptional service in the national interest

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 DE-AC04-94AL85000. SAND NO. 2011-XXXXP

Background & Motivation

- Molten salt thermal battery contains stack of electrochemical cells; anode, separator, cathode pellets
- Powders are made by blending constituents and sizing
- Pellets are formed by compacting powders under static force
  - Manual pellet press: Powder charge is weighed and loaded by hand
  - <u>Automated pellet press:</u> Powder flows from hopper into die cavity
- Goal: Increase pellet production yields
  - Increase throughput, reduce schedule and cost, reduce material waste
- Design for manufacturing while maintaining performance
  - Design a powder that makes better pellets
  - Design a process to reclaim scrapped separator materials

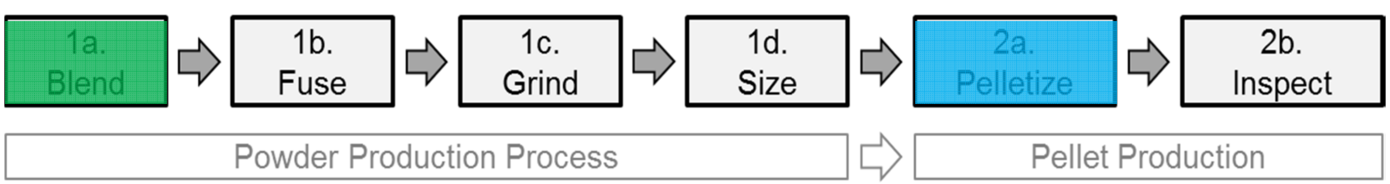




Powder Processing – Blending

Motivation and Background

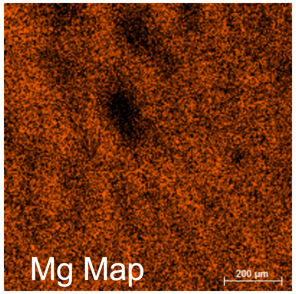
- LiCl/KCl eutectic mixed with MgO binder material
  - Powder homogeneity is critical parameter impacting flow characteristics to fill powder die
  - MgO has very poor flow characteristics (high angle of repose)
- Dry blending – Powder constituents mixed with traditional blending equipment (“V”-blender) with no additional materials added
  - Good homogeneity still difficult with multi-axis blenders (Turbula)
- Wet blending – The use of a medium to facilitate mixing
  - Guidotti (SNL, retired) investigated alternative blending media and identified Freon TF
  - Moya (SNL, retired) pioneered use of Vertrel XF



Powder Processing – Blending

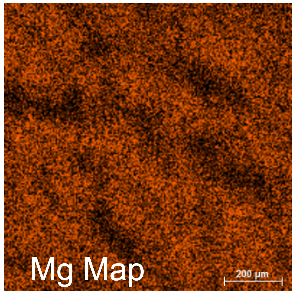
Experimental Results

- Wet blending reduced time to achieve homogenous blend by over one order of magnitude by acting as fluidization aid and decrease inter-particle friction
  - Required additional step to remove blending agent before fusing
- SEM/EDX indicate both blends are equally homogenous
- Experimental results using automated pellet presses demonstrated no quantifiable improvement on powder flow properties (pellet weight) or qualitative changes to compaction characteristics (pellet integrity)



Element	AN	Net	norm. C. [wt.%]	Atom C. [at.%]
Magnesium	12	85568	14.58	20.71
Chlorine	17	2422301	42.71	41.59
Potassium	19	774249	42.71	37.70
Rhodium	45	22661	0.00	0.00
		Total	100.00	100.00

Dry blend (left) and Wet blend (right) resulted in effectively same powder; equally homogenous and no obvious improvement to powder flow and/or compaction properties



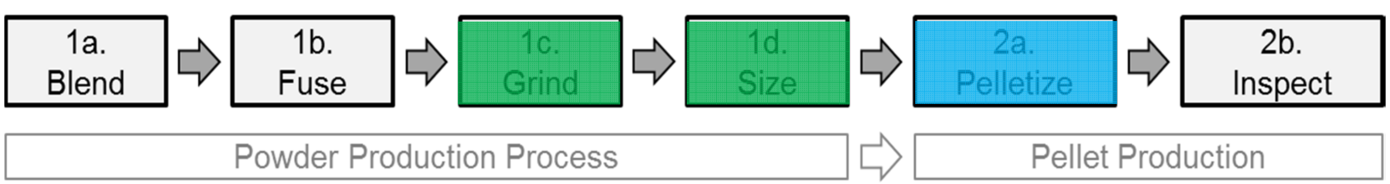
Element	AN	Net	norm. C. [wt.%]	Atom C. [at.%]
Magnesium	12	78689	13.82	19.72
Chlorine	17	2371196	42.22	41.29
Potassium	19	785190	43.96	38.99
Rhodium	45	22940	0.00	0.00
		Total	100.00	100.00

Powder Processing – Sizing

Motivation and Background

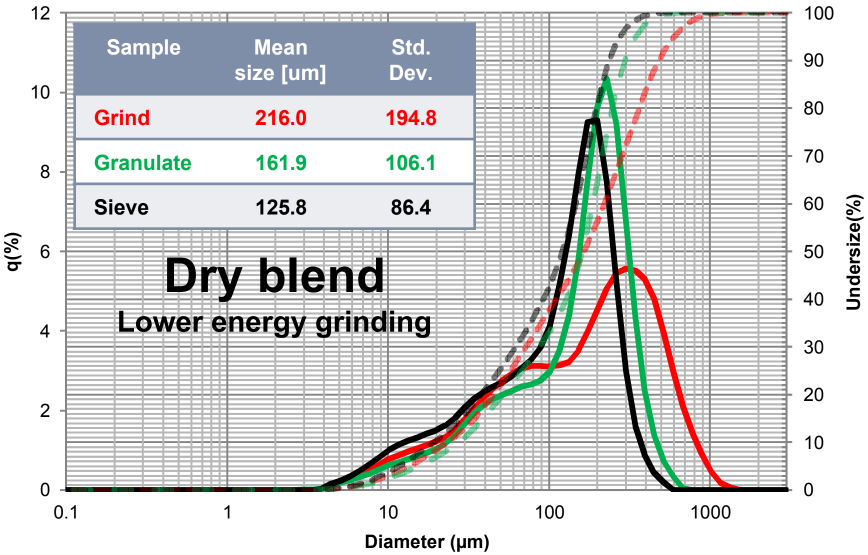
- After blending, powder is fused to melt the electrolyte
- Sizing operations result in powder of the desired particle size
  - Particle size distribution has significant impact on powder flow and compaction characteristics
- Powder was grinded using various mills through 0.033” screen
- Powder was then granulated and sieved through 0.010” screen

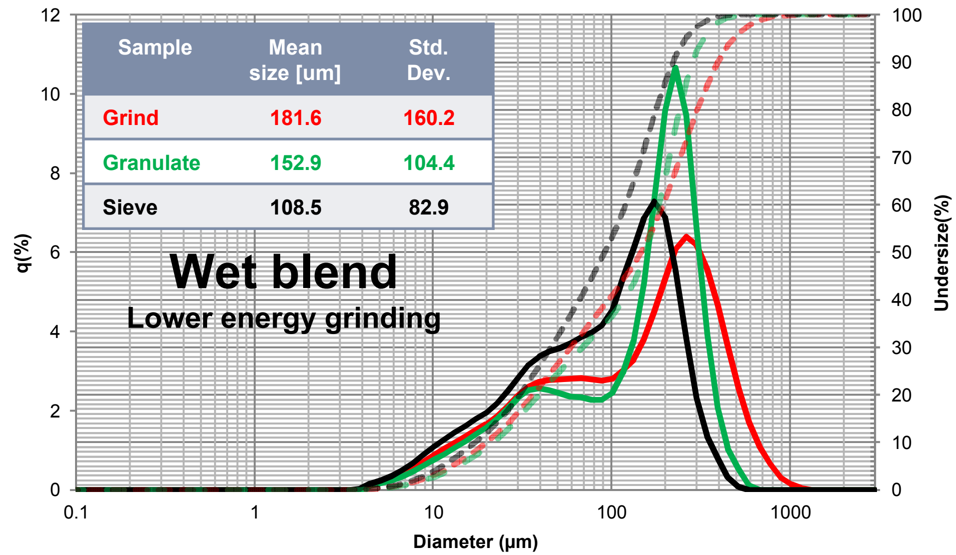
- Many sizing equipment is available that input different amounts of energy in order to grind very soft electrolyte-binder material
  - Particle size and distribution have significant effect on powder flow and compaction

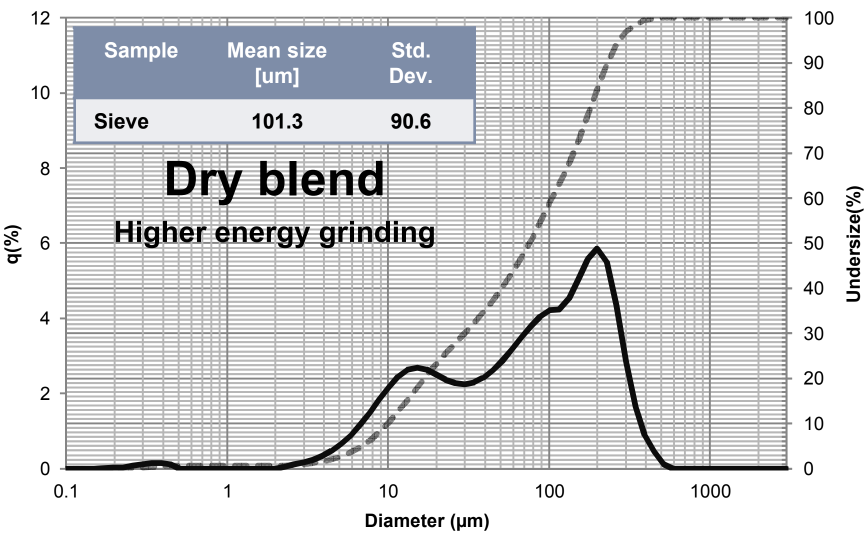


Powder Processing – Sizing

Experimental Results





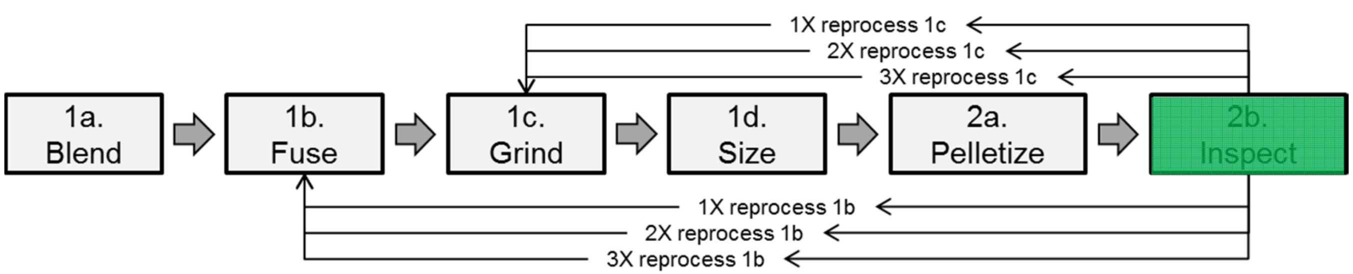


- Dry and wet blended powder showed similar particle size distribution
  - Homogeneity has no effect on grinding and sizing
- Lower energy grinding resulted in larger particle size and standard deviation
  - Additional sizing operations reduced particle size and standard deviation
- Grinding equipment has impact on particle size and distribution
- Experimental results on automated press showed no quantifiable differences in powder flowability

Pellet Reprocessing

Motivation and Background

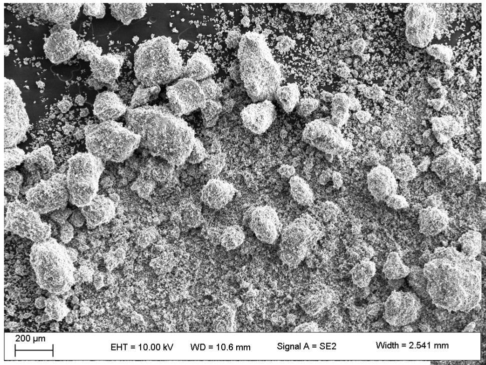
- Rejected and broken pellets make up large percentage of scrapped separator materials
  - Weight, density, bad edges, cracks, etc are all rejectable criteria
- Pellets were reprocessed using two methods
  - Re-melting the electrolyte
  - Immediately grinding pellets
- Materials were then pressed into new pellets and the process repeated 3 times to exaggerate mechanical or electrochemical impacts
  - Samples taken after each reprocess
  - Baseline pellets with no reprocessing



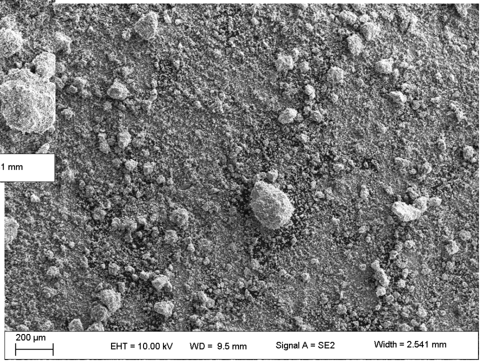
Pellet Reprocessing

Experimental Results - Mechanical

- Pellets could be pressed!
  - Reprocess 1b: Forming force required to be reduced by 10% between 1X and 2X
  - Reprocess 1c: No change to press settings
  - Manual presses → no data on flow characteristics
- Heat capacity (DSC)
  - Solid phase: Decreased but only estimated to be statistically significant for 1b 2X and 3X ($p<0.05$)
  - No change is estimated ($p>0.05$) at higher temperature range when electrolyte is molten
- Melting point and Heat of Fusion (DSC)
  - No change estimated – formulation of electrolyte remained unchanged throughout reprocess
- Surface area (BET)
  - By 3X, both processes resulted in decreased SA
- Mechanical slump
  - Reprocessed pellets measured less slump
- Hypothesis
  - Additional grinding steps reduce size of salt particles changes compaction characteristics
  - Results in change to pellet porosity which impacts mechanical characteristics: slump, surface area, heat capacity



Left: 1X reprocess 1c
Below: 3X reprocess 1c



Material	Cp avg		Melting Point Onset [°C]	Heat of Fusion [J/g]	BET Surface Area [m²/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

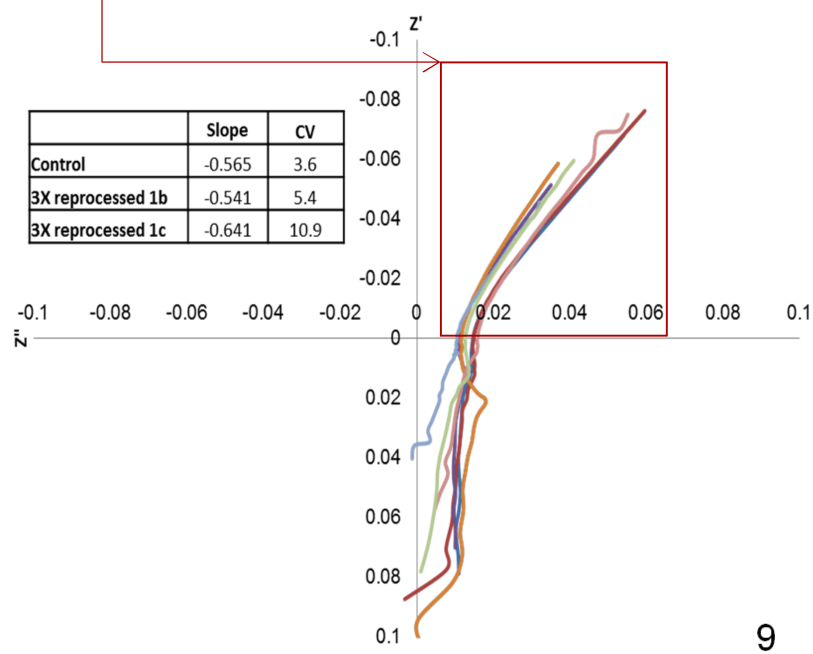
Pellet Reprocessing

Experimental Results - Electrochemical

- Electrochemical impedance spectroscopy
  - Single cell; 7.5 psi; 375, 400, 475, 500, and 550C; 1MHz → 1kHz with 5mV peak-to-peak
  - 3X pellets measured and compared to baseline looking for electrochemical impacts
- After heating up to 475C, spectrum remained same to 550C and cooling down
  - No hysteresis and therefore the battery will still function as it cools
- Linear portion of the impedance spectra used to compare pellets
- Reprocess 1b to control
  - 4% decrease to slope, small increase in variance
- Reprocess 1c to control
  - 13% increase to slope, large increase in variance
  - Change in slope driven by capacitive contribution from inhomogeneity of pellet
- Reprocessing scrapped pellets is viable
  - Reprocess 1b (re-melting electrolyte) behaves similarly to virgin pellet
- Future work in process
  - Full cell discharge
  - Battery configuration (Discharge and Mechanical environments)

Impedance Spectra at 550C

	Slope	CV
Control	-0.565	3.6
3X reprocessed 1b	-0.541	5.4
3X reprocessed 1c	-0.641	10.9



Conclusion

- Design for manufacturing of separator powder and separator pellet processes to improve yields while maintaining performance
- Further work is needed to design a powder that improves flow and compaction characteristics
  - Mixing operation: Homogenous mix in shortest process time
    - Experimental results shown no improvements using automated pellet press
  - Grinding and sizing operations: Desired particle size distribution for improved powder flow into die and compaction
- Reprocessing scrapped materials is viable process
  - Two reprocessing options explored; first re-melting or first re-grinding
  - Acceptable pellets could be pressed on manual press using either technique
  - 3X reprocessed pellets showed little mechanical or electrochemical impacts
- Reprocessing with first re-melting is preferred
  - No change to manual pellet press settings was required
  - No significant change to mechanical or electrochemical properties measured → no battery redesign required (including heat balance)
  - Future work exploring full cell and battery configuration test results

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)