

Development of Magnesium Oxide (MgO) Binder for Thermal Batteries

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Abstract: *Thermal batteries (TBs) are primary reserve batteries that employ inorganic salt electrolytes. These electrolytes are non-conductive solids at ambient temperatures. Pyrotechnic materials are used to provide sufficient thermal energy to melt the electrolytes and activate the cell. TBs are used in variety of Department of Defense applications including missiles and munitions. The fundamental unit cell of a thermal battery consists of an anode and cathode separated by a binder material infused with the salt electrolyte. The binder material provides structural support and separates the anode and cathode for the molten, liquid electrolyte when the battery is activated. The key performance characteristic of the binder material is the ability to provide reliable structural support while maximizing the electrolyte binding characteristics to minimize the required binder volume. Without an adequate performing material, the gap between the anode and cathode could not be maintained resulting in a voltage noise, localized heating, or an intracell short. The two highest performing binder materials commercially produced were Maglite S and Marinco OL, both of which were discontinued by their manufacturers more than 20 years ago due to economic reasons. No documentation of the precursor or manufacturing processes used was ever made available to allow the products to be recreated. Subsequently, TB manufacturers have been using the dwindling stockpile and/or developed stop-gap non-optimal (lower performing) but adequate solutions to meet military need. These binders have suffered from process instability and intermittent failures and the government has spent millions in an attempt to accommodate the lack of reliability. Qynergy, in order to stabilize the supply chain of critical TB materials, has developed a magnesium oxide (MgO) binder material (“GoMax”) for the binary LiCl:KCl electrolyte that outperforms the existing binder materials used in the industry. Qynergy has scientifically engineered the material in such a way that it can now be produced from several suppliers of precursors, thus mitigating supply chain risk. Qynergy’s GoMax MgO will both secure the supply chain for current thermal battery manufacturing and lead to performance enhancements in the TB applications space. The mechanism and powder properties driving the binder’s performance have been studied. This understanding allows for optimization and control of the binder material properties to specific thermal battery applications, as well as enabled the scaled production achieved under the Office of the Secretary of Defense (OSD) Manufacturing Science and Technology Program (MSTP). In this paper the link between salient*

powder properties such as pore volume and surface area as a function of binder performance will be presented. Multiple precursor sources were evaluated as potential suppliers for MgO binder production. Powder characterization and performance test data from MgO produced using one of these sources will be presented and compared to Maglite S. The powders were characterized using laser scattering, and mercury porosimetry. Performance was evaluated using deformation tests.

Keywords: thermal batteries; magnesium oxide; binder; separator; deformation; pore volume; particle size.

Introduction

Thermal batteries are constructed as stacks of bipolar electrochemical cells; each cell consisting of an anode, a separator, a cathode, and a heat pellet (Figure 1). The pellets are composed of different pressed powder mixes. The separators contain MgO as a binder to keep the molten electrolyte in place after the battery is activated. As produced, the pellets are dry, solid, and inert. The cell stack is contained in a stainless steel can and covered with a header containing terminals for electrical connections. The can and cover are placed under pressure (the stacking or closure force) and then hermetically sealed by welding.

The mechanical properties of the separator pellet are extremely important for proper operation of thermal batteries. Excessive deformation of the pellet while the electrolyte is molten can result in voltage noise, localized heating due to a high-resistance shunt path, and worst case, intracell shorting. Insufficient deformation can result in poor wetting of the electrodes resulting in high electrical resistance at the separator-anode and separator-cathode interface. Consequently, a nominal deformation of 15% to 30% has been empirically determined to be ideal, [1] with 20% as an optimal target [2]. With halide electrolytes a reduction in density of 20-25% going from solid to liquid phase is typical. For this study the LiCl-KCl eutectic electrolyte is utilized as it has been well described in literature, is commonly used in thermal batteries, and has the lowest solid and liquid densities; ρ_s of 2.02 g/cm³ and ρ_l of 1.59 g/cm³. [2] Although the separator pellet is processed with the electrolyte in solid form the electrolyte density in the liquid form determines the volume of electrolyte that must be retained by the MgO binder during battery operation. The properties of the MgO binder material such as pore volume etc. then dictate the optimum volume fractions of electrolyte and binder.

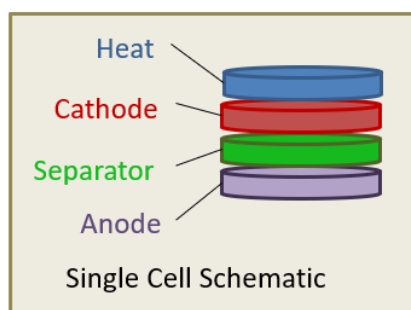


Figure 1. Schematic of Thermal Battery Single Cell Stack

Select physical and chemical properties of MgO materials were evaluated by Sandia National Laboratories (SNL) in the mid-1990s for correlation to deformation performance including purity, surface area, particle size distribution, morphology, and pore-size distribution. In the referenced study, particle and pore size distributions appeared to affect deformation performance. Also, among the materials studied, Maglite-S was the only one with a bi-modal particle size distribution and a smaller particle size which they theorized provided better performance. Maglite-S also had slightly larger pore diameters than other materials. They attributed the binder performance to the ability of the molten electrolyte to penetrate these pores. [1]

Maglite-S MgO powder manufactured by the Calgon Company was used as the standard binder material for over 30 years throughout the industry, however production of the material was discontinued by the manufacturer for economic reasons [4]. Other MgO materials were screened by SNL to identify and qualify a substitute material [4]. After several years' effort, a substitute material, Marince OL was successfully qualified, but that manufacturer also decided to discontinue production shortly after the material was qualified [4]. Since that time efforts have been underway to produce MgO specifically for thermal battery applications [4]. Given the performance of Maglite-S these efforts have primarily focused on attempting to reproduce similar particle size distribution and pore volume [4].

Qynergy has been developing MgO binders for thermal battery applications since 2012, and has evaluated multiple precursor formulations, sources, and processing conditions. An MgO binder has been developed called GoMax that has been thoroughly characterized with the LiCl-KCl binary eutectic, and the deformation performance correlated with the particle characteristics. The performance and characteristics were compared to Maglite-S material evaluated under identical conditions. In the case of Maglite-S the deformation performance correlated with the available pore volume of the binder and the total volume of electrolyte that must be retained in the melt state. The deformation performance of GoMax, however, exceeded the predicted value based on available pore volume. Therefore, a secondary mechanism must be contributing to electrolyte retention. GoMax has a significantly larger active surface area than Maglite-S. The improved binding performance is

attributed to the active surface interacting/holding the molten electrolyte. The degree of surface activity can be controlled by processing conditions and precursor selection.

In this study, deformation performance of Maglite-S and GoMax is compared to demonstrate this mechanism by varying the ratio of electrolyte (LiCl-KCl eutectic) and binder in mixes processed and tested under identical conditions.

Methods and Materials

GoMax was prepared by continuous calcination of precursor in a rotary furnace. The resultant MgO was collected in a dry air environment in an O-ring sealed container which was then moved to storage in a dry air purged glove box. Samples of GoMax and Maglite-S were analyzed using laser scattering and Hg porosimetry for particle size distribution and pore volume, respectively.

Preparation of the electrolyte salts, EB mixes, and deformation testing closely followed a procedure described in literature [3]. All handling and processing of materials was performed in dry air purged glove boxes with nominal dew points of $-80\text{ }^{\circ}\text{C}$ ($-112\text{ }^{\circ}\text{F}$) or less.

Reagent-grade halide salts of LiCl and KCl were used in the preparation of the binary electrolyte. A ratio of 45 weight percent (w/o) LiCl 55 w/o KCl was used to produce an electrolyte with a melting point of $352\text{ }^{\circ}\text{C}$ ($665.6\text{ }^{\circ}\text{F}$). The appropriate amount of salts were blended in a Turbula mixer and fused at $650\text{ }^{\circ}\text{C}$ ($1202\text{ }^{\circ}\text{F}$) for 3 hours. After quenching in an Inconel tray the electrolyte was ground to 100 mesh using a Fitzmill.

Prior to blending with electrolyte, the MgO was baked at $600\text{ }^{\circ}\text{C}$ ($1112\text{ }^{\circ}\text{F}$) for 4 hours to ensure complete moisture removal as well as decompose any hydroxides or carbonates that may have formed during storage. EB mixes were prepared by blending the electrolyte and binder at ratios of 65:35, 70:30, 75:25, and 80:20. The mixtures were fused at $400\text{ }^{\circ}\text{C}$ ($752\text{ }^{\circ}\text{F}$) for 16 hours. Mixes were then ground to 80 mesh prior to pelletizing into separators for deformation testing.

3.1 cm diameter separator pellets were pressed to 70% of theoretical density with a final thickness of 1.5 mm.

Heated thickness deformation analysis was performed to evaluate the effectiveness of the separator. Separator pellets were secured between mica sheets and stack thickness recorded prior to testing. The pellet was compressed at 14 psi and $500\text{ }^{\circ}\text{C}$ ($932\text{ }^{\circ}\text{F}$) in an argon glove box using Qynergy's heated deformation tester (shown in Figure 2). The final thickness reading was taken after 30 seconds (at which point the thickness was stabilized in response to the compaction force). Final percent (%) thickness deformation was then calculated. A minimum of three separator pellets were tested for each EB mix ratio to ensure uniformity.



Figure 2. Qynergy Heated Thickness Deformation Tester

Results

Particle size distributions for Maglite-S and GoMax are compared in Figure 3 and shows the overall larger particle size of GoMax (~2x). When interpreting cumulative pore volume and surface area characteristics using Hg intrusion porosimetry it is necessary to differentiate between interparticle porosity and intraparticle void space. In this evaluation pore diameters larger than 25% of the median particle size determined via laser scattering were considered intra-particle pores and, therefore, excluded. This is shown graphically in Figure 4.

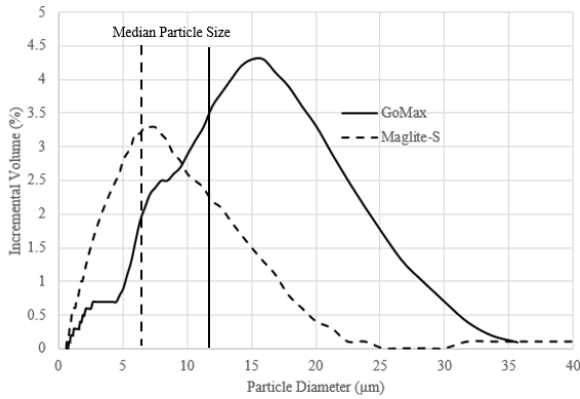


Figure 3. Comparison of Particle Size Distribution for GoMax and Maglite-S

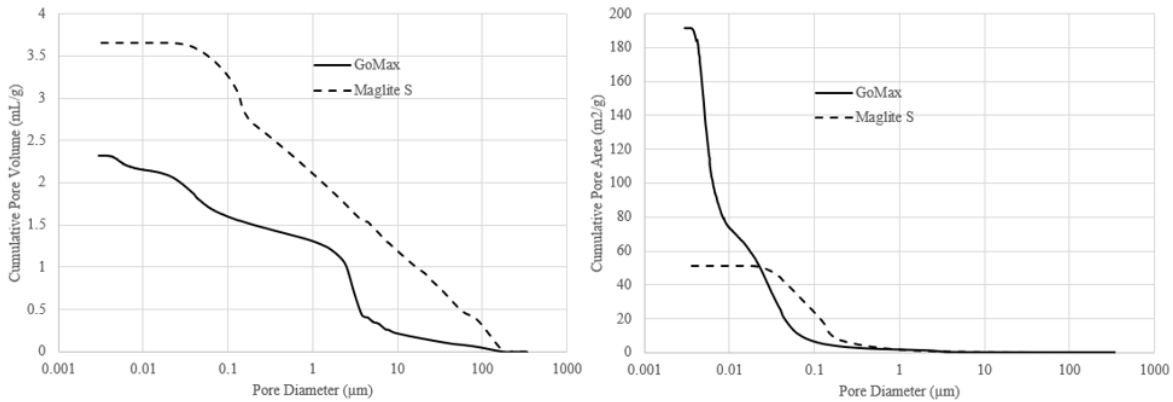


Figure 5. Cumulative Pore Volume (Left) and Cumulative Pore Area (Right) Distributions for GoMax versus Maglite-S

Figure 5 shows the cumulative pore volume and pore area distributions for GoMax and Maglite-S and shows that Maglite-S has greater overall pore volume while GoMax has significantly higher pore area due primarily to the contribution of extremely small diameter surface porosity. Values for median particle size, pore volume and pore area are summarized in Table 1 which shows the 2x larger median particle size, slightly reduced pore volume and nearly 4x greater pore area of GoMax versus Maglite-S.

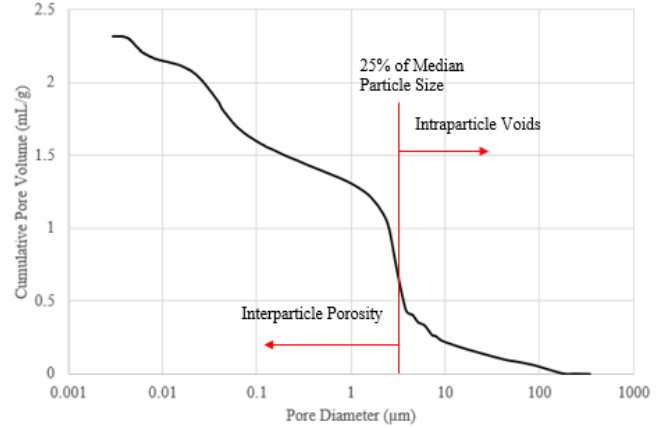


Figure 4. Pores Larger Than 25% of Median Particle Size are Excluded from Total Pore Volume and Area Calculation

Table 1. Summary of Particle Size, Pore Volume, and Pore Area

Sample	Particle Size (µm)	Pore Volume (mL/g)	Pore Area (m ² /g)
	\bar{x}	Σ	Σ
GoMax	11.98	1.561	191.179
Maglite-S	6.056	1.733	48.701

Based on a ρ_l of 1.59 g/cm³ total required pore volume in mL/g was calculated for EB-mix ratios ranging from 65:35 to 80:20 and is shown in Table 2 along with the % thickness deformation results. Figure 6 graphically shows the comparison of % thickness deformation versus theoretically required pore volume. From Figure 6 it is apparent that deformation performance for Maglite-S correlates well with total pore volume, while GoMax deformation remains low well beyond the predicted threshold.

Table 2. Heated Thickness Deformation Test Results

EB Mix Ratio:	65/35	70/30	75/25	80/20
Maglite-S (1.733 mL/g)	14.60%	22.00%	37.60%	71.10%
GoMax (1.561 mL/g)	9.20%	12.30%	28.60%	79.50%
Required Pore Volume (mL/g) (ρ_l 1.59 g/cm ³)	1.161	1.458	1.875	2.500

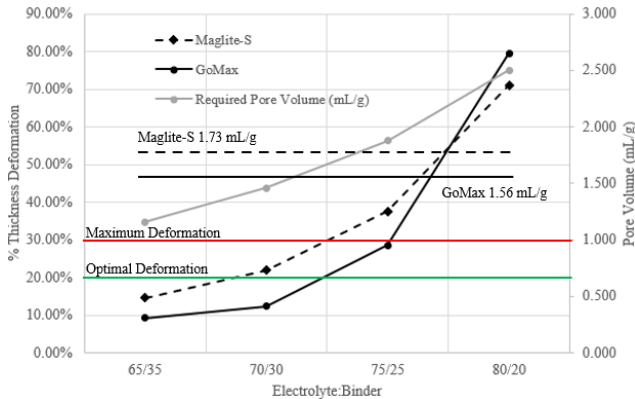


Figure 6. Comparison of Thickness Deformation and Required Pore Volume

Conclusions

Binding characteristics of MgO have been attributed to molten electrolyte being retained in the pores only. Varying pore volume and pore area and evaluating deformation performance with a range of electrolyte to binder ratios

indicates that pore volume alone is not entirely responsible for immobilization of electrolyte when high surface activity MgO is evaluated (as in GoMax). These high surface active MgO materials continue to perform better in deformation testing even when the quantity of liquid electrolyte exceeds the available pore volume. When liquid electrolyte exceeds pore volume in a non-surface active or low surface area MgO deformation performance is dramatically reduced. Surface activity is a property that can be modulated via MgO processing conditions and provides a second parameter that can be controlled to optimize binder performance. Qynergy has developed scaled processes for manufacturing production quantities of GoMax MgO binder materials.

Acknowledgements

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