SAND2007-1870C

Influence of MgO Filler on Deformation of MgO and Li-Halide Composites

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Abstract

MgO powder properties, electrolyte and composition were optimized for electrolyte-MgO powder pellet deformation. Two different MgO powder sources were used to process the composites and each was calcined to 600, 800 and 1000 °C for 4 hours to control the particle size and surface area of the powder. The composites were then mixed with two different electrolytes, LiCl-KCl and LiCl-LiBr-KBr, and pressed into pellets of the same density. The melting points of the electrolytes range from 300-350°C and were mixed into MgO:electrolyte ratios of 65:35, 70:30 and 80:20. The deformation of the pellets was measured using a thermal mechanical analyzer and measured from room temperature to 550 °C under a constant load. These measurements were then used to calculate viscosity and modulus values at temperature. The powder properties and composite viscosity values are used to discuss proposed interaction mechanisms for electrolyte-MgO powder pellets at temperature.

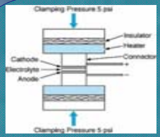
Introduction

Magnesium oxide is studied to understand the effect of oxide morphology on compaction response and electrolyte interaction with MgO. The MgO-electrolyte mix powders will be used as a separator pellet in thermal batteries. The MgO powder must exhibit properties that will enable an optimal flow of ions, but not leak out of the battery, causing a short circuit.

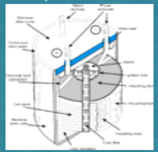
Thermal Batteries are used in a widespread range of applications:

- Ejector seats in fighter aircrafts
- emergency energy sources for industry purposes (safety systems for drilling platforms, surveillance systems, etc.)
- Space launchers

Thermal Batteries



Above: single cell thermal battery. **Below**: multi cell thermal battery assembly



Images provide by Lewis Research Center, Cleaveland, Ohio

Made up of several cells, each containing an anode, electrolyte, cathode, and heat source

- Solid electrolyte-MgO mix prevents electron flow from cathode to anode. The thermal battery stays inert before ignition
- After ignition of heat source, electrolyte is fluid and is conductive, allowing ions to flow
- Used in applications that require high energy and power density
- Can be stored for long times without degradation and can deliver full power and energy in less than a second
- Non-rechargeable, one-time use

The MgO in electrolyte-MgO mixes is important for the operation of the thermal battery. The MgO supports the electrolyte, and allows flow of ions from the anode to the cathode. If the electrolyte dewets the MgO powder, the electrolyte will flow out, but if there is no interaction, the ions will not flow. The MgO must be processed for optimal interaction with the electrolyte.

Material Properties

Inframat MgO Powder

Impurities	Al_2O_3	B_2O_3	CaO	Fe_2O_3	MnO_2	Na_2O	NiO	SiO_2	ZnO
Max Level (ppm)	200	2	500	10	10	10	5	10	5

Inframat Advanced Materials LLC, 74 Batterson Park Road, Farmington, CT 06032 USA

Maglite S MgO Powder

Impurities	Ca	Si	Na	Fe	Al	Li	B	Mn
Max Level (ppm)	400	600	60	150	80	4	350	30

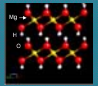
Merck/Calgon Corporation

MgO Properties

- Hygroscopic
- High surface area
- High melting point (2800C)

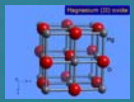
Thermal Decomposition of Brucite

Precursor structure of Inframat and Mag S powders is brucite ($Mg(OH_2)$). Upon calcination, H_2O is given off, leaving a MgO structure. Depending on the ramp rate used, the precursor morphology can be retained in this process. A lower ramp rate creates an oxide structure where the overall shape is that of the brucite crystals, retaining the external shape and apparent porosity of 54%.



$$Mg(OH)_{2(s)} \xrightarrow{\Delta} MgO_{(s)} + H_2O_{(g)}$$

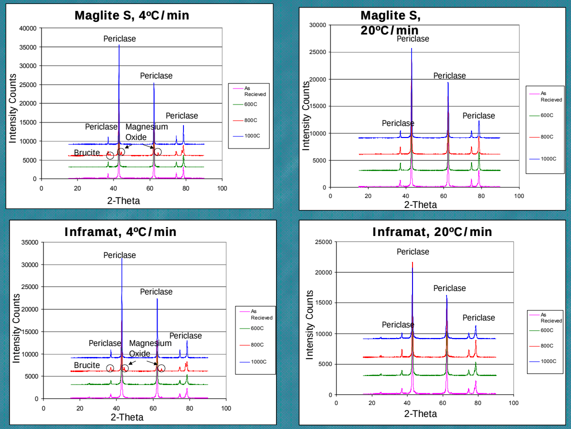
Brucite → Periclase



Brucite ($Mg(OH_2)$)
Crystal Structure: hexagonal

Periclase (MgO)
Crystal Structure: cubic

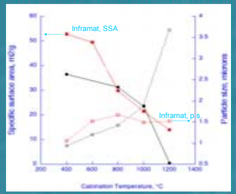
X-Ray Diffraction



- 4°C/min: brucite and MgO structure apparent at 800°C
- Periclase is present at all calcination temperatures. Fast ramp rate indicates that brucite morphology is not retained. Skips meta stable intermediate at 800°C.
- Materials behavior identically

Surface Area/Particle Size Analysis

Surface Area and Particle Size at High Ramp Rate



Effect of Heating rate on Surface Area

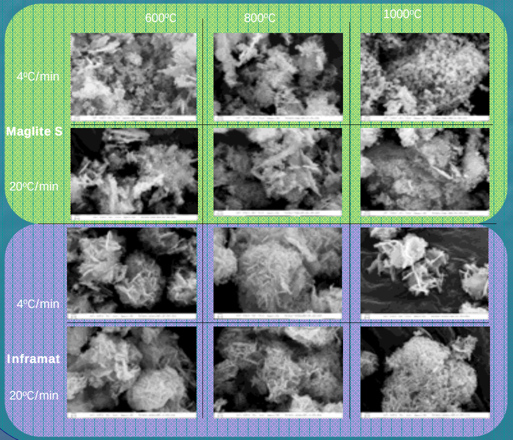
	Mag S, 800C		Inframat, 800C	
	4C/min	20C/min	4C/min	20C/min
Area (m^2/g)	29	33	29	36

- Higher heating rates lead to higher surface area
- As surface area decreases as particle size decreases

Surface area analysis done using BET

Particle size analysis done using dynamic light scattering (DLS)

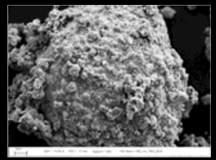
Scanning Electron Microscope Images of Calcination Series



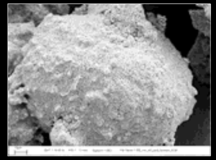
- Inframat has a plate-like structure, not seen in Maglite S.
- Mag S and inframat have different crystal morphology.

Scanning Electron Microscopy

EB Mix Series



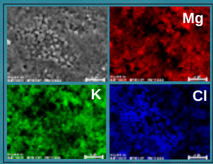
Maglite S MgO-E1C mix calcined to 600°C



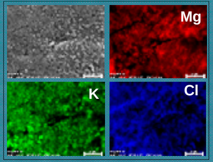
Inframat MgO-E1C mix calcined to 600°C

Different morphologies of EB mix powders show that electrolyte interacts differently with Mag S than with inframat. Inframat is wet by the electrolyte while the Mag S is not.

Energy Dispersive X-Ray Spectroscopy (EDS) Maps



Mag S EB mix powder

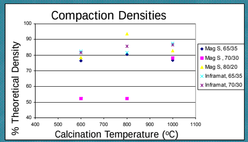


Inframat-EB mix powder

EDS uses x-ray that are emitted from the analyte upon bombardment by an electron beam. It characterizes the elemental composition of the analyte. Using this technique, it can be determined whether the MgO-electrolyte mixes are homogeneous or heterogeneous.

- Mag S EB mix powder is heterogeneous
- Inframat EB mix is uniform

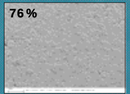
Compaction Density



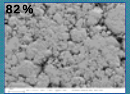
Theoretical Densities

Wt% MgO	Wt% LiCL-KCL	Theoretical Density (g/cm^3)
35	65	2.43
30	70	2.37
20	80	2.26

- Higher electrolyte in pellet gives higher density
- Inframat pellets are closest to theoretical densities

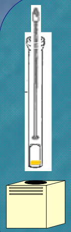


Maglite S:LiCl-KCl (35:65) Pellet Calcined to 600°C

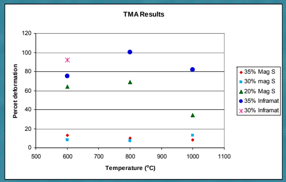


Inframat:LiCl-KCl (35:65) Pellet Calcined to 600°C

Thermal Mechanical Analysis



TMA applies a constant pressure of 20mN on the pellet. The furnace preheated to 600oC and is then lifted over the sample. The height of the pellet is monitored to give percent deformation as a function of Temperature.



- Pellets with higher electrolyte content deforms most
- Inframat deforms more than Maglite S

TMA test were run under a constant force of 20mN and an inert atmosphere to 600C

Mag S-E1C

Largest deformation: 69%; 800C, 20% MgO

Smallest deformation: 7%; 800C, 30% MgO

Inframat-E1C

Largest deformation: 100%; 800C, 35% MgO

Smallest deformation: 75%; 600C, 35% MgO

Conclusions

- The operation of a thermal battery is affected by the oxide morphology and the wetting behavior of the MgO powder
- The oxide morphology is dependent on calcination rate and calcination temperature
- Oxide morphology of Maglite S is not identical to that of Inframat
- A higher density leads to higher deformation; there is an optimal compaction density

Future Work

- Long term calcination of Mgo using lower ramp rate to study if meta stable structure is dependent of temperature only
- Wetting study to understand the interaction between the MgO and the electrolyte

Acknowledgements

Bonnie Mckenzie for SEM images. Denise Bencoe for TMA training. Funding provided by Process Development Program at Sandia national Laboratories, advanced power sources. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000