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Nanostructured MgO Binders for Thermal Battery Separators

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ECS, (G3) Separators and Membranes
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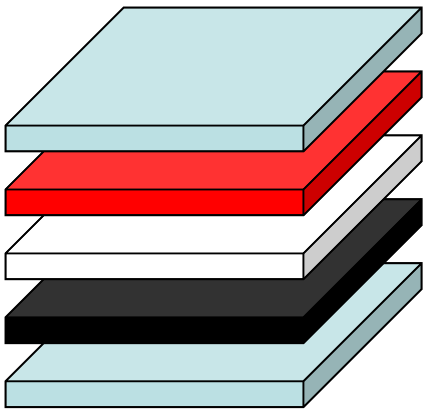
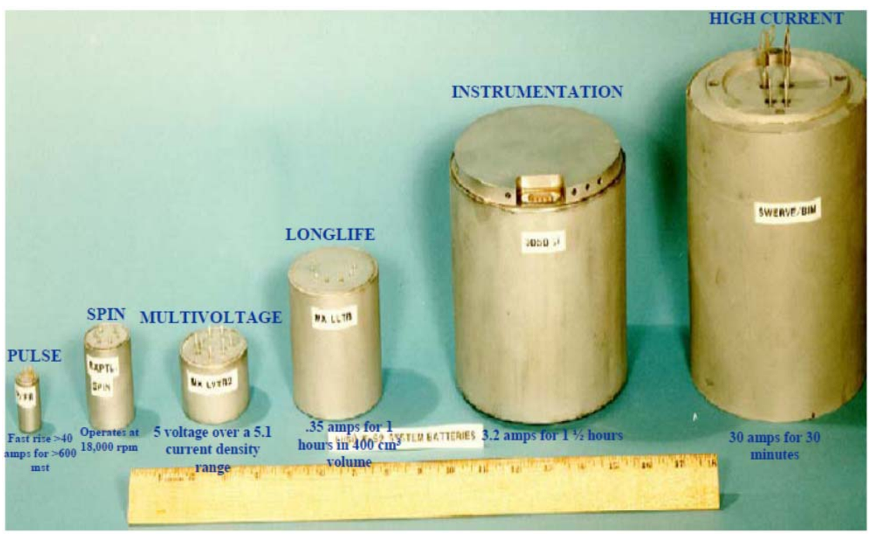
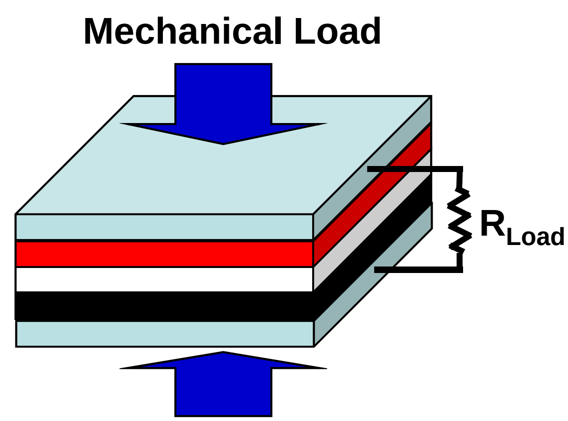
Thermal Batteries



Primary reserve battery:

- Low self-discharge
- Long shelf life (decades)
- Reliable
- Operating temperatures > 320 ^{o}C (molten salt)





Load improves electrical contact between electrodes and separator at operating temperature

Thermal Battery Separator Binders

Characteristics:

- Temperature stability (> 400 ^{o}C)
- Chemical compatibility
- Mechanical stability
- Electrochemical stability

No polymers
Only limited ceramics
Porosity/surface area restrictions
No semiconductors

Candidate binder materials: Al_2O_3, BeO, MgO, ZrO_2

30+ years of research has shown only one commercial source to match these criteria….

Objective: Develop a synthetic approach to give high surface area, porous MgO to be used as a the electrolyte binder in a TB separator

(….must be scalable, reproducible, easy to process, inexpensive, etc.)

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Variables for Separator Performance

- ***Materials Characteristics***
  - Particle size
  - Surface area
  - Morphology
  - Compaction behavior
  - Wettability (surface chemistry)
- ***Processing***
  - Fusing (temp, rate, time)
  - Mixing (speed, time)
  - Pellet Pressing (density, load)
  - Composition (electrolyte:binder)

Performance Targets
- Deformation
- Ionic conductivity
- Electrochemical performance

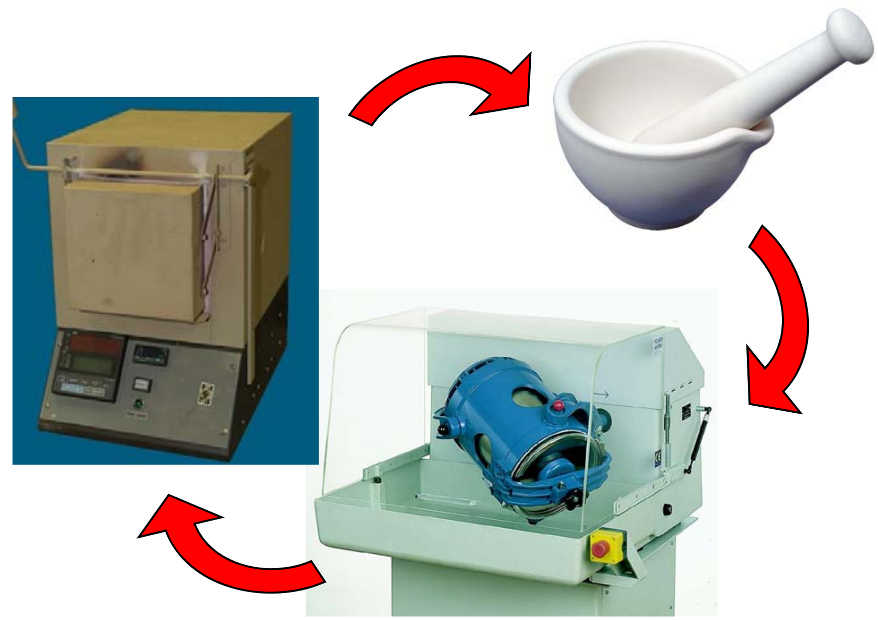
Synthetic chemistry can address a large number of these issues and could minimize the number of processing variables

Existing MgO Material Processing

- ***Existing MgO processing conditions:***
  - Calcinate MgO
  - Grind MgO
  - Sieve MgO
  - Dry MgO
  - Sieve Electrolyte
  - Mix MgO + Electrolyte
  - Fuse MgO + Electrolyte
  - Grind MgO + Electrolyte
  - Sieve MgO + Electrolyte
  - Dry MgO + Electrolyte
  - Press MgO + Electrolyte Pellets
  - Dry Pellets

Shortcomings:

- Specific for one MgO powder
- Unforgiving to other MgO materials
- Labor intensive (5 days)



Desperately need a more generic process

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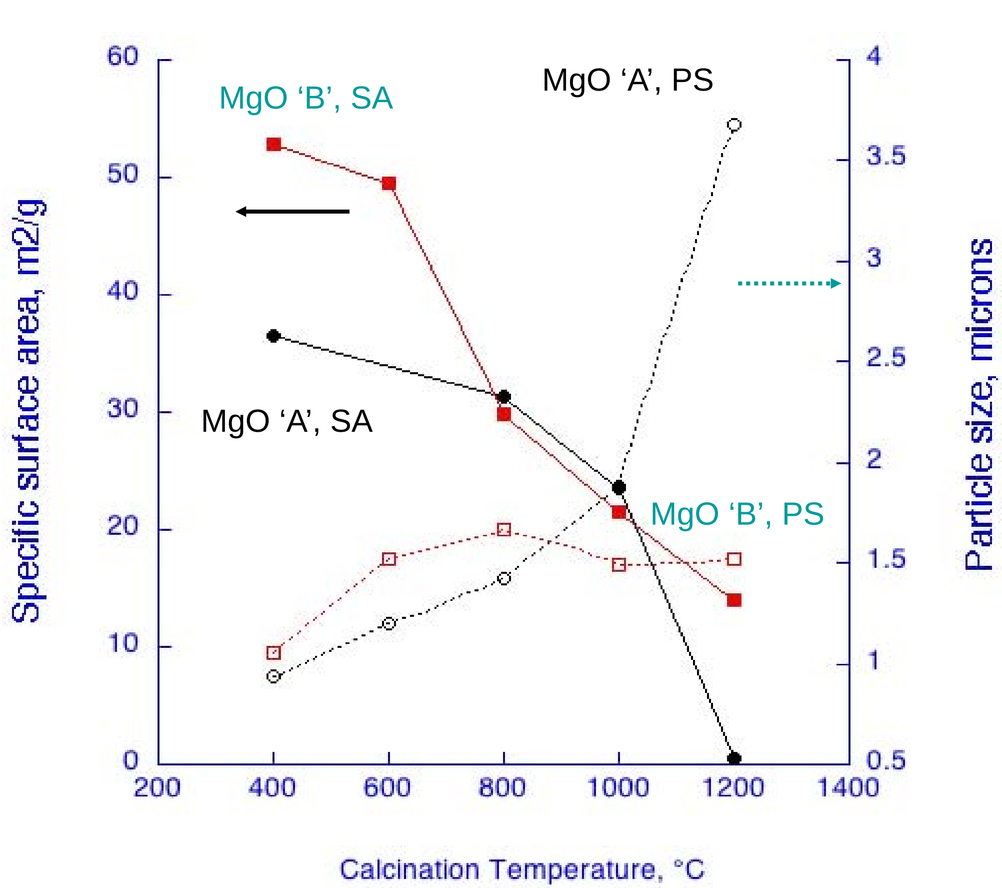
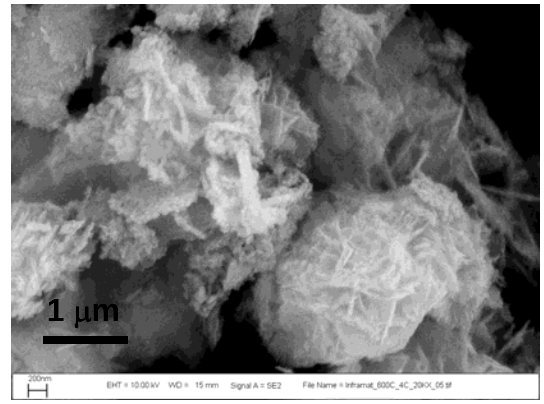
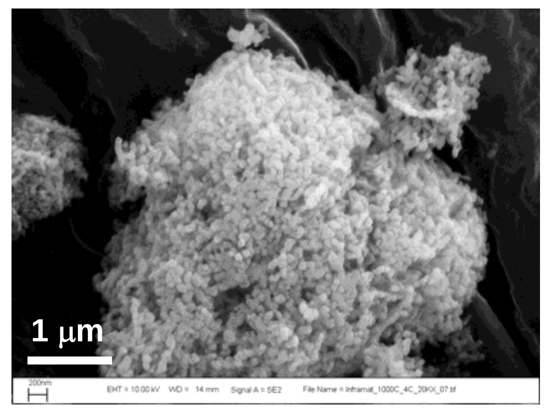
Temperature-Dependent Morphology





Calcined @ 600 ^{o}C

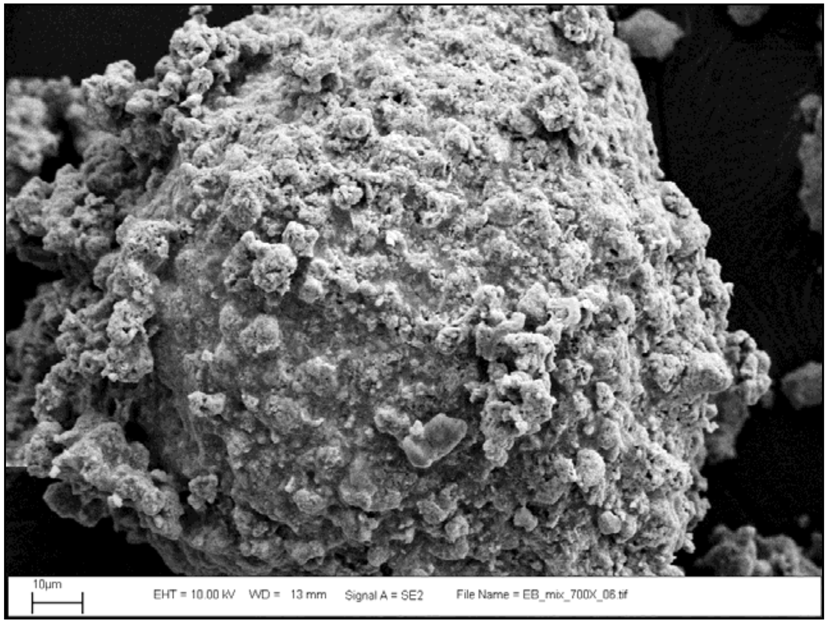


Calcined @ 1000 ^{o}C

Starting with higher surface area binder allows for greater flexibility in the subsequent processing steps

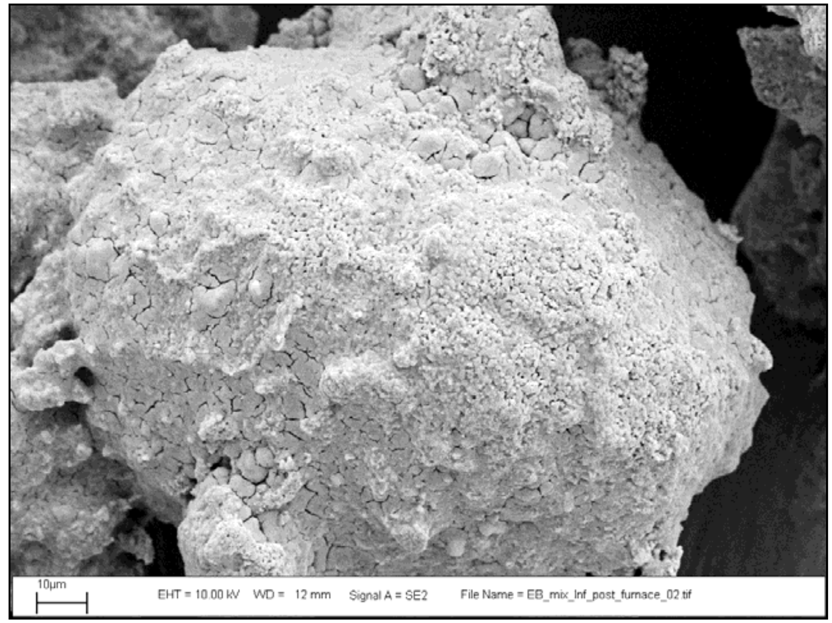
Erica L. Corral and Ronald E. Loehman

MgOParticle Surface Chemistry



MgO ‘A’ + Electrolyte

Heterogeneous wetting



MgO ‘B’ + Electrolyte

Homogeneous wetting

SEM images and EDS spectra support heterogeneous wetting of electrolyte on MgO ‘A’ and homogeneous wetting of electrolyte on MgO ‘B’, suggesting a *difference is MgO surface chemistry*

Erica L. Corral and Ronald E. Loehman

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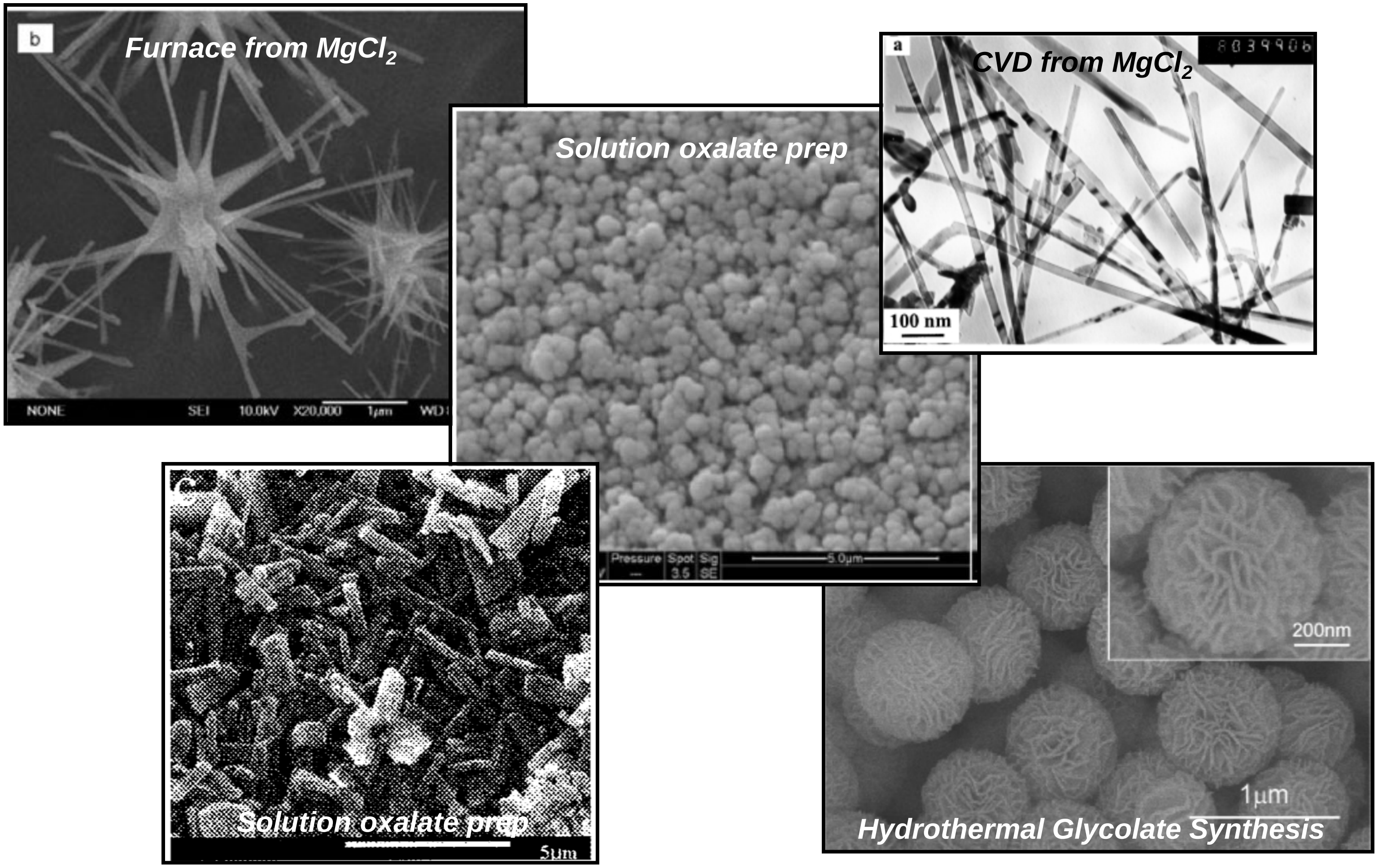
Synthetic Objectives for MgO

- ***High surface area (nanostructured, porous)***
  - Allows for flexibility in the subsequent powder processing steps
  - May provide better mechanical strength
  - Tunable surface chemistry to control electrolyte wetting
- ***Anisotropic structural features***
  - Enhance mechanical stability
- ***Materials adaptable to a generic set of process conditions***

Interest in Magnesium Oxide

Bulk of the work from catalysis community:



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Kumar, A. et al. *J. Phys. Chem. Solids* **2008**, *69*, 2764
Bain, S. –W. et al. *J. Phys. Chem. C* **2008**, *112*, 11340

Fang, X. –S. et al. *Small* **2005**, *1*, 422
Zhang, J. et al. *Appl Phys A* **2001**, *73*, 773

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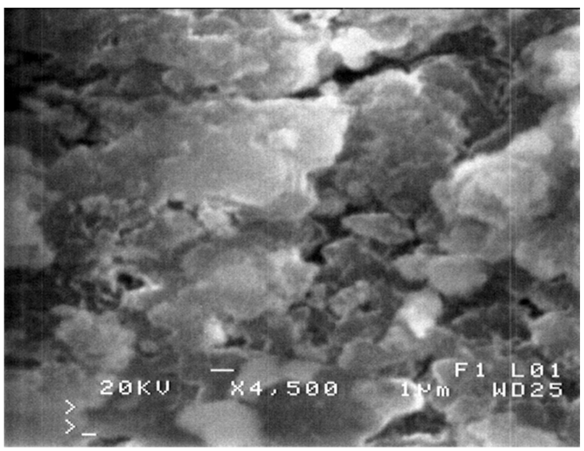
Synthesis of Magnesium Oxide

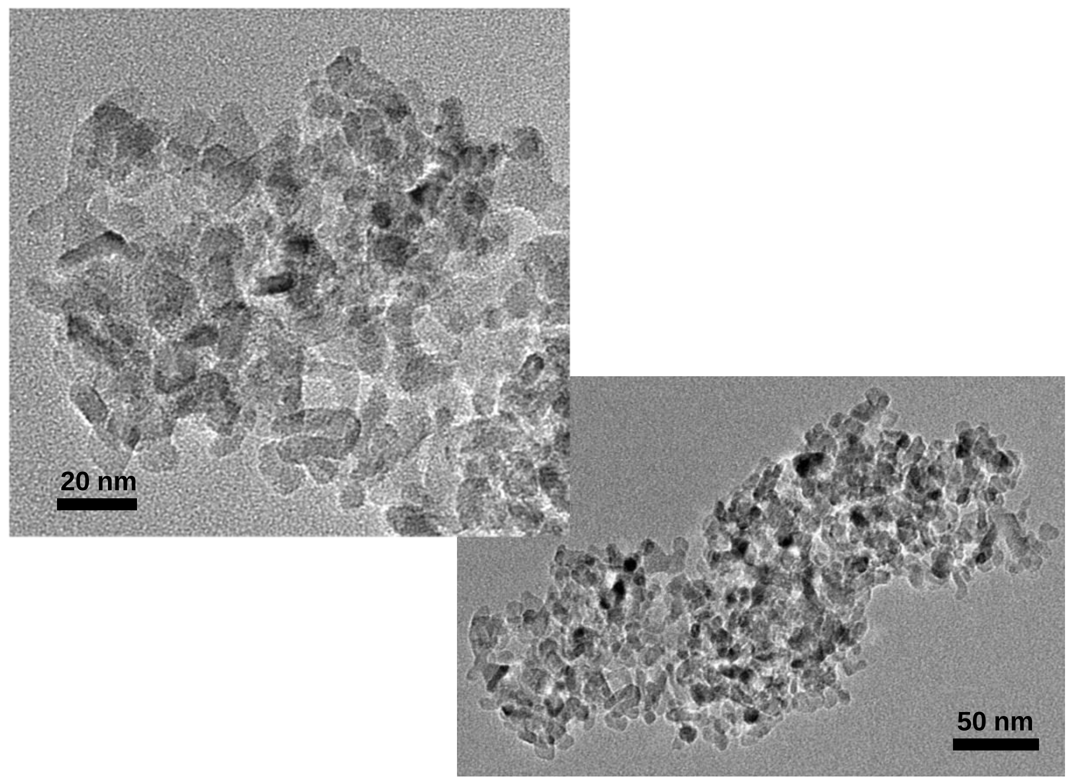
Hydrolysis of Magnesium Methoxide:

$$Mg(OCH_3)_2 + H_2O \text{ (or aqueous NaOH)} \longrightarrow Mg(OH)_2^* \xrightarrow{\Delta} MgO$$

*literature suggests that the product could also be $Mg(OH)(OCH_3)$

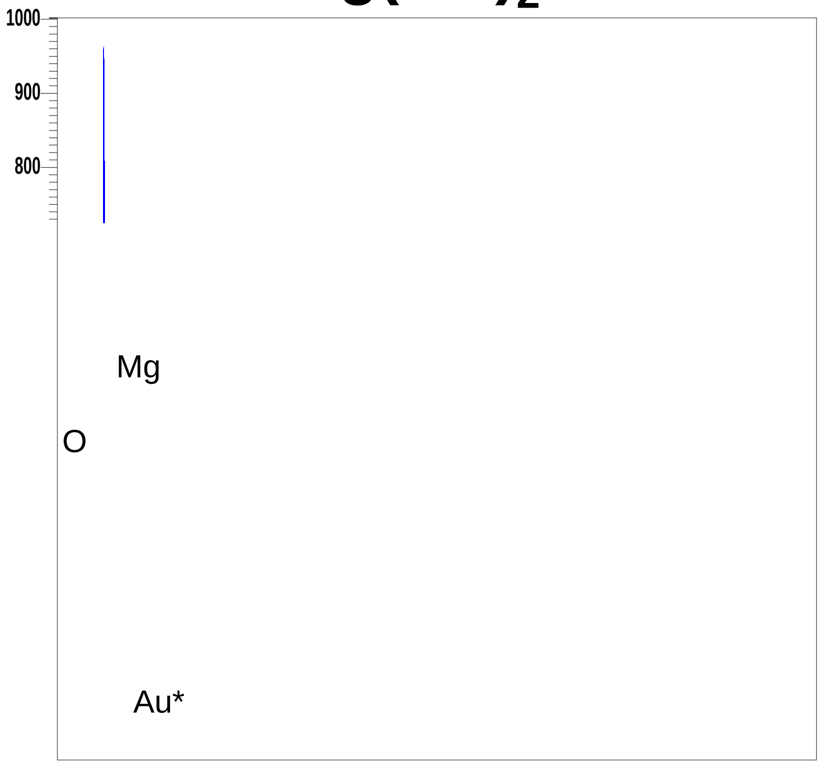


Specific surface area = 145 m^2/g

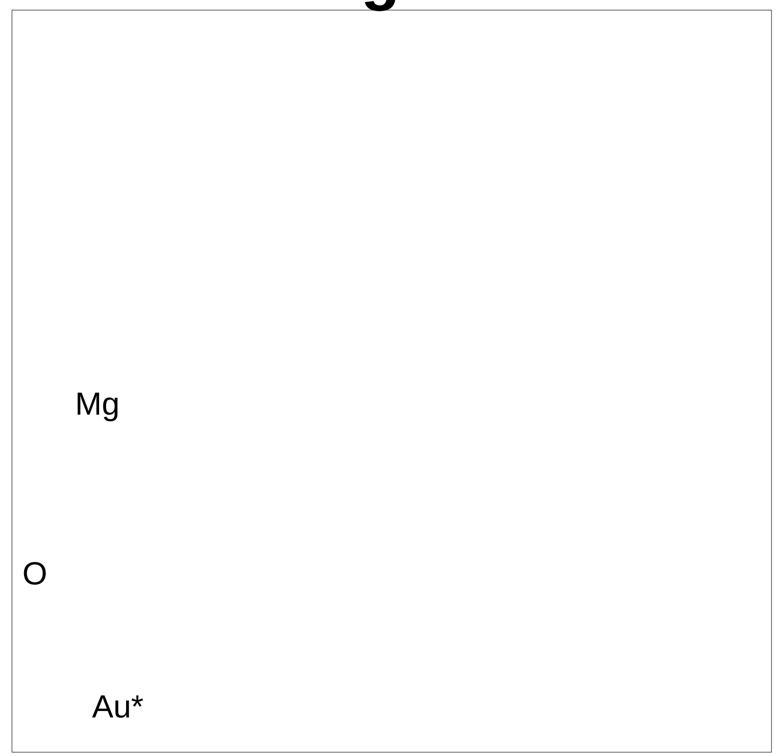


Hydrolysis of Magnesium Methoxide

$Mg(OH)_2$



MgO



*Normalized to the Mg Kα line, the O Kα line intensity decreases by a factor of 2, consistent with the stoichiometry as $Mg(OH)_2$ → MgO (*samples are Au coated)*

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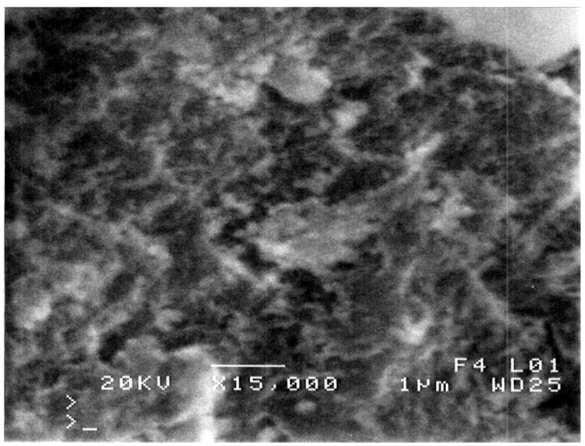
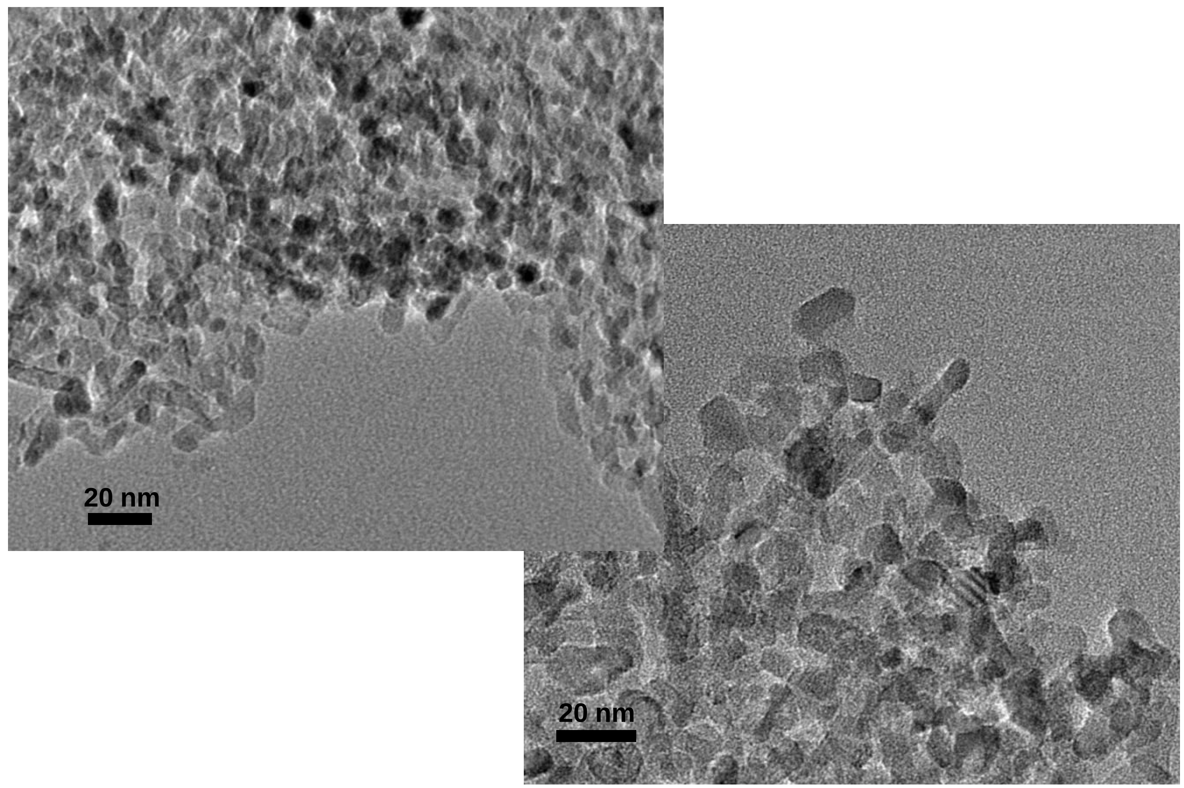
Synthesis of Magnesium Oxide

Synthesis and Calcination of Magnesium Oxalate:

$$Mg(CH_3COO)_2 + H_2C_4O_2 \xrightarrow{\text{Ethanol}} Mg(C_2O_4) \xrightarrow{\Delta} MgO$$



Specific surface area = 225 m^2/g

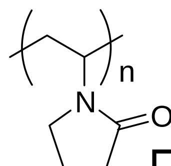


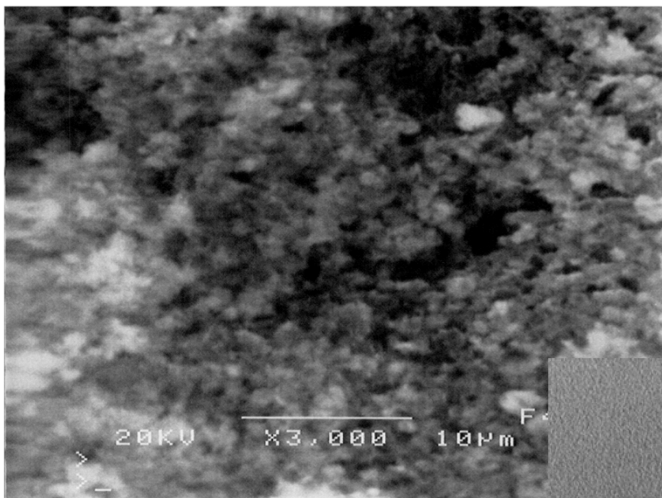
Synthesis of Magnesium Oxide

Synthesis and Calcination of Magnesium Glycolate:

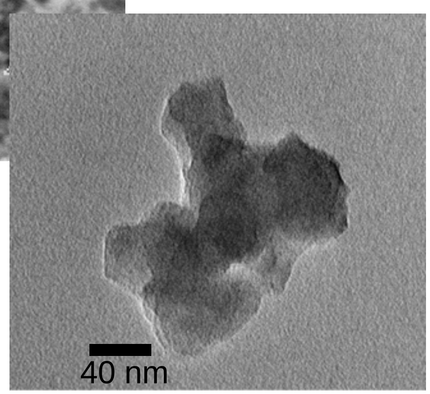
$$Mg(CH_3COO)_2 + PVP \xrightarrow[180\ ^{o}C,\ 30\ min]{Ethylene\ Glycol} Mg(C_2H_4O)_2 \xrightarrow{\Delta} MgO$$

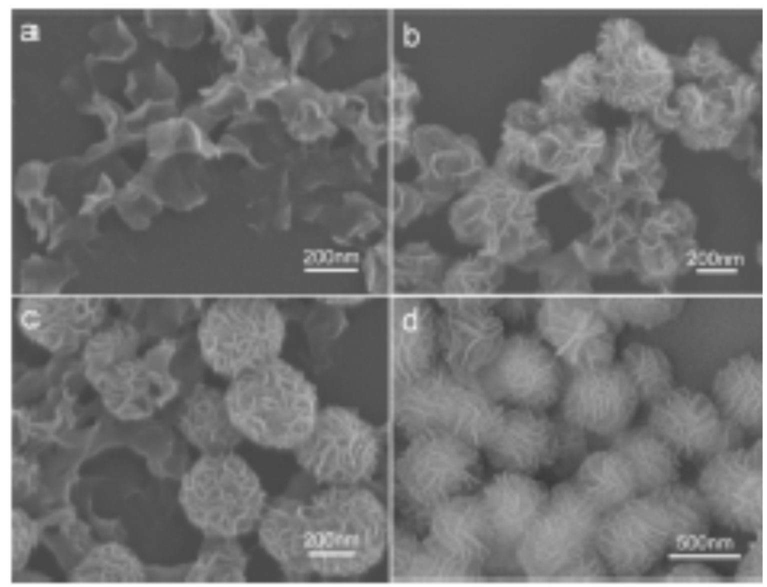
Poly(vinylpyrrolidone) (PVP) =





Specific surface area, TBD





Bain, S. –W. et al. *J. Phys. Chem. C* **2008**, *112*, 11340

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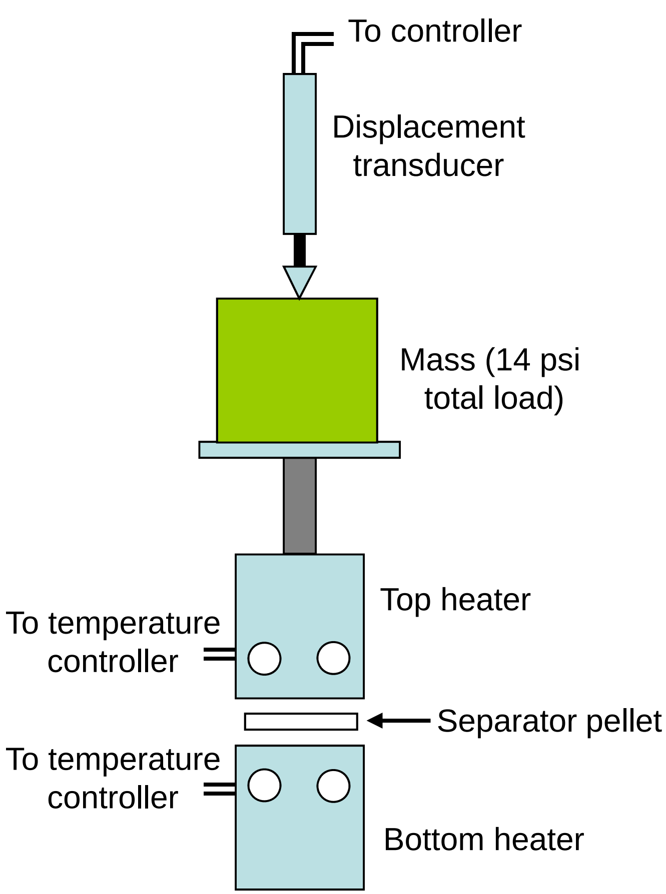
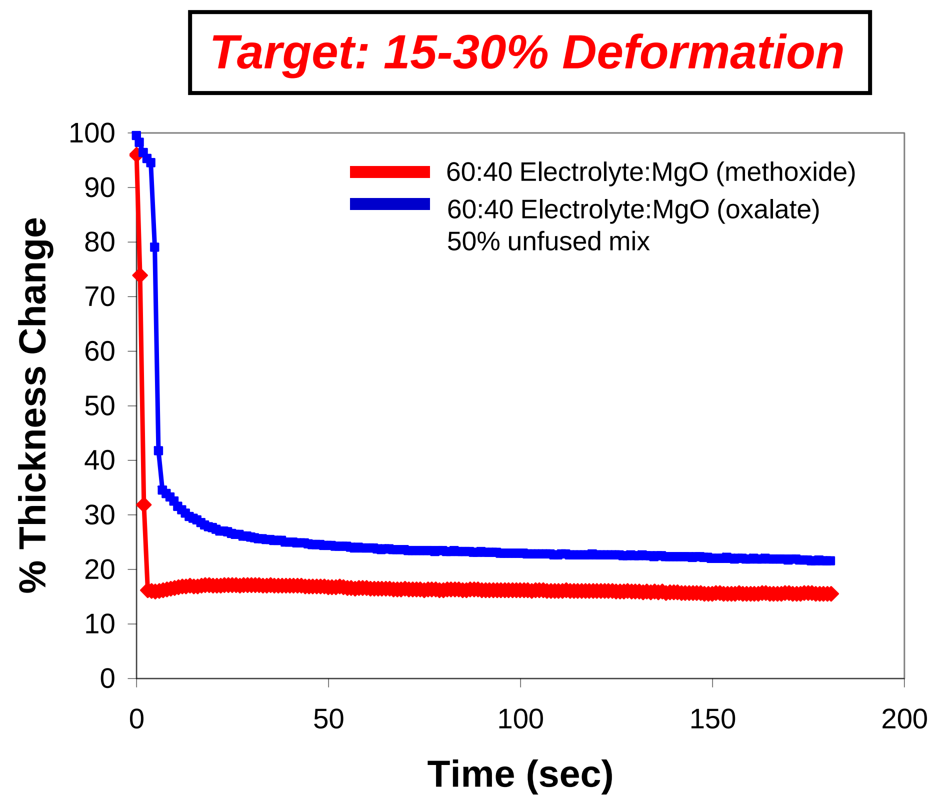
Mechanical Integrity - Deformation





- *75-85% Deformation*
- *Addition of unfused MgO alone may improve mechanical strength by simulating heterogeneous electrolyte wetting*

Acknowledgements

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