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JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

The Impact of Surface Films on Magnesium Electrodeposition and Dissolution in Inorganic Salt Electrolytes

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Sandia National Laboratories

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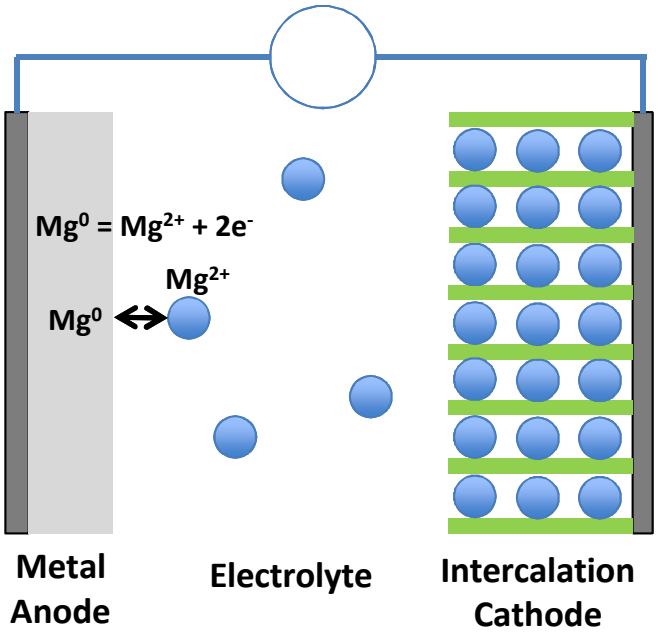
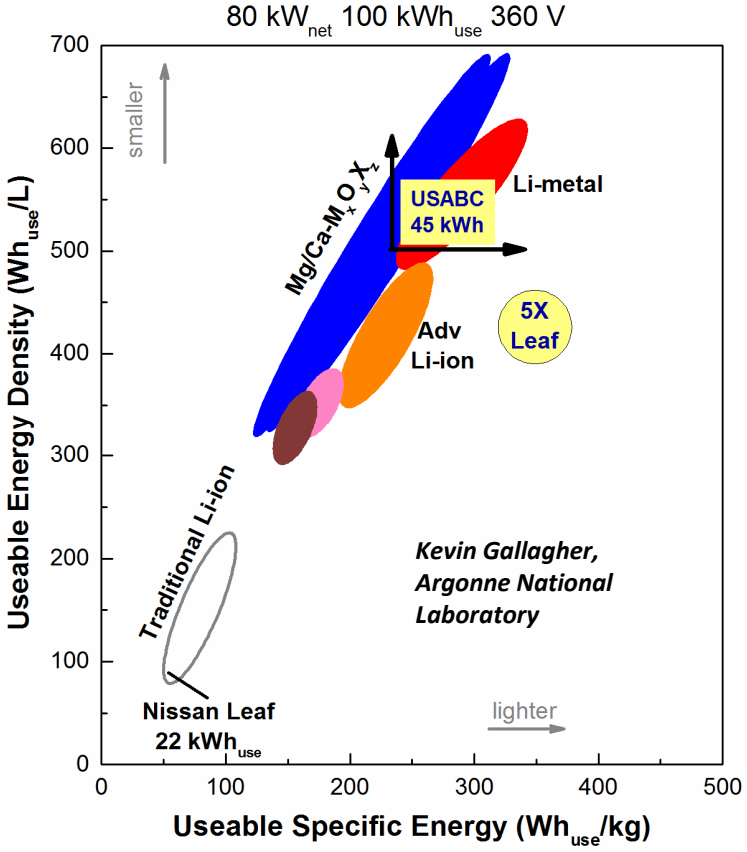
Mg Batteries = Promising Beyond Li-ion Energy Storage Technology



Anode	mAh/cm³	$/1000 kg metal[1]	V vs. SHE
LiC_6	780	$ 39600[2]	-2.9
Mg	3830	$ 2700	-2.4
Ca	2090	$ 3500	-2.9



- **Competitiveness of MV batteries hinges on the utilization of a metal anode**

[1]www.alibaba.com
[2]Based on Li_2CO_3 price of $7500

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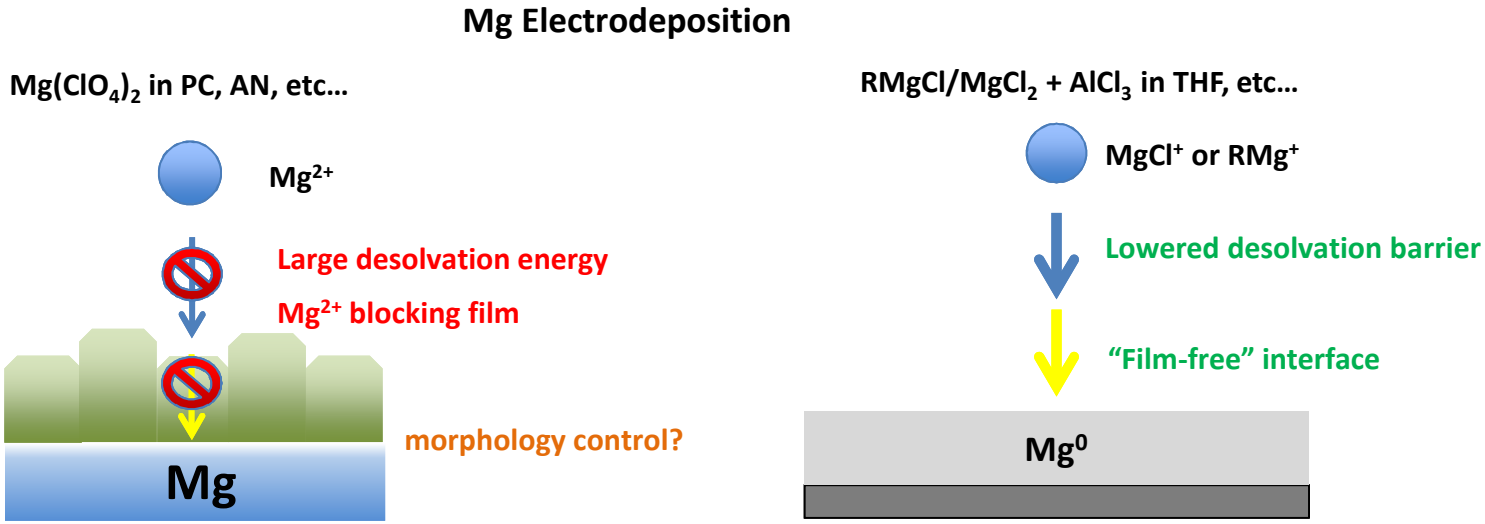
Metal Anode Challenges

Technical challenge

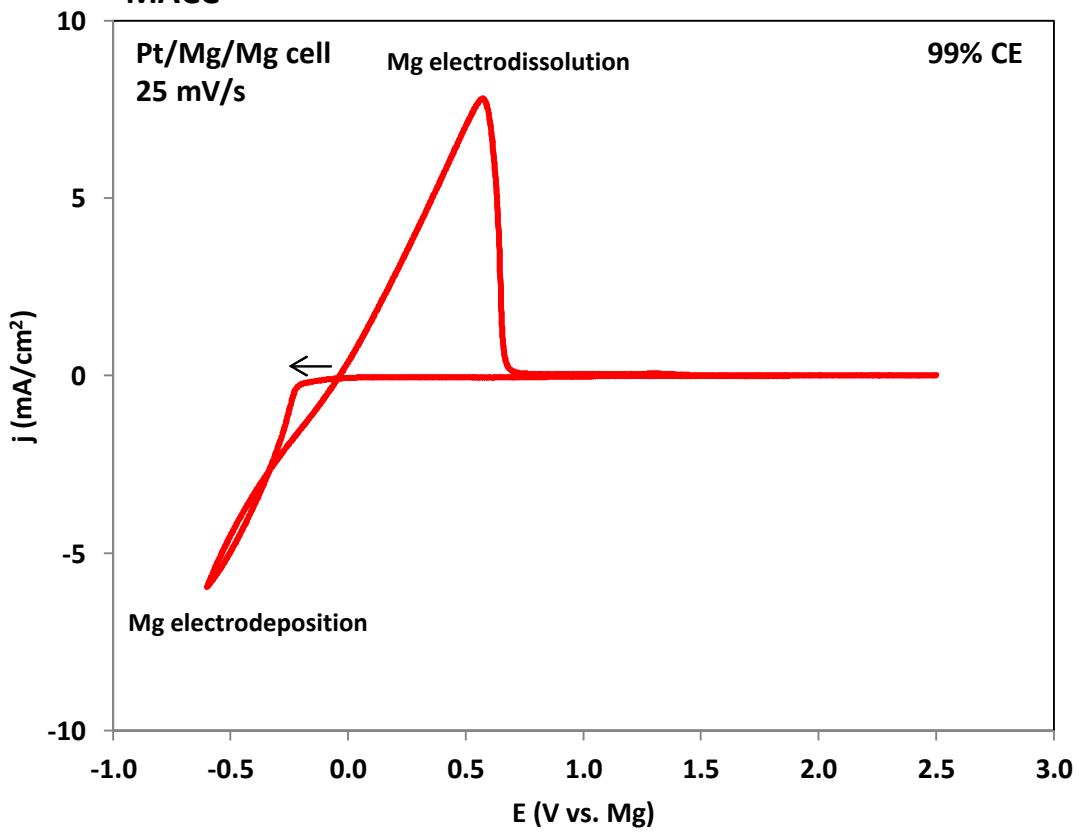
- Develop and implement the design rules necessary to achieve Li and Mg (Ca, Al, ...) cycling for 1000 cycles at >99.9% coulombic efficiency at relevant rates & capacities



- **Traditional views:**
  - electrolytes that can deposit Mg are able to because they don't form surface films
  - inorganic Mg-salts cannot deposit Mg due to film formation
- **Our approach:**
  - Understand the nature and impact of Mg surface films as a function of electrolyte composition

Chloroaluminate Example

0.25M $MgCl_2$ + 0.125M $AlCl_3$ in THF
"MACC"[1]

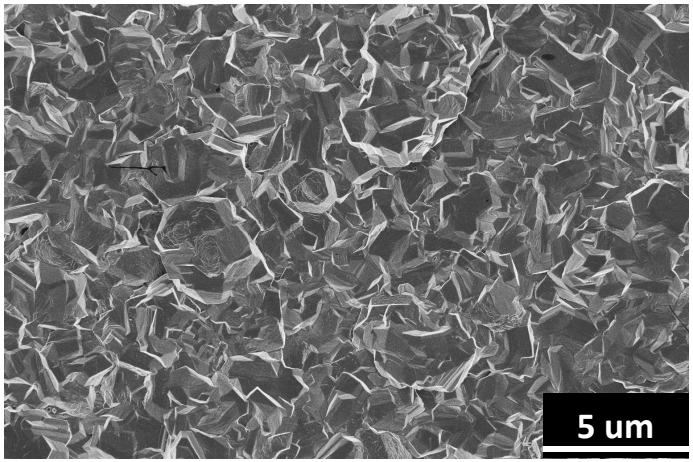


[1]Doe et al., Chem. Commun. 2013

- High coulombic efficiency
- Reasonable anodic window (~3 V)

- What happens to Mg surfaces at open circuit?

Mg deposited on Au (111)



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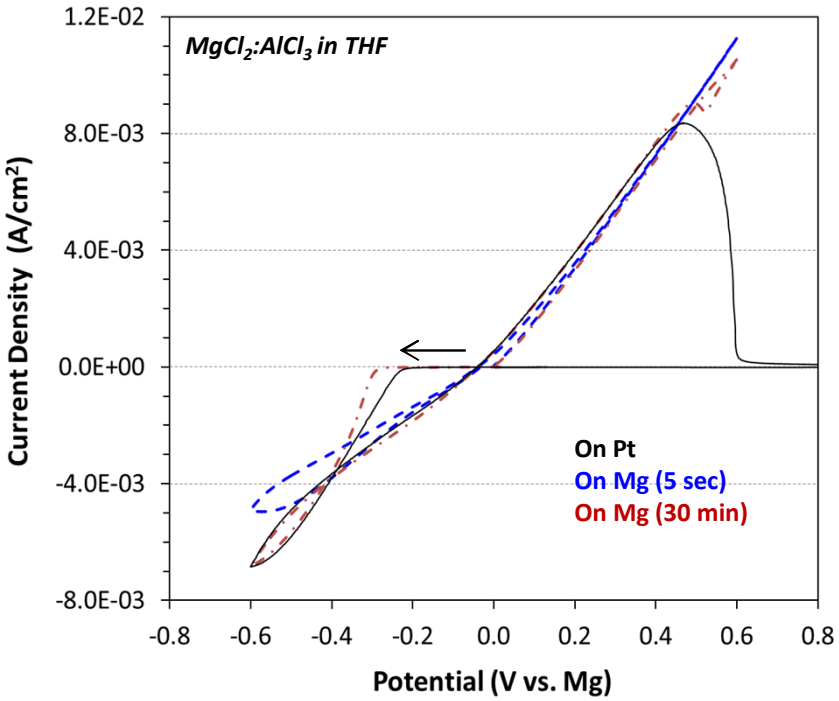
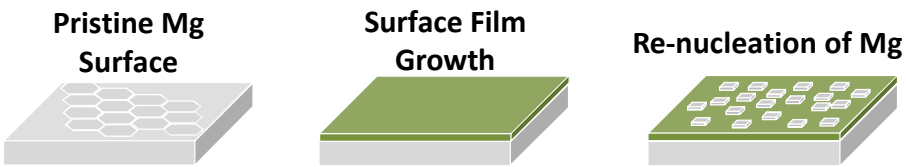
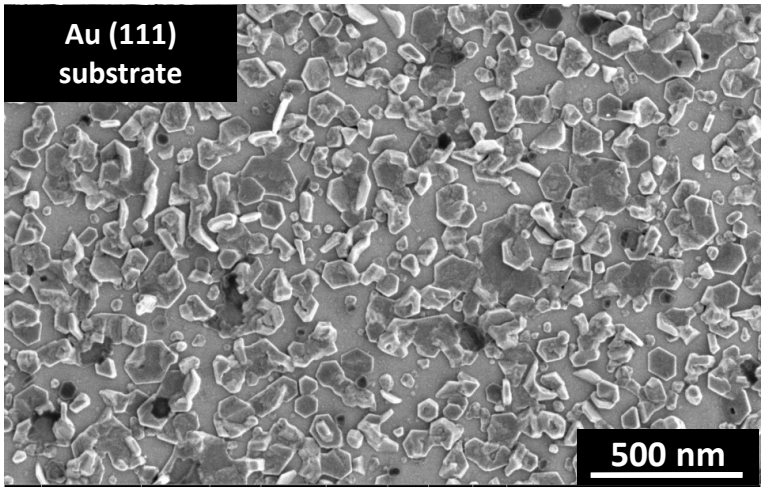
Deactivating surface films form on Mg at open circuit in chloroaluminates

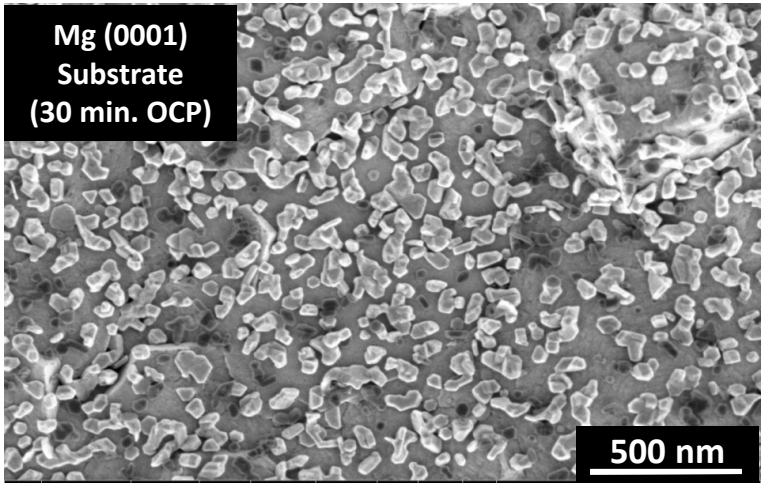




- Equilibrated Mg surfaces behave like foreign substrates w.r.t nucleation

Current-controlled nucleation density correlates with nucleation overpotential





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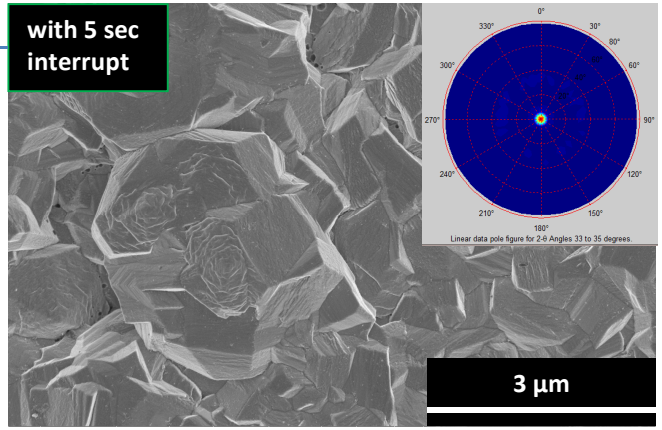
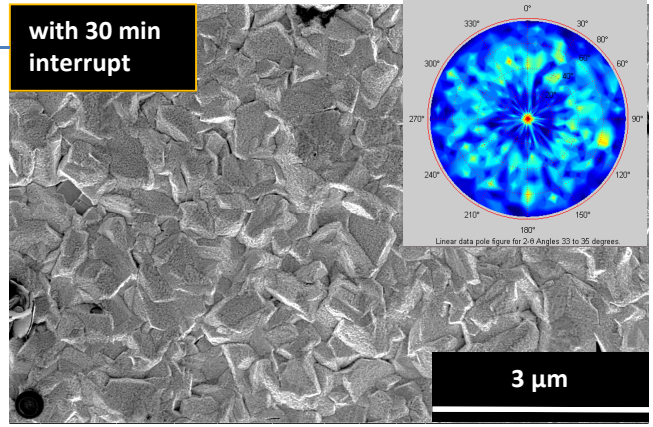
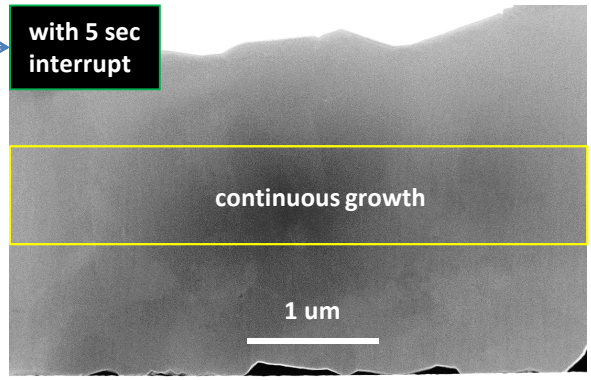
Renucleation in MACC compromises anode structure

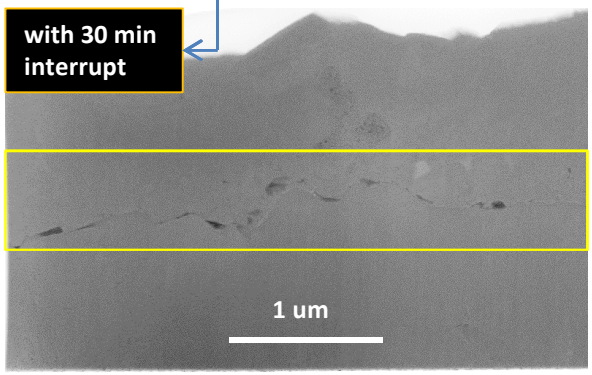
Crystallographic re-texturing occurs when Mg deposition is interrupted for significant periods

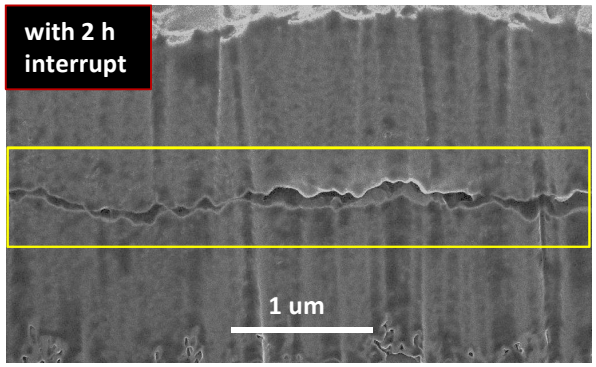




Interfacial voiding increases with equilibration time







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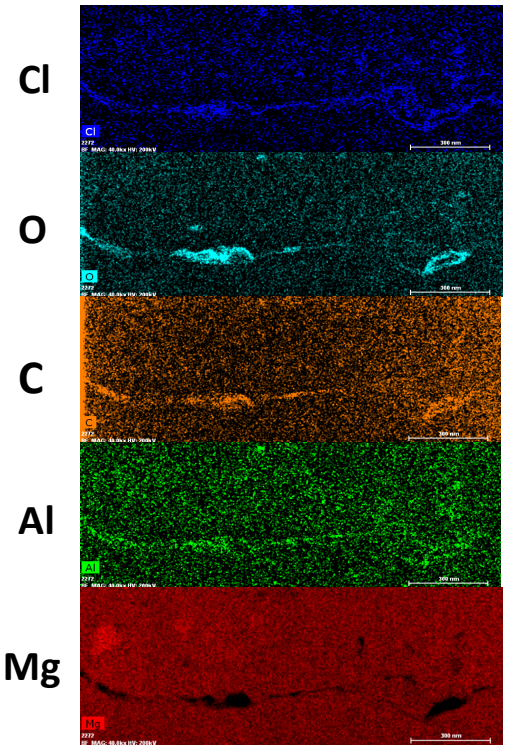
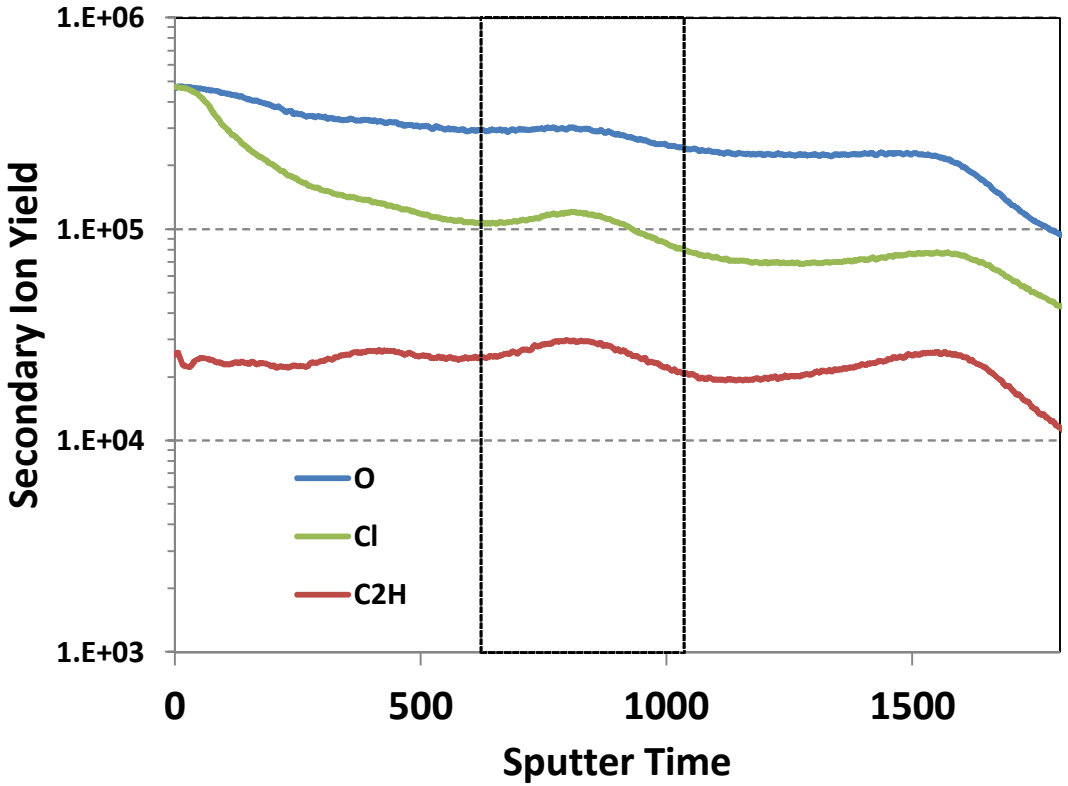
Interfacial layer contains non-Mg electrolyte constituents

Cross-sectional EDS

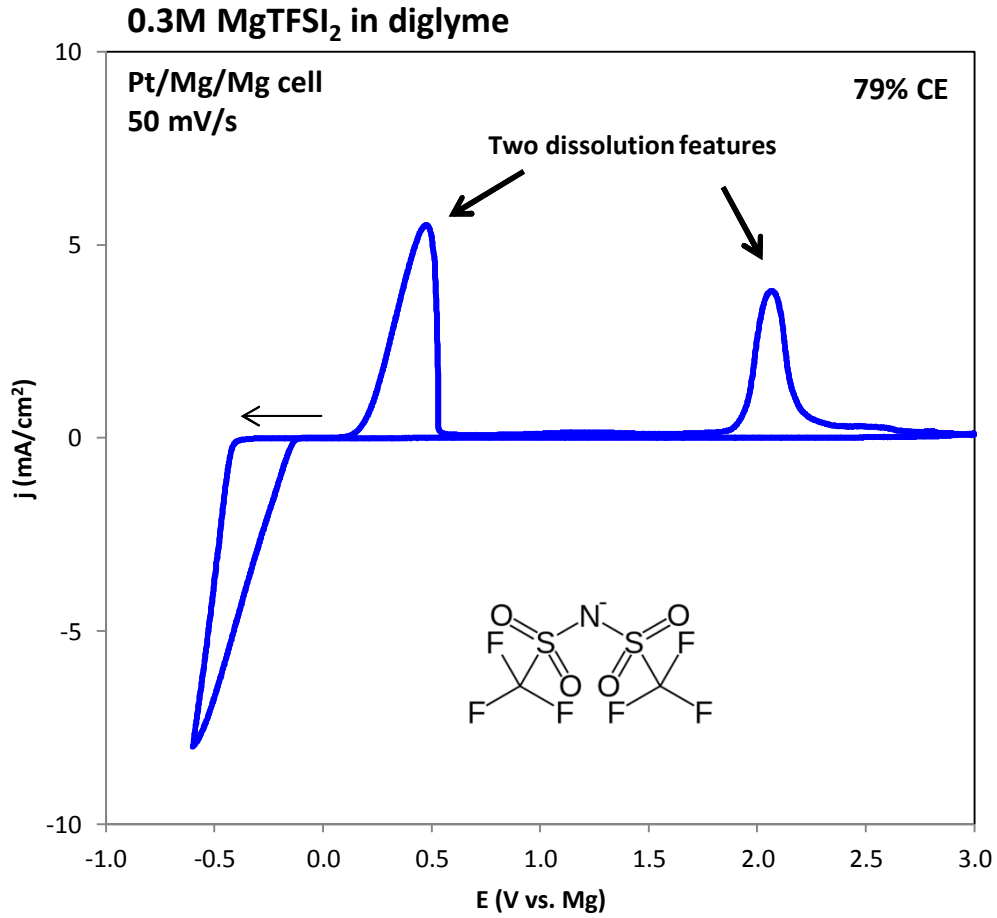


ToF-SIMS Negative Ion Depth Profiles



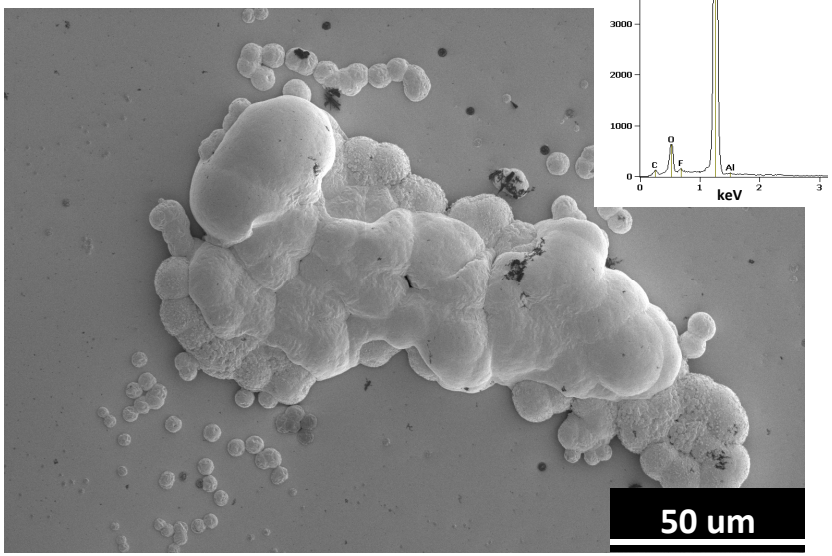
- Non-Mg electrolyte constituents are enriched within the film region
- Contribution of trapped electrolyte masks true film composition

Conventional Salt Example



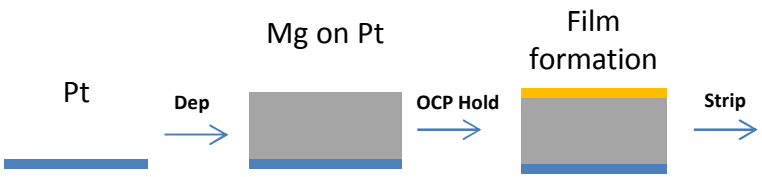
- Mg electrodeposition is possible from conventional weakly-coordinating salts
- Unique voltammetric behavior
- Unique deposition morphology
- To what extent does film formation influence behavior?

Mg deposited on Au (111)

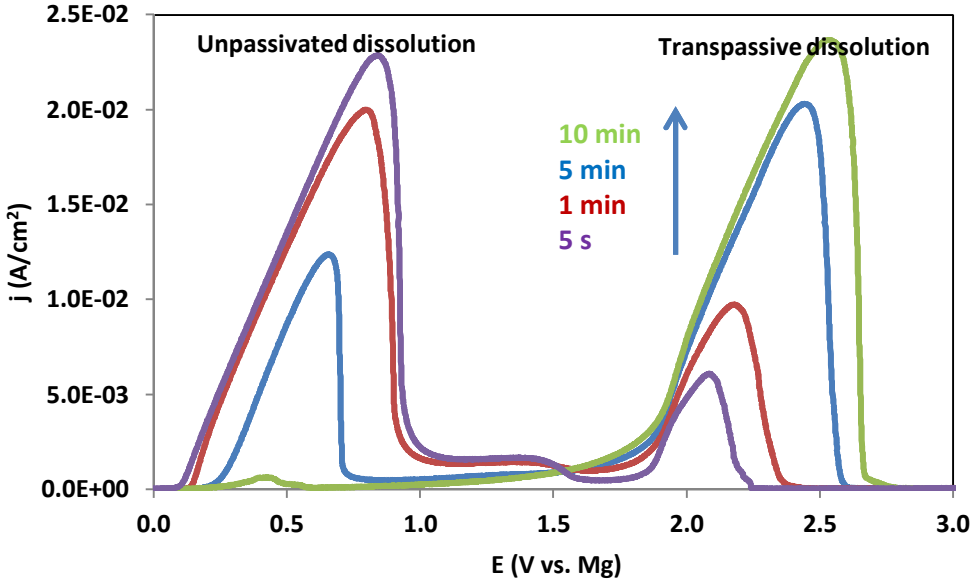


Passivating films form on Mg in $MgTFSI_2$-diglyme

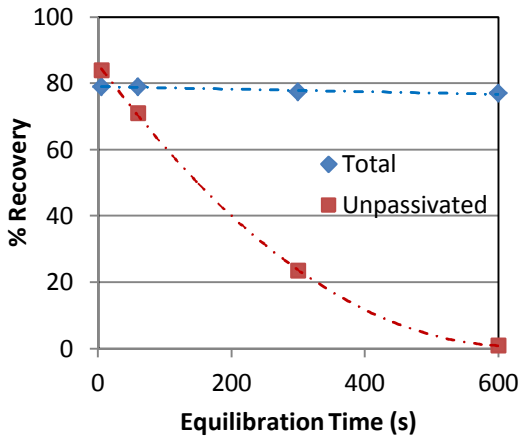
Open Circuit Equilibration Experiment:

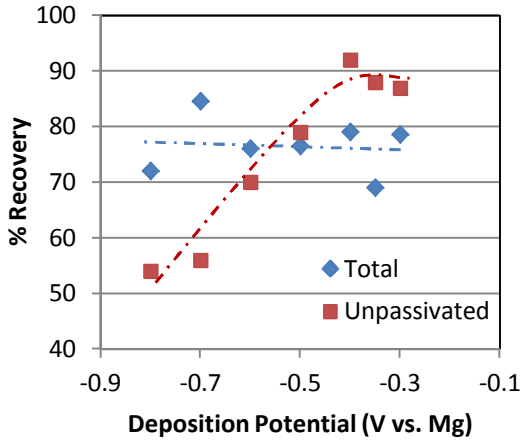


LSV strip after 500 nm Mg deposition



- Equilibrated Mg surfaces tend toward passivation within several minutes
- Extent of passivation increases if the deposition potential is reduced





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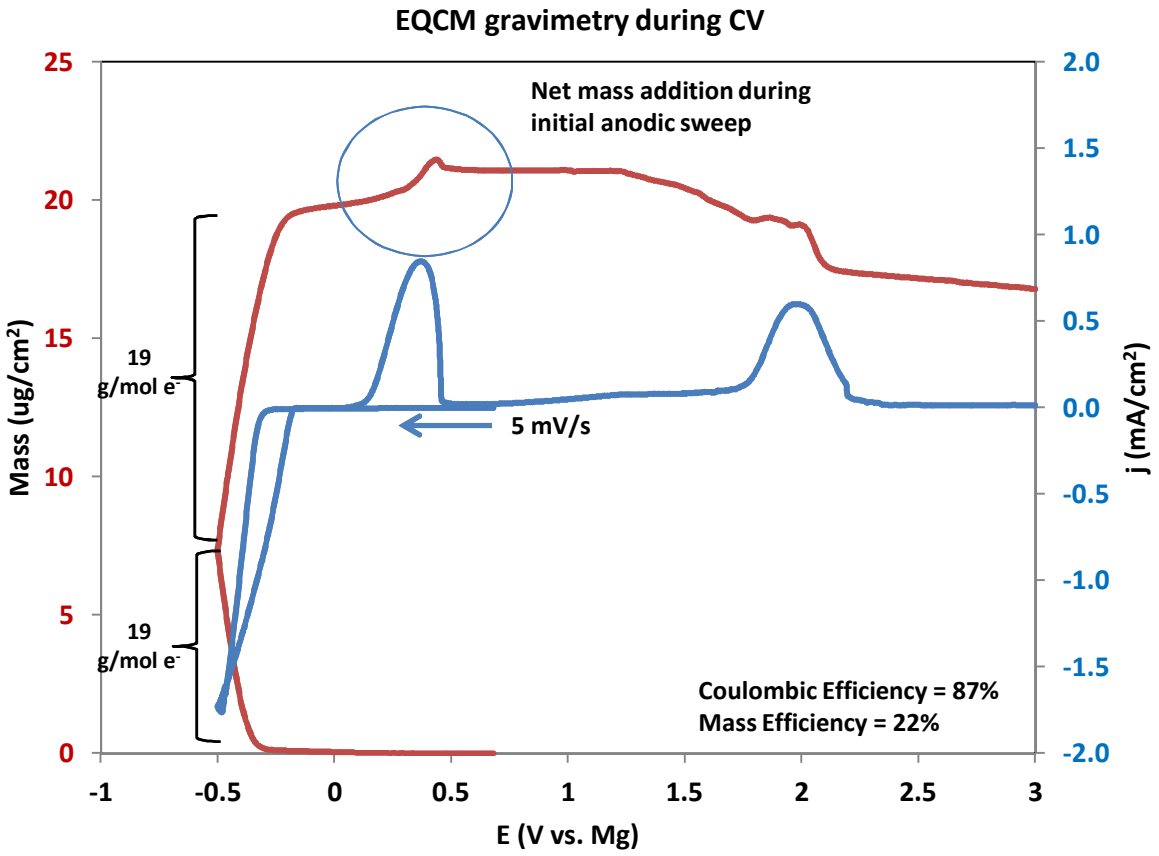
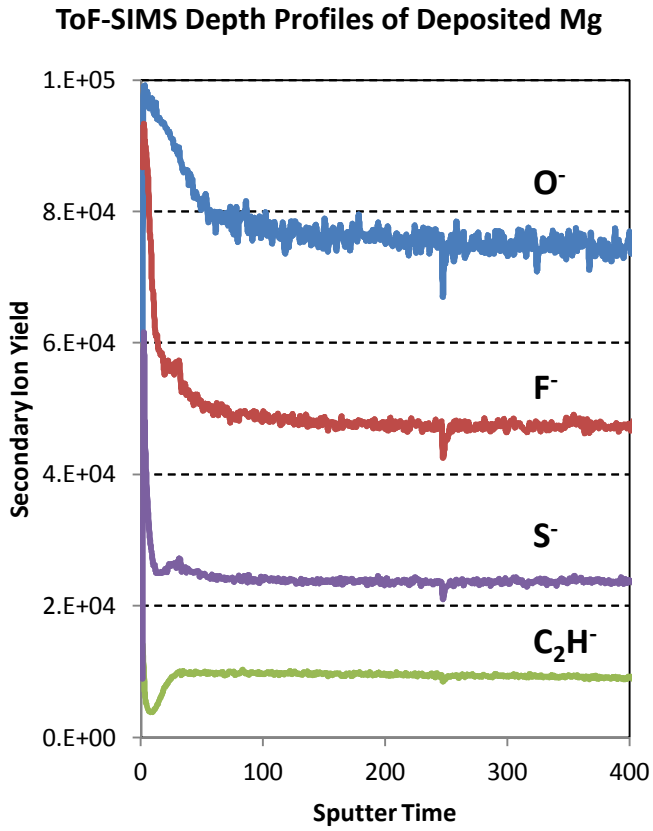
In-situ gravimetry demonstrates film formation





- Parasitic reduction and incorporation of electrolyte constituents during deposition
- Mass increases during initial dissolution stage - evidence for an anodically-driven film formation process

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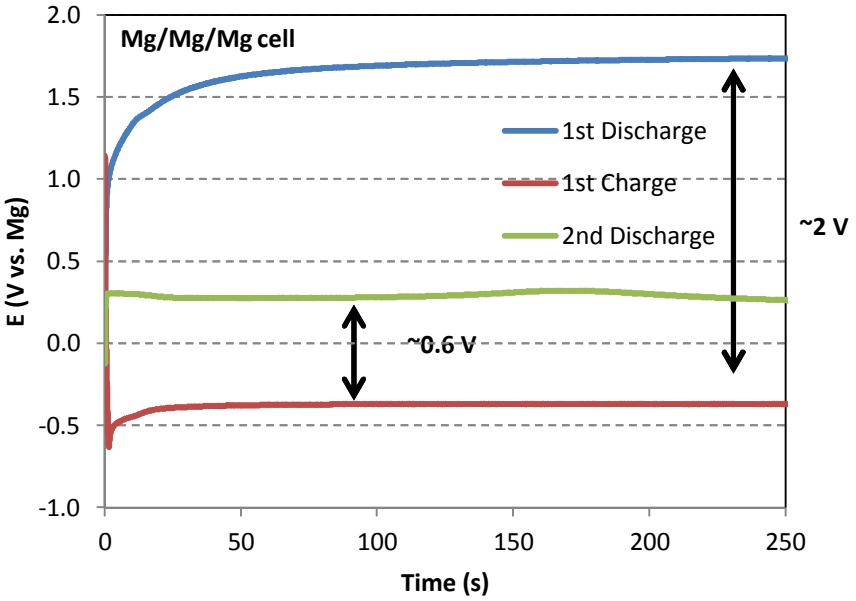
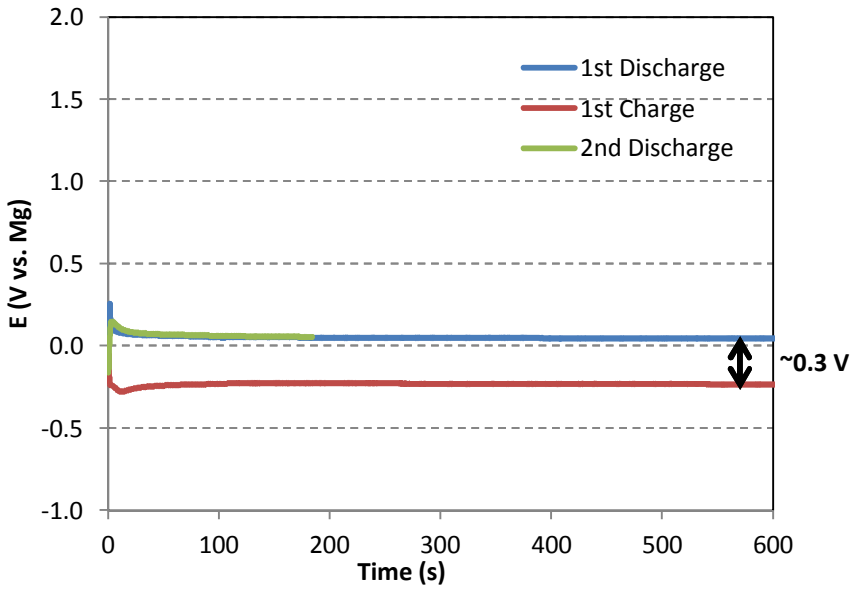
Anodically-driven passivation leads to large dissolution overpotentials at Mg anodes

Galvanostatic cycling @ > 2 mA/cm² after 15 min. equilibration



Cycling @ < 1 mA/cm² after 15 min. equilibration



- Passivated response is favored when the equilibrated Mg surface is driven to high potentials
- Cathodic polarization modifies the surface film to enable low overpotential dissolution during subsequent discharge

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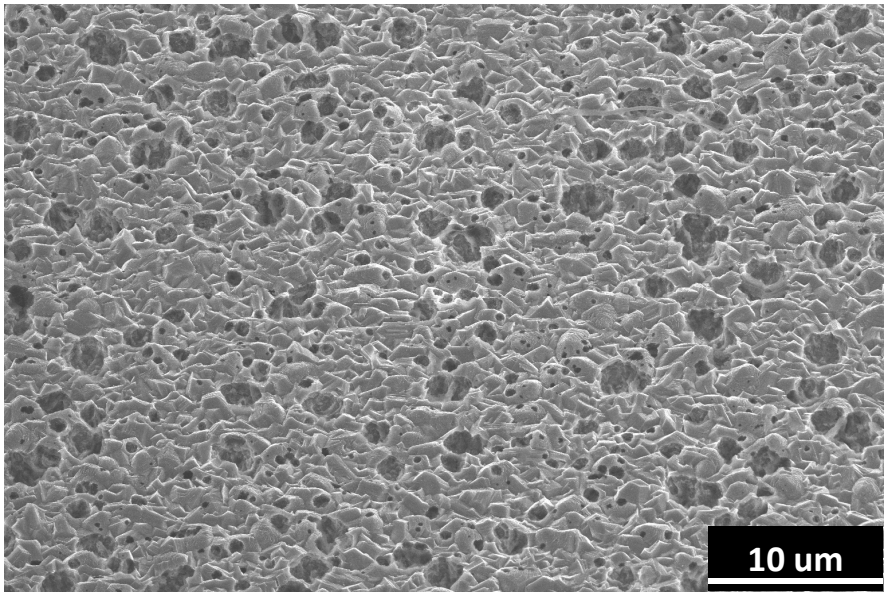
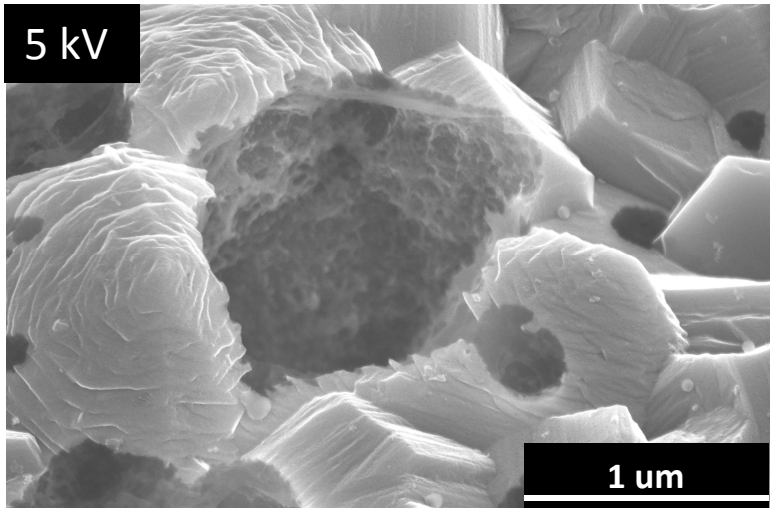
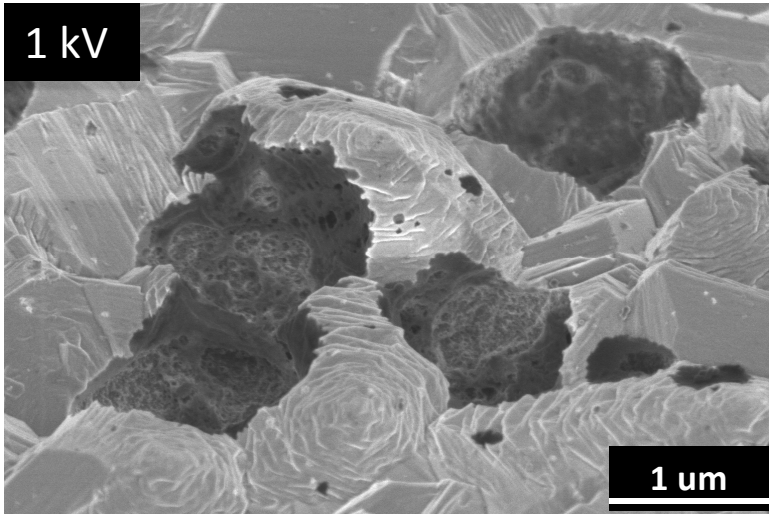
High overpotential dissolution is accompanied by pitting

Mg anode dissolution @ 1.5 mA/cm²







- Dissolution is confined entirely to pits (remainder of Mg appears untouched)
- Dissolution pits are coated by an amorphous film

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Take Home Messages

- Surface films matter
- Surface films form at open circuit in chloroaluminates
  - Voiding
  - Re-texturing
- Surface films passivated Mg deposited in $MgTFSI_2$-diglyme
  - Open circuit equilibration
  - Anodic passivation
- Paths forward for electrolyte development
  - Anions with better reductive stability
  - Strategies for stabilizing $TFSI^-$ against Mg^0

Acknowledgements

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