SAND2015-3110C

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Understanding the Morphological Evolution of a Mg Anode with Galvanostatic Cycling in Chloride-based Ether Electrolytes – Application to Mg Batteries

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Sandia National Laboratories

MRS, April 8, 2015

Supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science. Sandia is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the U.S. DOE's NNSA under contract DE-AC04-94AL85000.

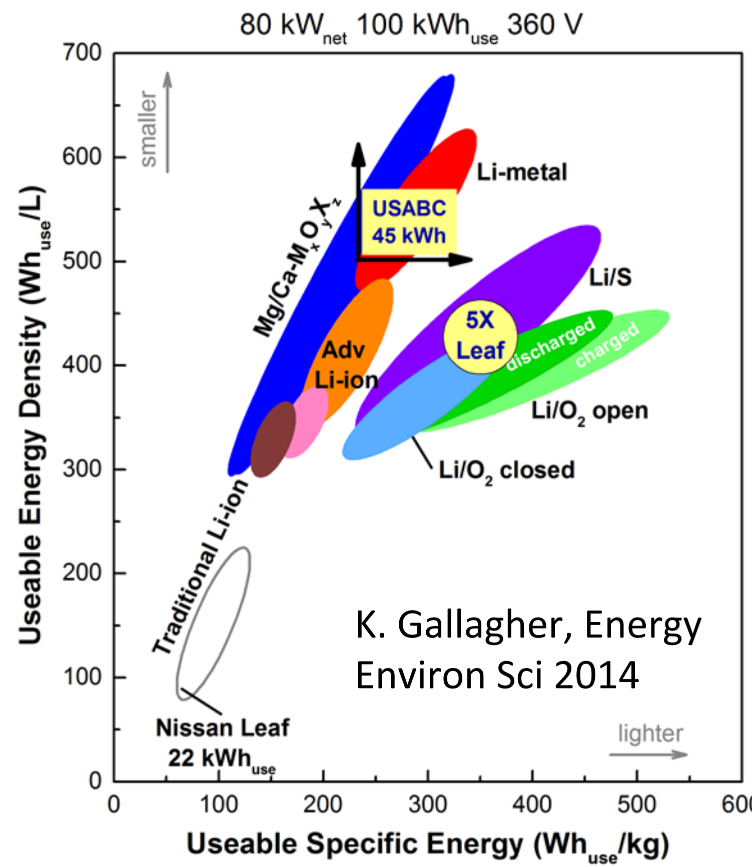
Switching the Working Ion to Mg and to Metals

Advantages of Mg:

- divalency
- high density
- less electropositive
- non-dendritic deposition, 99.9% CE demonstrated
- cost & availability

Anode	Ah/L	$/1000 kg metal[1]	V vs. SHE
LiC_6	818	$ 39600[2]	-2.9
Li	2026	$ 39600[2]	-3.1
Mg	3840	$ 2700	-2.4
Ca	2090	$ 3500	-2.9

[1]Bulk prices from alibaba.com
[2]Based on Li_2CO_3 price of $7500



Cell: 3 V insertion cathode (750 Wh/kg), 50% excess Mg

Outcomes: $100 /kWh, 500 Wh/l

Disadvantages of Mg:

- relevant rate anode morphology is unknown
- electrolytes compatible with high voltage cathodes
- viable high voltage cathodes do not exist - mobility

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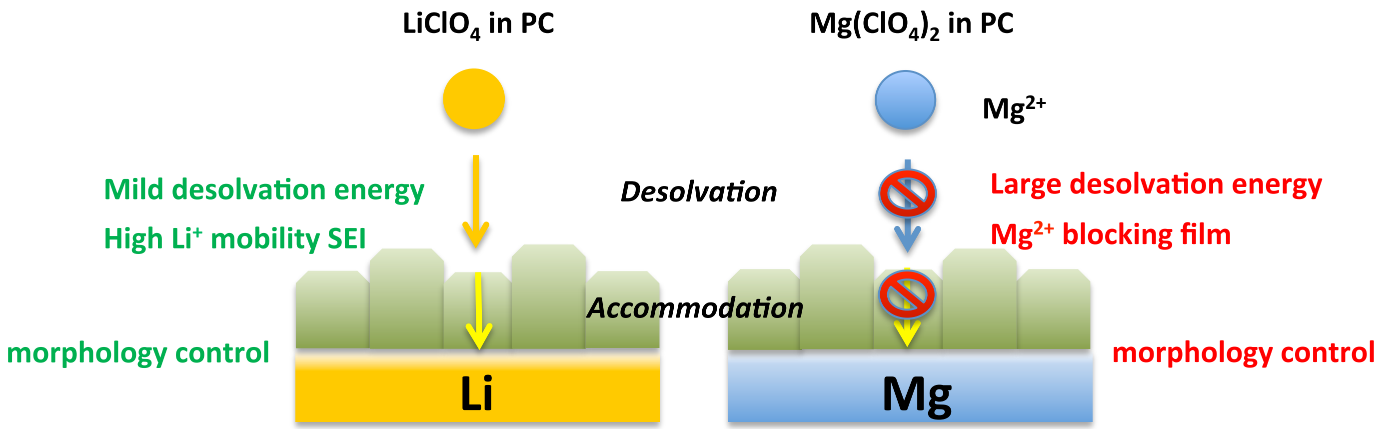
Metal Anode Challenges

Technical challenge

- Develop and implement the design rules necessary to achieve Mg (Ca, Al, ...) cycling for 10^3 cycles at >99.9% Coulombic efficiency at relevant rates & capacities

Li vs. Mg Anode Plating



Science challenges and research

- Efficient cation desolvation
- Efficient cation accommodation
- Electrolyte stability
- Metastability - Activation, Corrosion, Protection

Anode Dimensional Control is Required at High Rates

$100/kWh, 100 kWh battery, 100 kW pulse, 15 kW continuous, 60 kW charge, 120 kW fast charge

Magnesium - MX_y	
target areal capacity	6 mAh/cm^2
anode active loading	2.7 mg/cm^2
anode thickness	16 μm
cathode specific capacity	250 mAh/g
cathode active loading	24 mg/cm^2
cathode thickness	100 μm

Pulse power c.d.	6 mA/cm^2
Cont. power c.d.	0.9 mA/cm^2
L3 charger c.d.	3.6 mA/cm^2
Super charger c.d.	7.2 mA/cm^2

16 μm of Mg

large quantity of metal to move!

6 mA/cm^2 of Mg

high rates of metal transformation!

Key Messages

- Surface films form in 100’s of seconds – open circuit equilibration
    - These films are not benign – they direct structure evolution
- Repeated exposure of the dissolution front creates a structurally complex interface
    - Film and electrolyte incorporation, voiding, and porosity
    - Efficiency is not changed over limited (50) continuous cycles
- Periodic equilibration interrupts during cycling magnifies structural evolution
    - Performance degrades - 1-2% decrease in efficiency
    - Stranded Mg – electrical and structurally isolated

Organic vs. Inorganic Mg Chloroaluminate Electrolytes

All Phenyl Complex (APC): 2 $PhMgCl:AlCl_3$ in THF

D. Aurbach et al., *Energy Environ Sci* 2013

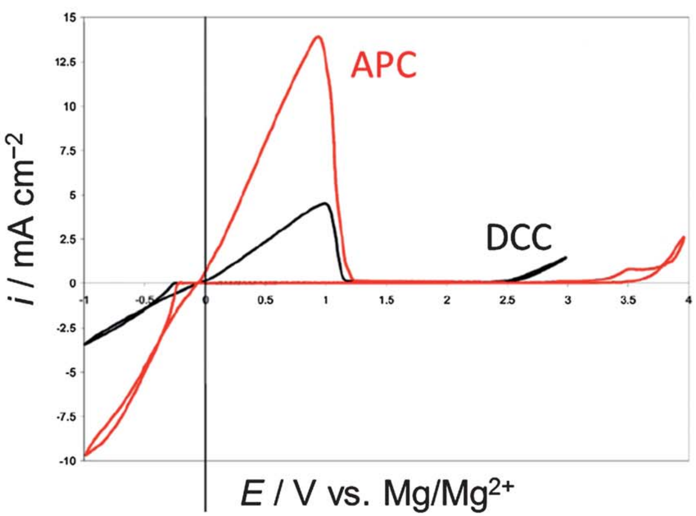
Magnesium Aluminum Chloride Complex (MACC): 2 $MgCl_2:AlCl_3$ in THF or DME

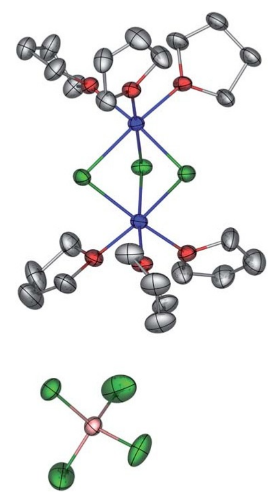
R. Doe et al., *Chem Comm* 2014

$9PhMgCl + 4.5AlCl_3 \rightarrow Ph_4Al^- + 2Ph_2AlCl_2^- + PhAlCl_3^- + 0.5AlCl_4^- + 4.5\mathbf{Mg_2Cl_3^+}$

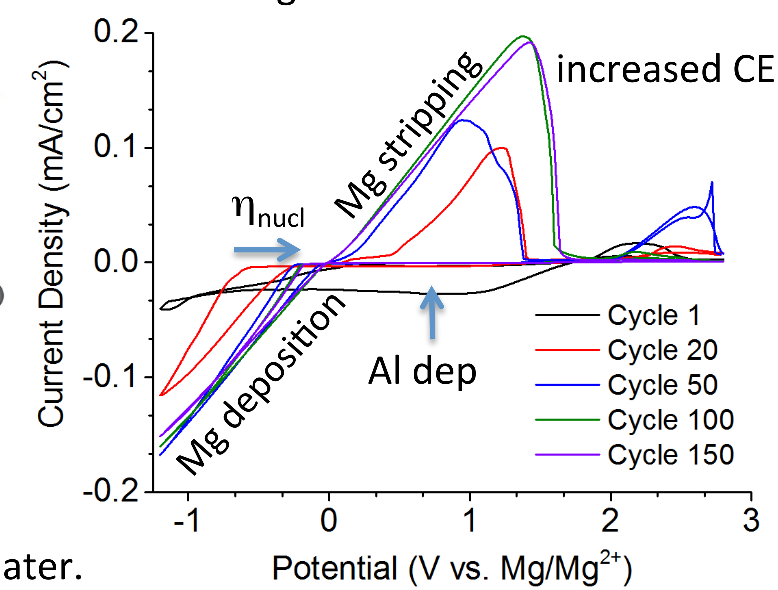
$2MgCl_2 + AlCl_3 \rightarrow \mathbf{Mg_2Cl_3^+} + AlCl_4^-$

Mg:Al increases from 2 to 2.6





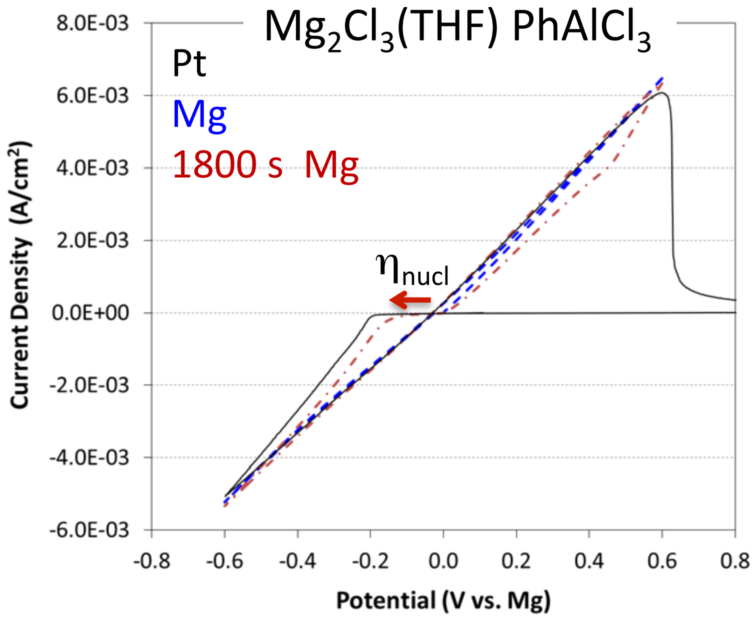
T. Liu et al., J. Mater. Chem. A, 2014

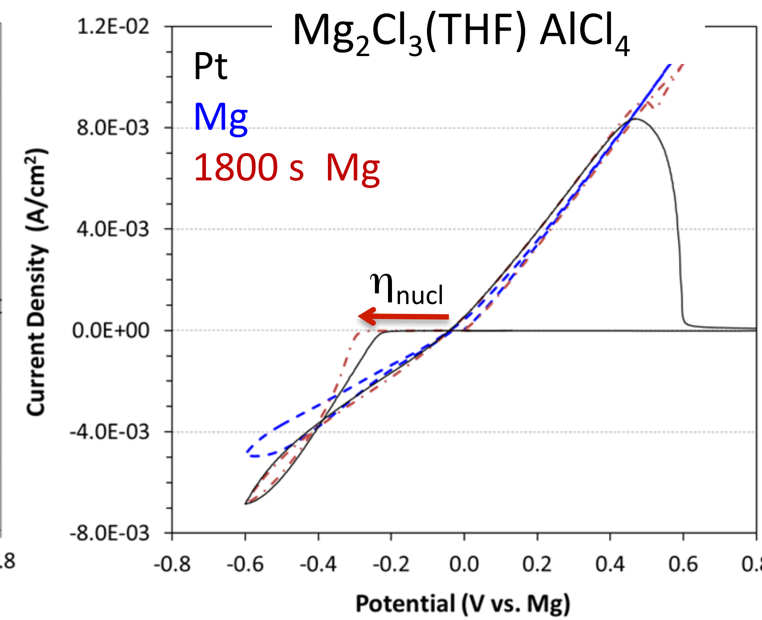


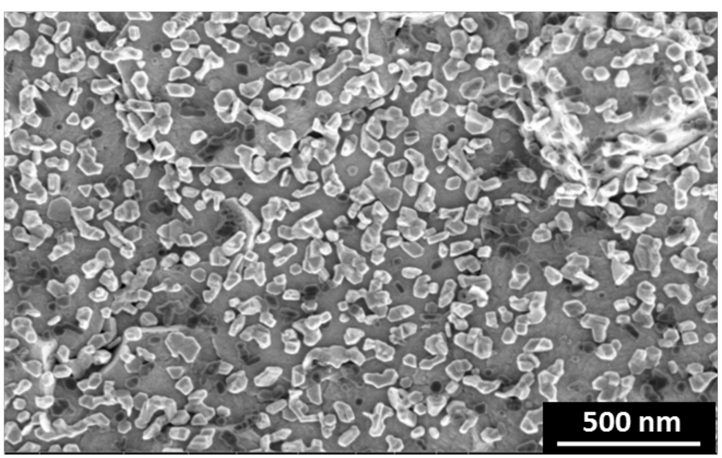
C. Barile et al., J Phys Chem C 2014

Multimers define bulk speciation $Mg_2Cl_3^+(THF)_n$

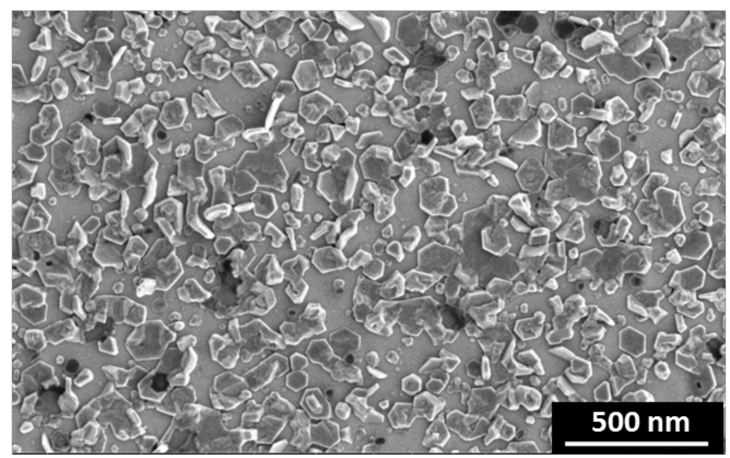
Re-nucleation is required at the filmed Mg interface







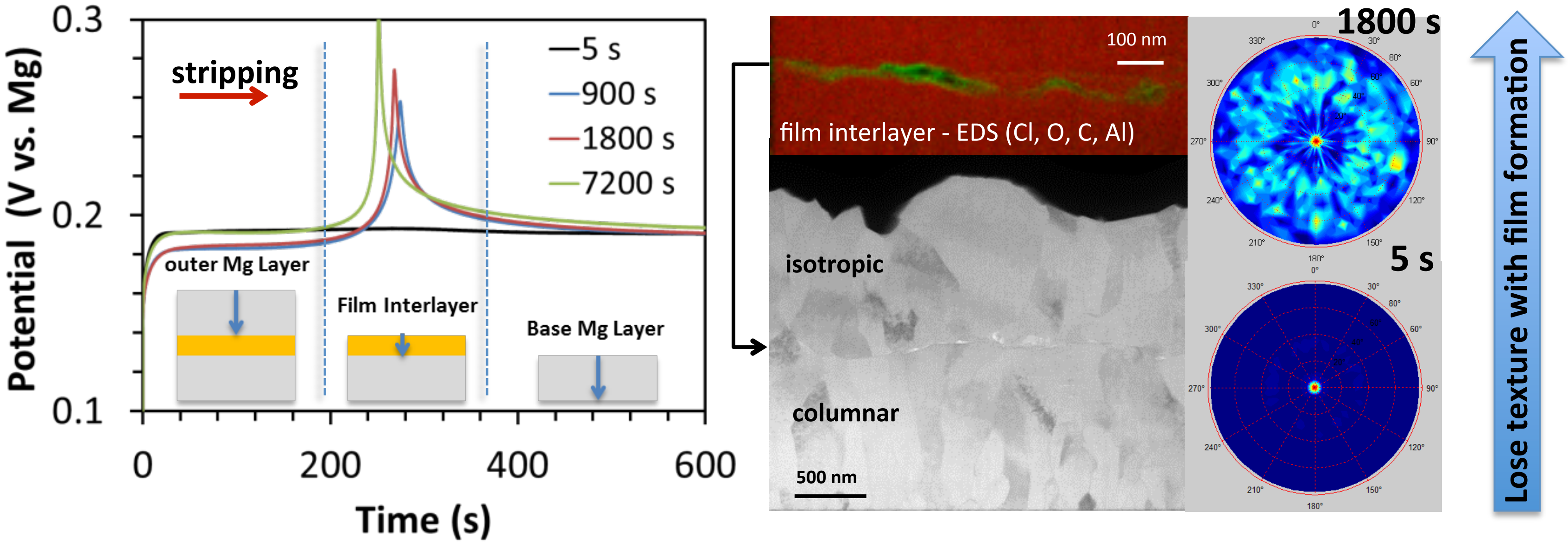
Mg on 1800 s equilibrated Mg



Mg on clean Au

N. Hahn et al. 2015 submitted

The filmed interface directs subsequent Mg growth



Surface films form in chloroaluminate electrolytes

- Protective – reduce self-discharge to < 2 nm/hr
- Directive – direct morphology development of the subsequent Mg deposit
- Disruptive – filmed interface incorporates - mechanical flaws within the deposit
- May contribute to incoherent Mg deposition observed in JCESR Mg prototype cells

N. Hahn et al. 2015 submitted

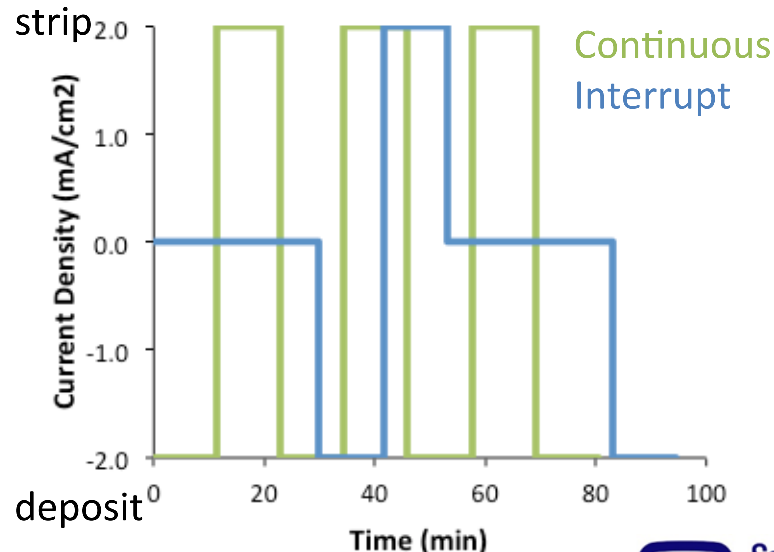
Quantifying the Impact of Surface Films

	Coulombic Efficiency[1]		
Electrolyte	Single cycle	50 cycles continuous	50 cycles with 1800 s interrupt
APC	99.5	99.3 →	97.4
MACC	99.2	99.2 →	98.1

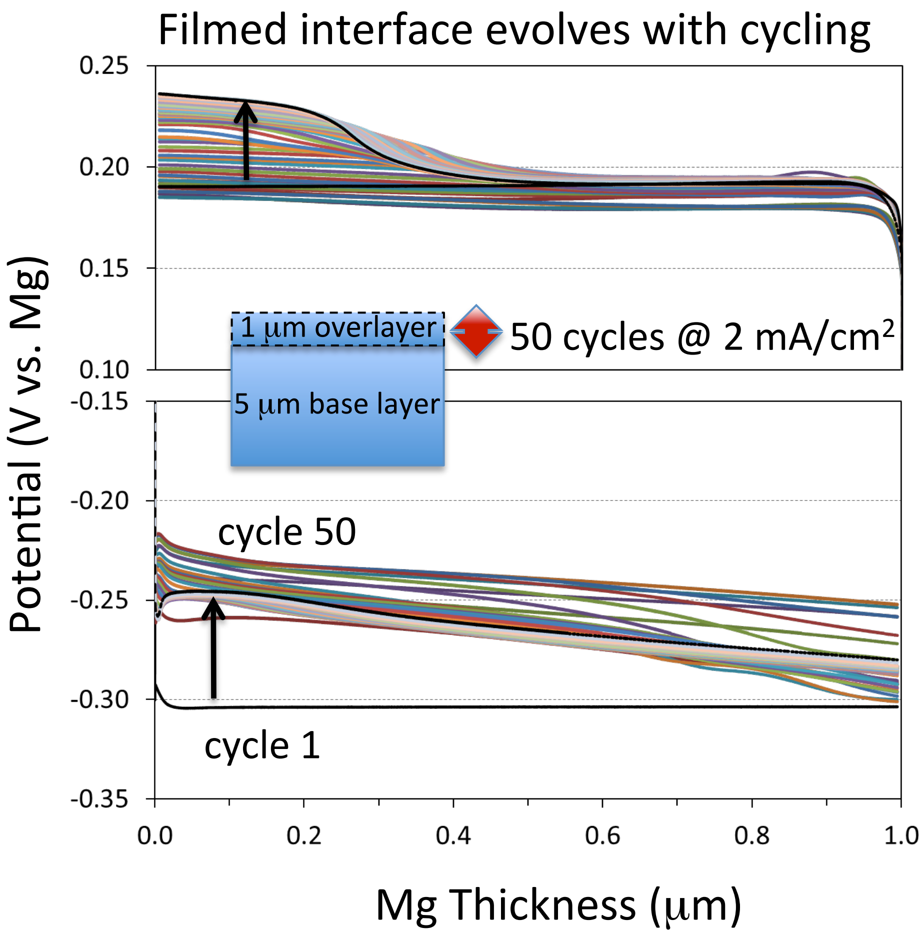
[1]±0.1 % found for 3 to 6 replicate runs of single cycle chronopotentiometric titration

Efficiency is maintained with continuous cycling

Efficiency is decreased with introduced open circuit equilibration – mimics a practical use profile



Performance signatures exist for changes in morphology/structure



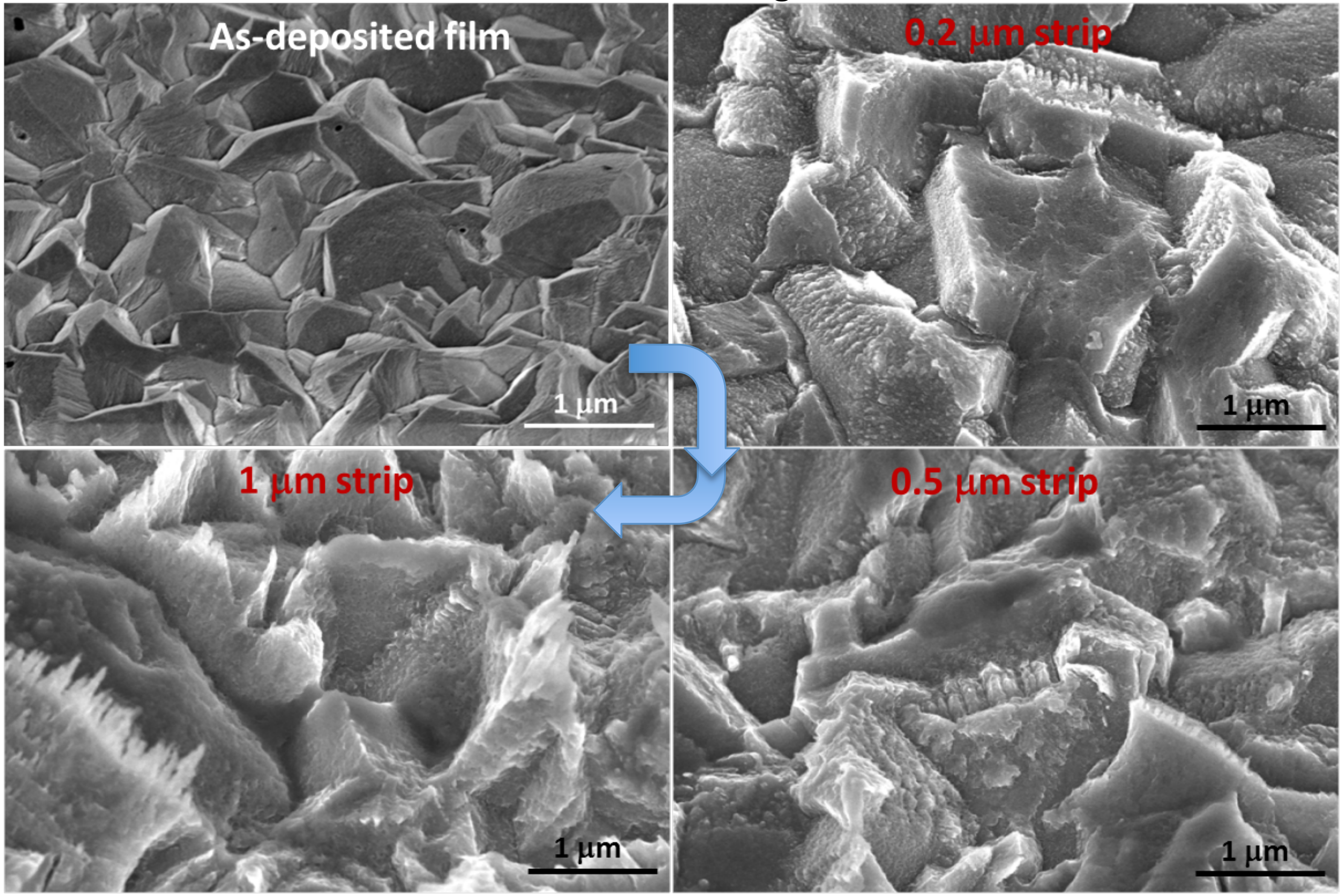
Increased polarization with repeated exposure of the dissolution front

Reduced polarization for initial Mg redeposition

N. Hahn et al. 2015 submitted

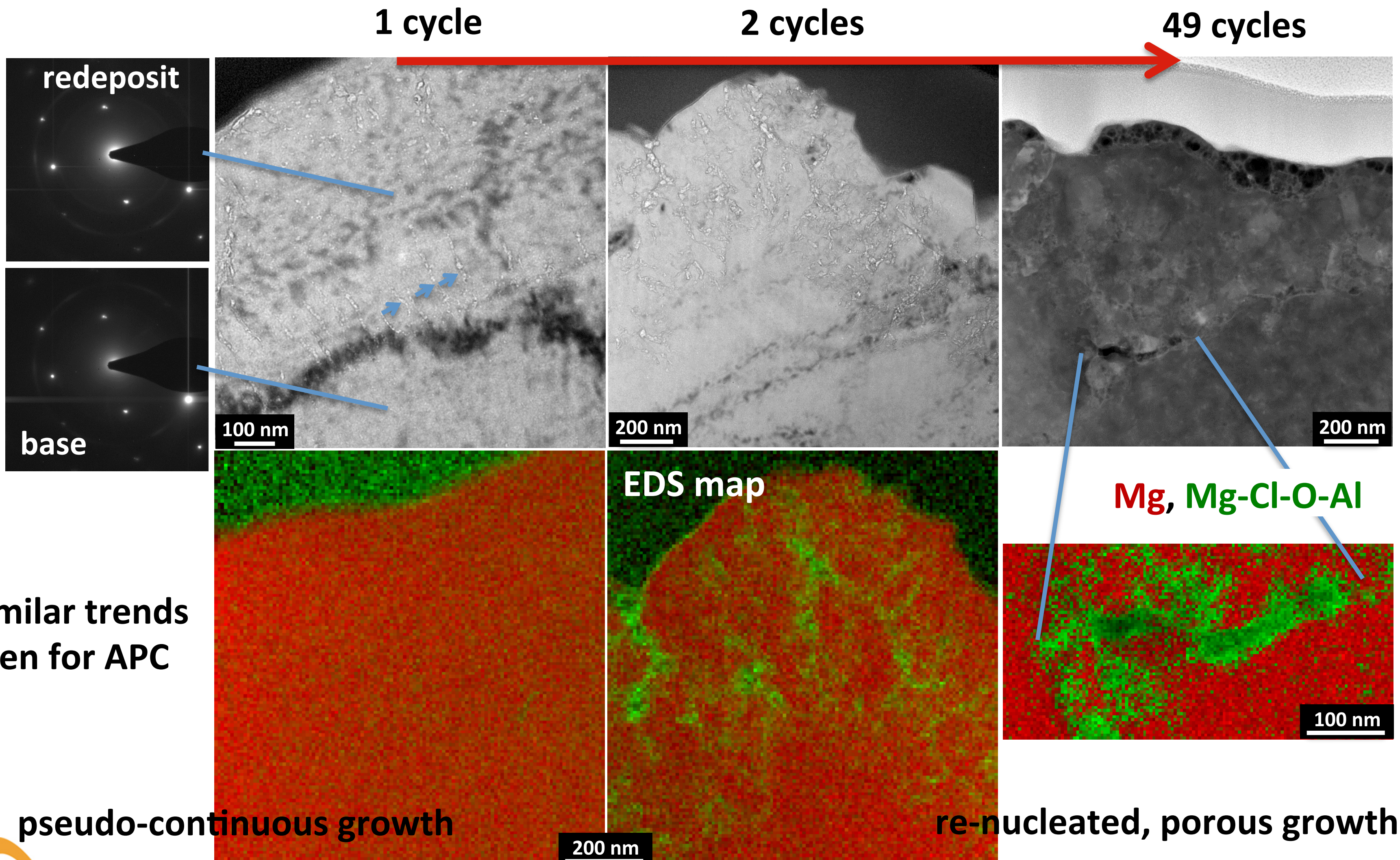
Mg deposition and dissolution are asymmetric processes in the chloroaluminates

nanostructure evolves on the facets during dissolution at 2 mA/cm^2



starting point for cycling: enhanced surface area – lower true current density
increased defects – enhanced nucleation & early stage growth

Evolution of the Interface in MACC with Continuous Cycling

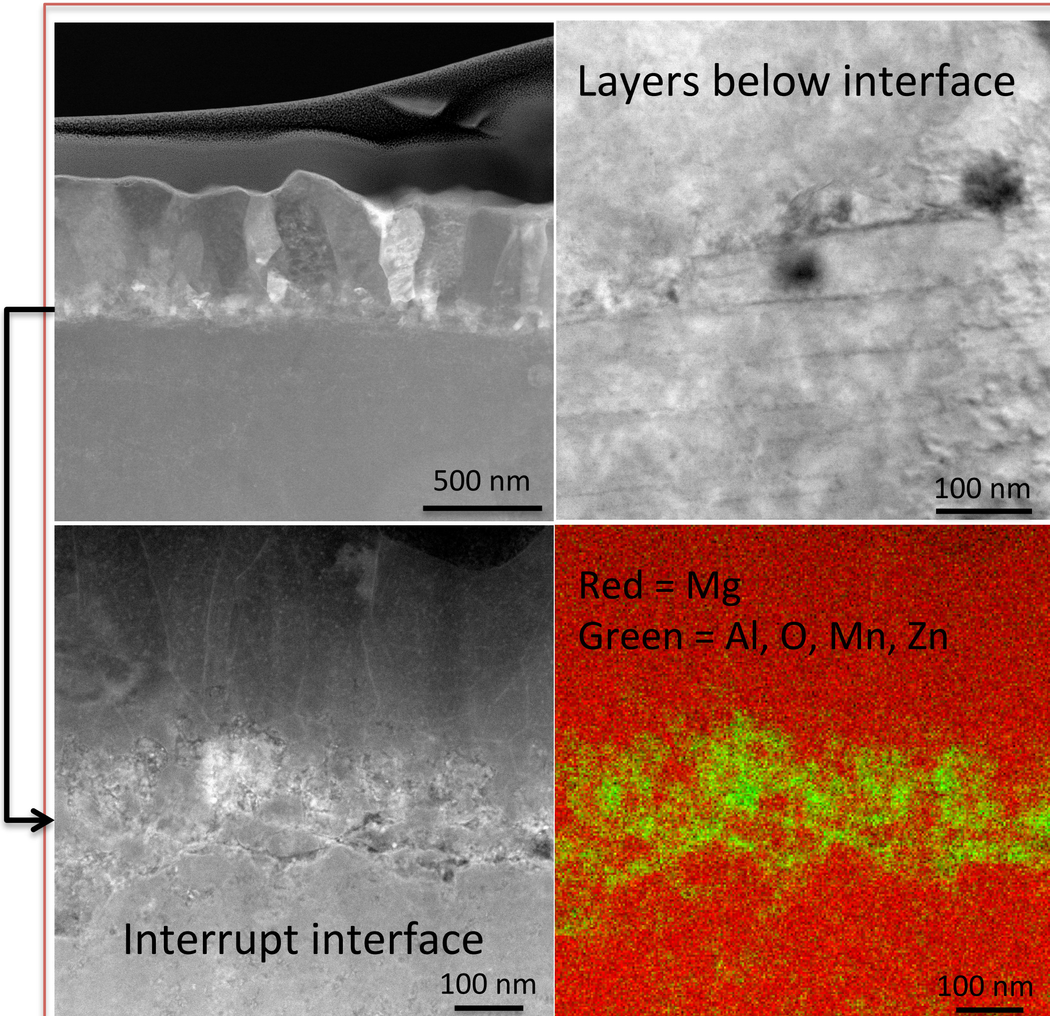


Similar trends seen for APC

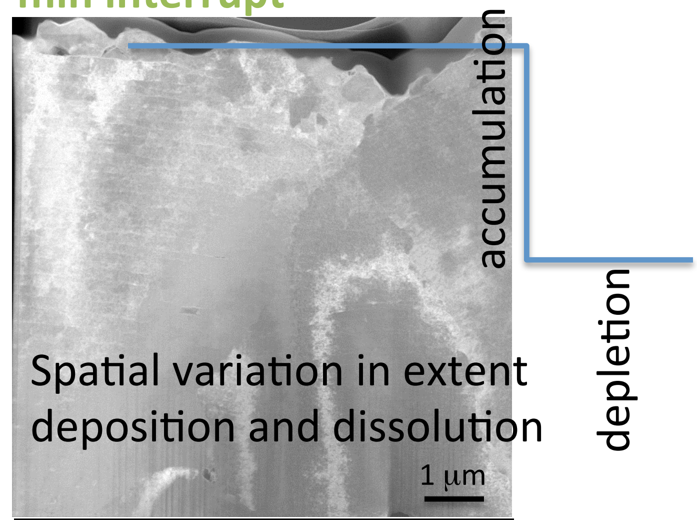
N. Hahn et al. 2015 submitted

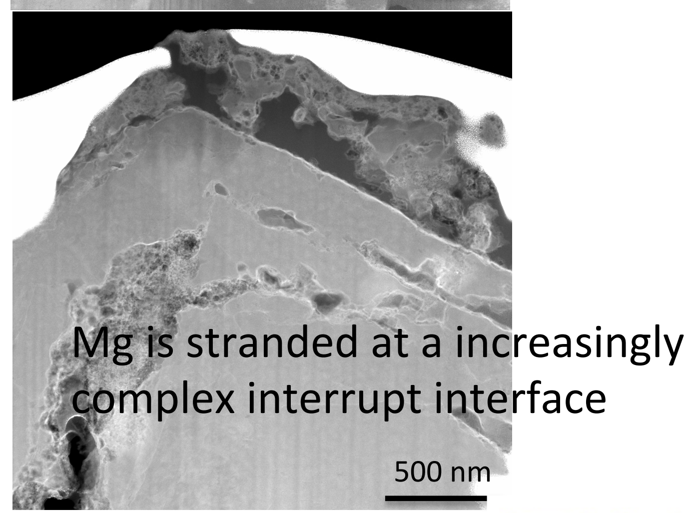
Discontinuous cycling produces stranded Mg

APC @ 50 cycles with 30 min interrupt



MACC: @ 50 cycles with 30 min interrupt



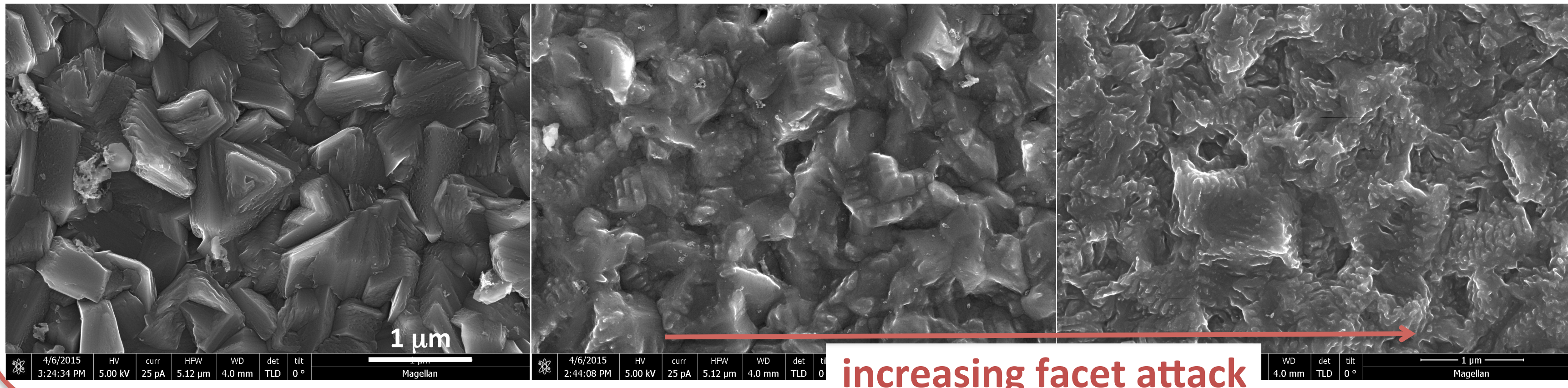


Dissolution morphology appears independent of rate within the relevant current density window

APC: 1 μm Mg:Au high rate strip (6 mA/cm²)

- 50 nm

- 100 nm



MACC: 2 μm Mg:Au strip 200 nm

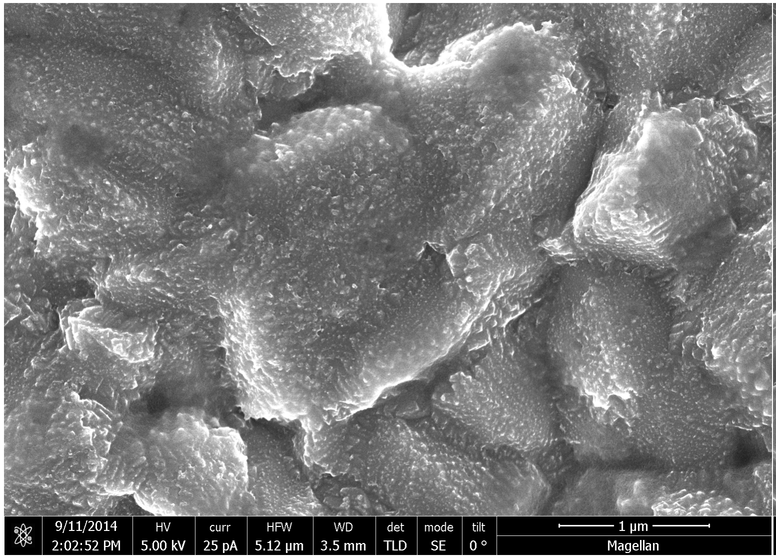
2 mA/cm²

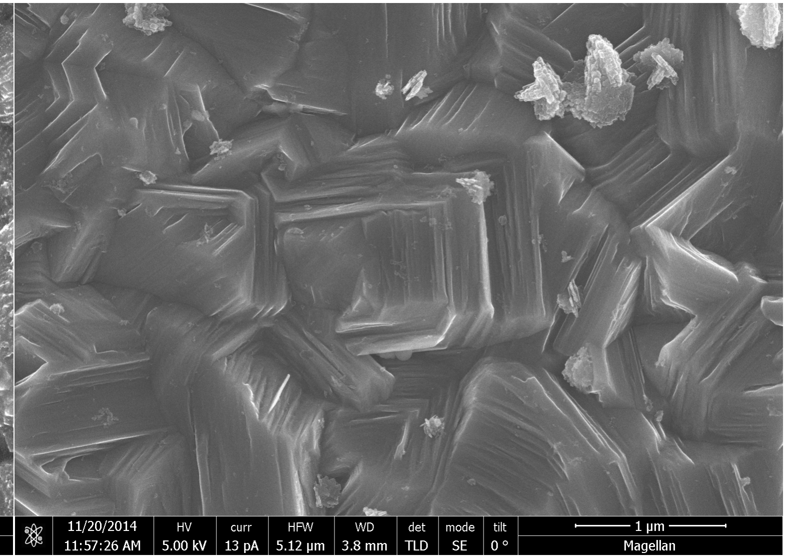
1 mA/cm²

0.5 mA/cm²

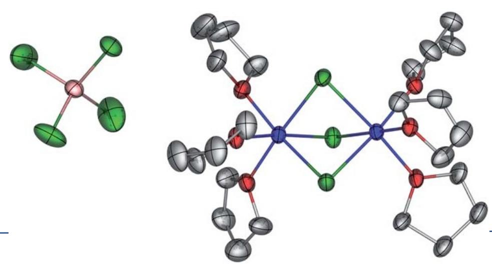
Kinetic roughening is an attribute of slow complexation reaction for Mg^{2+}_{solv}

MACC:THF @ 2 mA/cm^2 | 200 nm strip | $MgTFSI_2$:Diglyme @ 1.4 mA/cm^2

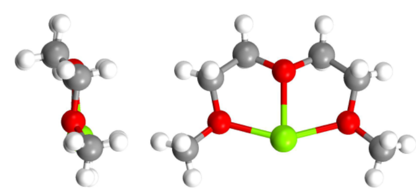




$$Mg \rightarrow Mg^{2+}_{ads}$$
$$Mg^{2+}_{ads} + Cl^- + nTHF \rightarrow MgCl^+{:}THF_n$$
$$MgCl_2 \leftrightarrows MgCl^+ + Cl^-$$
$$2MgCl^+{:}THF_n + Cl\text{-} + nTHF \leftrightarrows Mg_2Cl_3^+{:}THF_n$$



$$Mg \rightarrow Mg^{2+}_{ads}$$
$$Mg^{2+}_{ads} + 2G2 \rightarrow Mg^{2+}{:}2G2$$
$$Mg^{2+}{:}2G2 + TFSI^- \leftrightarrows MgTFSI^+{:}G2 + G2$$

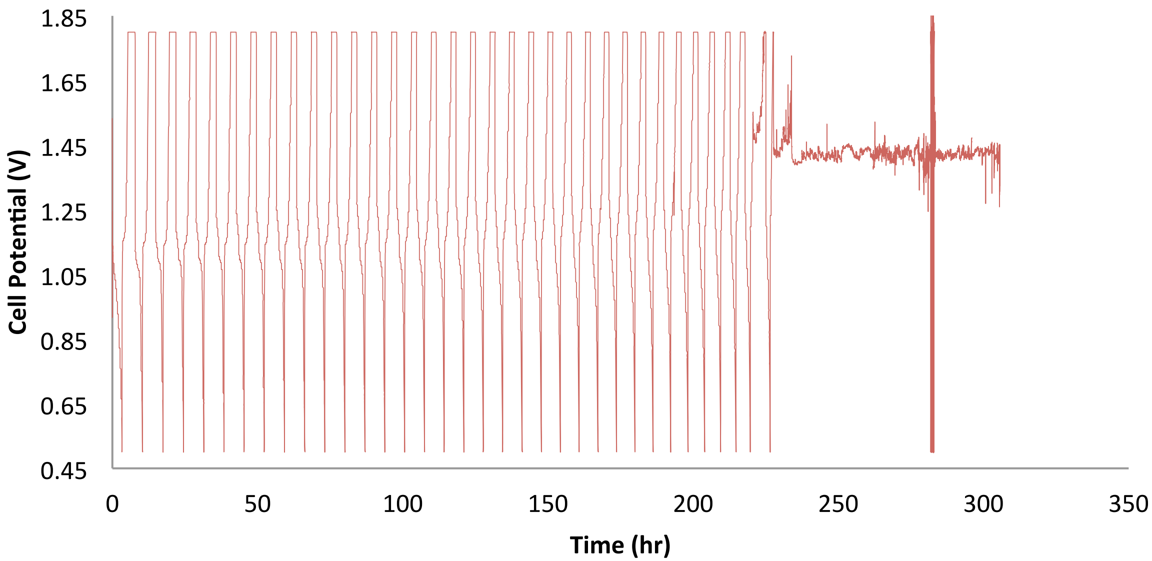


G2 chelation of Mg^{2+}

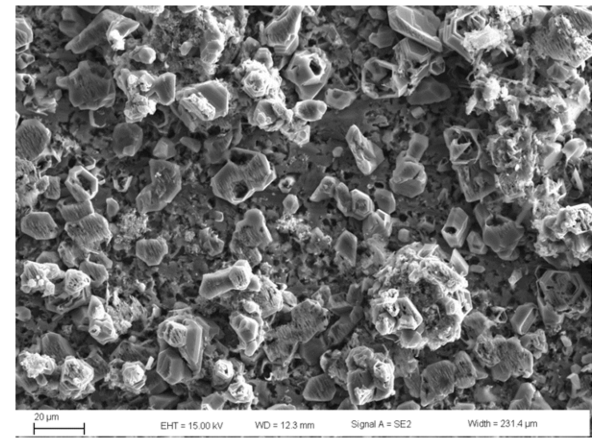
Loss of mechanical cohesion of Mg – capacity loss through electrical isolation

Chloroaluminate electrolyte can fail with cycling

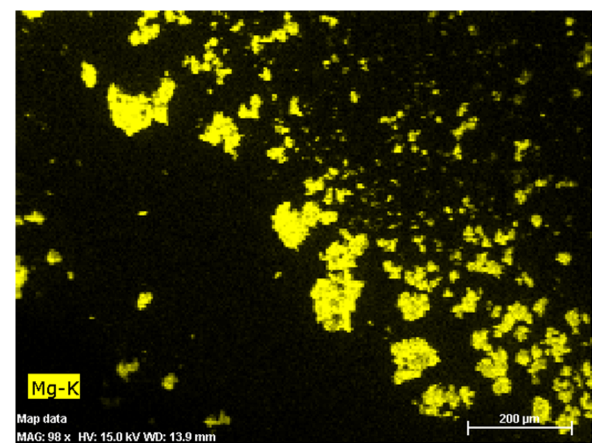
$Mg|Mg^{2+}$, APC | Mo_6S_8



Mg anode after cycling



Anode side of separator after cycling



B. Perdue, SNL

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Conclusions

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  - These films are not benign – they direct structure evolution
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  - Film and electrolyte incorporation, voiding, and porosity
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Acknowledgements

Nathan Hahn, Katie Harrison, SNL
David Wetzel, Marvin Malone, Ralph Nuzzo, UIUC

Chris Barile, Russell Spatney, Andy Gewirth, UIUC

Stephen Dewitt, Katsuyo Thornton, U Mich

Mukesh Bachhav, Emmanuelle Marquis, U Mich

Kevin Gallagher, ANL

Experimental Team: P. Kotula, T. Alam, M. Brumbach, T. Ohlhausen, M. Rye, D. Grant, SNL