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Origins of Non-ideal Coulombic Efficiency in Magnesium Electrodeposition and Electrodissolution

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Sandia National Laboratories

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Switching the Working Ion to Mg and to Metals

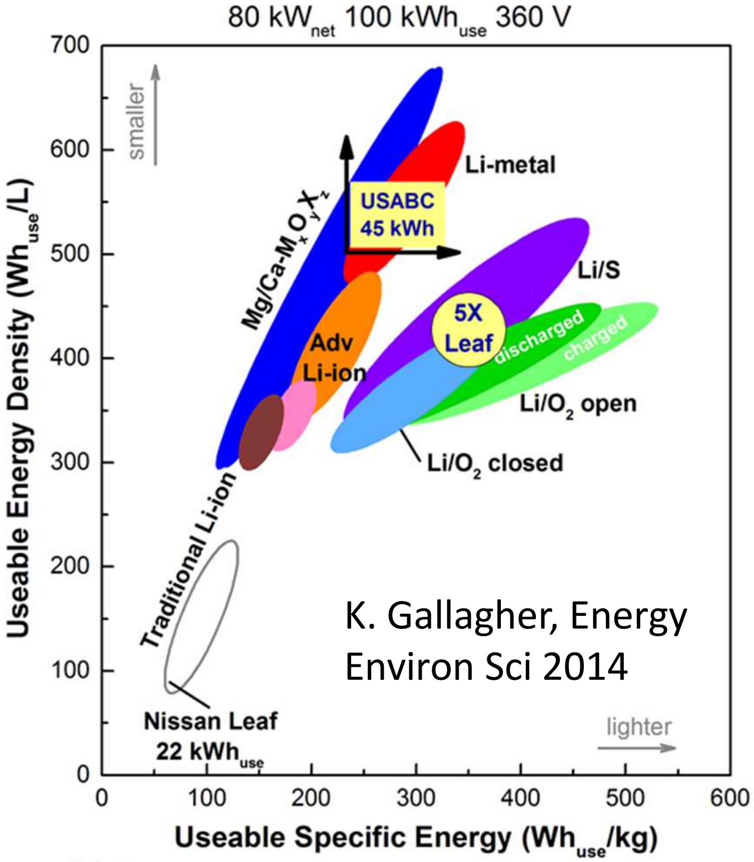
Advantages of Mg:

- 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



K. Gallagher, Energy Environ Sci 2014

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

Anode Dimensional Control is Required at High Rates and Capacities

$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

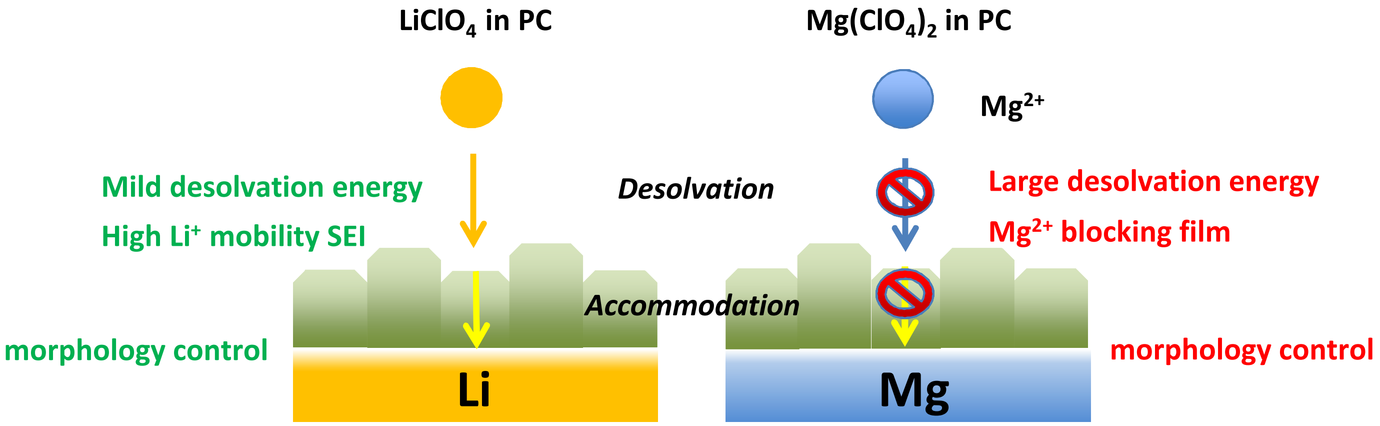
high rates of metal transformation!

Metal Anode Challenges

Technical challenge

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

Li vs. Mg Anode Plating

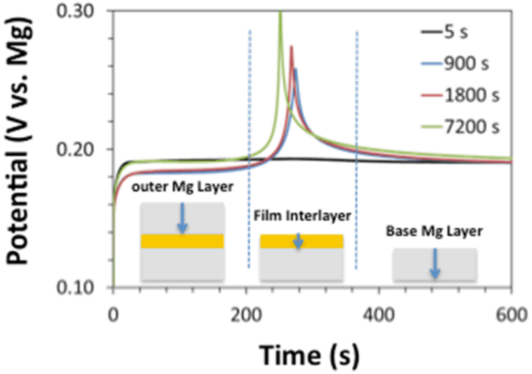


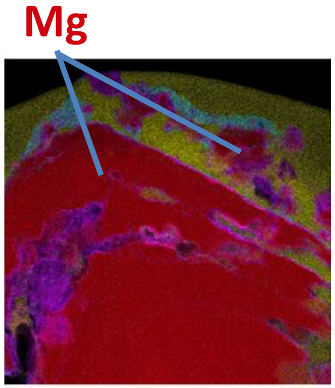
Science challenges and research

- Efficient cation desolvation
- Efficient cation accommodation – cathode & anode
- Electrolyte stability
- Metastability - Activation, Corrosion, Protection

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



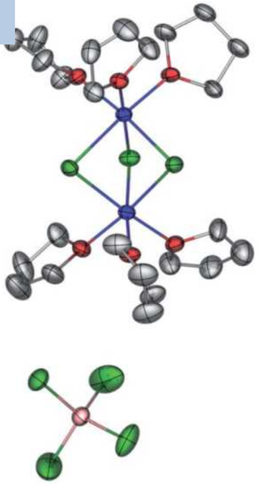


Mg Chloro Complex Forming Electrolytes

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

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

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



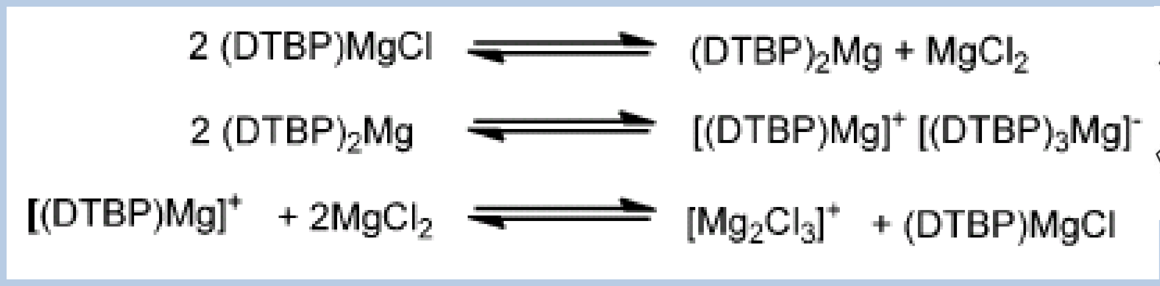
Magnesium Aluminum Chloride Complex (MACC): 2 $MgCl_2:AlCl_3$ in THF or DME

R. Doe et al., *Chem Comm* 2014; C. Barile et al., J Phys Chem C 2014

$$2MgCl_2 + AlCl_3 \rightarrow Mg_2Cl_3^+ + AlCl_4^-$$

Lewis acid – free Alkoxide Magnesium Chloride : $ROMgCl:MgCl_2$ in THF

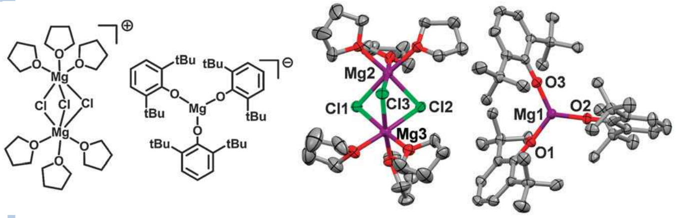
B. Pan et al., *Chem Comm* 2015



$$2\,(DTBP)MgCl \rightleftharpoons (DTBP)_2Mg + MgCl_2$$

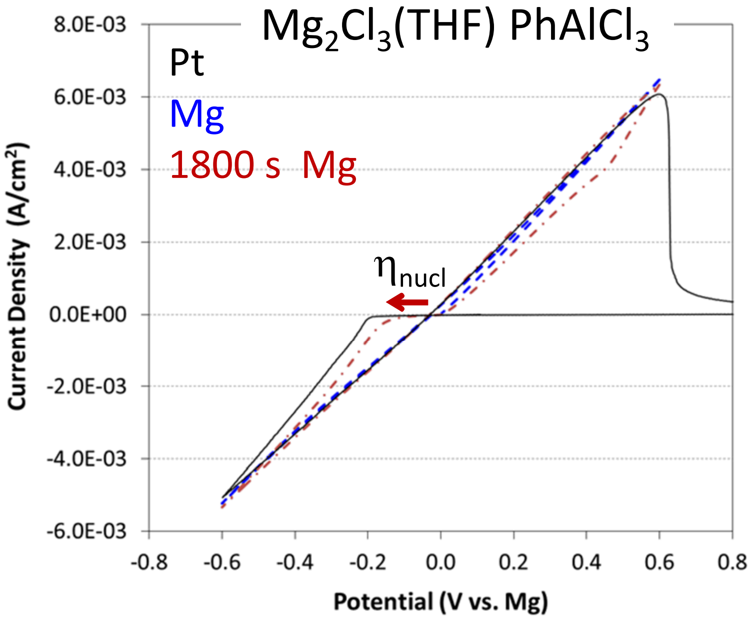
$$2\,(DTBP)_2Mg \rightleftharpoons [(DTBP)Mg]^+\,[(DTBP)_3Mg]^-$$

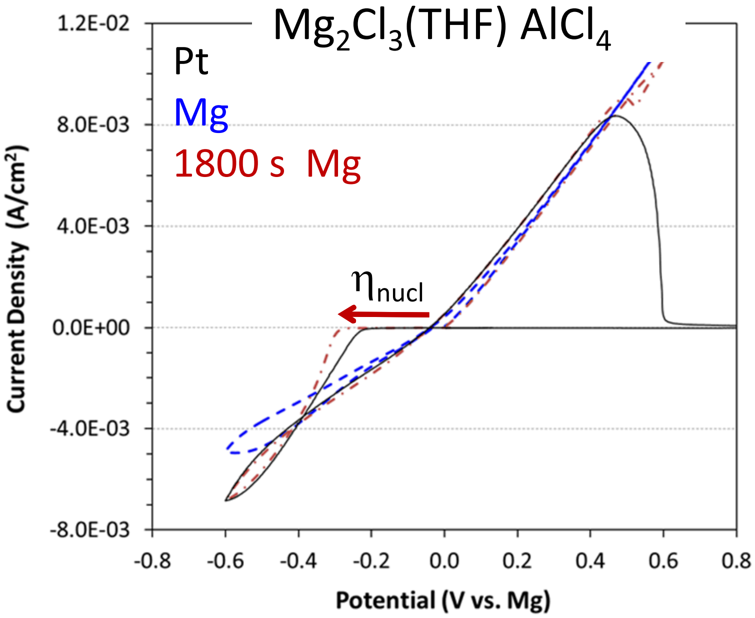
$$[(DTBP)Mg]^+ + 2MgCl_2 \rightleftharpoons [Mg_2Cl_3]^+ + (DTBP)MgCl$$

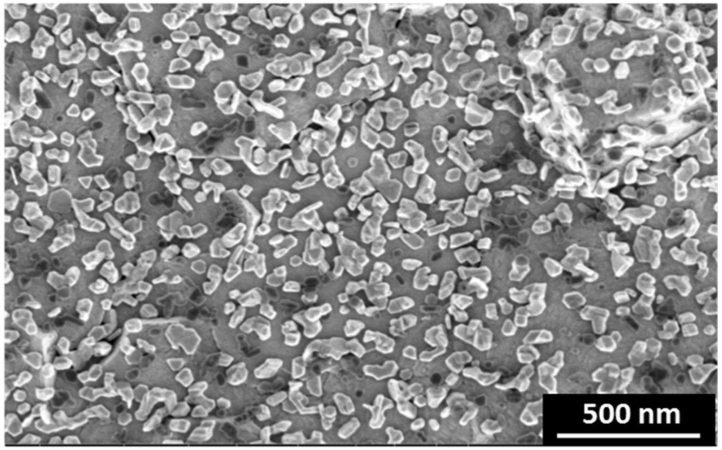


Multimers may define bulk speciation $Mg_2Cl_3^+(THF)_n$

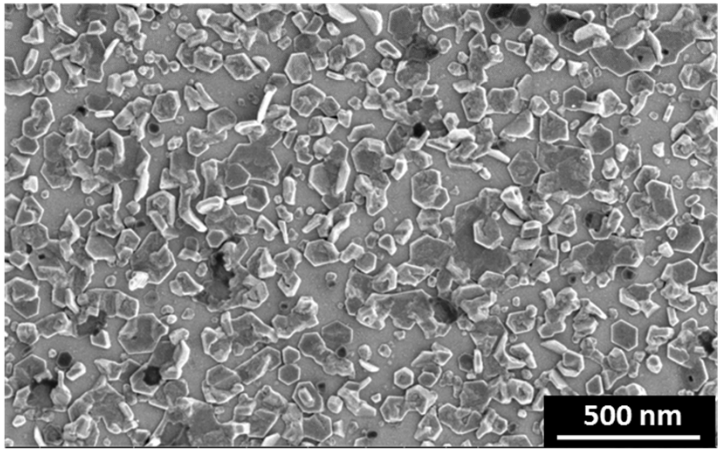
Mg re-nucleation is required at the filmed interface







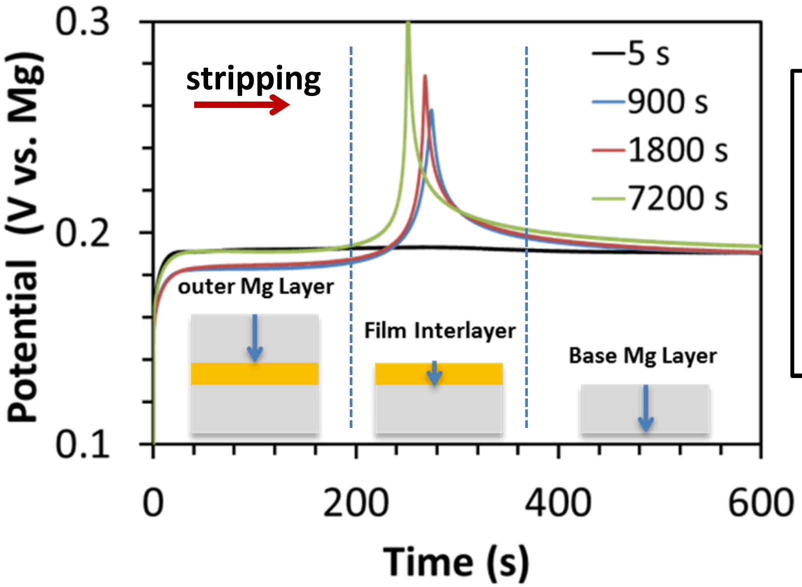
Mg on 1800 s equilibrated Mg

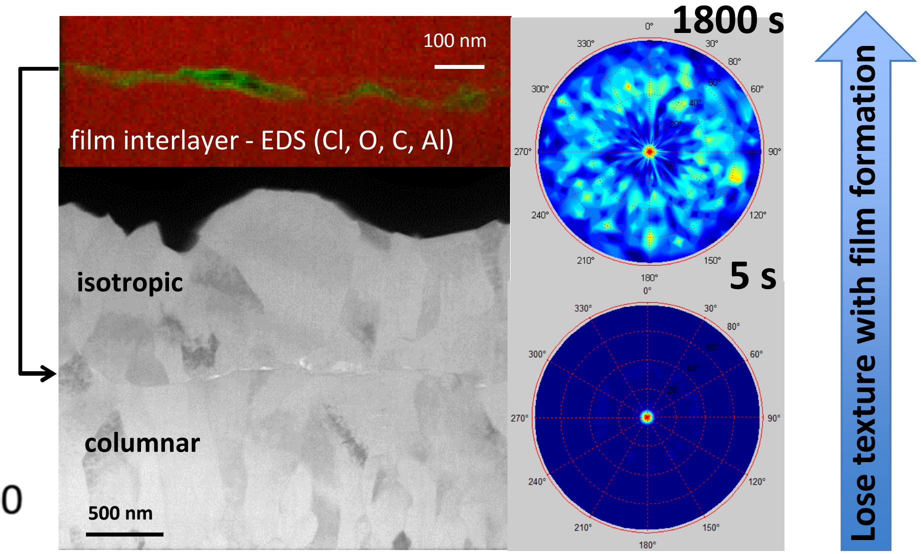


Mg on clean Au

N. Hahn et al. 2015 submitted

The filmed interface directs subsequent Mg growth



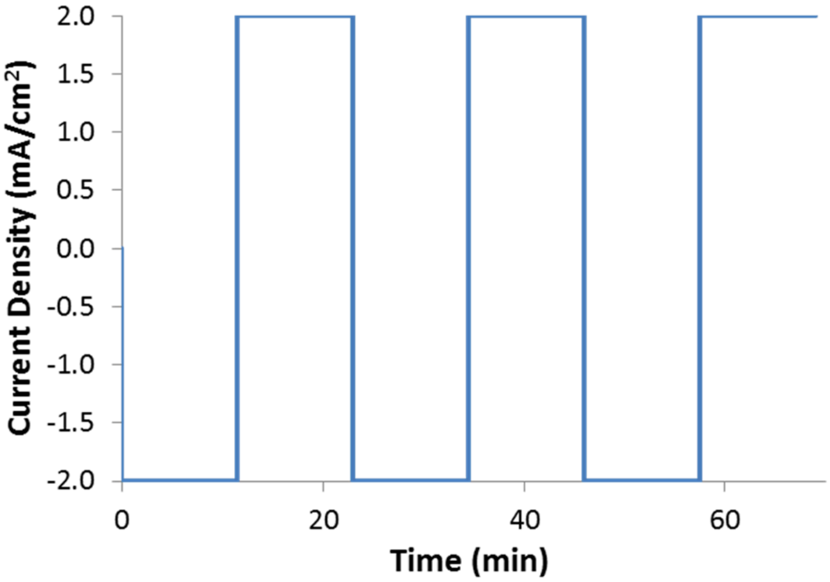


Surface films form in chloroaluminate electrolytes

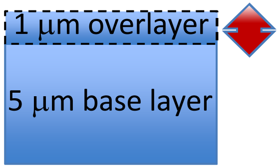
- Protective – reduce self-discharge to < 2 nm/hr
- Directive – direct morphology development of the subsequent Mg deposit
- Disruptive – filmed interface incorporates - mechanical flaws within the deposit
- May contribute to incoherent Mg deposition observed in JCESR Mg prototype cells

N. Hahn et al. 2015 submitted

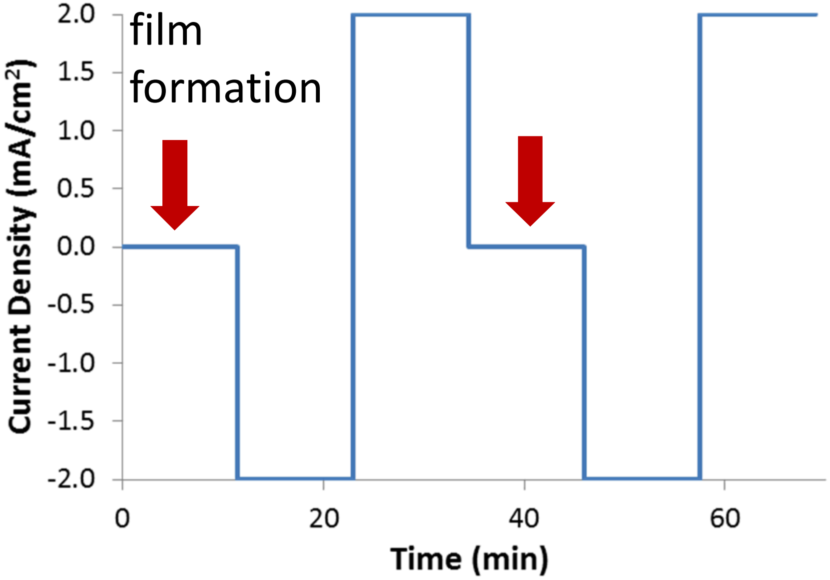
Probing the Performance Impact of a Film



continuous cycling



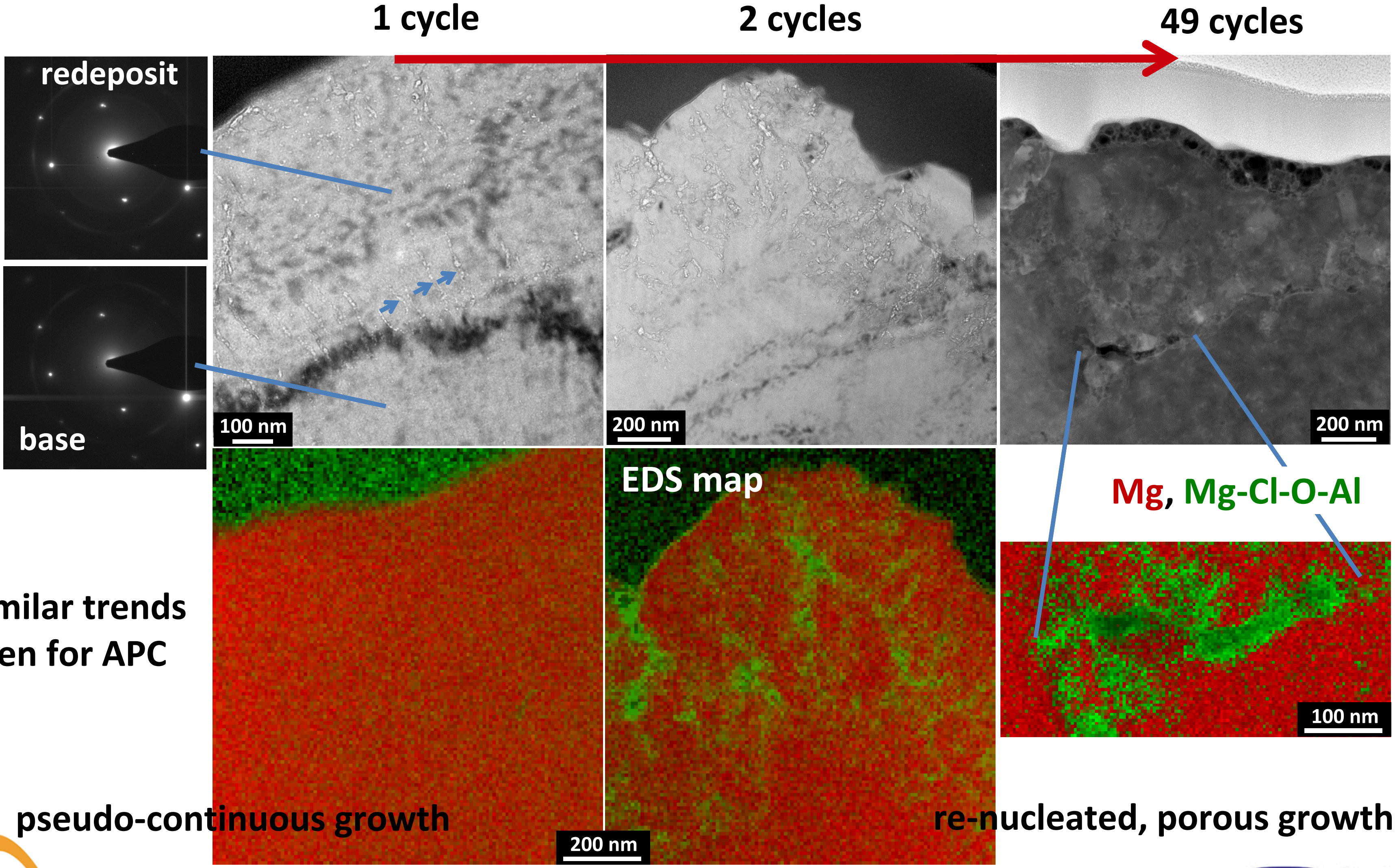
50 cycles @ 2 mA/cm^2



discontinuous cycling

CE = Qstrip/(cycles x Qdeposit)

Evolution of the Interface in MACC with Continuous Cycling



Similar trends seen for APC

pseudo-continuous growth

re-nucleated, porous growth

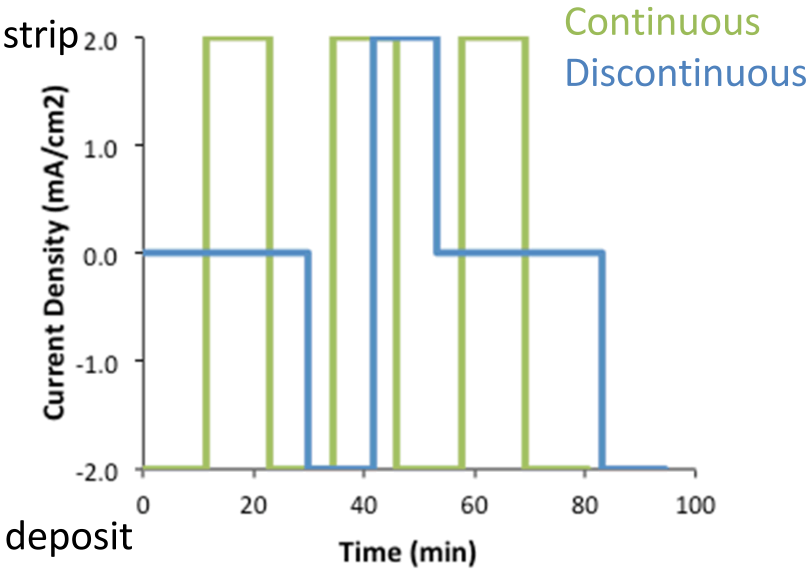
N. Hahn et al. 2015 submitted

Quantifying the Impact of Surface Films

	Coulombic Efficiency, %			
Electrolyte	**Single cycle**	**50 cycles continuous**		**50 cycles with 1800 s interrupt**
APC	99.7	99.3	→	97.4
MACC	99.2	99.2	→	98.1
ROMgCl	99.6	97.0	→	92.7

Efficiency is maintained with continuous cycling

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

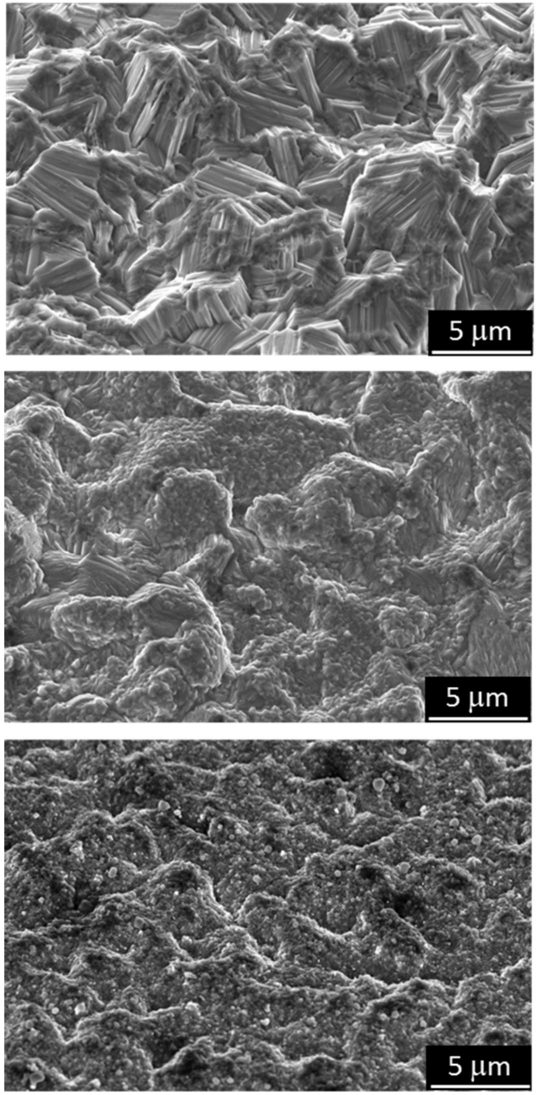


Variation in Coulombic Efficiency with an Introduced Surface Film

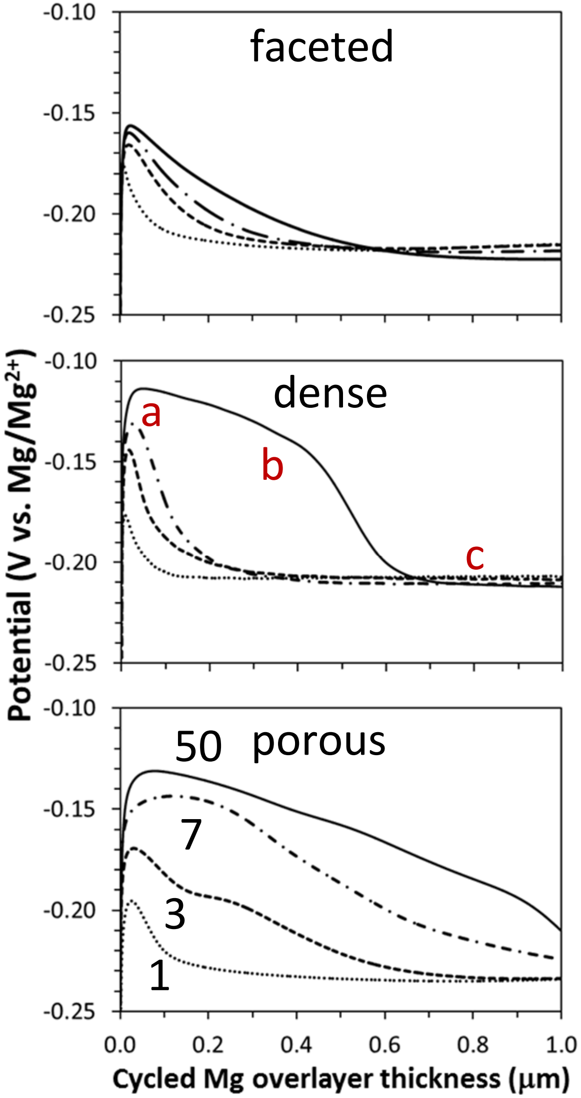
Electrolyte	Structure	Control	50 cycles continuous	30 min, 50 cycles discontinuous	2 hr, 50 cycles discontinuous
APC	faceted	99.7 ± 0.3	100.2 ± 0.3	100.0 ± 0.1	96.6
	dense	99.4 ± 0.2	99.4 ± 0.1	99.3 ± 0.1	97.3
	porous	99.4 ± 0.3	99.0 ± 0.5	98.1 ± 0.9	96.9
MACC	faceted	100.3 ± 0.2	----	99.9 ± 0.1	----
	dense	99.6 ± 0.2	99.4 ± 0.3	97.8 ± 0.2	----
	porous	99.1 ± 0.2	98.9 ± 0.3	98.2 ± 0.1	----
TBMC	faceted	99.6 ± 0.1	99.6 ± 0.1	99.3 ± 0.1	99.0

Films also impact structure during the dissolution phase

redeposit morphology



redeposit traces



re-deposition tracks the consumption of surface defects:

a - low η with kink and step infill

b – η increase with transition to step flow

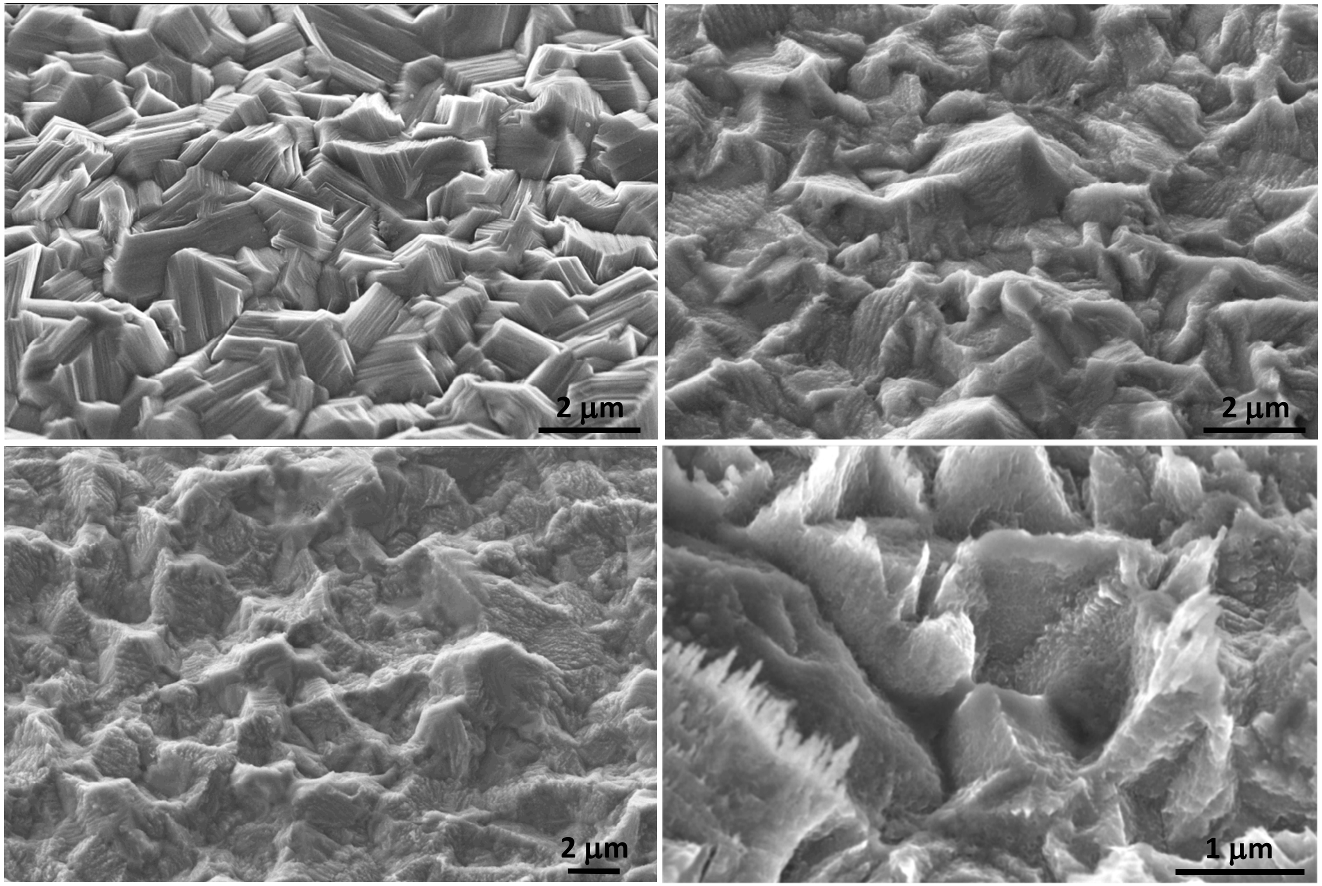
c – resumption of step flow at critical facet size

Surface films can passivate select facets

stop on the dissolution half cycle

faceted: base

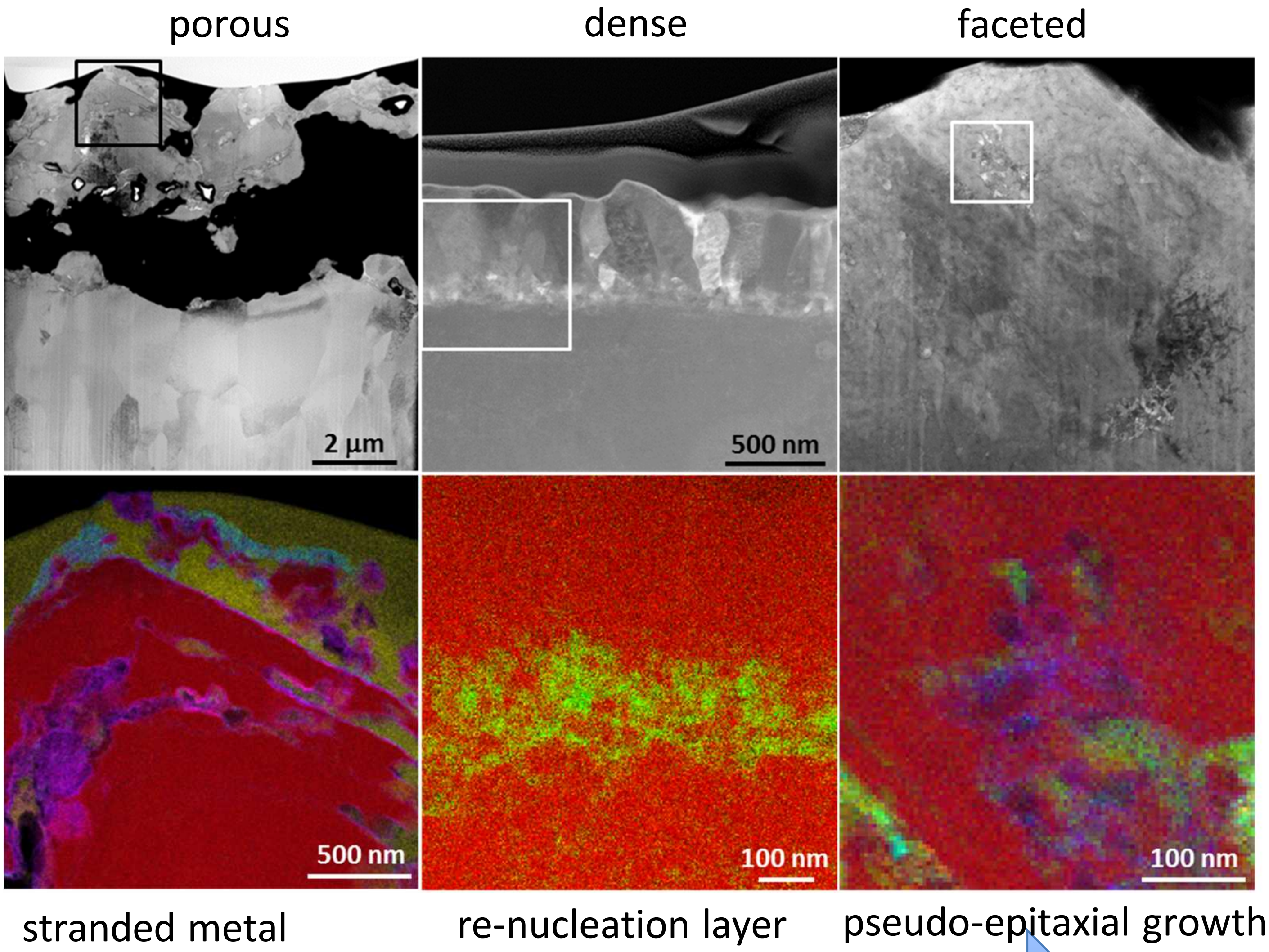
faceted: 1 cycle



dense: 8 cycles

porous: 1 cycles

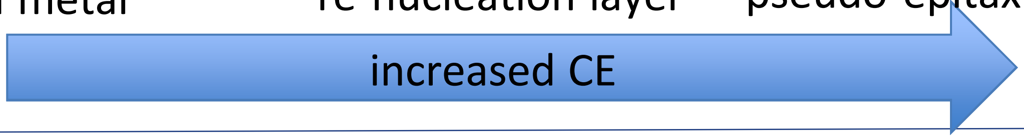
Structure Evolution with Discontinuous Cycling



stranded metal

re-nucleation layer

pseudo-epitaxial growth



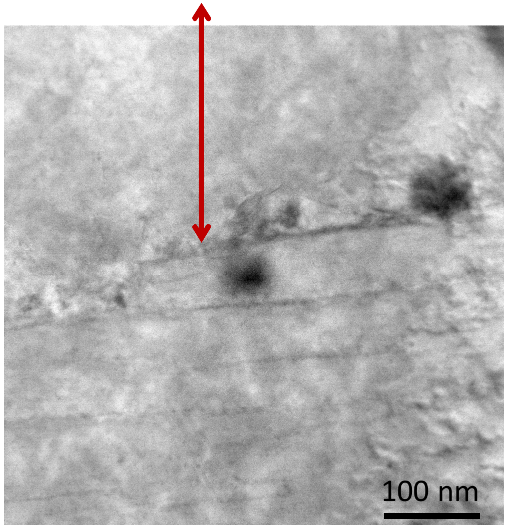
99%

100%

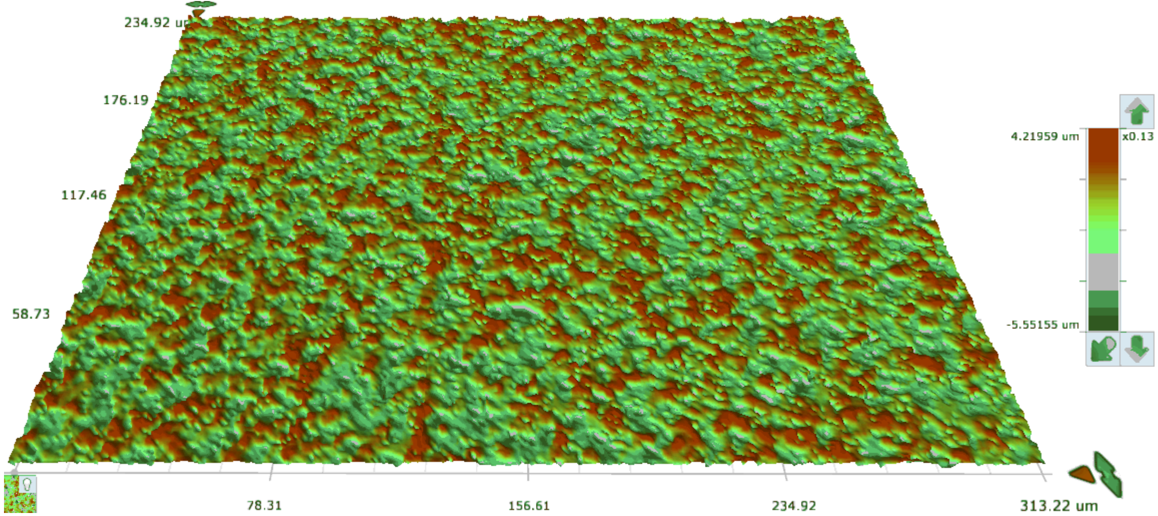
Evidence for Large Scale Loss of Dimensional Control

APC @ 50 cycles with 30 min interrupt

final 1 µm thick re-deposit layer



9 µm variation in height



regions of net accumulation and removal

Conclusions

- 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
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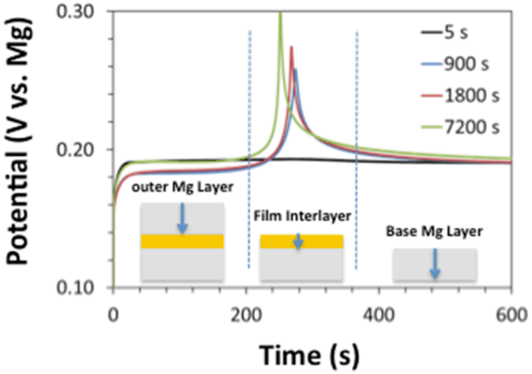
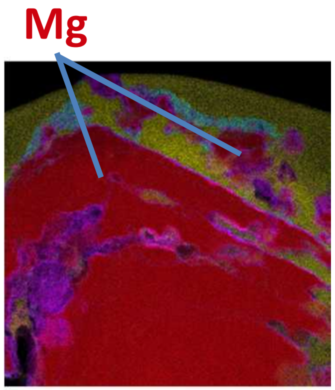
    - Stranded Mg – electrical and structurally isolated





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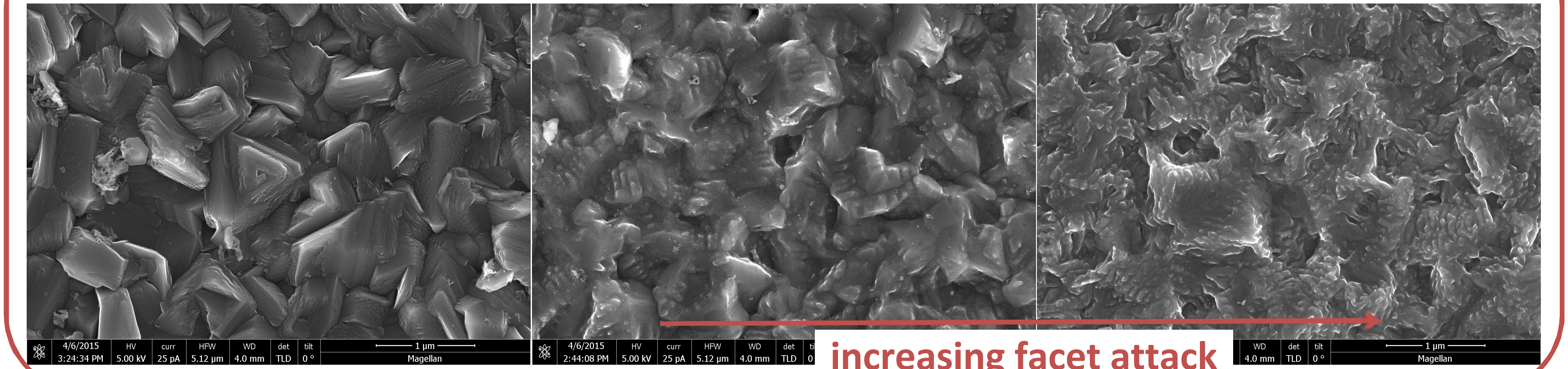
Experimental Team: P. Kotula, T. Alam, M. Brumbach, T. Ohlhausen, M. Rye, D. Grant, SNL

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

APC: 1 μm Mg:Au high rate strip (6 mA/cm^2)

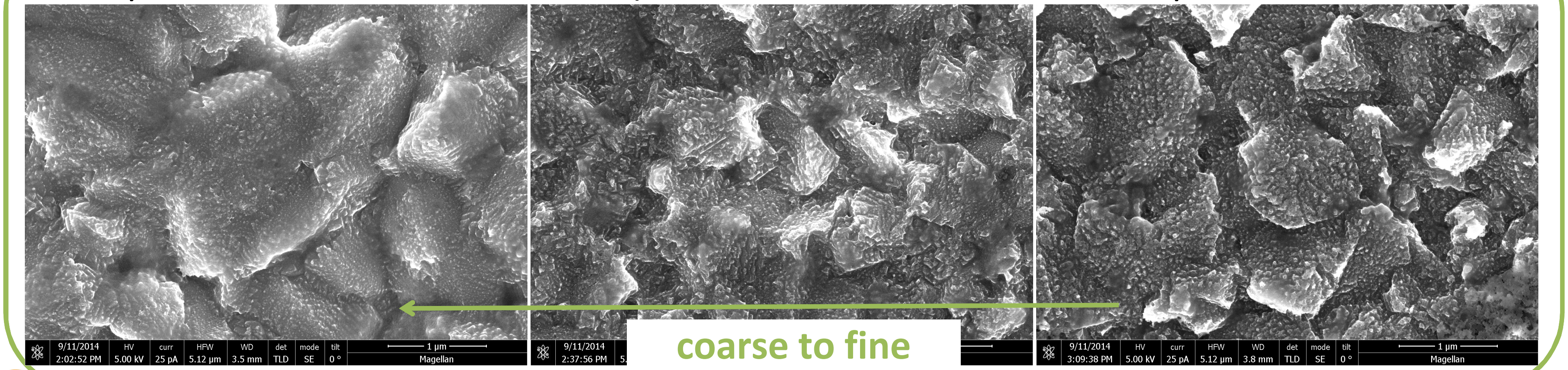


- 50 nm

- 100 nm

increasing facet attack

MACC: 2 μm Mg:Au strip 200 nm



2 mA/cm^2

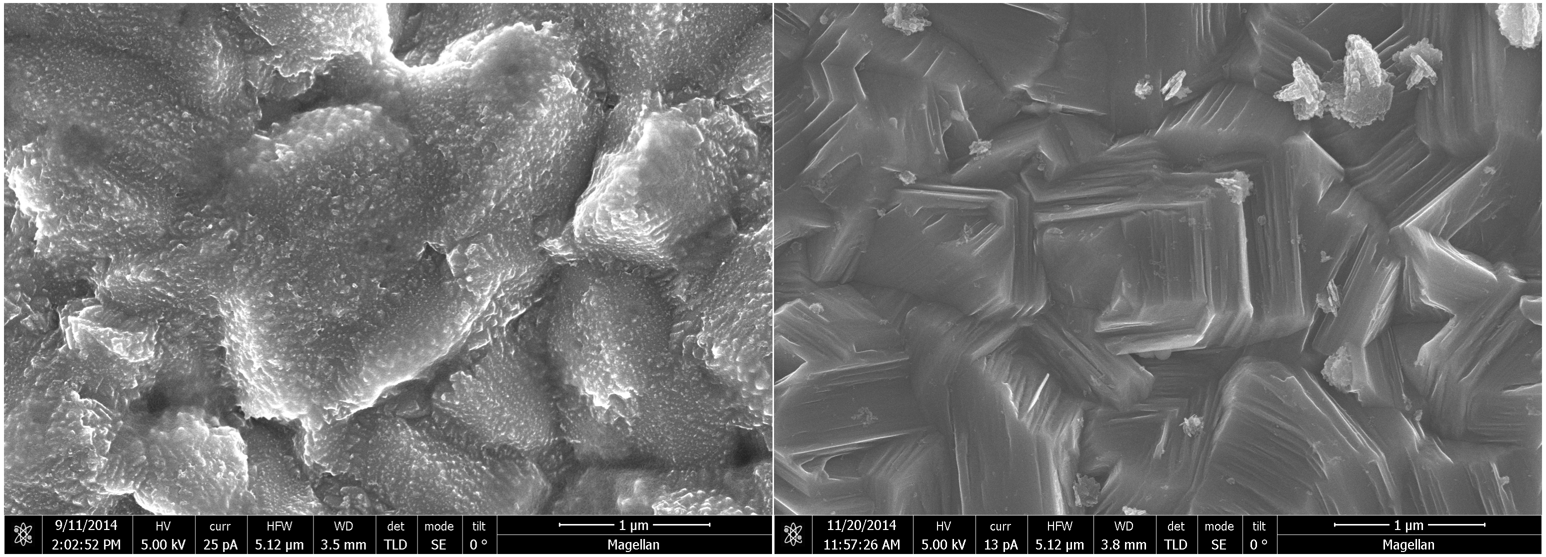
1 mA/cm^2

0.5 mA/cm^2

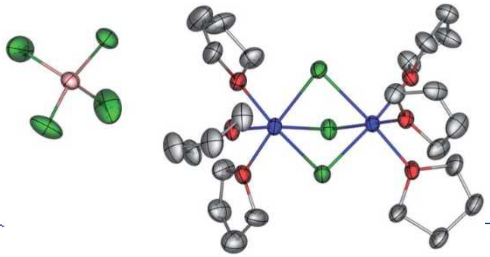
coarse to fine

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

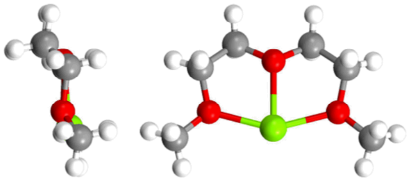
MACC:THF @ 2 mA/cm^2 200 nm strip MgTFSI$_2$:Diglyme @ 1.4 mA/cm^2



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



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

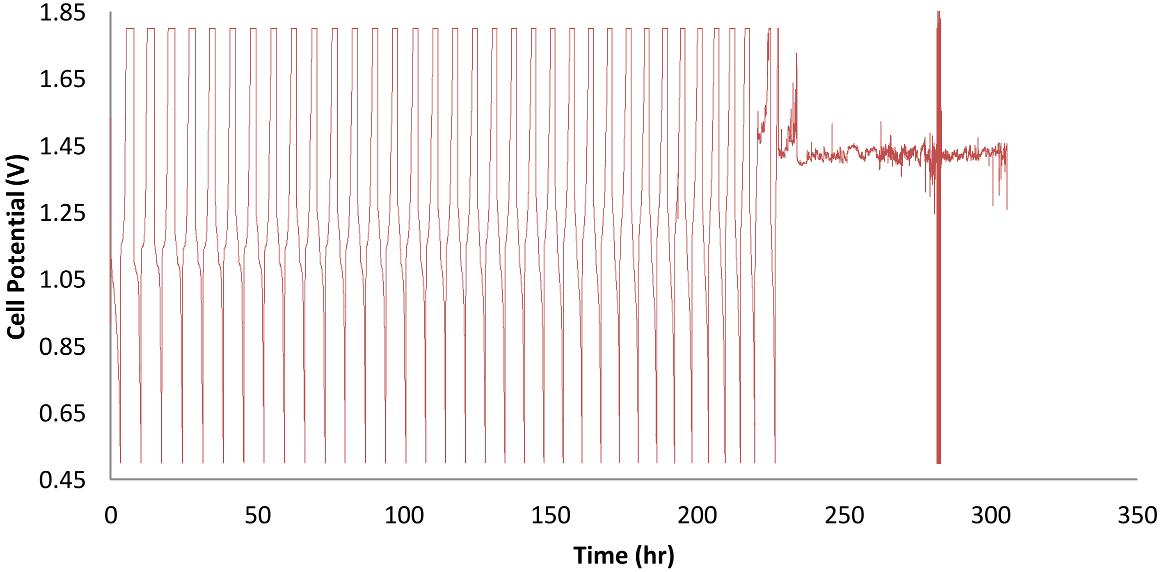


G2 chelation of Mg^{2+}

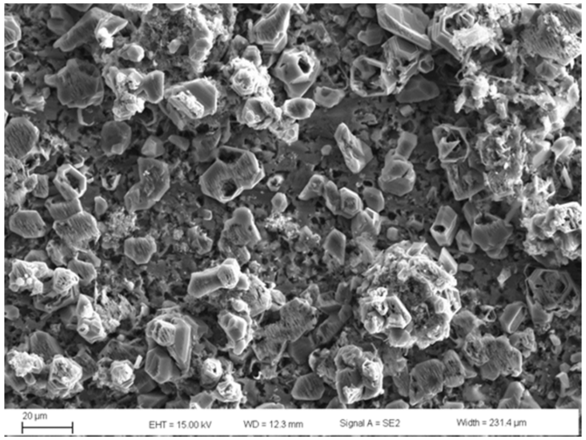
Loss of mechanical cohesion of Mg – capacity loss through electrical isolation

Chloroaluminate electrolyte can fail with cycling

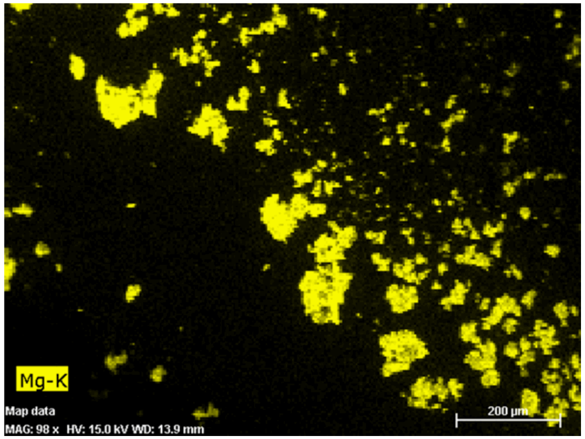
Mg|Mg^{2+}, APC | Mo_6S_8



Mg anode after cycling



Anode side of separator after cycling



B. Perdue, SNL