SAND2014-20174C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Alkaline Earth Metal Anodes for Energy Storage – Understanding the Limits of Efficient Electrodeposition/Dissolution

K.R. Zavadil

Sandia National Laboratories

MRS Fall, December 1 -5, 2014

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.

JCESR: Energy Innovation Hub with Transformative Goals

TRANSPORTATION

$100/kWh

400 Wh/kg 400 Wh/L

800 W/kg 800 W/L

1000 cycles

80% DoD C/5

15 yr calendar life

EUCAR

GRID

$100/kWh

95% round-trip
efficiency at C/5 rate

7000 cycles C/5

20 yr calendar life

Safety equivalent to a
natural gas turbine

Vision

Transform transportation and the electricity grid with high performance, low cost energy storage

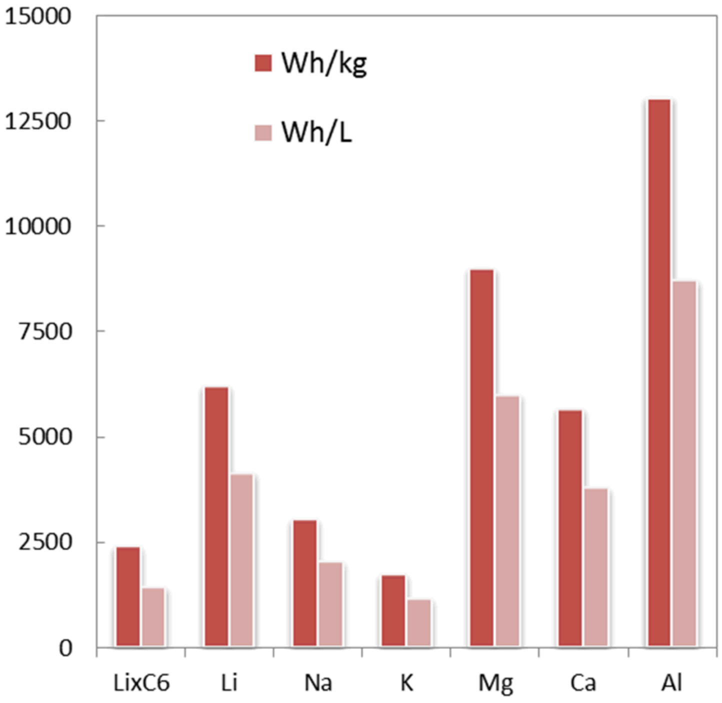
Mission

Deliver electrical energy storage with five times the energy density and one-fifth the cost of today's commercial batteries within five years

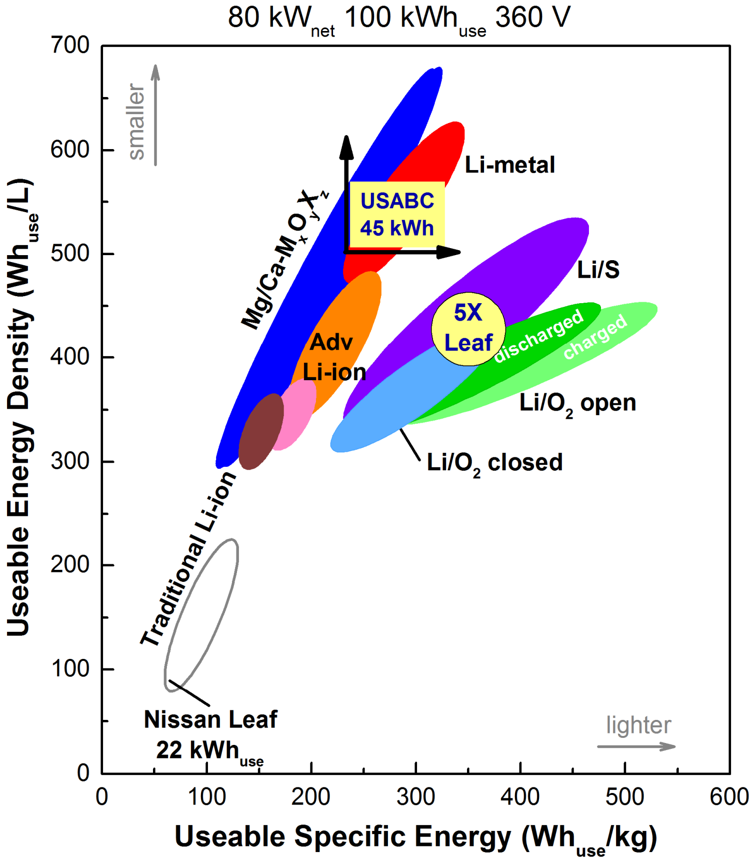
Legacies

- **A library of the fundamental science** of the materials and phenomena of energy storage at atomic and molecular levels
- **Two prototypes, one for transportation and one for the electricity grid**, that, when scaled up to manufacturing, have the potential to meet JCESR's transformative goals
- **A new paradigm for battery R&D** that integrates discovery science, battery design, research prototyping and manufacturing collaboration in a single highly interactive organization

Metal Anodes are the Key to Increased Energy Density



System Analysis



Techno-economic model:

3 V insertion cathode (750 Wh/kg), 50% excess Mg → $100 /kWh, 500 Wh/l

System Level Requirements for Metal Anodes

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

Lithium - Sulfur		**Magnesium - MX_y**	
target areal capacity	10 mAh/cm^2	target areal capacity	6 mAh/cm^2
anode active loading	2.6 mg/cm^2	anode active loading	2.7 mg/cm^2
anode thickness	49 μm	anode thickness	16 μm
cathode specific capacity	1200 mAh/g	cathode specific capacity	250 mAh/g
cathode active loading	8.3 mg/cm_2	cathode active loading	24 mg/cm_2
cathode thickness	139 μm	cathode thickness	100 μm

49 μm of Li

large quantity of metal to move!

16 μm of Mg

Pulse power c.d.	10 mA/cm^2	Pulse power c.d.	6 mA/cm^2
Cont. power c.d.	1.5 mA/cm^2	Cont. power c.d.	0.9 mA/cm^2
L3 charger c.d.	6 mA/cm^2	L3 charger c.d.	3.6 mA/cm^2
Super charger c.d	12 mA/cm^2	Super charger c.d.	7.2 mA/cm^2

10 mA/cm^2 of Li

high rates of metal transformation!

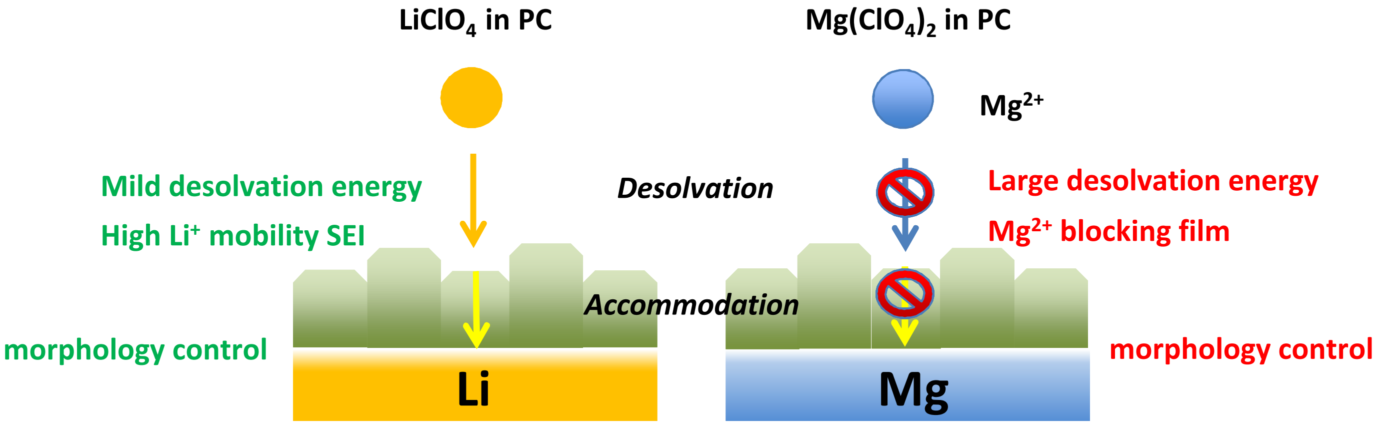
6 mA/cm^2 of Mg

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

Li vs. Mg Anode Plating



Science challenges and research

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

Mg Electrolyte Roadmap

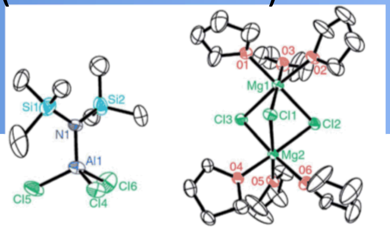
Lewis Acid – Base Complexes

Al-, B-hydrides 1957

Acid/base derived Organo-Mg complexes
Gregory 1990

Mg Organochloroaluminates
RMgX + $AlCl_3$
(Aurbach 2000, 2008)

Eliminating the organic radical
R_2NMgX + $AlCl_3$
(Muldoon 2011)



Inorganic source of Mg
$MgCl_2$ + $AlCl_3$
(Aurbach 2014)

Replace the Lewis acid
$MgCl_2$ + **BR_3**
(Muldoon 2013)

stabilizing the Lewis acid toward oxidation

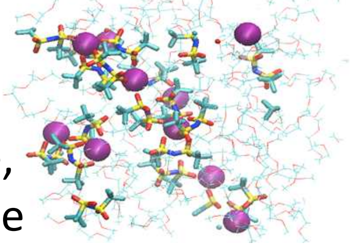
identifying critical speciation - controlling anode morphology

Conventional solvent/salt – *understanding speciation provides new design rules to guide electrolyte discovery*

Competitive coordination
$Mg(BH_4)_2$ + $LiBH_4$
Competing cation to drive dissociation (PNNL 2013)

Non-directed ligand exchange
$MgTFSI_2$ + $MgCl_2$ (Pellion 2013) Anion redistribution

Simple Mg Salts
$MgTFSI_2$ in glyme, (Ha, 2014) Can we Eliminate chloride?



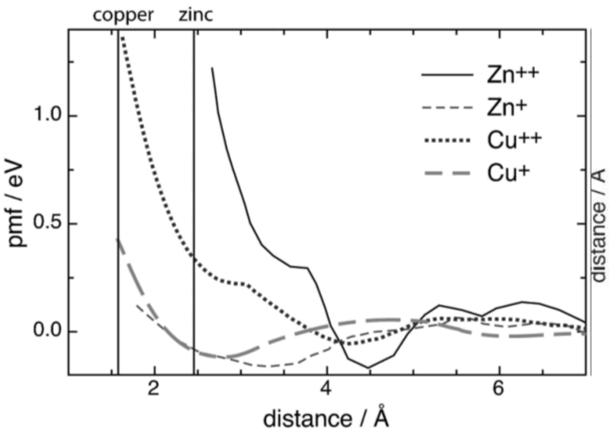
Determining the role (necessity) of halides – impact of surface films

Chloroaluminates: the $Mg_2Cl_3^+$/$MgCl^+$ Concept is Reassuring from the Desolvation Perspective

Computationally – are energies and rates consistent with known activity?

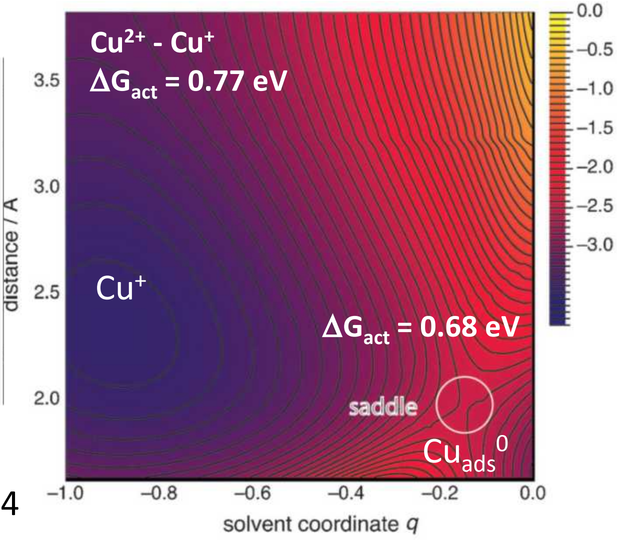
The Challenge

Interface proximity vs. desolvation energy

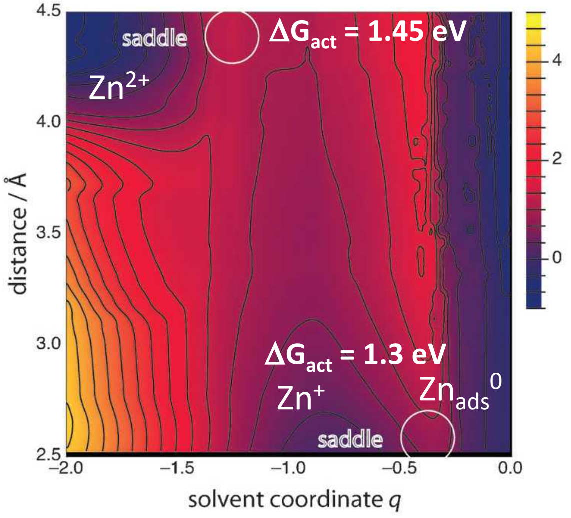


Schmickler et al. ChemPhysChem 2014

Yes for Cu2+:Cu(100)
Mod ΔG_{act}, moderate rates
Cu deposits



No for Zn2+:Zn(0001)
High ΔG_{act}, slow rates
Zn deposits



Desolvation is not the whole story
Double layer and metal surface structure not accounted for

Organometallic-free Chloroaluminate electrolytes for Mg Electrodeposition/dissolution

How Mg^{2+} is delivered for deposition in a chloroaluminate electrolyte is unresolved.

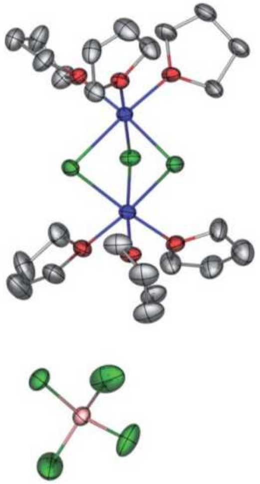
The answer is instrumental in designing electrode compatible electrolytes.

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

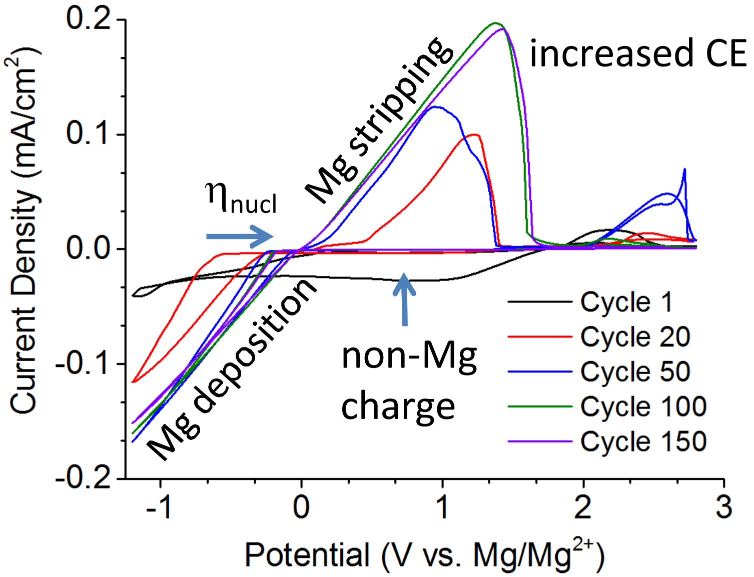
R. Doe et al., *Chem Comm* 2014

Isolation of 2 $MgCl_2$:$AlCl_3$ (THF) reaction product yields a $Mg_2Cl_3 \cdot 6THF^+$ $AlCl_4^-$ dimer complex

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

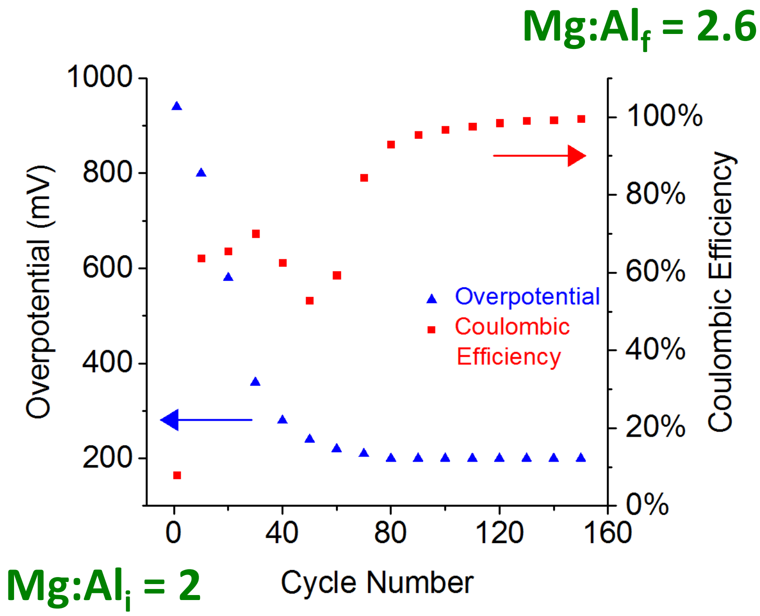


electrochemical cycling ("conditioning") is required for a functional electrolyte



C. Barile et al., 10.1021/jpc506951b

Electrolyte activity and composition are correlated



slow swept CV cycling

- produces a minimum, limiting nucleation overpotential
- produces a CE increase to 99.9%
- produces a decrease in bulk Mg:Al ratio to 2.6

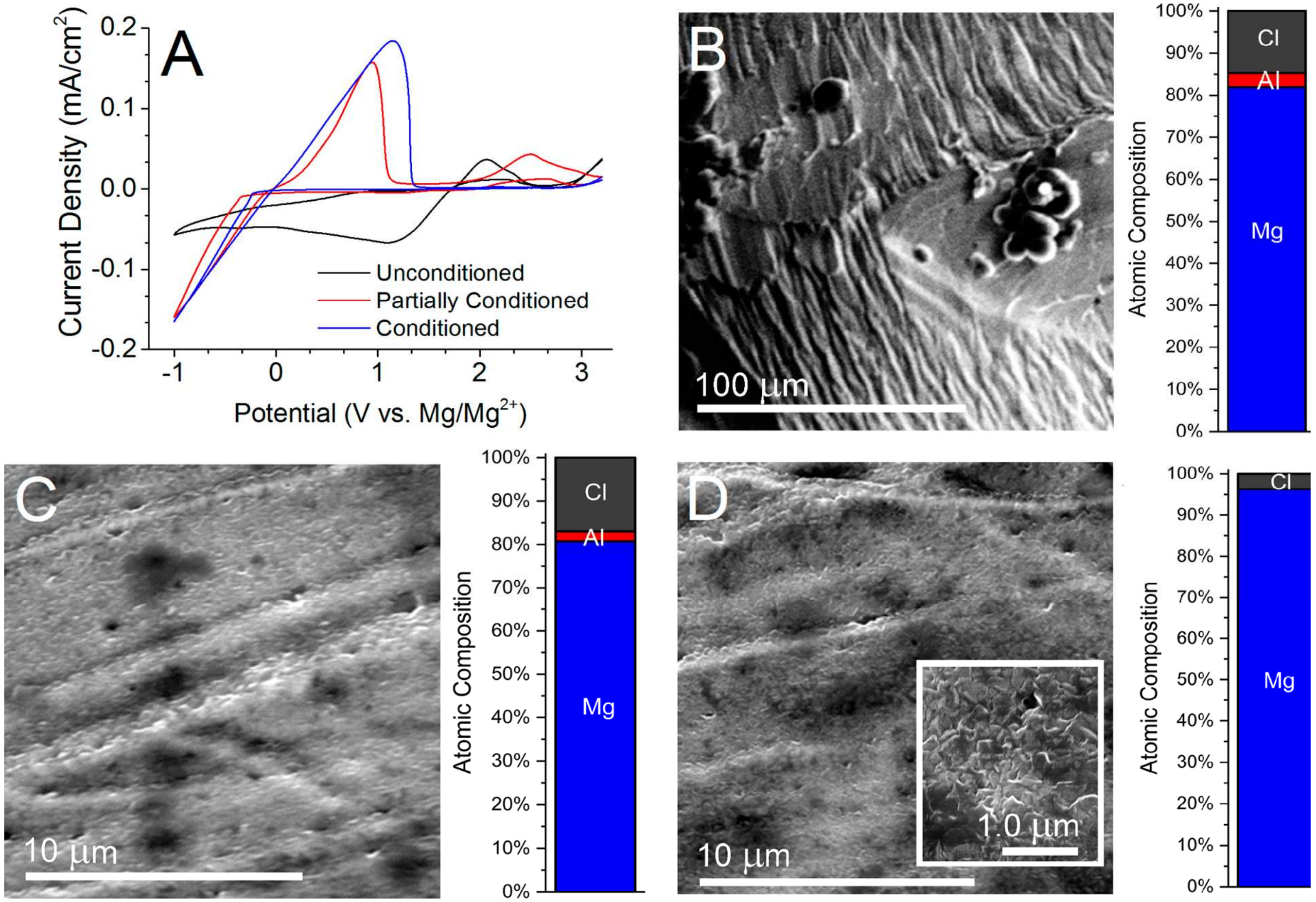
- cannot create a functional MACC by targeting a ~2.6 ratio
- $MgCl_2$ and $AlCl_3$ additions to conditioned MACC inhibit Mg

Nominal Molar Mg:Al Ratio	Sample	Found Molar Mg:Al Ratio	Coulombic Efficiency
1:1	Freshly synthesized	(0.98 ± 0.01):1	16%
	Conditioned	(2.6 ± 0.1):1	(99.8 ± 0.3)%
2:1	Freshly synthesized	(1.9 ± 0.2):1	14%
	Conditioned	(2.58 ± 0.06):1	(99.9 ± 0.2)%
3:1	Freshly synthesized	(2.7 ± 0.1):1	13%
	After 800 cycles	3.5:1	0%

Loss of activity appears related to THF oligomers

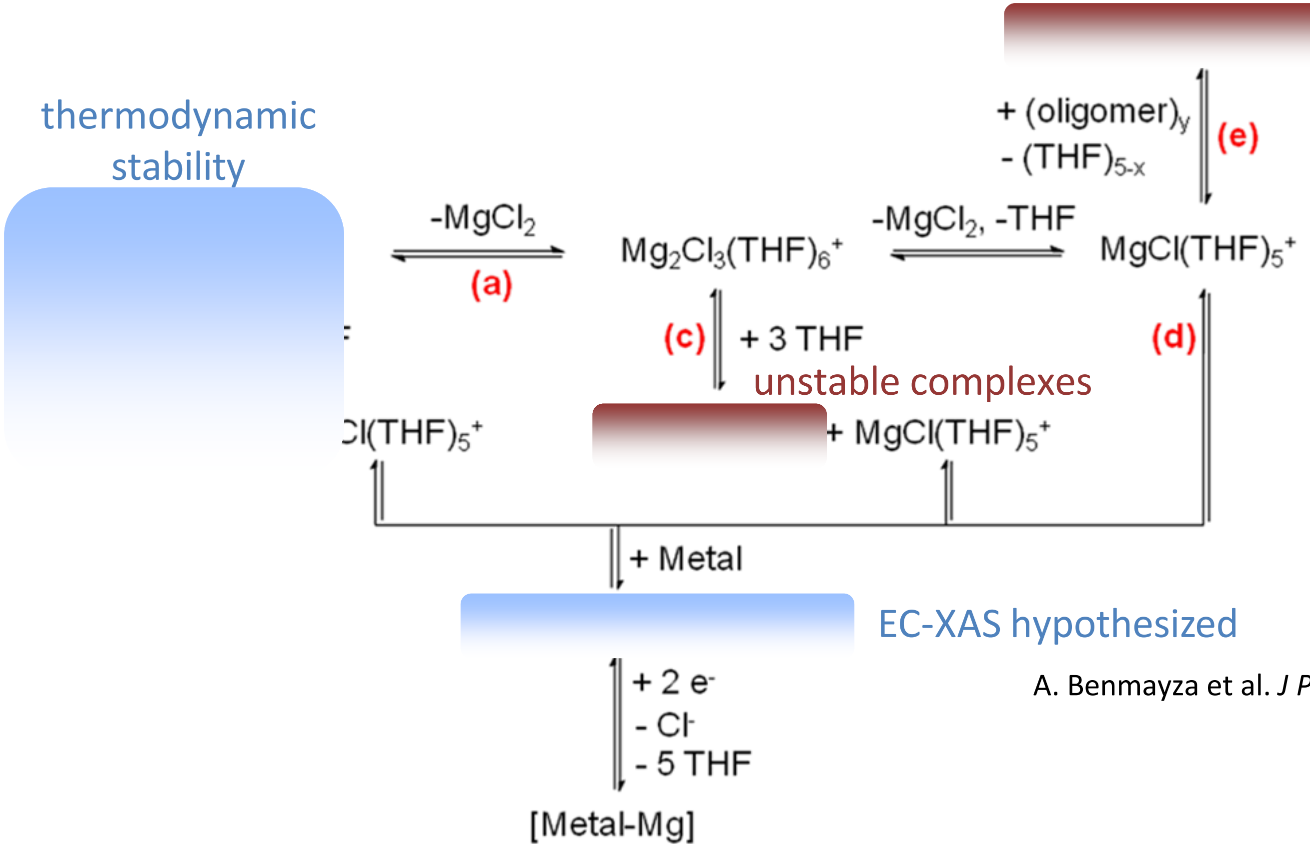
C. Barile, et al. 10.1021/jpc506951b

Conditioning consumes excess Al in the deposit



C. Barile, et al. 10.1021/jpc506951b

Proposed Mechanisms for Mg Deposition in MACC



competitive complexation

thermodynamic stability

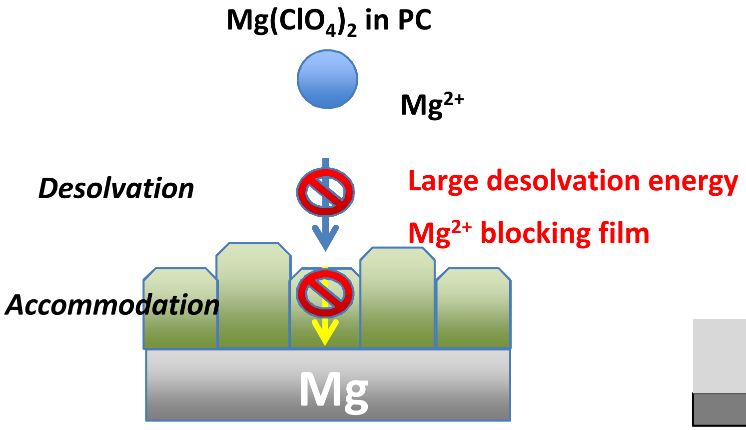
unstable complexes

EC-XAS hypothesized

A. Benmayza et al. *J Phys Chem C* 2013

C. Barile, et al. 10.1021/jpc506951b

Conventional Mg Salts Produce Blocking Layers – don’t they?



$Mg(ClO_4)_2$ in PC

Mg^{2+}

Desolation

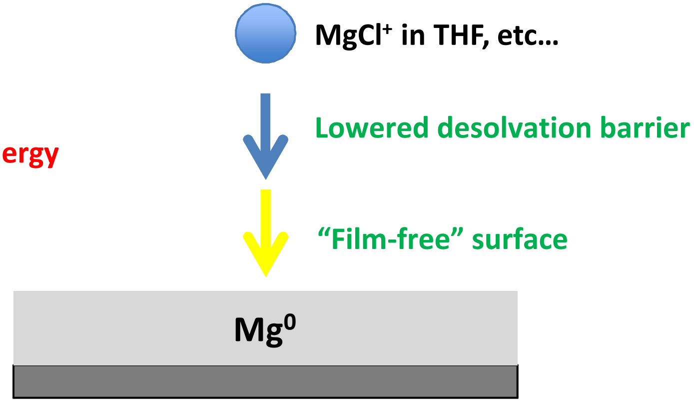
Accommodation

Large desolvation energy

Mg^{2+} blocking film

Mg

Mg Plating in Ethereal Chloro-Complex Electrolytes



$MgCl^+$ in THF, etc…

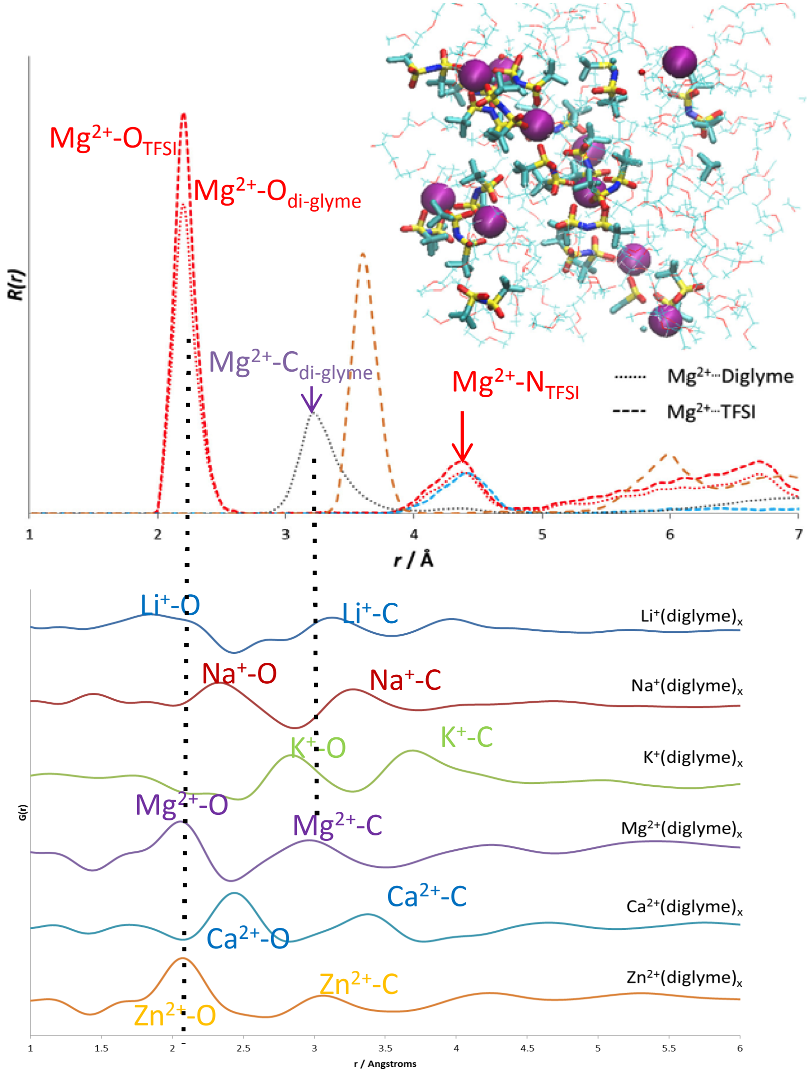
Lowered desolvation barrier

“Film-free” surface

Mg^0

- A body of literature exists documenting electrolyte decomposition
- What does the lack of a high efficiency response in CV on a foreign substrate really tell us?

Tailoring Mg2+ Coordination to



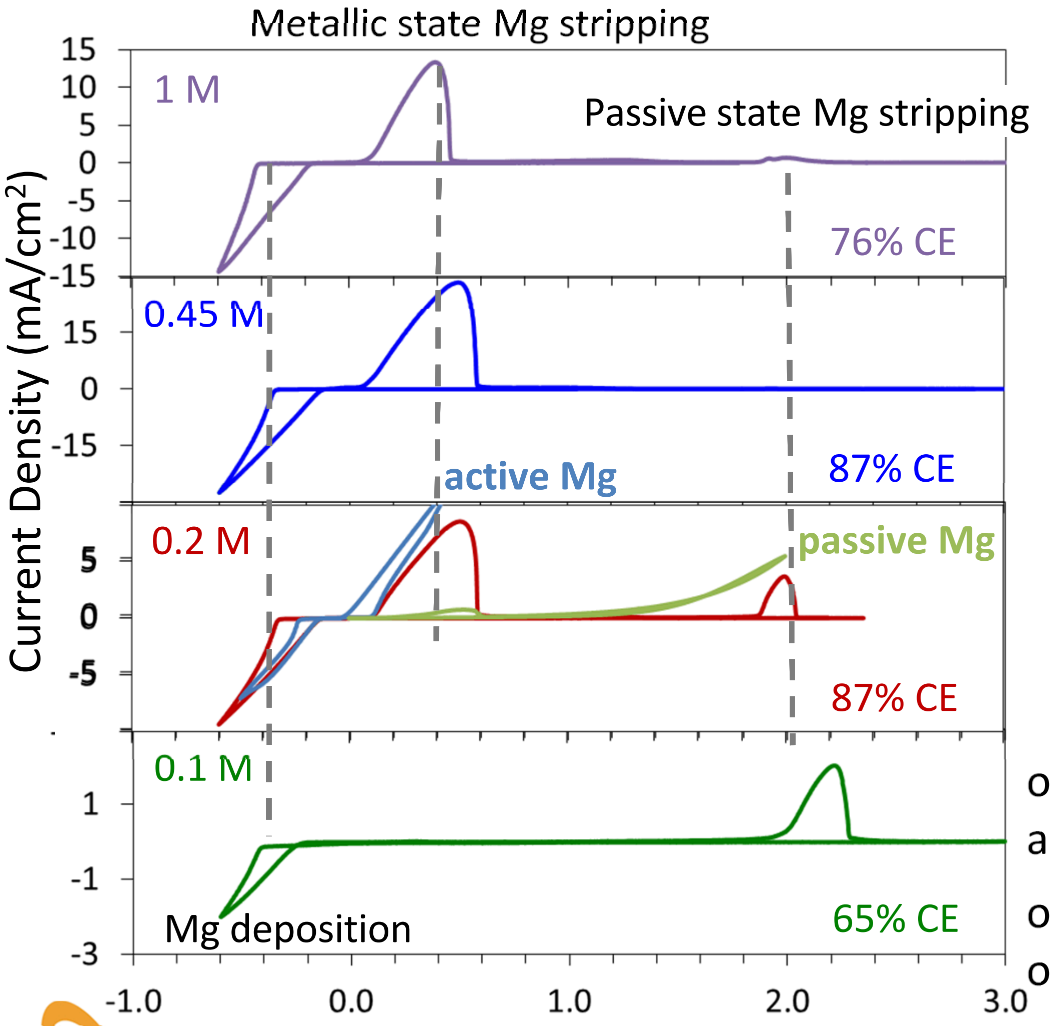
$Mg(TFSI)_2$ in diglyme forms an electrolyte with solvent-shared ion pair interactions

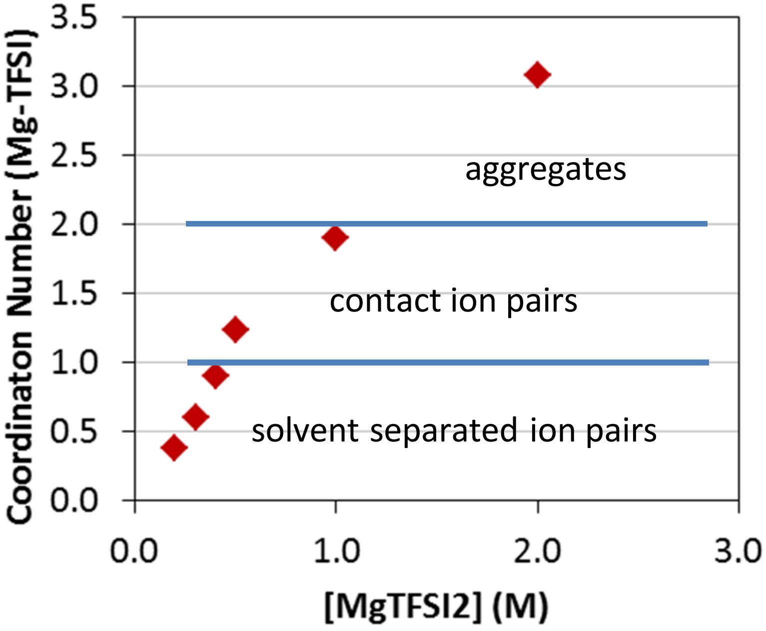
	Coordination Number
Mg-TFSI	0.9
Mg-diglyme	2.3

	Desolvation Energy (kcal/mol)
Mg^{2+} -TFSI in Diglyme	~17
Li^+ in EC/DMC	~12

S.H. Lapidus, et al. *Phys Chem Chem Phys* 2014

Mg Delivery with a Weakly Coordinated Anion



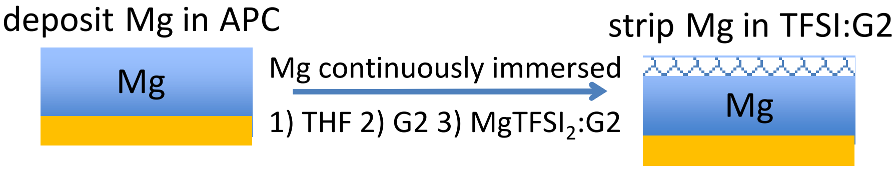


N. Rajput, et al. LBNL

origin of low Coulombic efficiency - G2 and/or TFSI decomposition

origin of passivity – G2, TFSI, or remnant oxidant (H_2O) reaction

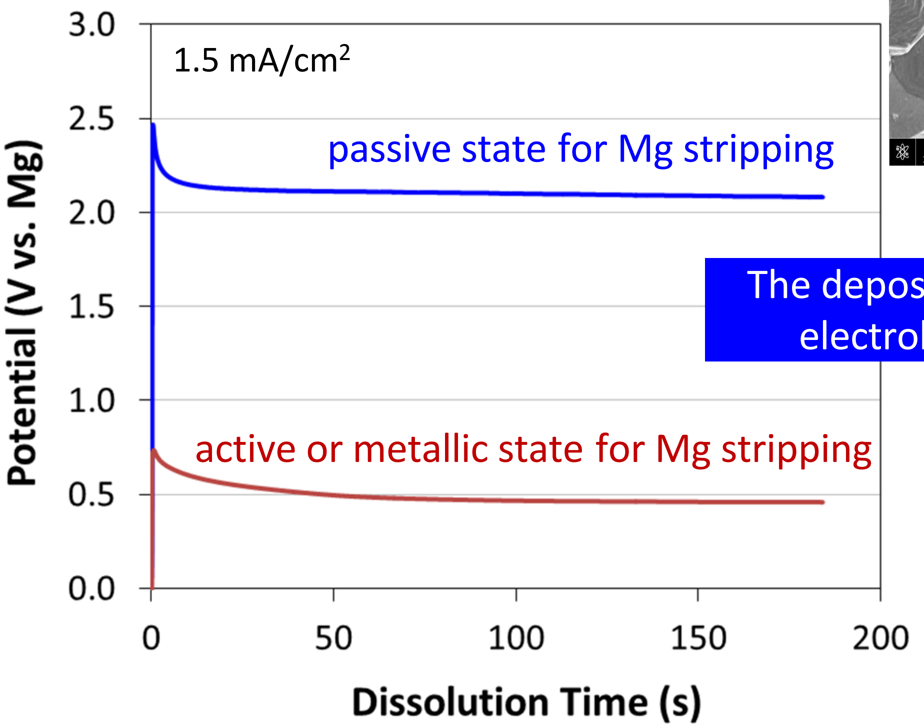
Mg Exhibits Passive and Active States in the TFSI:G2 Electrolyte (confirm passive states)


deposit Mg in APC

Mg continuously immersed

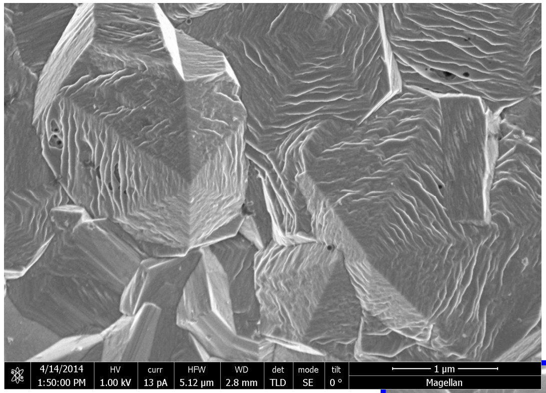
1) THF 2) G2 3) $MgTFSI_2$:G2

strip Mg in TFSI:G2

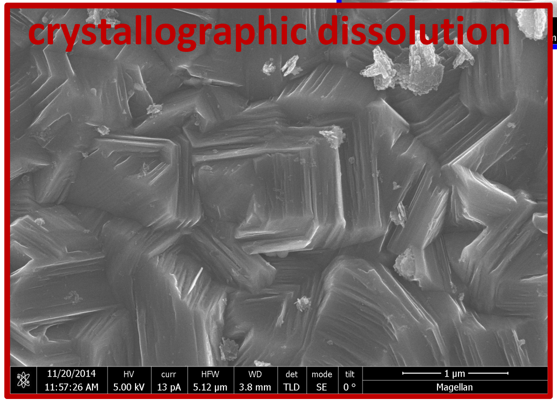


The deposit is passive with electrolyte exchange

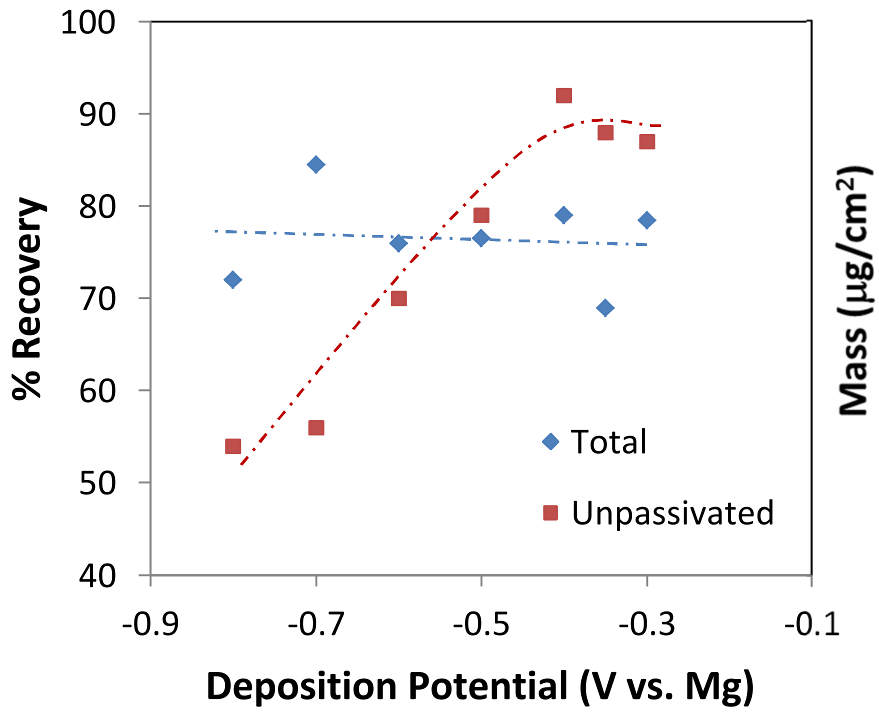
The deposit is activated with cathodic polarization

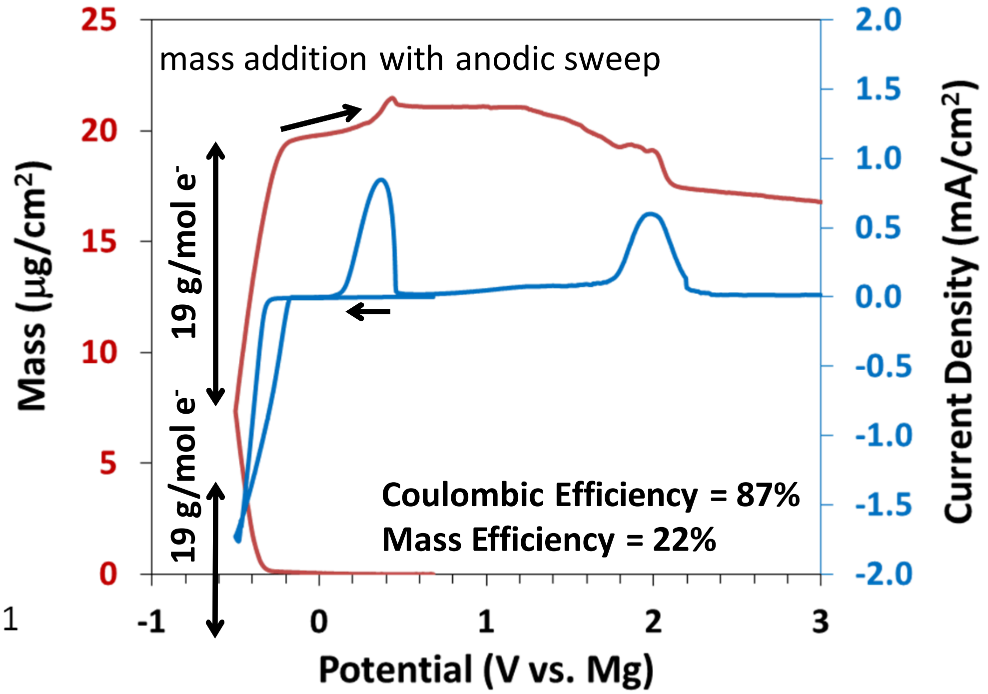



localized dissolution - pitting


crystallographic dissolution

Precursor to passivation is created during Mg deposition





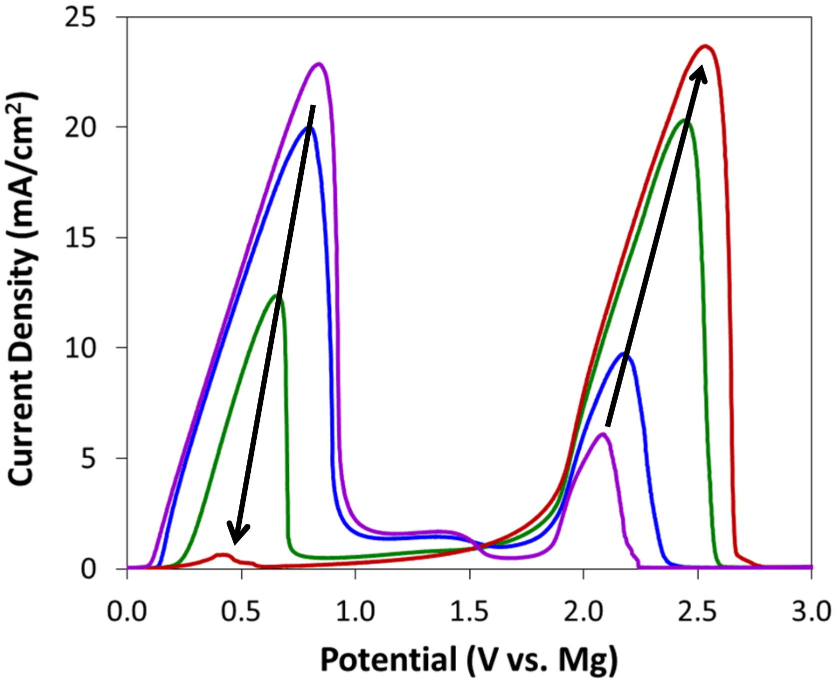
Coulombic Efficiency = 87%
Mass Efficiency = 22%

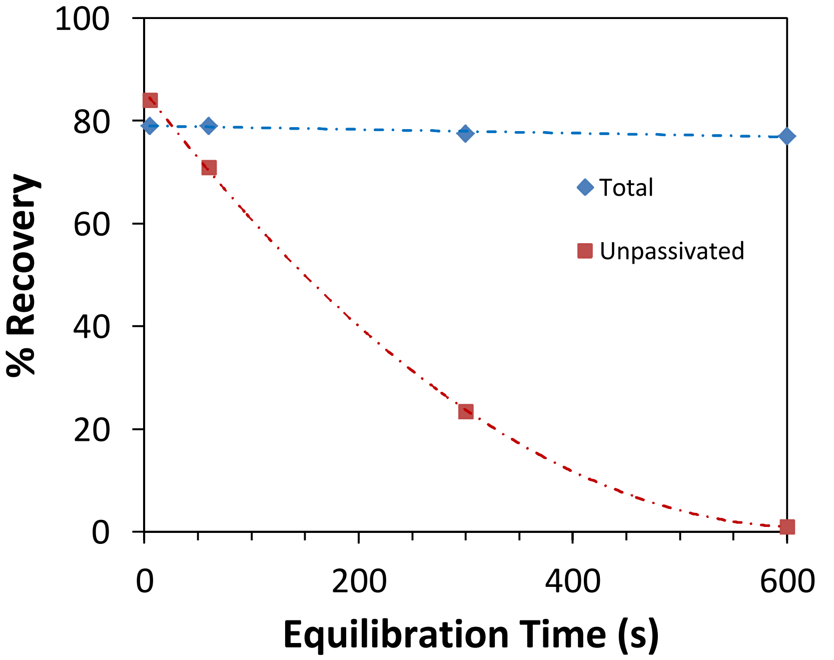
Efficiency is independent of potential – passivation is increased with cathodic polarization

Non-Mg mass is accrued during deposition
Assembly of an interfacial film

- remains coupled to the electrode surface
- retains discharged Mg^{2+}?

Equilibration time at open circuit is sufficient to induce passivation



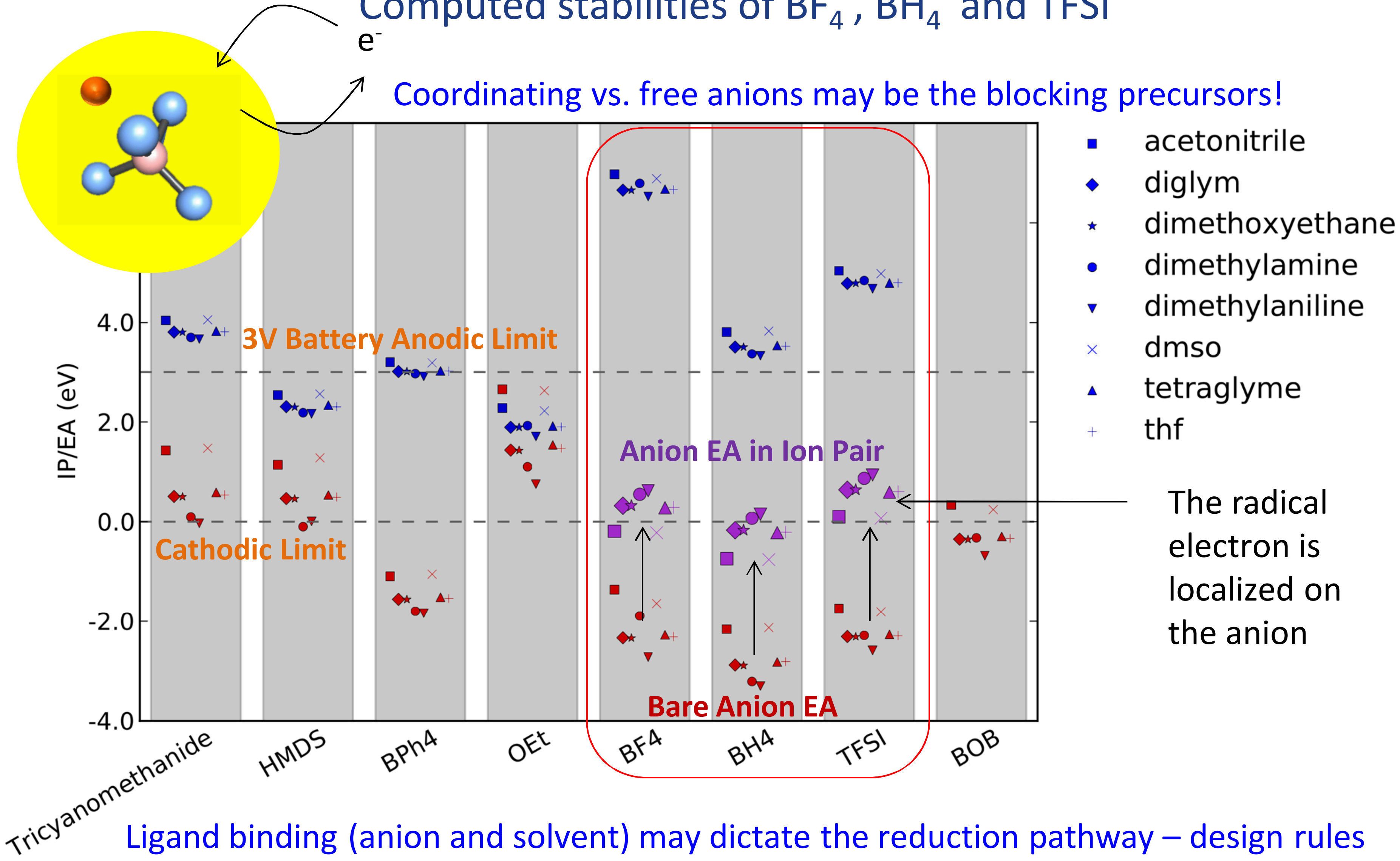


A slow process results in modification of the interface and the onset of passivity

- slow reaction of accumulated solvent or anion reaction products

Do we anticipate TFSI reductive decomposition?

Computed stabilities of BF_4^-, BH_4^- and $TFSI^-$



Coordinating vs. free anions may be the blocking precursors!

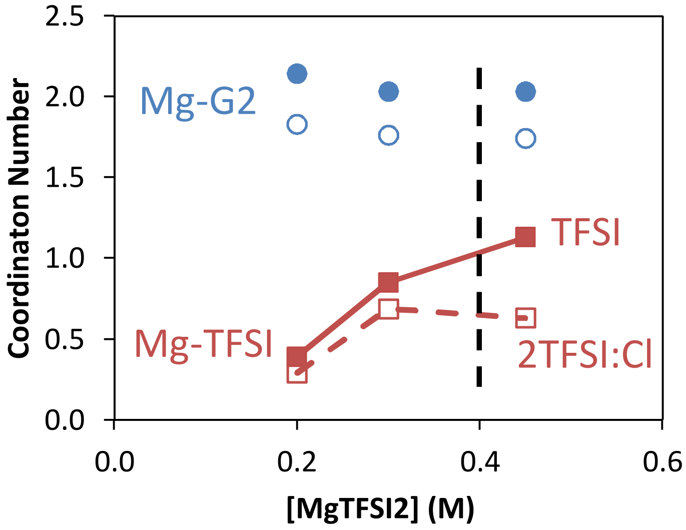
The radical electron is localized on the anion

Ligand binding (anion and solvent) may dictate the reduction pathway – design rules

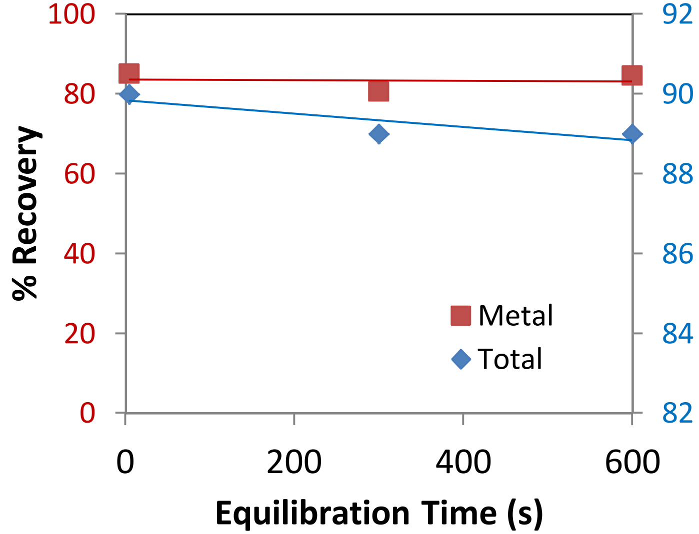
Chloride Addition Inhibits Passivation

TFSI is displaced by Cl in the CIP regime – 0.3 M $MgTFSI_2$:0.15 M $MgCl_2$

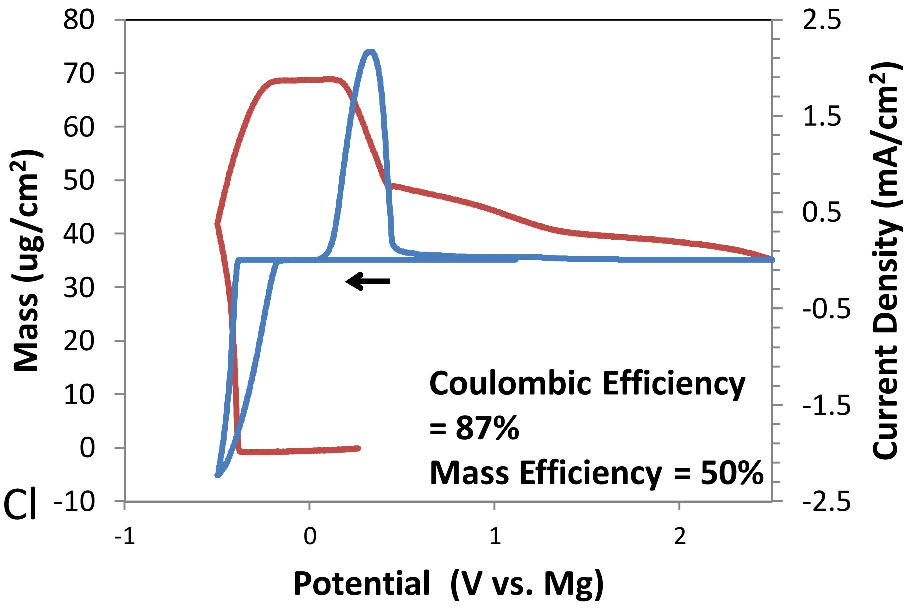
Consistent with 25Mg NMR + 5 ppm shift at 2TFSI:Cl



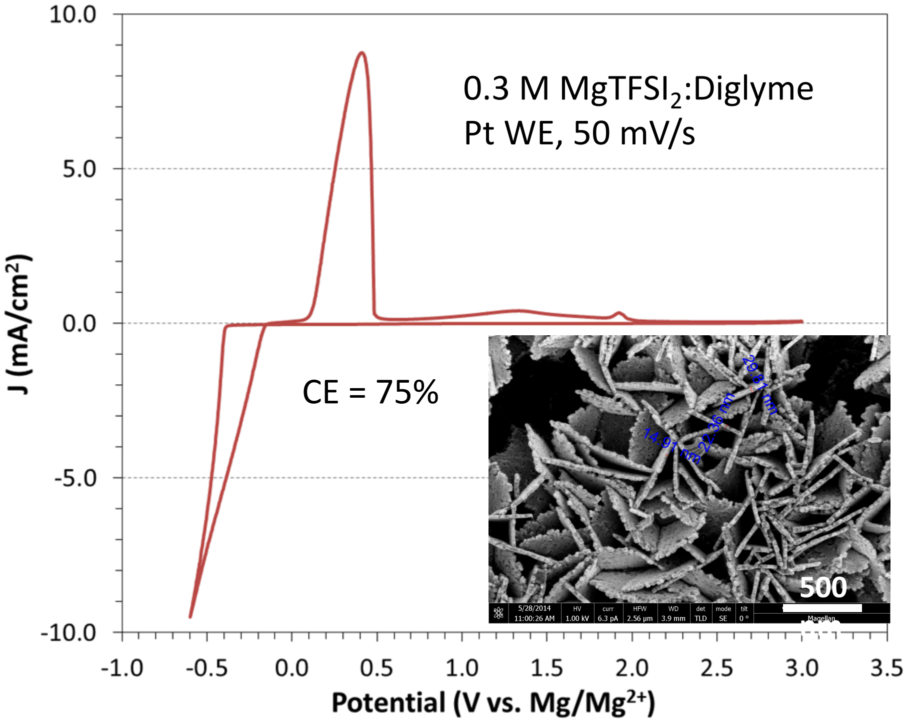
Cl inhibits passivation



3-fold increases in mass/charge ratios with Cl vs. without

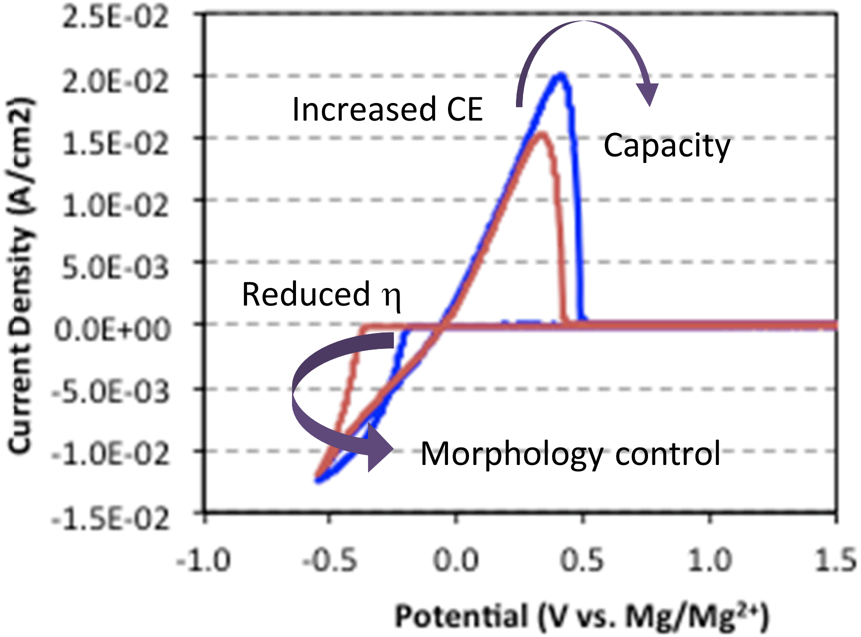


TFSI-derived Mg Deposits have unusual structural motifs



0.3 M $MgTFSI_2$:Diglyme
Pt WE, 50 mV/s

CE = 75%



Increased CE

Capacity

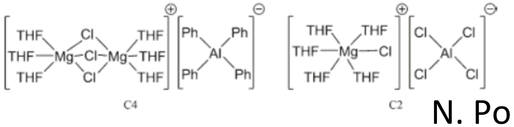
Reduced η

Morphology control

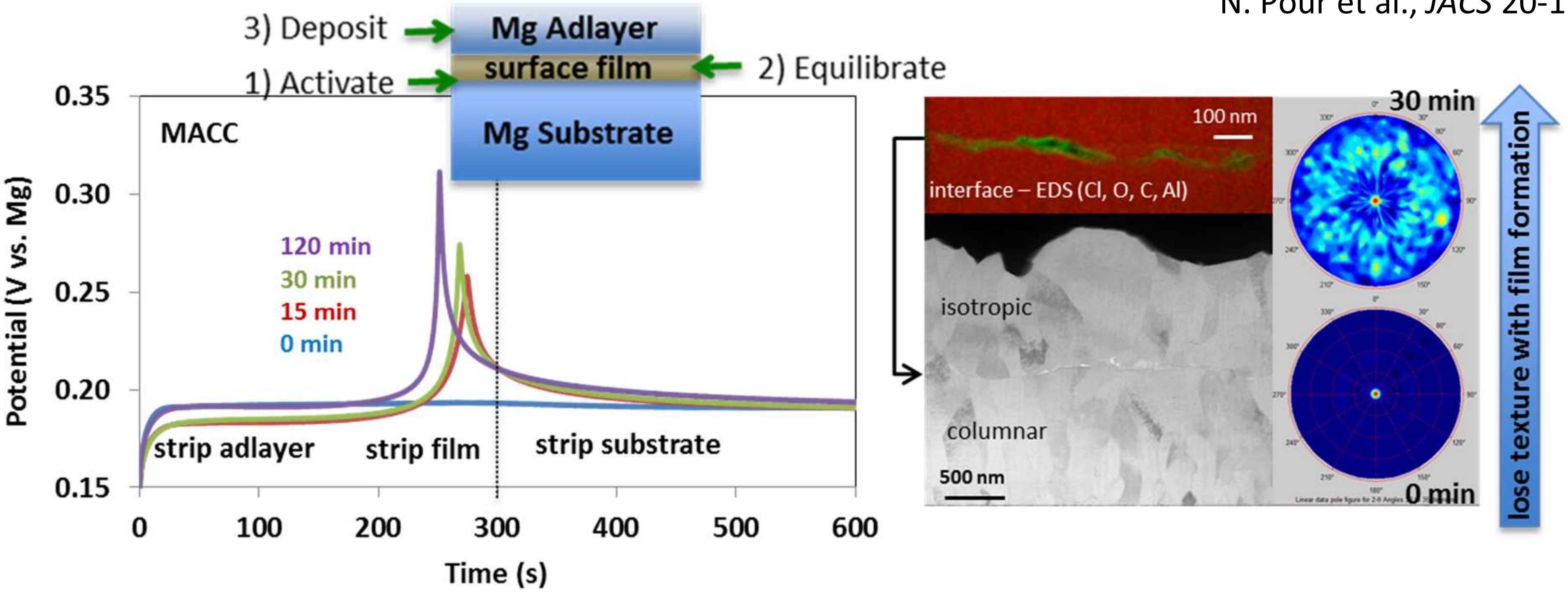
Hypothesis: what reacts at the interface is what is carried to it through coordination

Can chloroaluminate electrolytes provide effective Mg accommodation at relevant rates?

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



N. Pour et al., *JACS* 20-11

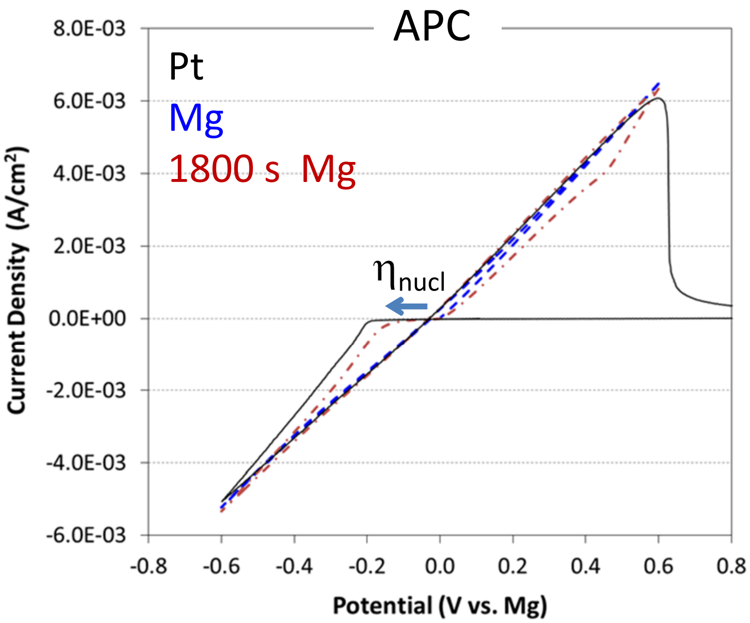


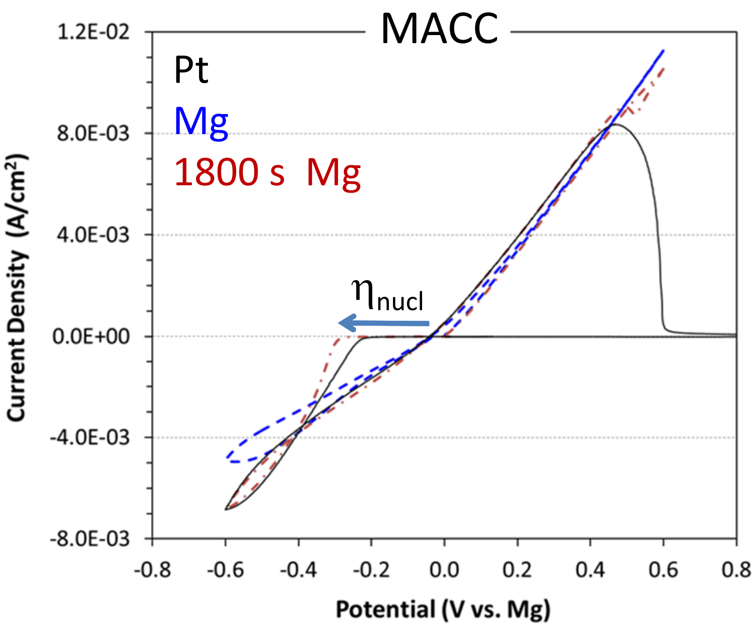
Surface films form in chloroaluminate electrolytes

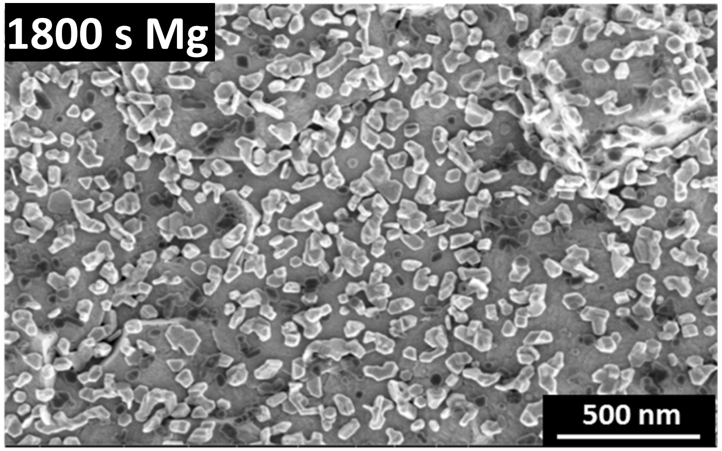
- Protective – reduce self-discharge to < 2 nm/hr
- Directive – direct morphology development of the subsequent Mg deposit
- Disruptive – filmed interface incorporates - mechanical flaws within the deposit
- May contribute to incoherent Mg deposition observed in JCESR Mg prototype cells

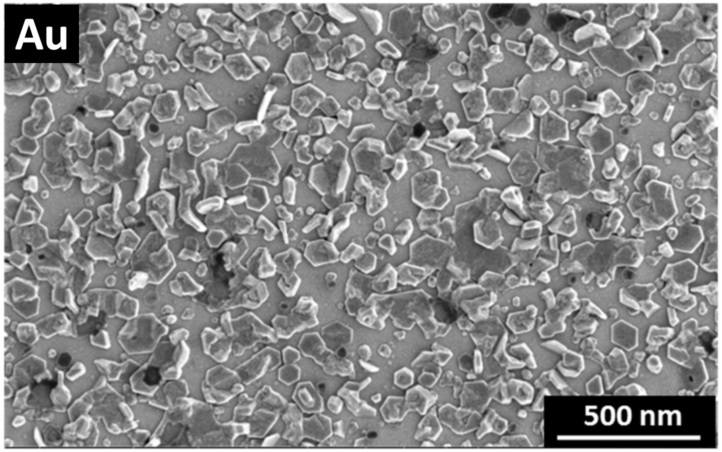
N. Hahn et al. J Phys Chem C 2014 submitted

Renucleation of Mg is required at the filmed interface





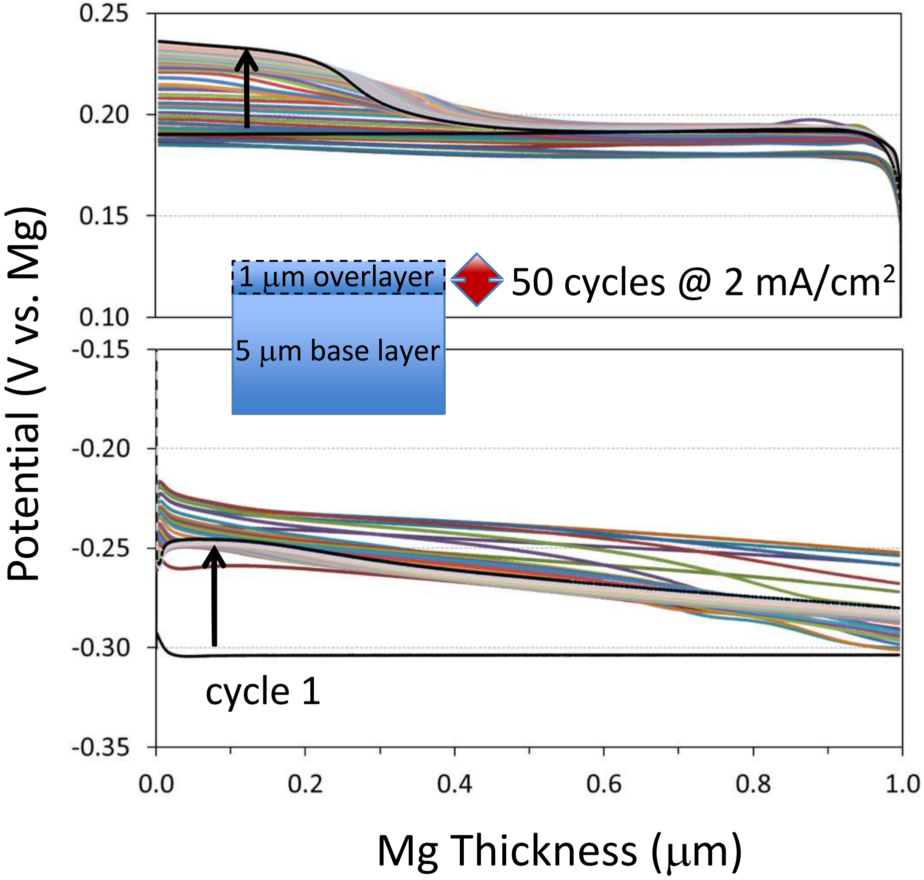




N. Hahn et al. J Phys Chem C 2014 submitted

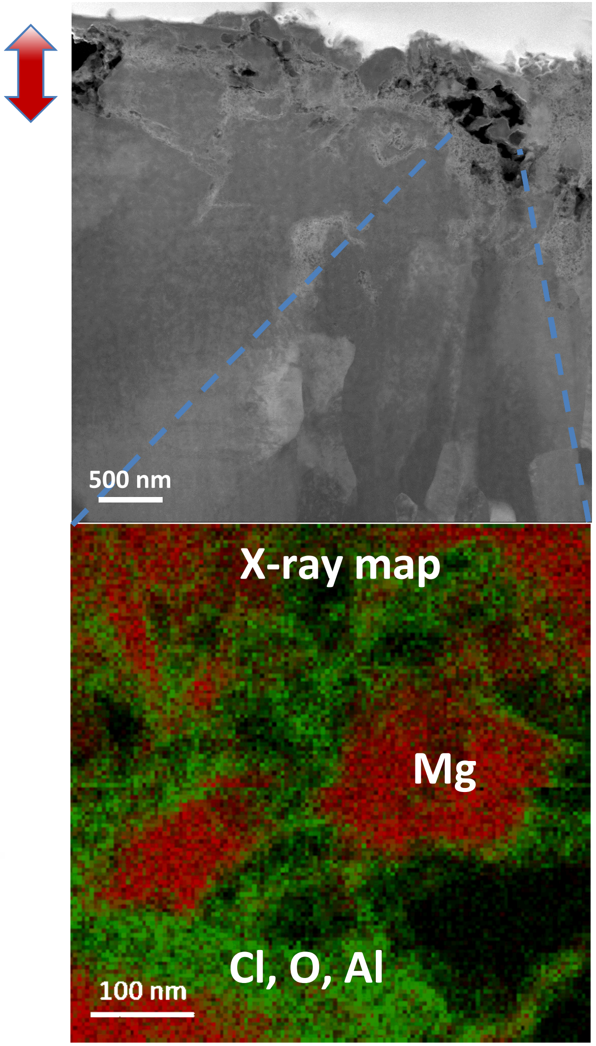
Morphology Control is a Problem for Mg at High Rates in a Chloroaluminate

Filmed interface evolves with cycling



observed for APC and MACC (var. solvent)

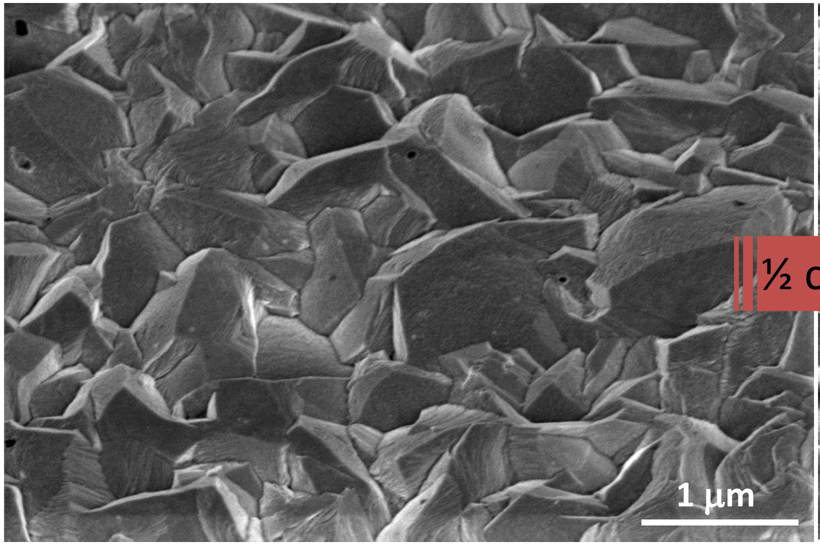
Void formation



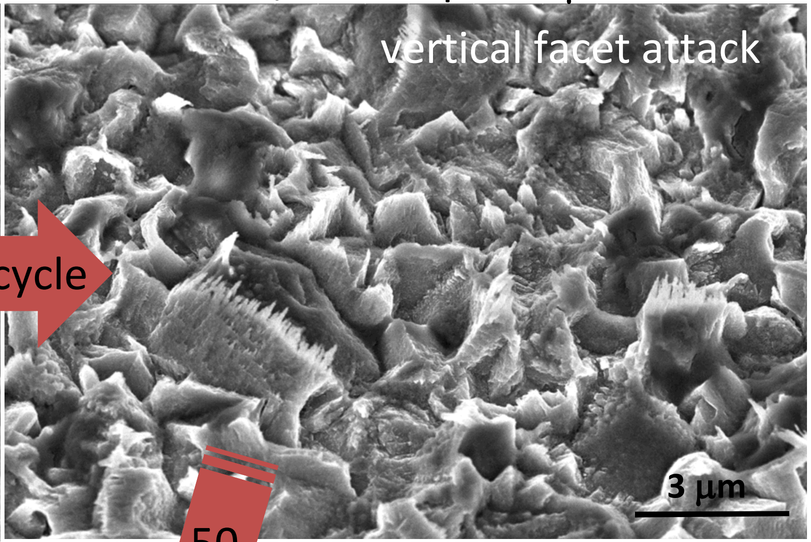
N. Hahn et al. J Phys Chem C 2014 submitted

High Rate Dissolution is Crystallographically Anisotropic

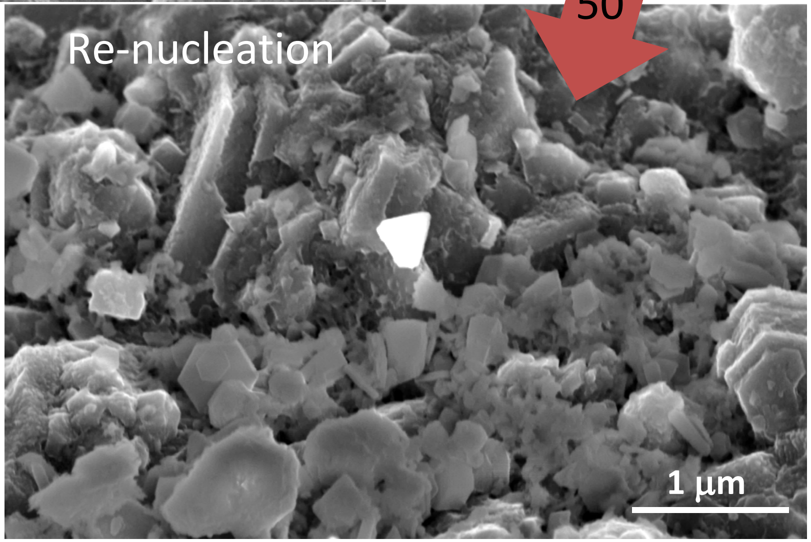
2 mA/cm^2 deposition in a Chloroaluminate



2 mA/cm^2 strip of 1 μm



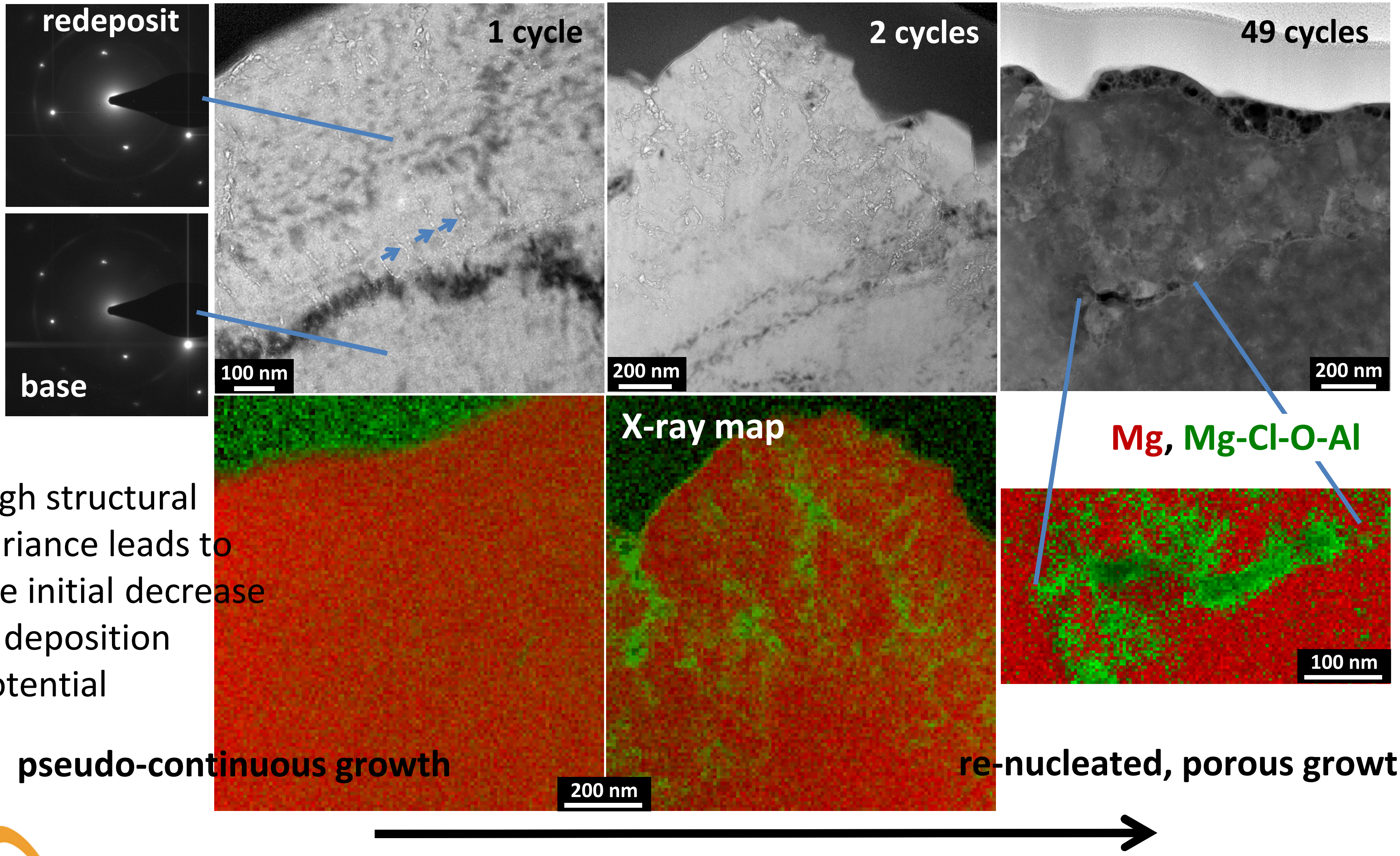
High structural variance leads to the initial decrease in deposition potential



50 cycles ±1 μm at 2 mA/cm^2

N. Hahn et al. J Phys Chem C 2014 submitted

Similar evolution of the MACC Interface



High structural variance leads to the initial decrease in deposition potential

pseudo-continuous growth

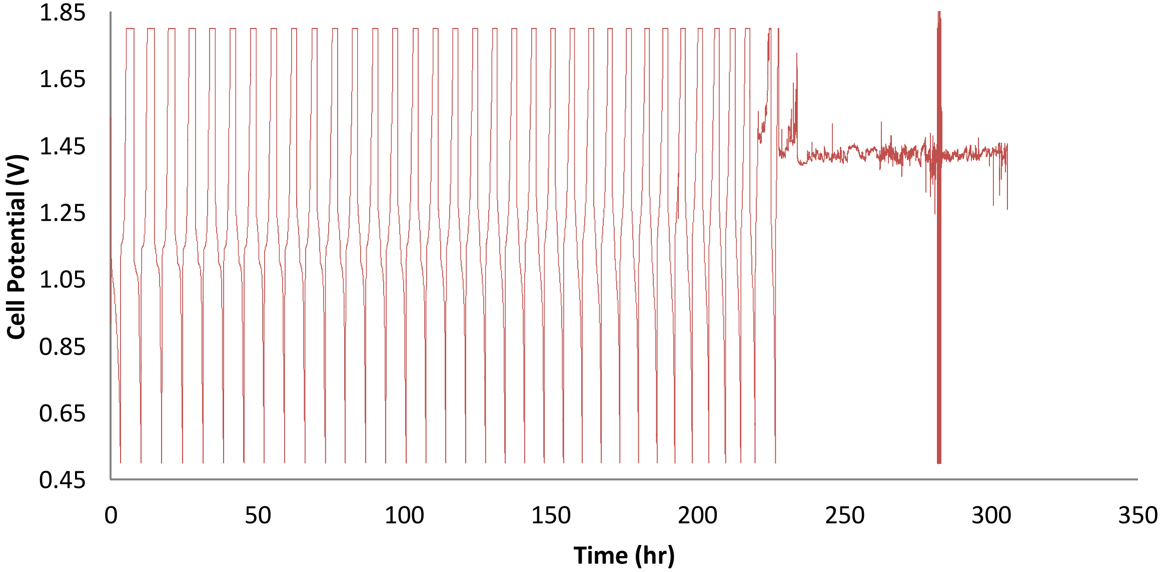
re-nucleated, porous growth

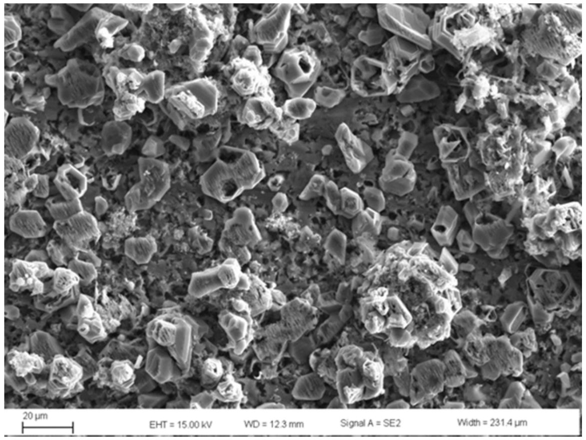
N. Hahn et al. J Phys Chem C 2014 submitted

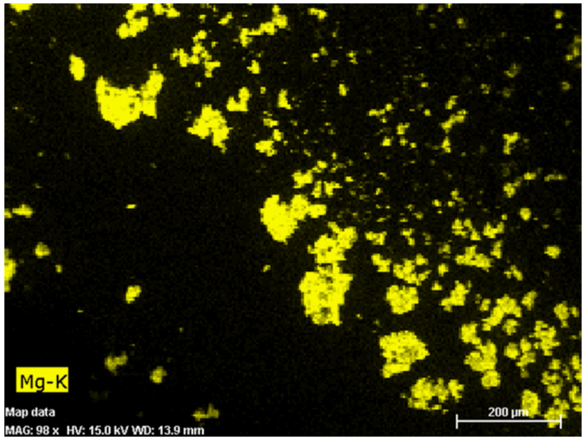
Loss of mechanical cohesion of Mg – capacity loss through electrical isolation

Chloroaluminate electrolyte fail with cycling

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







B. Perdue, SNL

What about Ca^{2+} and other MV Cations

- Efficient Ca deposition and stripping has not been demonstrated
  - No fundamental reason exists to make this impossible
- The power of analogy from established Mg(II)/Mg(0) work
  - Mixed Ca^{2+} ion systems look like a reasonable starting point
  - Lewis Acid – Base chemistries are also reasonable
  - The larger size Ca^{2+} cation and corresponding coordination sphere - different solvent sensitivity
  - Utilize speciation control
  - surface films will play a more dominant role

Acknowledgements

Nathan Hahn & Katie Harrison, SNL

Chris Barile, Russell Spatney, Andy Gewirth, UIUC
David Wetzel, Marvin Malone, Ralph Nuzzo, UIUC

Yuyan Shao and Jun Liu, PNNL

Chen Liao, Tony Burrell, ANL
Kevin Gallagher, ANL

Nidhi Rajput, Kristin Persson, LBNL

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