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JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Decoupling the Solvation and Accommodation Challenges to Enable Alkaline Earth Metal Anodes

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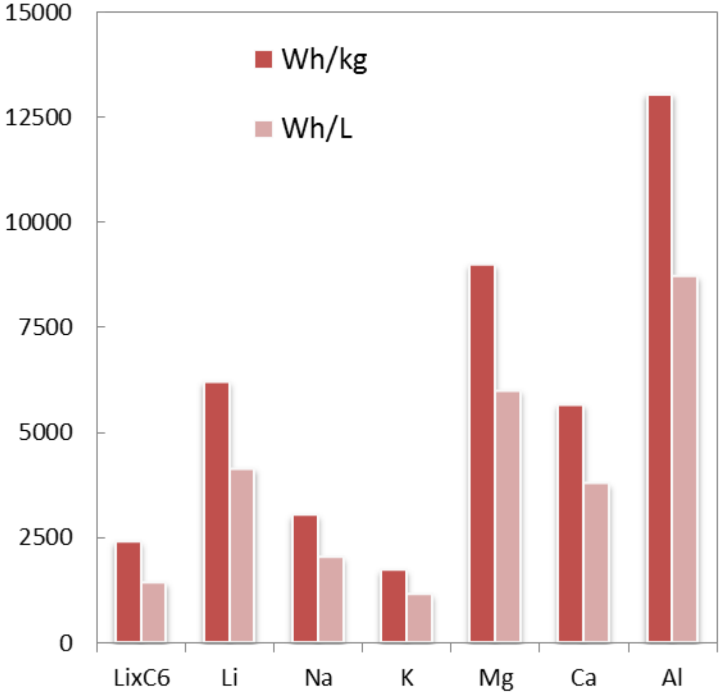
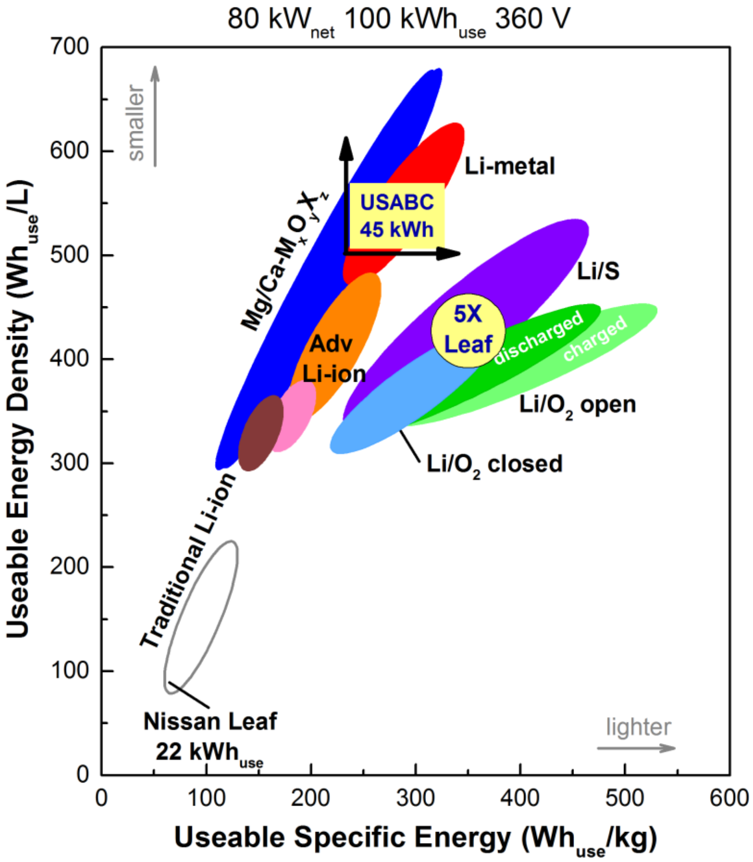
Metal Anodes are the Key to Increased Energy Density



System Analysis



Techno-economic model:

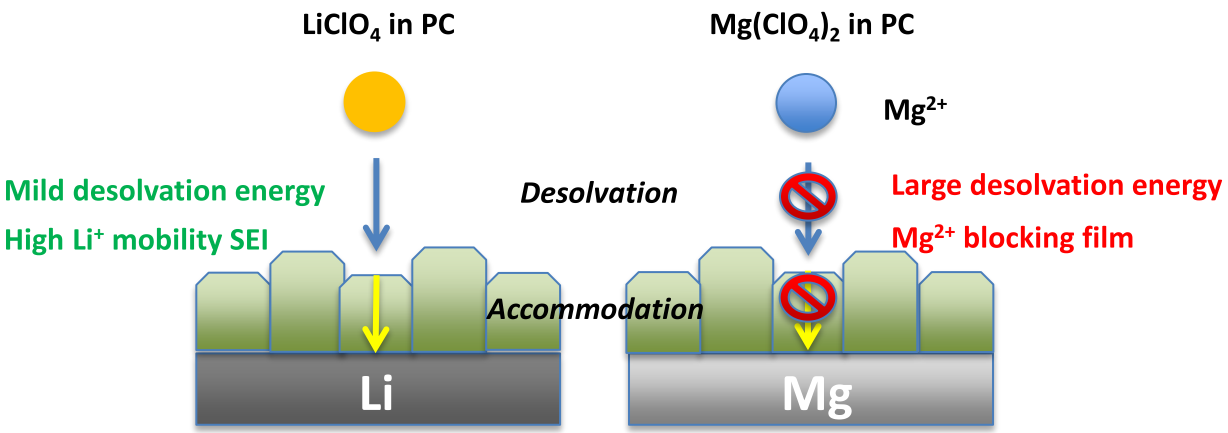
3 V insertion cathode (750 Wh/kg), 50% excess Mg → $100 /kWh, 500 Wh/l

MV Metal Anode Challenges

Technical challenge

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

Li vs. Mg Anode Plating



$LiClO_4$ in PC

$Mg(ClO_4)_2$ in PC

Mg^{2+}

Mild desolvation energy

High Li^+ mobility SEI

Desolvation

Accommodation

Large desolvation energy

Mg^{2+} blocking film

Science challenges and research

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

Metal Anodes Function is Tied to the Electrolyte

Desirable attributes:

- High Coulombic efficiency
- Modest to low overpotentials for deposition and dissolution
- Readily activated anode surface
- Low self-discharge
- High ionic conductivity over full operational temperature
- Oxidant and impurity free (H_2O, O_2, …)
- Compatibility with cathode
- Low cost
- Reliable
- Safe

Current Anode Electrolyte Concepts

Lewis Acid - Base Complex Formation

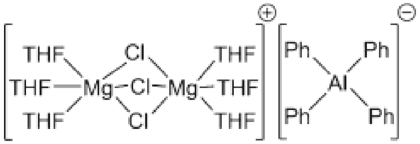
Mg supply via Grignard reagent:
2PhMgCl:$AlCl_3$ All Phenyl Complex - APC (Aurbach)
Transmetallation of Ph
Cl redistribution

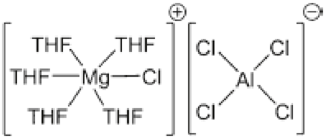
Eliminating the organic radical:
(HMDS)MgCl:$AlCl_3$ (Muldoon)
$Mg(HMDS)_2$:2$AlCl_3$ (Fichtner)
ROMgCl + $AlCl_3$ (Liao)

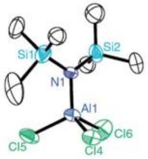
Inorganic source of Mg:
2$MgCl_2$:$AlCl_3$ Magnesium Aluminum Chloride Complex - MACC (Aurbach)

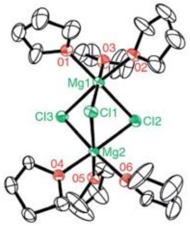
$MgCl_2$:$AlPh_3$

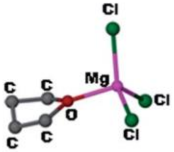
Complex Responsible for Mg Delivery

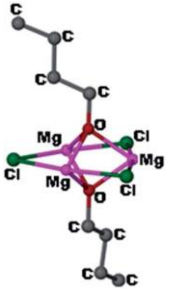


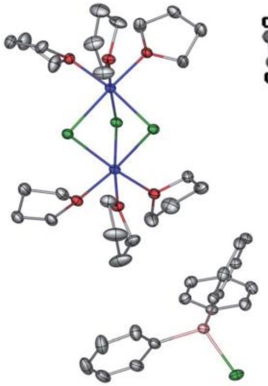






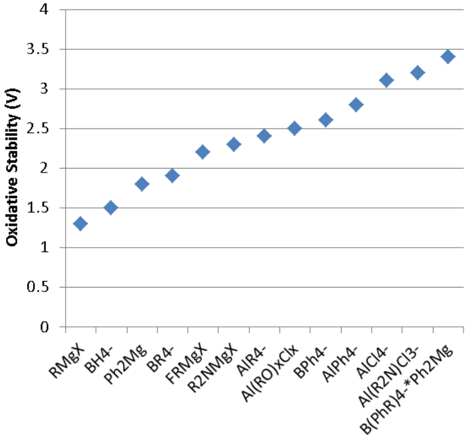






Design Goals

Increased anodic oxidation limit



Elimination of the nucleophile
Compatible electrolyte for expanded cathode chemistry

“New” Anode Electrolyte Concepts

Competitive Coordination:

$Mg(BH_4)_2$:$LiBH_4$

Competing cation to drive dissociation (PNNL 2013)

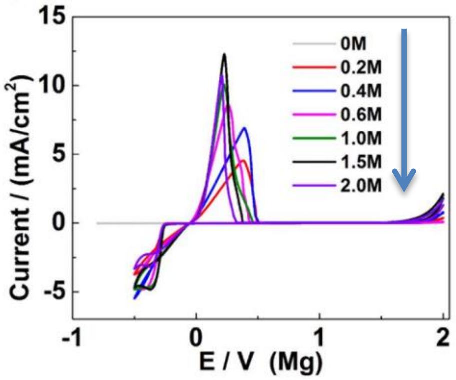
[Li^+] and ether solvent both matter

- Why not MgTFSI:LiTFSI?

Complex Responsible for Mg delivery

NMR & Computation

Li drives a covalent to ionic transition in Mg^{2+} - BH_4 interaction: cations to drive dissociation



Non-directed ligand exchange:

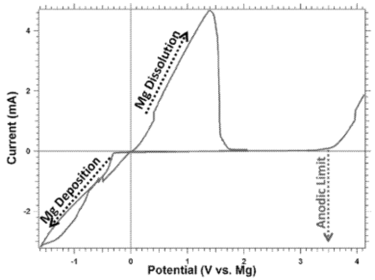
$3MgTFSI_2$:$MgCl_2$ (Pellion 2013)

Redistribution of anion ligands

- Solvent aided?

Speciation information not available

Expect strong solvent effect – solvent as a ligand



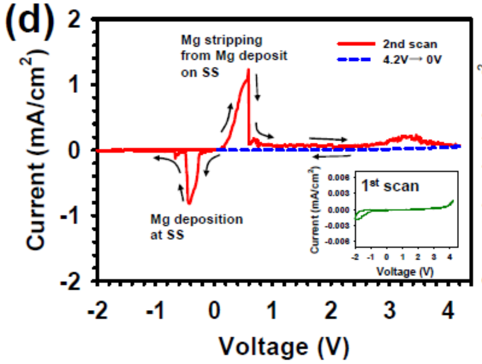
Simple Mg Salts:

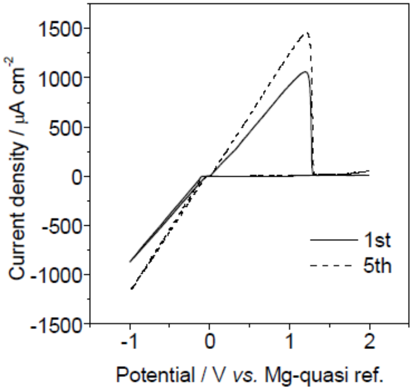
$MgTFSI_2$: glyme/diglyme (Ha, 2014)

$MgBr_2$:n-BME (Abe, 2013)

Speciation unknown

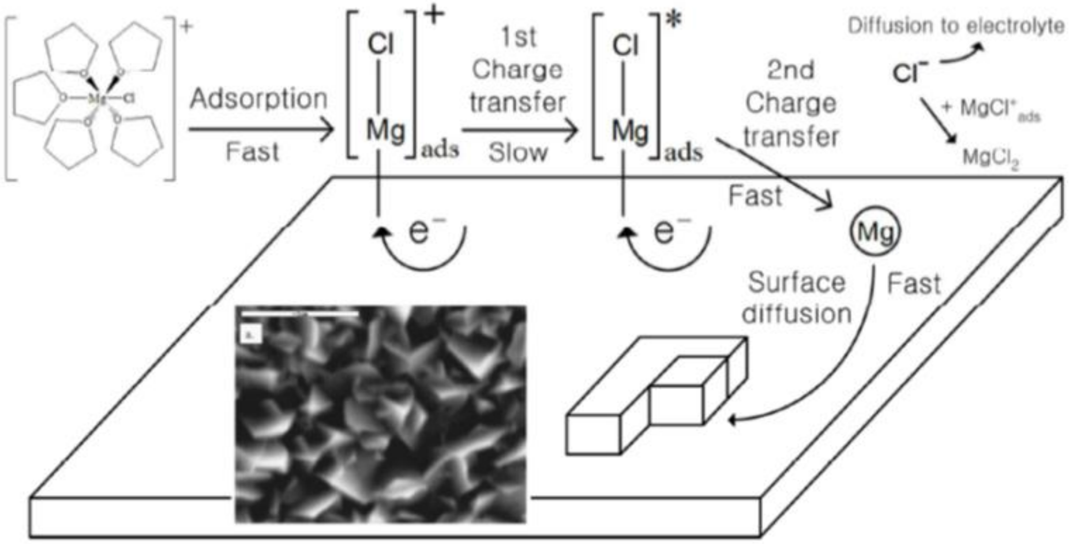
Activity is restricted to a limited range of DN





The Essential Mg Complex

de-solvation **accommodation**

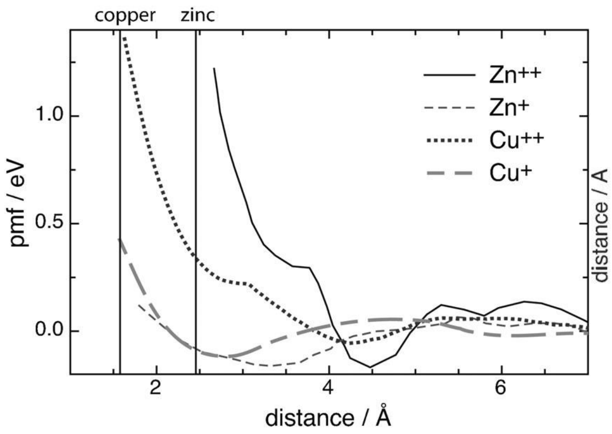


Aurbach Energy Environ Sci 2013

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

The Challenge

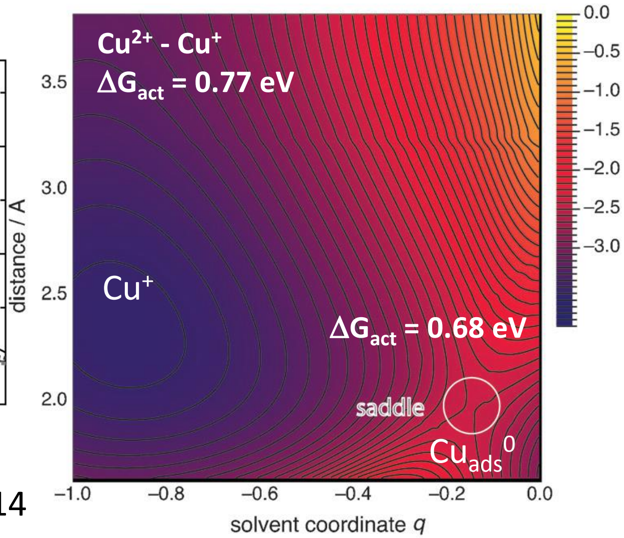
Interface proximity vs. desolvation energy



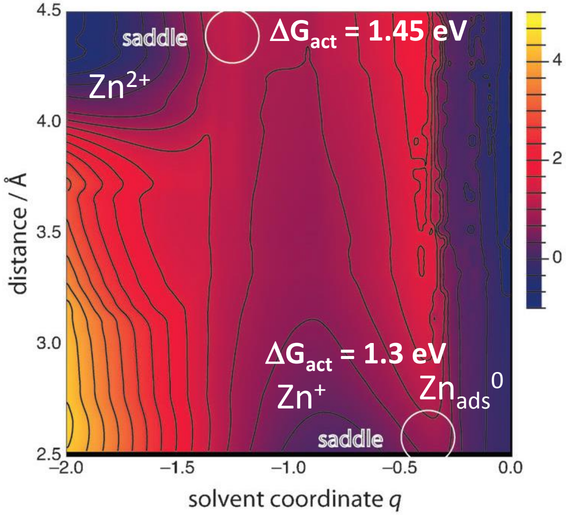
Schmickler et al. ChemPhysChem 2014

Computationally – are energies and rates consistent with known activity?

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



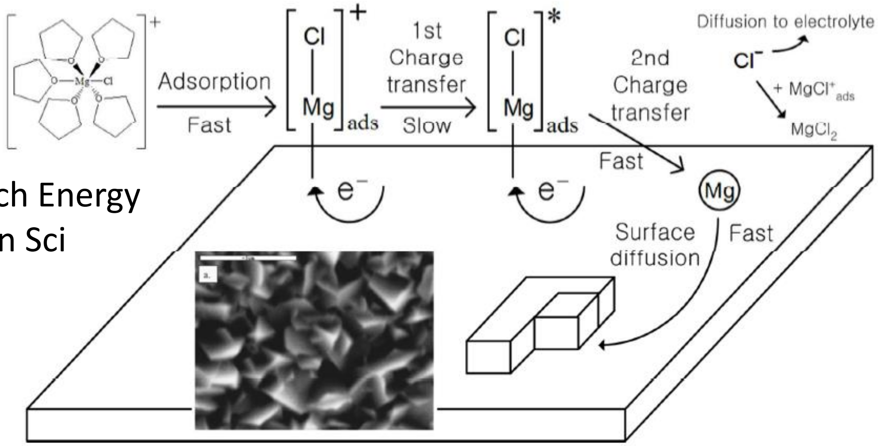
No for Zn2+:Zn(0001)
High ΔG_{act}, slow rates
Zn deposits



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

Efficient Mg Cycling: if I solve the de-solvation problem my problems are over – aren't they?

- Mg^{2+} must transit the double layer, must undergo two electron transfers, must accommodate in the surface lattice (diffuse and fill a step edge site) and in doing so must displace and disrupt interfacial structure



Aurbach Energy Environ Sci 2013n

- The Grignard chemistry is quite specialized: reducing environment allows for some degree oxidant tolerance
- The Grignard chemistry has problems: complex speciation, stability of the organo-Al species, limited anodic window, corrosive nature of the halide

- **Halo-Mg complexes transcend the Grignards – demonstrations of Mg deposition from MgX_mL_n complexes without the organo-Mg and with an extended anodic limit**
- **Opportunities to learn from working systems as JCESR designs new electrolytes and tailored interfaces**

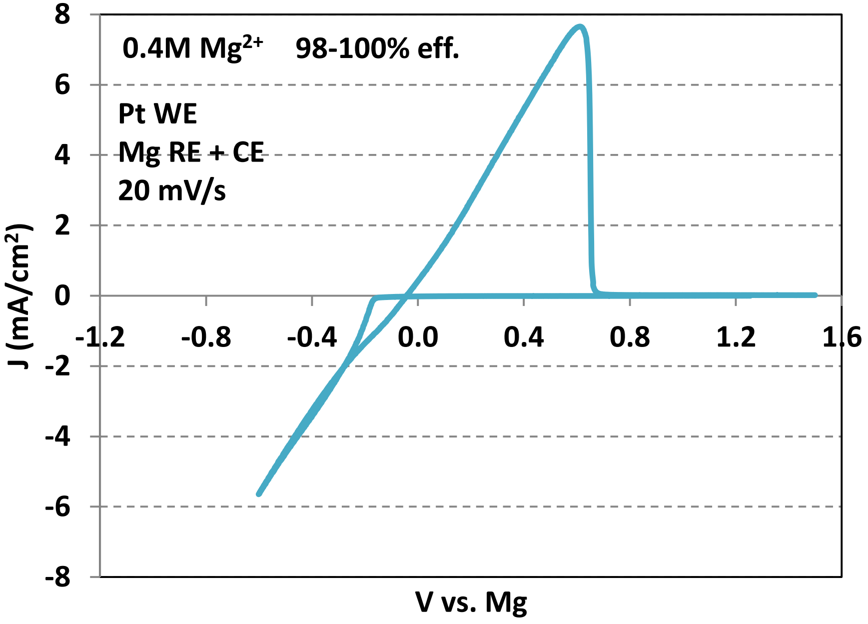
Organohaloaluminates as a Case Study of What Works for Magnesium

Mg Chloroaluminates Electrolytes Perform

“APC” electrolyte

$2PhMgCl + AlCl_3 = [Mg_2Cl_3]^+[AlPh_xCl_{4-x}]^-$

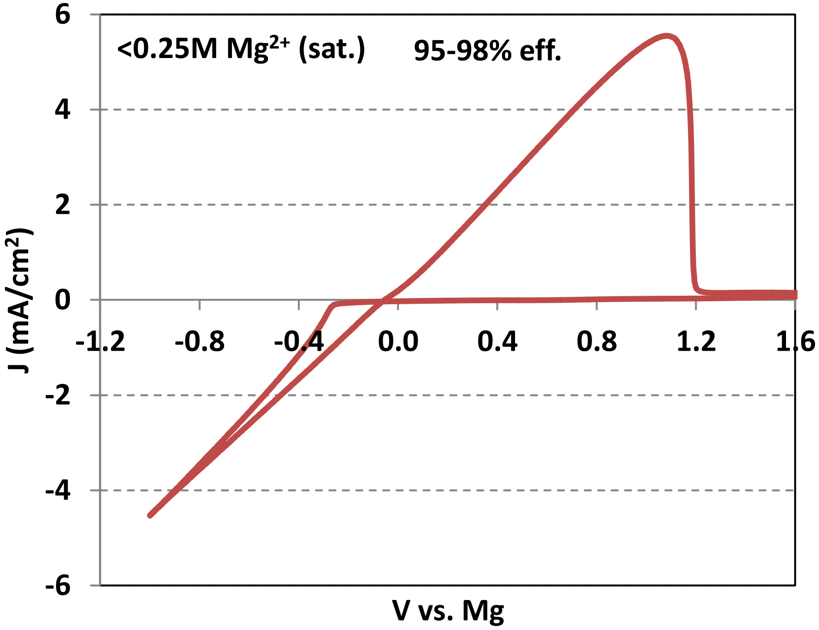
In THF



“MACC” electrolyte

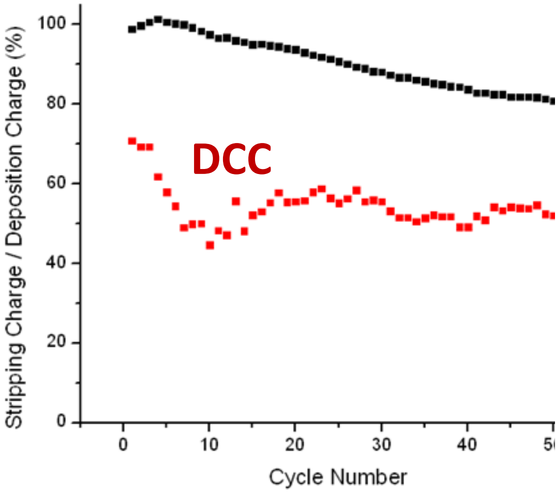
$2MgCl_2 + AlCl_3 = [Mg_2Cl_3]^+ [AlCl_4]^-$

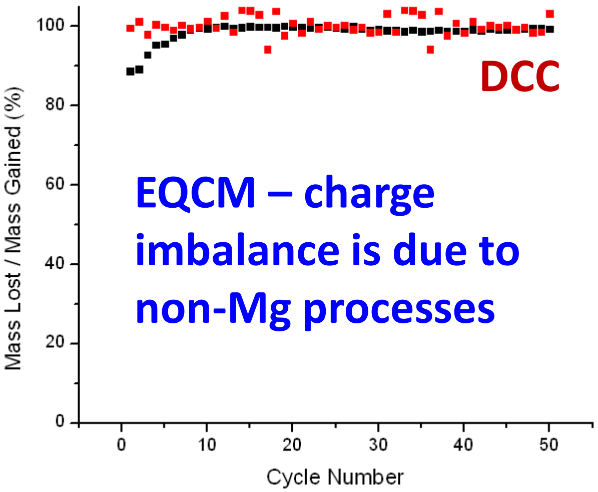
In THF



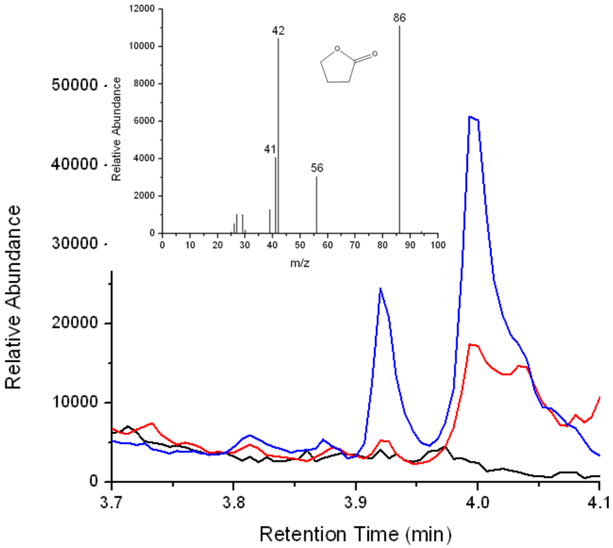
- Current literature approach uses continuous charge/discharge demonstrate kinetics and efficiency
- The behavior and impact of an equilibrating Mg deposit in new electrolytes is largely ignored
    - Deactivation?
    - Open circuit dissolution?

Organohaloaluminate Electrolytes Degrade





EQCM – charge imbalance is due to non-Mg processes

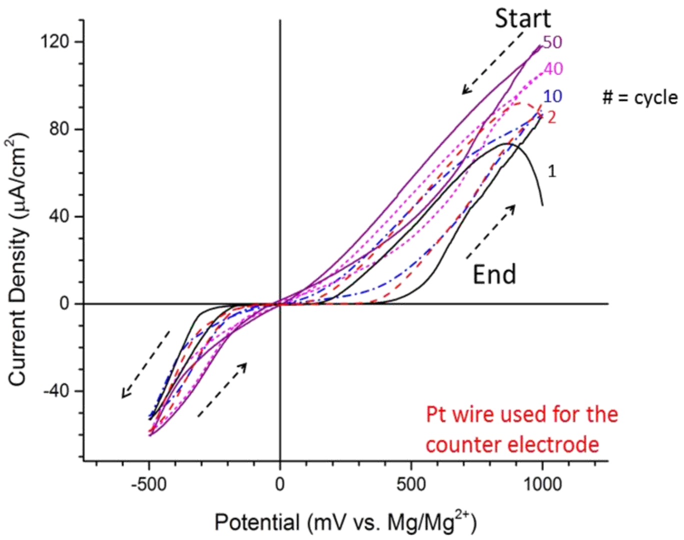


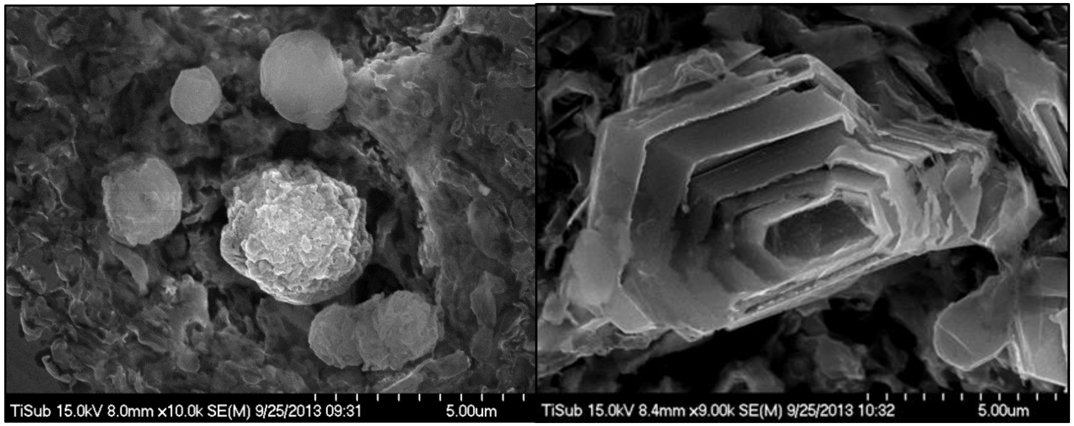
C. Barile et al. J Phys Chem C 2014

- The safe bet is that all electrolytes will undergo some degree of change with time.
- The THF conversion to butyrolactone raises questions of reactions unique to electron transfer and the interface
- Similar decomposition reactions reported for APC and MACC

Activation Processes Govern Mg Deposition and Dissolution in Organohaloaluminates

Mg response to potential and galvanostatic cycling





D. Wetzel et al. UIUC

Inhibited deposition and dissolution

Deposition requires activation - localized corrosion

Deposition is restricted to the evolving corrosion pits

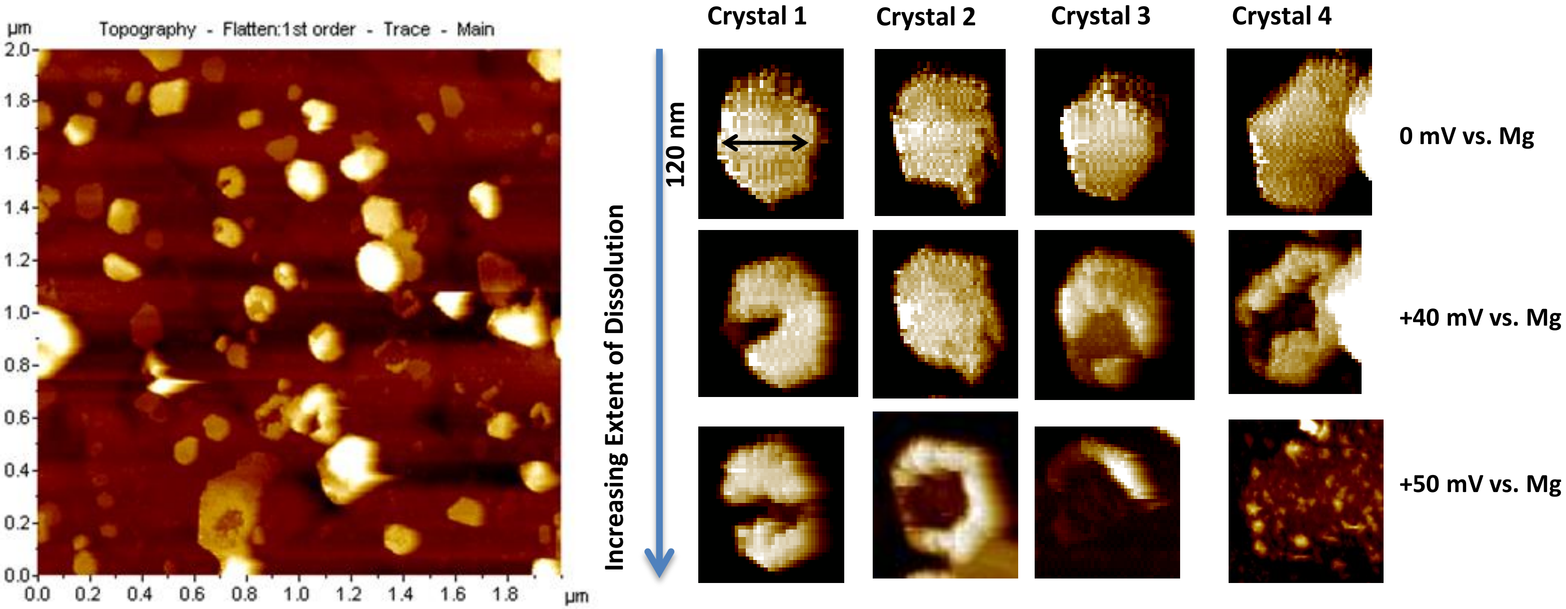
The consequence is that only a fraction of the surface is accessed

Anisotropic dissolution governed by passive film formation – halides as a key factor

Surface Films Dominate the Mg Chloroaluminate System

- Nucleate and grow Mg crystallites onto a Au(111) terraces
- Potentiostatically dissolute the Mg crystallites and monitor details of shape change

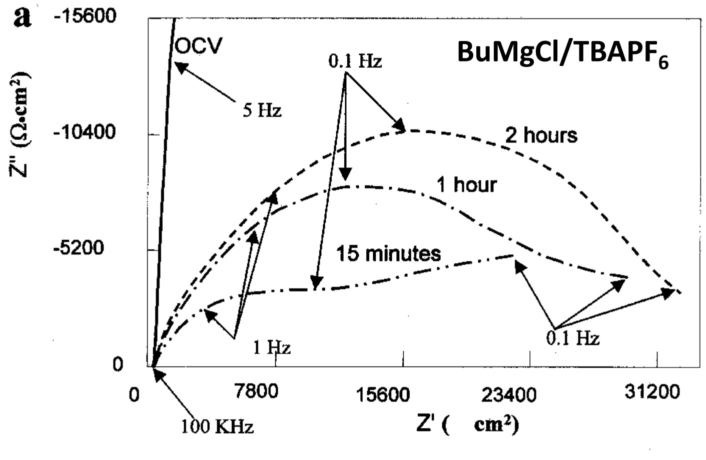
In situ AFM of Mg in 0.5M PhMgCl/THF



- dissolution is localized – breakdown of a surface film
- remnant film decorates the Au surface

N. Hahn et al. in preparation

Surface Films Regulate Mg Cation Transport



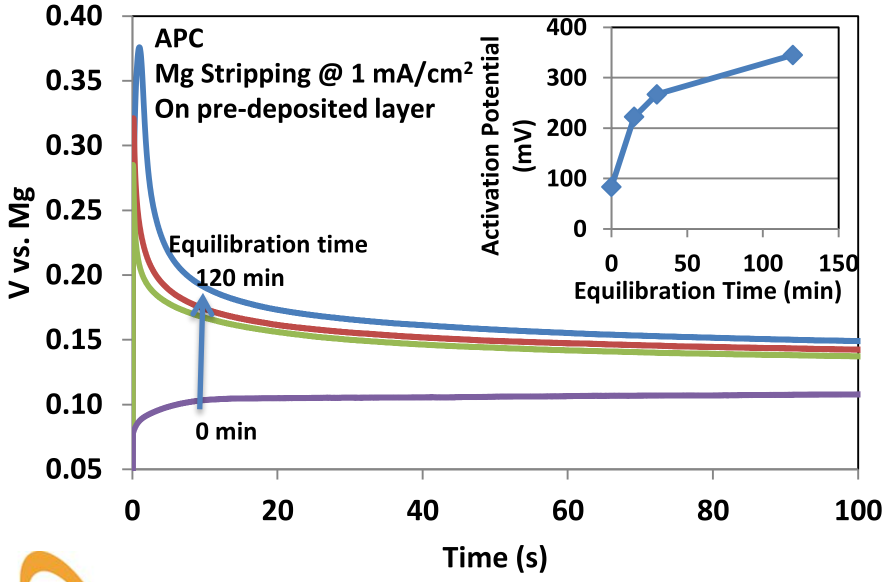
Aurbach et al., Electrochem. Solid State Lett., 2000

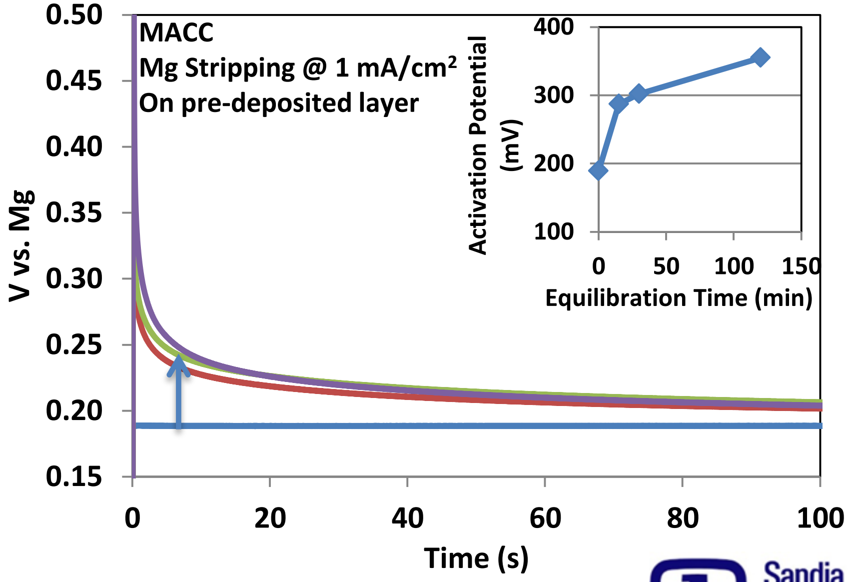
“…adsorption phenomena are responsible...”

“…both Mg deposition and dissolution processes occur via a breakdown of the electrode passivation.”

“…no indications of the formation of stable surface films on Mg...”

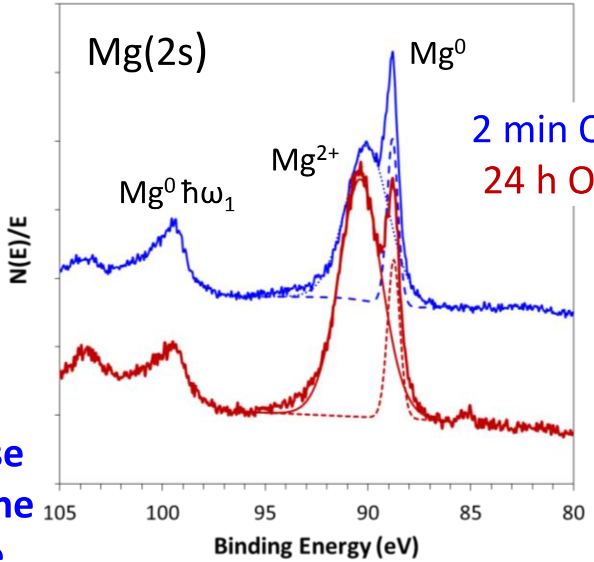
- Activation potential trends indicate that films regulate Mg-cation transport beyond the initial application of current





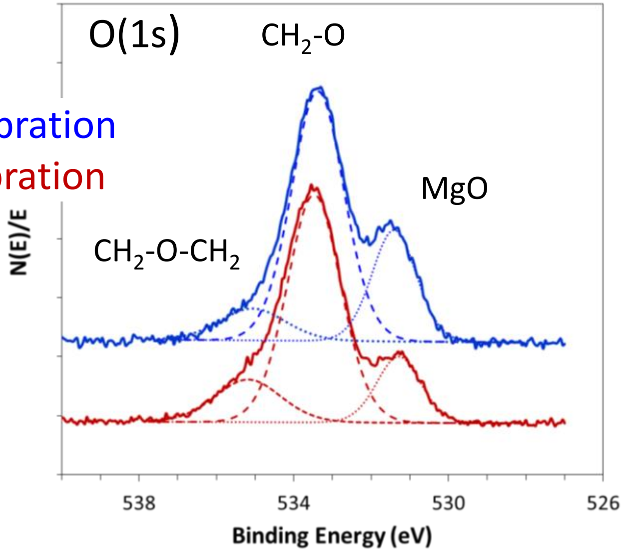
Composite Films Forms

BuMgCl:BuDiglyme (200 ppm H_2O) – rinsed in BuDiglyme and DME – Ar transferred to UHV

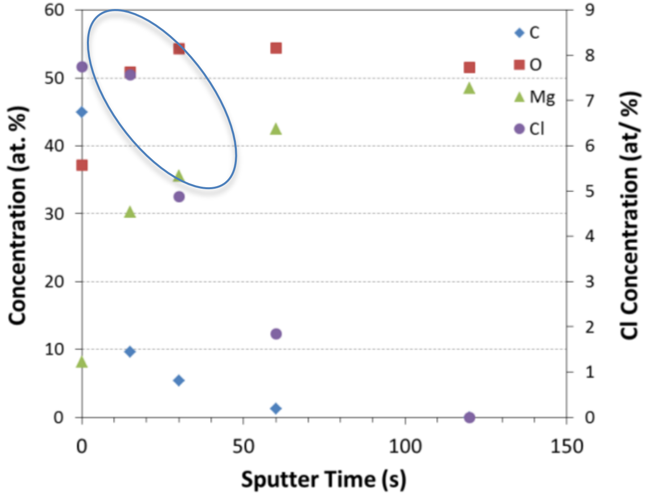


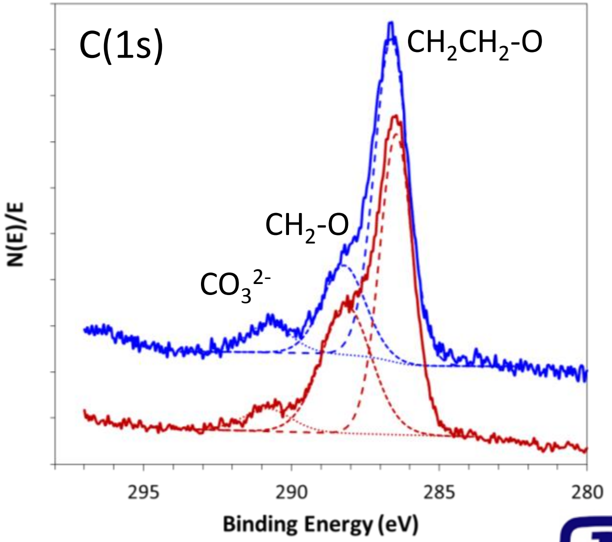
2 min OC equilibration

24 h OC equilibration



ex situ **- as close as allowed to the deposited state**





Are We Even Capturing a Glimpse of the Surface at It's Deposition State?

Unlikley, but we do see differences that suggest the environment produces changes

Cl increase w/ $[H_2O]$ w/ equilibration

Mg^0 signal - thicker cumulative surface layer with $[H_2O]$

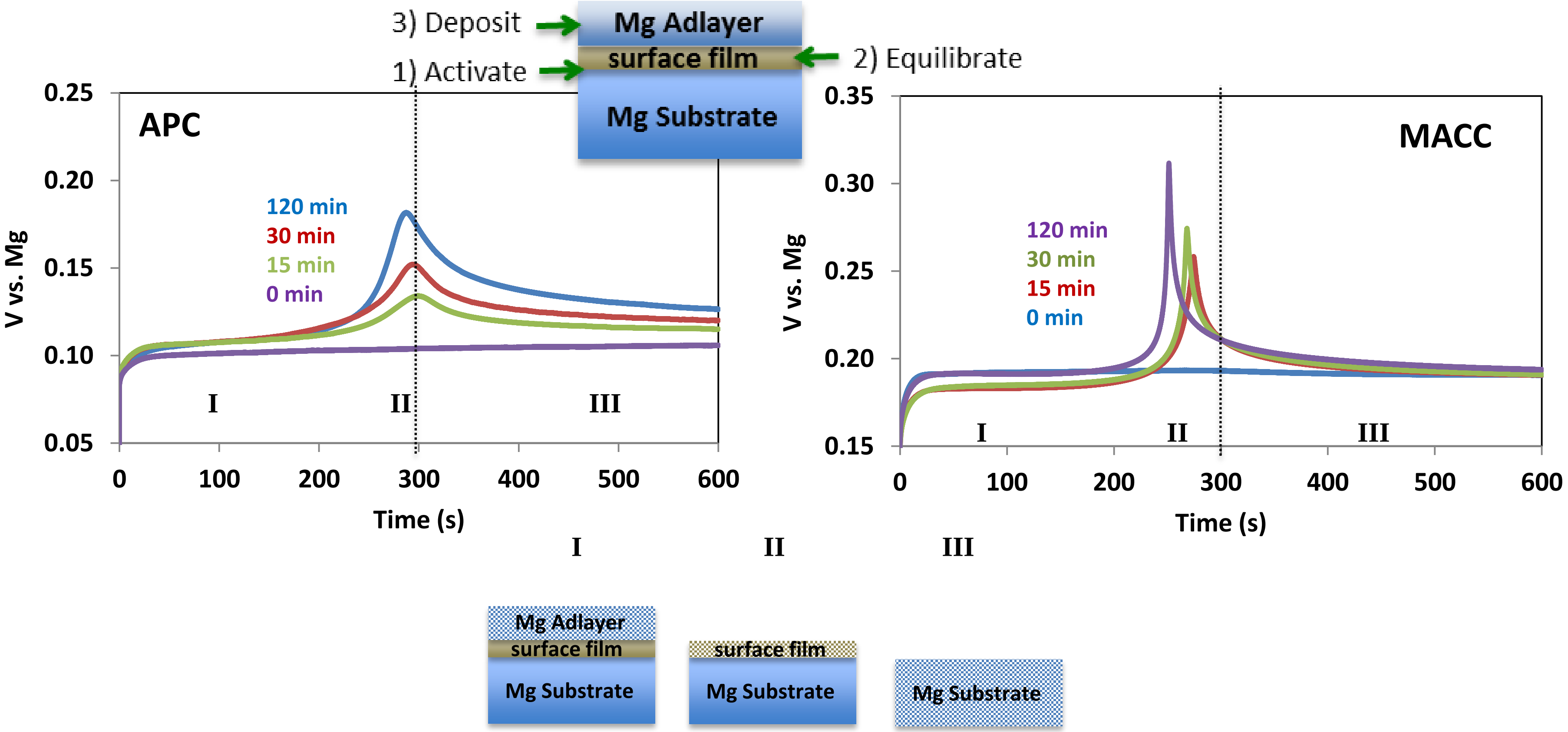
at %

$[H_2O]$	t_{eq}	Mg	C	O	Cl	Mg(0) R	Org O R	Org C/O
200 ppm	2 min	17.7	60.0	17.1	5.2	22.8	89.9	0.317
200 ppm	24 hr	14.2	57.7	20.3	7.8	15.2	82.0	0.428
20 ppm	2 min	17.2	61.2	18.5	3.1	22.5	63.9	0.350
20 ppm	120 min	18.6	60.1	17.2	4.1	24.0	81.5	0.475

relative organic C:organic O increases w/ equilibration – more parent ether?

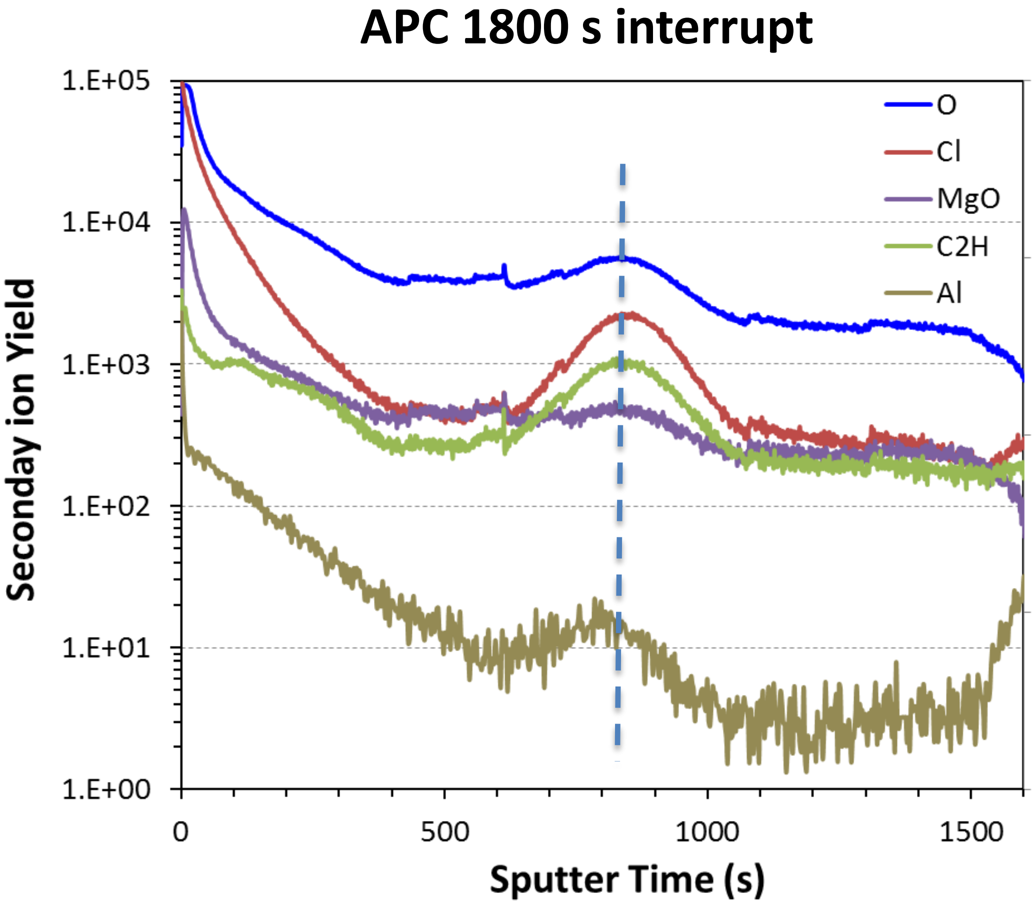
We appear to be sensitive to changes beyond post reaction with vapor phase O_2 and H_2O once emersed!

Surface Film Formation has a Long Lived Impact

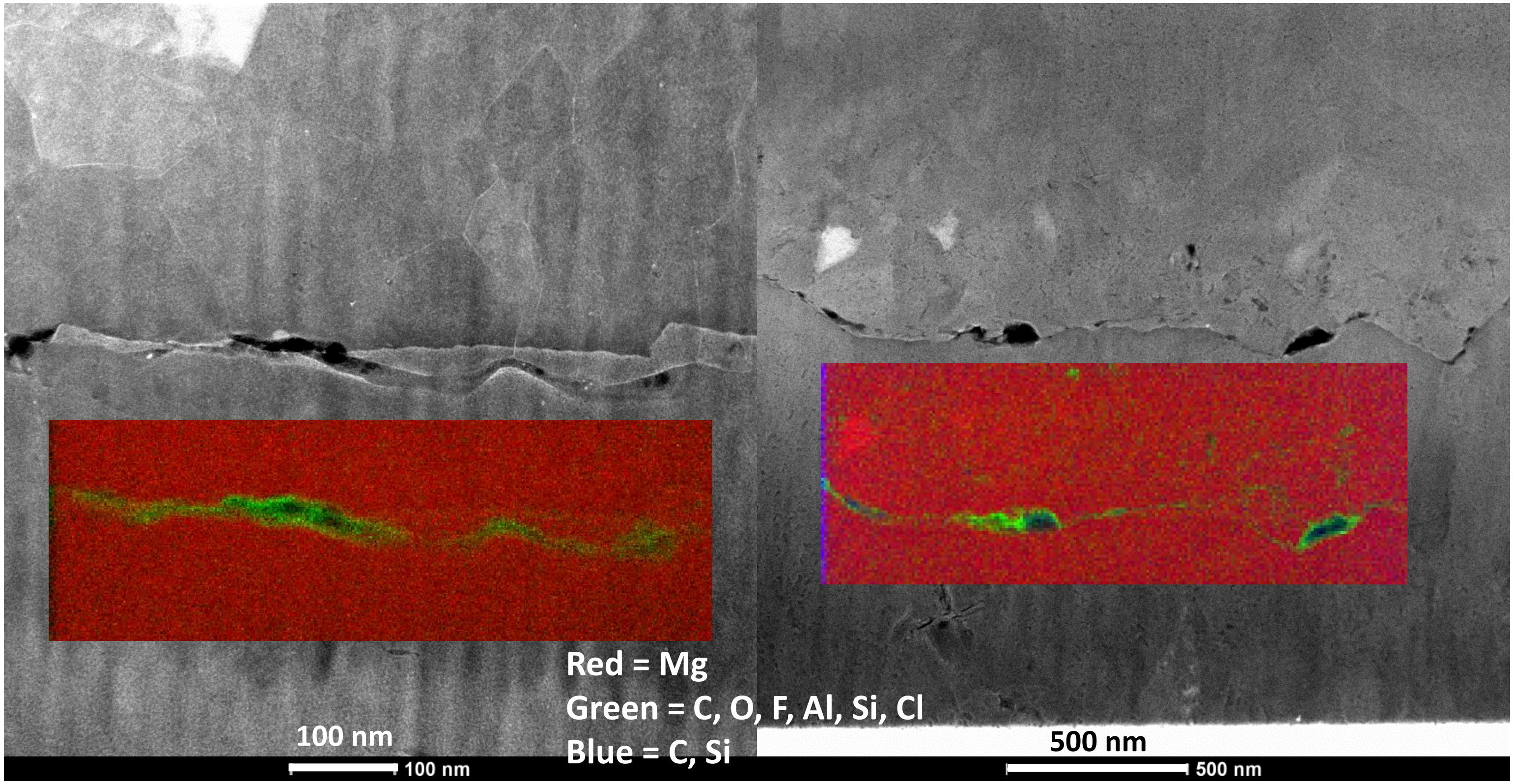


- Deposition has occurred onto or within the film layer without disrupting it
- Film regulates Mg-ion transport until it is fully disrupted/exfoliated

Depth Profile Measurements Indicate a Buried Interface Exists



The Growth Interrupt Interface is what is observed both Electrochemically and Spectrometrically



APC 1800 s interrupt

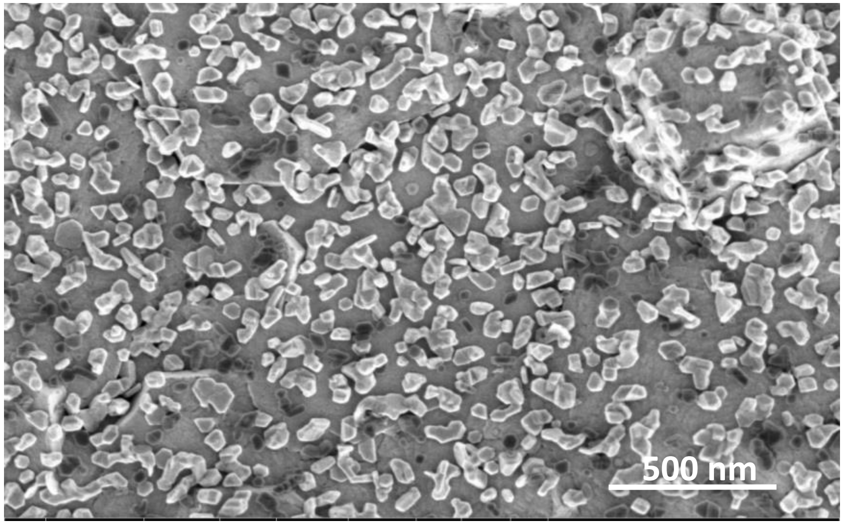
MACC 1800 s interrupt

Red = Mg
Green = C, O, F, Al, Si, Cl
Blue = C, Si

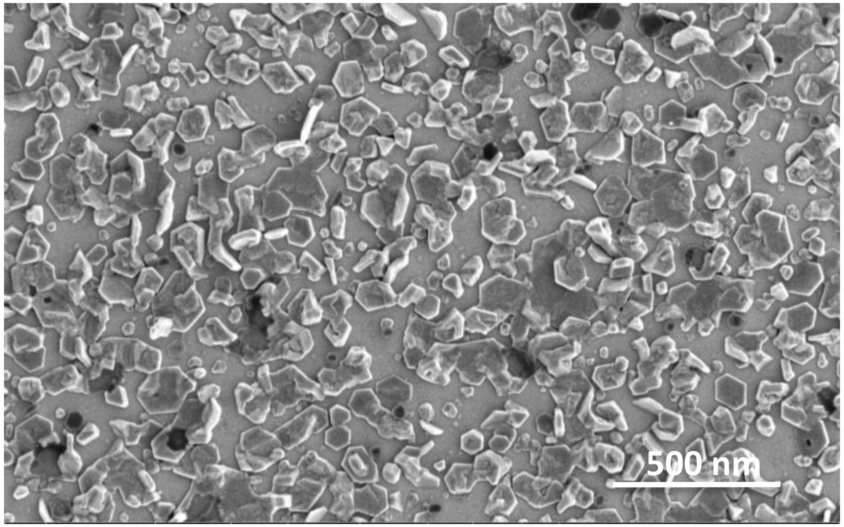
Surface Films formed during Equilibration Force Re-nucleation

SEM of Mg deposited in APC electrolyte

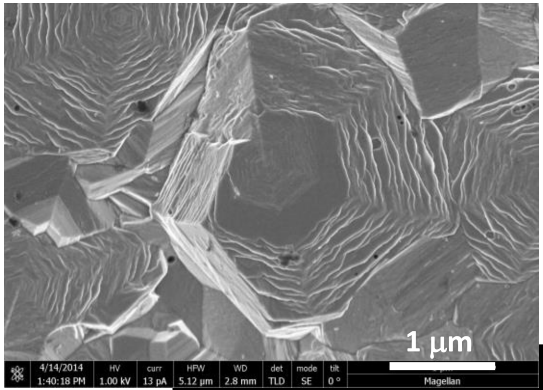
20 nm deposition on Mg (30 min. equilibrated)



20 nm deposition on Au

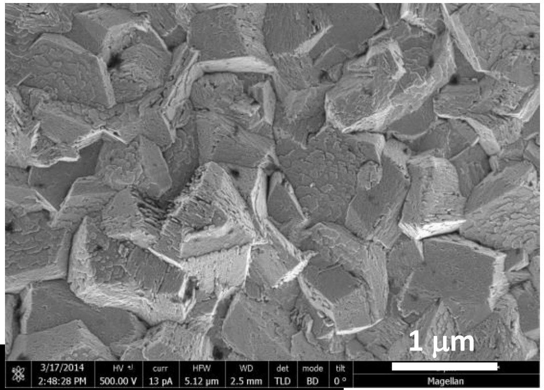


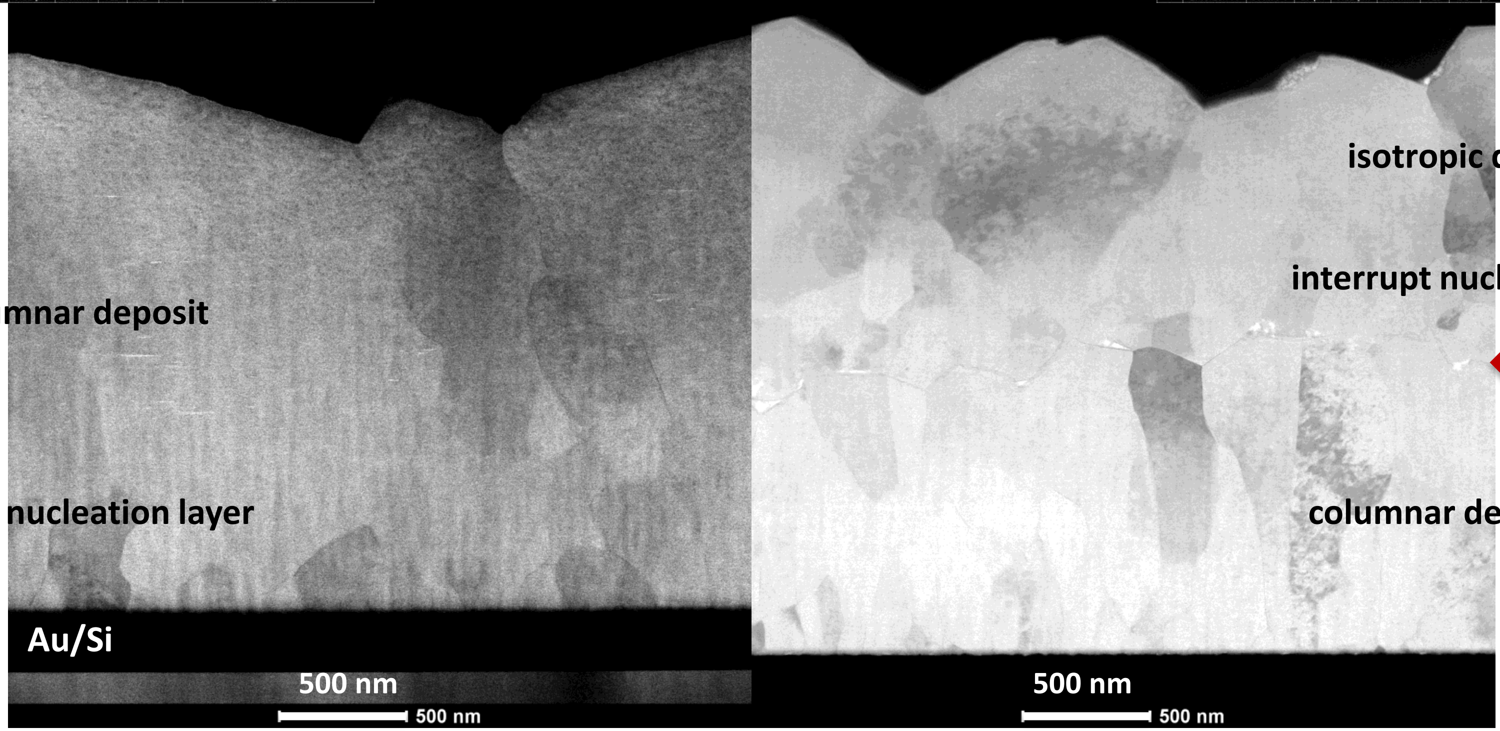
Deposit Structure is Redefined with Re-nucleation



APC 5 s interrupt

APC 1800 s interrupt





columnar deposit

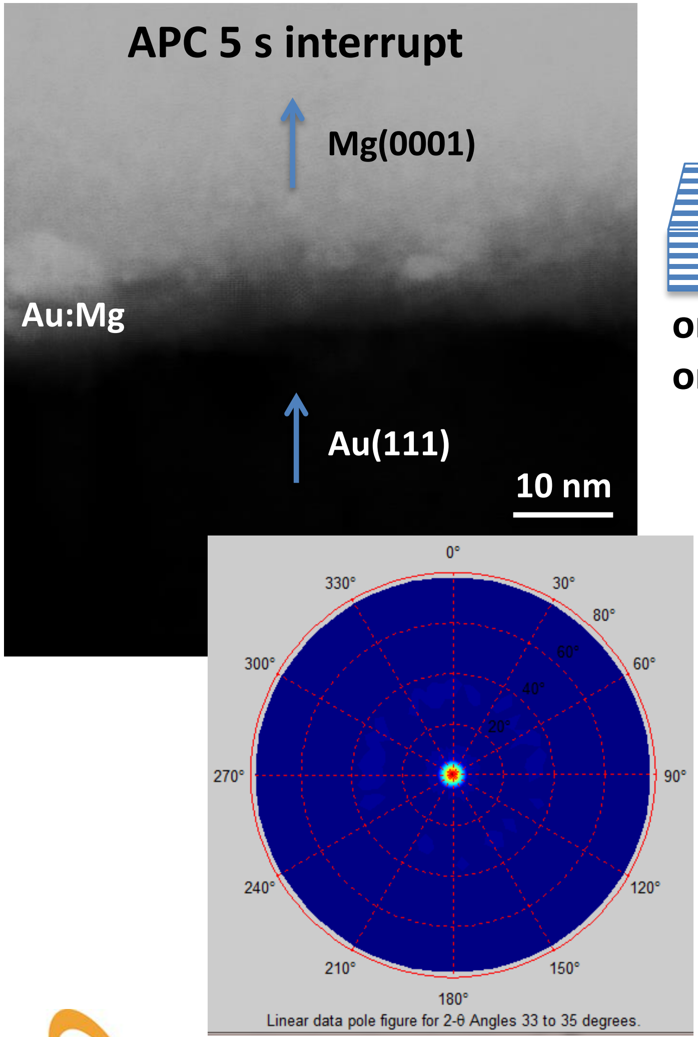
Base nucleation layer

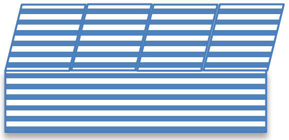
isotropic deposit

interrupt nucleation layer

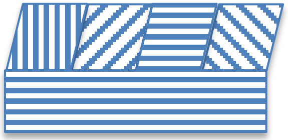
columnar deposit

Additional Mg Deposition behaves as if on a Non-aligning Foreign Substrate



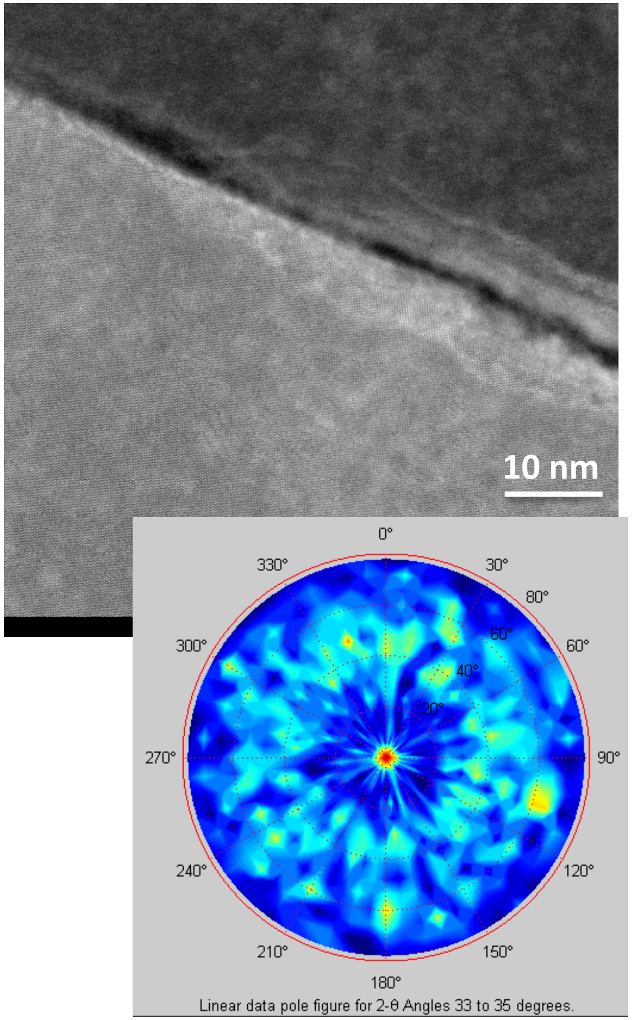


oriented overlayer
oriented base

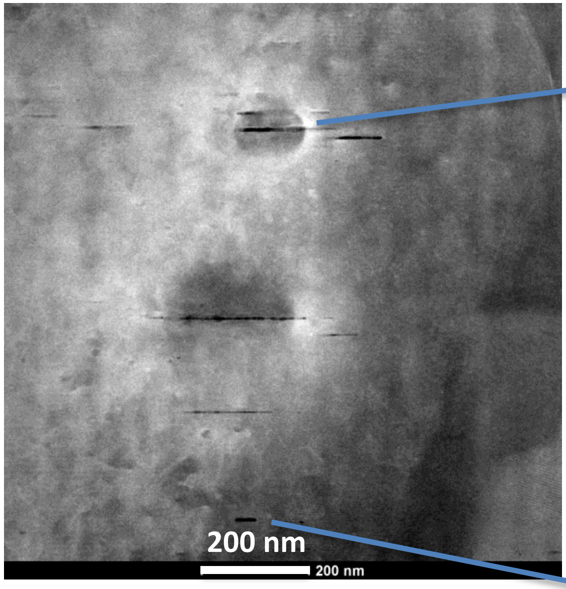


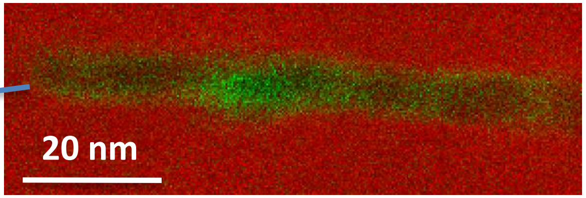
random overlayer
oriented base

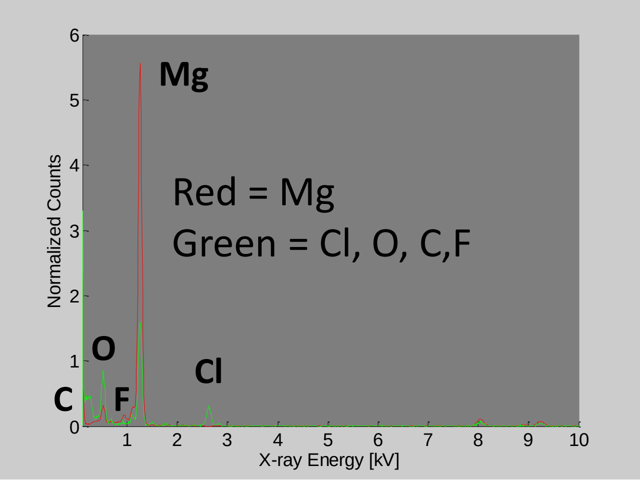
APC 1800 s interrupt



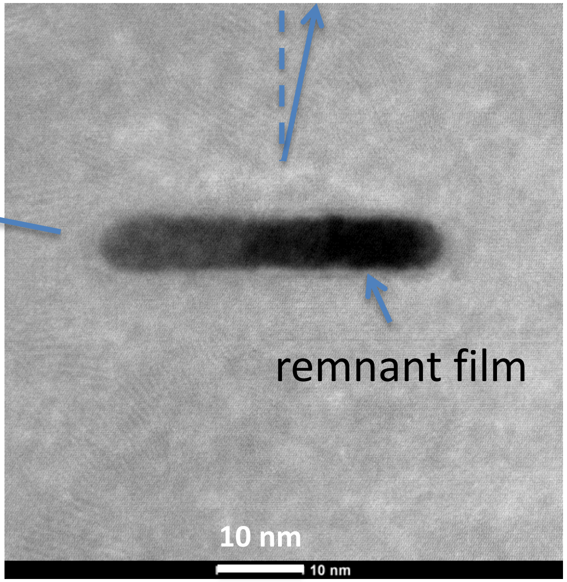
Is the Metal Accommodation Rate Limited in the Chloroaluminates?



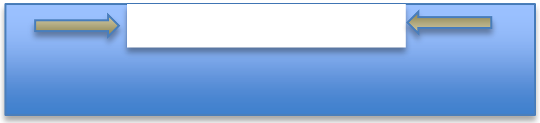


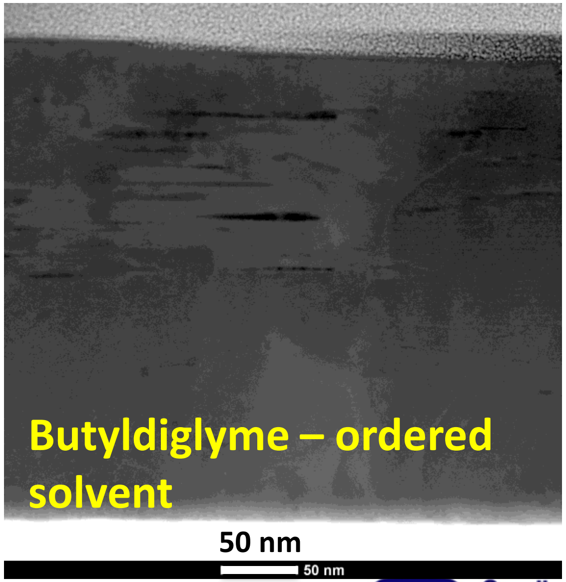


with 6° of c axis



2 to 5 nm high linear voids are present on the Mg basal plane

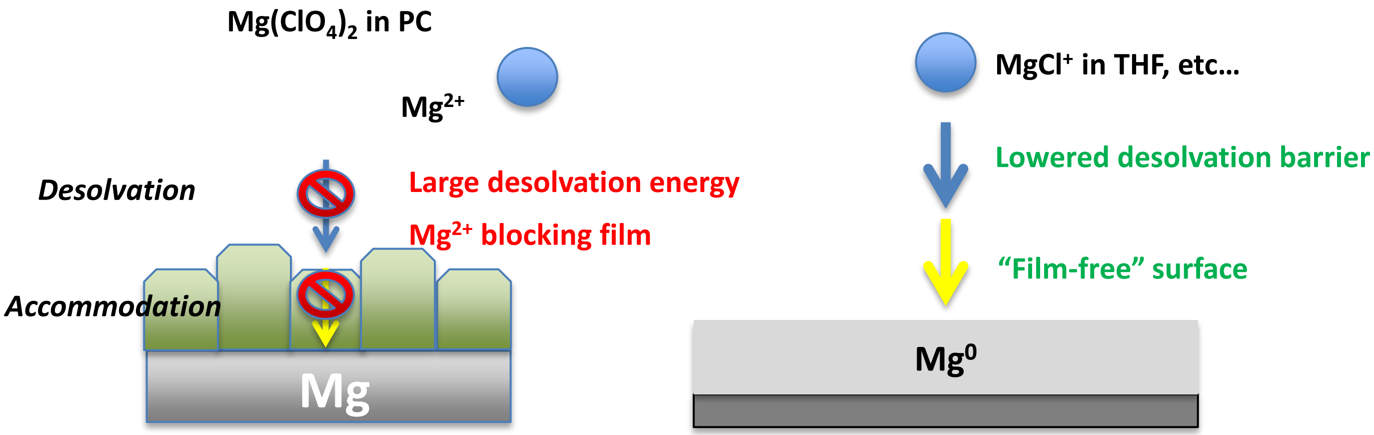




Butyldiglyme – ordered solvent

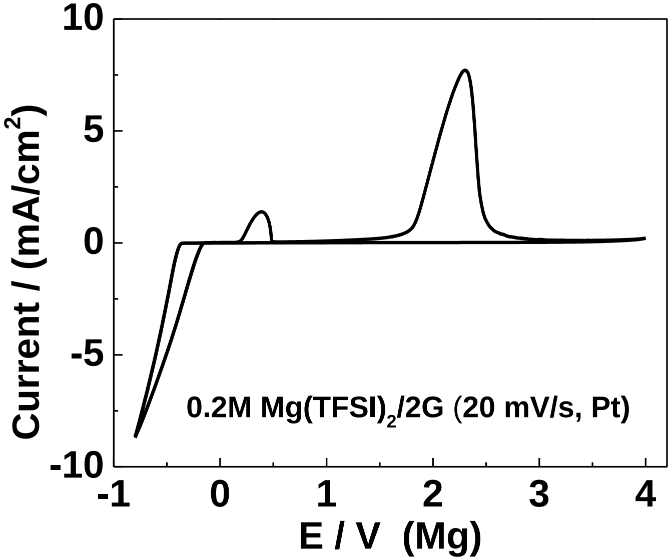
Conventional Mg Salts Produce Blocking Layers – don’t they?

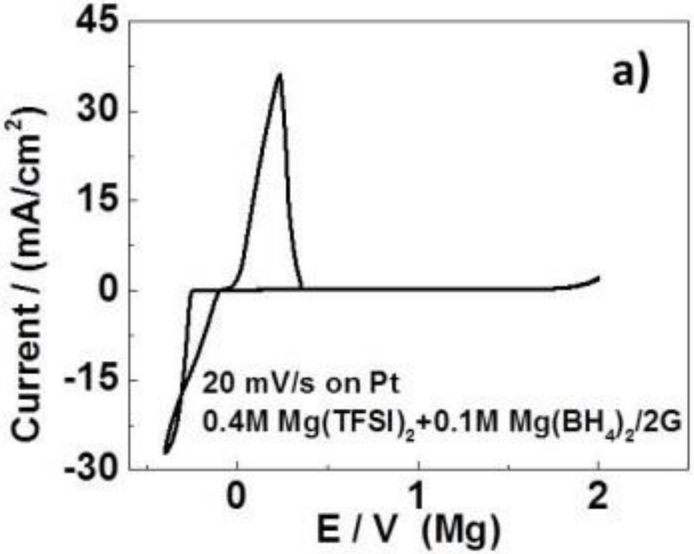
Mg Plating in Ethereal Chloro-Complex Electrolytes

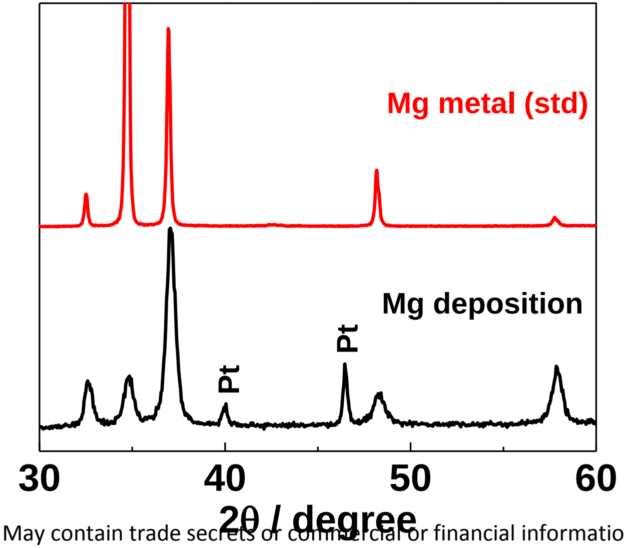


- A body of literature exists documenting electrolyte decomposition
- What does the lack of a high efficiency response in CV on a foreign substrate really tell us?

Mg can be Deposited using Weakly Coordinating Anion Ligands







With Mg(BH$_4$)$_2$

- XPS does not show TFSI decomposition
- No sign of passivation
- 98.8% CE

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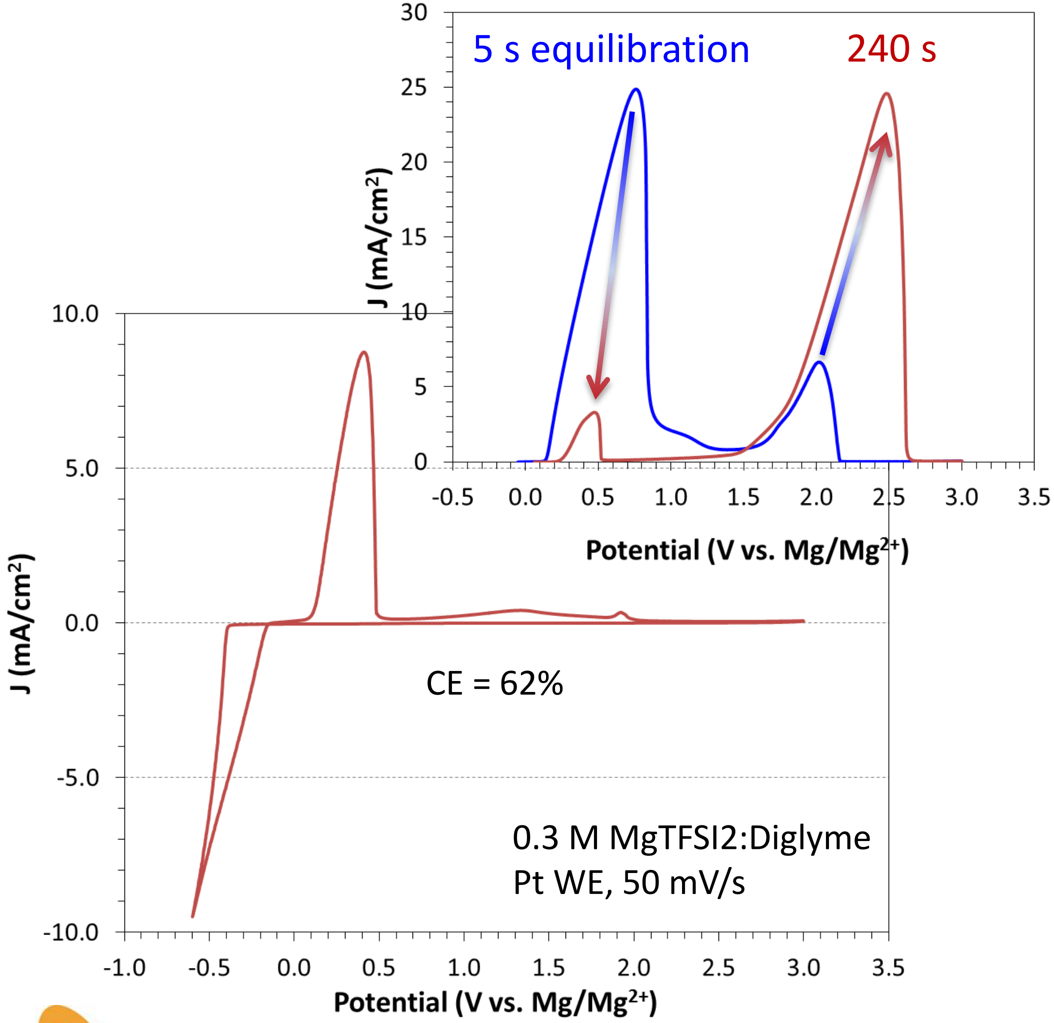
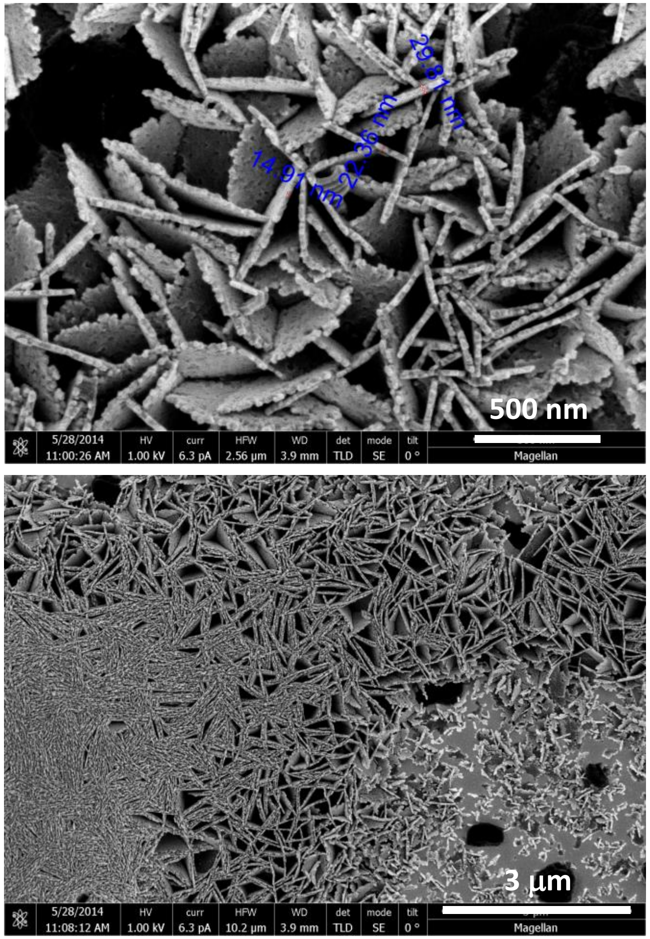
Mg Passivation Occurs After the Deposition



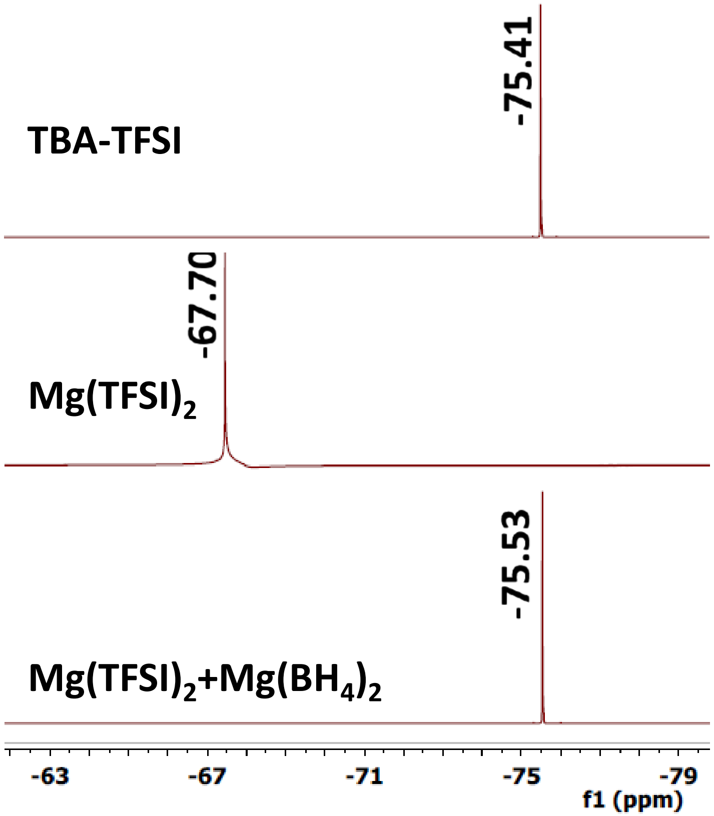
CE = 62%

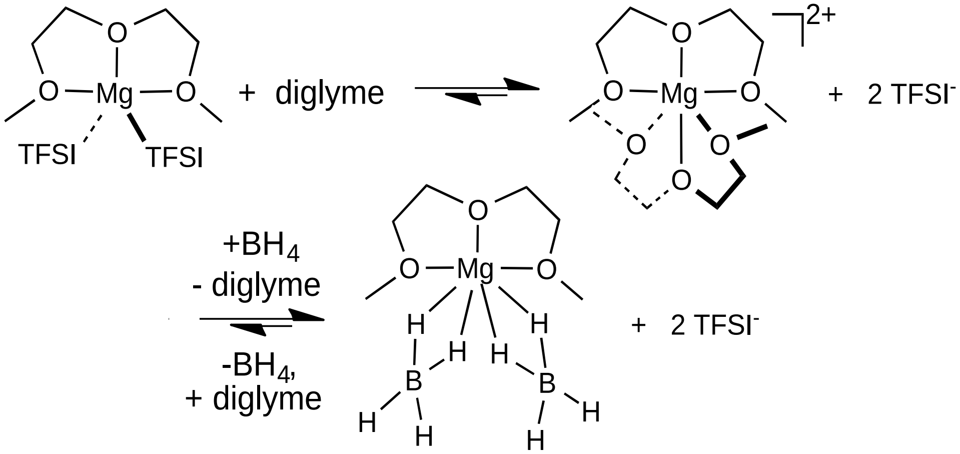
0.3 M MgTFSI2:Diglyme
Pt WE, 50 mV/s

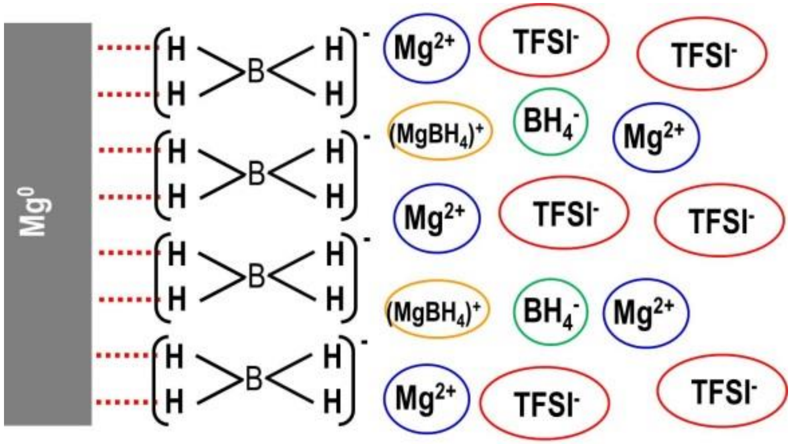
Mg deposit - dendritic platelets



Surface Adsorbates as an Alternate Strategy?







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

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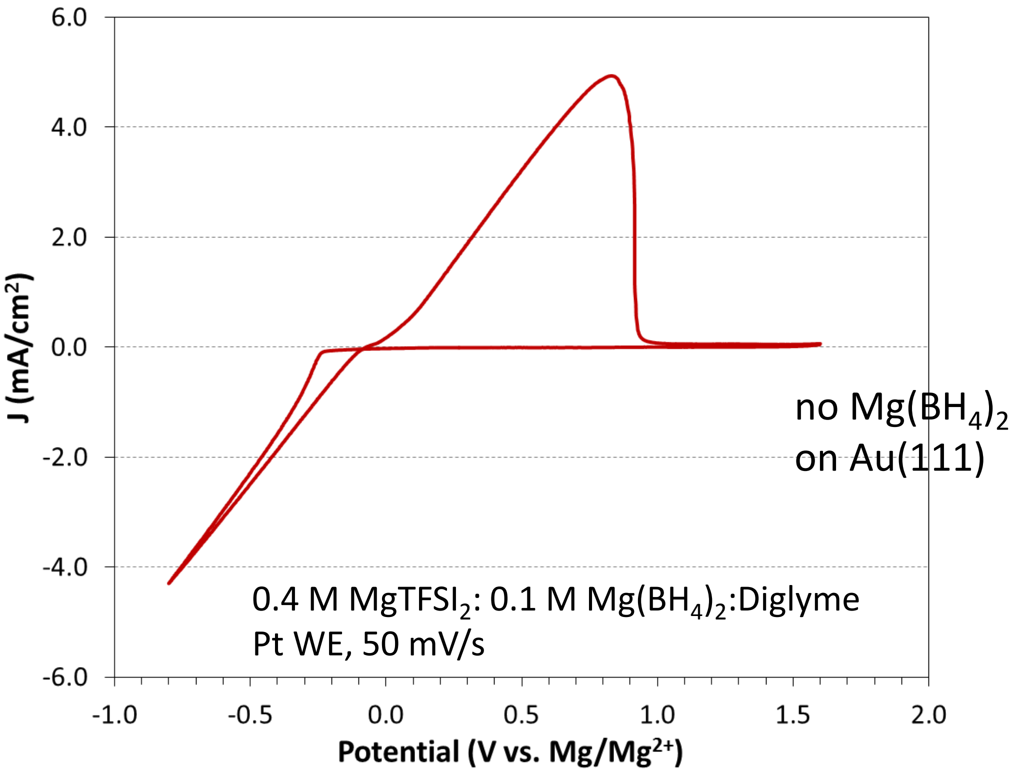
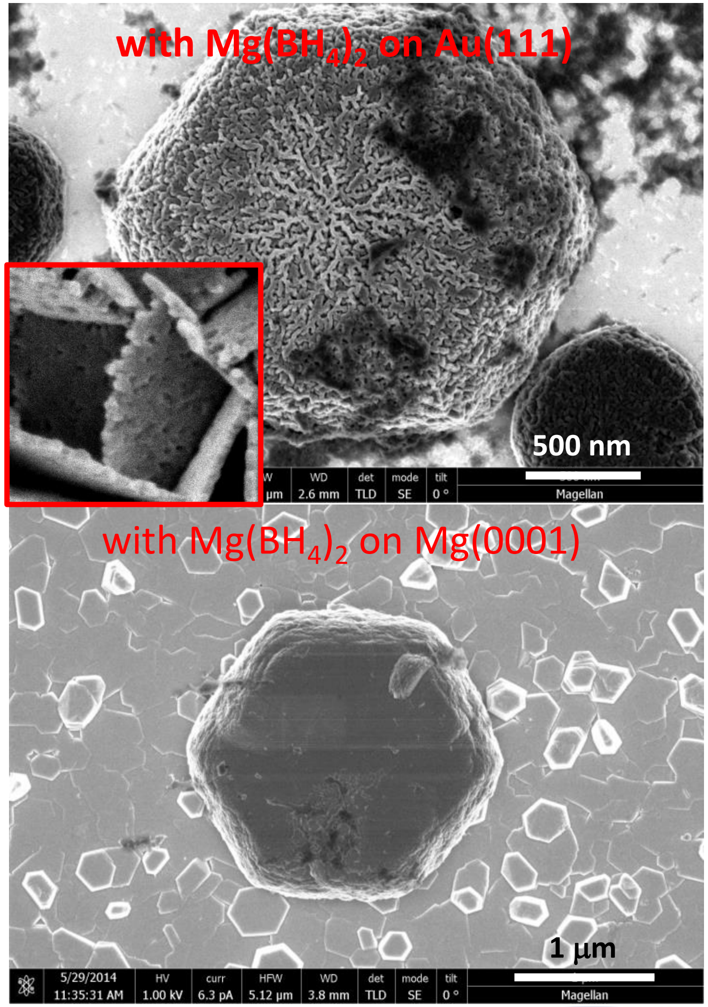
The Mg Structural Motif is Unchanged with *Adsorbate*



no $Mg(BH_4)_2$ on Au(111)

0.4 M $MgTFSI_2$: 0.1 M $Mg(BH_4)_2$:Diglyme
Pt WE, 50 mV/s

1 mA/cm^2: dendritic sheets



Protection without altering growth mode

What if the Primary Reactants are the Coordinating Ligands?

If the Mg-L(e^-) is the activated complex that dictates how reaction progresses

Then:

- Tuning interfacial speciation becomes an impactful strategy
- Start with the bulk by displacement with stable ligands
- Move toward structured double layers that force the coordination change
- Is a highly ordered double layer really a molecular scale membrane?
- Have we thought about exploiting IL’s for this structural attribute?

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
- 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
- Al^{3+} deposition is well established in acidic Ils (EMICl)
  - $Al_2Cl_7^-$ complex

What the Chloroaluminates have Taught Us

- The importance of establishing a chemical inventory – bulk speciation and the source term for Mg^{2+} delivery
  - IR, Raman, NMR spectral libraries, X-ray RDF
  - Computation to support spectroscopic assignments
- Two problems need solutions – desolvation & accommodation
- Speciation at the interface - what exists in the bulk does not reflect the critical components responsible for efficient deposition/dissolution or insertion/extraction
  - Role of organic adsorbates, adsorbed Cl^- (anion), surface film formation
  - APC does not work with oxides
- Evolution of the electrolyte – the electrolyte changes (electrolytic, hydrolytic)
  - Role of byproducts

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