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JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Metal Anode Interfacial Reactions and Protection Strategies

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Sandia National Laboratories

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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

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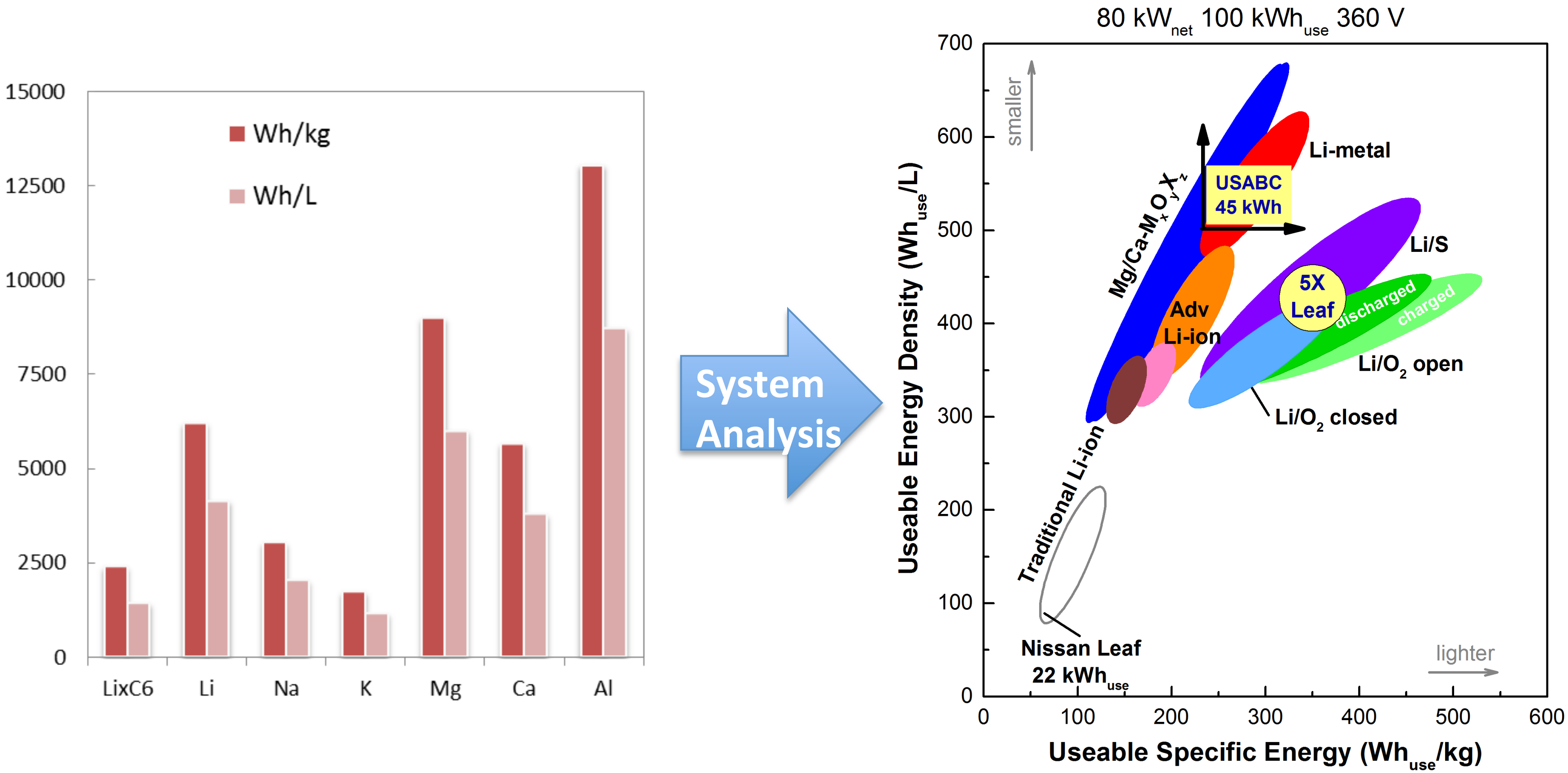
Metal Anodes are the Key to Increased Energy Density



Techno-economic model:

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

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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

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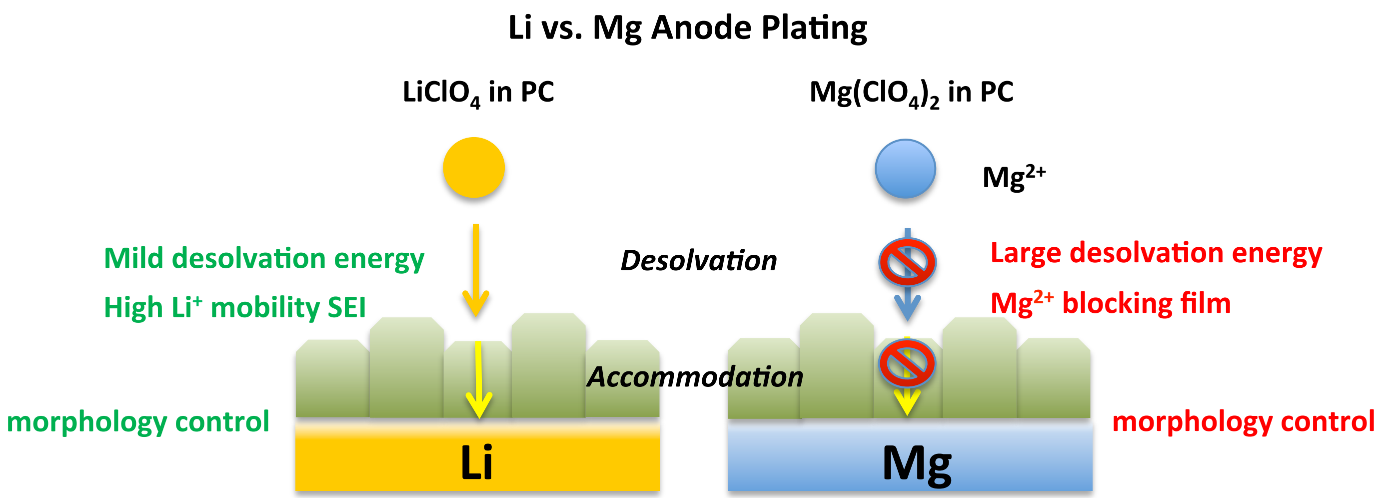
Metal Anode Challenges

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



Science challenges and research

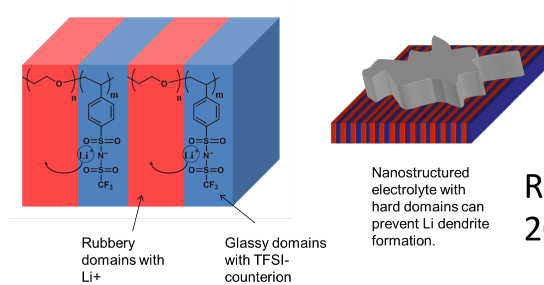
- Efficient cation desolvation
- Efficient cation accommodation – cathode & anode
- Electrolyte stability
- Metastability - Activation, Corrosion, Protection

Strategies for Li Morphology Control & Protection

Microscopic mechanical systems

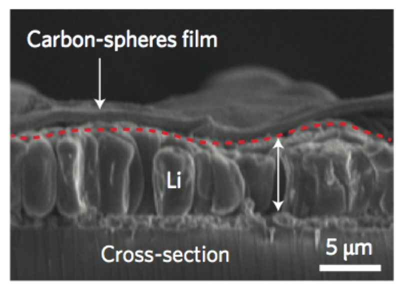
PolyPlus PLE

Microscopic membranes



R. Bouchet et al. *Nat. Mater.* 2013

Nanoscopic architectures

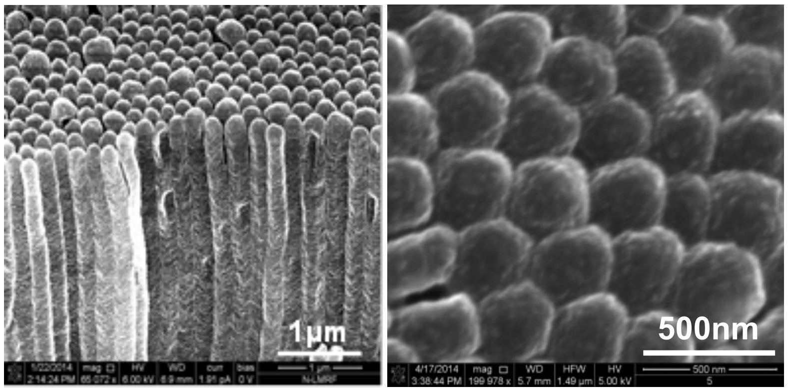


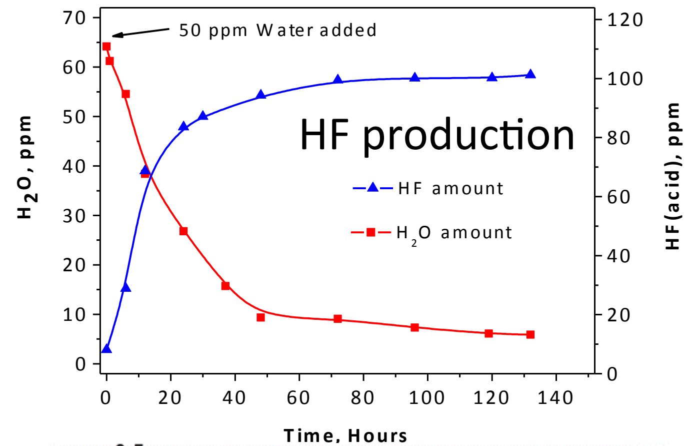
G. Zheng et al. *Nat. Nanotech.* 2014

Nanometric films – tailored solid electrolyte interphases

Nanometric Films as a Means of Controlling Morphology

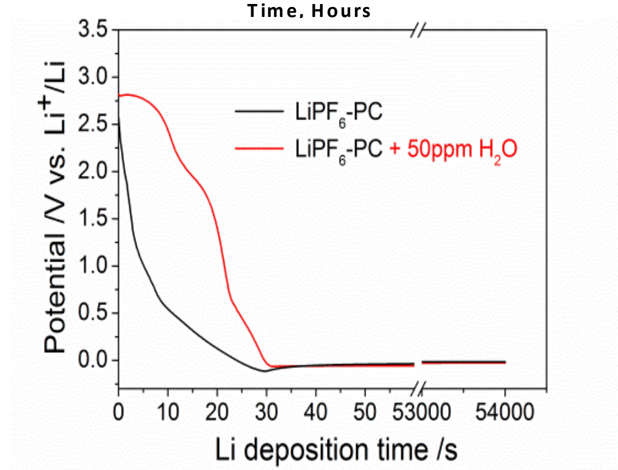
Could electrolyte chemistry be used to direct Li growth?





Addition of H_20 (25 – 50 ppm) in $LiPF_6$/PC electrolytes produces a Li^o nanorod morphology – maintained with cycling

HF reduction leading to LiF film formation during initial deposition on Cu



J.-G. Zhang and team

Pacific Northwest NATIONAL LABORATORY

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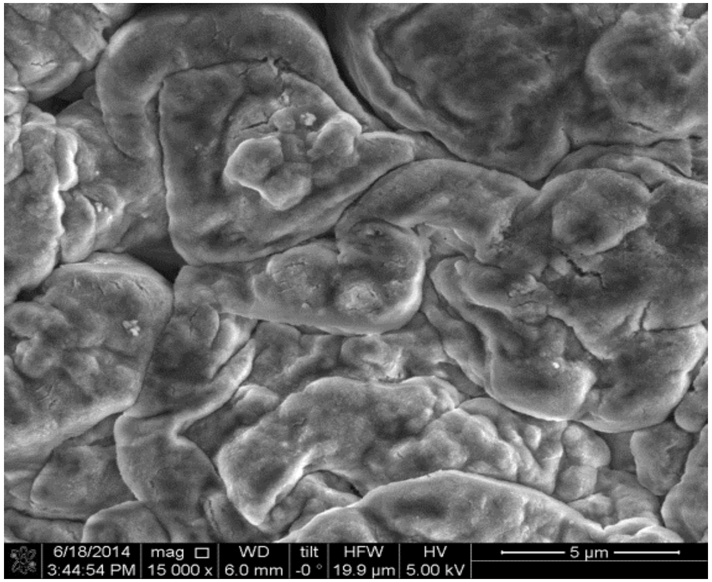
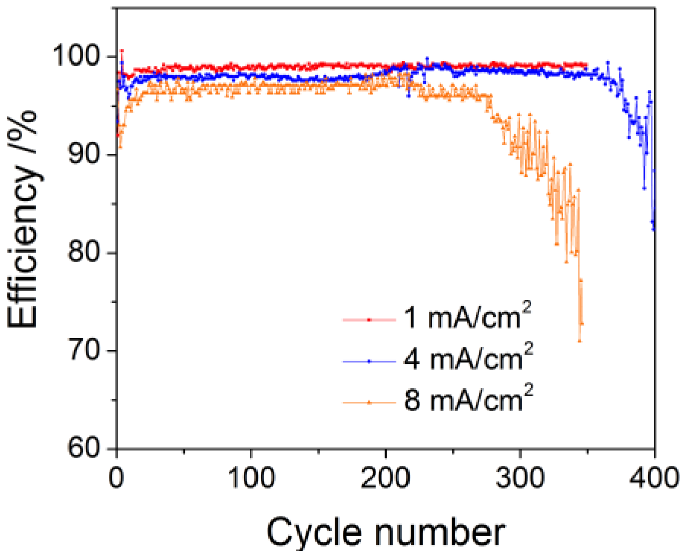
Dendrite-free Li Deposition at Relevant Current Densities

lithium bis(fluorosulfonyl)imide:1,2-dimethoxyethane





LiFSI-DME electrolyte demonstrates superior Li cycle performance with high Coulombic efficiency at high current densities.

J.-G. Zhang and team Pacific Northwest NATIONAL LABORATORY

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Mg Electrolyte Roadmap

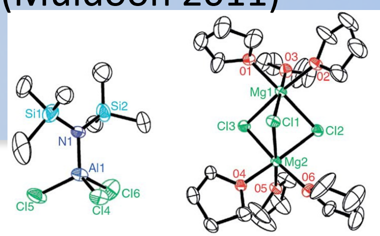
Lewis Acid – Base Complexes

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

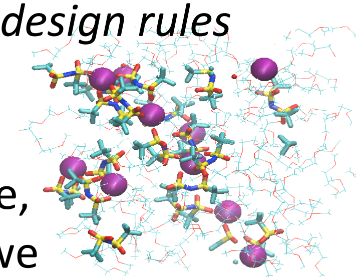
JCESR demonstrates speciation is different than expected

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

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

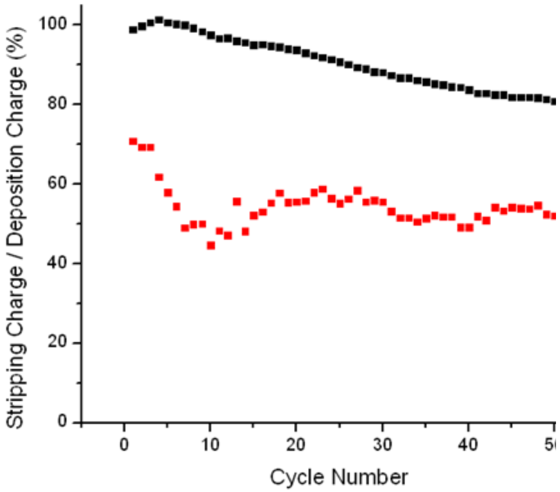
Non-directed ligand exchange
$MgTFSI_2$ + $MgCl_2$ (Pellion 2013) Anion redistribution

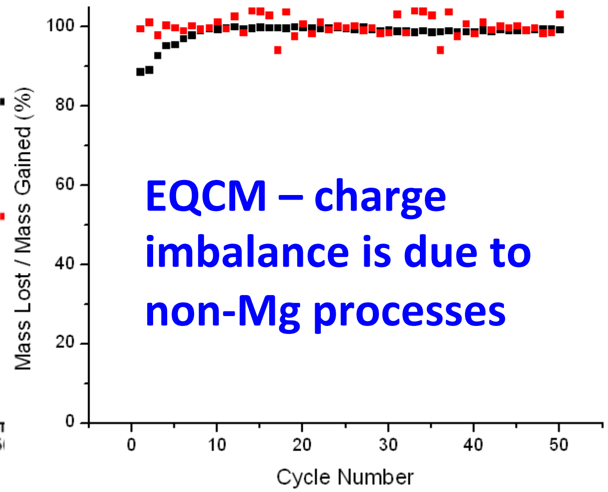
Simple Mg Salts
$MgTFSI_2$ in glyme, (Ha, 2014) Can we Eliminate chloride?

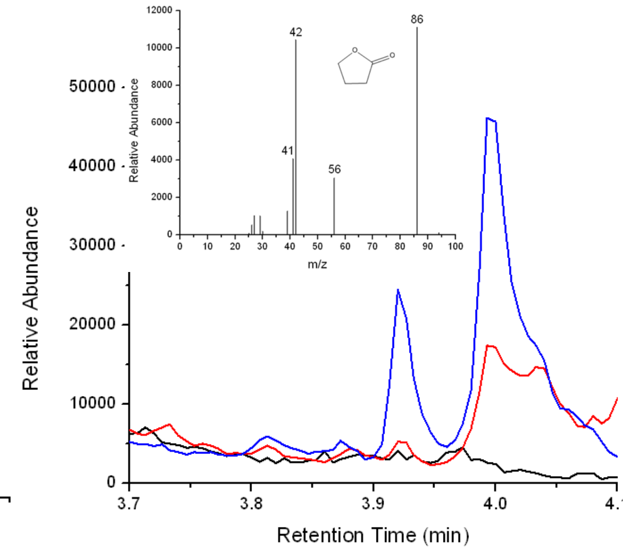


JCESR demonstrates conventional systems yield unexpected activity

Organohaloaluminate Electrolytes Degrade







- 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

C. Barile et al. J Phys Chem C 2014

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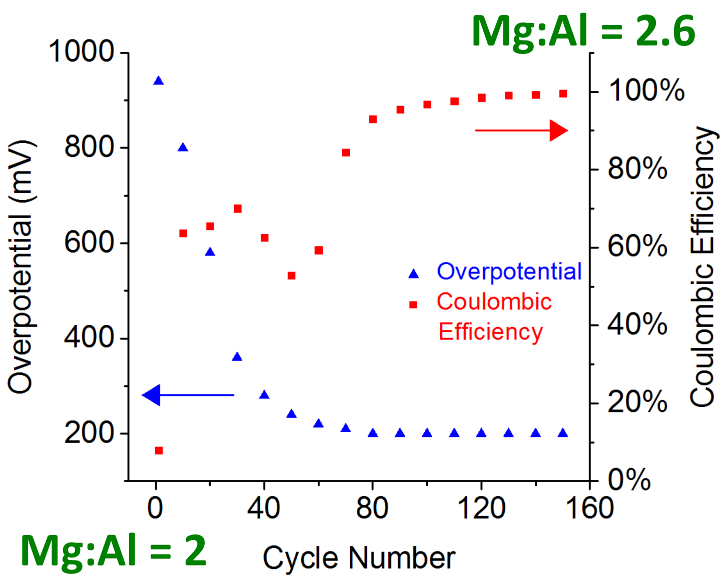
Anode Functionality is Directly Tied to the Electrolyte

How Mg^{2+} is delivered for deposition in a chloroaluminate electrolyte is unresolved. The answer is instrumental in designing electrode compatible electrolytes.

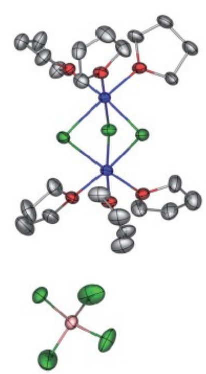
Repeated deposition and stripping *conditions* the electrolyte – changes its composition



Sample	Ions Detected
Unconditioned MACC in THF	$[(THF)_n\text{-}C_2H_4{+}H]^+$ $[(THF)_n\text{-}C_2H_4\text{-}CH_2{+}H]^+$ $[AlCl_3O(THF)_n\text{-}H_2{+}H]^+$
Conditioned MACC in THF	$[GBL{+}H]^+$
Conditioned MACC in THF after one week at OCP	$[(THF)_n\text{-}C_2H_4{+}H]^+$ $[(THF)_n\text{-}C_2H_4\text{-}CH_2{+}H]^+$ $[AlCl_3O(THF)_n\text{-}H_2{+}H]^+$
$AlCl_3$ in THF	$[(THF)_n\text{-}C_2H_4{+}H]^+$ $[(THF)_n\text{-}C_2H_4\text{-}CH_2{+}H]^+$ $[AlCl_3O(THF)_n\text{-}H_2{+}H]^+$

ESI-MS THF ring opening

- $Mg_2Cl_3(THF)_n^+$ (dimer)does not deliver Mg cation!
- $AlCl_3$ catalyzed cyclic ether polymerization creates inhibiting oligomers



JCESR hypothesis

$Mg_3Cl_5(THF)_6^+ \leftrightarrows MgCl\,(THF)_5^+$ + dimer

$\downarrow\uparrow$

$[MgCl(THF)_5]_{ads}$

monomer delivers Mg cation!

C. Barile et al. *J Phys Chem C* 2014 accepted

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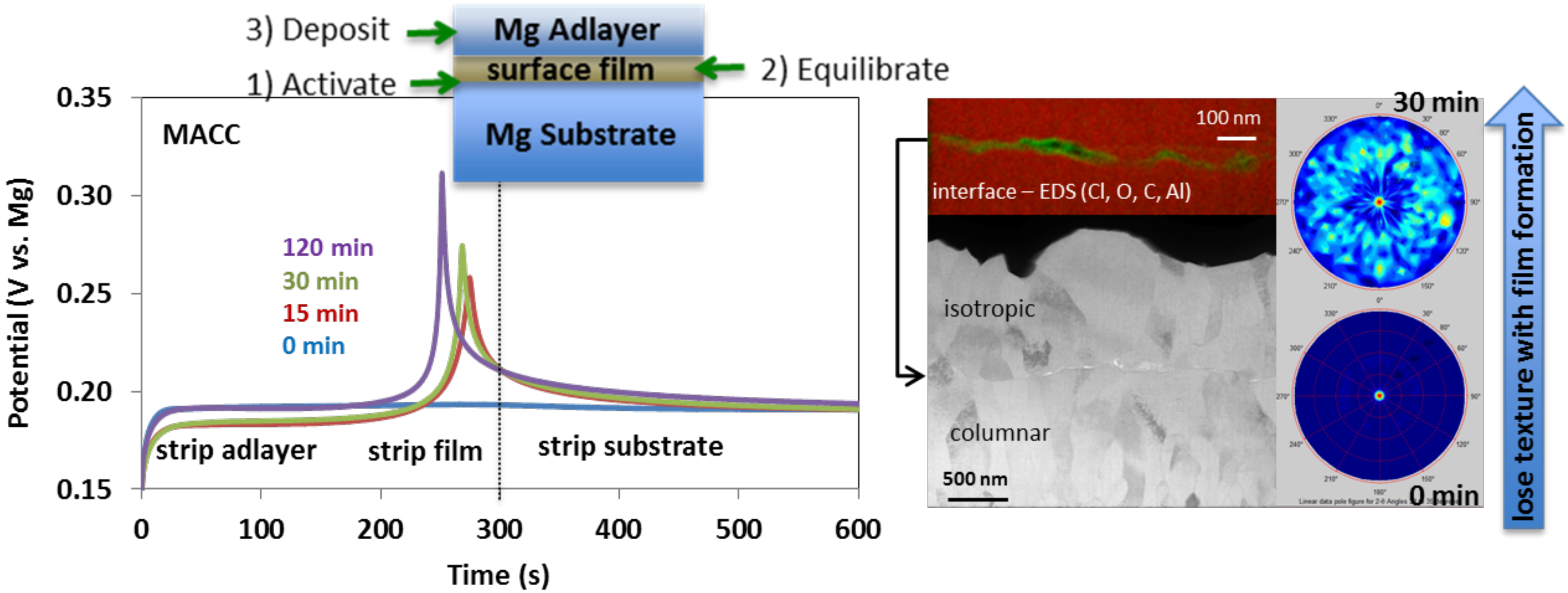
Mg Anode Surface Films Dictate Deposit Structure in Chloroaluminate Electrolytes



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

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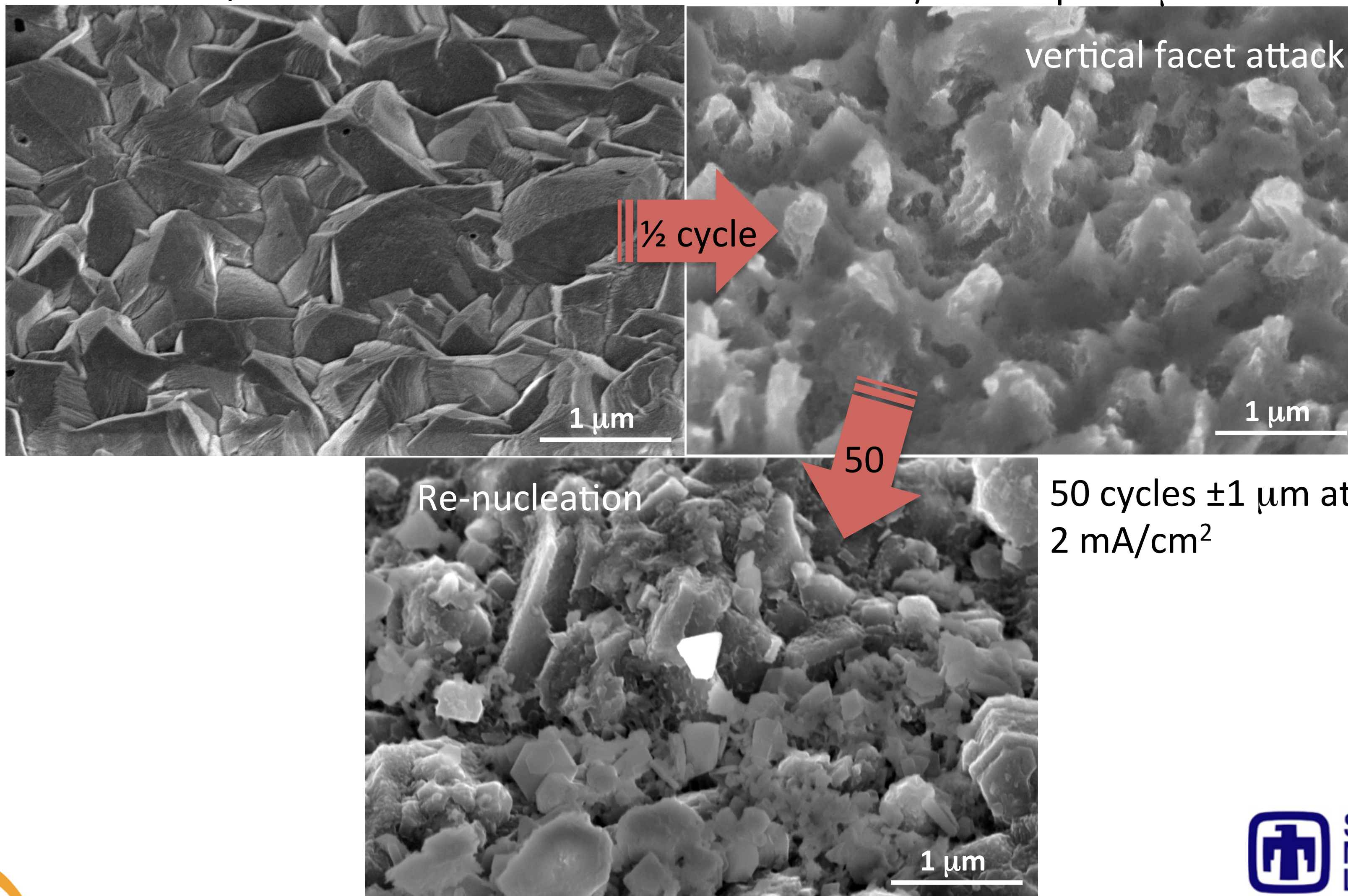
High Rate Dissolution is Crystallographically Anisotropic

2 mA/cm^2 deposition in a Chloroaluminate

2 mA/cm^2 strip of 1 μm



50 cycles ±1 μm at 2 mA/cm^2

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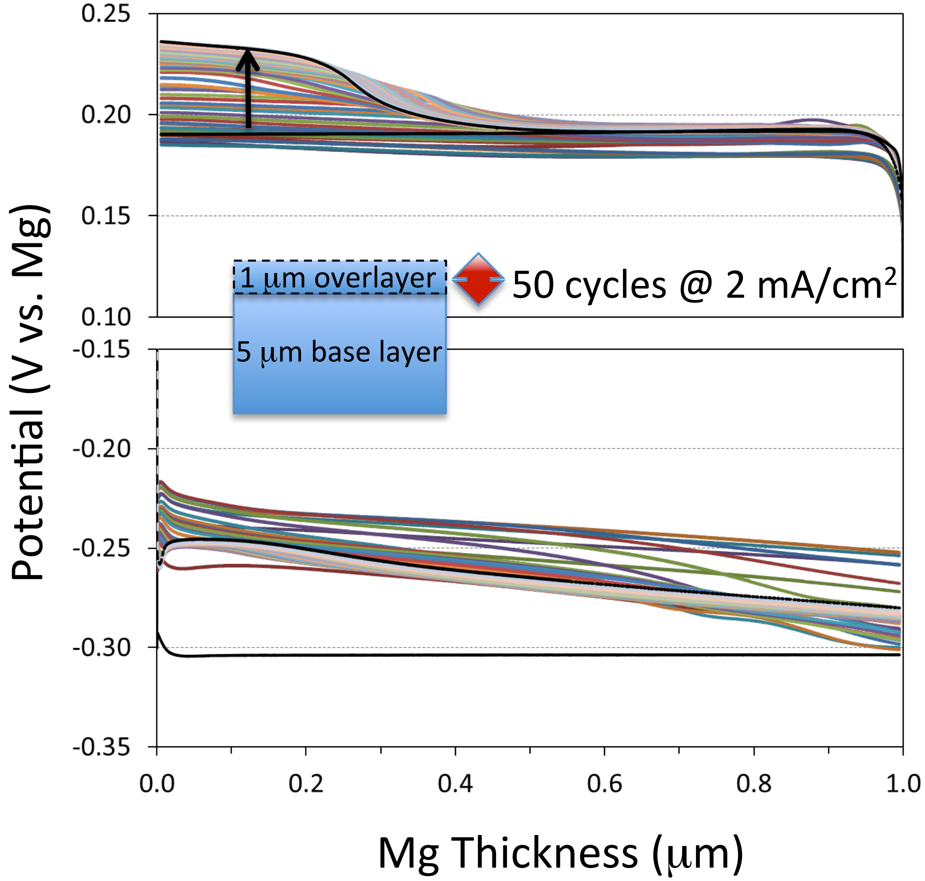
N. Hahn et al. J Phys Chem C 2014 submitted

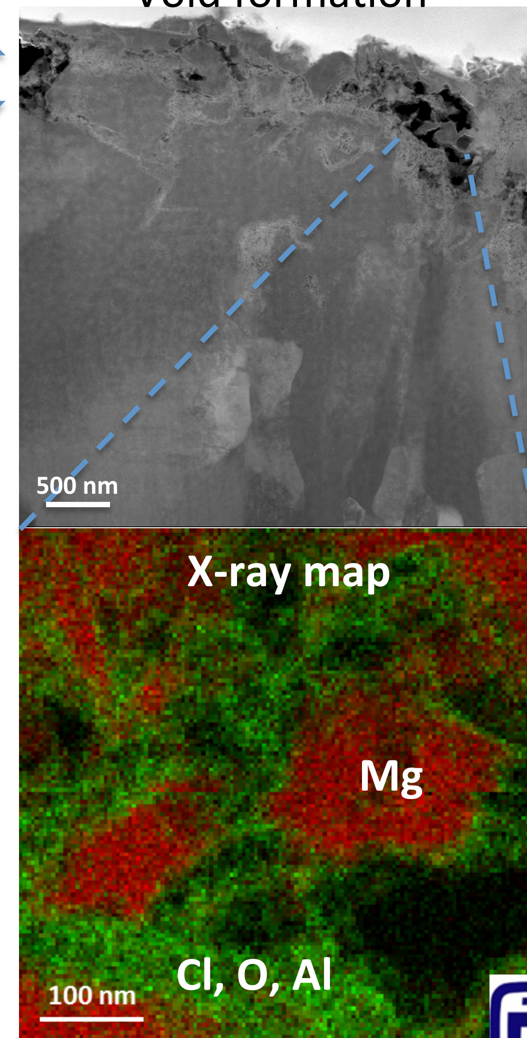
Morphology Control is a Problem for Mg at High Rates

Filmed interface evolves with cycling



observed for APC and MACC(var. solvent)

Void formation



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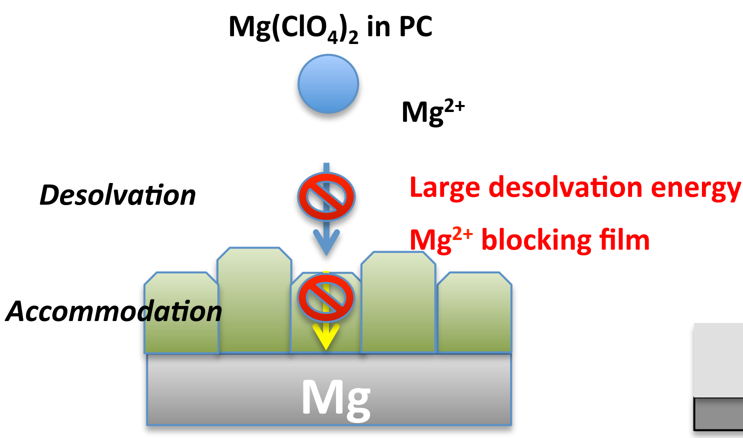
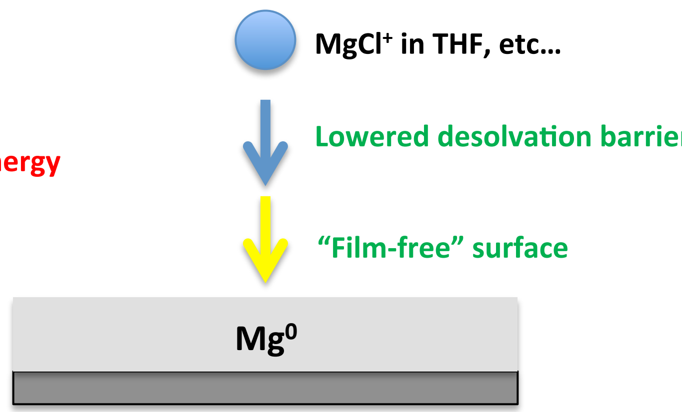
N. Hahn et al. J Phys Chem C 2014 submitted

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?

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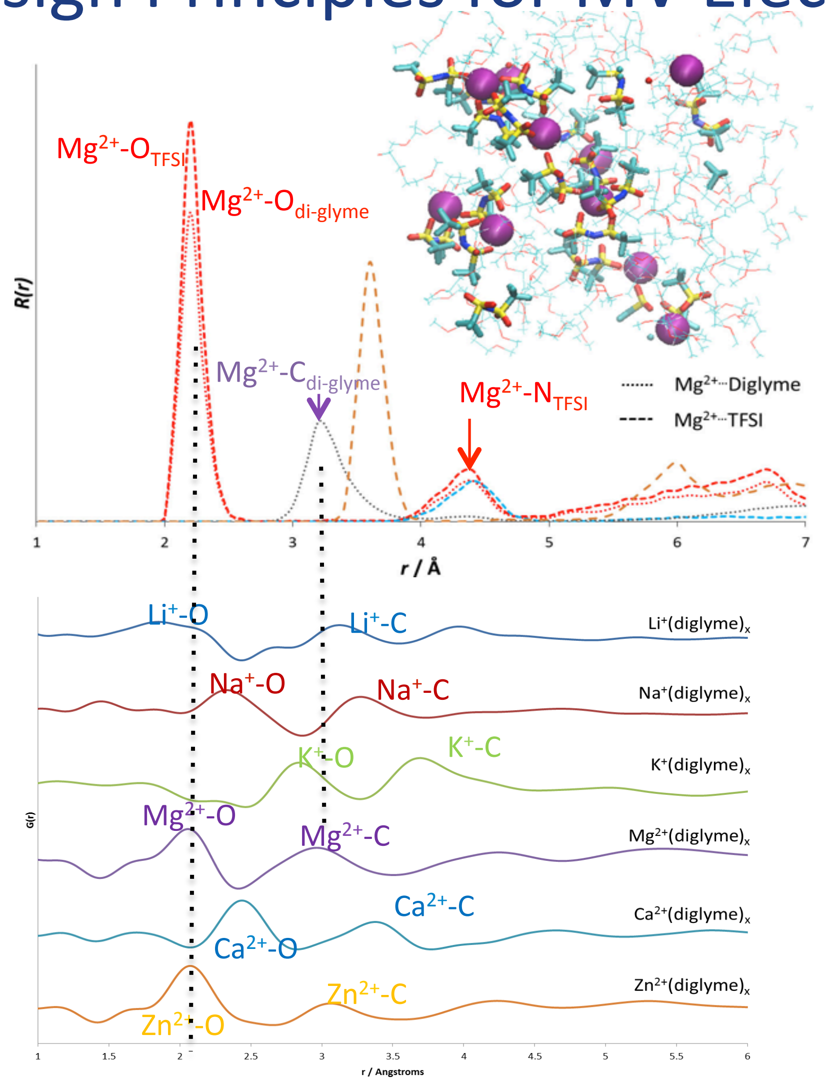
Experimental feedback to the Electrolyte Genome Reveal Design Principles for MV Electrolytes



$Mg(TFSI)_2$ 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. *J Phys Chem Lett* 2014

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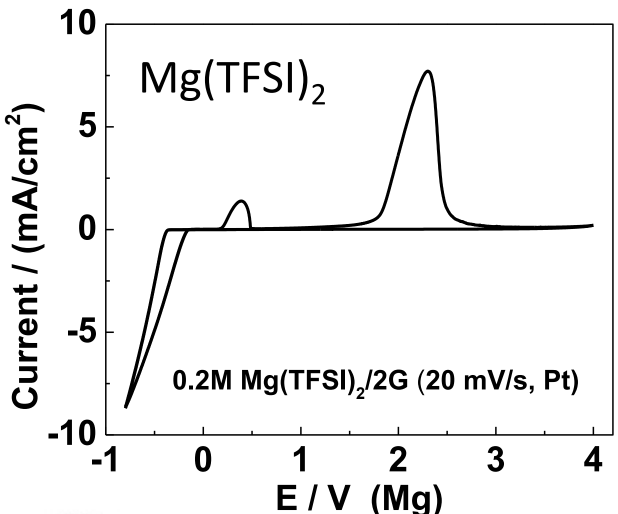
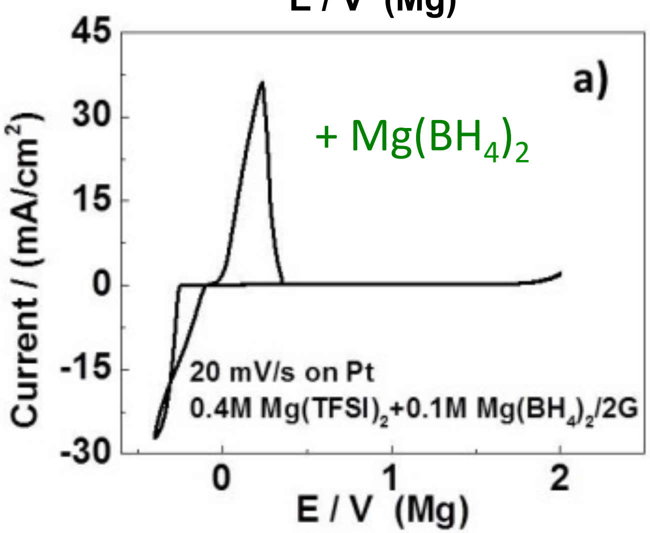
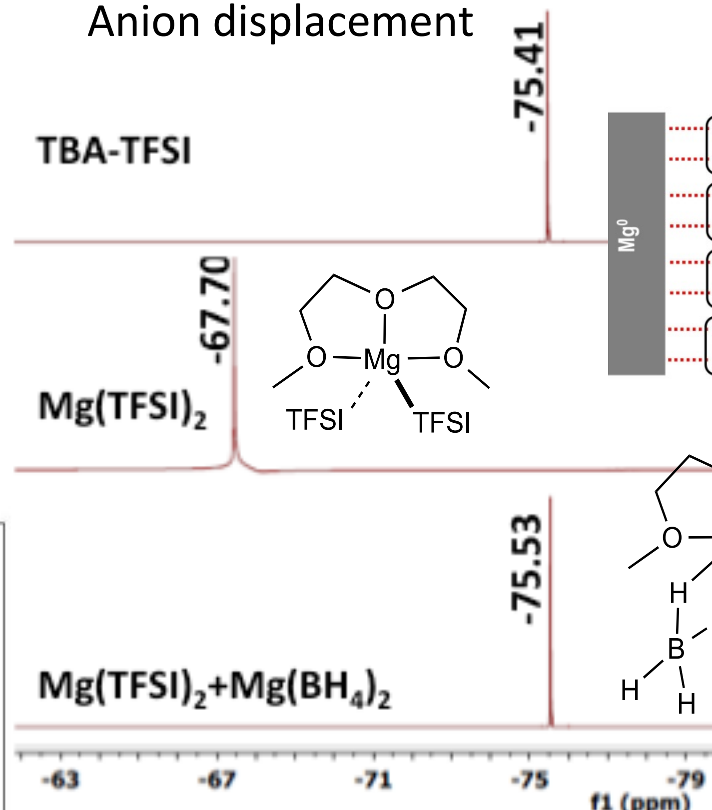
Surface Adsorbates as an Alternate Protection Strategy?

Eliminate TFSI reductive decomposition

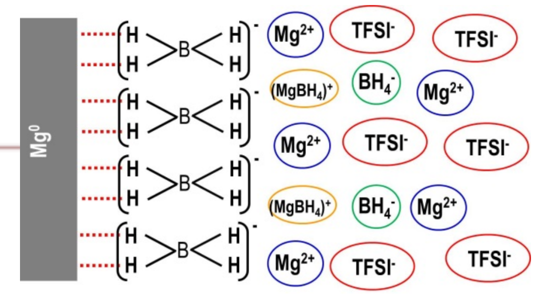


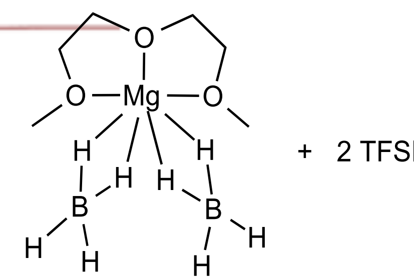


Anion displacement



BH_4^- binding





Y. Shao and team

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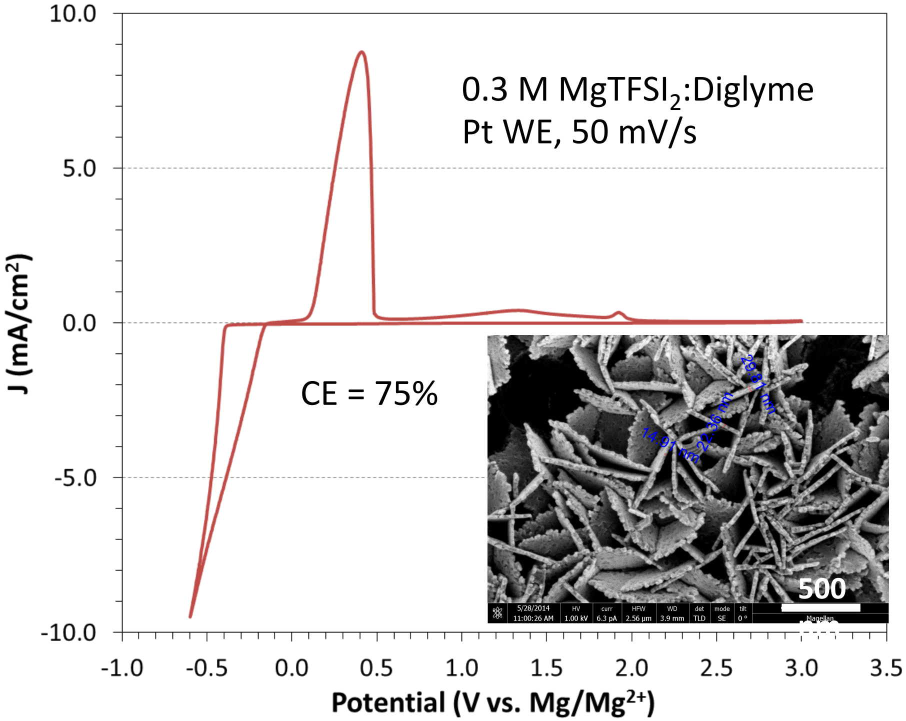
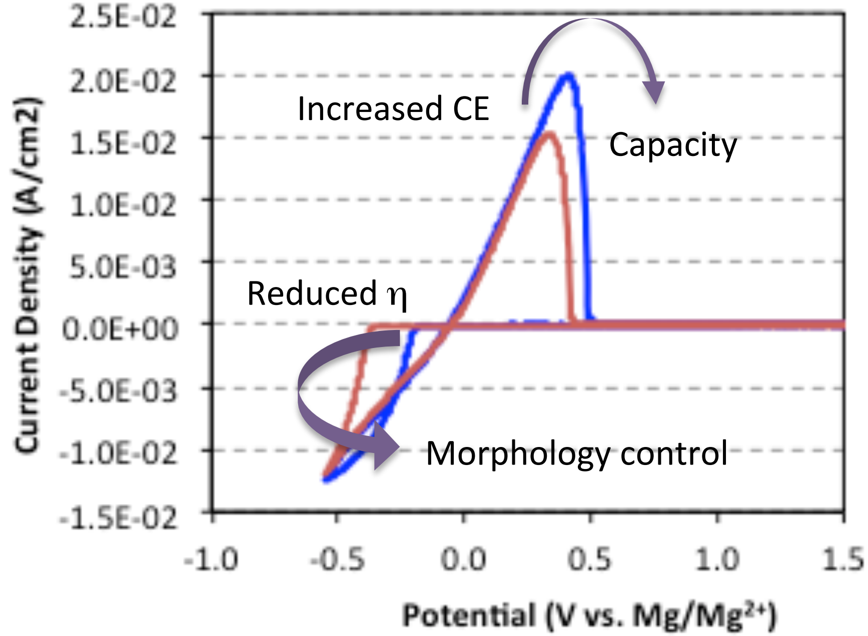
Intrinsic Films & Manipulation of a Blocking Layers





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

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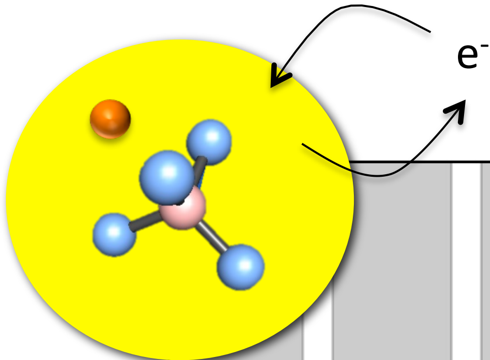
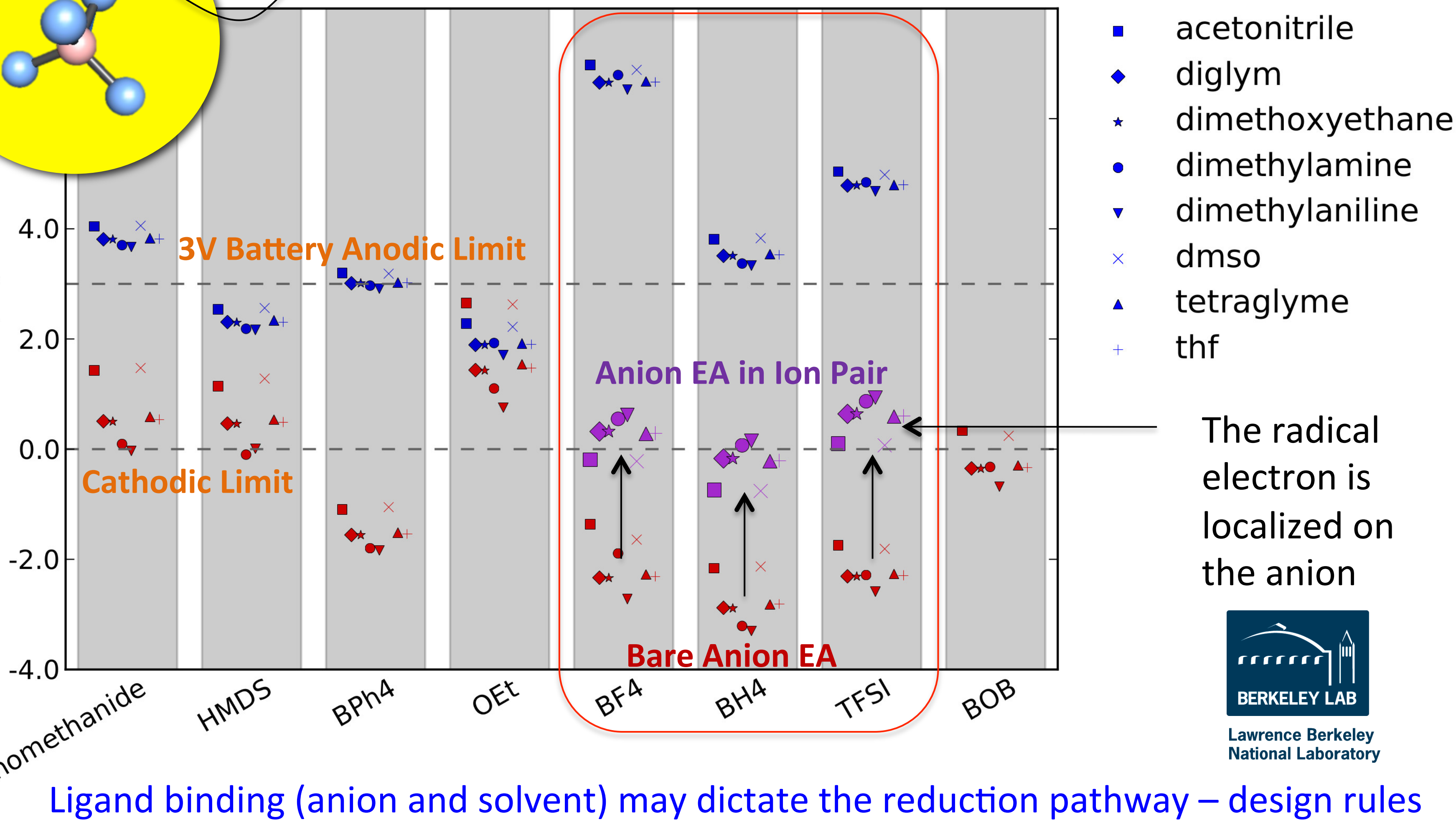
Mg^{2+} ‘Attacked’ Redox Potential of Anions

(BF_4^-, BH_4^- and $TFSI^-$)



Coordinating vs. free anions may be the blocking precursors!



Lawrence Berkeley National Laboratory

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

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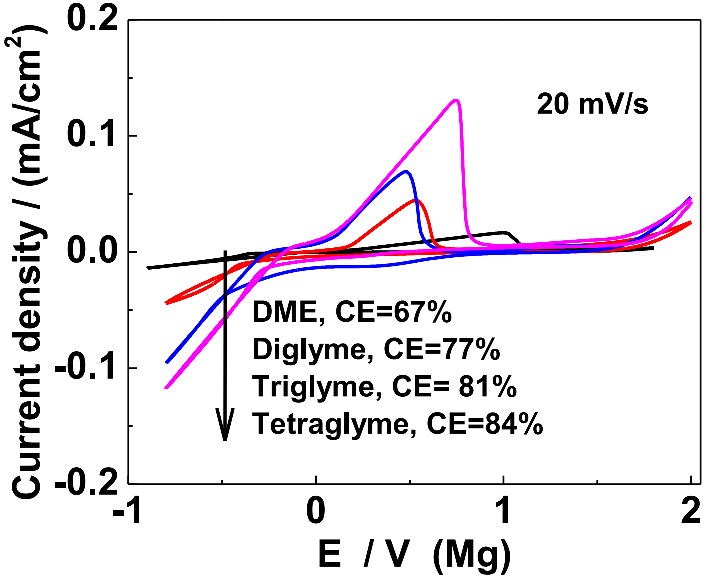
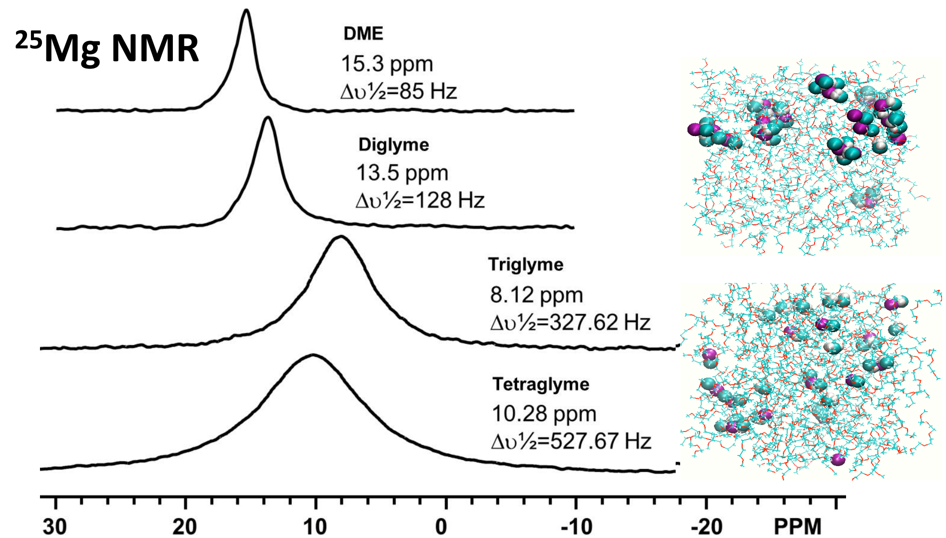
Establishing Electrolyte Structure – Function Relationships

Electrolyte design rules are derived from exploration of MV cation – anion – solvent

Activity varies with strength of solvent interaction



NMR yields relative strength of coordination by anions vs. solvent



DFT computation of Mg^{2+} shielding argue systematic decrease in anion coordination strength with denticity of glyme

Experimental (^{25}Mg chemical shift/ppm)		Calculation (^{25}Mg chemical shift/ppm)	
$Mg(BH_4)_2$/DME	15.3	22.26	$Mg_2(BH_4)_4$-$(DME)_3$
$Mg(BH_4)_2$/Diglyme	13.5	21.23	$Mg(BH_4)_2$-Diglyme
$Mg(BH_4)_2$/Triglyme	8.12	5.961	$Mg(BH_4)_2$-Triglyme
$Mg(BH_4)_2$/Tetraglyme	10.28	-12.597	$Mg(BH_4)_2$-Tetraglyme
$Mg(BH_4)_2$/Tetraglyme	10.28	7.329	$[MgBH_4]^+$-Tetraglyme

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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

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