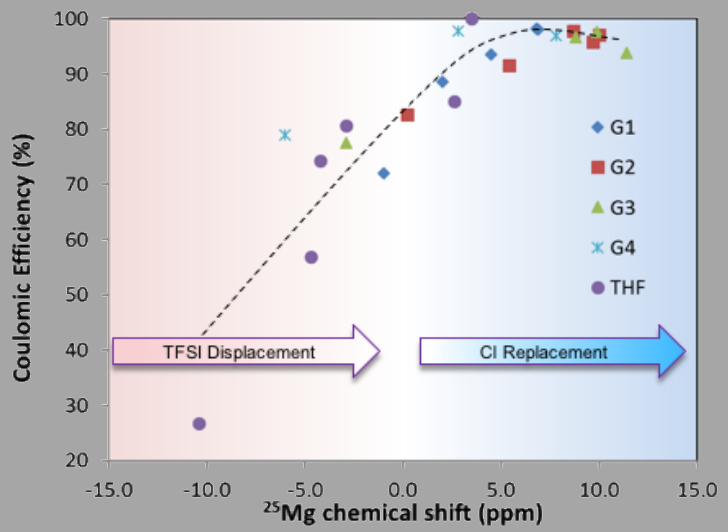
SAND2017-9496C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Stable Electrolytes for High Voltage Mg Ion Batteries: Decoupling Weakly Coordinating Anion and Solvent Stability to Reveal Design Principles



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Beyond Li Ion X
June 27-29, 2017

U.S. DEPARTMENT OF ENERGY

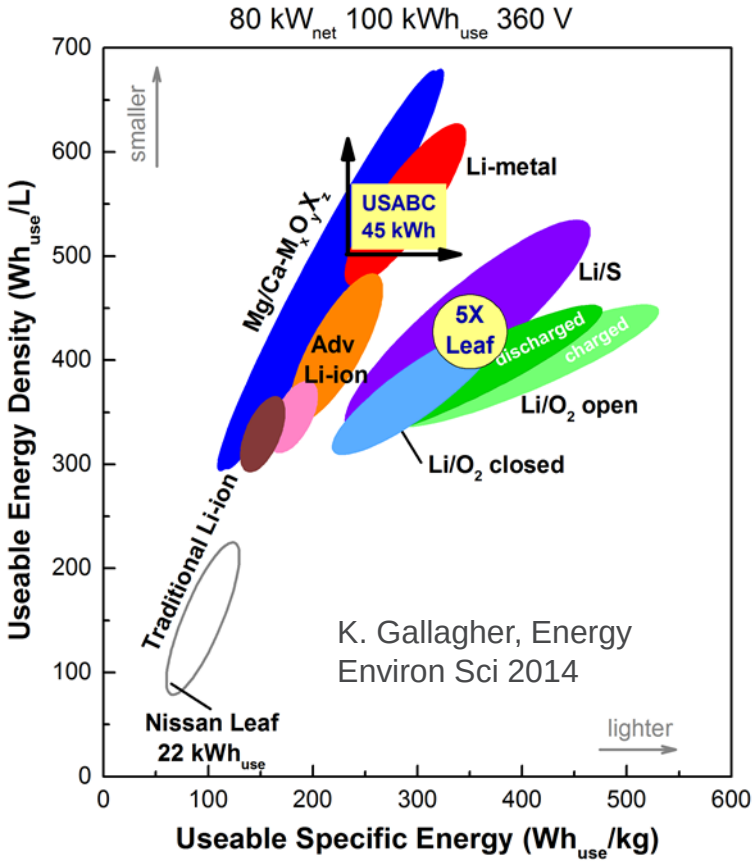
Switching the Working Ion to Mg^{2+} and the Anode to Metal

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

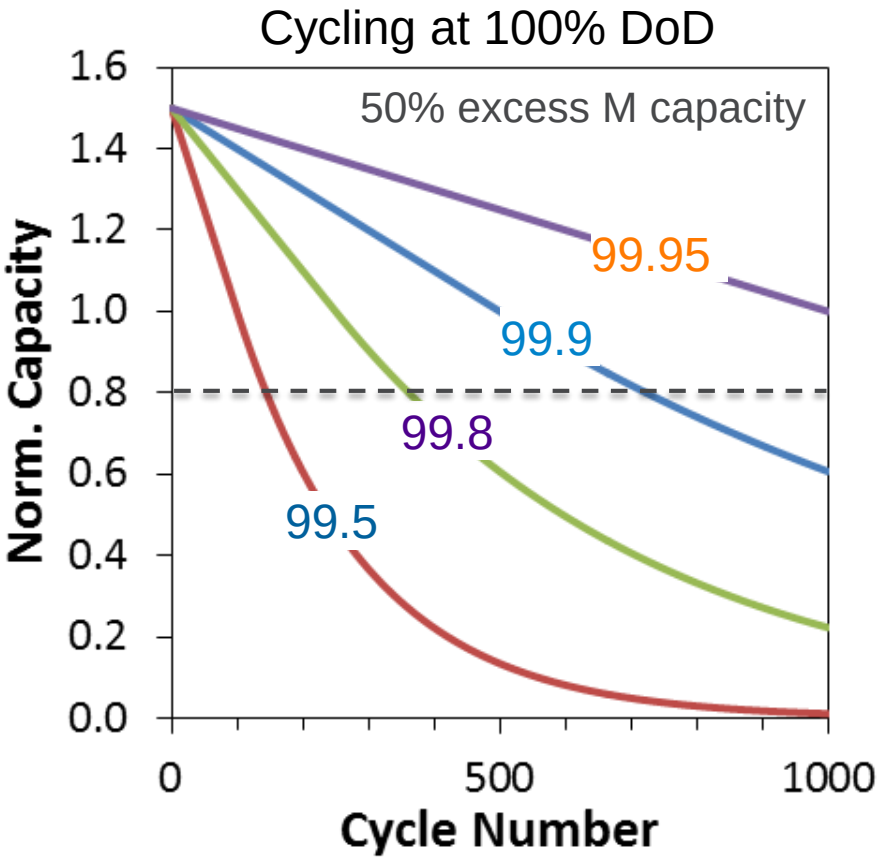
Outcomes: $100 /kWh, 500 Wh/l

Disadvantages of Mg:

- relevant rate metal CE
- electrolytes compatible with high voltage cathodes
- viable high voltage cathodes – JCESR's >3.5 V

Near-unit Coulombic Efficiency is Required for a Viable Metal Anode

Coulombic efficiency: Q_{Ox}/Q_{Red}(%)



<100% CE:

Origin	Symptom	Outcomes
parasitic reactions	electrolyte loss	reduced cycle life
		reduced round trip efficiency
		reduced energy density
inefficient metal dep/dsln	metal loss	reduced cycle life
		capacity fade
		reduced energy density

Maintaining the cell chemical inventory matters!

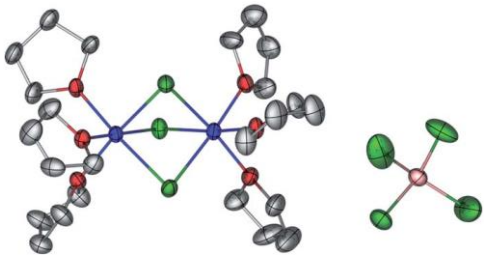
Electrolyte loss is the greater concern

Chloroaluminate Electrolytes are the Benchmark

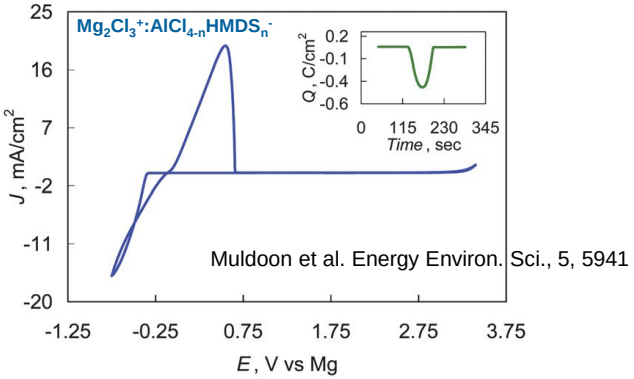
$Mg_2Cl_3^+$ $AlCl_{4-y}R_y^-$

$R_xMgCl_{2-x} + AlCl_3$ —THF→

Aurbach et al.



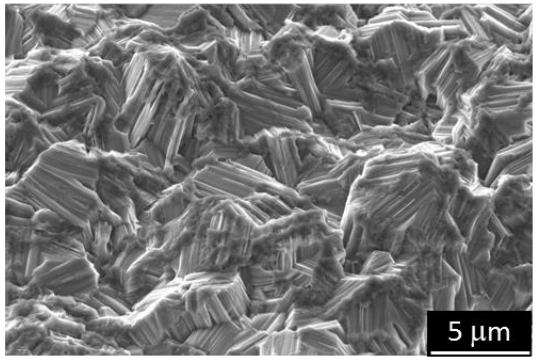
High CE afforded by reductive stability + role of Cl^-?

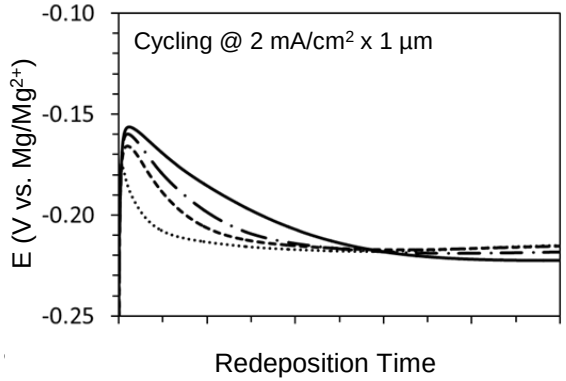


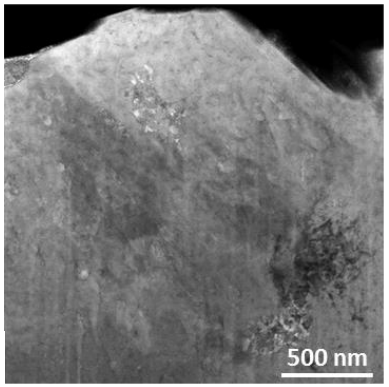
Near unit Coulombic efficiency and classic electrocrystallization, even during interrupted galvanostatic cycling

PhMgCl:$AlCl_3$/THF

CE 100
± 0.1%







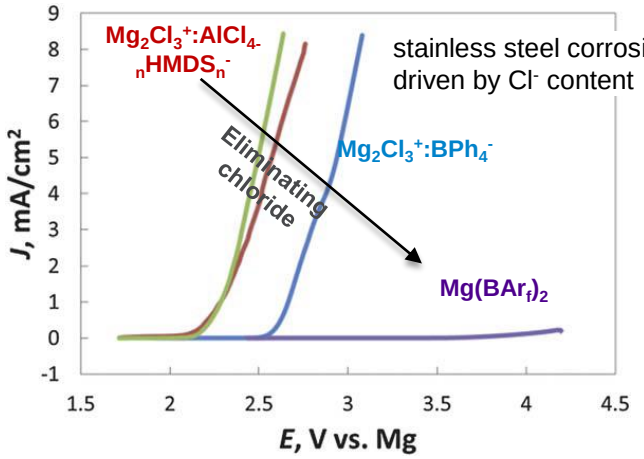
N.T. Hahn et al, submitted

epitaxy

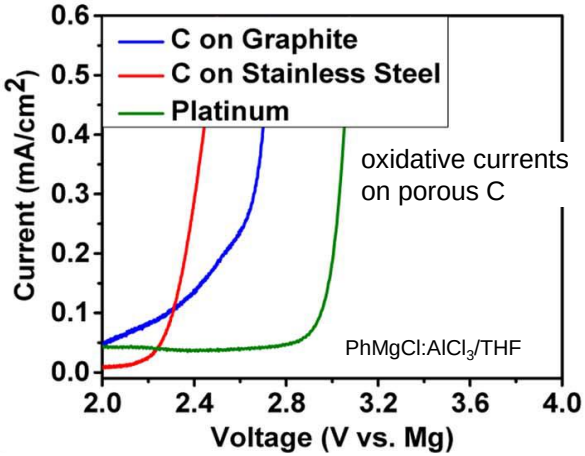
Mg maintains faceted structure

Chloroaluminate Issues: Anodic Instability and Rate Capability

Electrolyte Oxidation/Incompatibility Limits Attainable Cell Voltage

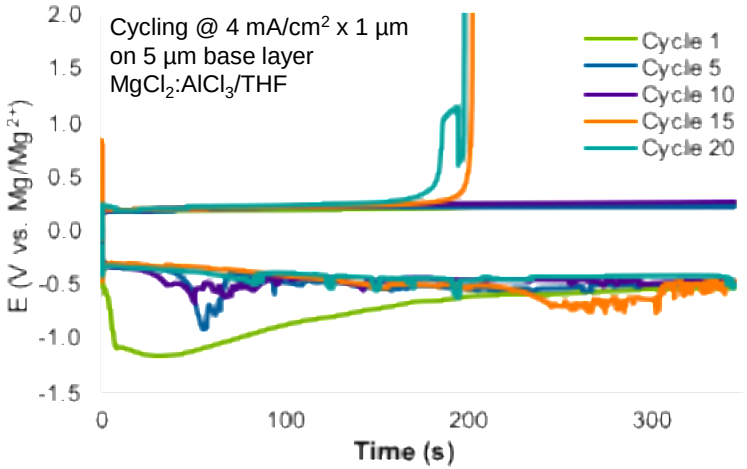


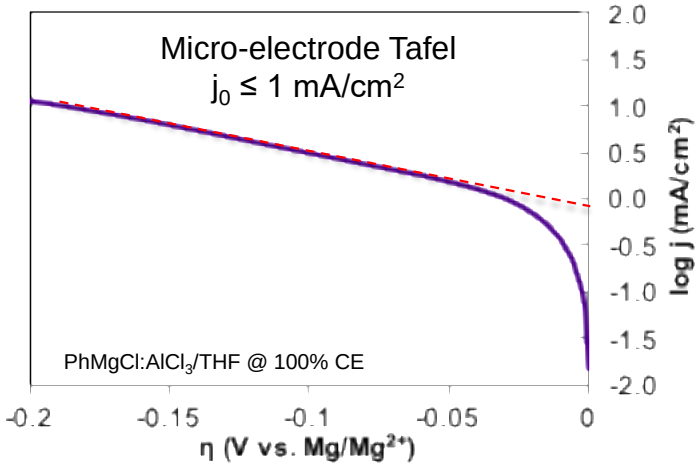
Muldoon et al. *Energy Environ. Sci.*, ***6***, *482*



Lipson et al. *JECS*, **163** A2253

High Rate Charging Limited by Mass Transport and Deposition Kinetics





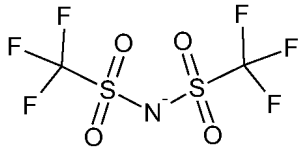
N.T. Hahn et al, submitted

Can anodic stability and rate capability issues be resolved using weakly coordinating anions?

Distribute desolvation energy – reconfigurable coordination at the interface

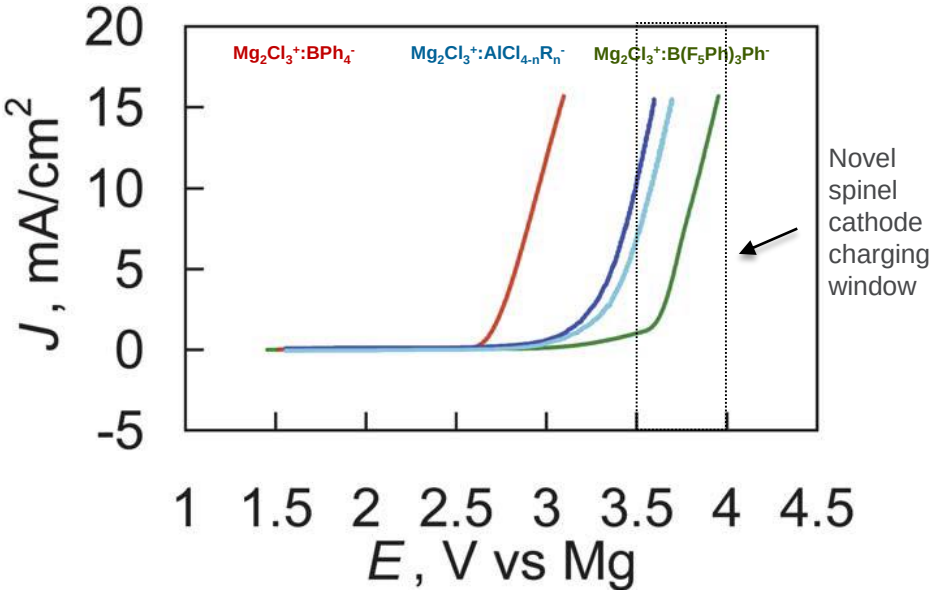
$Mg(TFSI)_2$ as a Weakly Coordinating Test Case

- High solubility/conductivity in glymes
- High oxidative stability



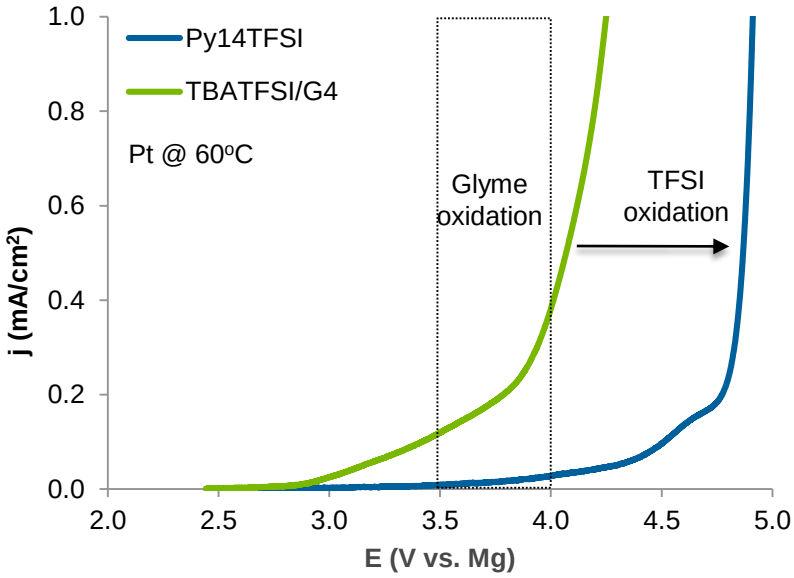
Weakly Coordinating, non-Cl^- Species Hold Promise for High Voltage Cathodes

Cl^--based electrolytes pinned < 3.7 V vs. Mg on Pt



Muldoon et al. Energy Environ. Sci., 5, 5941

TFSI-based electrolytes pinned by glyme solvent



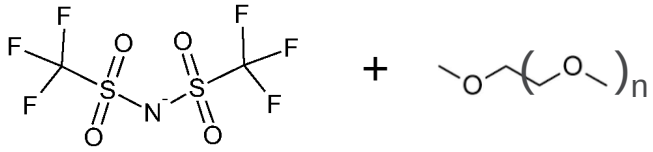
TFSI affords high anodic stability

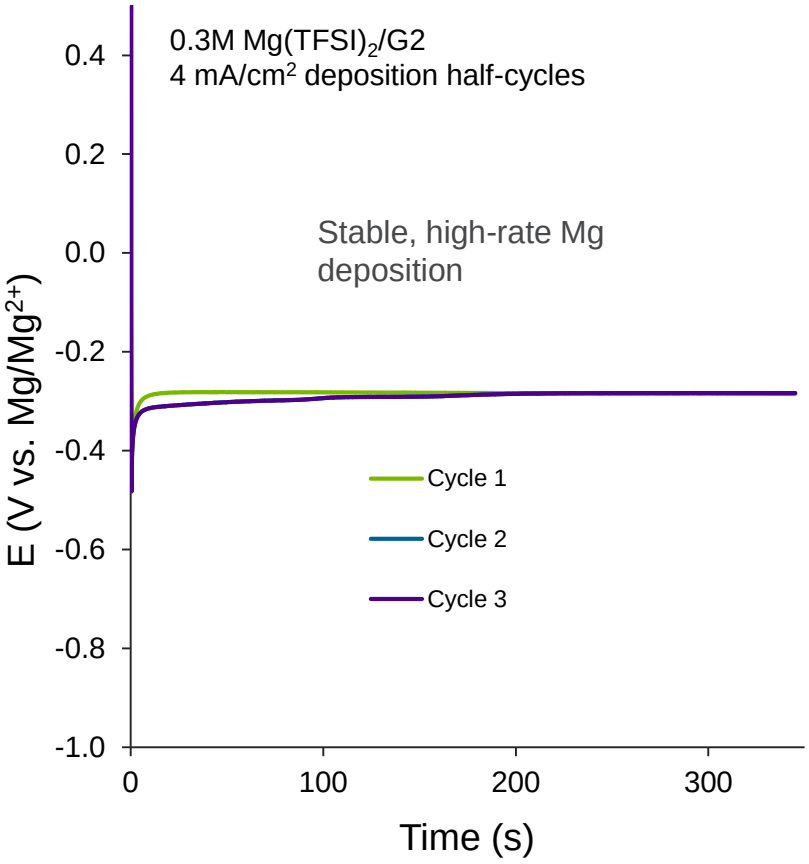
$Mg(TFSI)_2$ Performance at the Anode

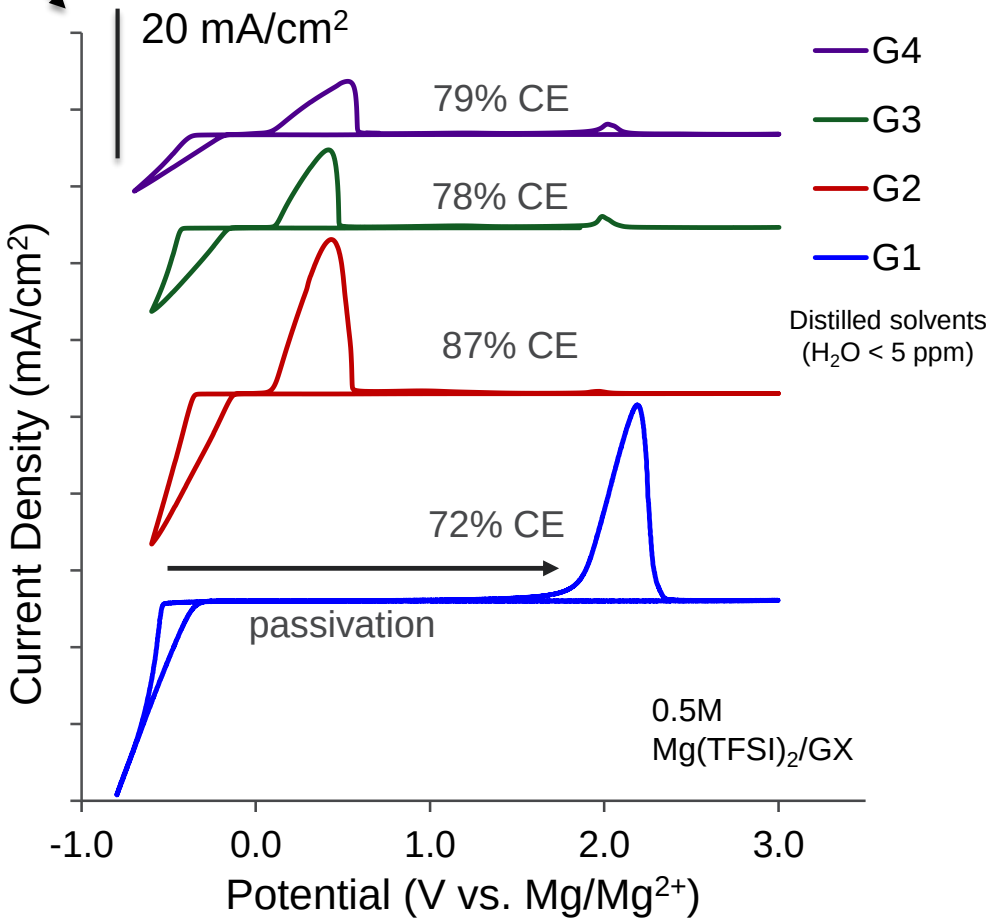
Superior rate capability

But…

Lower metal CE & passivation?



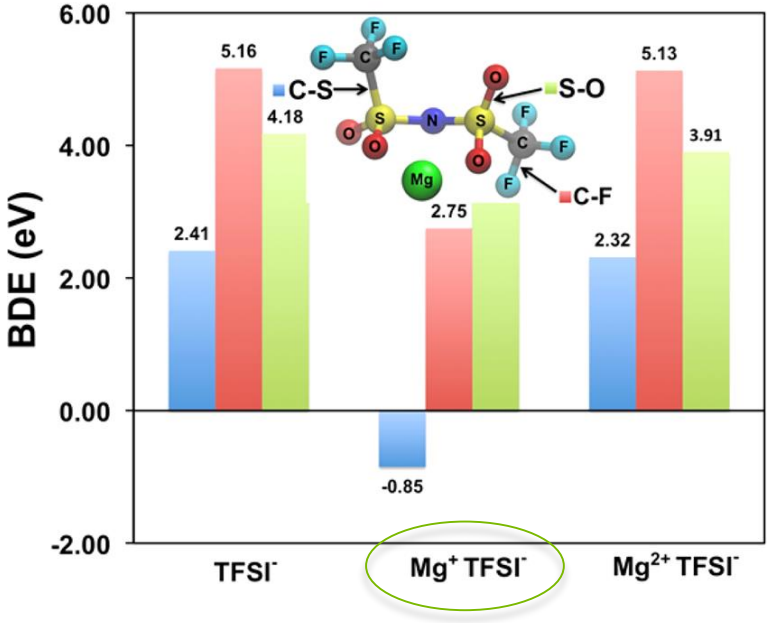




TFSI reduction + impurity influences limit anode response

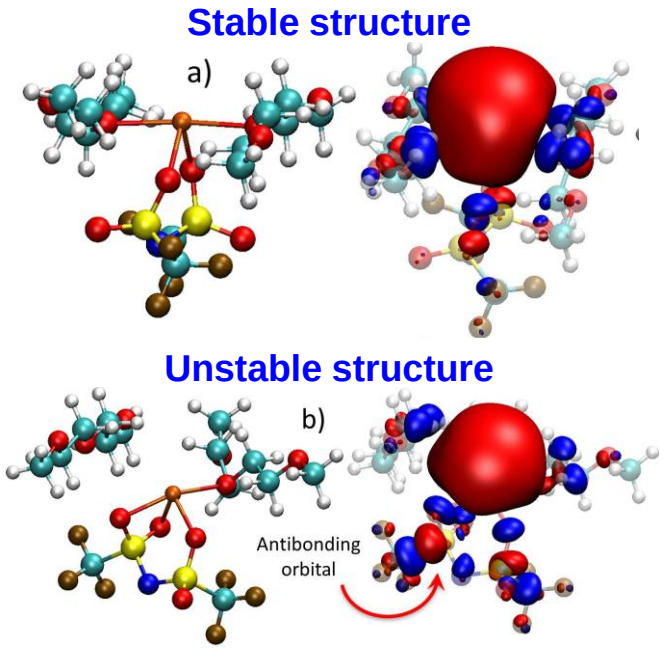
Reductive Decomposition of TFSI Limits Efficiency

Mg-TFSI$^+$ reduction results in C-S bond scission



N. Rajput et al. J. Am. Chem. Soc. 2015, 137, 3411−3420

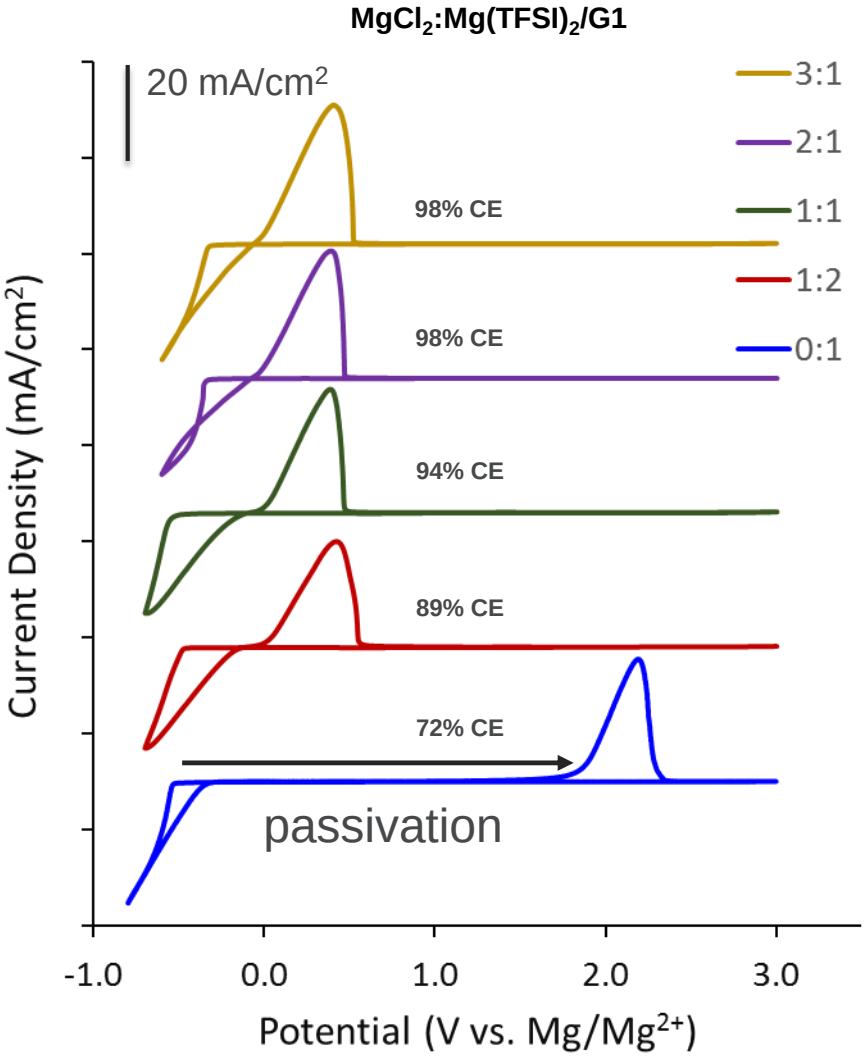
Instability of Mg-TFSI$^+$ complex depends on configuration

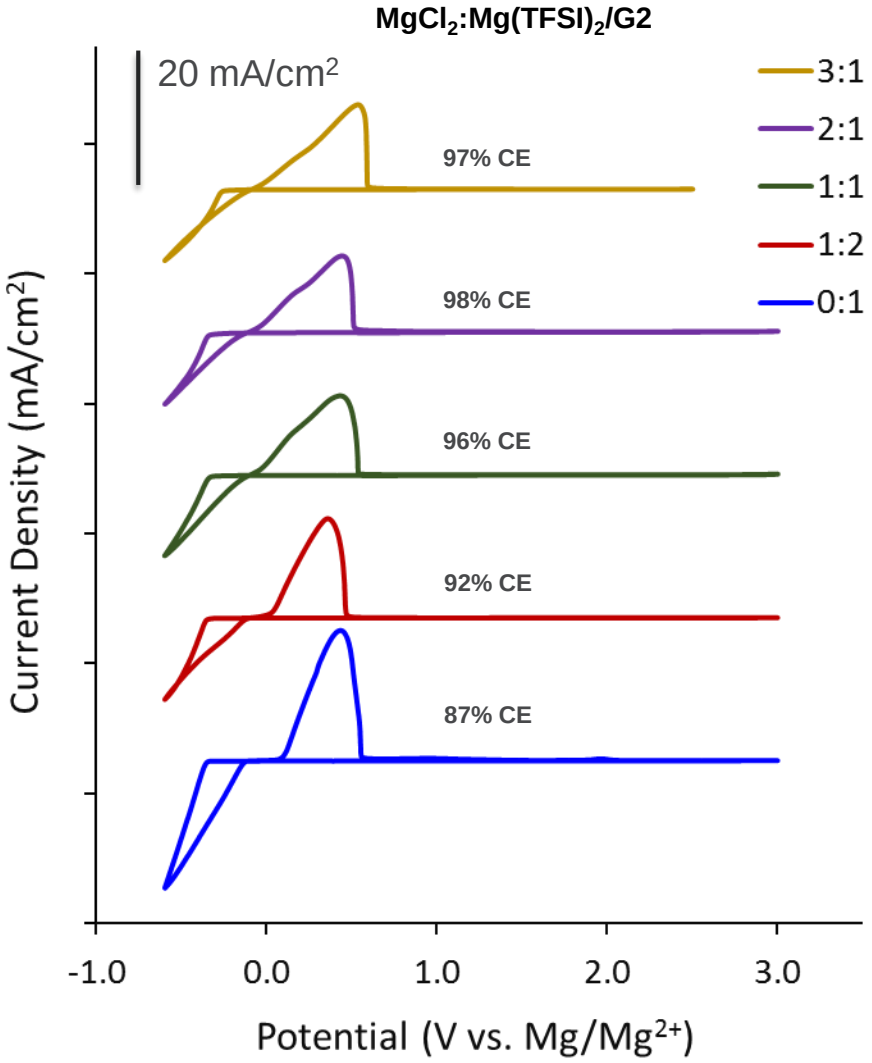


A. Baskin et al. J. Phys. Chem. C, 2016, 120 , 3583–3594

Limiting the Mg-TFSI interaction is critical for high CE

TFSI:Glyme Coulombic Efficiency is Improved by Chloride Addition

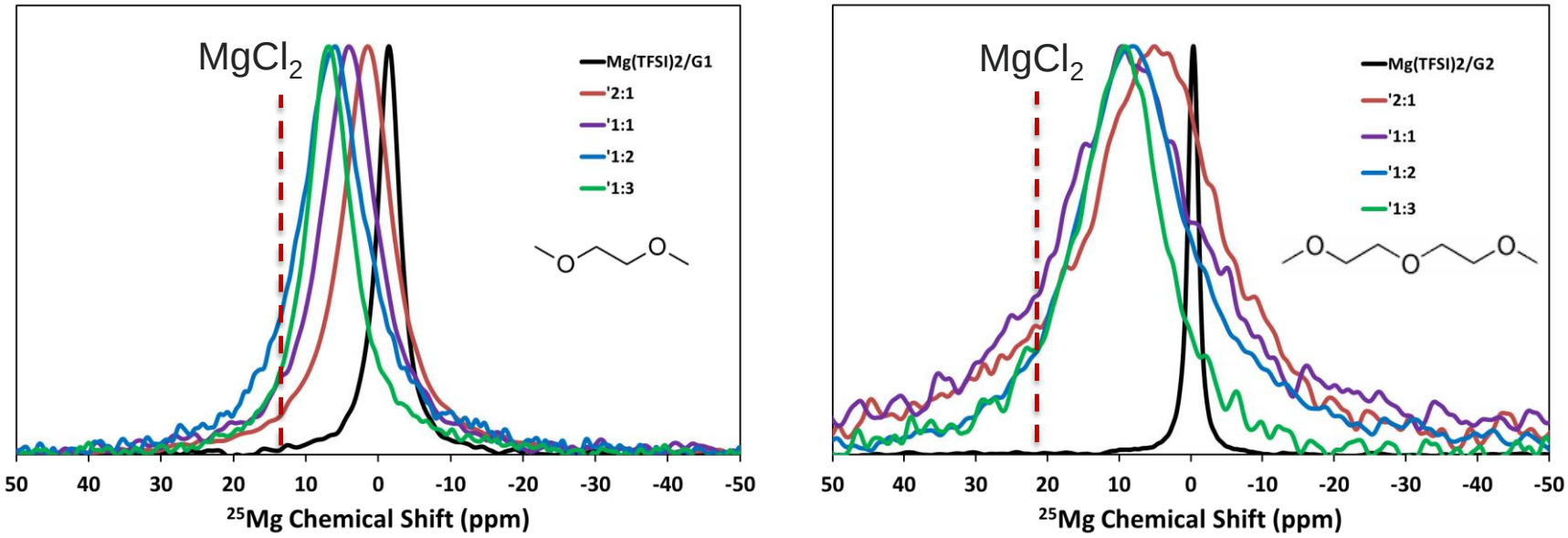




Cl^- addition restores high metal CE and suppresses passivation – by limiting Mg-TFSI interaction?

Improved Efficiency Correlates with Changes in Mg^{2+} Coordination

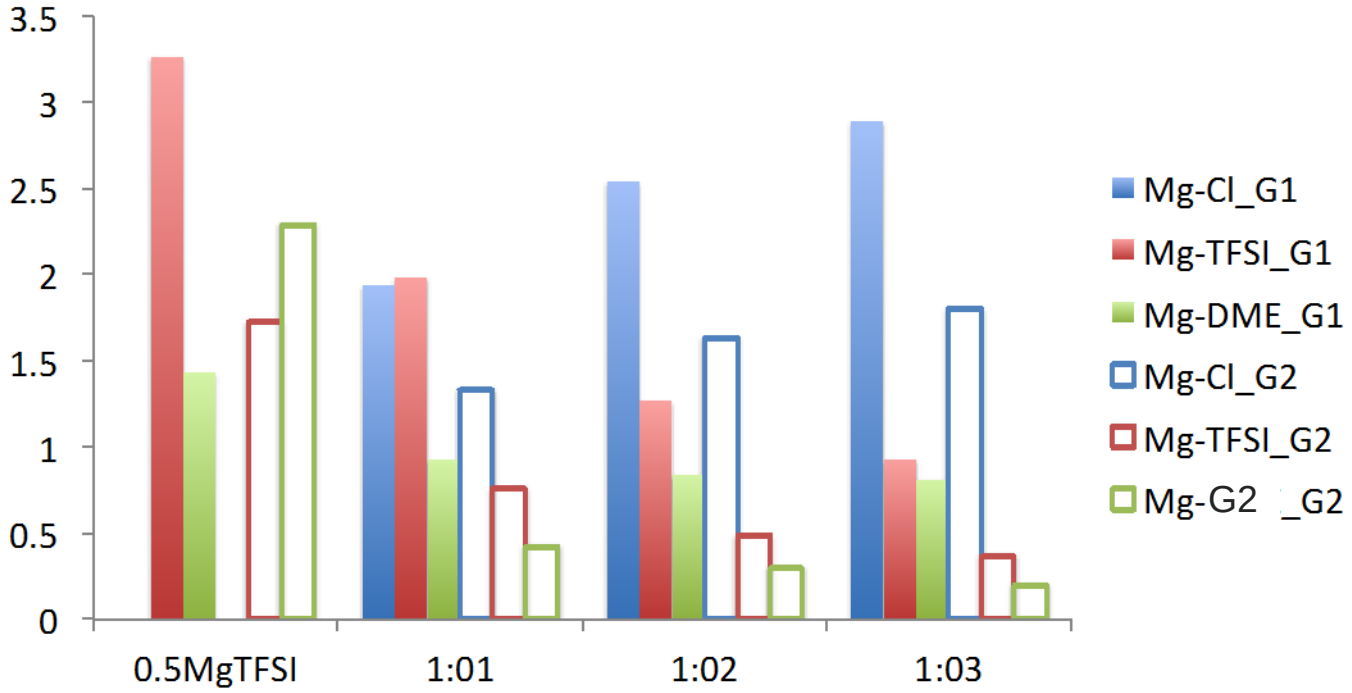
^{25}Mg NMR is an effective probe of local environment



Cl^- displaces $TFSI^-$ as a first shell coordinator

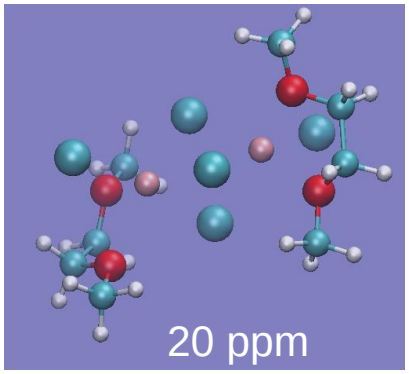
$$Mg^{2+}:TFSI^-:Solv + Cl^- \rightarrow Mg^{2+}:Cl^-:Solv + TFSI^-$$

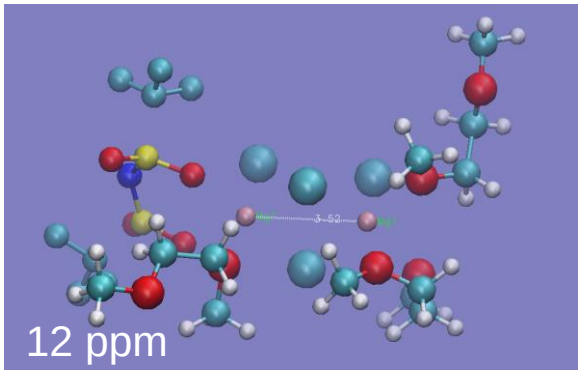
AIMD simulation results are consistent with reduced TFSI coordination

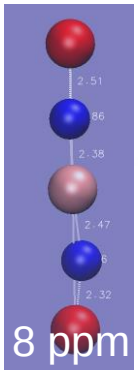


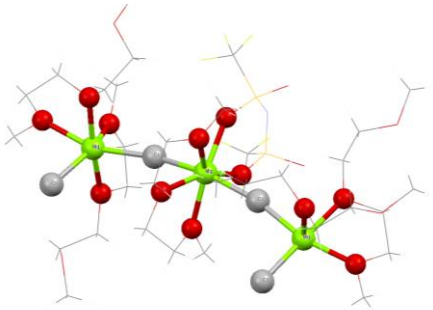
- Chloride displaces both the TFSI anion and the solvent
- Displacement occurs to varying extents for these two polyethers

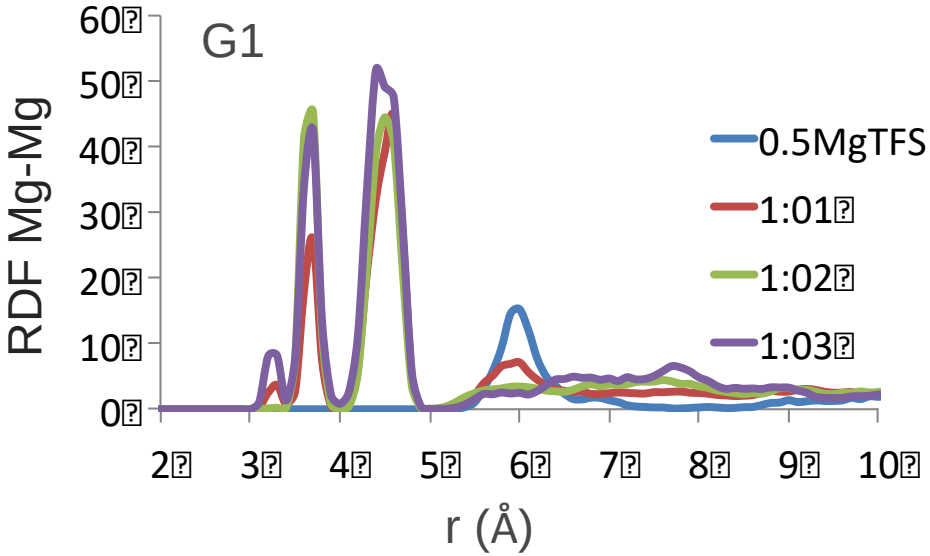
Width of the ^{25}Mg Resonance Results from Variation in Coordination

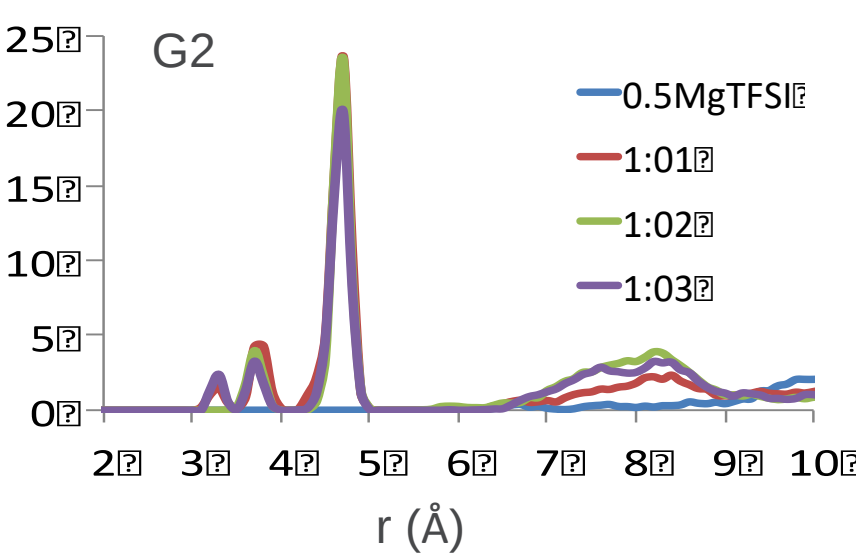










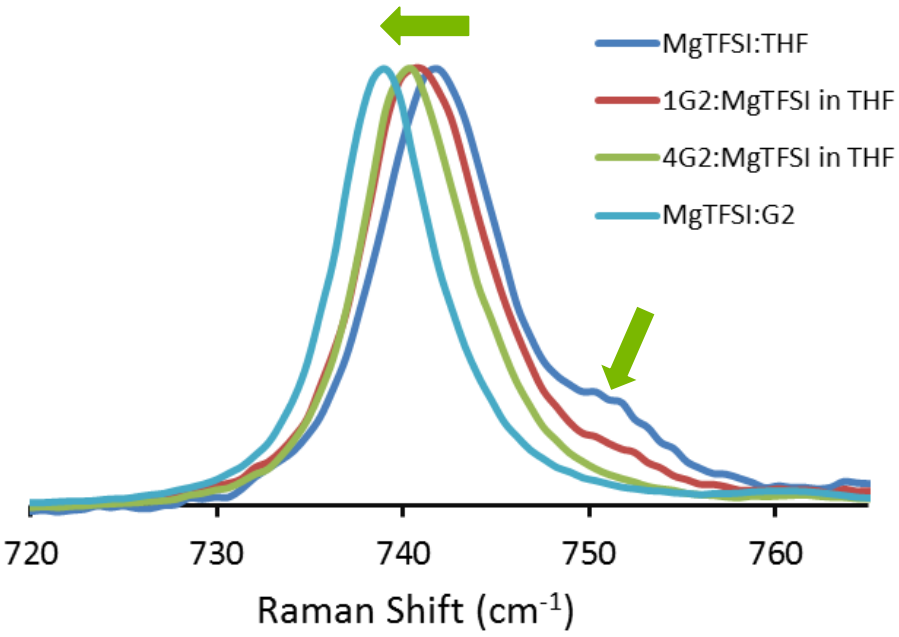


Shorter Mg-Mg (3.2 - 3.6 Å) - face or edge shared Cl^-'s, dimer-like structures

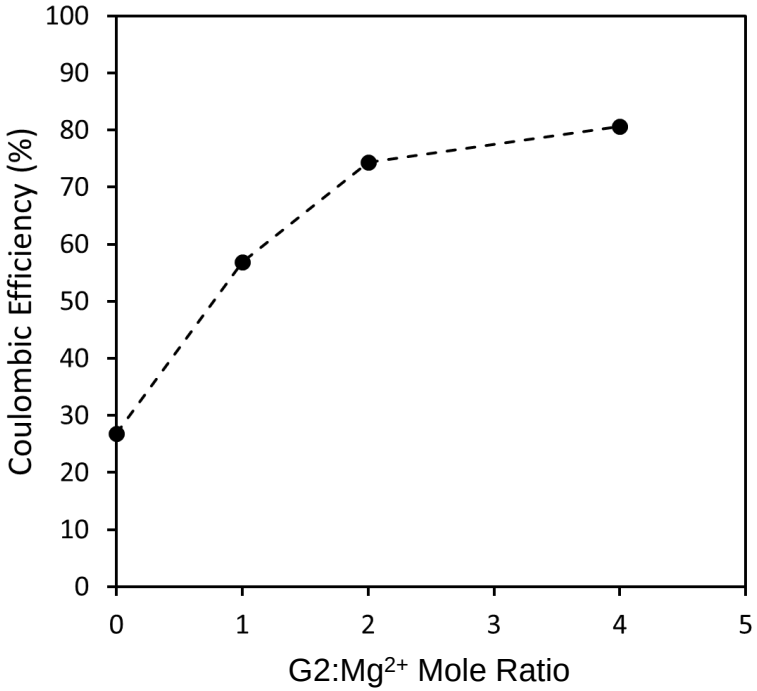
Longer Mg-Mg (4.6 Å) – corner shared Cl^-'s, linear complexes

Anion displacement is driven by solvent choice

Mg-TFSI ion pairing is significant in THF



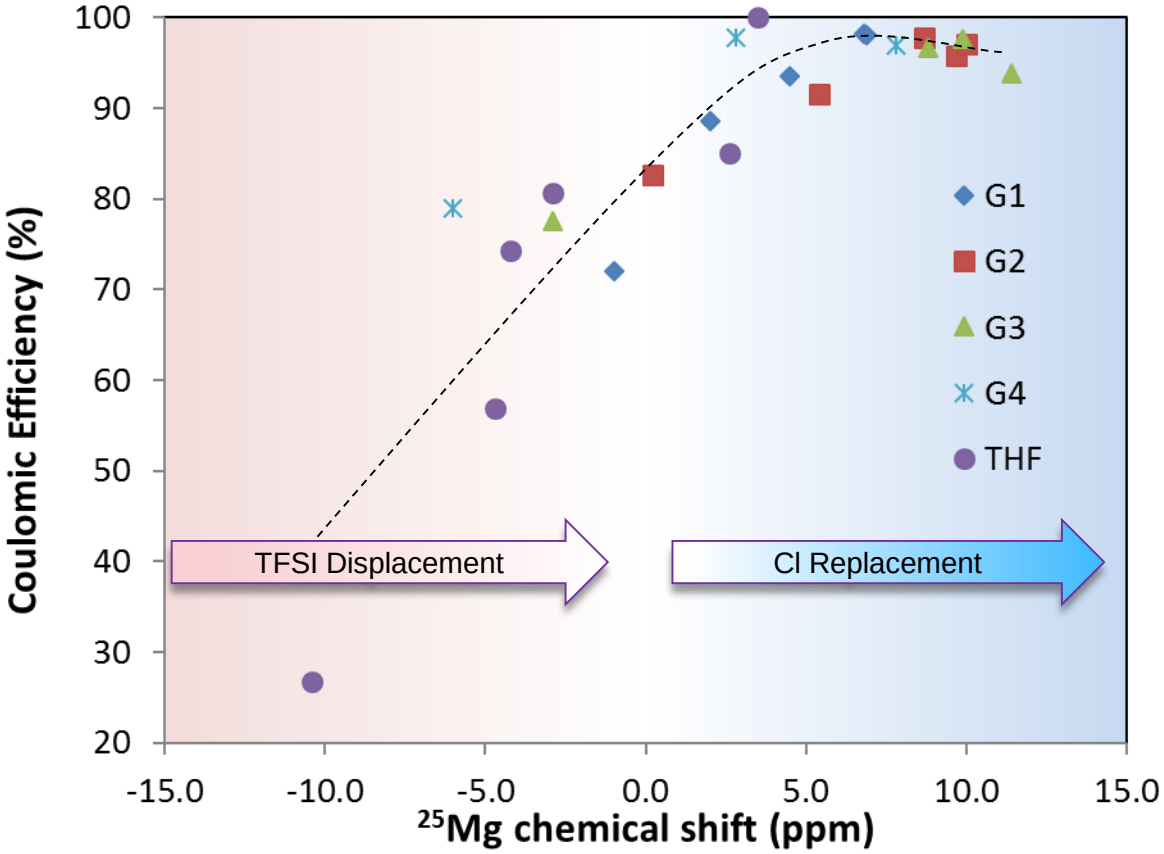
Addition of chelating G2 suppresses ion pairing

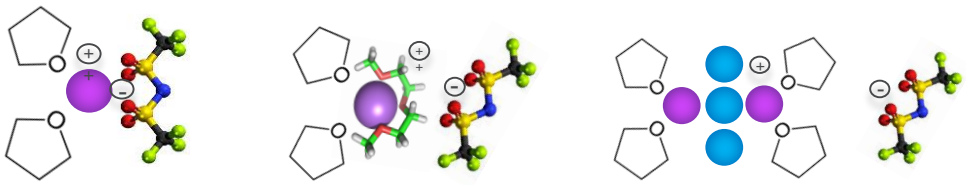


Mg deposition efficiency is enhanced with TFSI displacement

Weakly Coordinating Anion Displacement is a Generalized Phenomena

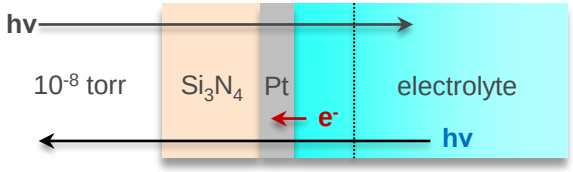
Observed across a range of cyclic and linear polyethers





The Electrode Interface also Changes with Cl^-

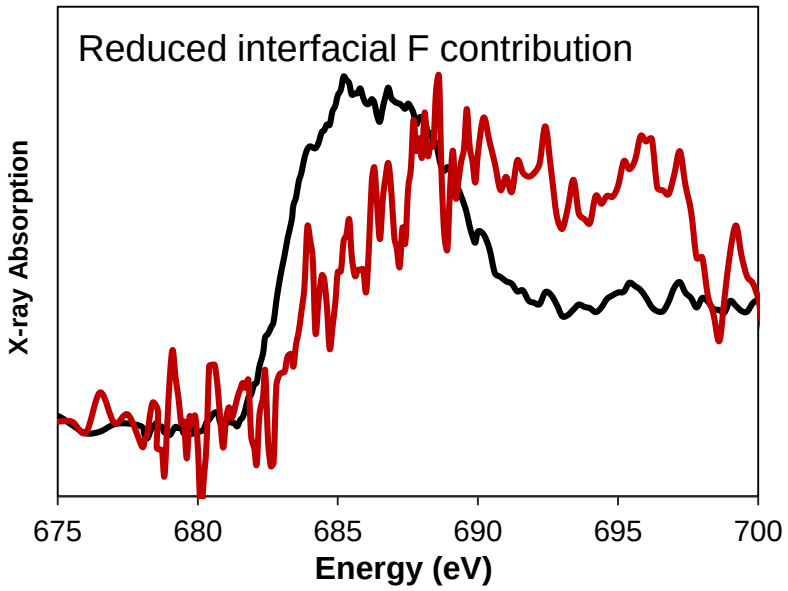
- In-situ X-ray absorption at ALS BL-8.0.1
- **Fluorescence yield -> bulk species**
- **Electron yield -> interfacial species**



ALS BL 8.0.1 in-situ XAS cell

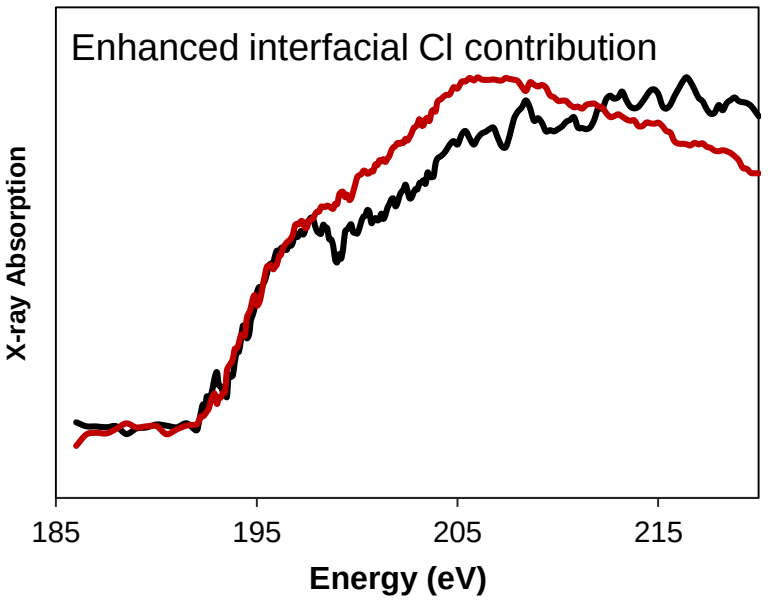
2:1 $MgCl_2$:$Mg(TFSI)_2$/G1

F K-edge



2:1 $MgCl_2$:$Mg(TFSI)_2$/G1

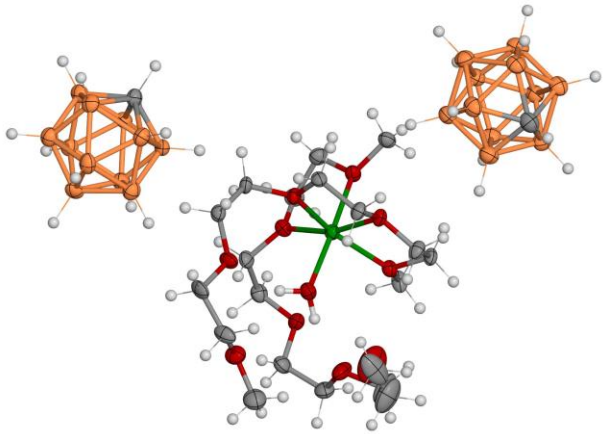
Cl L-edge



Preferential Cl^- surface adsorption inhibits TFSI decomposition

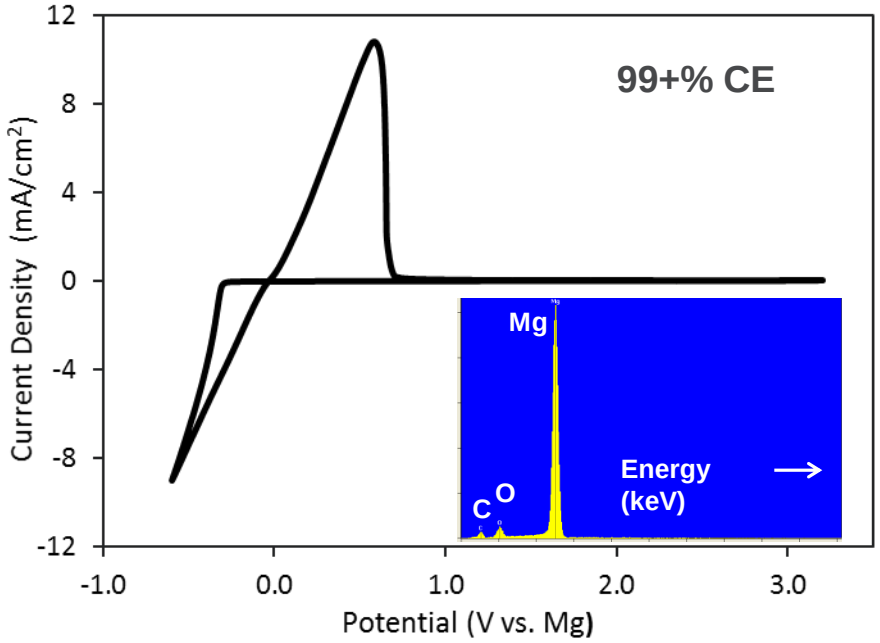
Pushing to more stable, weakly coordinating anions

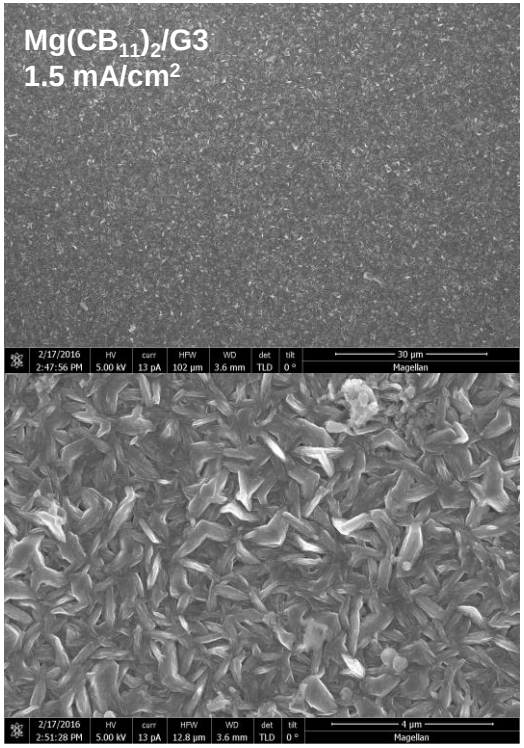
Carborane Anions: Combining Reductive Stability and Weak Coordination



First reported use of $Mg(CB_{11})_2$ in glyme G3 and G4 – solvent separated ion pairs found in crystallized electrolytes O. Tutusaus et al. 10.1002/anie.201412202

High deposition efficiency from $Mg(CB_{11})_2$ in G3

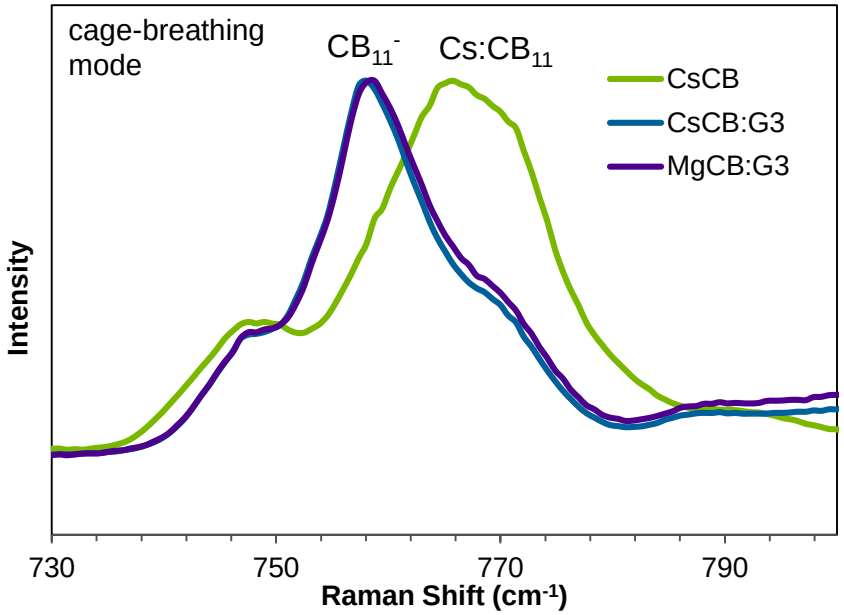




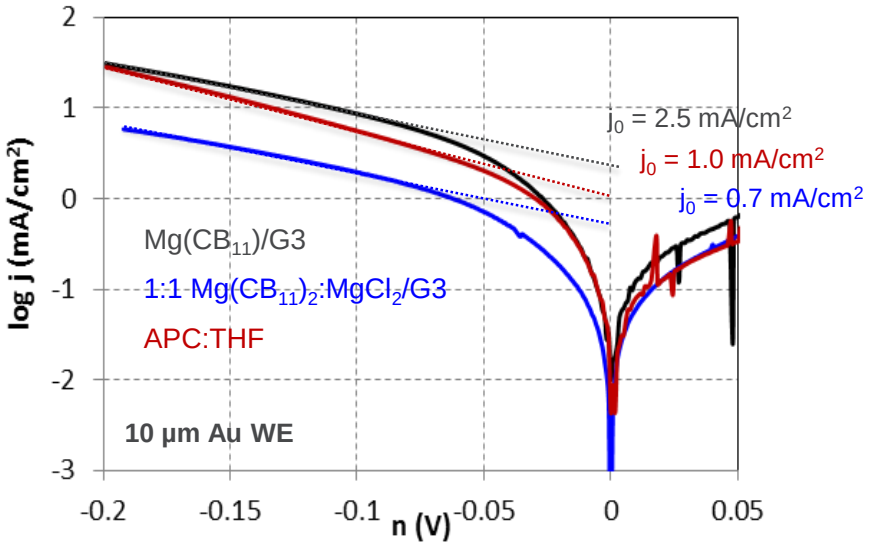
N.T. Hahn submitted

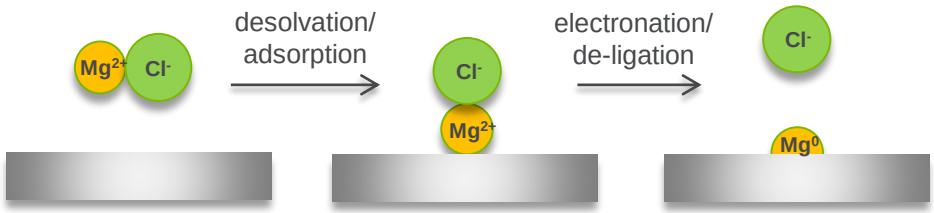
Anion-free Mg^{2+} Facilitates Faster Deposition Kinetics

Similarity between $CsCB_{11}$ and $Mg(CB_{11})_2$ in G3 argues for nearly complete dissociation



Dissociated Mg^{2+} yields higher exchange current density vs. Cl^- complexation



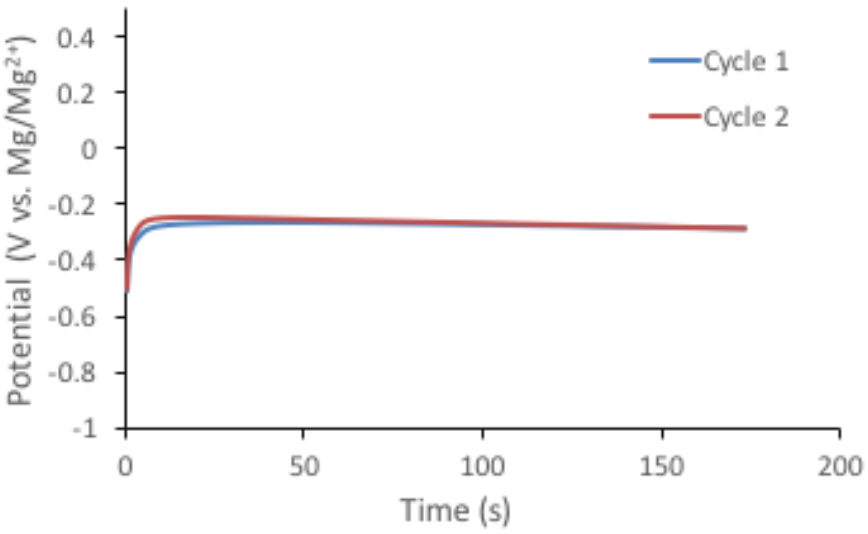


- Cl^- facilitates Mg^{2+} delivery via complexation

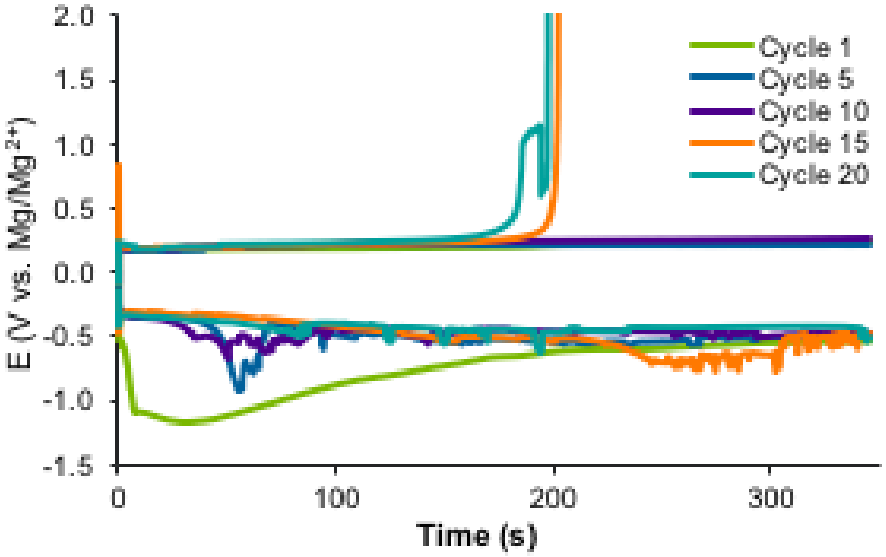
- $(Mg\text{-}solv)^{2+}$ as effective as $(Mg\text{-}Cl)^+$ for delivery
- Chloro-complexes do not provide more efficient Mg^{2+} delivery route

Stable Deposition/Stripping is Supported at Faster Rates

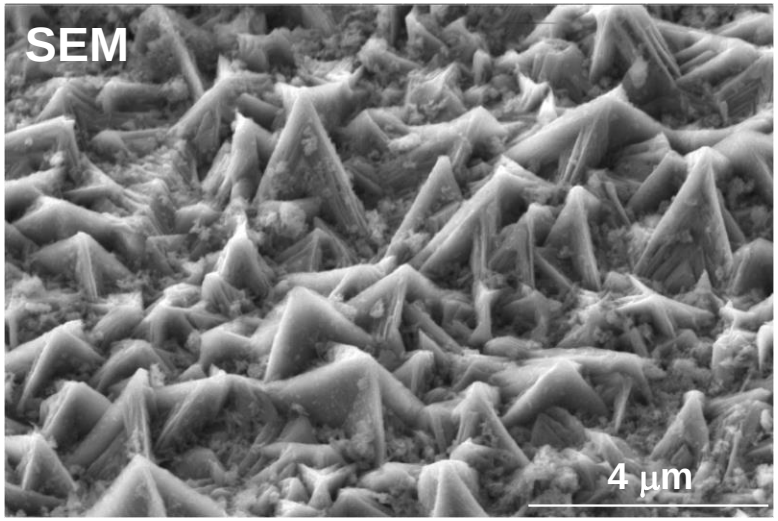
$Mg(CB_{11})$/G3, 4 mA/cm^2 deposition

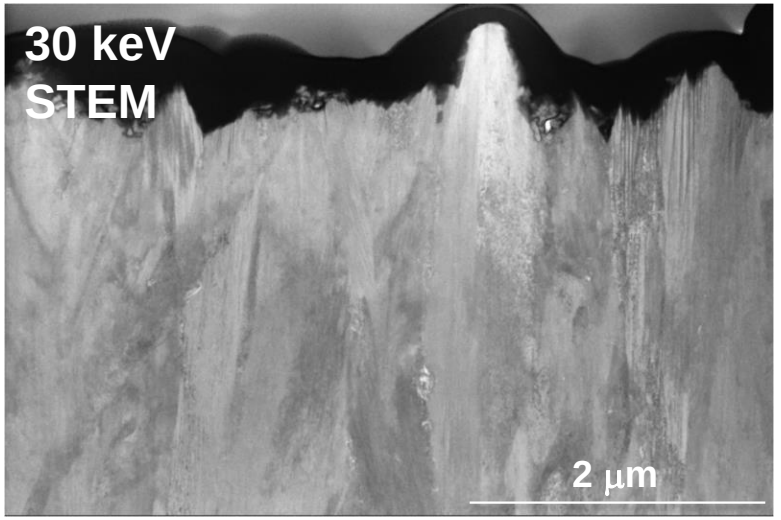


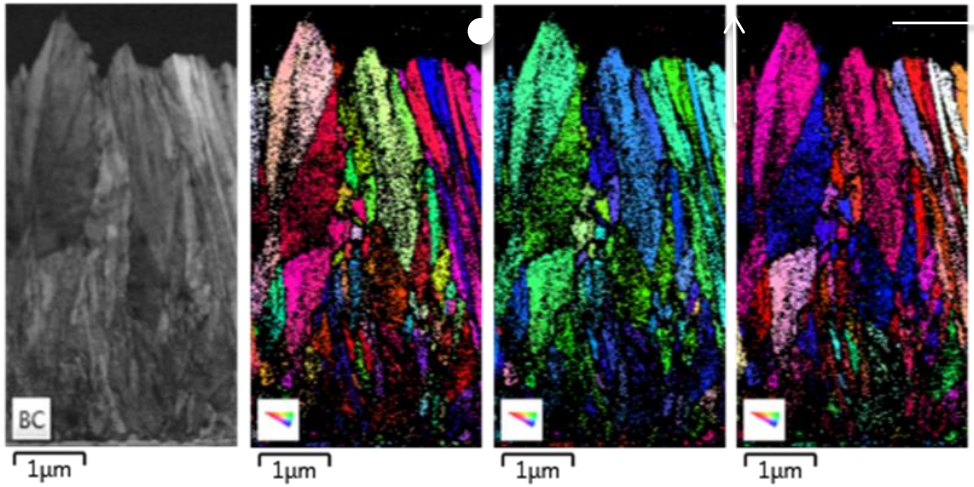
$MgCl_2$:$AlCl_3$/THF, 4 mA/cm^2 deposition



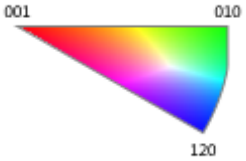
Chloride-free Mg^{2+} Produces Unique Mg Deposit Structure







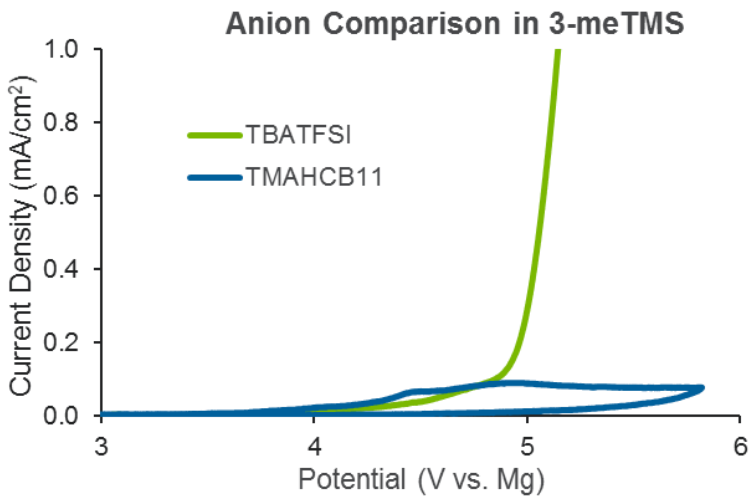
EBSD Indexing

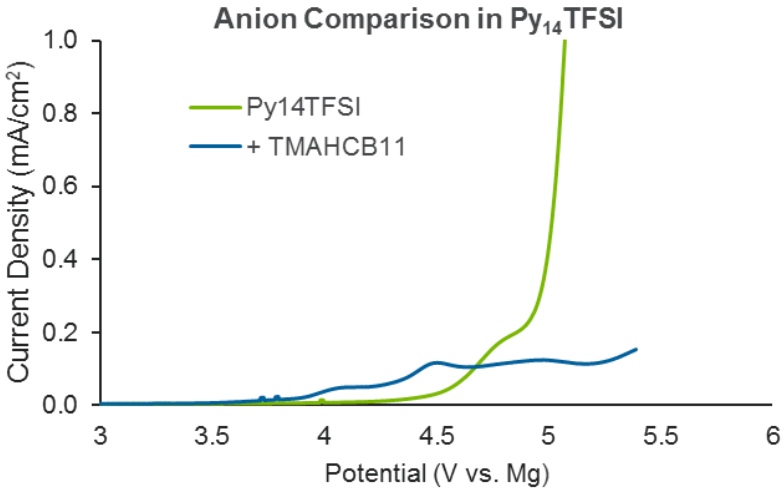


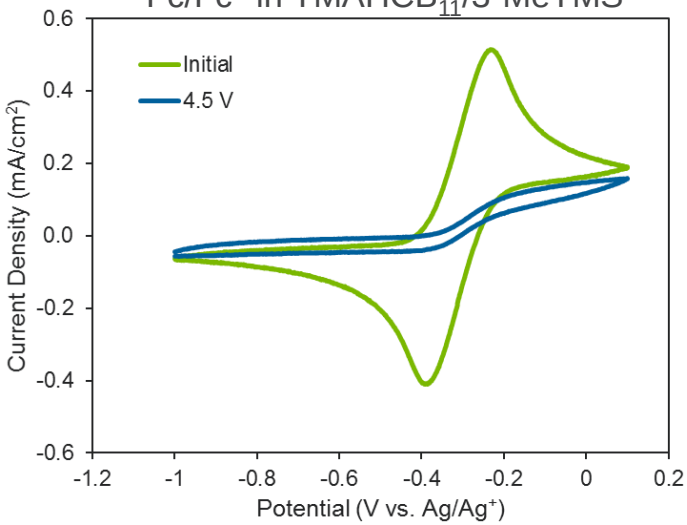
Classic electrocrystallization not seen in absence of Cl^-

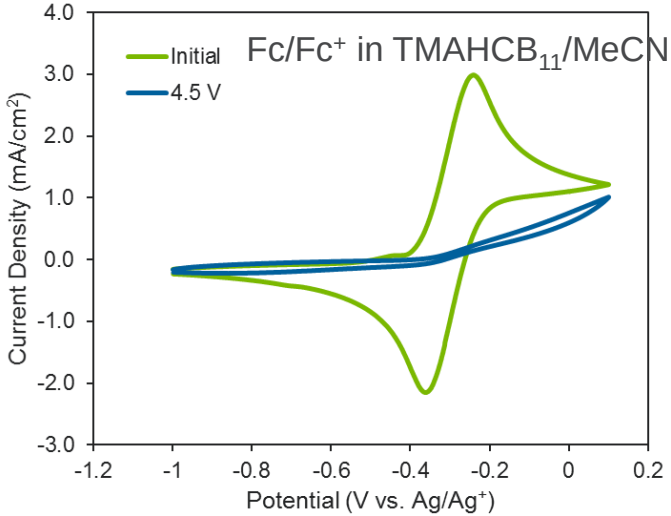
Carborane Anion Drives Passive Film Formation

Independent of solvent, cation, substrate



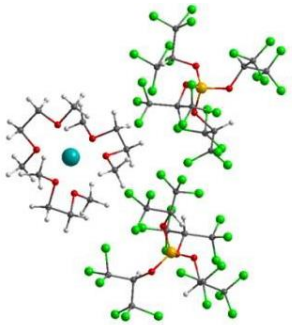




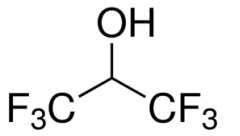


$CB_{11}H_{12}^{\bullet}$ facilitates film formation • stabilize through functionalization

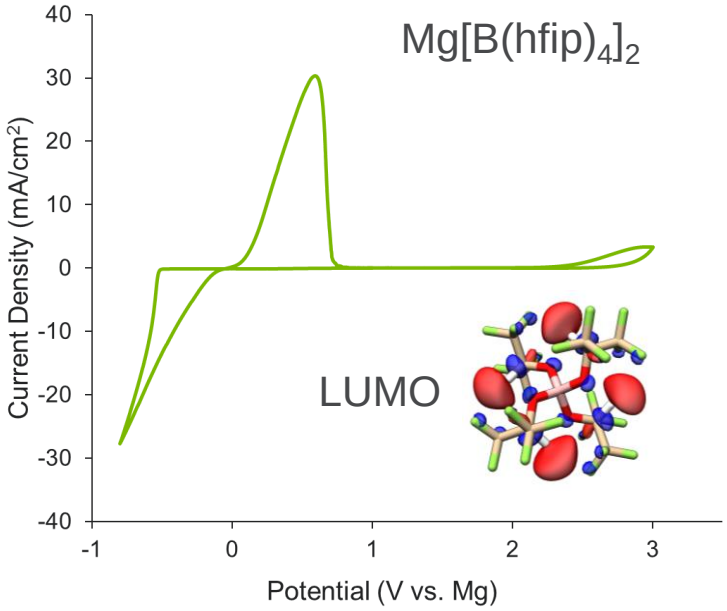
Mg-Fluoroalkoxyborates Salts to Tailor Stability

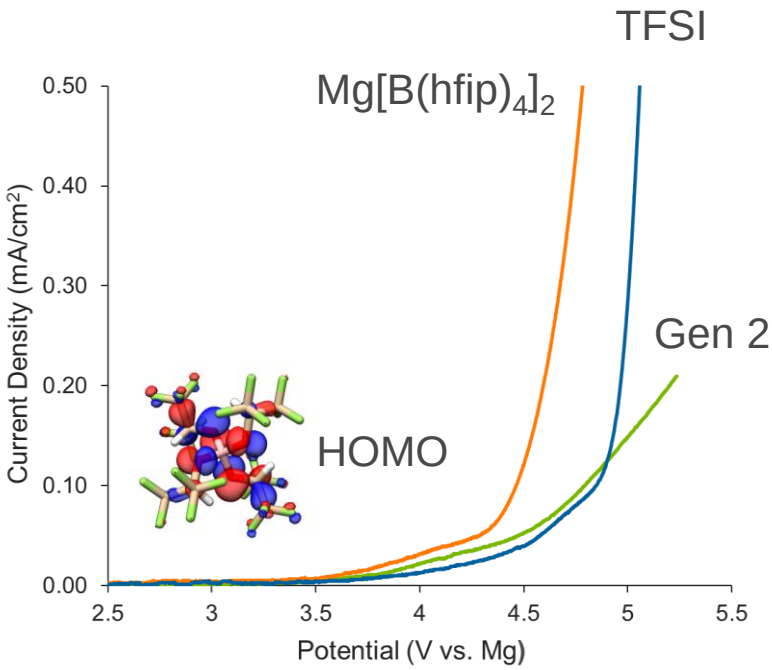


Mg- fluoroalkoxyborates first reported by Fichtner J Mater Chem A 2017



$Mg[B(hfip)_4]_2$

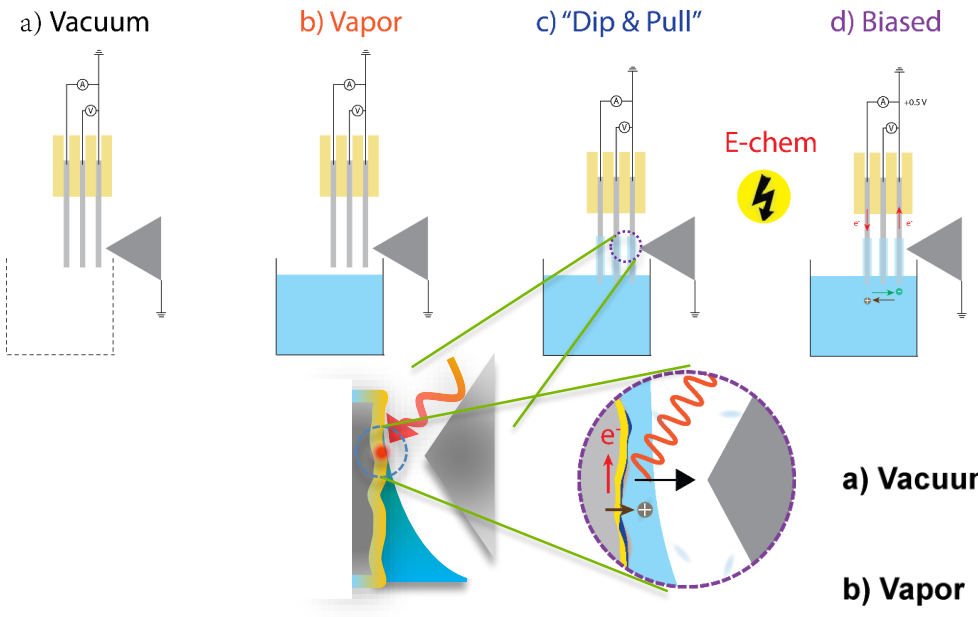




JCESR is tailoring the ligands to tune cathodic and anodic stability

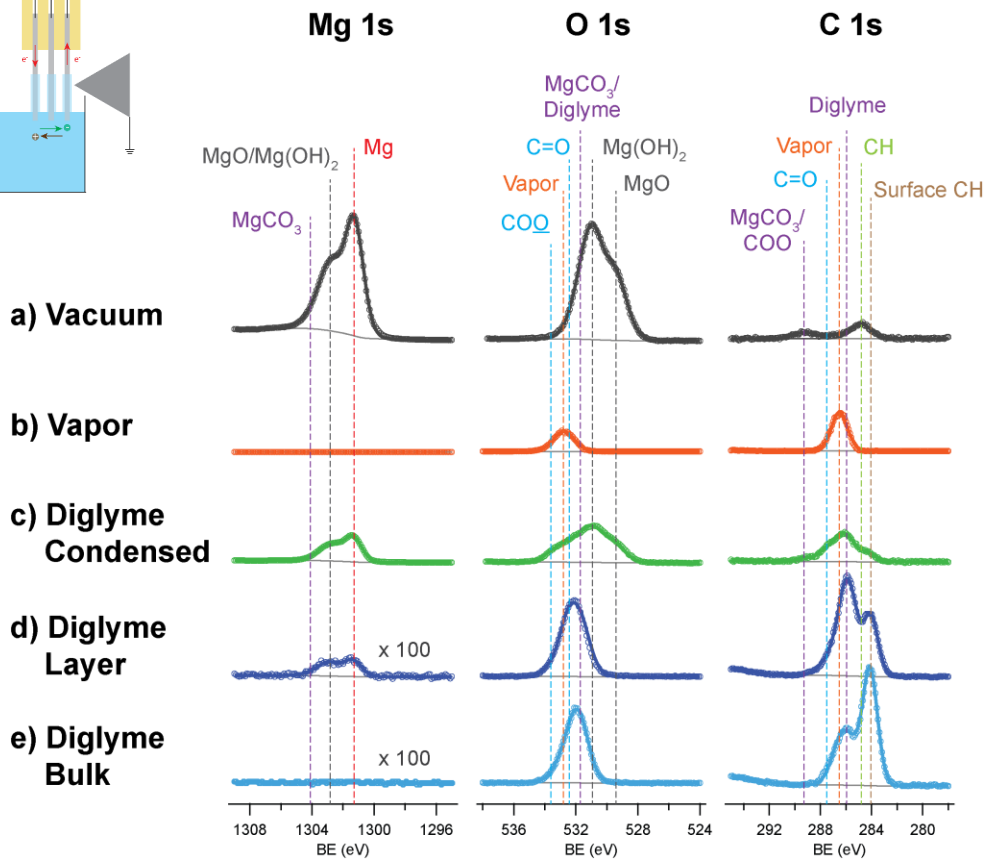
Limitations imposed by impurities?

Evidence for Spontaneous Oxidation of G2



XPS signatures indicate:

1) expected oxidation of Mg anode surface
2) formation of additional organic moieties due to diglyme decomposition



Examination of thin (10s—100s nm) meniscus using tender X-rays permits high kinetic energy electrons to escape and be detected while electrochemical processes advance

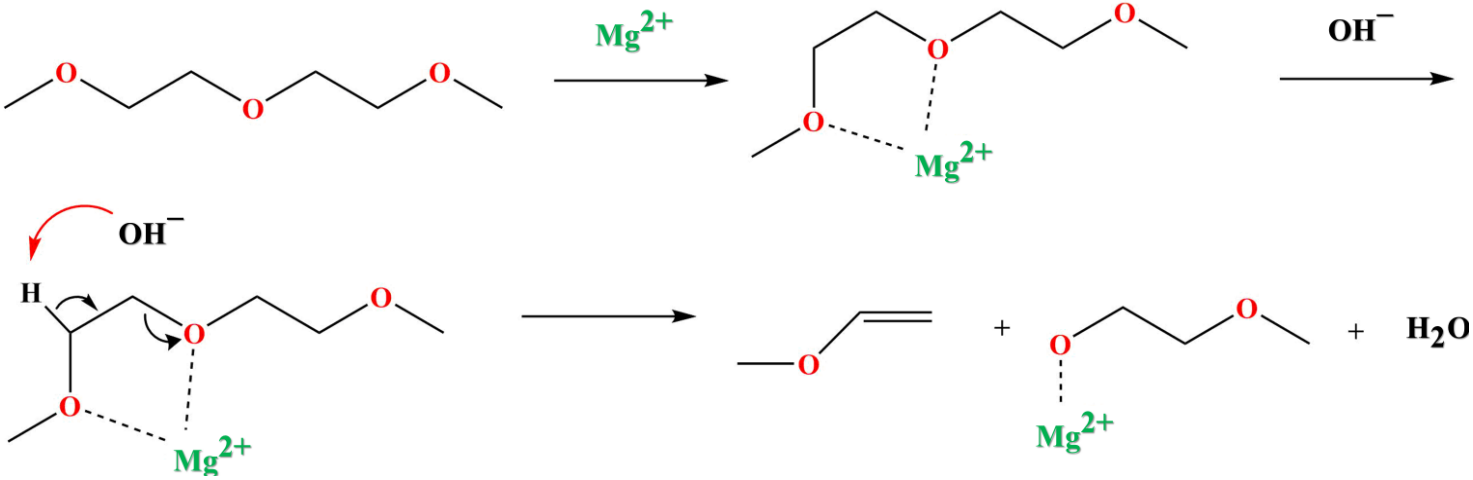
Study of Mg anode in symmetric cell in contact with diglyme solvent

Electrochemistry performed with dissolved $Mg(TFSI)_2$

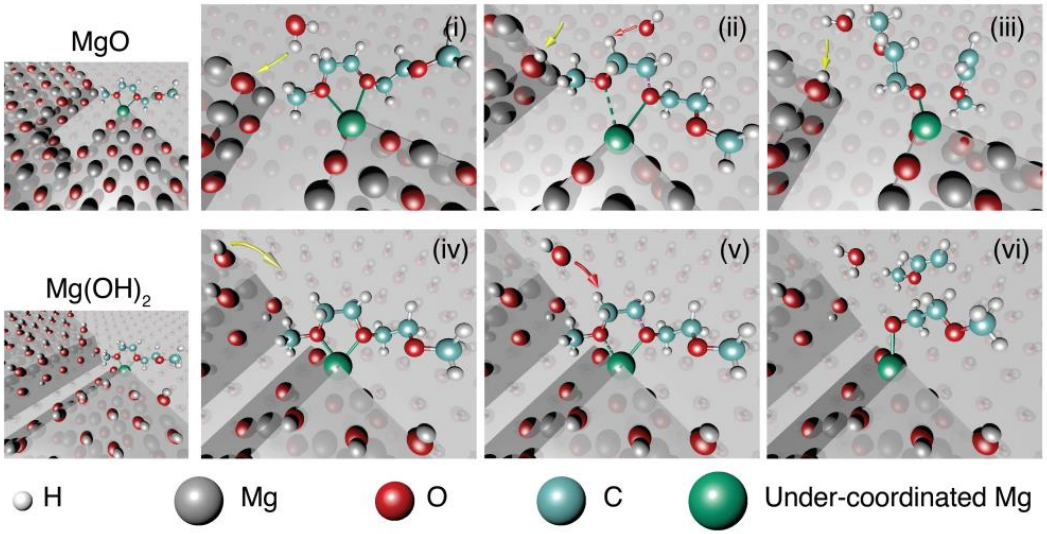
Yu, Baskin et al. *under review Nat. Comm.*

Diglyme decomposition at Mg-anode

Cation chelation enables proton abstraction)



Reactions on “rough” oxidized Mg-anode surface



DFT calculations indicate spontaneous reactivity of Mg^{2+}-chelating diglyme with free hydroxide

We imagine competitive Mg-OH bond prevented by pinning of diglyme at anode surface

No proton abstraction upon chelation of softer cations (Na^+, K^+)

$(Mg\text{-}TFSI)^+$ ion-pair also unstable to OH^-

Yu, Baskin et al. *under review Nat. Comm.*

Conclusions

- Chloroaluminates (and other chloro-Mg complex electrolytes) provide benchmark for metal anode activity but have issues

- Weakly coordinating salts can overcome anodic stability and deposition rate limitations
  - Shortcomings of $TFSI^-$ largely anode related

    Cl^- addition highligths the path to free dissociated Mg^{2+}
  - Carborane is limited at the cathode – passivation

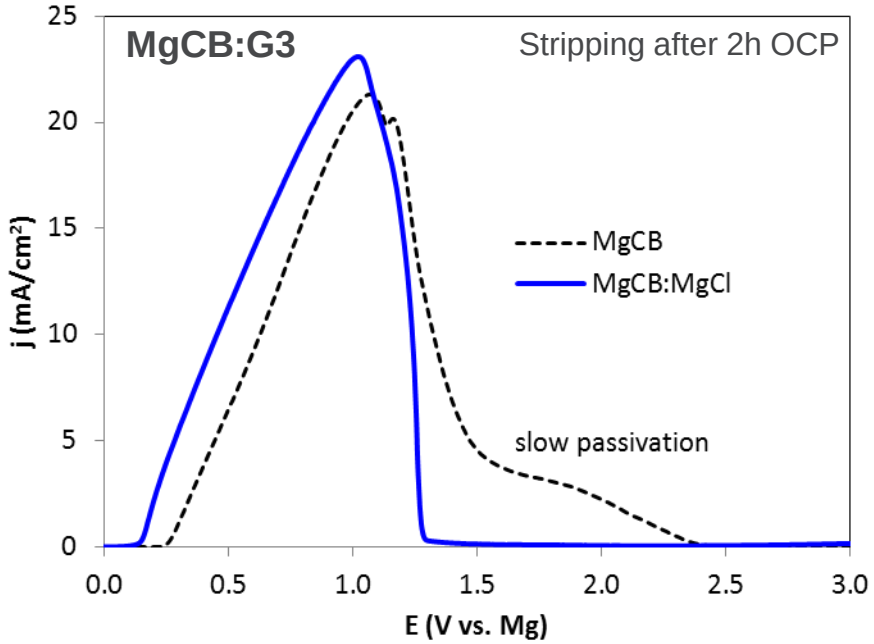
    Alkoxyborates show promised cathodic and anodic limits
  - Path forward will couple functionalization and performance

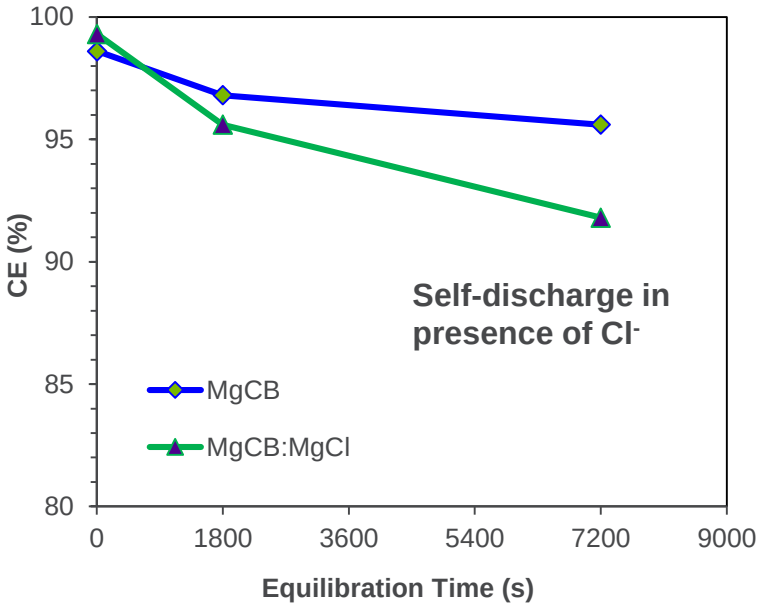
    Computational guidance is essential

- Stability of the weakly coordinating anion and impurity control are critical
  - Clean synthesis
  - Dry solvents

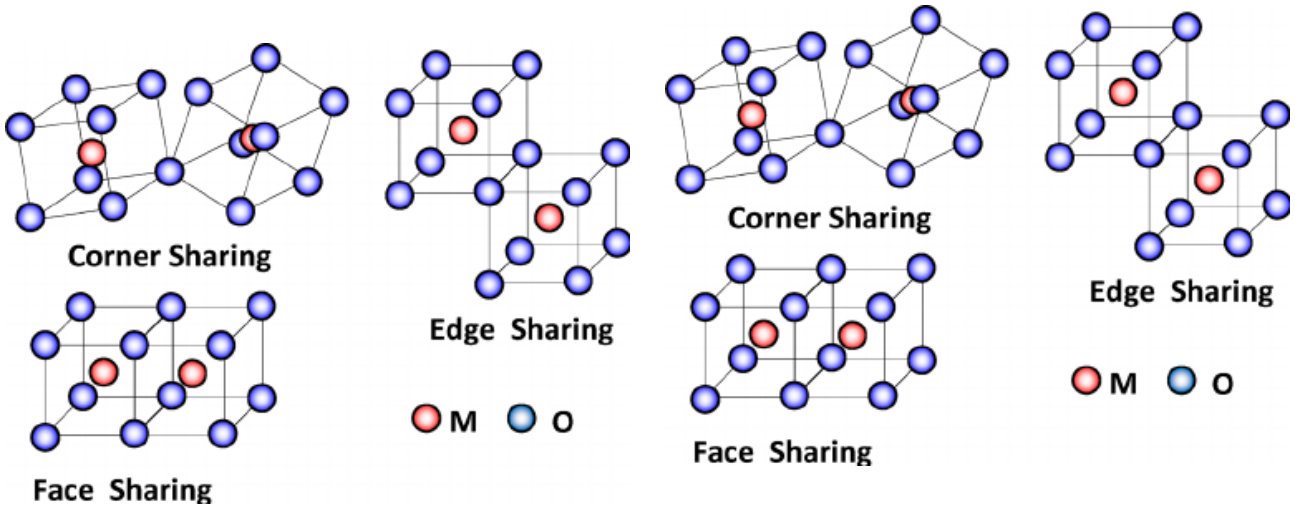
Questions

Chloride-free and Scavenger-Free Electrolytes are prone to surface deactivation





- Cl^- suppresses passivation in by facilitating breakdown of modified Mg surface layer
- Absence of stable surface layer at OCP may enable self discharge


Corner Sharing
Edge Sharing
Face Sharing
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Corner Sharing
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