This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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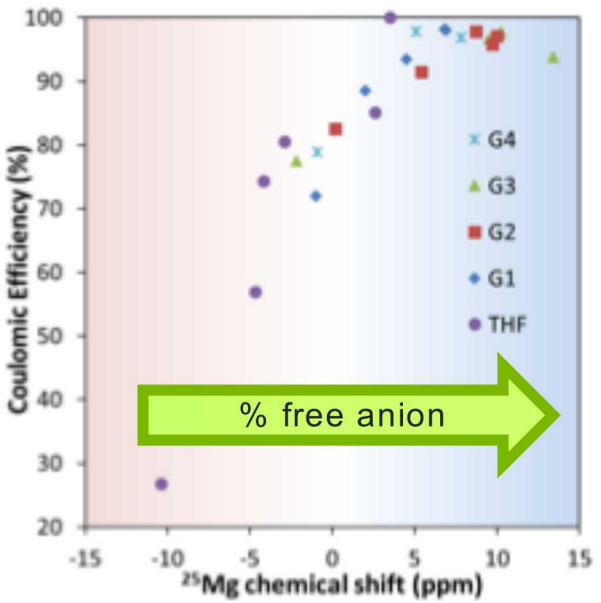
JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Decoupling Electrolyte Anion and Solvent effects in Magnesium Electrodeposition for Rechargeable Batteries



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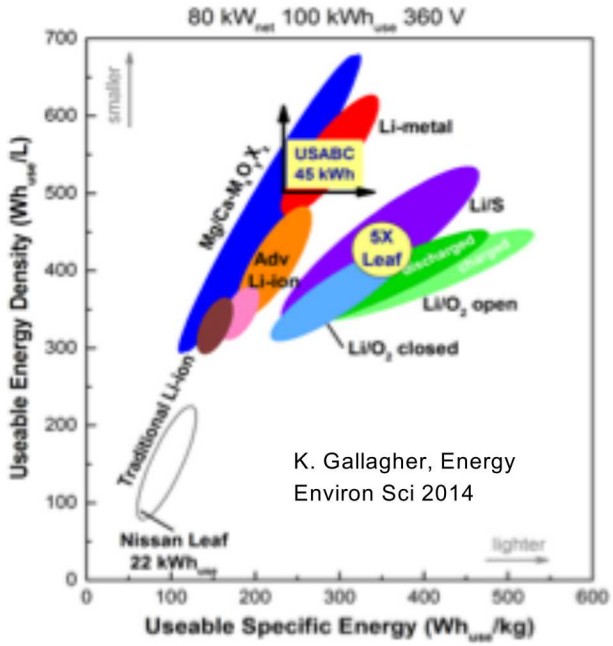
Sandia National Laboratories

The Promise of Mg Batteries

- ***Mg metal anode + high voltage cathode = transformative energy storage***
- Significant growth in Mg electrolyte development
  - Aimed at expanding the stability window
- Growing electrolyte toolkit provides opportunity for systematic investigation



Mg Electrolyte Concept Development

$R_2Mg:AlR_xCl_{3-x}$ "DCC" — $RMgCl:AlCl_3$ "APC" — $MgX_2:MgCl_2$ X = OR, NR_2 — $MgTFSI_2:MgCl_2$

Cl-based Electrolytes

($Mg_2Cl_3^+$ + etc.)

more basic/reactive (lower anodic stability)

less basic/reactive (higher anodic stability)

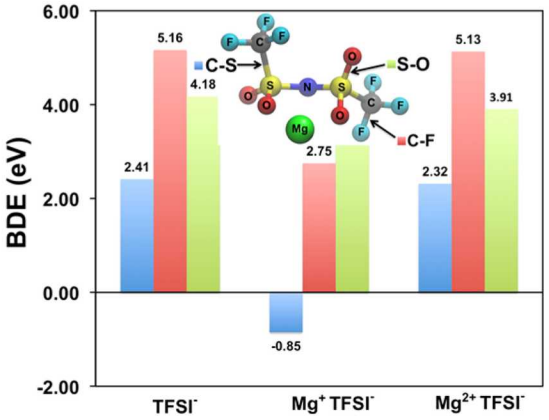
$Mg(BR_4)_2$ — $MgTFSI_2$ — $Mg(HCB_{11}H_{11})_2$ — $Mg(MOR^F{}_4)_2$

WCA-based Electrolytes

(Mg^{2+})

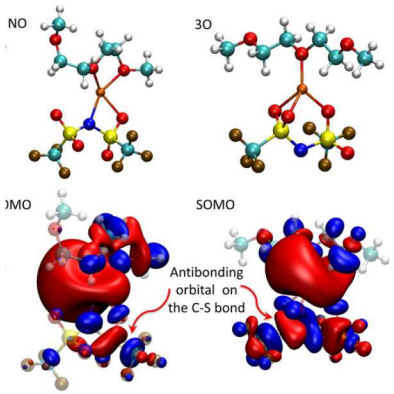
Instability of the TFSI Anion

Efficiency is argued limited by Mg^{2+}-$TFSI^-$ reduction during electron transfer



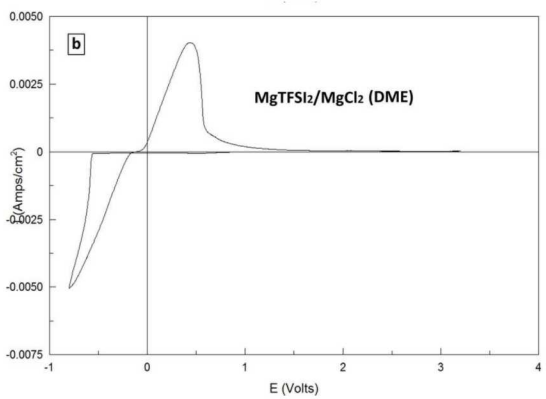
N. Rajput, J. Am. Chem. Soc. 2015, 137, 3411−3420

Extent of molecular orbital rehybridization dictates e- localization on anion



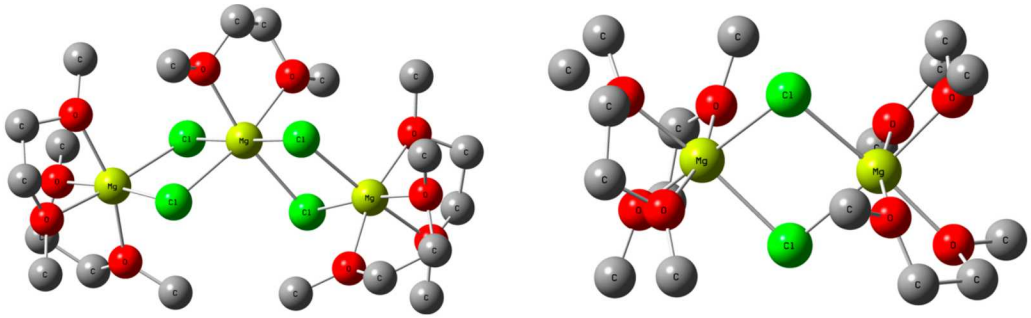
A. Baskin, J. Phys. Chem. C 2016, 120, 3583

Cl^- addition - a CIP anion - improves efficiency



M. Salama, J. Phys. Chem. C 2017, 121, 24909

$Mg_2Cl_2^{2+}$ and $Mg_3Cl_4^{2+}$ complexes are proposed as deposition species in Cl:TFSI mixtures based recrystallized on solvates – unique wrt $Mg_2Cl_3^+$



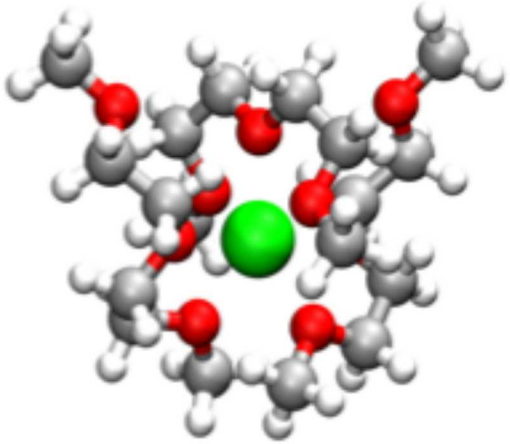
I. Shterenberg *JES*, 162 (13) A7118 (2015)

Outstanding Questions – New Approach

Does unbound TFSI contribute significantly to inefficiency?

Can we draw more universal conclusions of TFSI's role in limiting efficiency?

What lessons from TFSI can be applied to WCA's

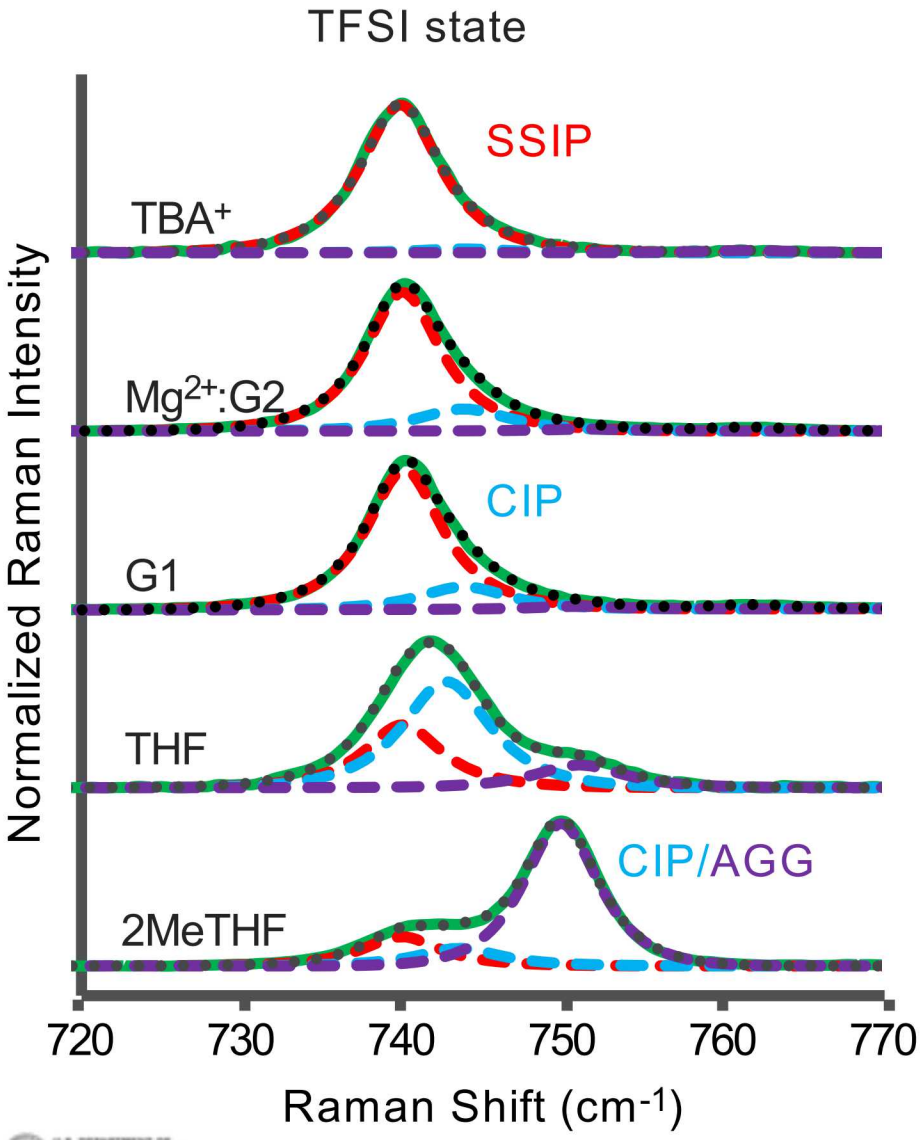


Our approach:

Explore impact of competitive solvent and anion complexation on efficiency.

- Treat the ether – glyme solvent series as a continuum of energy of complexation
- Treat contact ion pairing anions as displacive ligands

Mg Coordination Environment is Dictated by Solvent

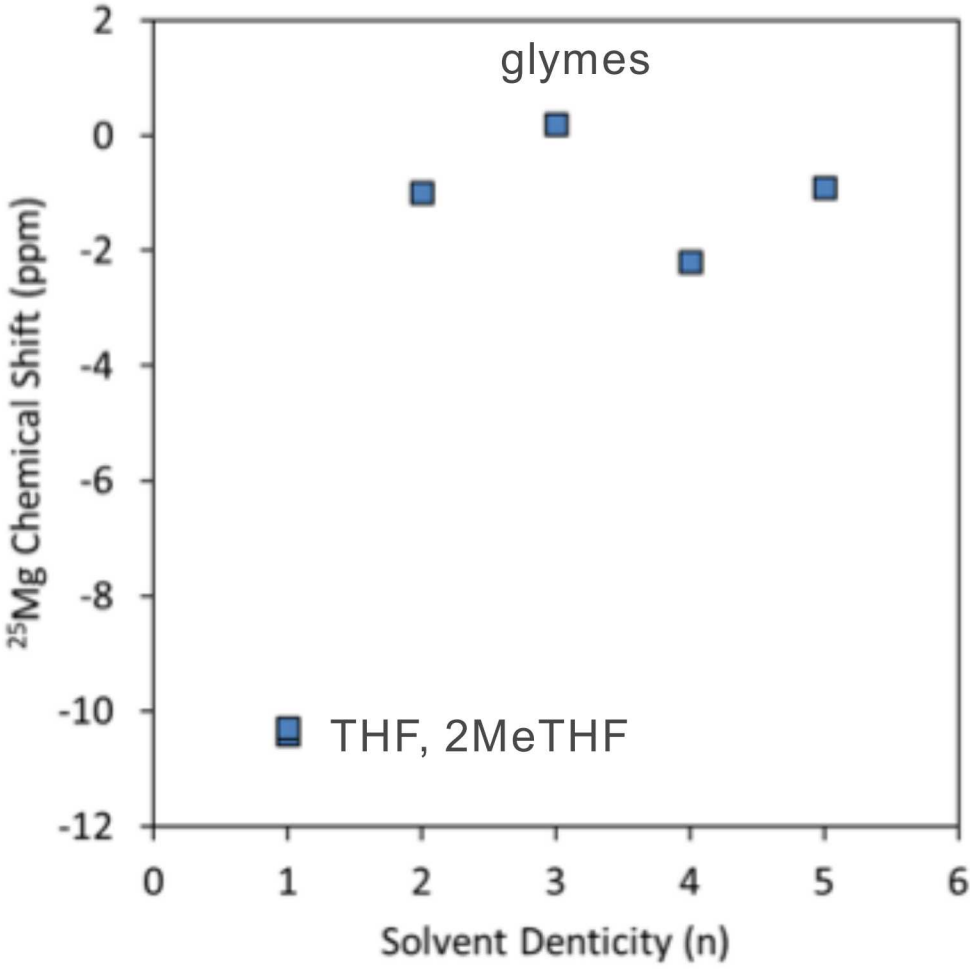


Solvent	TFSI SSIP
TBA^+:G2	>97
G4	74
G3	83
G2	84
G1	83
THF	31
2MeTHF	16

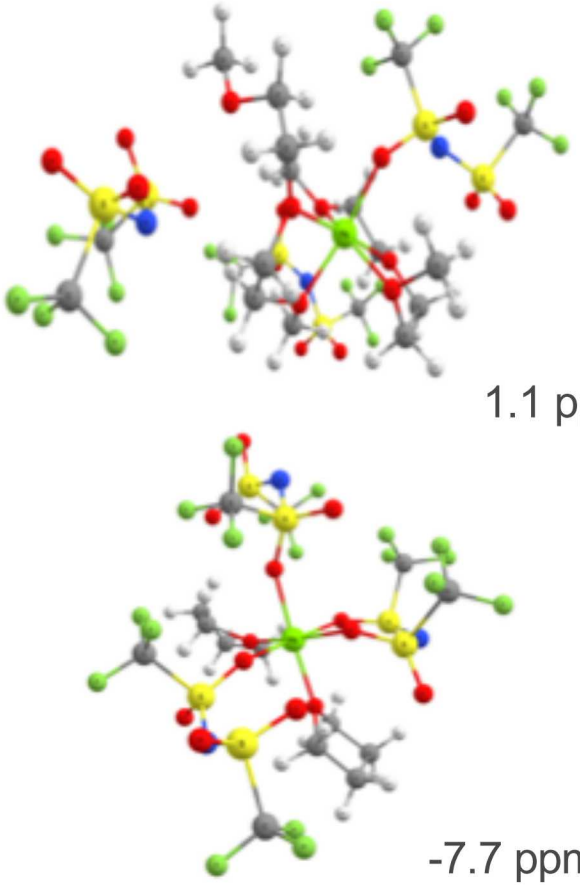
Solvent and anion compete for cation coordination

Greater denticity – reduced ion pairing

Reduced Ion Pairing is Reflected in ^{25}Mg NMR



CMD derived, DFT optimized

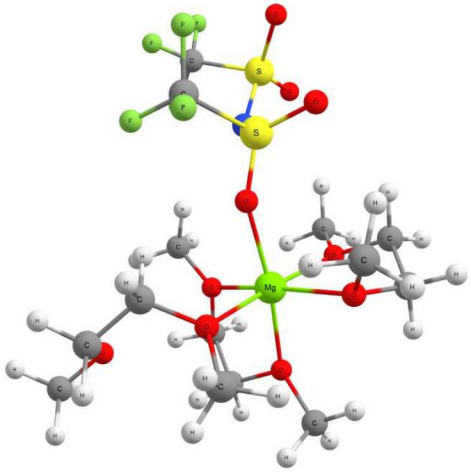


1.1 ppm

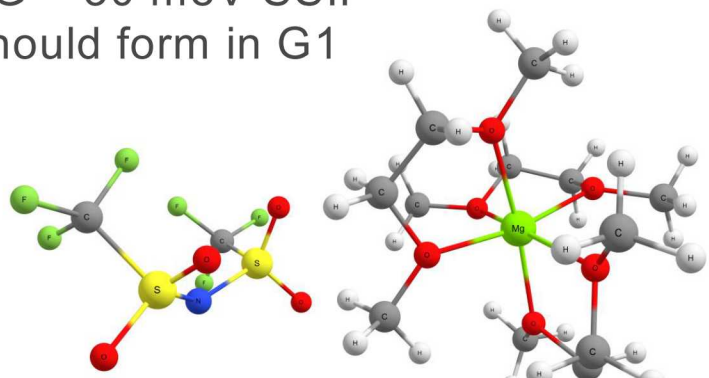
-7.7 ppm

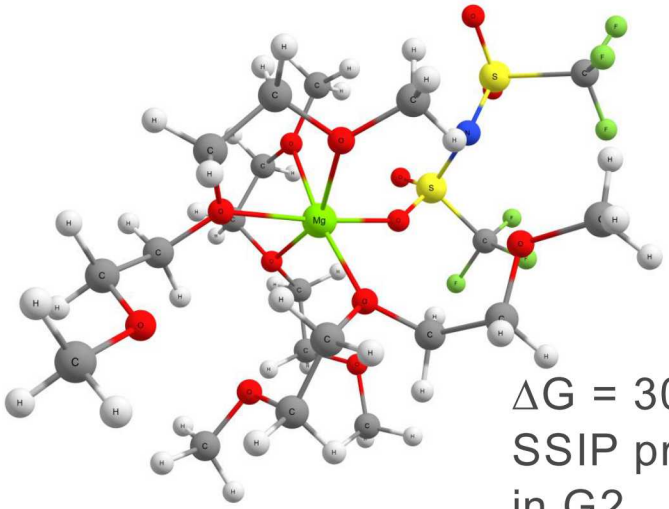
Competitive Complexation is Expected

Comparing ΔG formation of $Mg(solv)_5TFSI$ and $Mg(solv)_6$

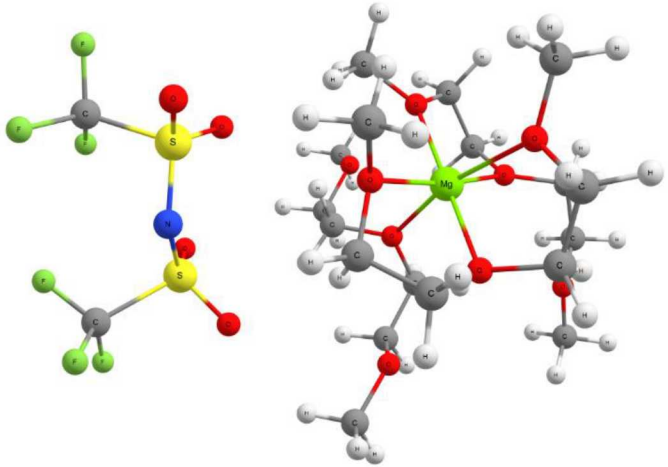


ΔG = 30 meV SSIP should form in G1

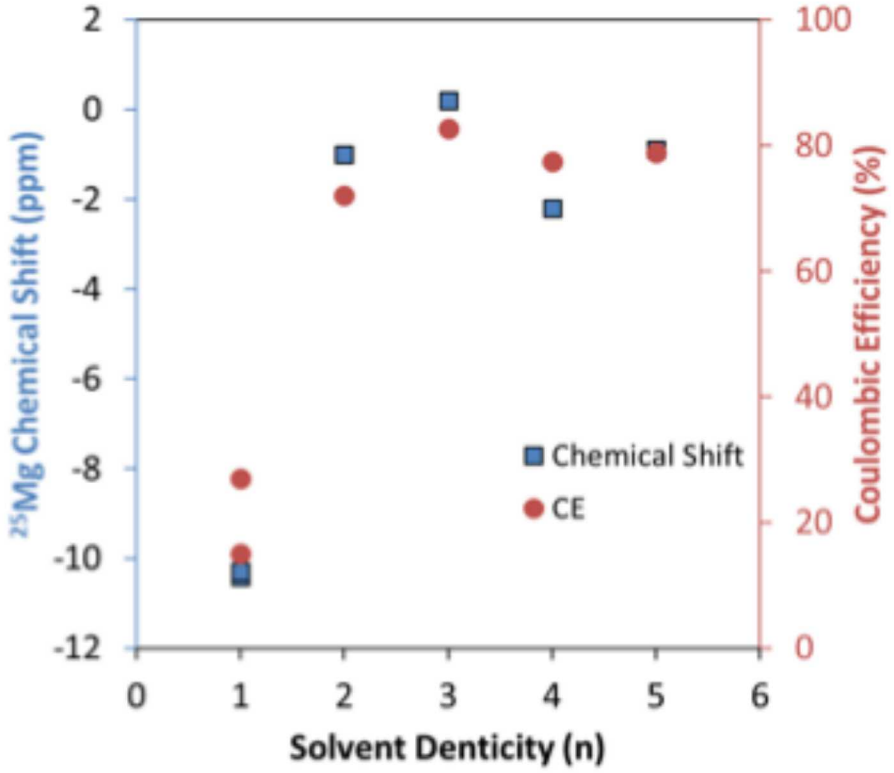


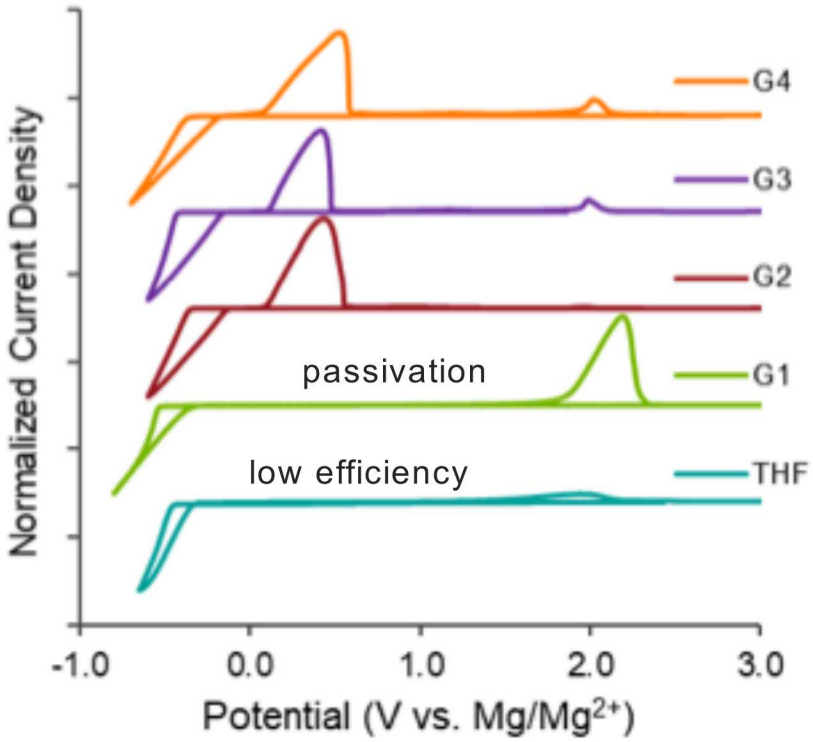


ΔG = 300 meV SSIP preferred in G2



Speciation Impacts Electrolyte Cathodic Performance

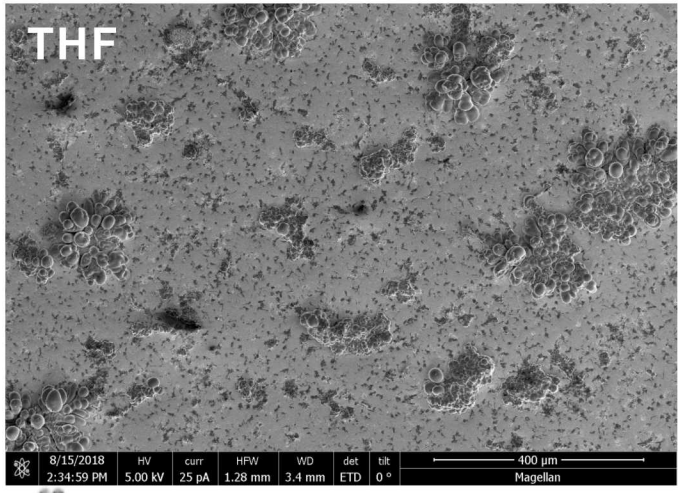


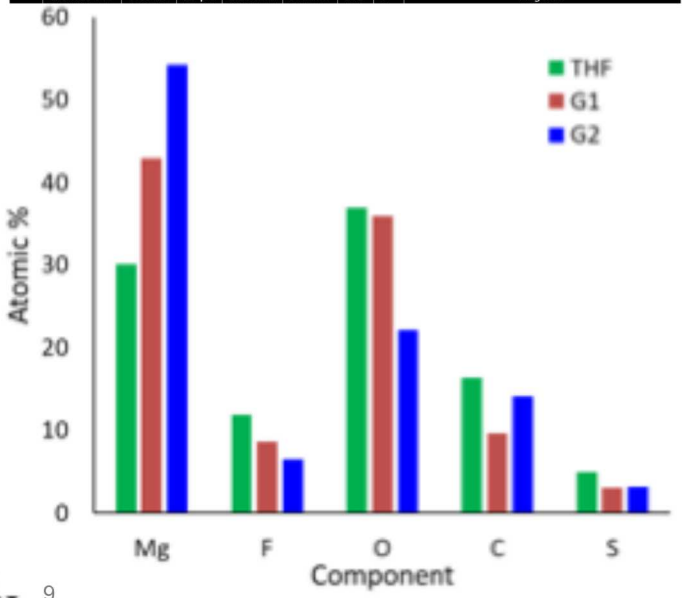


Reduced TFSI Decomposition with Displacement

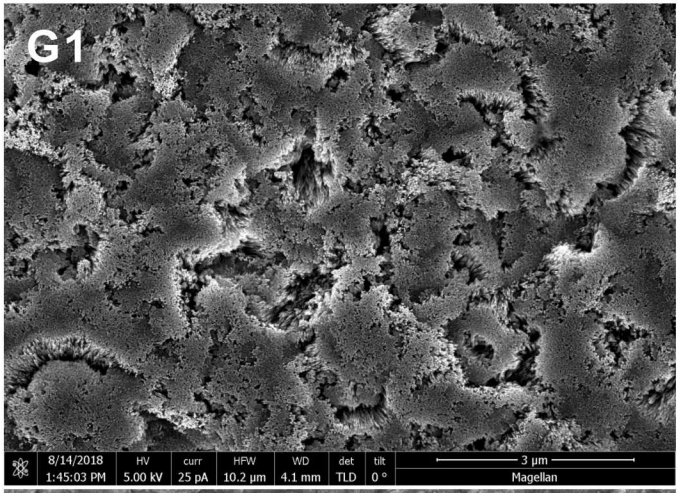
Interphase composition should yield less TFSI products with THF ⇢ G2

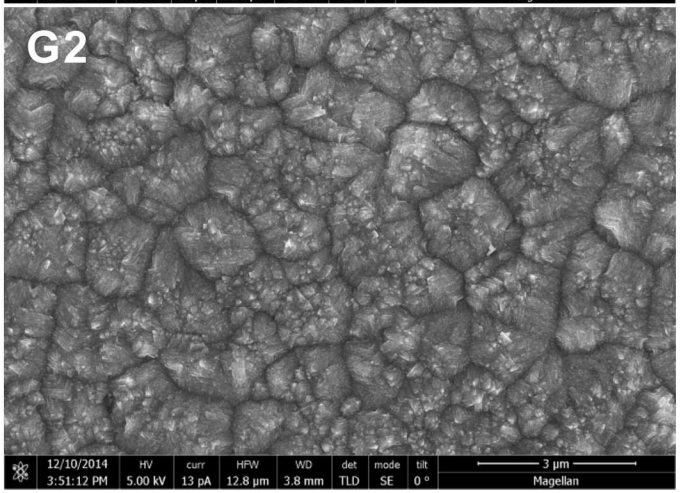
Localized deposit – filmed substrate





localized deposit – fibrous morphology





localized deposit – dense platelets

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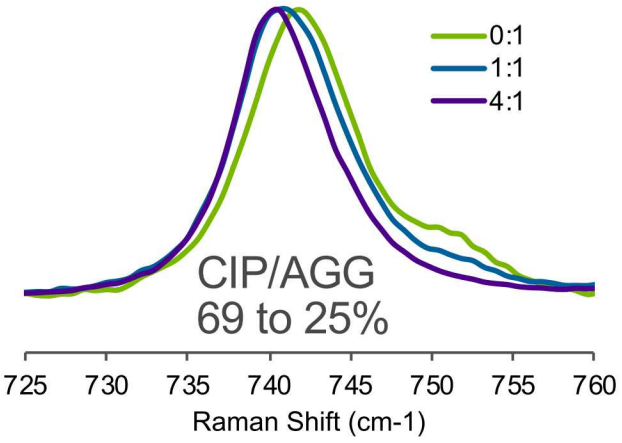
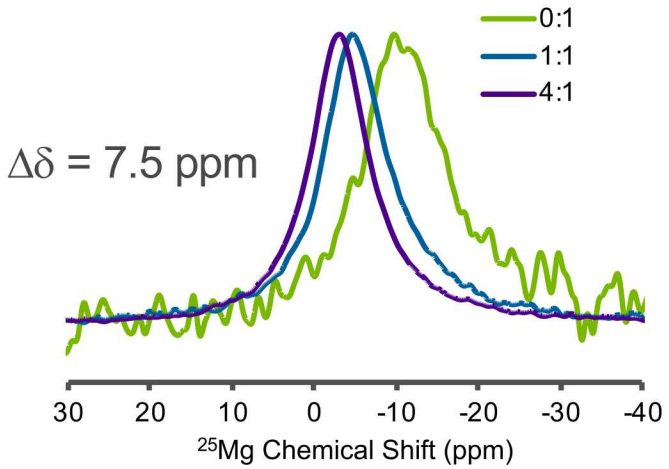
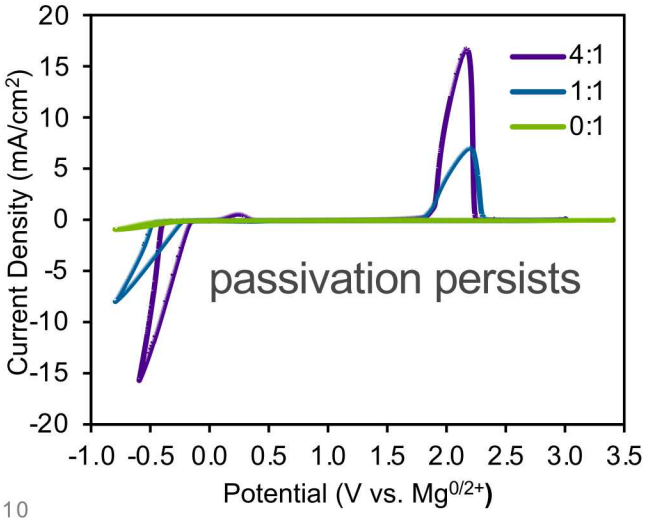
Anion Displacement through Co–Solvent Addition

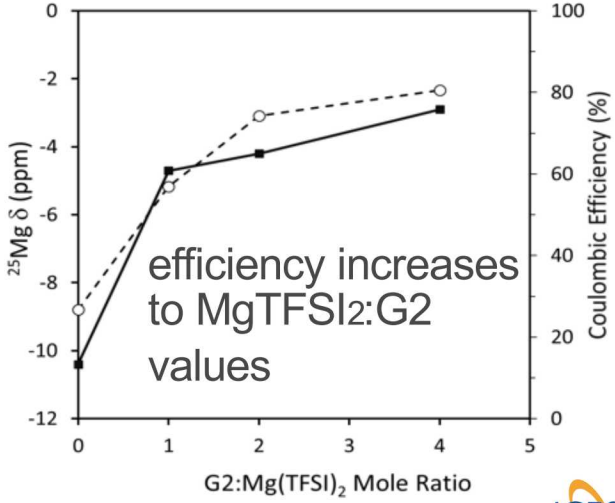
Can a more strongly complexing solvent displace coordinated TFSI?

0 to 4 molar ratios of G2:$MgTFSI_2$(THF), 4:1 only 0.14 x_{G2}



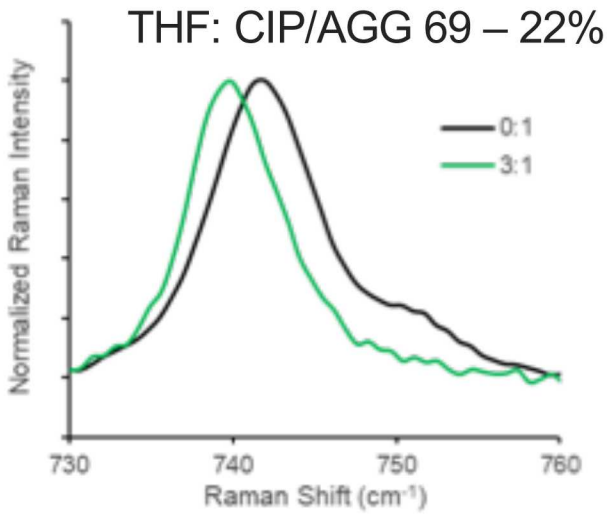


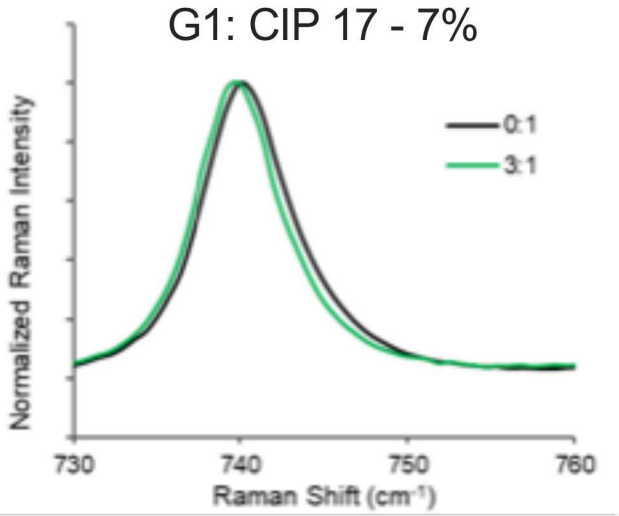


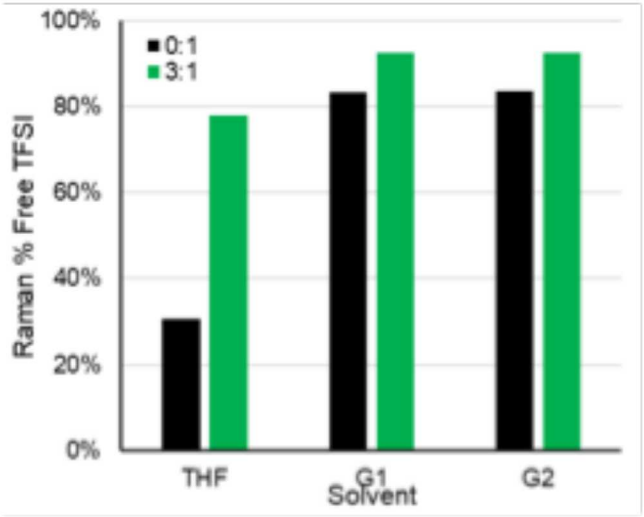


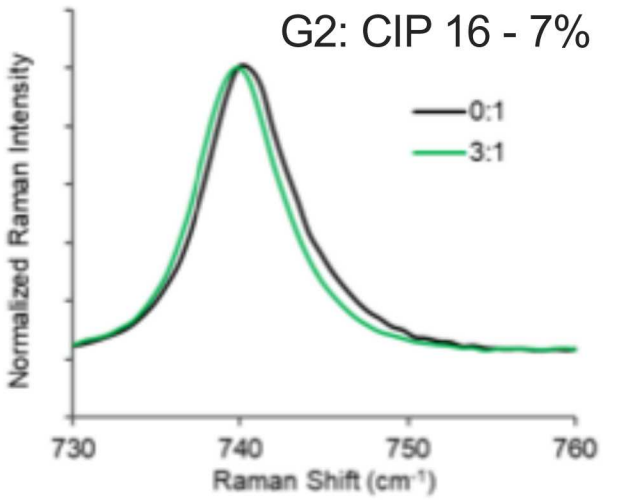
Anion Displacement through Co-Anion Addition

Co-anion electrolyte: 3:1 molar ratio of $MgCl_2$ to $MgTFSI_2$ (0.5 M Mg^{2+})

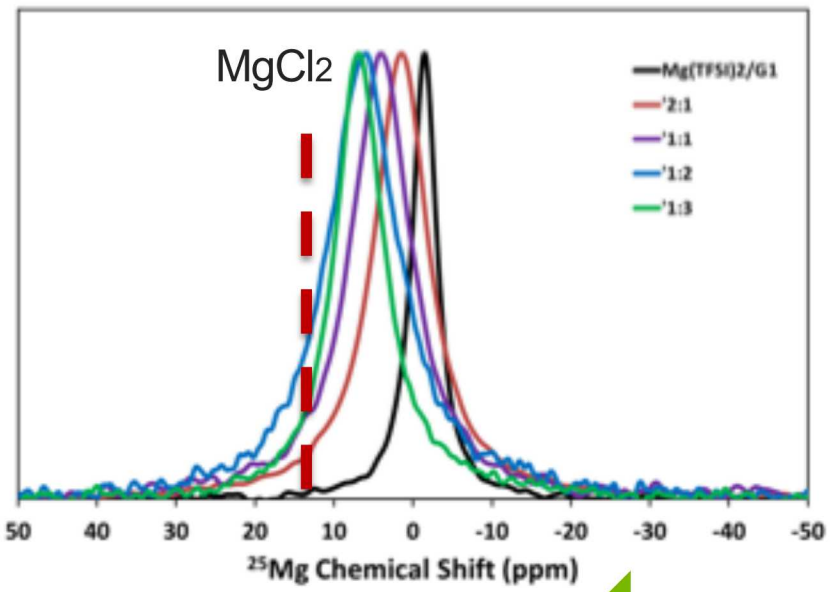


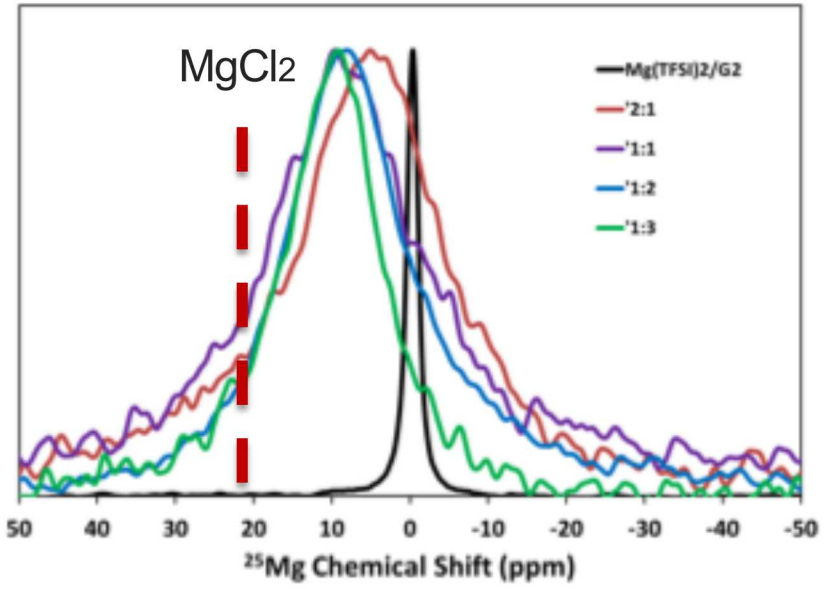






Deshielding of the ^{25}Mg Resonance with Co-Anion





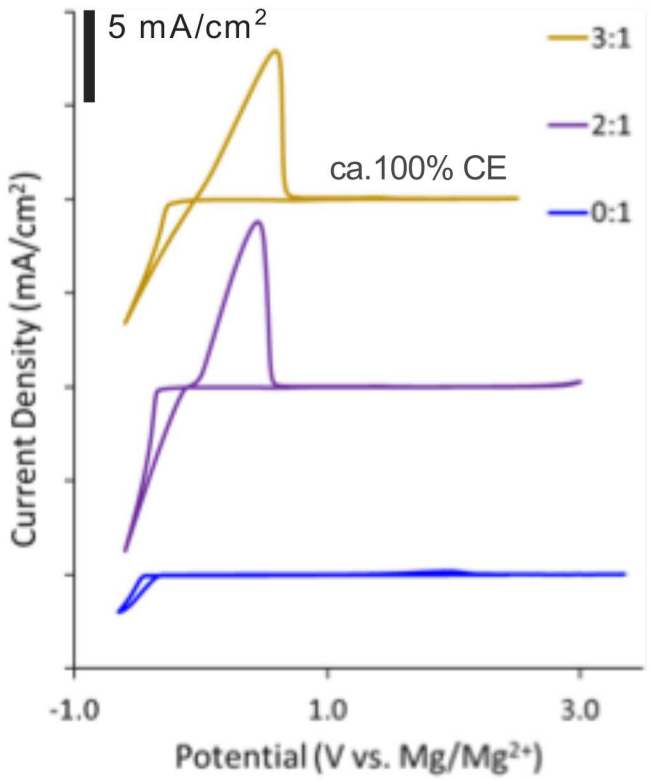
Increasing Cl^-

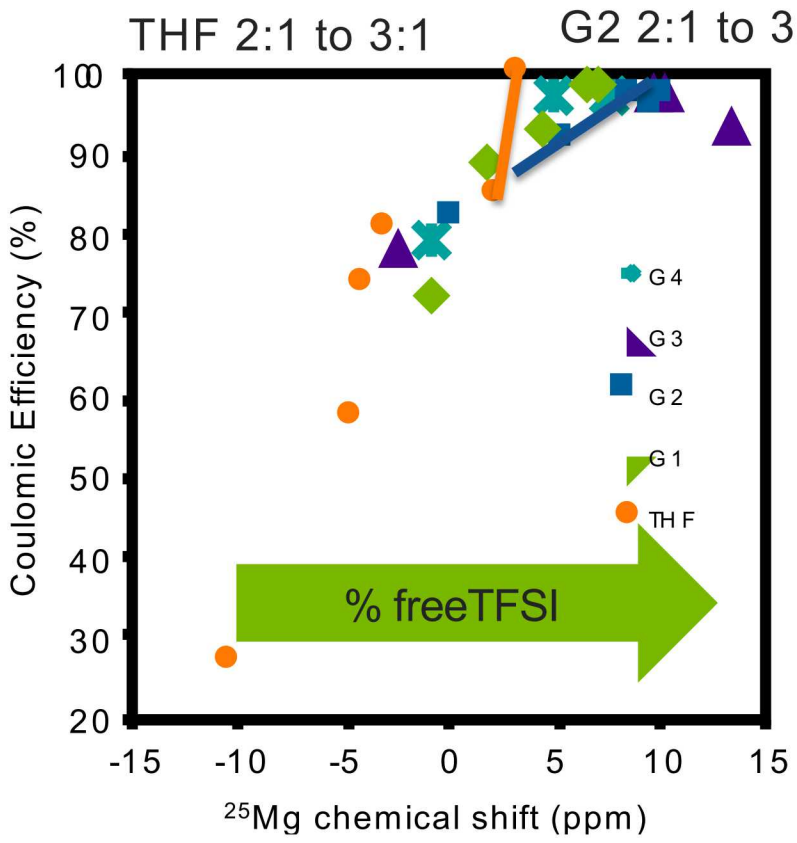
Show the systematic shift with Cl increase for a single solvent – need to capture FW
Create a scale with

Efficiency Increased Dramatically with Cl^- Addition

Two different trajectories – different speciation?

Cl:TFSI **THF** (0.5 M Mg^{2+})



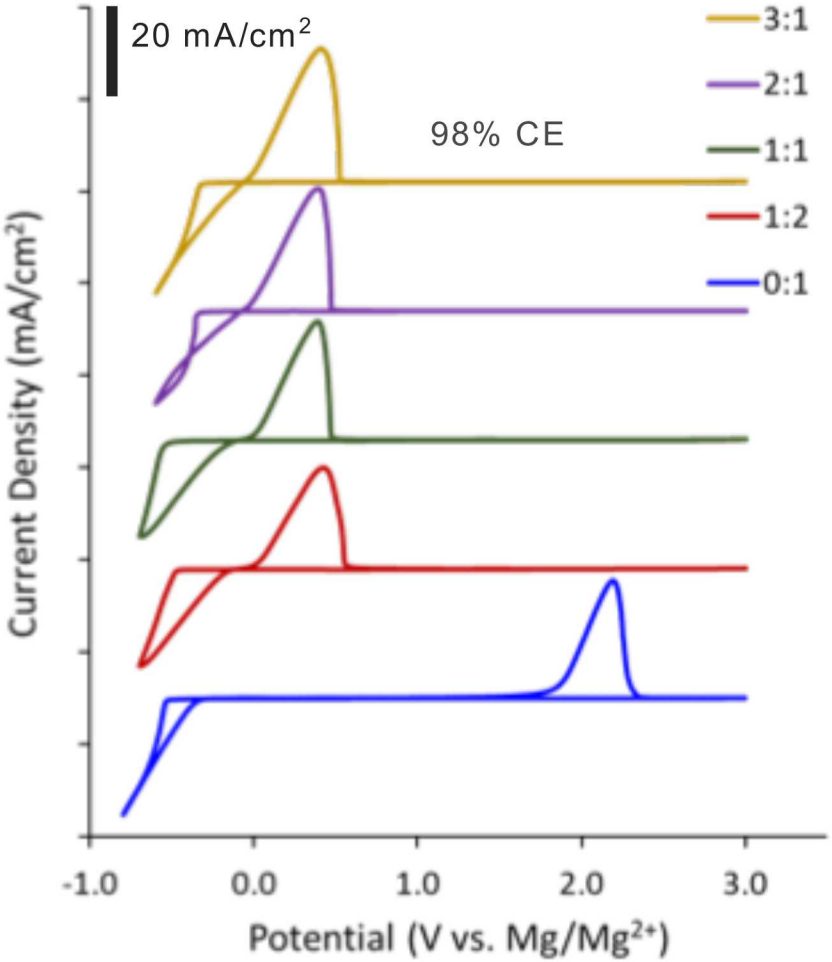


THF: 7% TFSI is paired 100% CE
G1: 7% TFSI is paired 98% CE

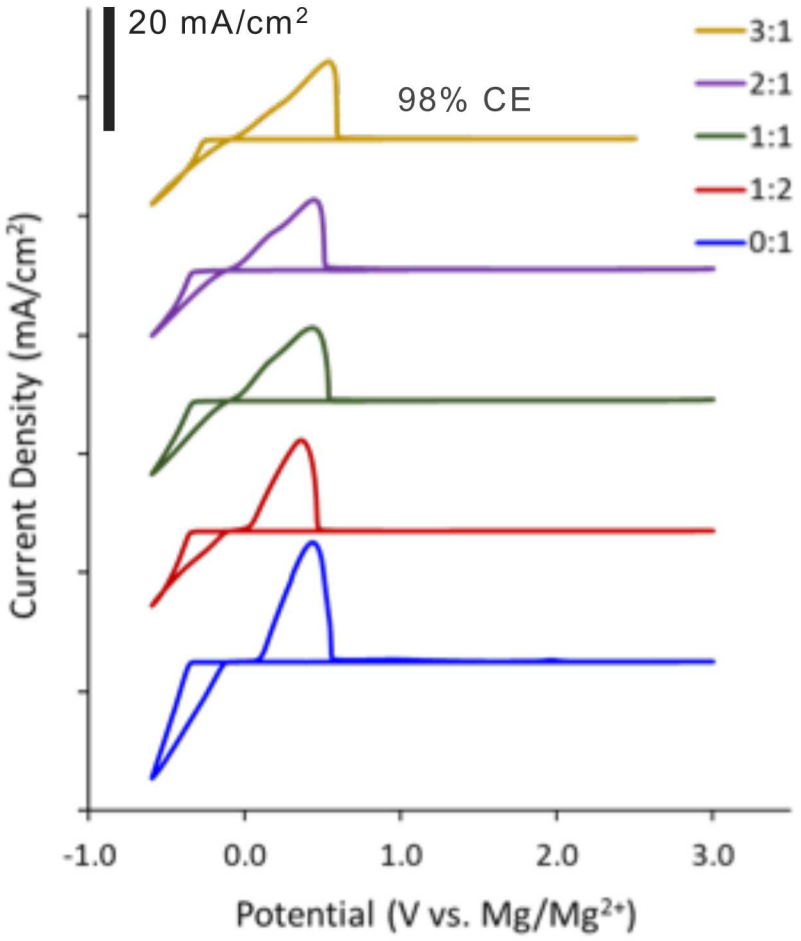
Why the difference?

Common Electrochemical Response Across Solvents

Cl:TFSI **G1** (0.5 M Mg^{2+})



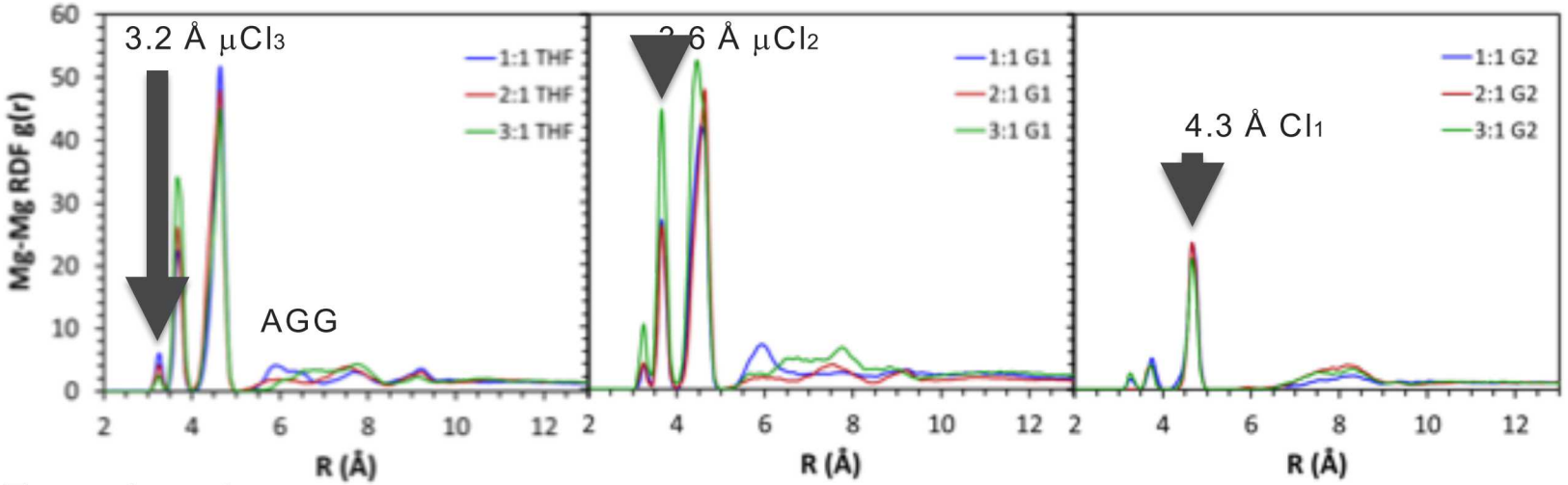
Cl:TFSI **G2** (0.5 M Mg^{2+})



G3 and G4 exhibit comparable changes in η_{red} and η_{ox}, kinetics are slowed

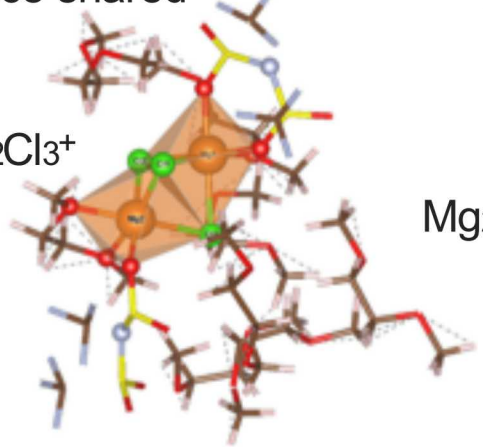
Classical MD Applied to Explore Speciation

MD simulations indicate multimeric complexes with characteristic Mg-Mg distances



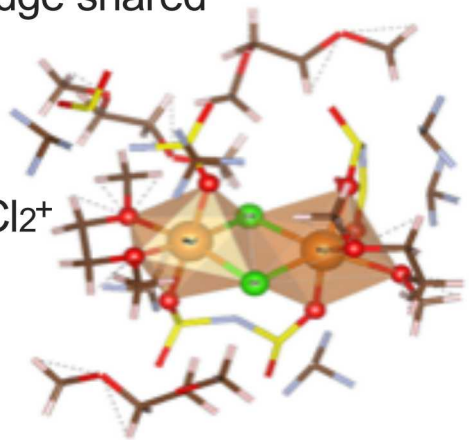
Face shared

$Mg_2Cl_3^+$



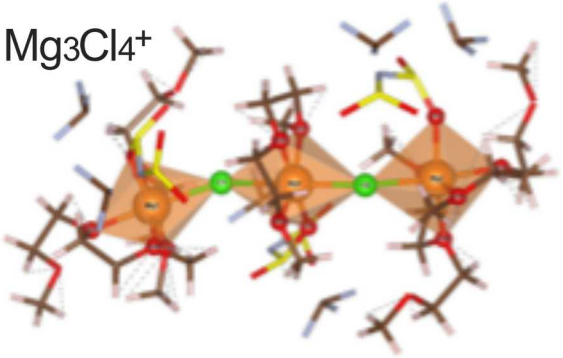
Edge shared

$Mg_2Cl_2^+$



Corner shared

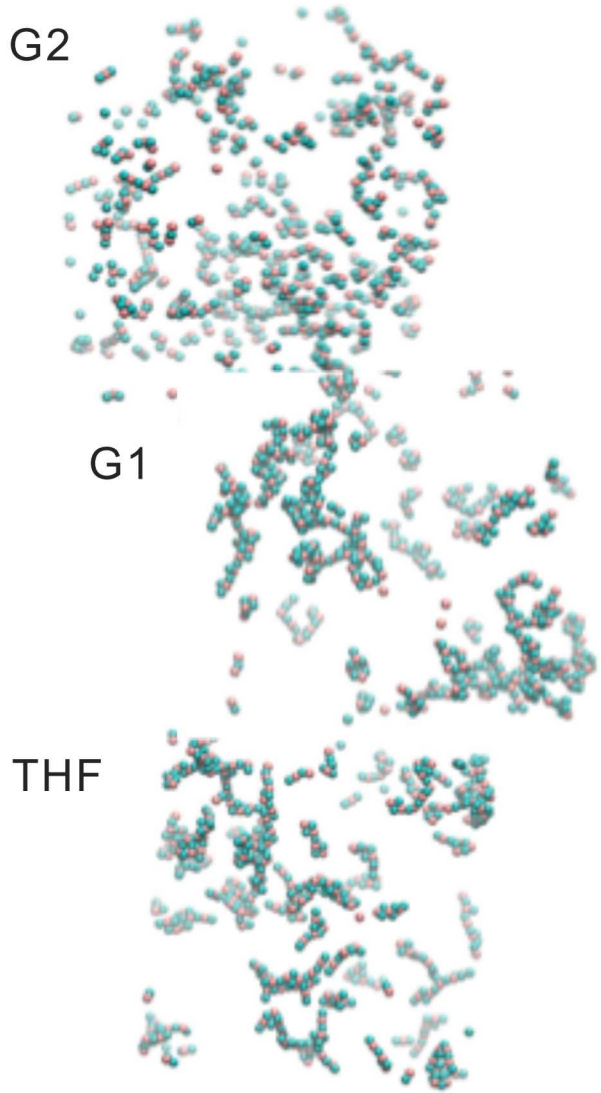
$Mg_3Cl_4^+$



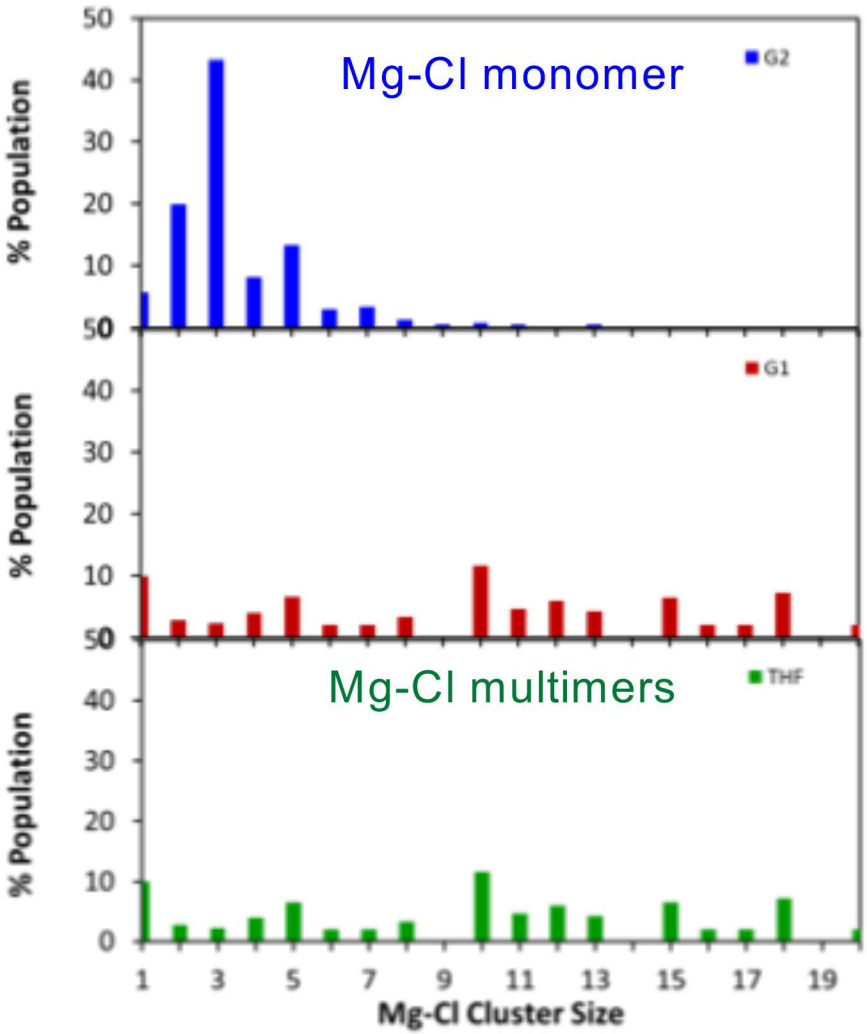
THF/G1 high multimer and μCl probability

G2 lower probability of multimers

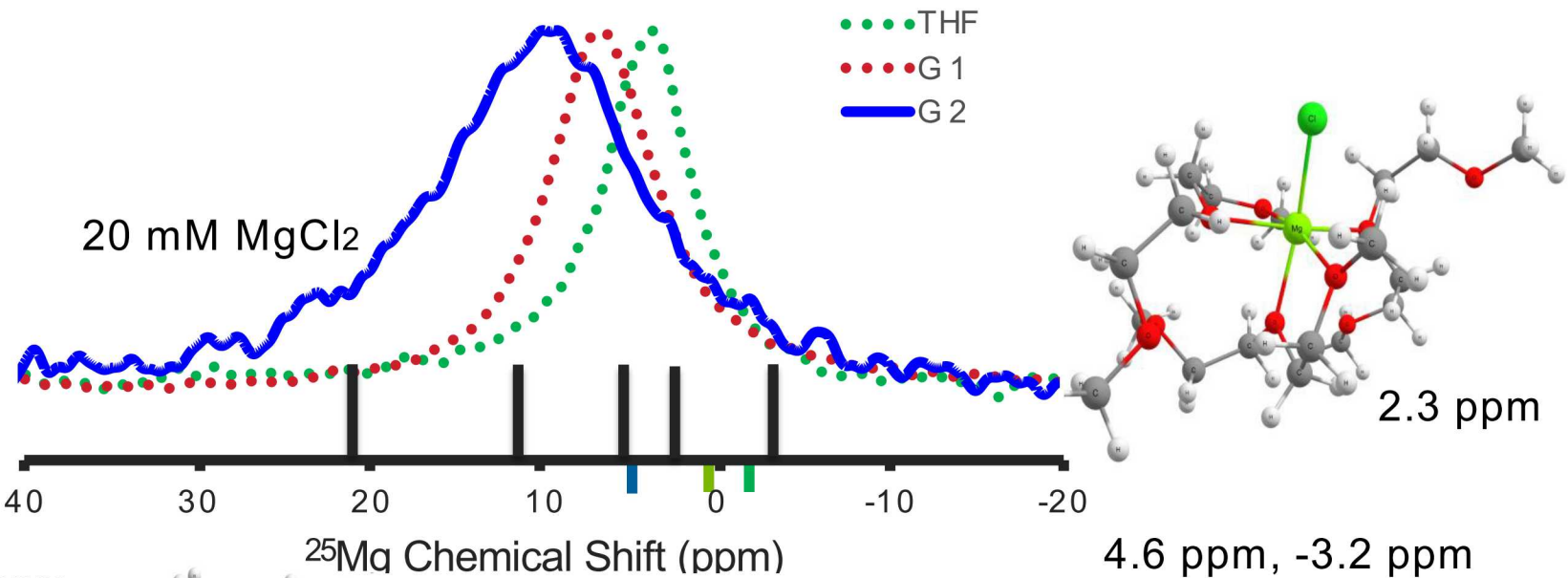
Cluster Analysis Indicates Speciation Differences

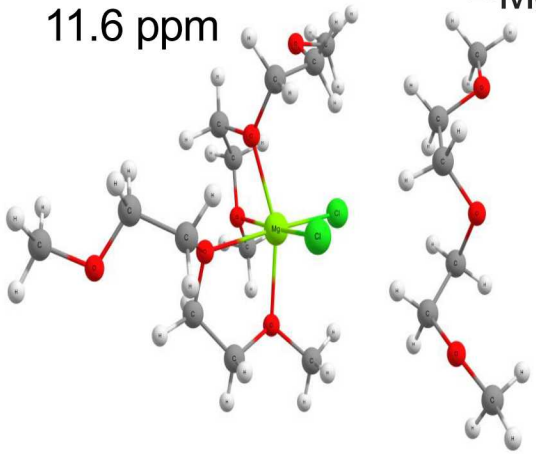


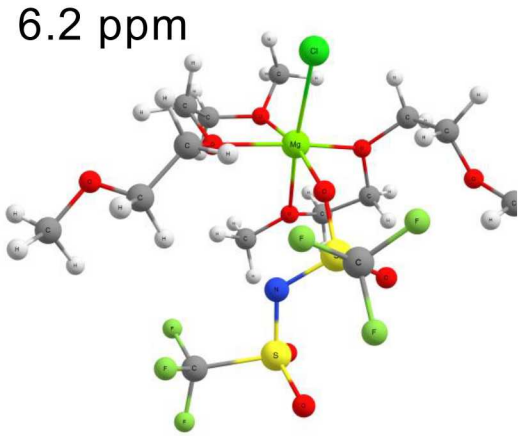
Variation in aggregates

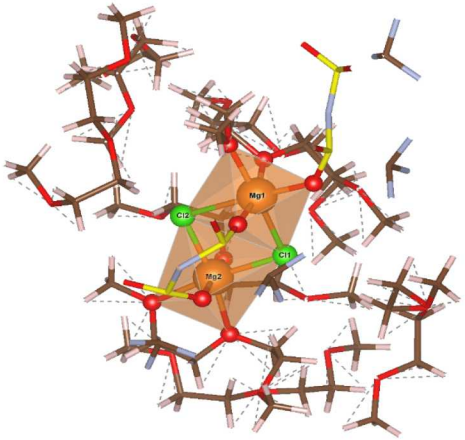


NMR Trends are Consistent with MD Speciation



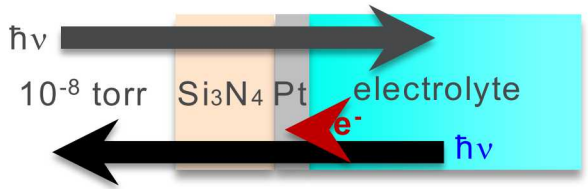






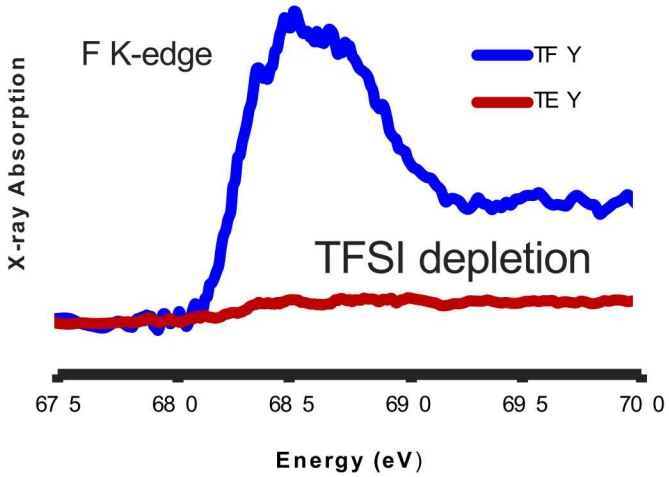
Multidentate Ether Dominates the Interface

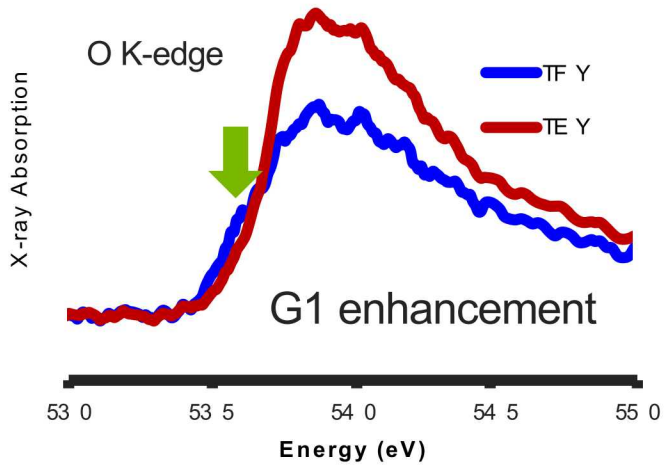
Operando XAS



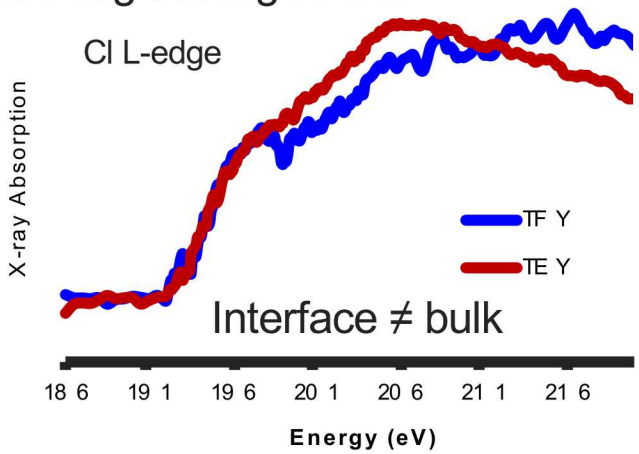
e- out interfacial

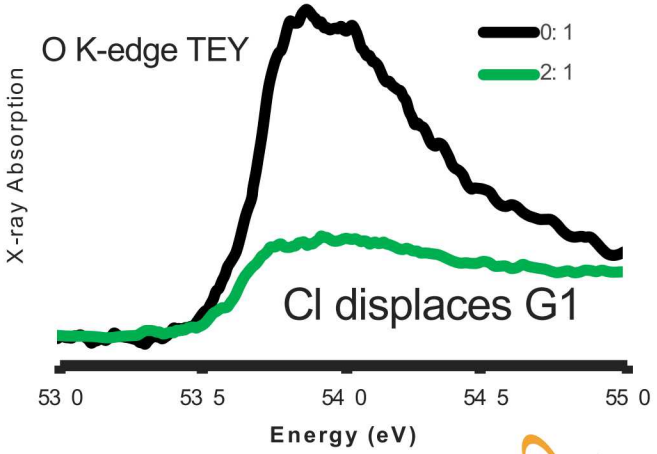
ħν out bulk electrolyte





2:1 molar ratio $MgCl_2$:$MgTFSI_2$

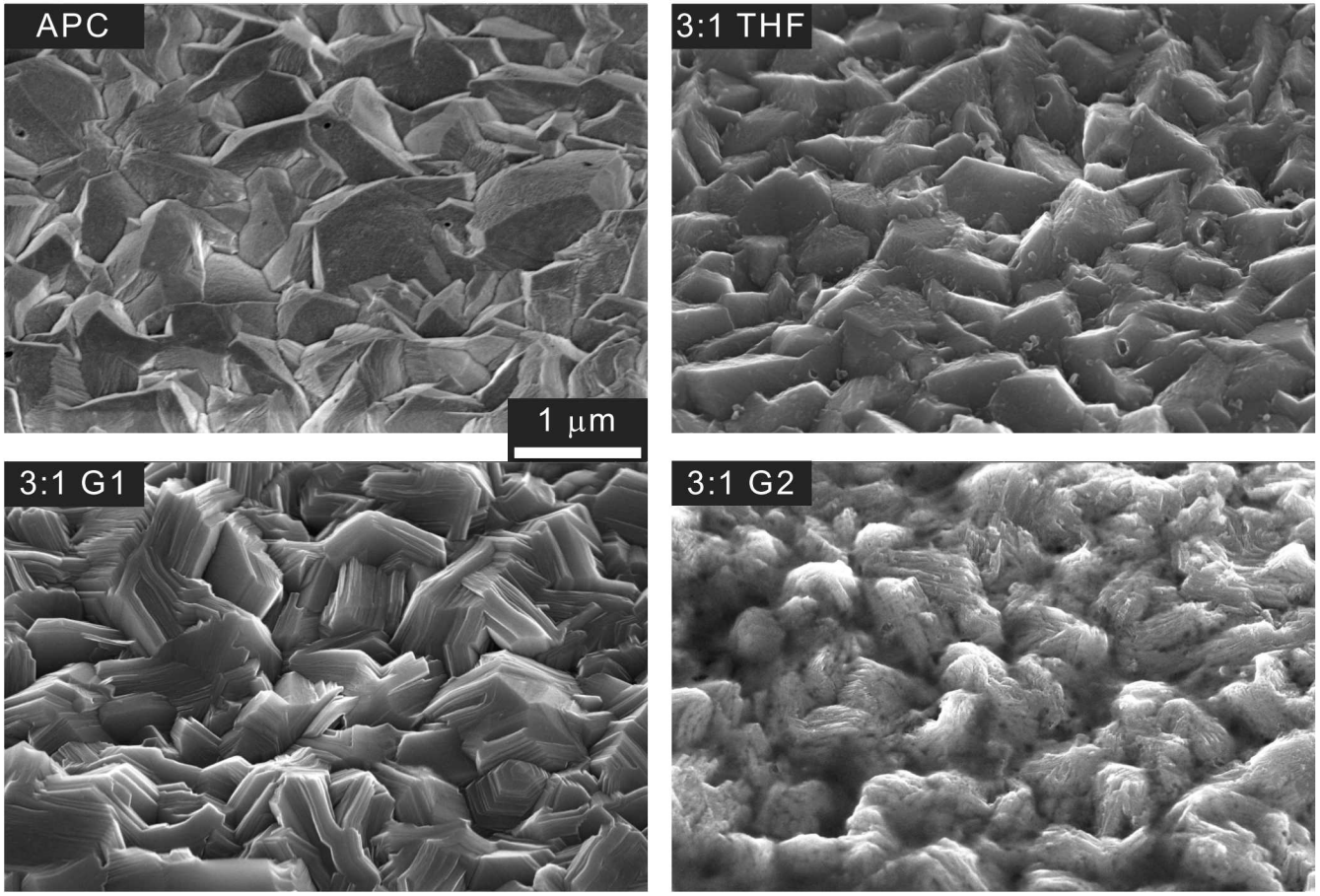




Multimer μ-Cl Systems Yield Defined Crystallography

Cl^- facilitates Mg nucleation at noble metals

Textured (0001) to random (p-1000)

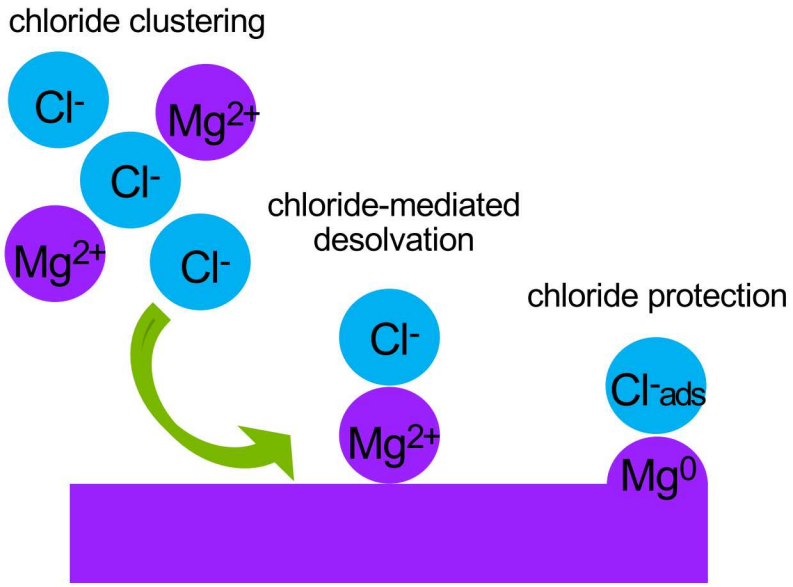


Reduced surface faceting

Chloride vs. WCA-based Electrolytes

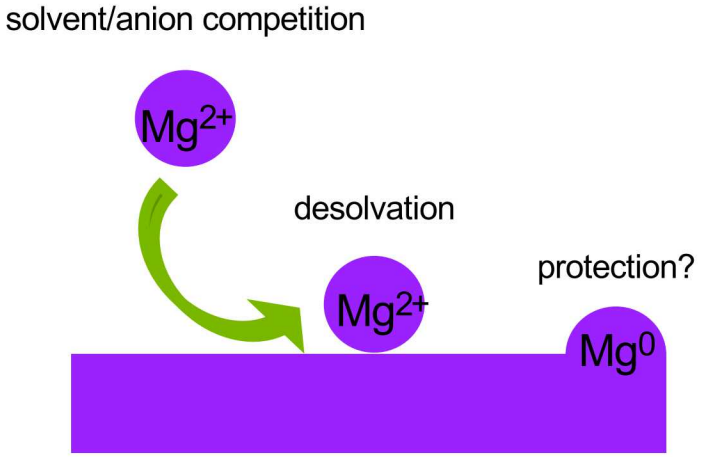
- General principle of operation: mitigate parasitic reductive decomposition to **avoid Mg^{2+} blocking film formation**

Strongly Coordinating Halide



- Chloride regulates response
- Provides apparent protection

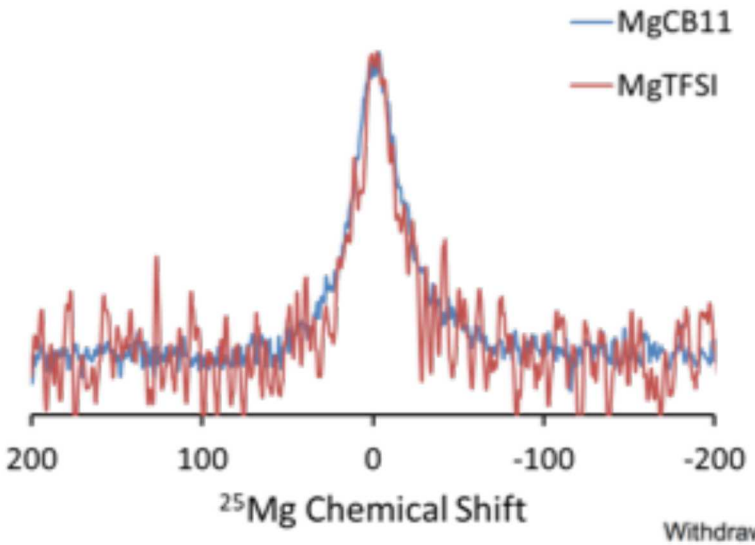
Weakly Coordinating Anion

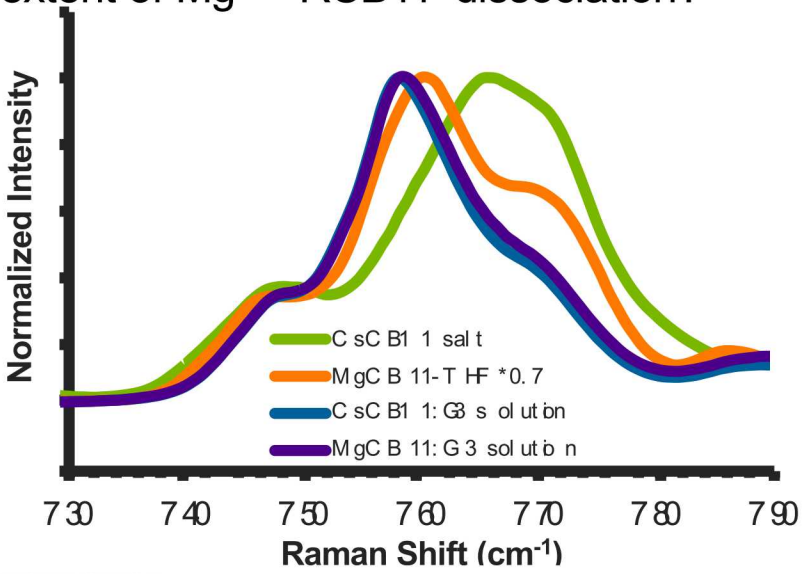


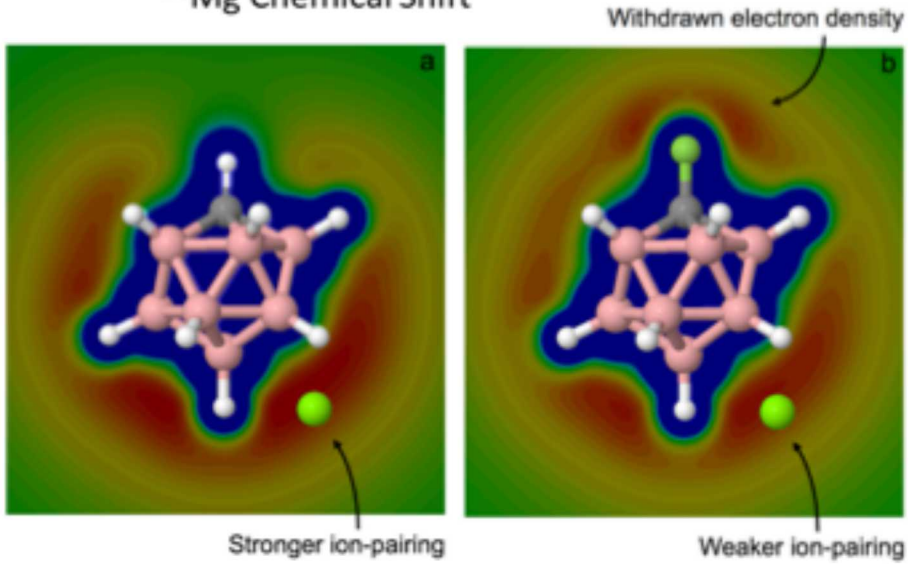
- Solvent vs. anion competition regulates response
- Greater susceptibility to passivation

Carbo-closo-dodecaborate is Mg Active

Does conductivity scale with expected extent of $Mg^{2+}\cdots RCB11^{-}$ dissociation?



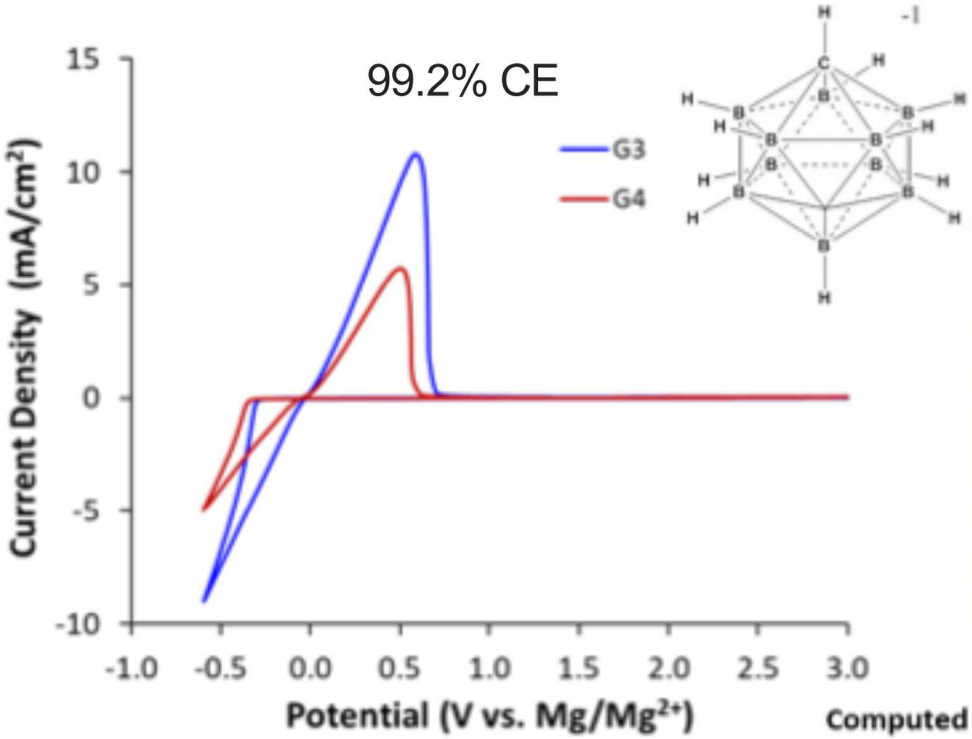




Reduced Ion-pairing strength translates to increased conductivity:
40% increase for FCB_{11} vs. HCB_{11}
(2.1 $mS \cdot cm^{-1}$ 0.4 M G3)

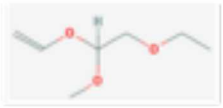
N. Hahn et al. JACS 2018 10.1021/jacs.8b05967

WCA Cathodic Efficiency is Governed by Impurities

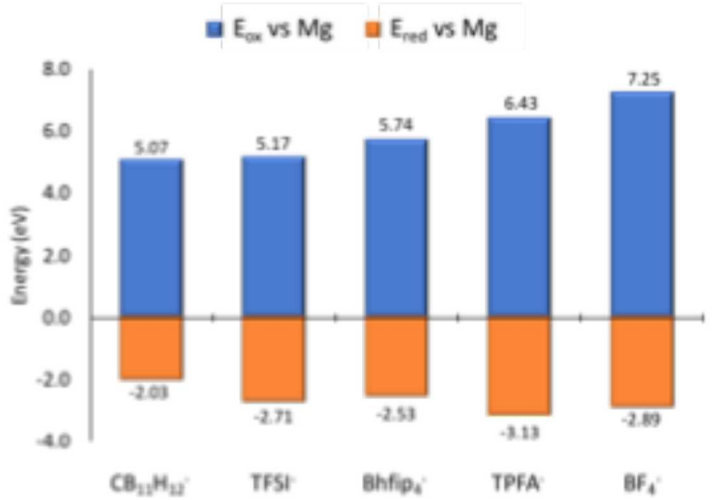


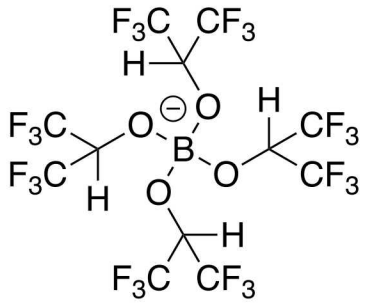
Solvent	Species	%
G3	**triglyme**	**97.27%**
	ethyldiglyme	0.55%
	1-tetradecene	0.33%
	butyldiglyme	1.86%
G4	**tetraglyme**	**99.35%**
	2-ethoxy-1-methoxyethoxy ethene	0.15%
	1-tetradecene	0.18%
	ethyldiglyme	0.11%
	1-butoxyethoxy-2-propanol	0.17%

Reduced protic levels in G3

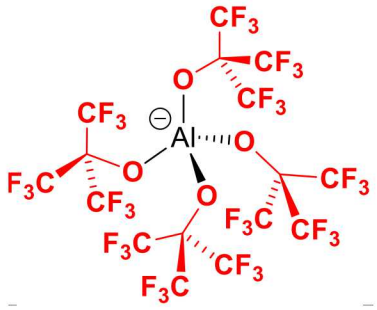
Computed pKa	Chemical Structure	Chemical Name
		1-tetradecene
33.1		butyl diglyme
33.1		ethyl diglyme
26.4		2-ethoxy-1-methoxyethoxy ethene
14.9		1-butoxyethyoxy-2-propanol

Impurities Likely Limit $Mg(MOR^F_4)_2$ Electrolytes

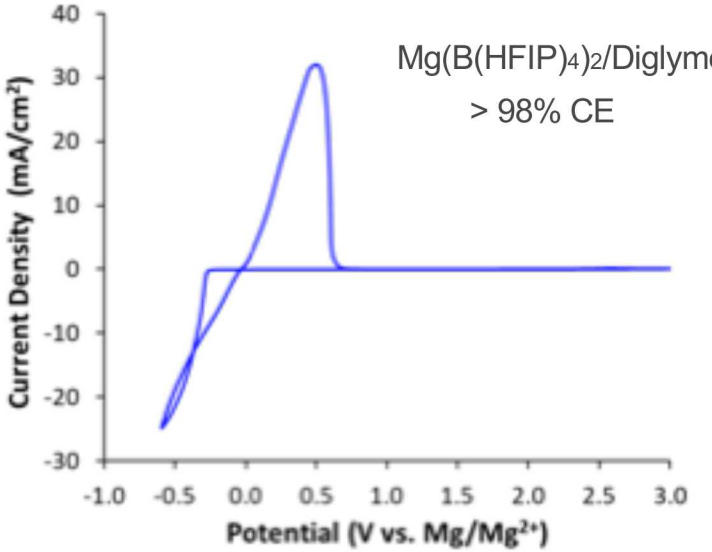


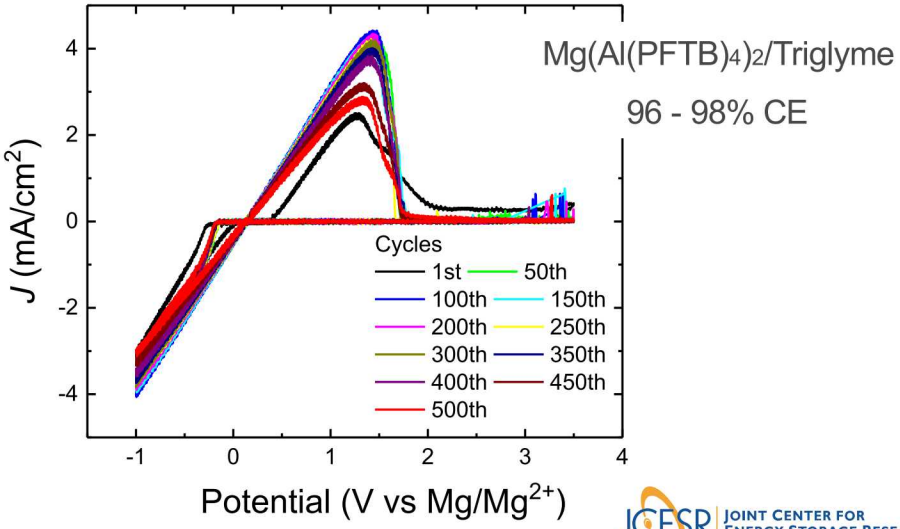


Zhao-Karger J. Mater. Chem. A, 2017,**5**, 10815



K.C. Lau, in preparation





Conclusions

Solvents of increasing complexation energy displace TFSI from Mg^{2+}

Coulombic efficiency increases as contact ion paired TFSI is eliminated

Cl^- anion more efficiently displaces TFSI and increases efficiency – but not completely

THF (2MeTHF) and glymes exhibit different efficiency trajectories

Computation argues complex Mg-Cl speciation

- Multimer dominated for compact ethers
- Monomer dominated with increased polyether denticity/size