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Multivalent Anode Interphases: Opportunities to Direct Interfacial Cation Transport

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Beyond Li Ion XII

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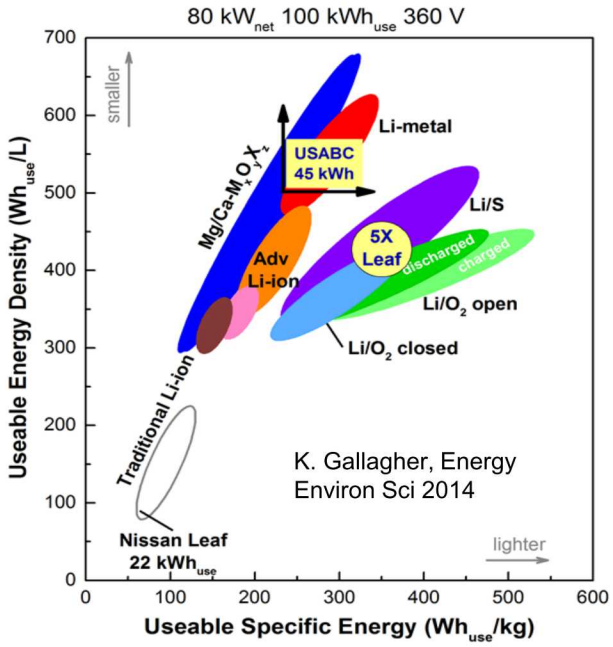
Snapshot of Mg Electrolyte Development

- ***Mg metal anode + high voltage cathode = transformative energy storage***
- Significant growth in Mg electrolyte development – expansion of stability window
- Growing electrolyte toolkit provides opportunity for systematic investigation - predictive electrolyte design



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)

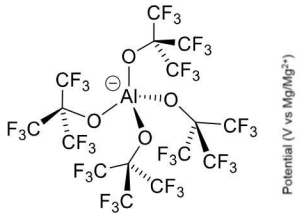
$Mg(BR_4)_2$ — $MgTFSI_2$ — $Mg(RCB_{11}H_{11})_2$ — $Mg(MOR^F{}_4)_2$

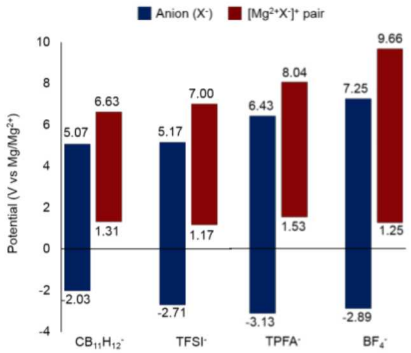
WCA-based Electrolytes

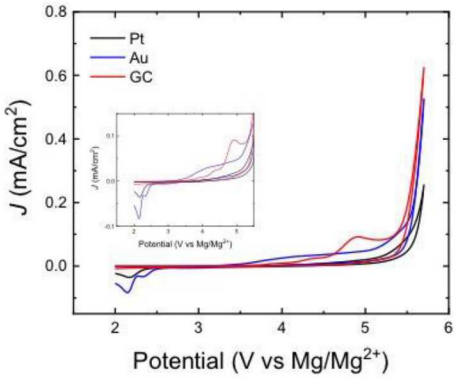
(Mg^{2+})

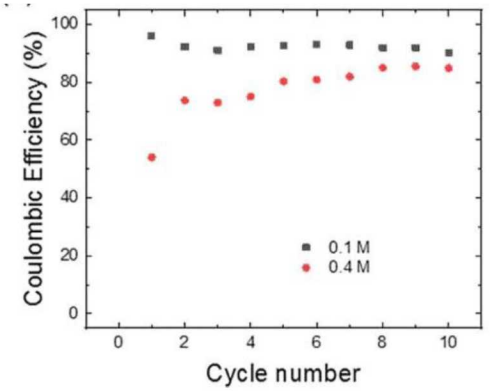
Computational Screening Drives New WCA Development

Computational screening of ion association and redox stability leads to $Mg(AlOR^F{}_4)_2$ with expanded redox window



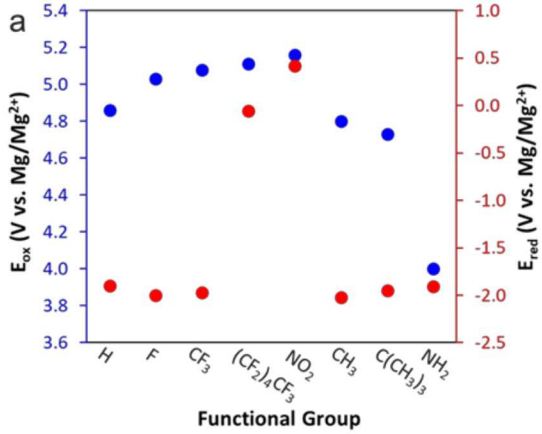


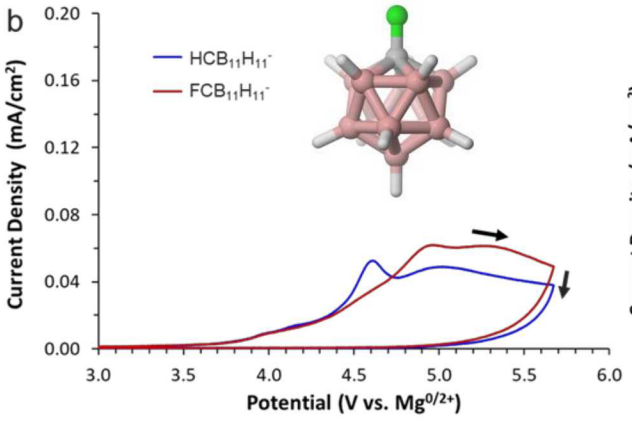


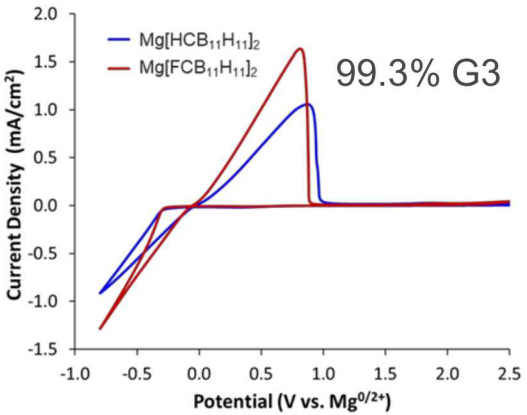


K.C. Lau et al. J. Electrochem. Soc. 2019 DOI: 10.1149/2.0751908jes

Computational screening of $Mg(RCB_{11}H_{11})_2$ target derivatives leads to improved anodic stability with no penalty to cathodic stability



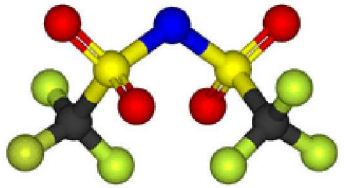




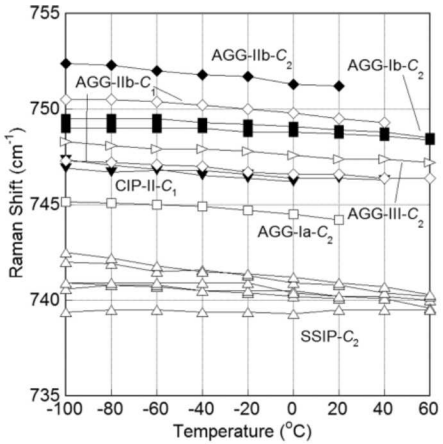
N. Hahn et al. J. Am. Chem. Soc. 2018 DOI: 10.1021/jacs.8b05967

$TFSI^-$ as a Benchmark Weakly Coordinating Anion

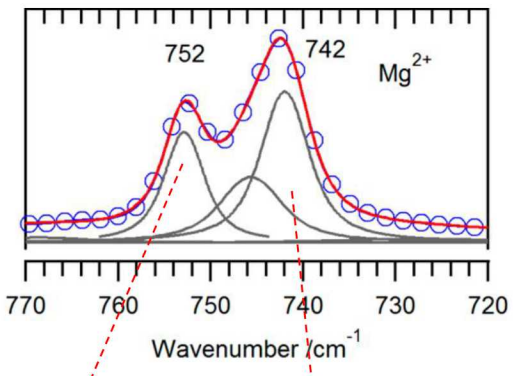
TFSI provides diverse conformations and interactions



TFSI Conformational Sensitivity

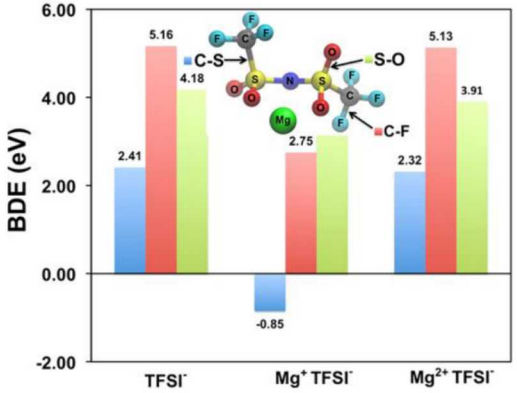


Seo et al. J. Phys. Chem. B 2014, 118, 13601−13608

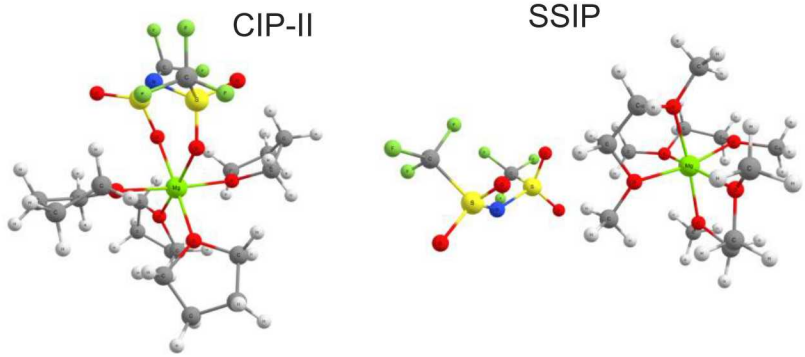


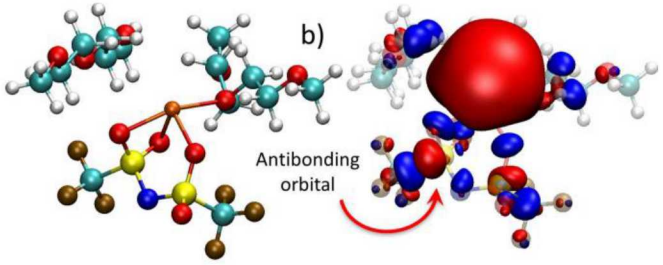
Giffin et al. J. Phys. Chem. C 2014, 118, 9966−9973

Predicted Stability Dependence



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



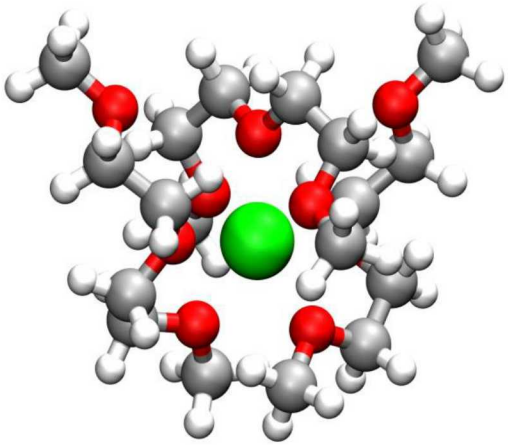


A. Baskin et al. J. Phys. Chem. C, 2016, 120 , 3583–3594

Outstanding Questions – New Approach

What is the role of the solvent in dictating the following:

- TFSI reactivity?
- the limits of efficiency?
- performance of WCA's?

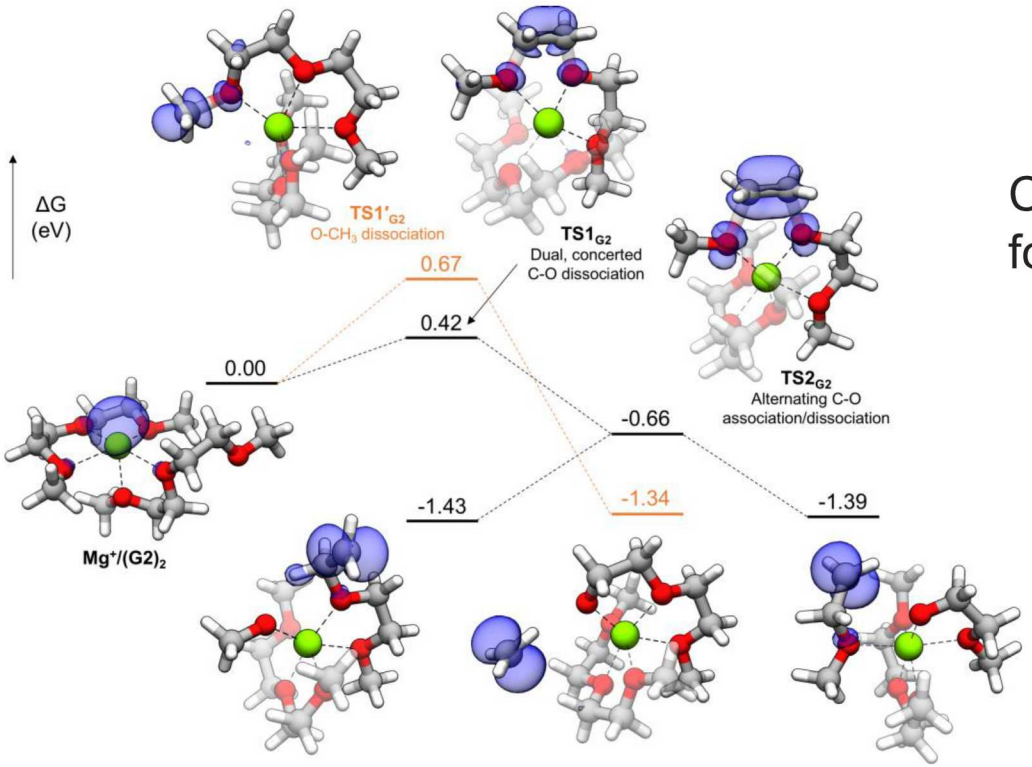


Our approach:

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
- Bulk speciation – interfacial speciation - reactivity

What about intrinsic reductive stability of the solvent?



Comparable free energy barriers for Mg^+-solv reduction

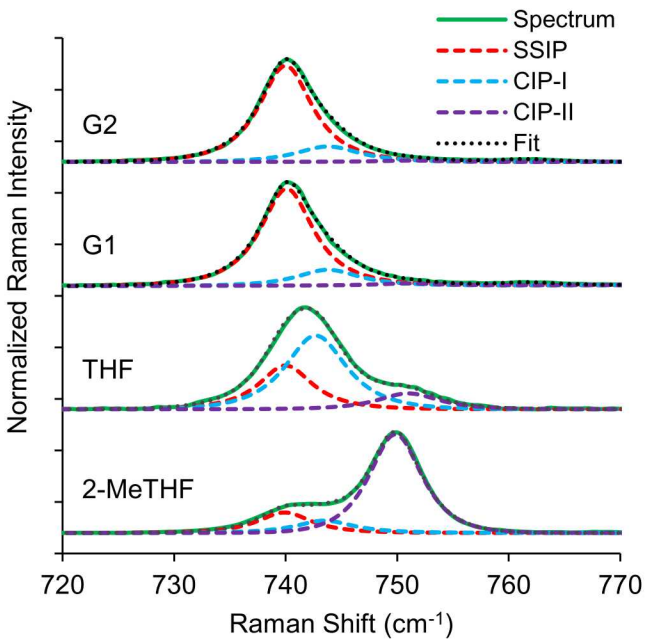
$$\Delta E^{\ddagger} = \Delta E_{dist}(glyme) + \Delta E_{int} + \Delta E_{red}(glyme) + \Delta E_{ox}(Mg^+)$$

Solvent	$\Delta G^{\ddagger}$	$\Delta E^{\ddagger}$	ΔE_{dist}(glyme)	ΔE_{red}(glyme)	ΔE_{int}	$\Delta E_{ox}(Mg^+)$
G1	0.54	0.68	0.91	1.63	-16.56	14.70
G2	0.42	0.55	0.98	1.68	-16.81	14.70
G3	0.51	0.58	0.77	1.56	-16.44	14.70

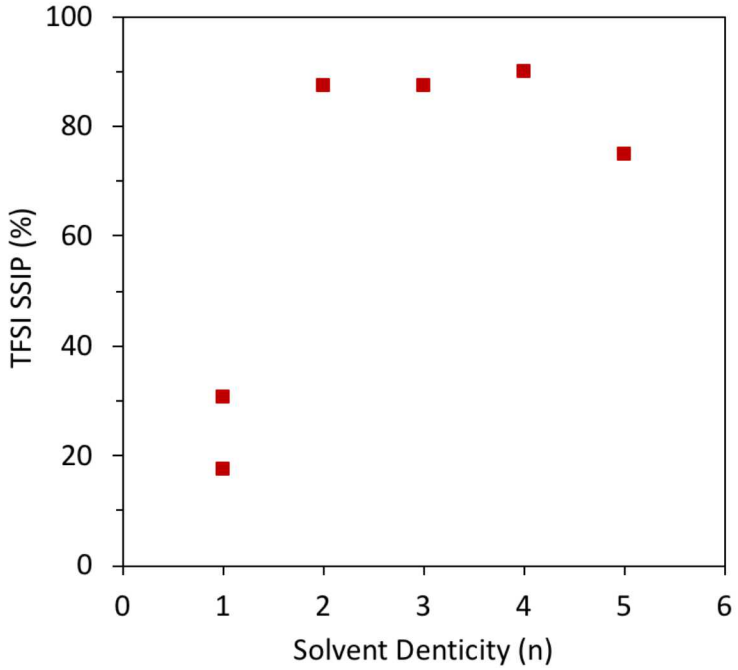
N.T. Seguin et al. Frontiers in Chemistry. 2019, 10.3389/fchem.2019.00175

Chelating ability of the ether drives ion separation

0.5 M $MgTFSI_2$:solvent



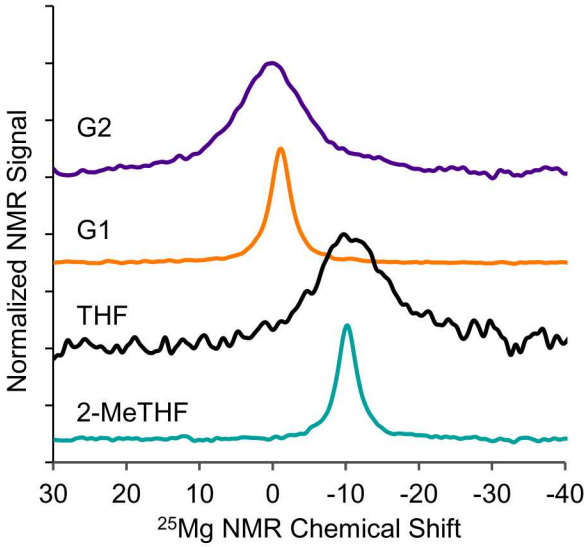
Structures or degree of association with ether type

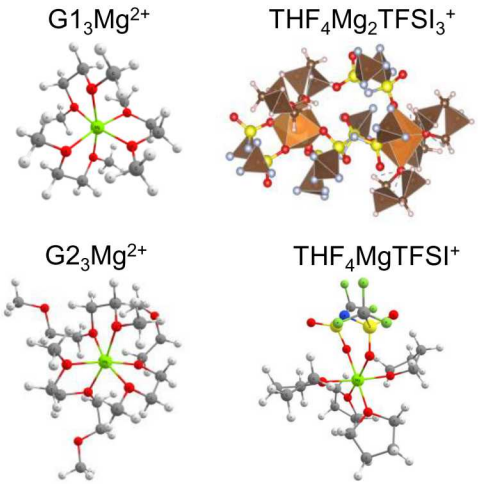


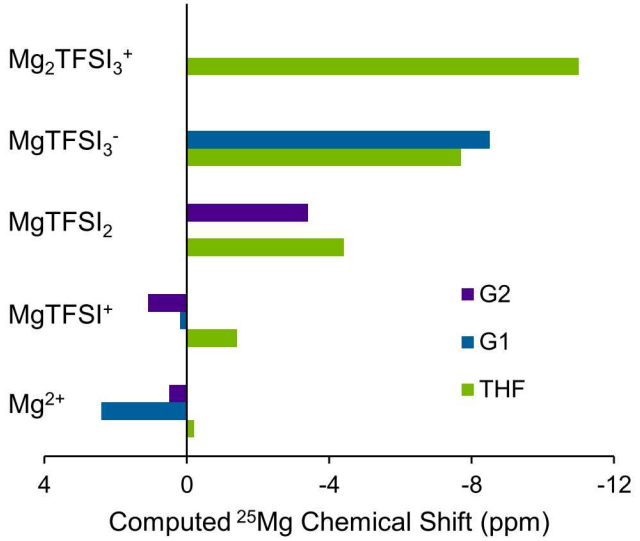
- Free or solvent separated ion pairs are dominant in multidentate ethers
- Contact ion pairs and aggregates are dominant in the cyclic ethers

Solvent – anion exchange is tracked by ^{25}Mg NMR

Relaxed MD or created complexes





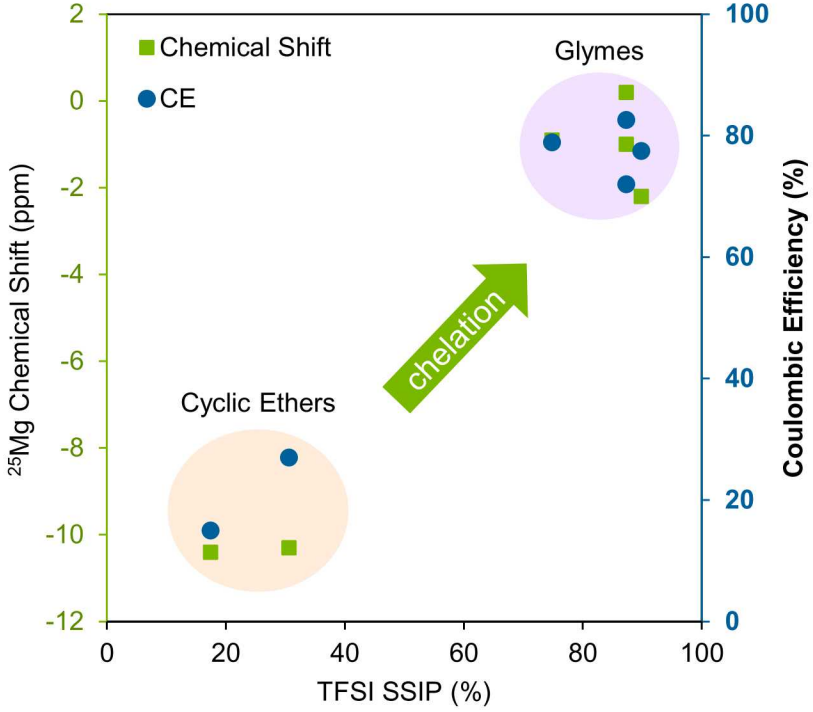


- Mg(solv)$_n$ complexes exhibit downfield shifts
- Mg-TFSI contact ion pairs and aggregates exhibit upfield shifts

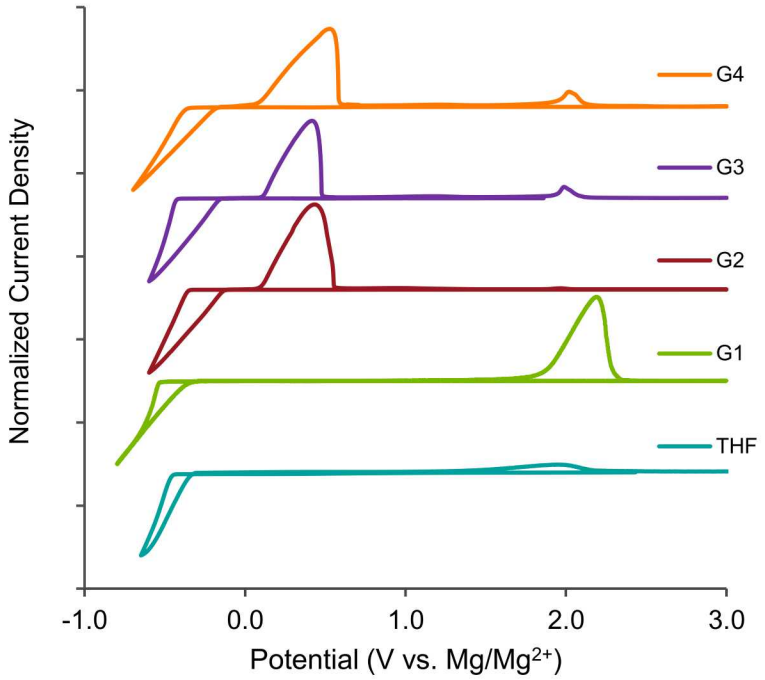
Deposition efficiency is correlated with ion separation

Descriptors for electrolyte properties and reactivity

Coordination environment



Coulombic efficiency

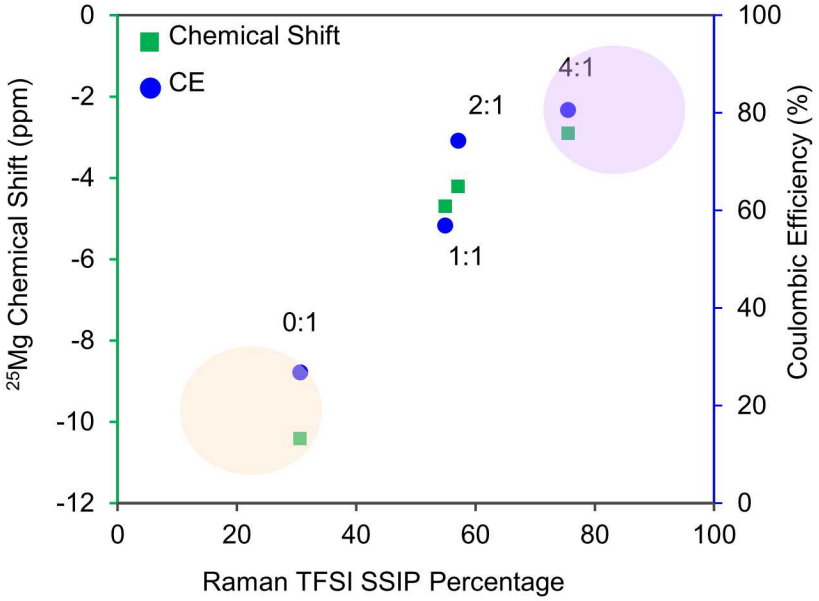


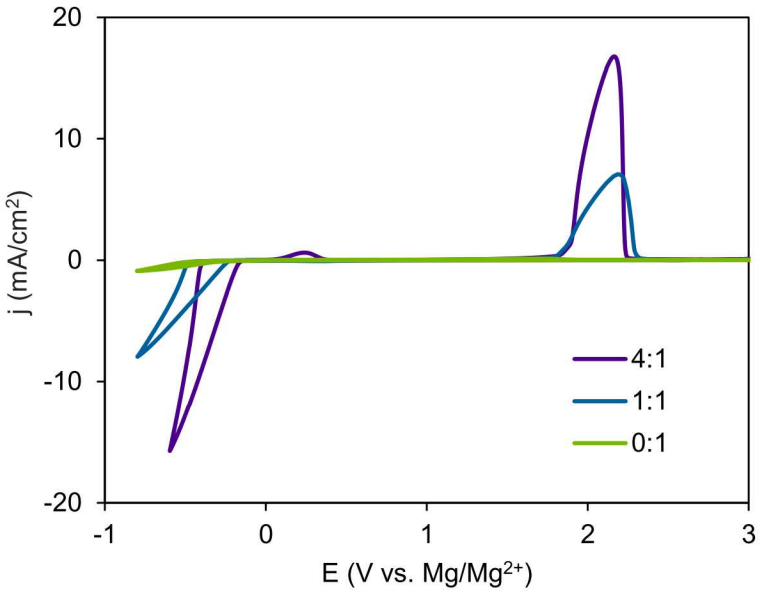
- Chelating ability of solvent drives ion separation
- Passivation (G1) remains an issue even at low Mg-TFSI pairing

Demonstration of Solvent Controlled Ion Separation

Add a stronger coordinating solvent to a highly ion associated electrolyte

G2 addition at select G2:Mg^{2+} molar ratios maintain Mg^{2+} at 0.5M



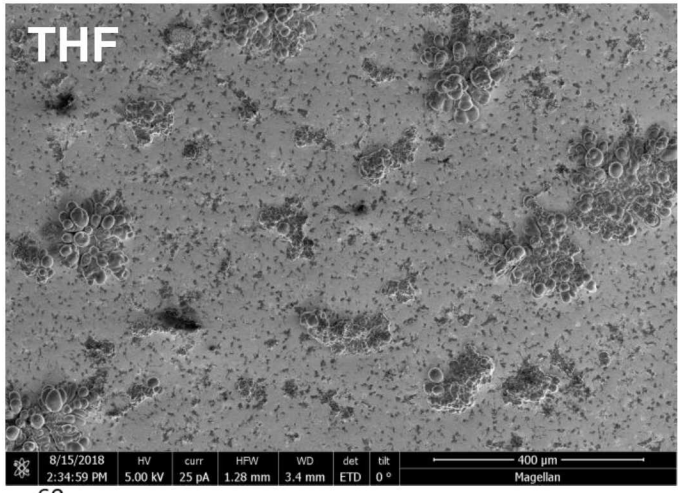


- G2 up to 17 mol% yields descriptors consistent with a glyme electrolyte
- Mg deposition is greatly enhanced
- Generalized strategy for regulating reactivity

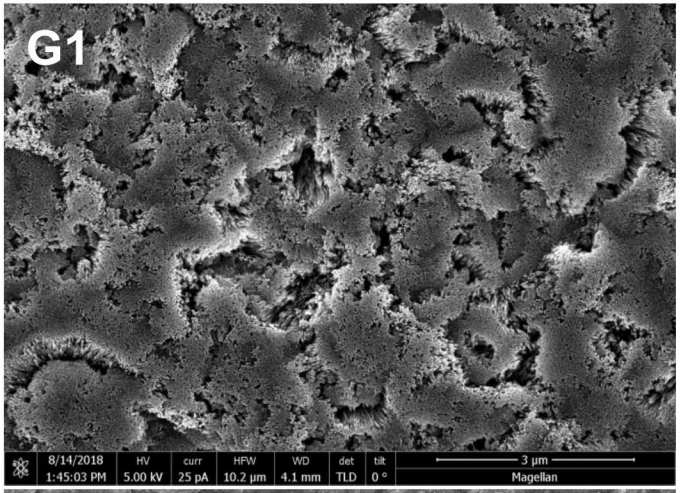
Reduced TFSI Decomposition with Displacement

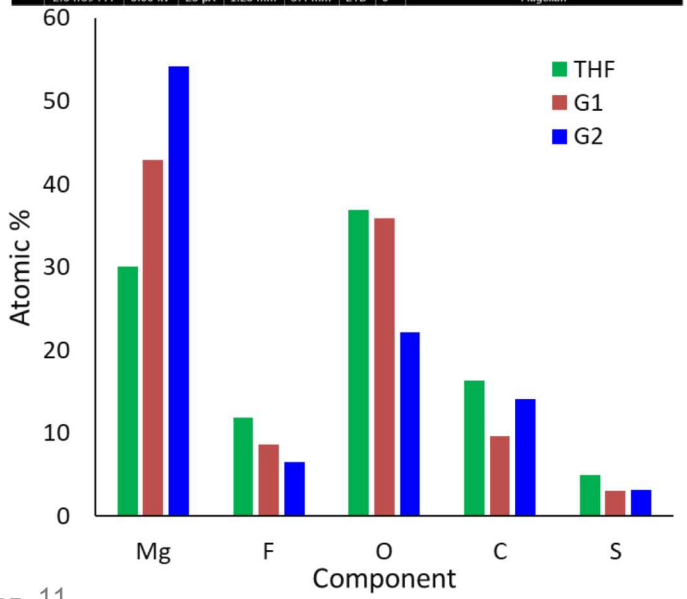
Interphase composition should yield less TFSI products with THF ⇢ G2

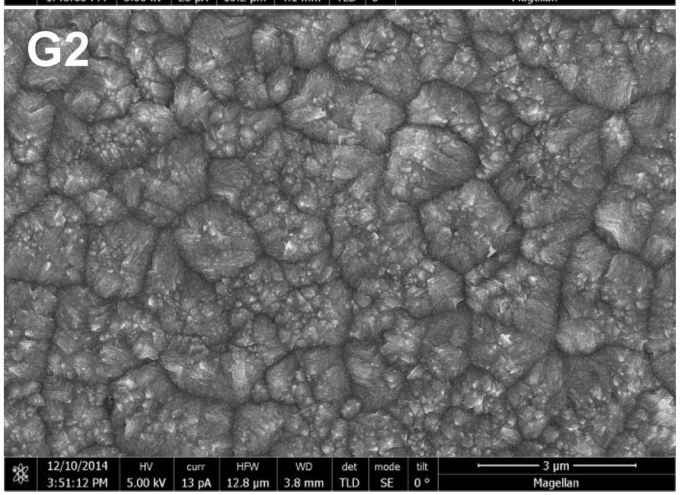
Localized deposit – filmed substrate



Localized deposit – fibrous morphology







Localized deposit –dense platelets

Mukesh's citation – CI or not?

Key Lessons

Solvent regulates the extent of Mg-TFSI ion pairing

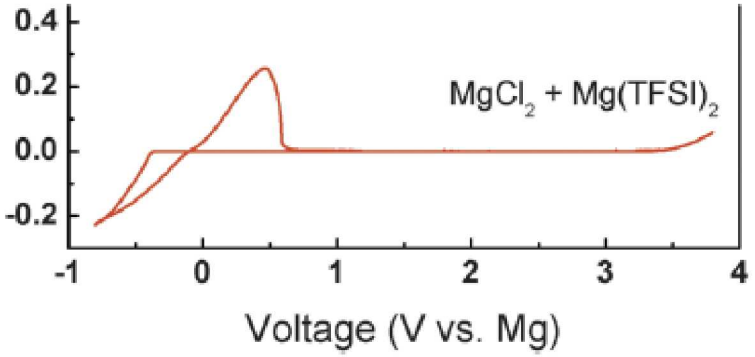
Ion pairing is always present at mid to high concentration for the cyclic to low order glyme series impacting Mg deposition efficiency

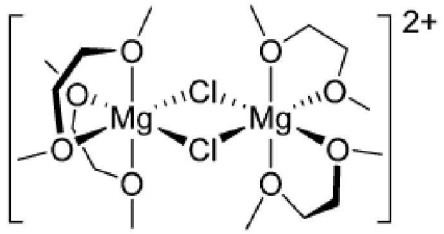
Stronger coordinating co-solvent addition reduces ion pairing - increases efficiency

Tuning Interactions with a $MgCl_2$ Co-salt

Previous work highlights the benefit of $MgCl_2$ addition to $MgTFSI_2$/G1

1:1 $MgCl_2$:$MgTFSI_2$





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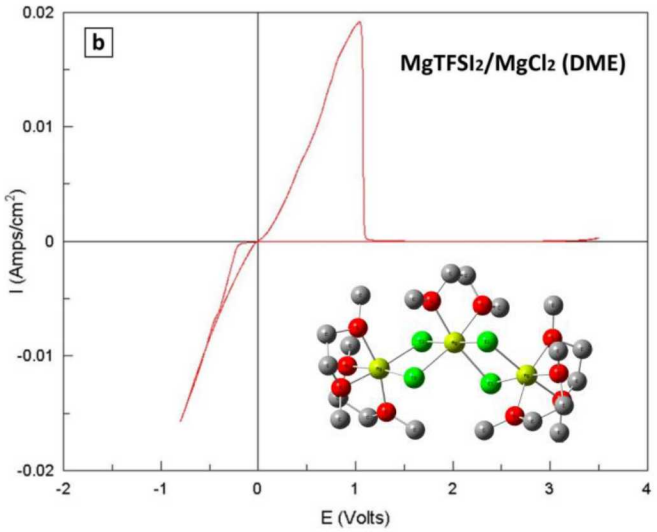
Cheng et al. Phys. Chem. Chem. Phys., 2015, 17, 13307--13314

2:1 $MgCl_2$:$MgTFSI_2$

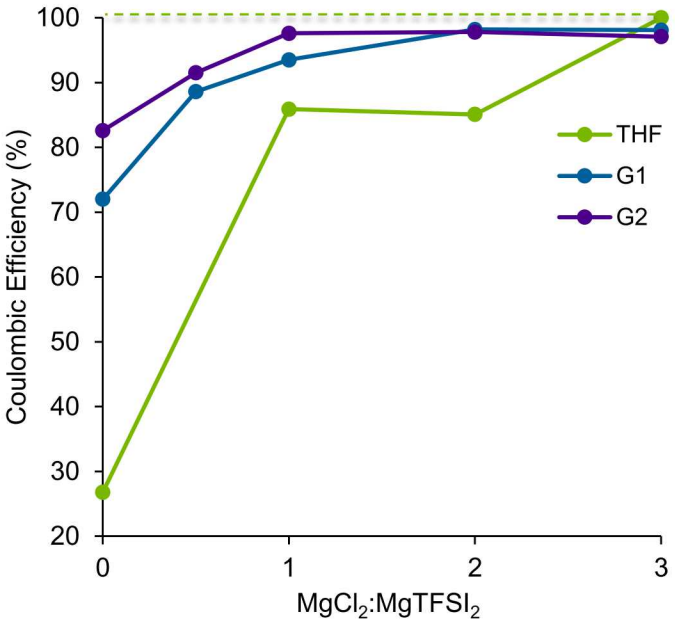


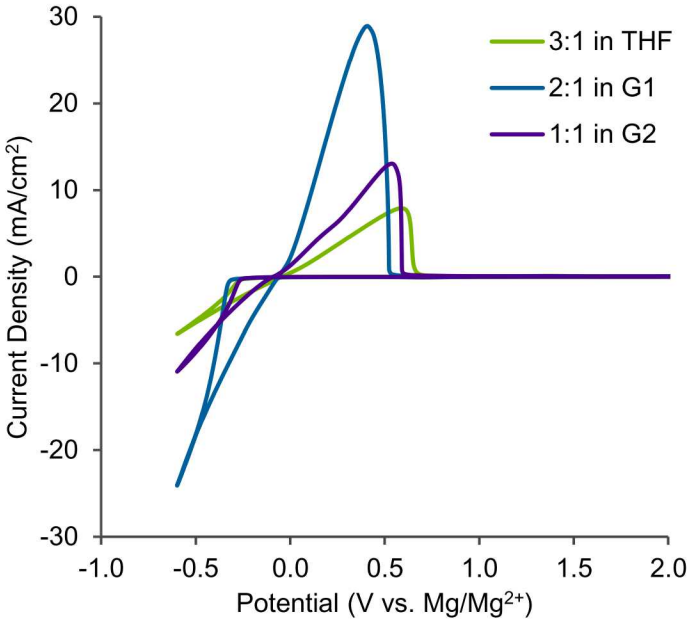
Shterenberg et al. Journal of The Electrochemical Society, **162** (13) A7118-A7128

What about the solvent impact with stronger coordinating anion addition?

Deposition behavior exhibits critical Cl^- concentration

Maintain Mg^{2+} at 0.5M – vary Cl^-:$TFSI^-$ molar ratio

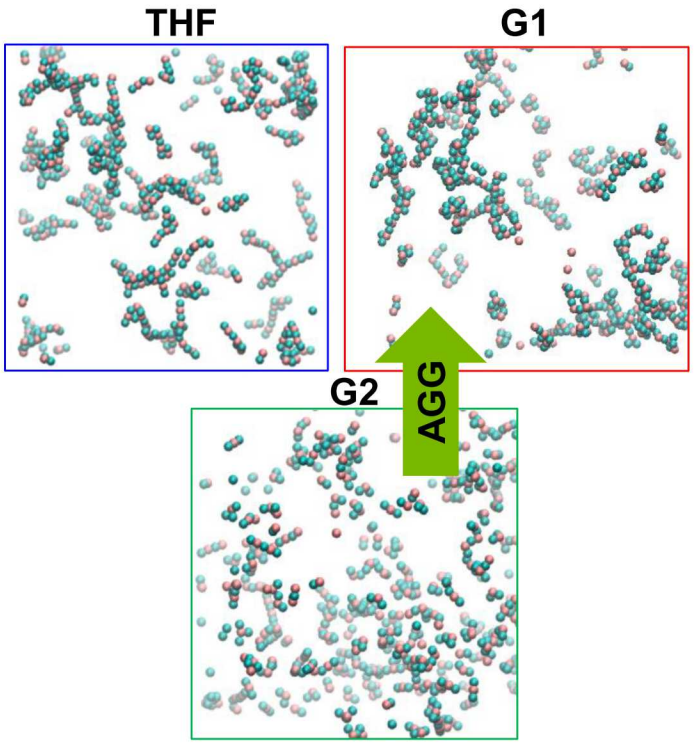


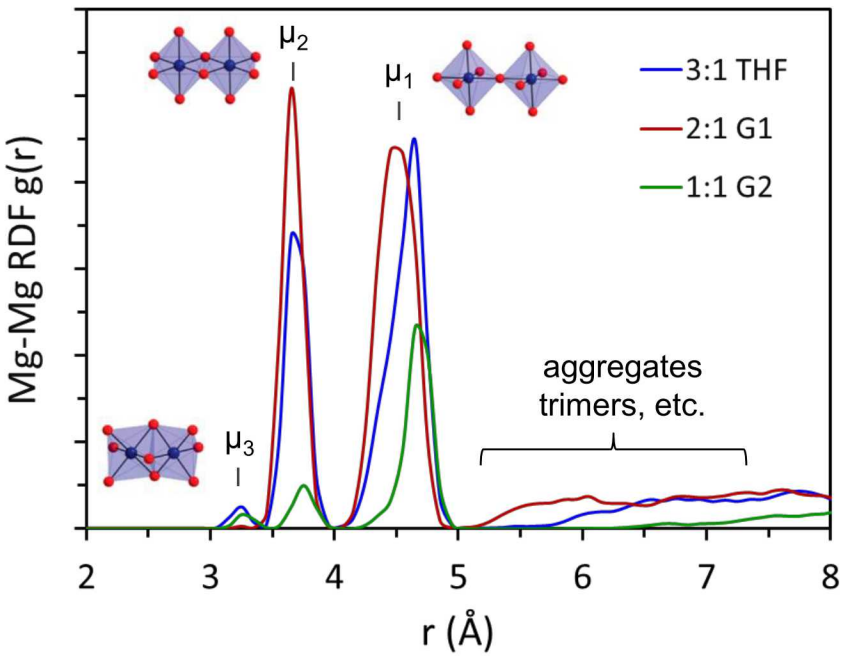


- Coulombic efficiency is maximized at a unique Cl^-:$TFSI^-$ ratio
- Overpotentials are lower than for $TFSI^-$ and comparable across ether

Solvent plays a key role in defining speciation

Details of the MD simulation

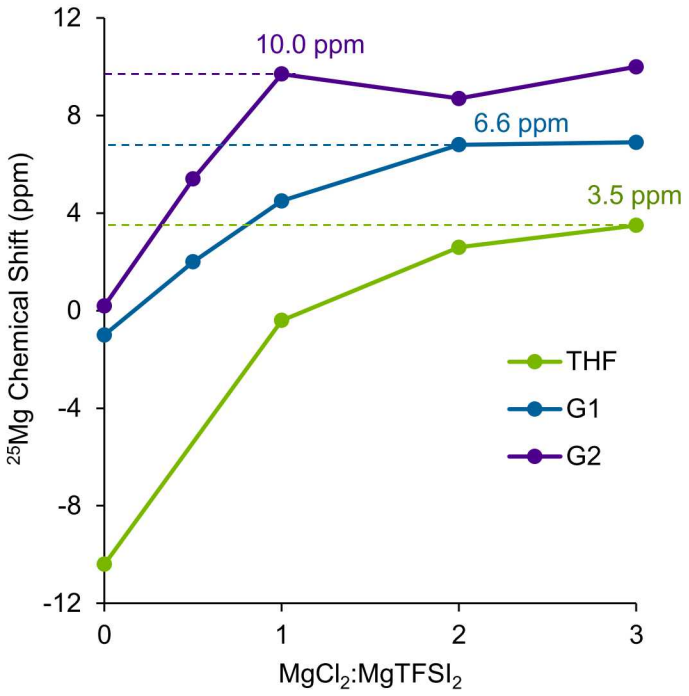


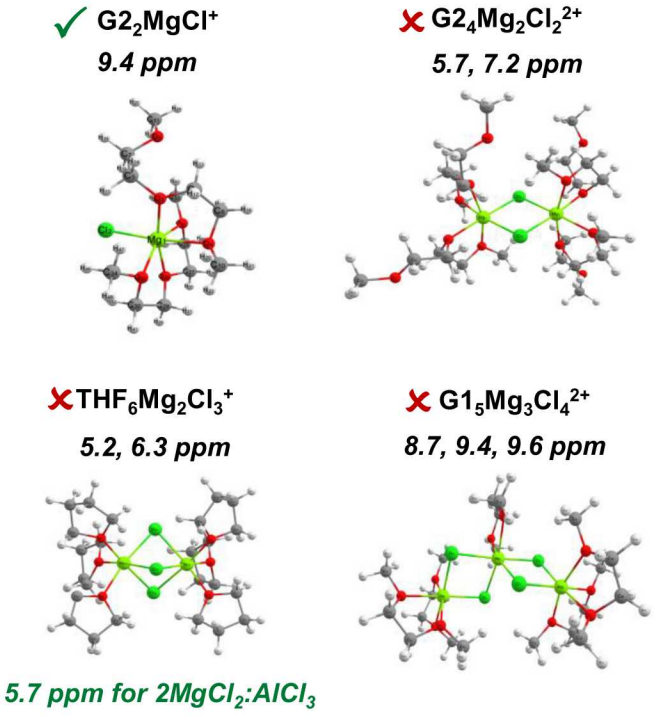


- Stronger chelating G2 limits μ_n-Cl dimer and multimer formation
- Minimal differentiation between THF and G1

Mg coordination environment exhibits a critical Cl^- concentration

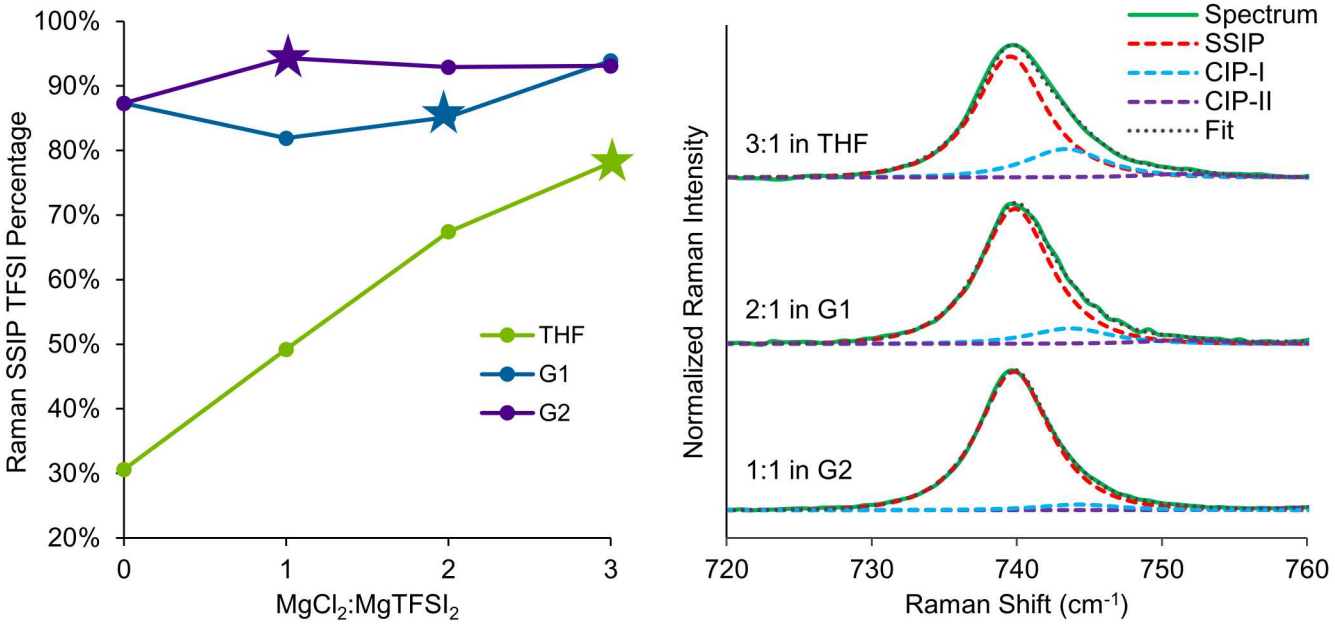
Compare measured and computed δ_{Mg} as a function of Cl^-:$TFSI^-$





- Mg environment is different than that of the expected μ_n-Cl complex
- Upfield δ_{Mg} consistent with the $TFSI^-$ induced shift

Without a strong chelating solvent, $TFSI^-$ continues to coordinate in the presence of Cl^-



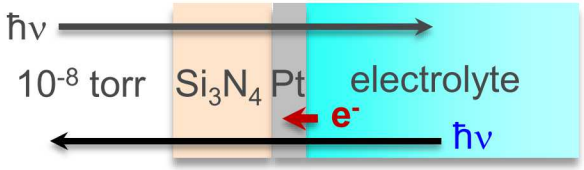
appreciable $TFSI^-$ coordination at critical [Cl^-] and max CE

- THF 23%, 100% > G1 15%, 98% > G2 7%, 98%

Why reduced activity? CIPs displaced from the interface, Cl^- prevents electron localization on TFSI, surface Cl^- plays a protective role

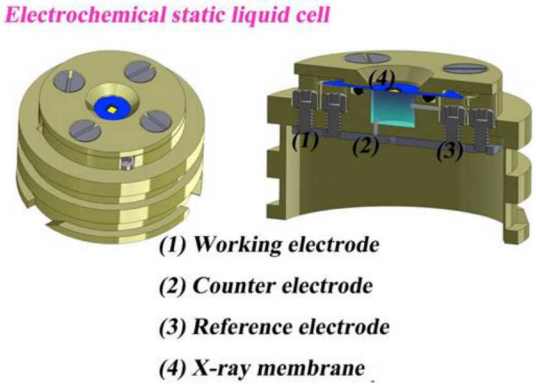
Methods for Determining Interfacial Speciation

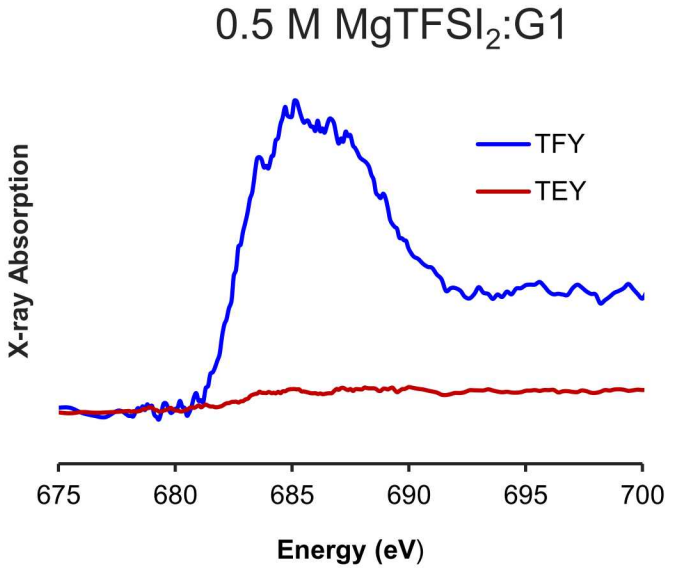
Operando XAS



e^- out = interfacial

ħν out = bulk electrolyte





potential dependent response of interface

soft and tender x-rays enable an interfacial compositional inventory
Cations: Mg, Ca, Zn
Ligands: B , Cl, C, O, F

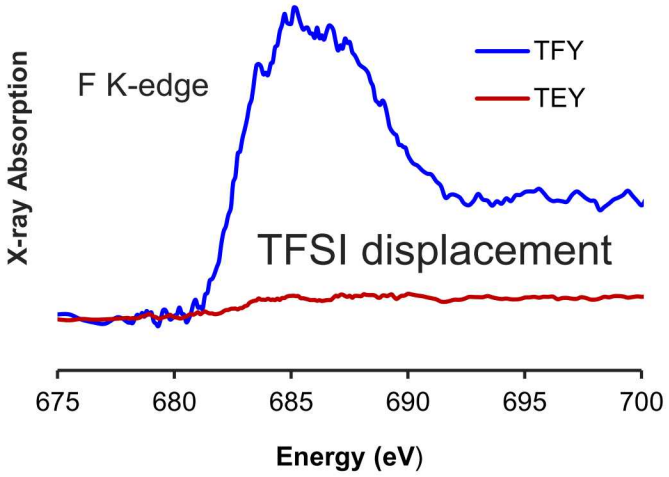
Anion Speciation at the Interface

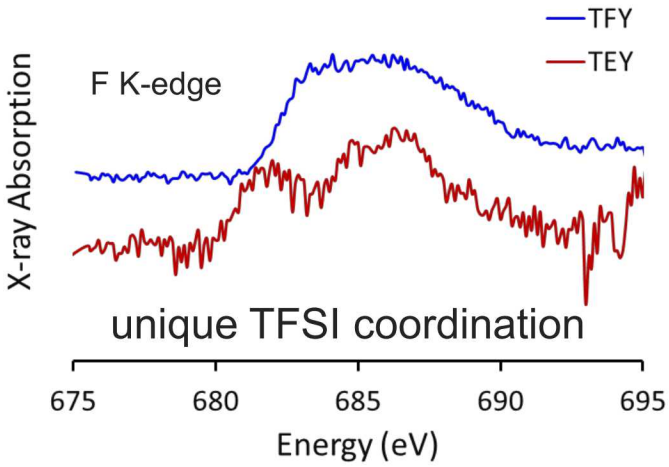
G1 ⟷ **Solvent impact** ⟷ 2MeTHF

$MgTFSI_2$

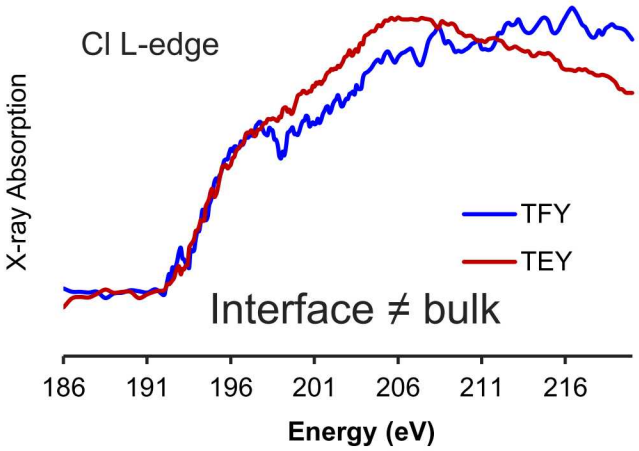
Anion impact

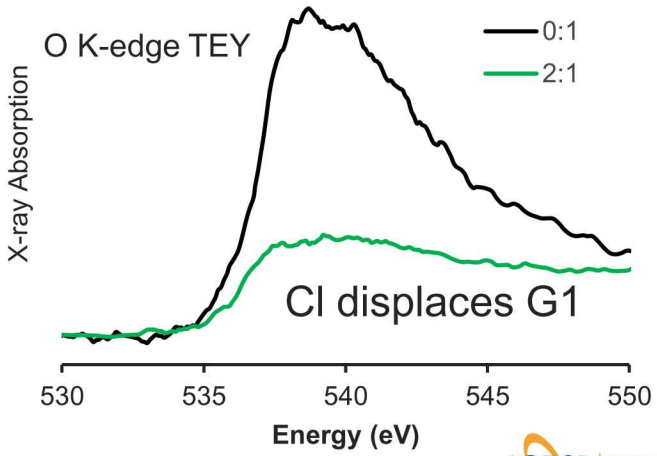
$MgCl_2$





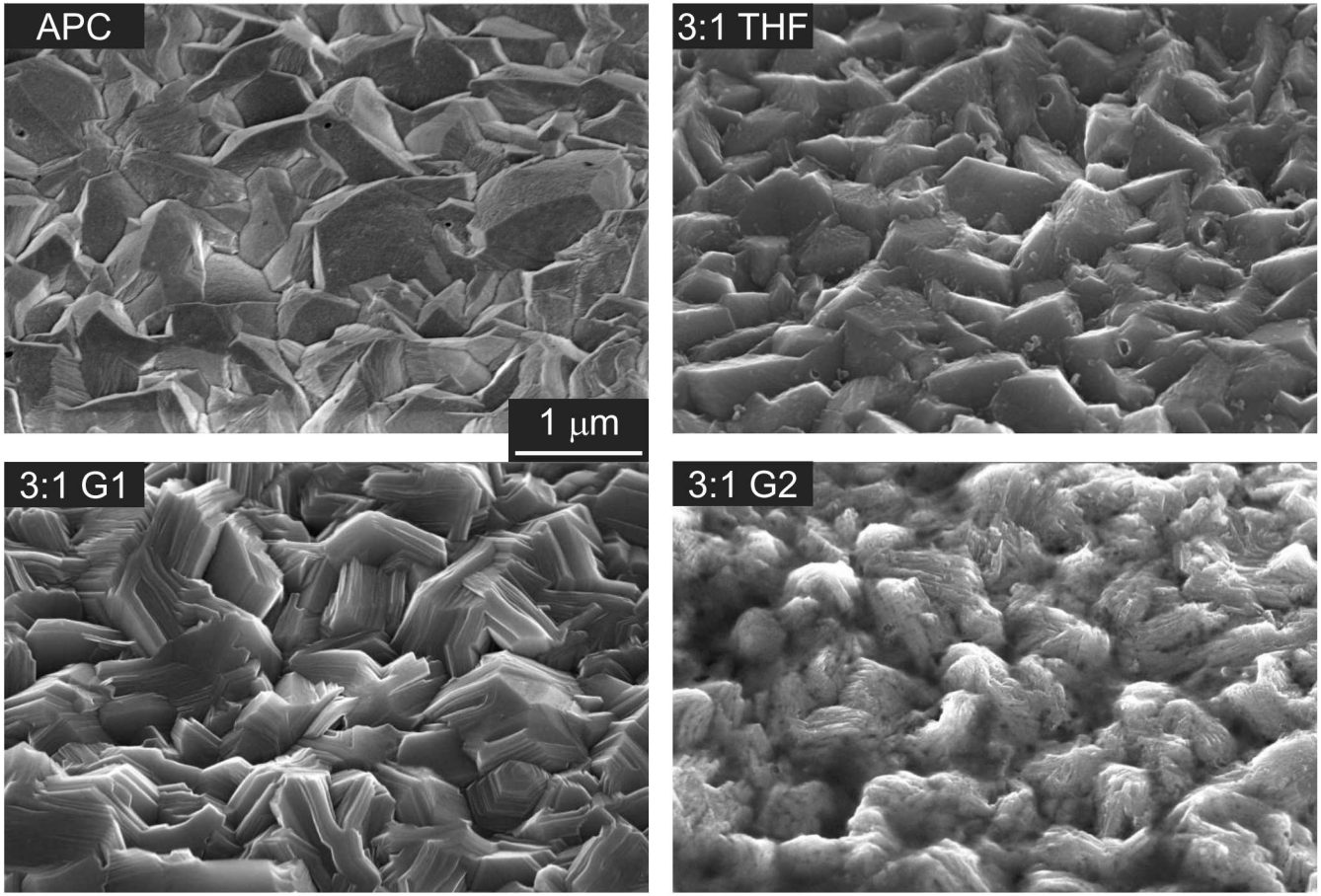
2:1 molar ratio $MgCl_2$:$MgTFSI_2$ G1





Multimer μ-Cl Systems Yield Defined Crystallography

Continuous deposits textured (0001) to random (p-1000)



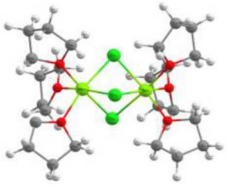
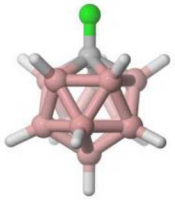
Reduced surface faceting

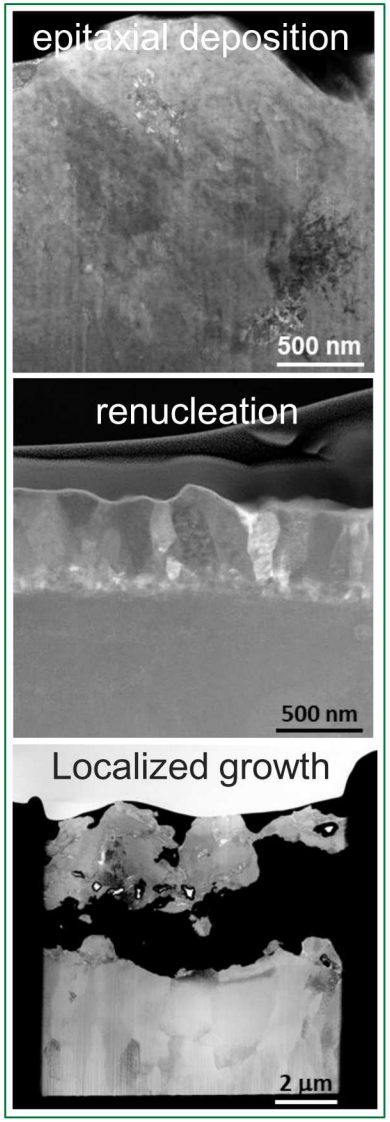
Key Lessons

- Ether solvent chelation regulates Cl:Mg^{2+} multimer structure and Mg^0 deposition efficiency
- Critical Cl:TFSI ratios exist
- Greater solvent chelation ability suppresses μ-Cl sharing
- More μ-Cl sharing favors high efficiency despite bulk TFSI interactions
- Interfacial behavior of these complexes require further exploration

Transitory nature of protection without an SEI

Penalty for moving divalent cations freely

		Coulombic Efficiency, %			
Electrolyte	**Structure**	**Control 1 cycle**	**50 cycles continuous**	**30 min, 50 cycles discontinuous**	**2 hr, 50 cycles discontinuous**
APC	faceted	99.7 ± 0.3	100.2 ± 0.3	100.0 ± 0.1	96.6
	dense	99.4 ± 0.2	99.4 ± 0.1	99.3 ± 0.1	97.3
	porous	99.4 ± 0.3	99.0 ± 0.5	98.1 ± 0.9	96.9
MACC	dense	100.3 ± 0.2	----	99.9 ± 0.1	----
	dense	99.6 ± 0.2	99.4 ± 0.3	97.8 ± 0.2	----
	porous	99.1 ± 0.2	98.9 ± 0.3*	98.2 ± 0.1	----
$MgCB_{11}H_{12}$:G3	TBD	99.2±0.3	98	95	



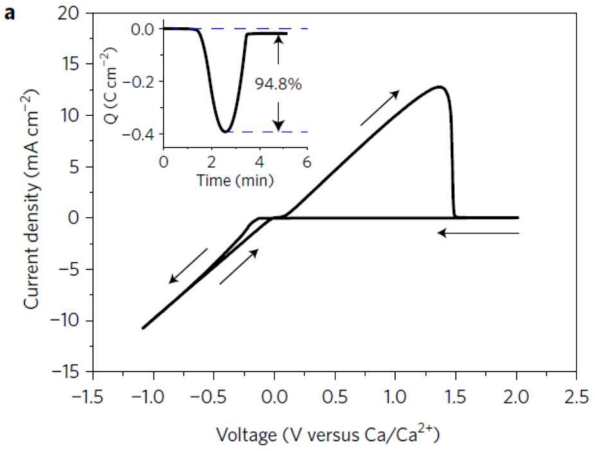
Free Cl- plays a vital but temporary role in stabilizing Mg

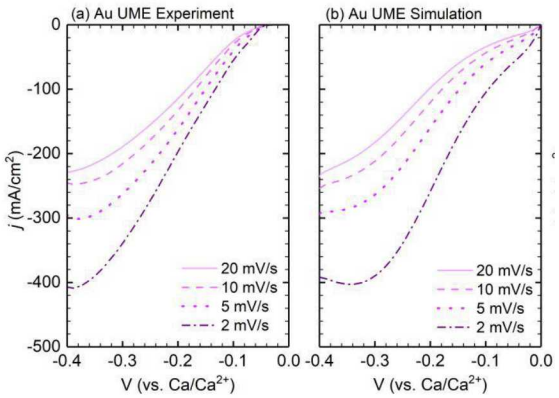
No equivalent effect for a WCA – ether combination

How is reversible Ca deposition enabled?

- First demonstration of reversible Ca deposition and stripping coupled
- CaH_2 formation as a passivant to further reactivity
- Dehydrogenation of solvent

D. Wang et al. *Nature Materials* **2017**



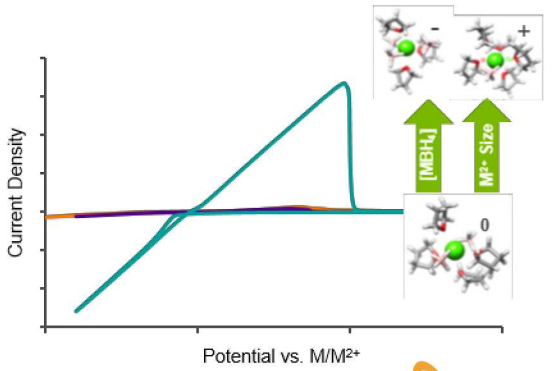


K. Ta et al. *ACS Appl Mater Interfaces* **2019**

- CE mechanism S + BH_4^- + THF → S-H^- + BH_3-THF
- CaH_2 produced by H^- abstraction from BH_4^- not dehydrogenation of solvent
- H- transfer subsequent surface transport and Ca^{2+} reduction are linked – continuous vs. localized deposition

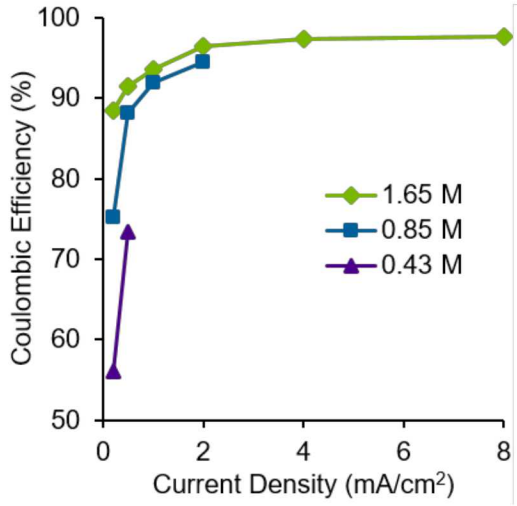
- Neither paper describes speciation nor links it to deposition mechanism

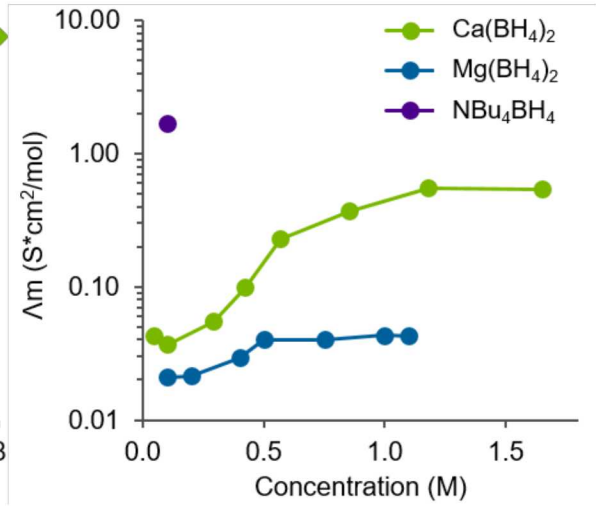
N. Hahn et al. *submitted*

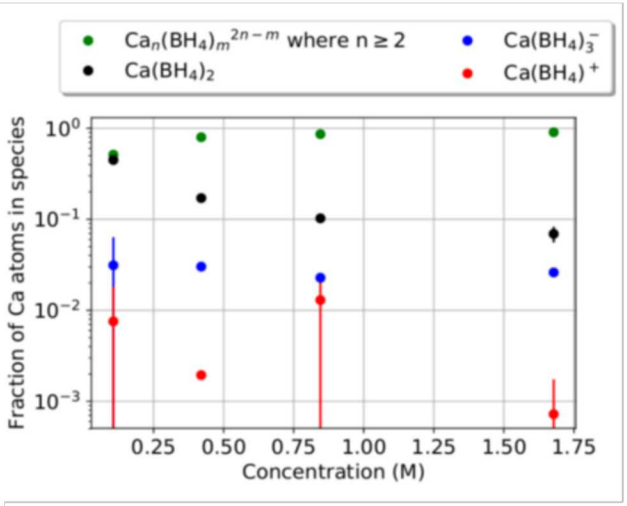


Unique Ca^{2+} speciation evolves with concentration

Experiment plus computation drives an understanding of speciation



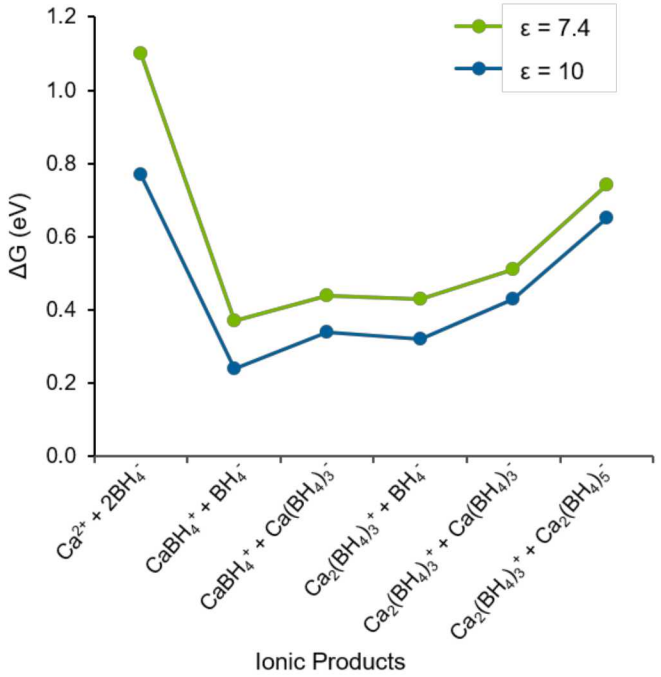


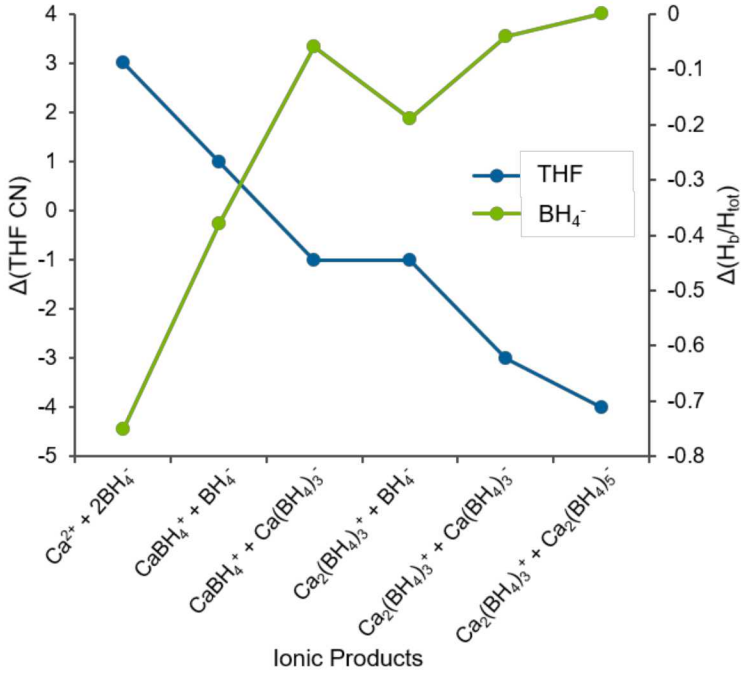


- Efficiency is a strong function of concentration and rate
- Increased concentration drives driving ion species formation
- Redistribution of BH_4^-
- Cationic multimers are the likely agents of Ca^{2+} delivery

Ca^{2+} polarizability facilitates ionization

Dissociation energetics dictate activity originates from minority species





Probable ionization products

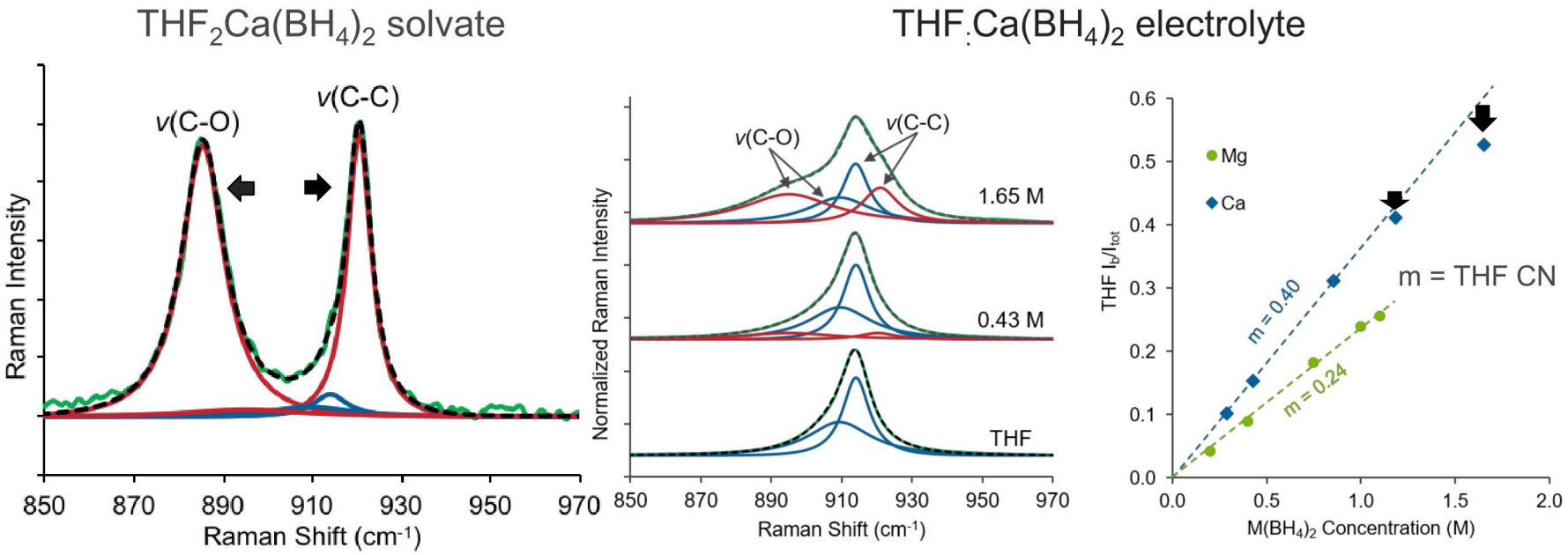
- are not free ions
- are ion aggregates – cationic mono- and di-mers

AGG stabilized with increased permittivity – solvation of neutrals

Multimer formation should drive

- decreased THF coordination
- decreased H bridging

Demonstration of decreased THF coordination with concentration

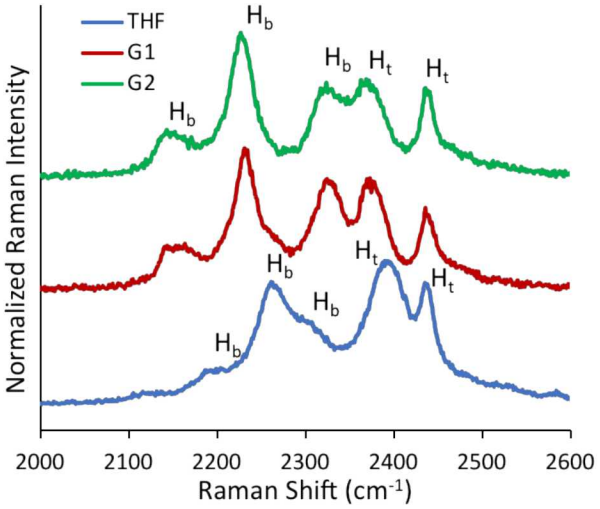


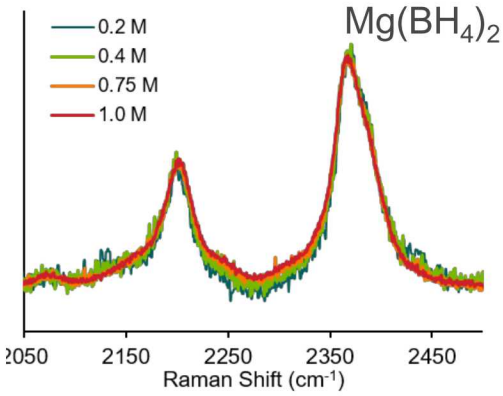
Ionic AGG population evolves for Ca^{2+}, static for Mg^{2+}

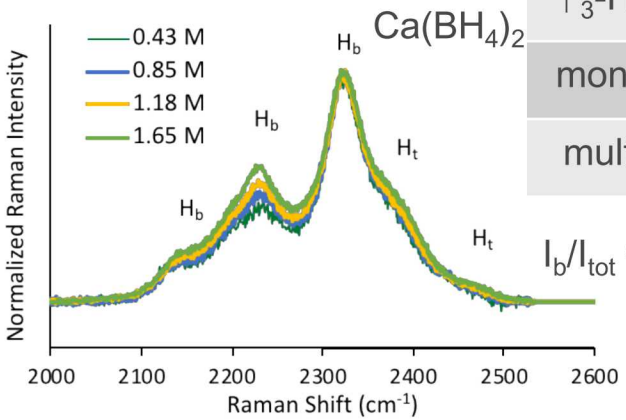
DFT shows BH_4^- formation does not drive lower THF CN, $Ca(BH_4)_3^-$ and $Ca_2(BH_4)_3^+$ do

BH_4^- exchange occurs among AGG – $Ca_2(BH_4)_4$ driven by Ca^{2+} polarizability

BH_4^- Coordination Signature is more Difficult to Decipher





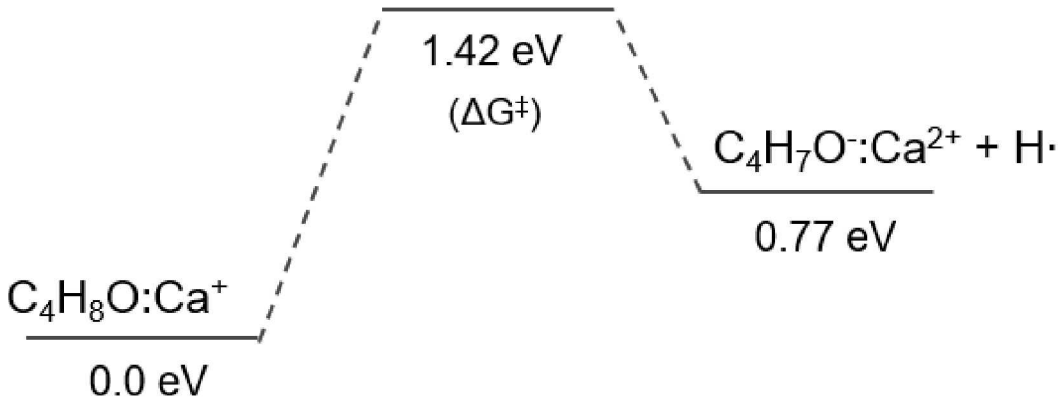


MBH_4	Mg	Li	Ca	Sr,Ba
α_2-H_2	✔	✔	✔	✔
α_3-H_3		✔	✔	✔
mono	✔	✔	✔	
multi		✔	?	✔

I_b/I_{tot} = 0.76 to 0.79

- ν(B-H) mode is sensitive to change in coordination
- ν(B-H) spectral change is consistent with conductivity – Ca^{2+} variant, Mg^{2+} invariant
- no free BH_4^-, < 2250 cm^{-1} neutral aggregate formation

Dehydrogenation of THF is unlikely



Reaction profile for reduction of THF via dehydrogenation by a reduced Ca^+ species

Large thermodynamic and kinetic barriers – reaction improbable

Key Messages

Transport and deposition are driven by charged aggregates formed through BH_4^- exchange between neutral aggregates

Strong association of Ca^{2+}- BH_4^- no free cation and minimal free anion

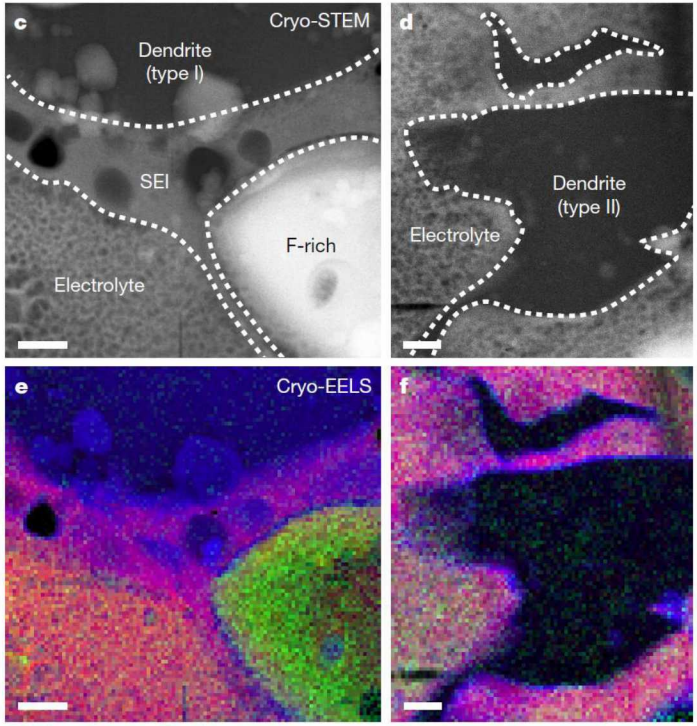
Proposed chemical reaction step could be due to AGG dissociation

Dehydrogenation of THF is energetically and kinetically disfavored

New Techniques for Characterizing Interphases

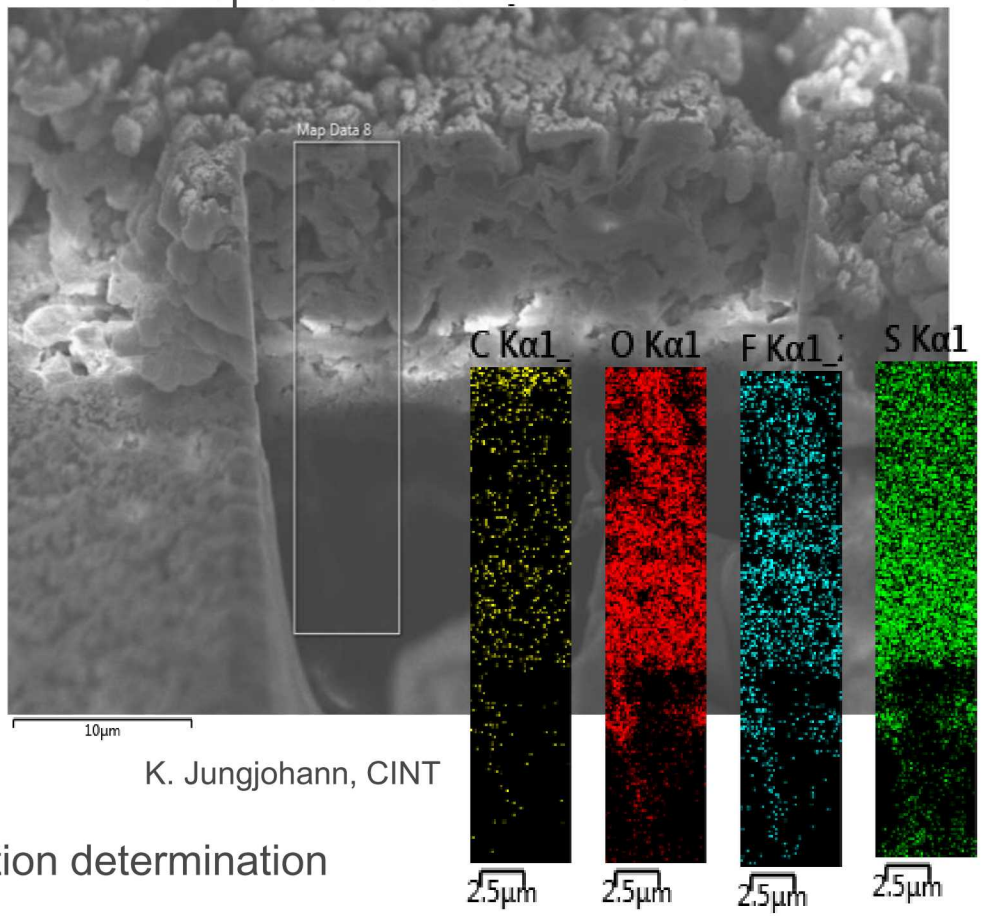
Cryogenic characterization of cycled lithium anodes using electron microscopy

Cryo-EELS in STEM of Li Dendrites



Zachman et al. *Nature* **2018**

Cryo-SEM and X-ray Spectroscopy of Li Electroplated on Cu in 4 M LiFSI in DME



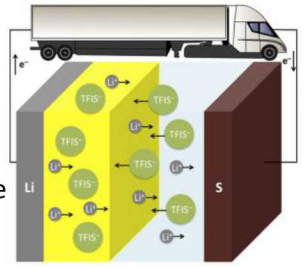
K. Jungjohann, CINT

Interfacial structure and composition determination with the electrolyte intact

Intentional Interphases for Selective Cation Transport

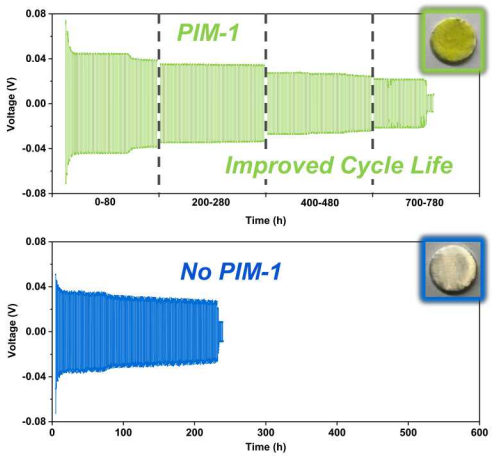
Polymer membranes as selective ion conducting hosts

Demanding EV applications require significant improvements in lithium anode cycle life to enable enable lithium metal batteries



Nanoporous polymer membranes (PIM-1) yield selective transport of the small radius Li^+ cation while constraining motion of the larger $TFSI^-$ anion

Liquid electrolyte-filled nanopores in rigid polymers are demonstrated to dramatically increase selective Li cation transport, in turn suppressing dendrite formation during lithium metal electrodeposition.



Li–Li cell cycle life comparison with and without PIM-1 membrane.

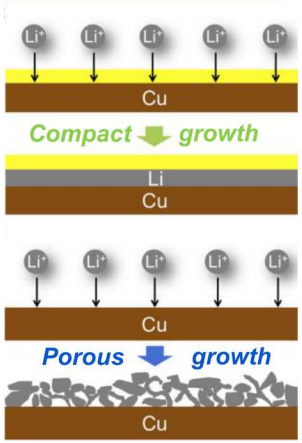


Illustration of lithium growth in the respective cells.

- The Li^+ transference number is measured to increase from 0.2 to 0.72 when a standard ether electrolyte is confined to the nanometer diameter pores of the structurally rigid PIM-1 membrane.
- The enhanced stability of the lithium anode results from repeated formation of compact, dense lithium metal deposits driven by selective Li^+ transport within the PIM-1 membrane.

Fixed anion scaffolds from polymers of intrinsic microporosity, porous aromatic frameworks, block copolymers

L. Ma, Nano Lett. 2019 DOI:10.1021/acs.nanolett.8b05101

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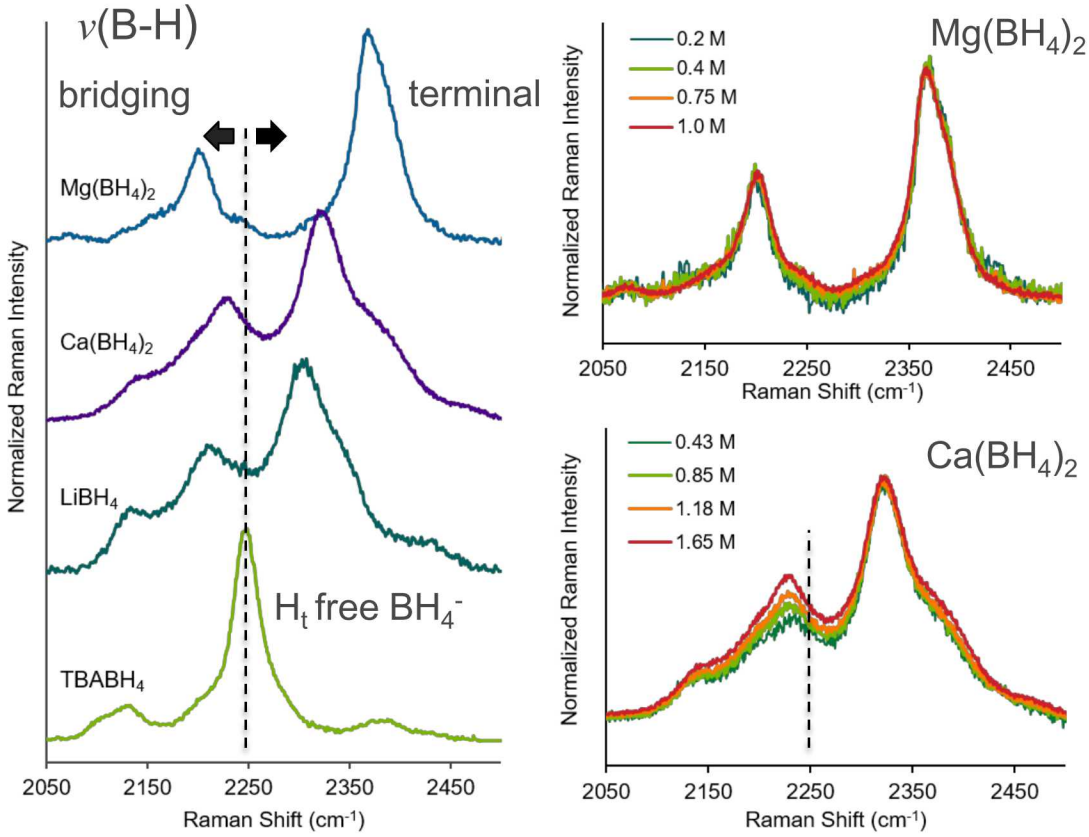
Vijayakumar Murugesan
Jian Zhi Hu

BH_4^- Coordination Signature is more Difficult to Decipher



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