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Tuning Mg^{2+} Battery Electrolyte Solvation and Behavior Through Organic Solvent Structure

Nathan Hahn, Kevin Zavadil
Sandia National Laboratories

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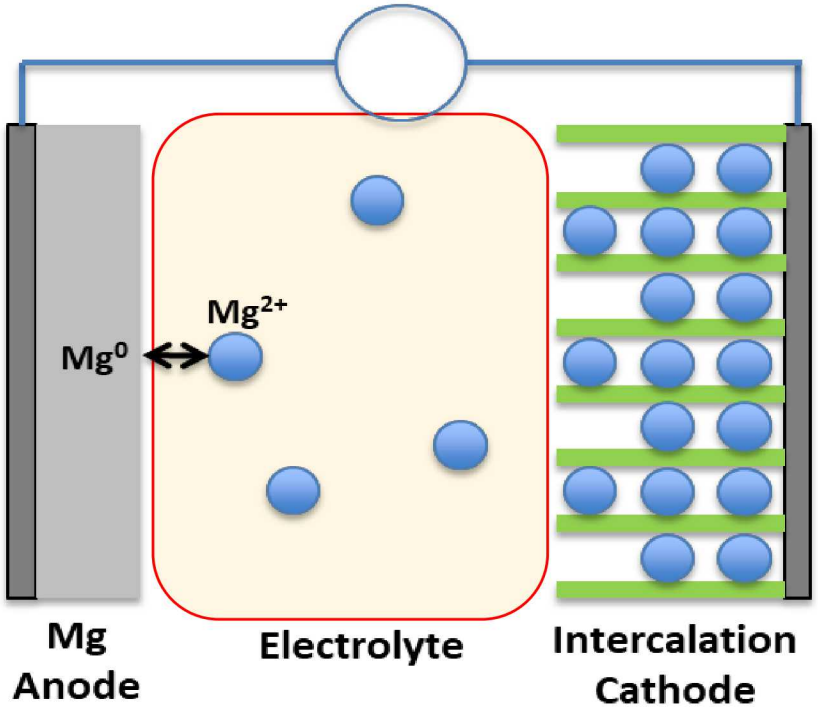
Multivalent Liquid Solvation Science

- **Goals:**
  - Develop scientific frameworks for understanding molecular-scale phenomena
  - Apply learned principles to the design of new battery materials

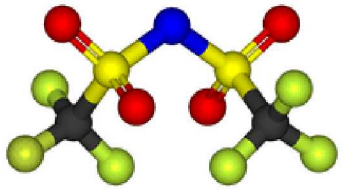
Mg^{2+} Electrolyte Science



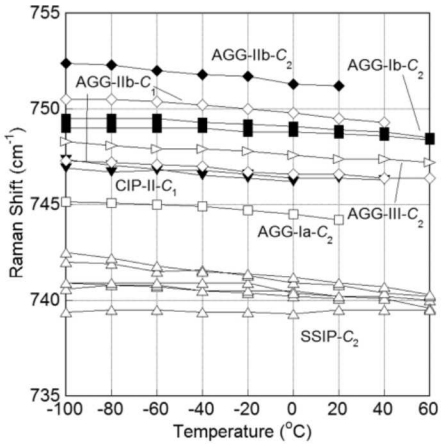
- Linking solvation interactions to supporting electrolyte stability

$MgTFSI_2$ as a Benchmark Salt

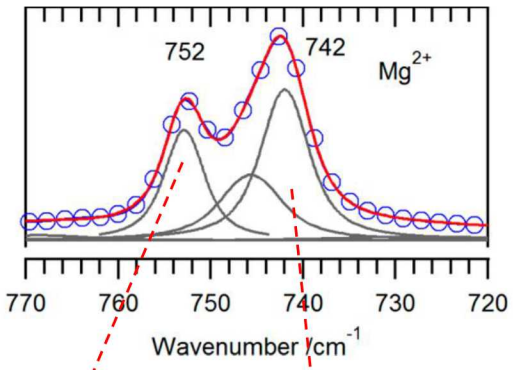
- **Benefits:** diverse conformations and interactions



TFSI Conformational Sensitivity

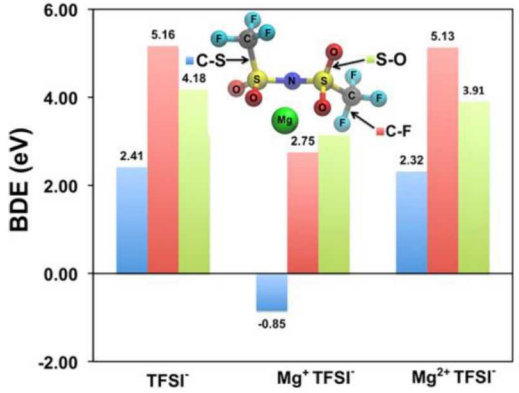


Seo et al. J. Phys. Chem. B 2014, 118, 13601−13608

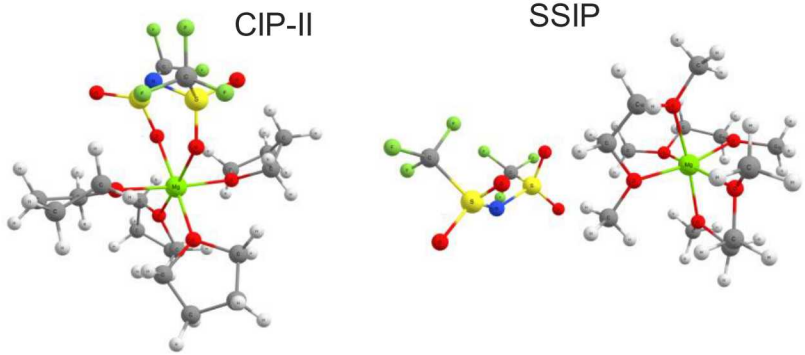


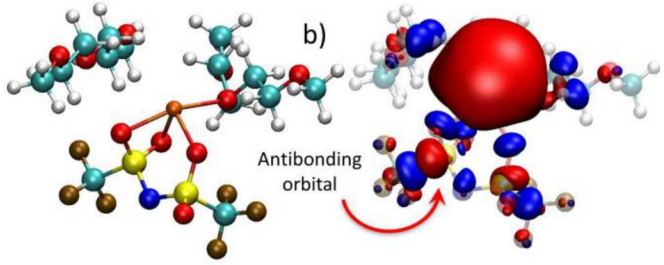
Giffin et al. J. Phys. Chem. C 2014, 118, 9966−9973

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

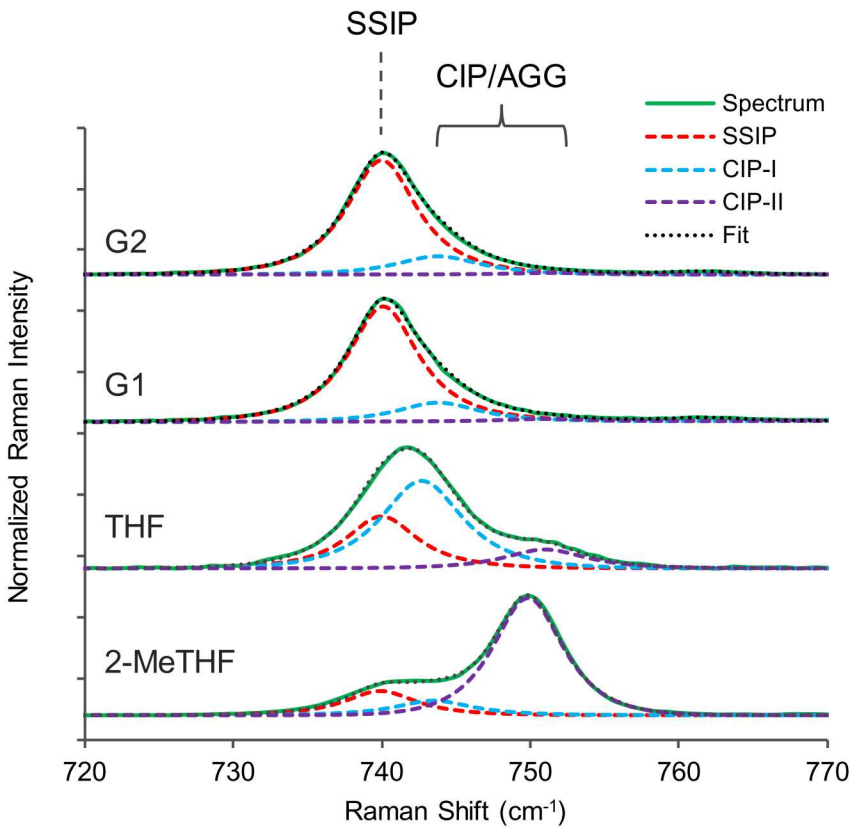
Key Takeaways

1. Ether solvent chelation regulates TFSI:Mg^{2+} interactions and thus electrolyte stability + transport

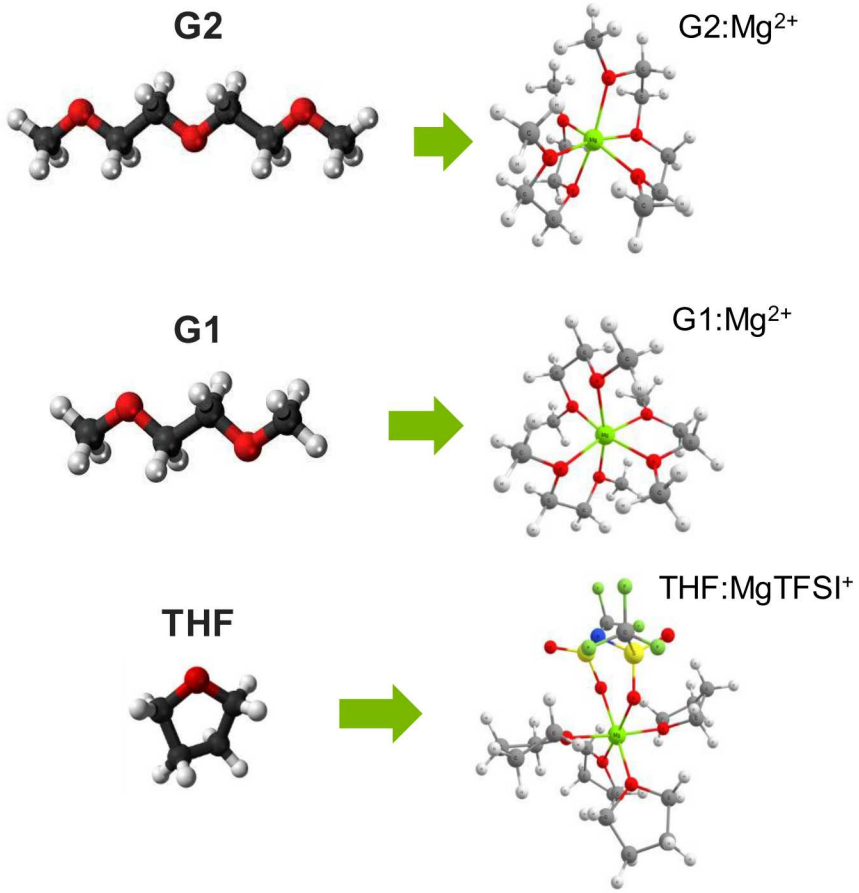
2. Ether solvent chelation regulates Cl:Mg^{2+} complex structure and Mg^{0} deposition efficiency

Ether Structure Controls TFSI:Mg^{2+} Interactions

Raman Analysis of TFSI Environments



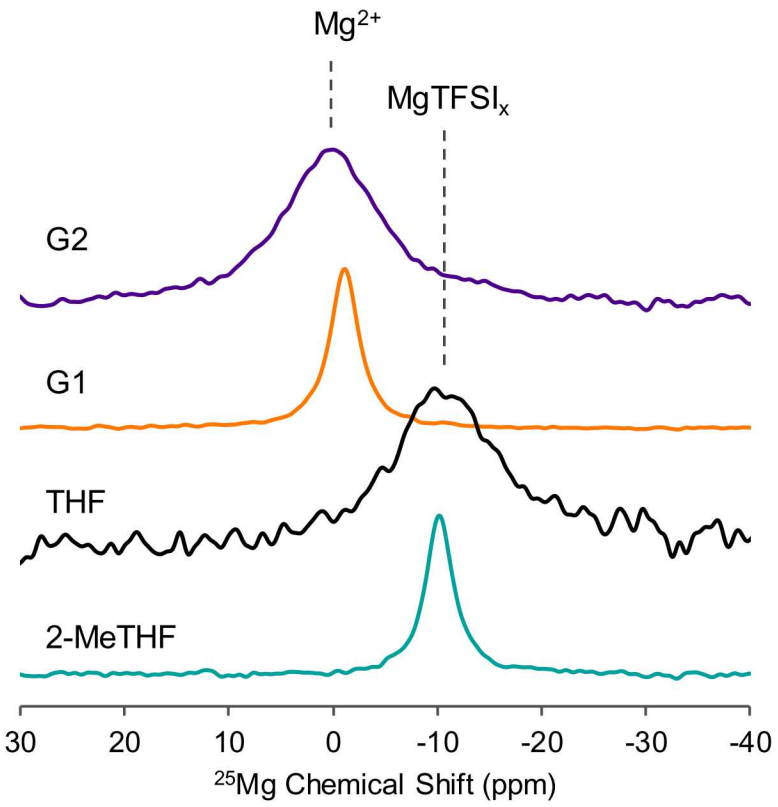
Chelation Ability Drives Ion Separation



- **Persistent ~10-15% coordinated TFSI even in G1 and G2**

Ether Structure Controls Ion Interactions

^{25}Mg NMR analysis of Mg^{2+} Environments

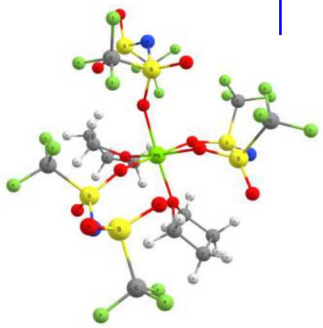


Computed Chemical Shifts (DFT Optimized)

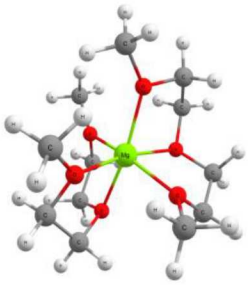
Mg-Species	THF	G1	G2
Mg^{2+}	-0.2	2.4	0.8
$MgTFSI^{+}$	-1.4	0.2	1.1
$MgTFSI_2$	-4.4		-3.4
$MgTFSI_3^{-}$	-7.7	-8.5	
$Mg_2TFSI_3^{+}$	-11		
$MgTFSI_4^{2-}$		-11.4	
$MgTFSI_5^{3-}$	-16		

More $TFSI^{-}$ = More Upfield

$Mg_xTFSI_y^{2x-y}$



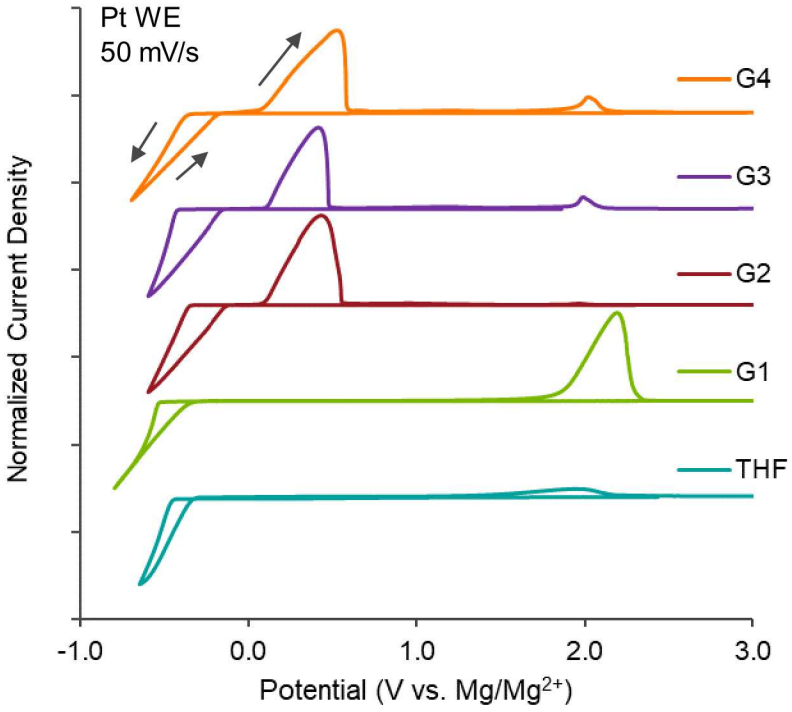
Mg^{2+}



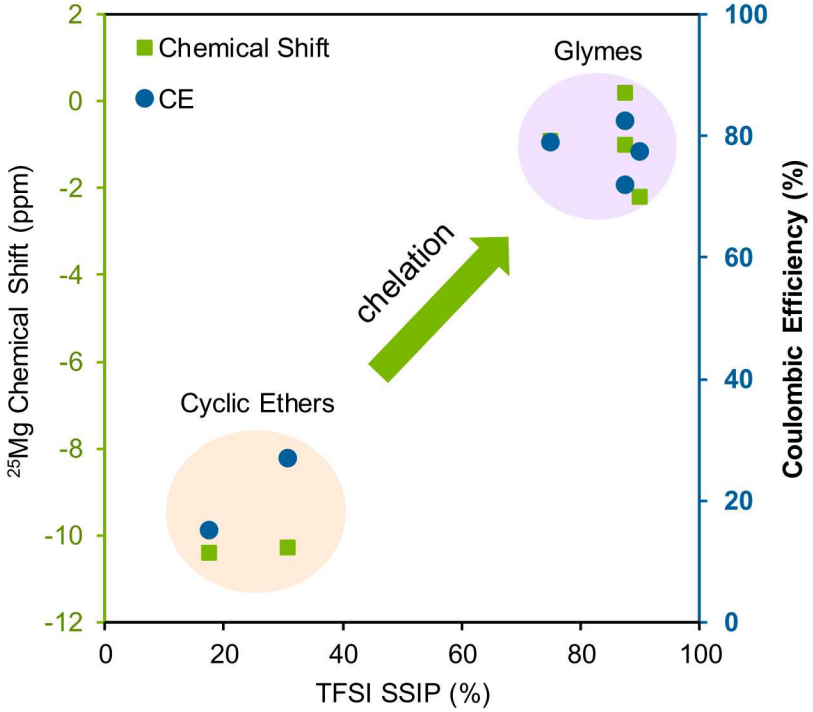
- Chemical shift depends on sulfonyl vs. ether oxygen coordination

Solvent Chelation is Key Performance Driver

Chelation Increases Efficiency + Reduces Passivation



Chemical Environment Correlates with Stability

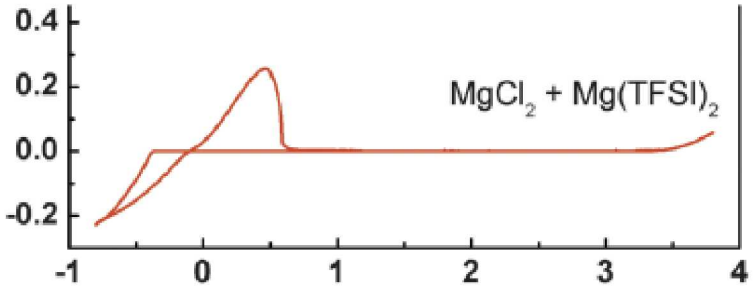


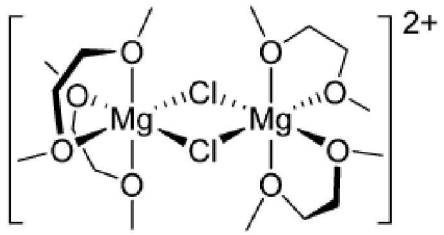
- Primary efficiency determiner is ion separation ability

Tuning Interactions with $MgCl_2$ Co-salt

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

1:1 $MgCl_2$:$MgTFSI_2$

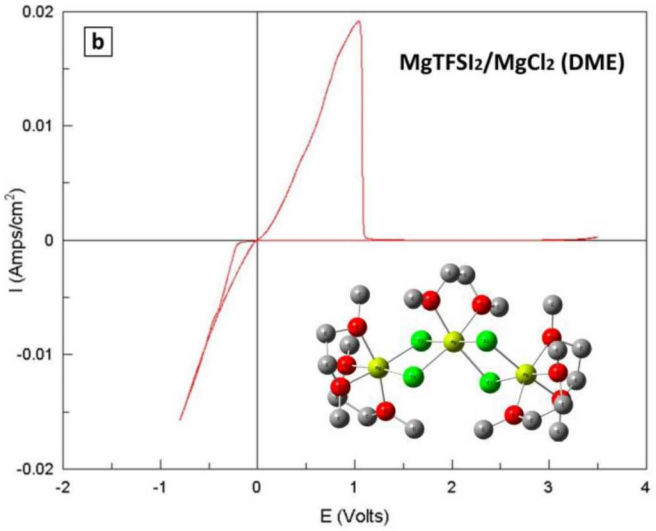




stable

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

2:1 $MgCl_2$:$MgTFSI_2$

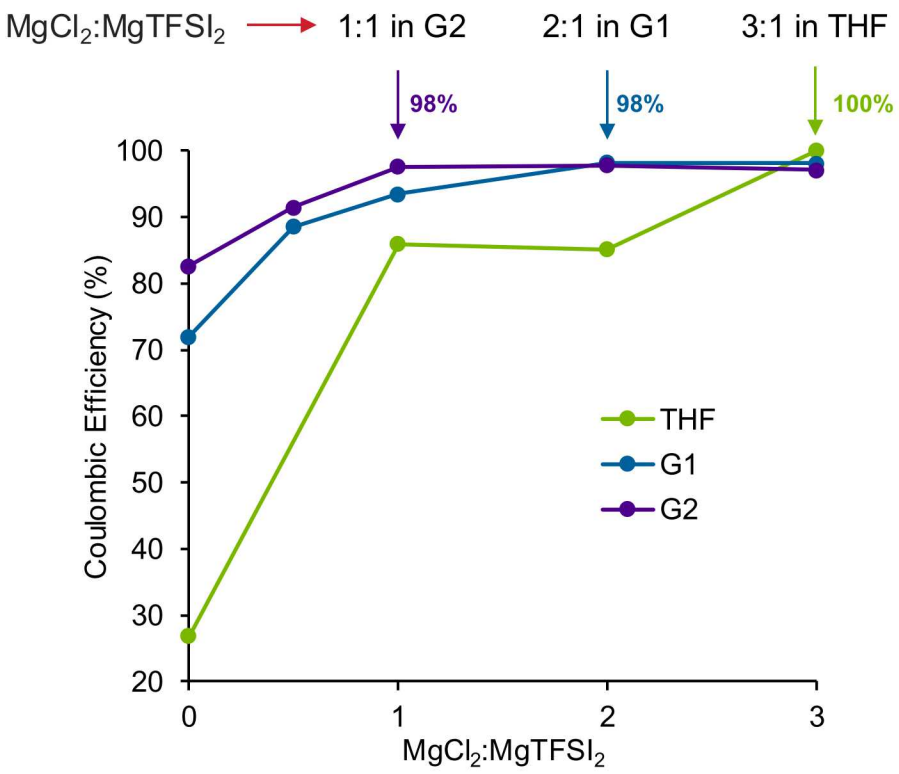


Shterenberg et al. Journal of The Electrochemical Society, **162** (13) A7118-A7128

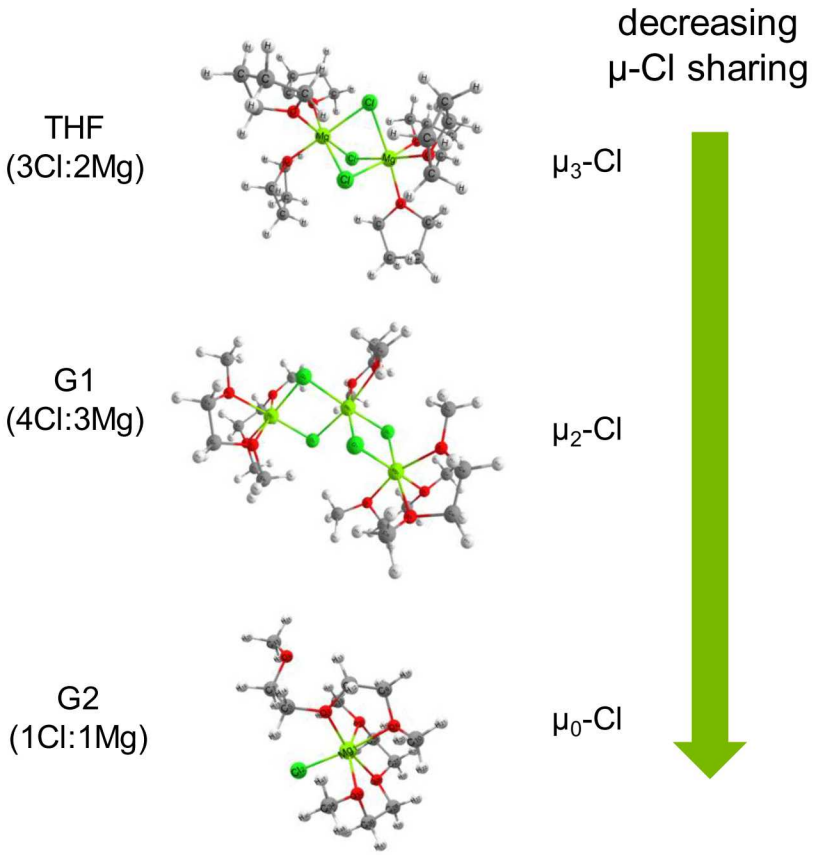
- How does solvent structure govern co-salt interactions?

Optimum Salt Ratio Depends on Solvent

Mg Plating Performance Trends



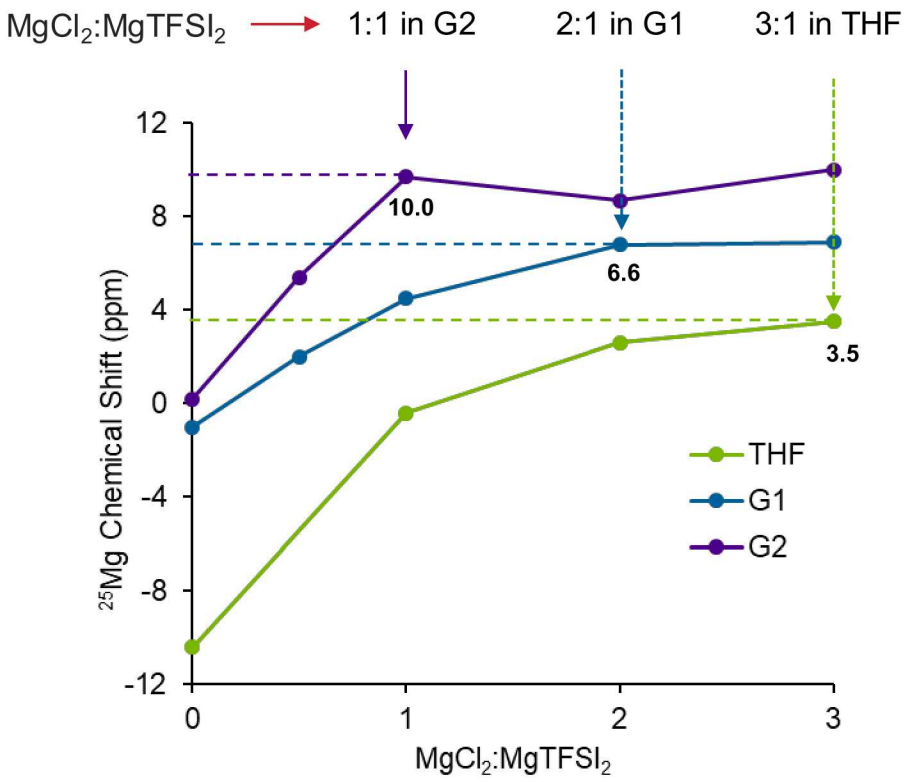
Speciation Trends



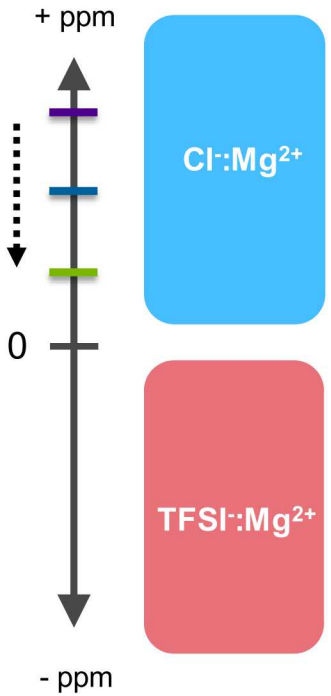
- Optimum ratio differences reflect unique Cl-Mg cluster formation tendencies
- Chelation ability disfavors Cl-sharing, consistent with MD simulations

Proposed Mg-Cl Complexes Aren't the Only Species

^{25}Mg NMR Tracks Critical Ratio

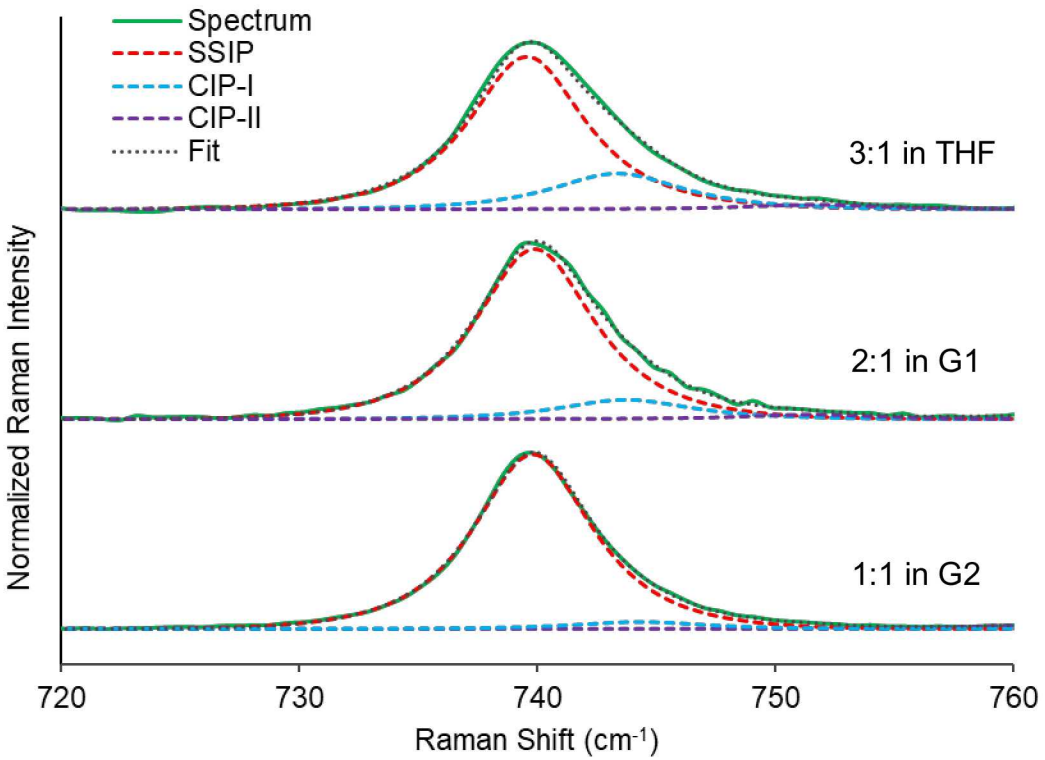


Limiting downfield shift correlates with chelation ability



- Chemical shift trend suggests residual influence of TFSI:Mg^{2+} as a function of chelation

Remnant TFSI:Mg^{2+} Depends on Chelation



~22% TFSI:Mg^{2+}

~14% TFSI:Mg^{2+}

~6% TFSI:Mg^{2+}

- Weaker chelation facilitates persistent TFSI:Mg^{2+}
- High deposition efficiency is still possible reflecting interfacial role

Conclusions

1. Ether solvent chelation regulates TFSI:Mg^{2+} interactions and thus electrolyte stability + transport
   - Chelation correlates inversely with TFSI and Mg^{2+} interactions
   - TFSI:Mg^{2+} interactions drive instability

2. Ether solvent chelation regulates Cl:Mg^{2+} multimer structure and Mg^{0} deposition efficiency
   - Greater chelation ability suppresses μ-Cl sharing
   - More μ-Cl sharing favors high efficiency despite bulk TFSI interactions
   - Interfacial behavior of these complexes is not well understood

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