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Competitive Solvent and Anion Coordination in Multivalent Battery Electrolytes

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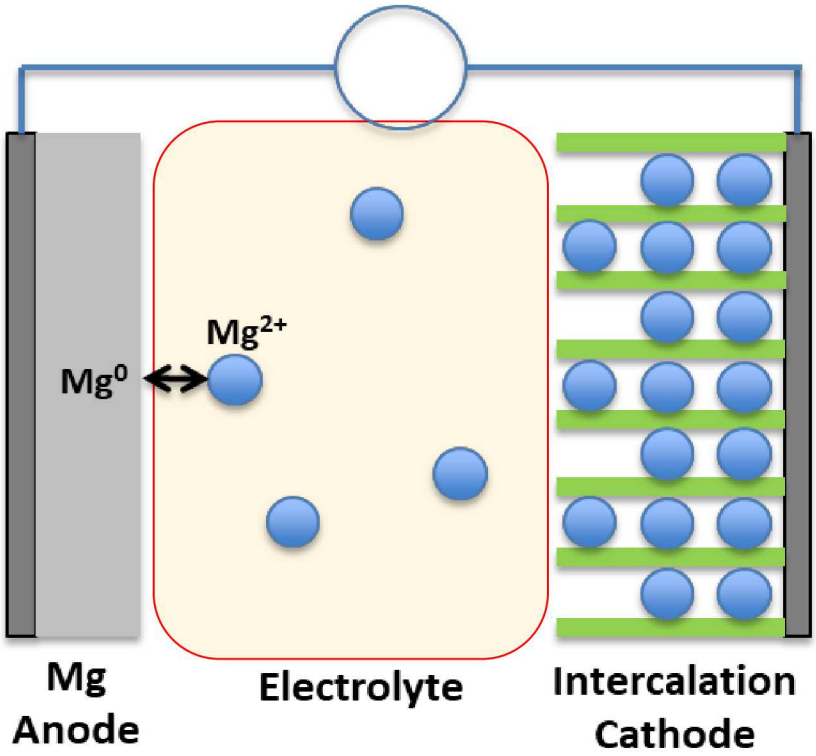
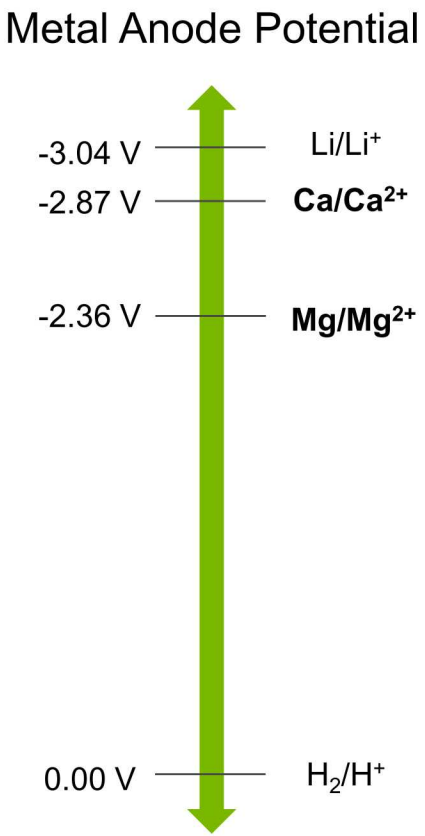
Opportunities for Divalent Electrolytes

- Mg^{2+} or Ca^{2+} both offer potential paths to ≥ 400 Wh/l batteries
- Electrolyte science challenges:
  - Stable and rapid delivery of M^{2+} active species
  - Metal anodes, high voltage cathodes

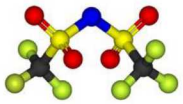


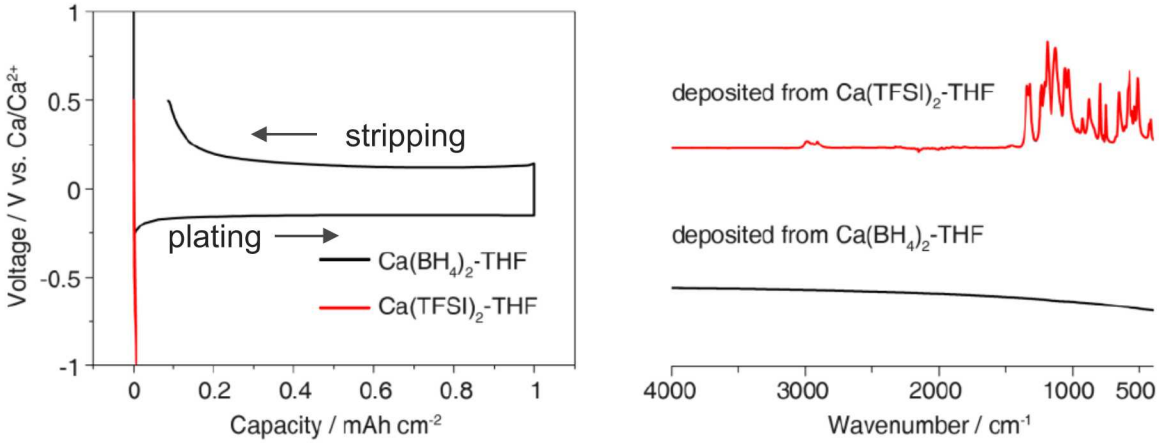


Calcium Electrolytes: plagued by instability

$Ca(TFSI)_2$/THF

$N(SO_2CF_3)_2^-$

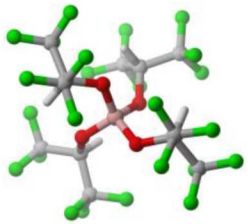


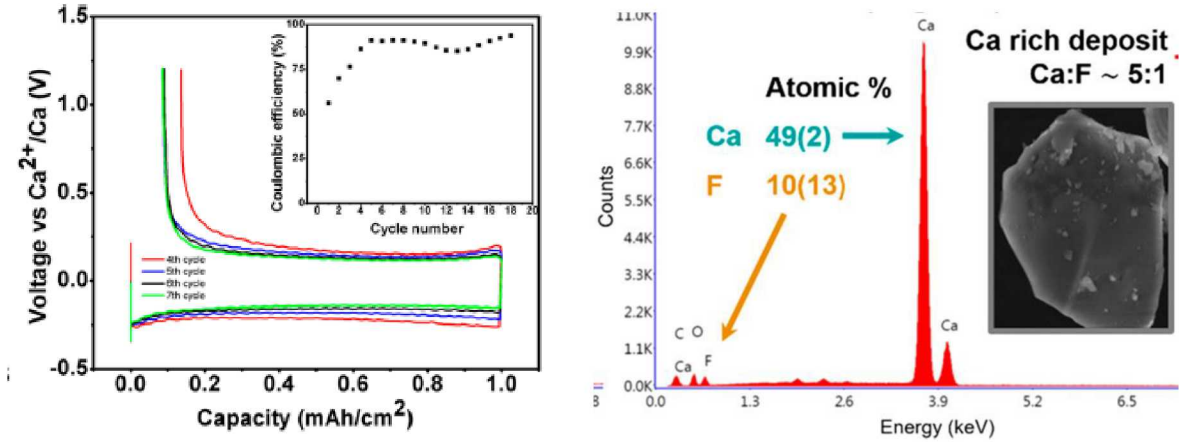


Bruce et al. Nature Mater. 2018

$Ca(BHFIP)_2$/G1

$B(OCH(CF_3)_2)_4^-$



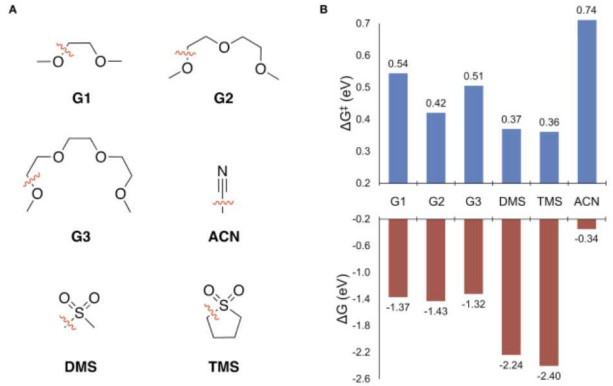


Nazar et al. ACS Energy Lett. 2019

Links Between Coordination and Stability

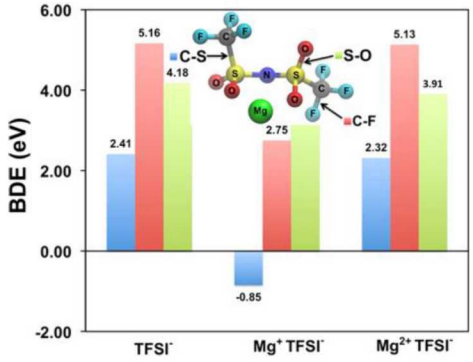
partly understood for Mg^{2+}; not understood for Ca^{2+}

solvent:Mg^{2+}



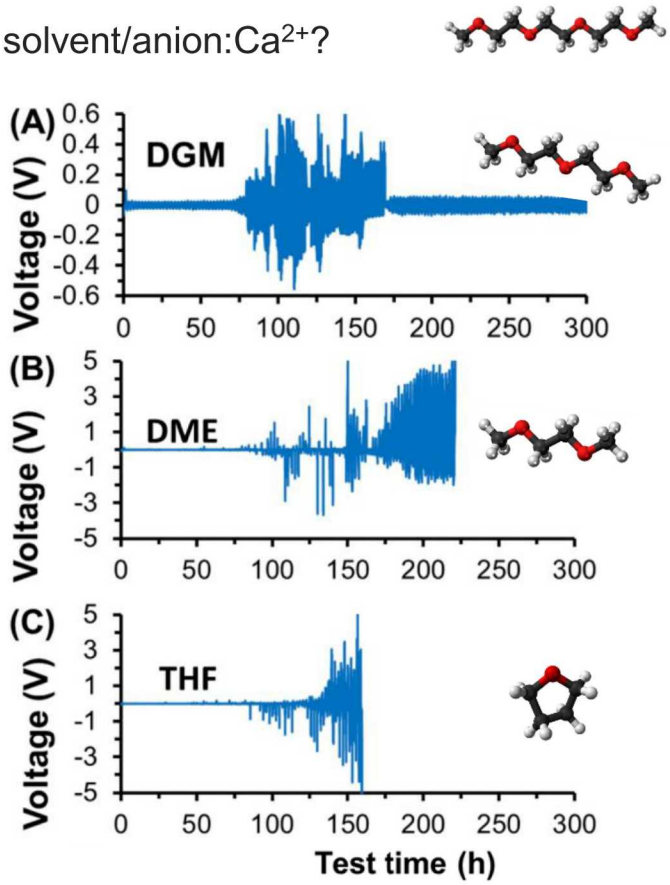
Persson et al. Front. Chem. 2019

anion:Mg^{2+}

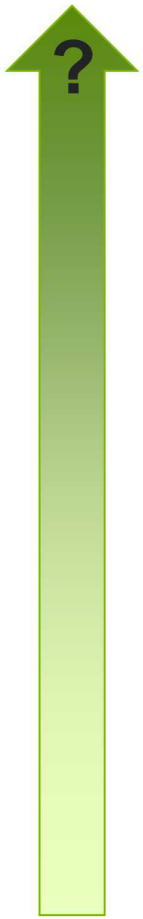


Persson et al. J. Am. Chem. Soc. 2015

solvent/anion:Ca^{2+}?



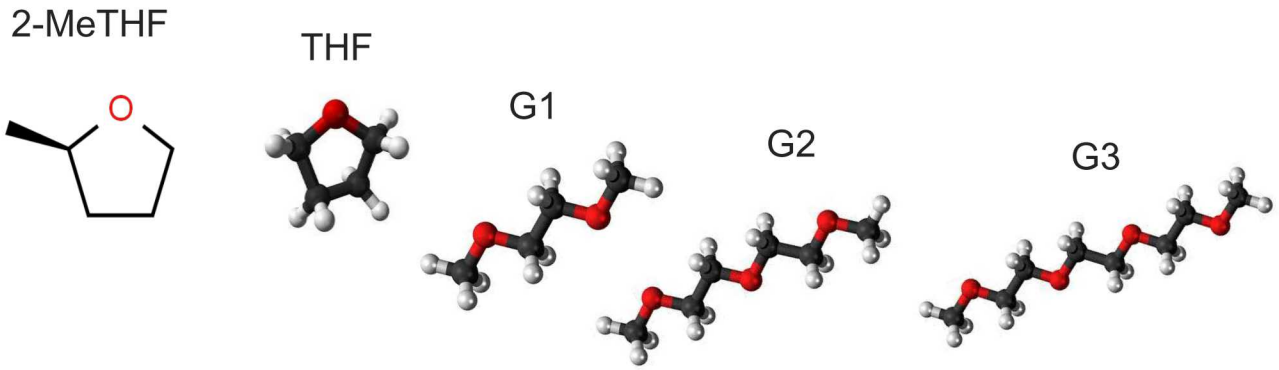
Liu et al. Batteries & Supercaps 2020



- Need to understand coordination to understand and guide stability

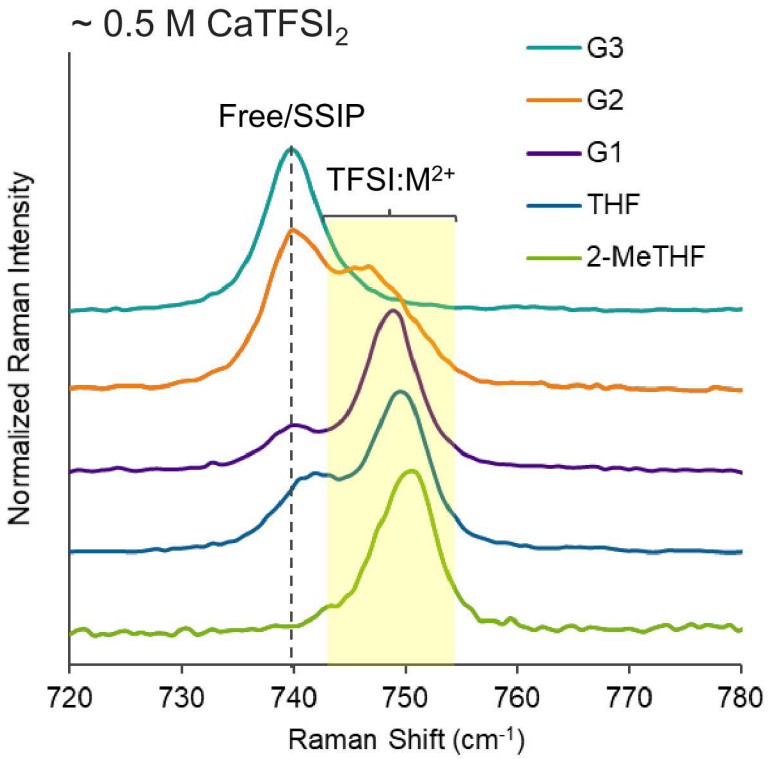
Goals of this Talk

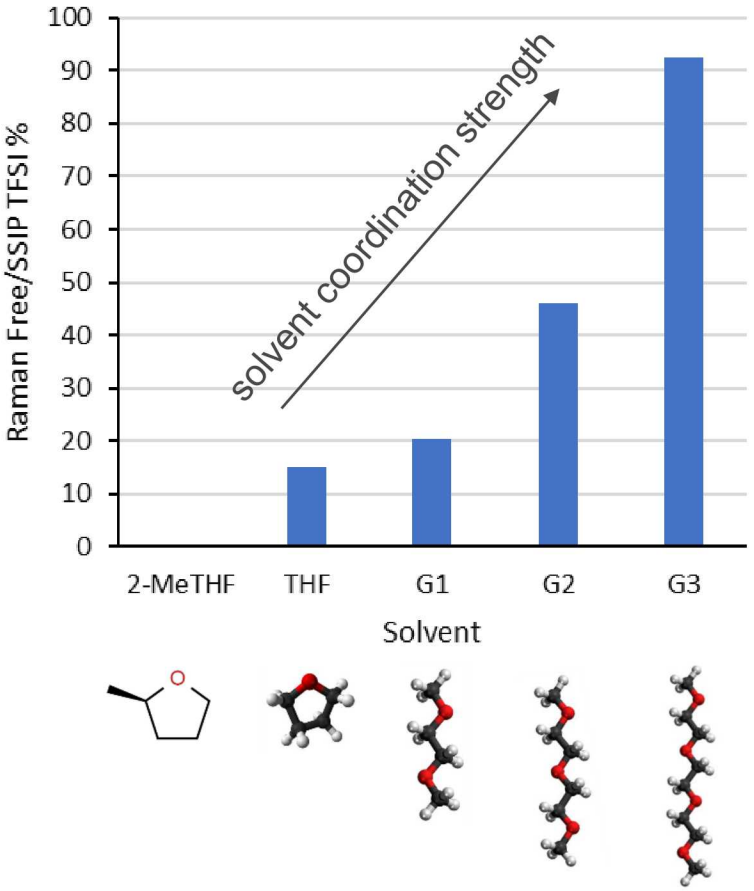
- Describe how ether/glyme structure controls coordination of Ca^{2+}
- Correlate coordination tendencies to metal plating behavior



Establishing Ether Coordination Strengths

Raman Analysis of TFSI Displacement

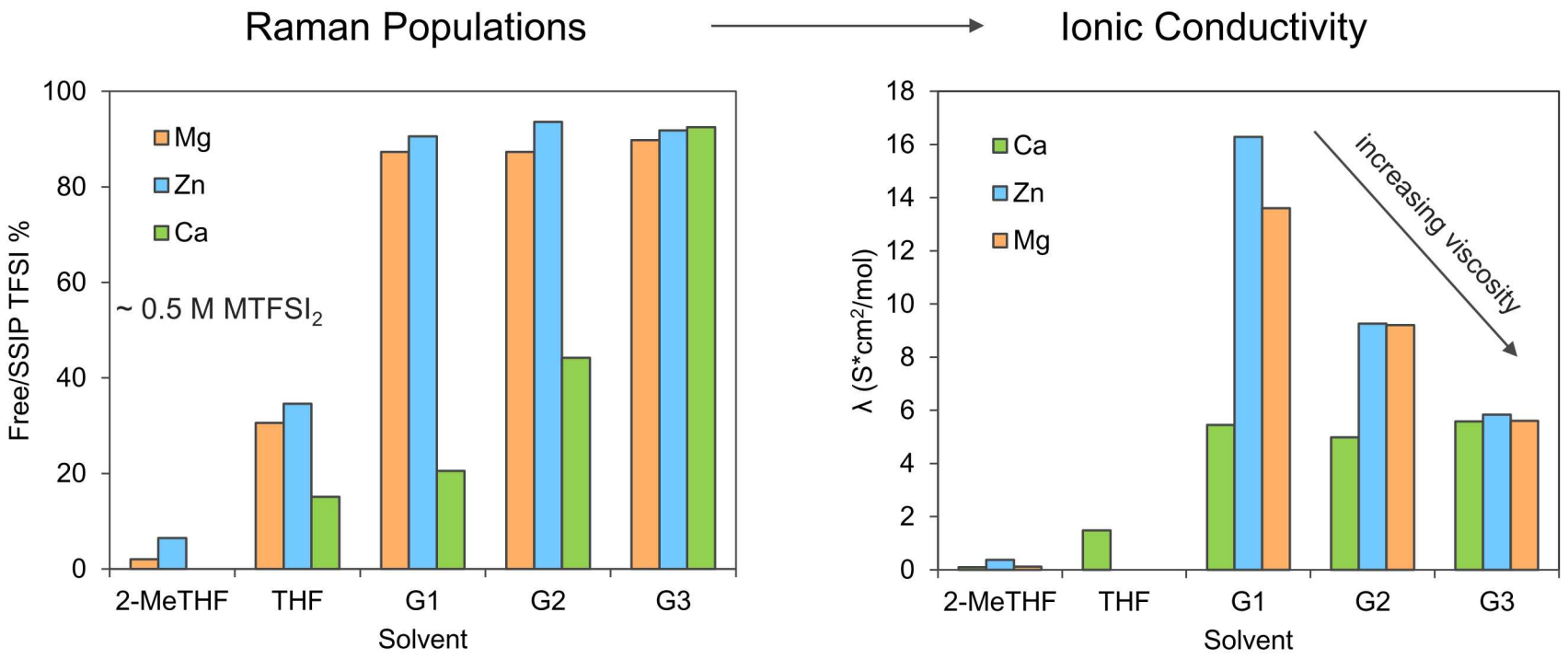




- Glymes > cyclic ethers
- Strength increases with glyme length

Hahn et al. ACS Appl. Energy Mater. 2020

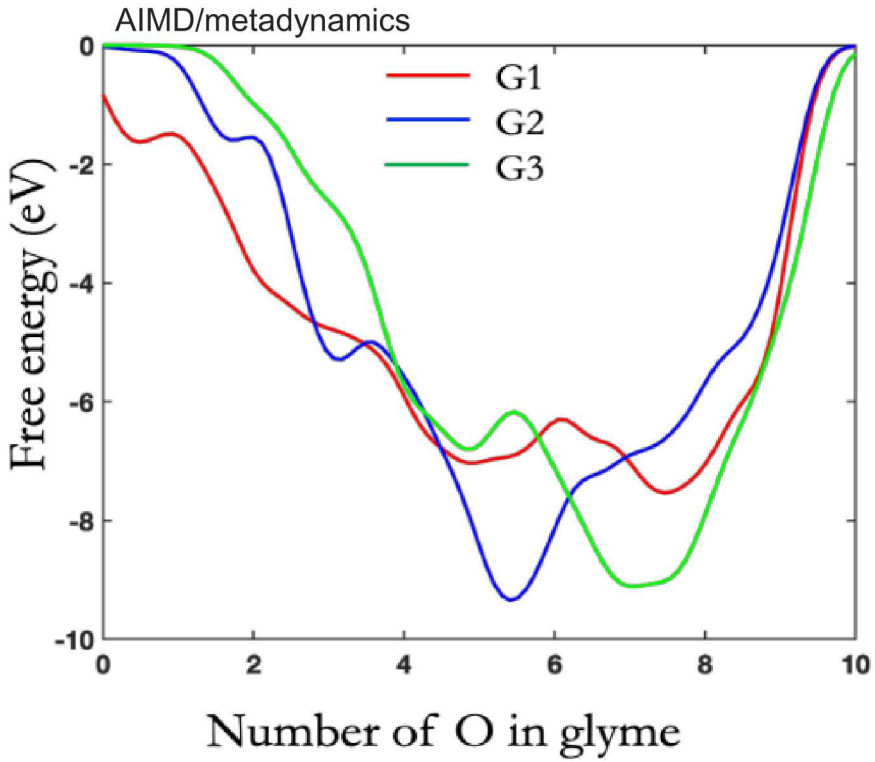
Glyme Coordination Trend Depends on Cation

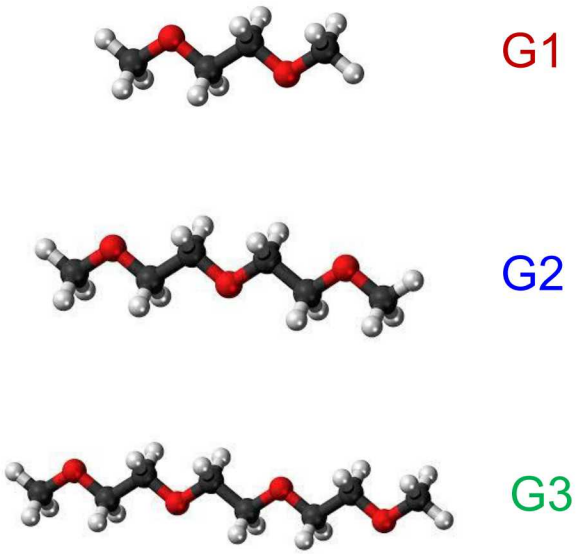


- Glyme chain length dependence is unique to Ca^{2+}
- Larger size + polarizability plays a role

Ca^{2+} Coordination Preferences vs. Glyme Length

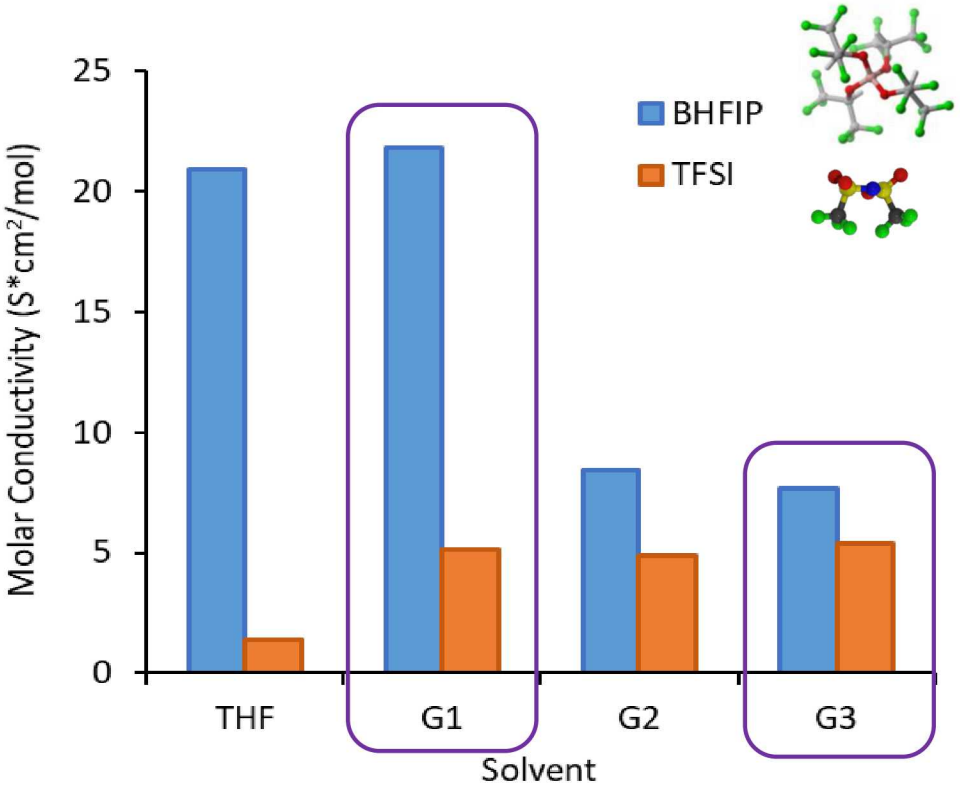
Glyme:Ca^{2+} Free Energy Profiles

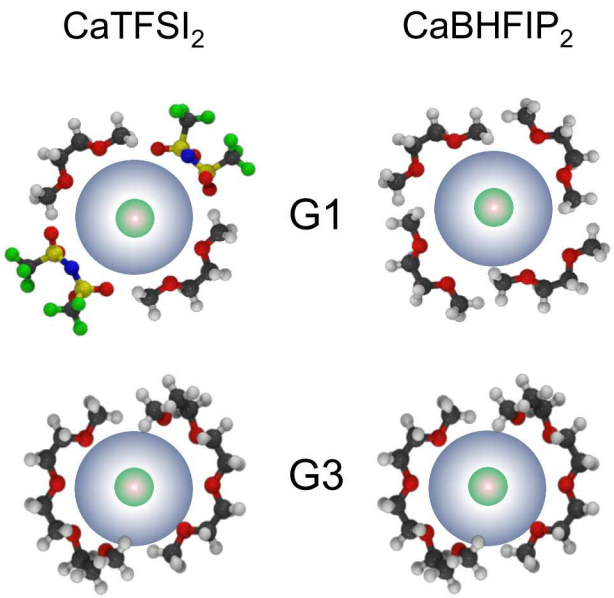




- G1 is more “accommodating” of different structures
- G2 has strong preference for lower CN
- G3 has strong preference for higher CN

Decoupling Anion Contributions



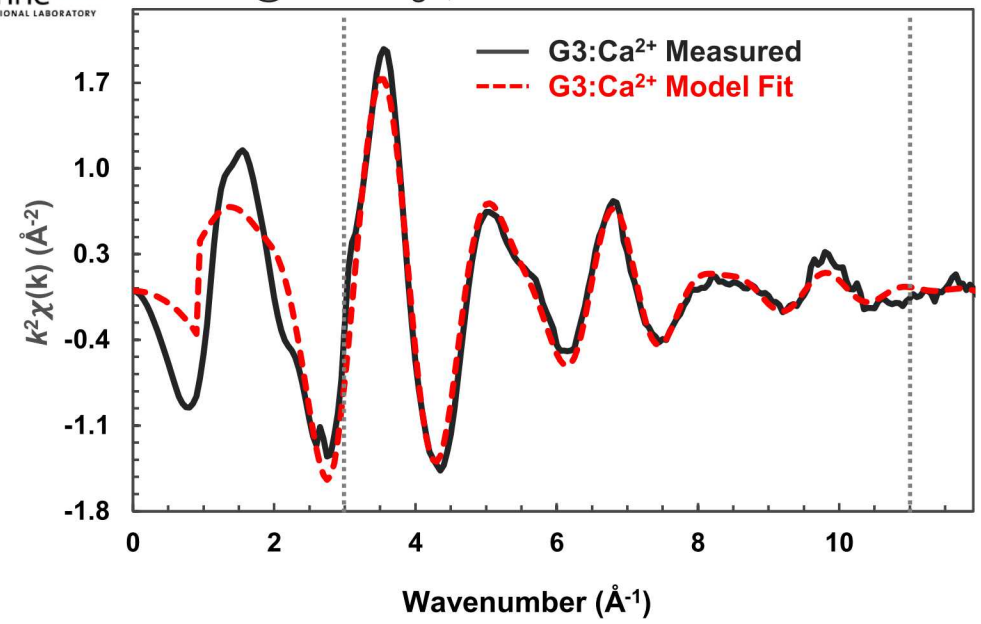


- BHFIP provides a strongly dissociating benchmark
- Relative ion interactions are regulated by specific solvent interactions

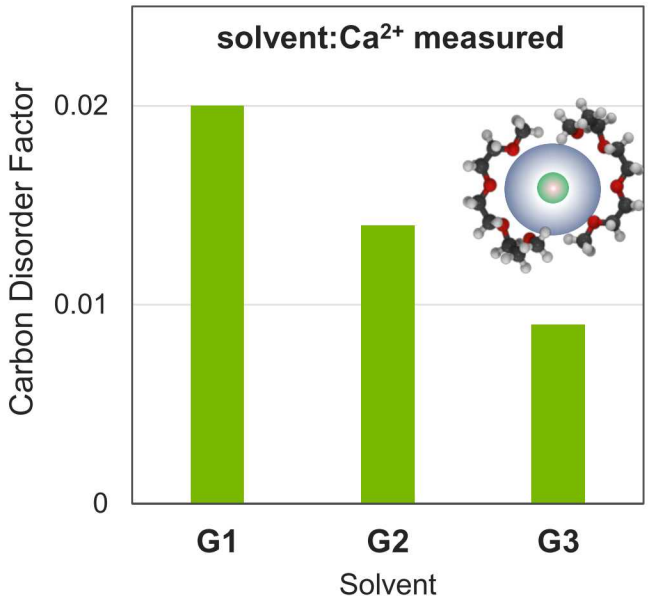
Comparison of 1st Shell Structures

All-solvent model matches EXAFS

EXAFS @ Ca K-edge; Advanced Photon Source



Disorder Decreases with Glyme Length

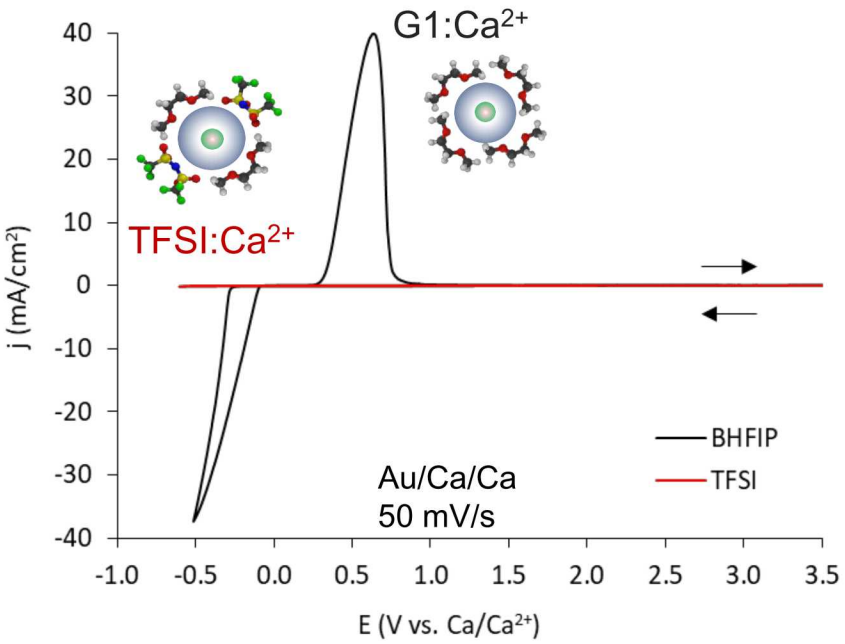


- G3 fully solvates Ca^{2+} regardless of anion
- Rigidity of glyme coordination increases as G1 < G2 < G3

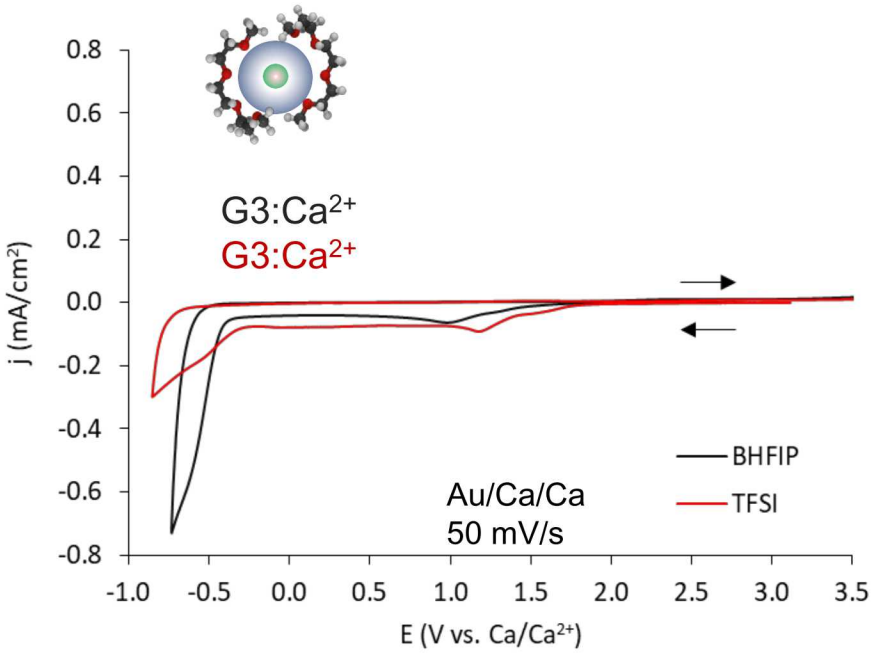
G3 sets itself apart by strong/rigid coordination

Impact of Coordination on Metal Plating

G1: full solvation enables deposition

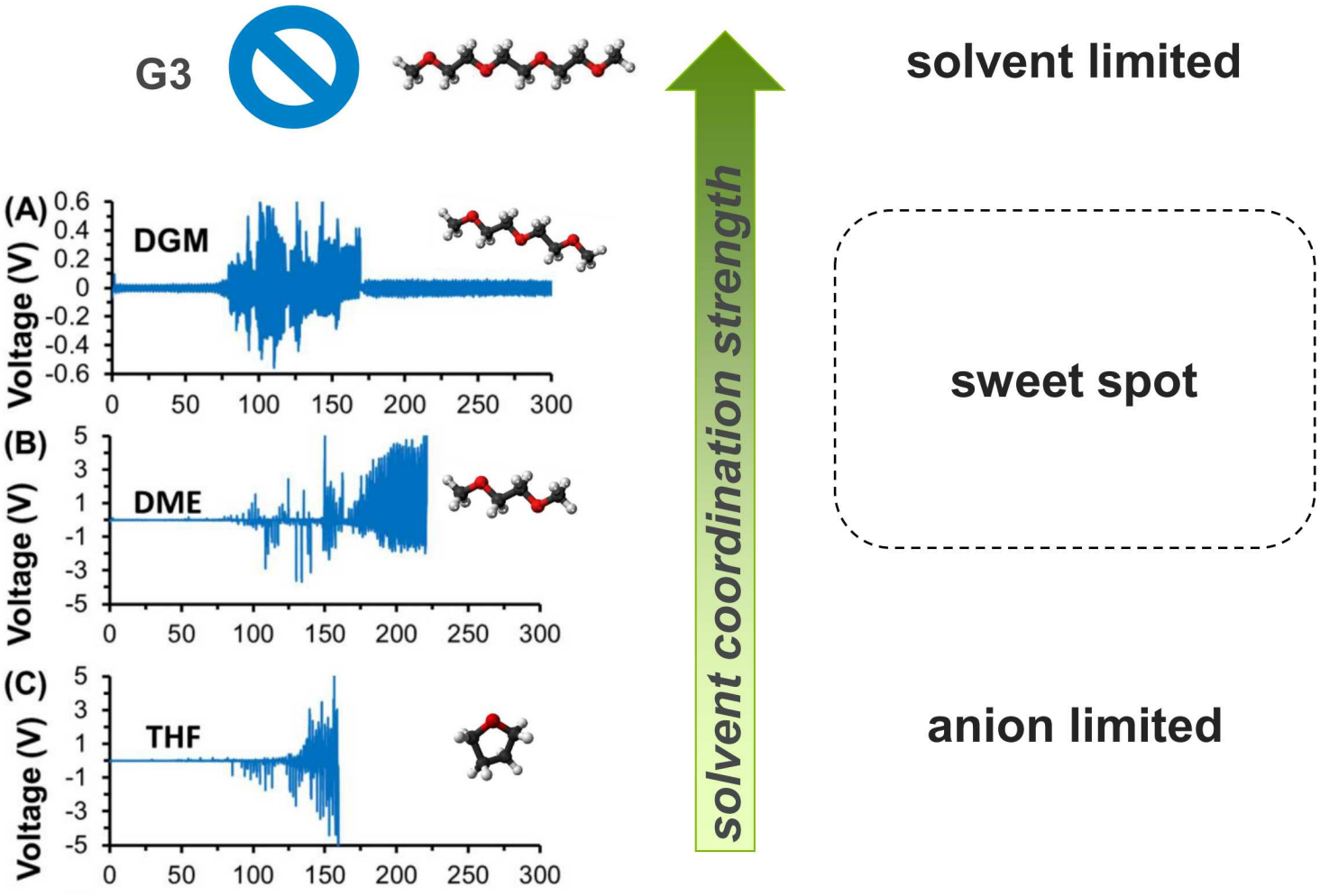


G3: full solvation inhibits deposition



- solvent:Ca^{2+} interactions must be optimized to allow stable desolvation
- difficulty of G3:Ca^{2+} reorganization at interface

Need to Tune Solvent:Ca^{2+} Coordination



Liu et al. Batteries & Supercaps 2020

Conclusions

- Dication size determines ethereal solvent coordination trends; solvent:Ca^{2+} coordination strength increases with glyme chain length up to G3
- Calcium deposition is correlated with solvent coordination strength/rigidity

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