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U.S. DEPARTMENT OF ENERGY

Enabling Oxidatively Stable Solvents for High Voltage Magnesium Battery Electrolytes

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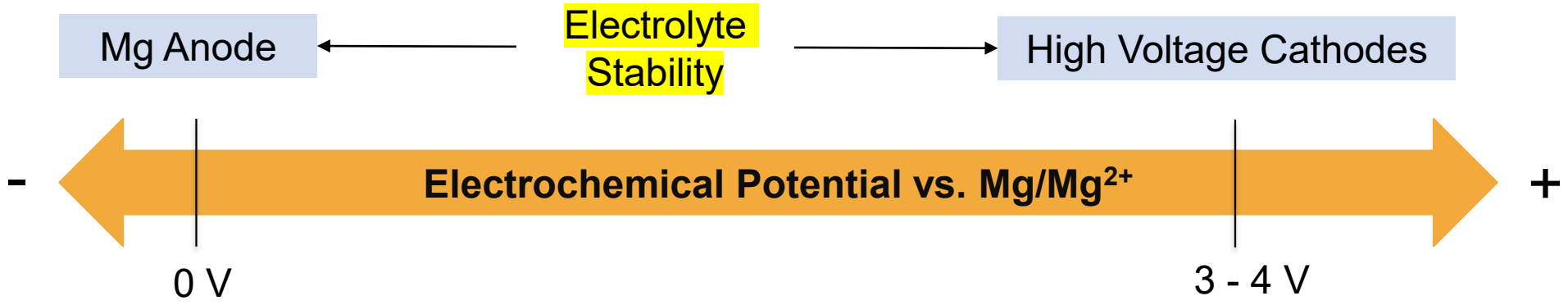
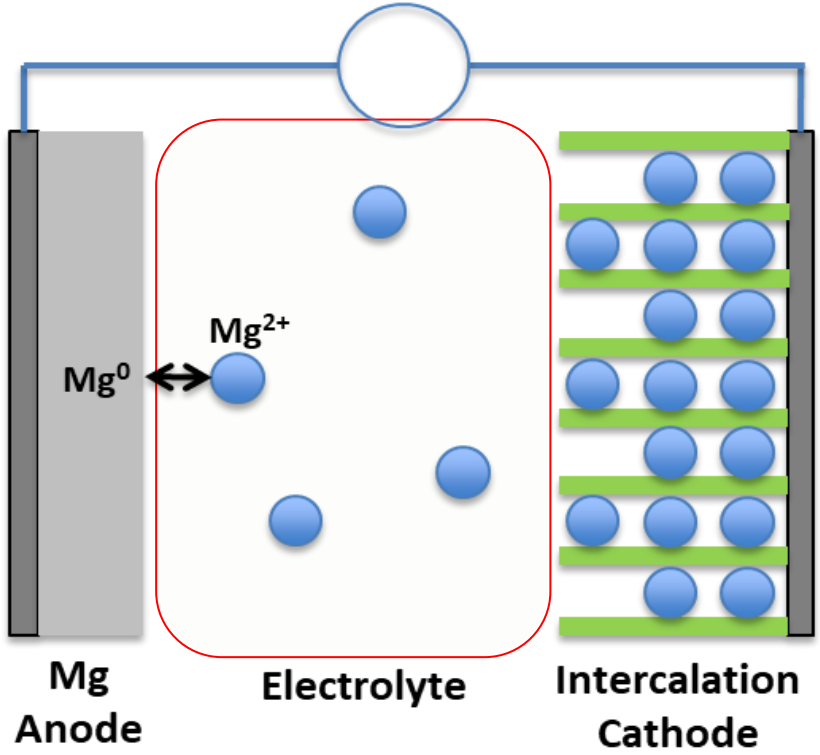
The Push Toward High Voltage Mg Batteries





- 400 Wh/L potential
- Potential improvements in safety/cost

The Push Toward High Voltage Mg Batteries

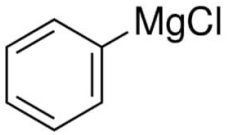
Mg Anode ← Electrolyte Stability → High Voltage Cathodes

\- **Electrochemical Potential vs. Mg/Mg^{2+}** +

0 V 3 - 4 V

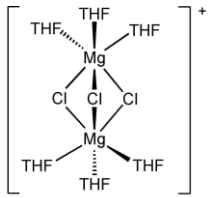
Mg Electrolyte Development

Grignards, BH_4^- → **Nucleophile Limit**



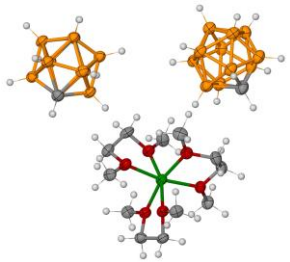
PhMgCl / THF

Chloro-Complexes → **Chloride Limit**



$Mg_2Cl_3^+AlR_xCl_{4-x}^-$ / THF

Designer WCAs → **Glyme Limit**



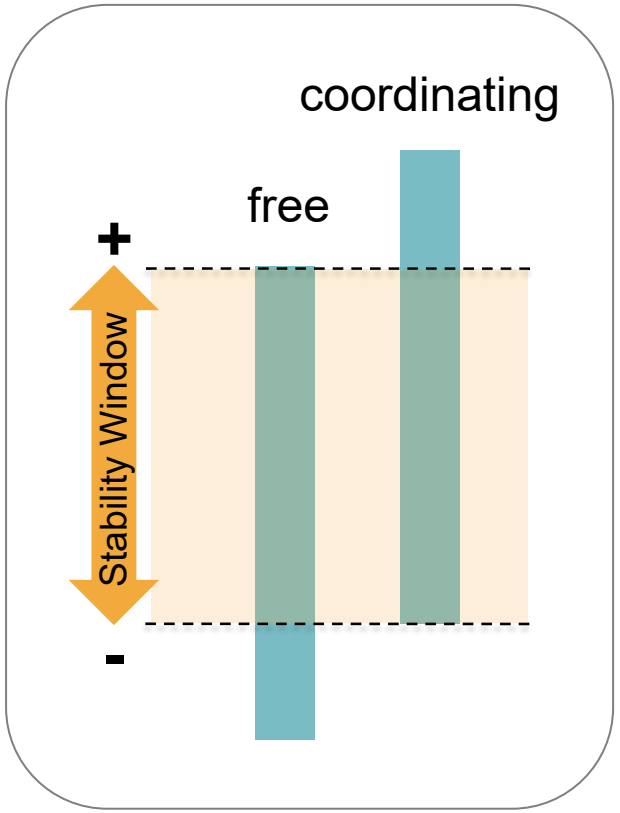
$Mg(CB_{11}H_{12})_2$ / GX

Oxidatively Stable Solvents → **Fundamental Limit?**

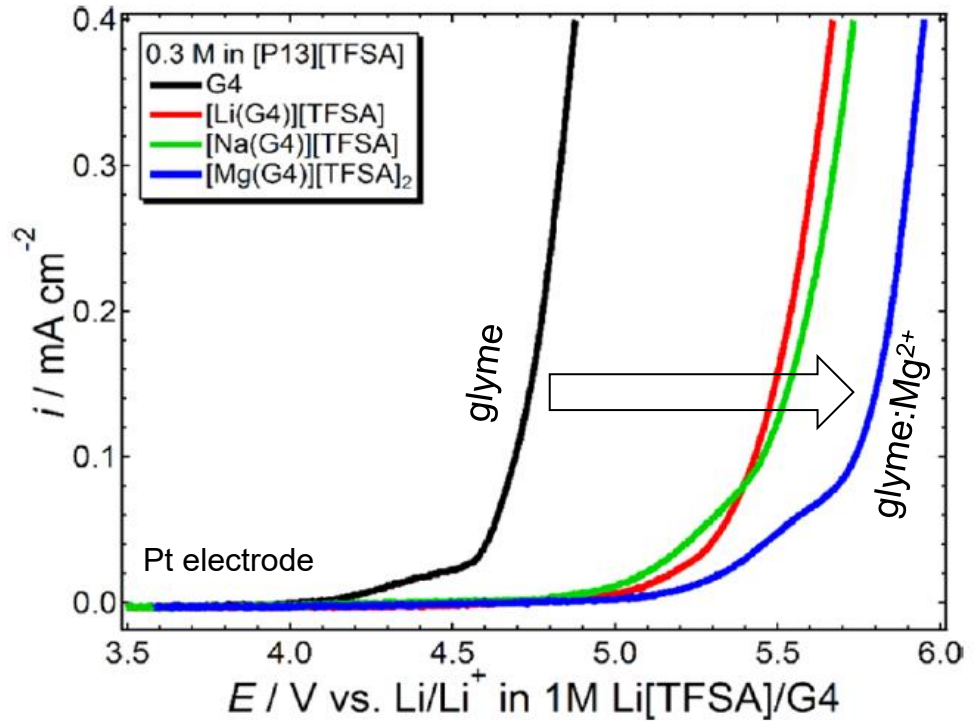
Electrolyte Stability Design Rules

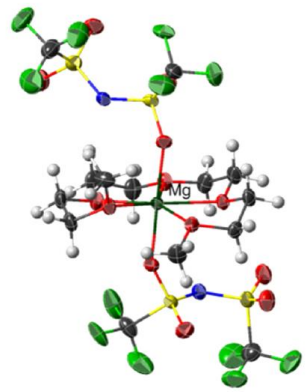
1. **<u>Mg-Coordinating</u> solvent determines <u>reductive</u> stability limit**

2. **<u>Free</u> solvent determines <u>oxidative</u> stability limit**



Coordination Increases Glyme Stability





Watanabe et al. J Phys Chem C 2016

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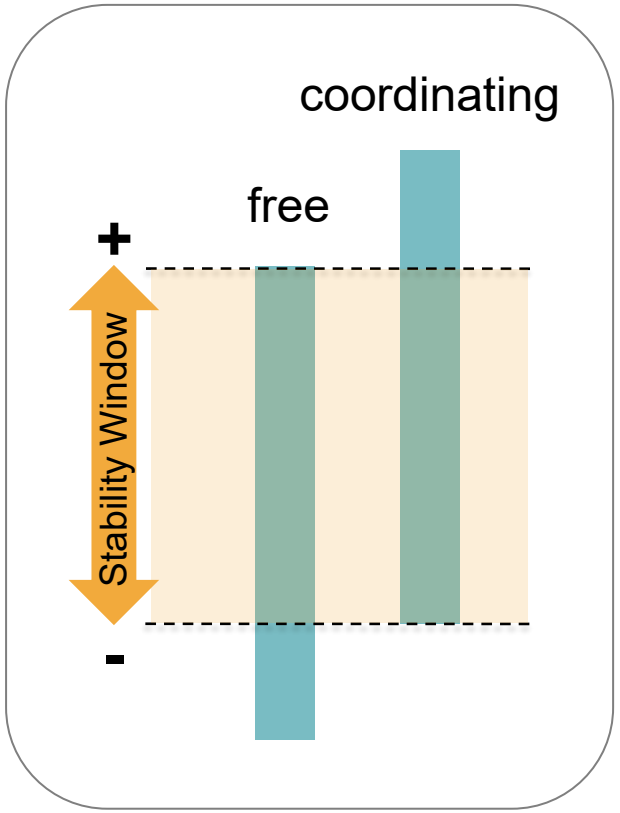
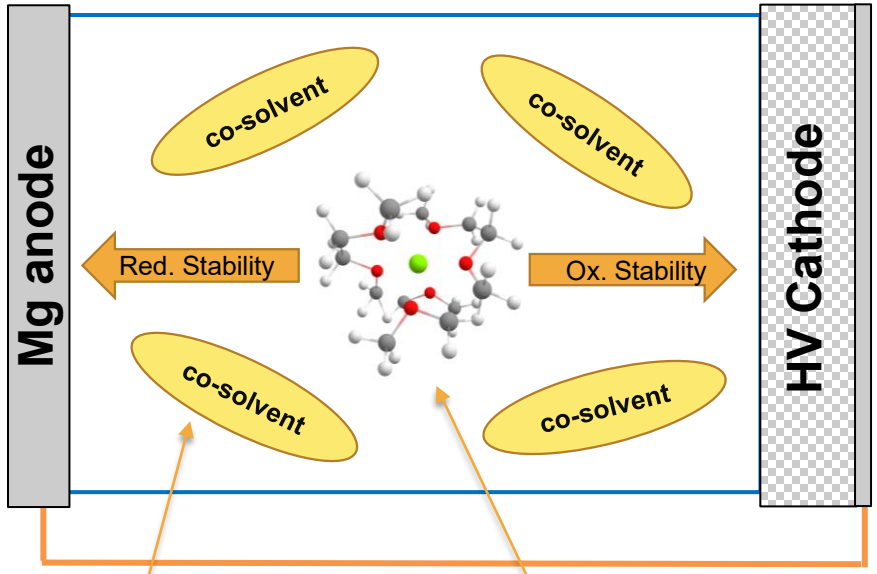


Strategy: Glyme Solvates in Co-Solvent



free co-solvent (majority)

coordinating glyme (minority)

Electrolyte Stability Design Rules

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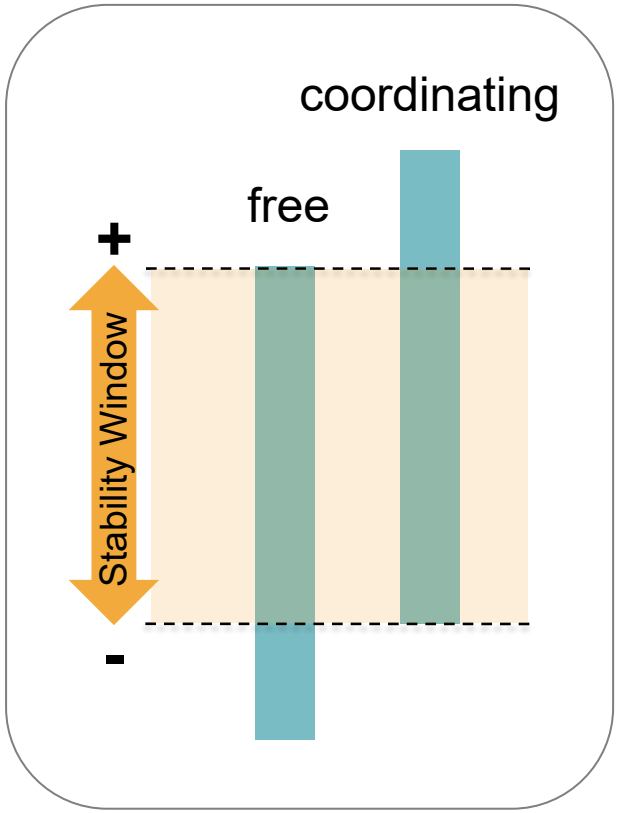
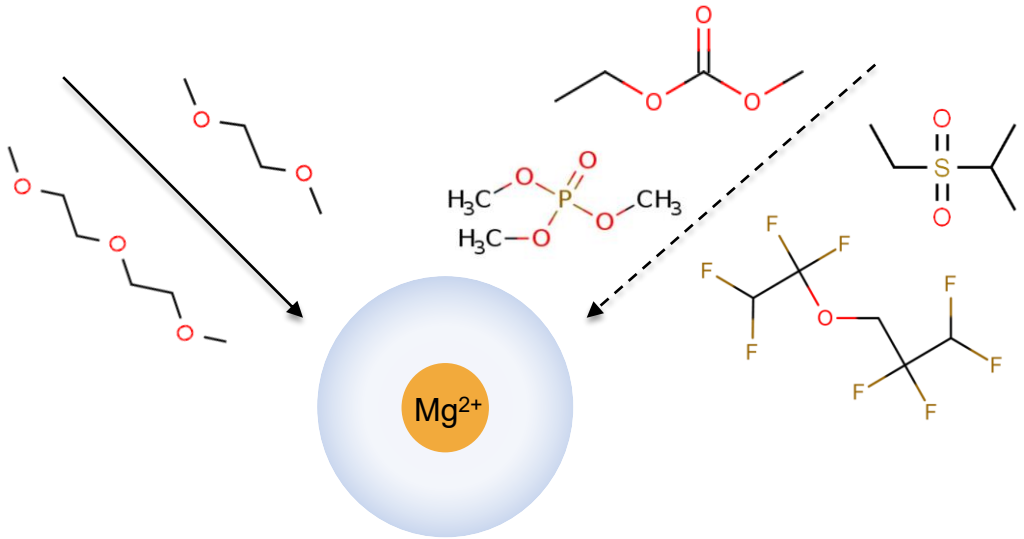


<u>Managing Coordination Selectivity</u>

Coordinating Glymes

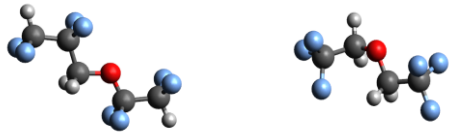
Non-Coordinating (?) Co-Solvents



Proof-of-Concept System

Non-Coordinating Co-Solvent

Hydrofluoroether (HFE)



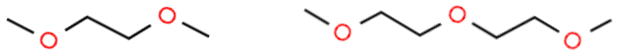
TTE BTFE

- High oxidative stability
- Weak solvating power

Electrolyte Composition

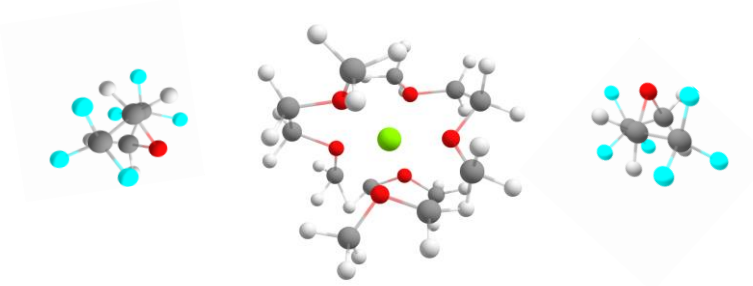
Salt: 0.5M $Mg(TFSI)_2$
Glyme: 1M G2 or 1.5M G1

Monoglyme (**G1**) Diglyme (**G2**)

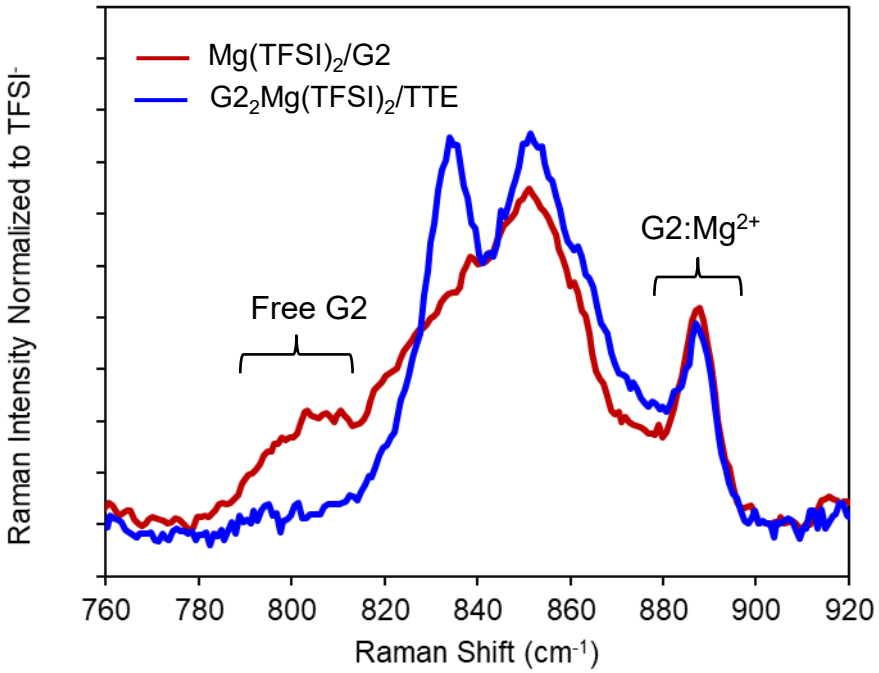


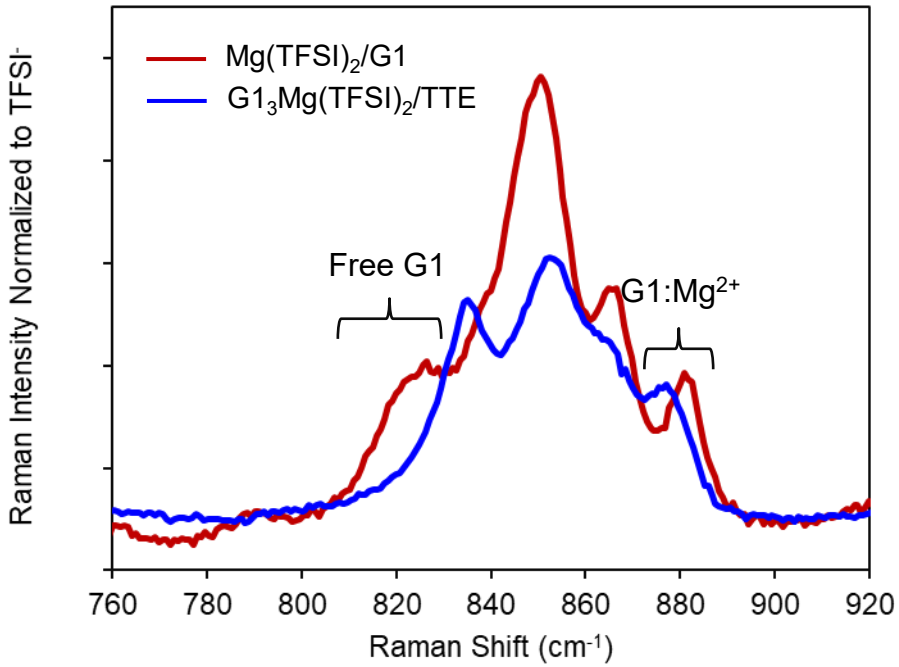
n = 3 n = 2

= 6 O_{glyme} per Mg^{2+}



Selective Glyme Coordination in HFE





- Elimination of free G2
- Consistent G2 solvation of Mg^{2+}

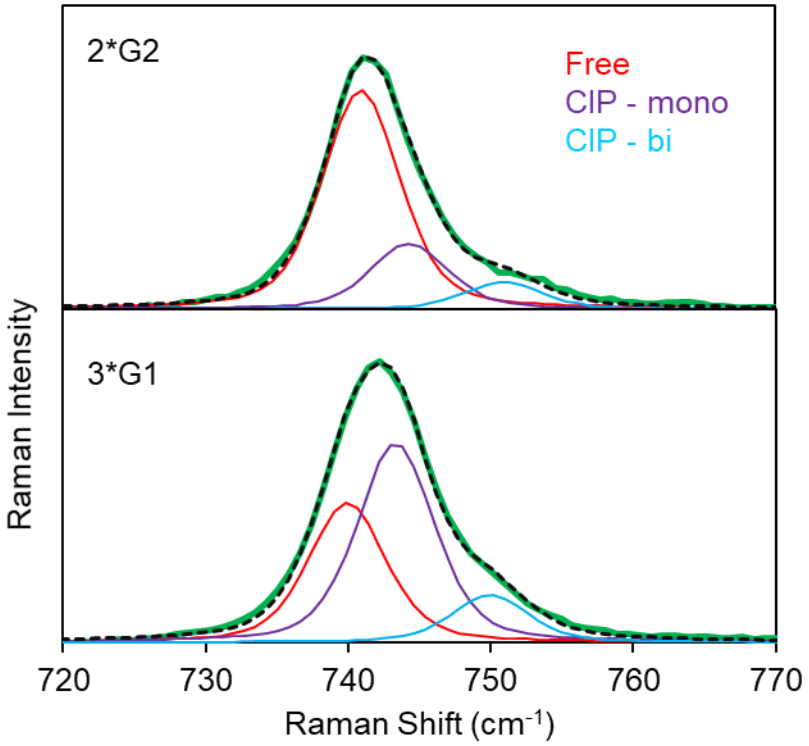
- Elimination of free G1
- Perturbed G1 solvation of Mg^{2+}

- <u>G2 more effective than G1 at fully solvating Mg^{2+} in HFE</u>

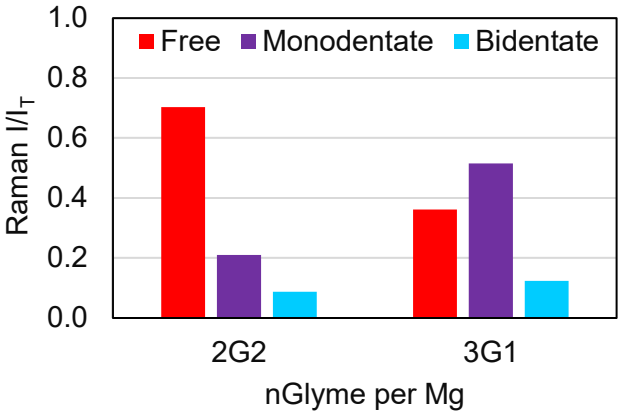
Primary Competition is Between Glyme and $TFSI^-$

$TFSI^-$ Coordination Behavior

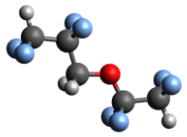
TTE example

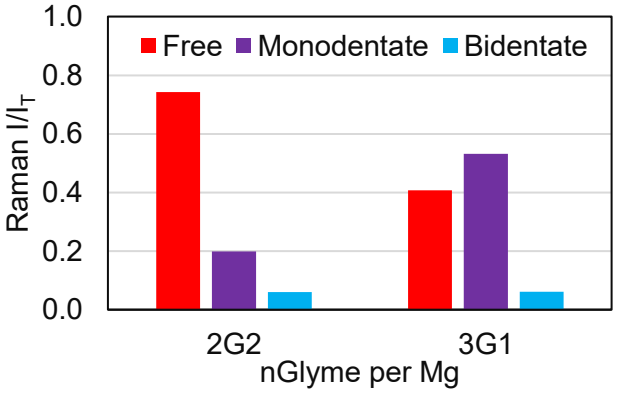


Coordination Statistics

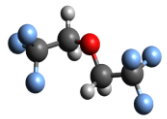


TTE





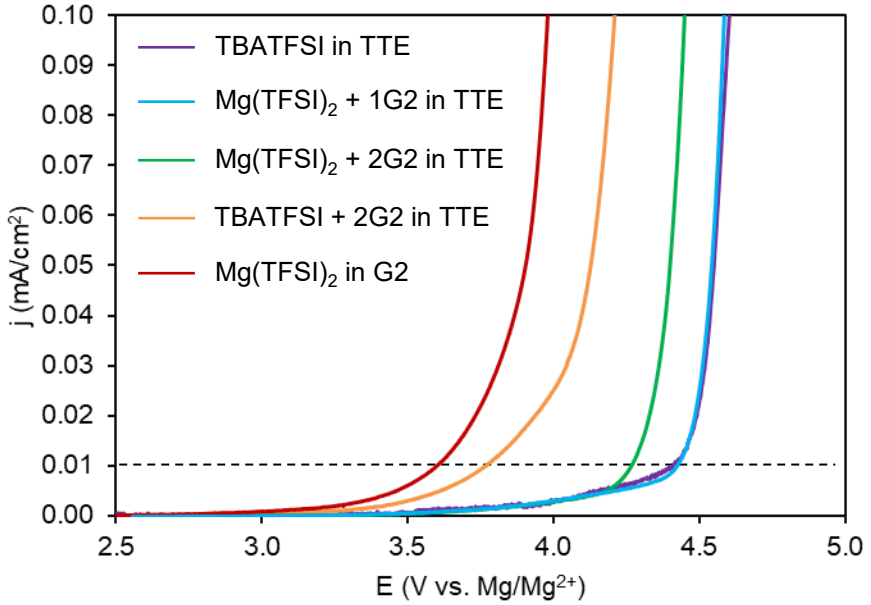
BTFE

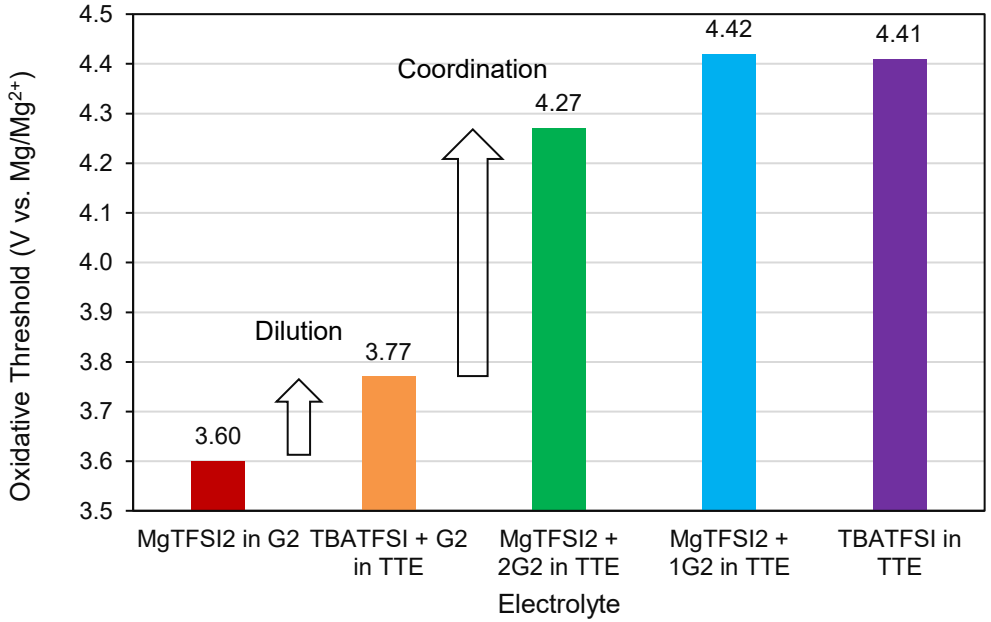


- Glyme structure influences $TFSI^-$ coordination
- HFE structure doesn't influence $TFSI^-$ coordination

Impact of Coordination on Oxidative Stabilization

Pt WE
Mg CE
Ag/Ag$^+$ RE (calibrated using Fc/Fc$^+$)
LSV @ 1 mV/s



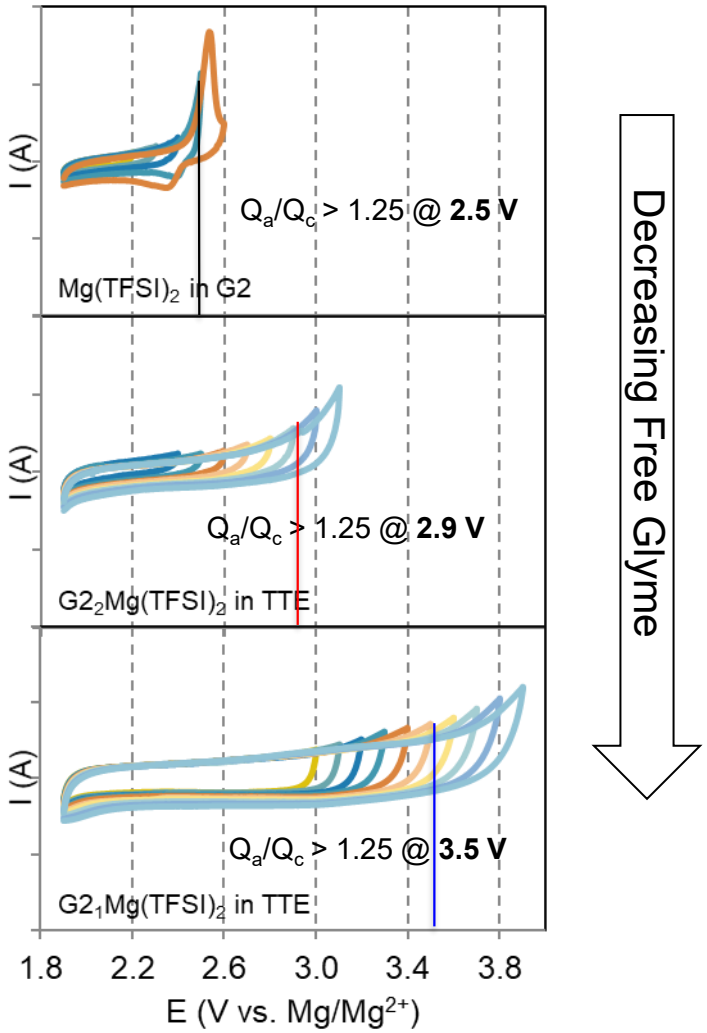


- Selective G2 coordination enables > 0.5 V oxidative stabilization

Stabilization on Oxide Cathode Surfaces

Progressive CV on $MgCr_2O_4$ Spinel

$MgCr_2O_4$/Mo WE
Mg CE
Ag/Ag^+ RE
CV @ 10 mV/s

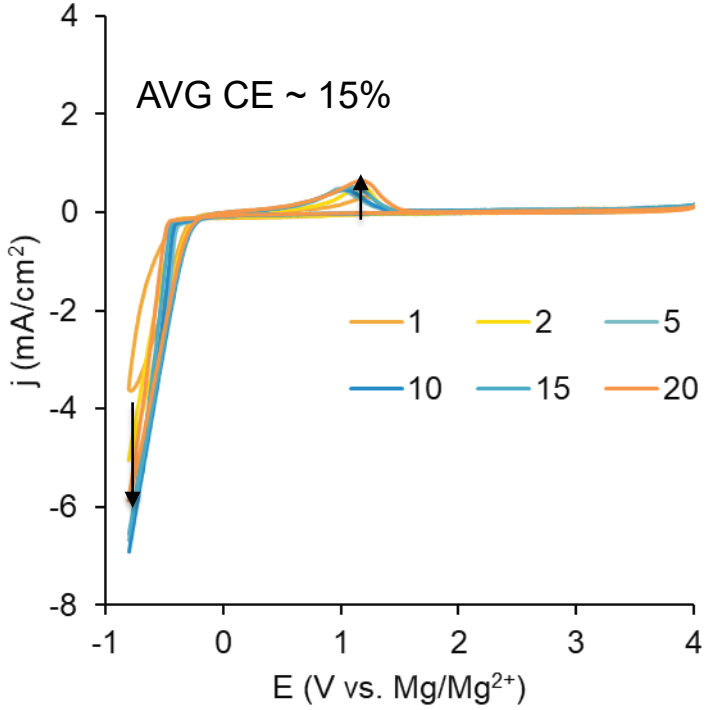


- Similar magnitude of stabilization cathode vs. Pt surface

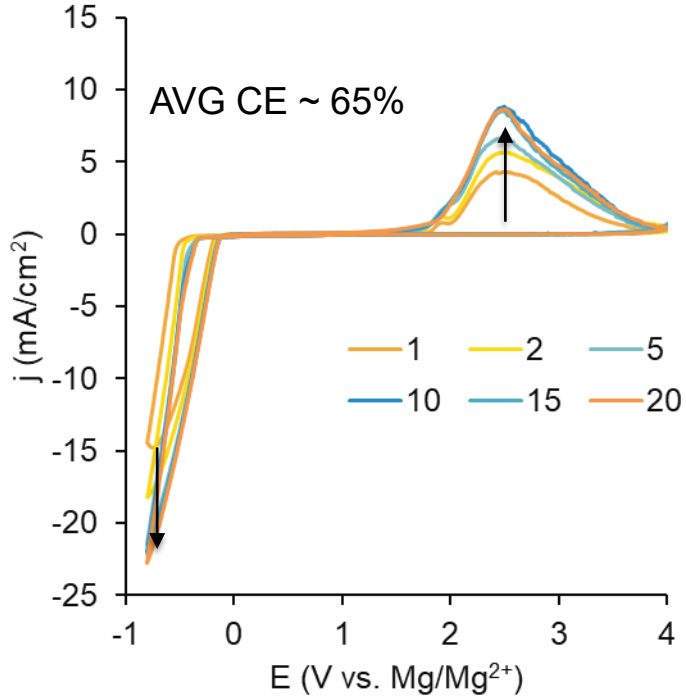
Mg Cycling in HFE Co-Solvents

Pt WE
Mg CE
Ag/Ag$^+$ RE
CV @ 50 mV/s

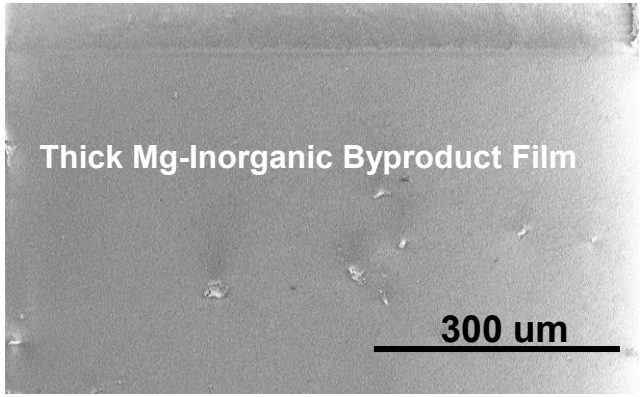
$Mg(TFSI)_2$ + 2G2 in TTE

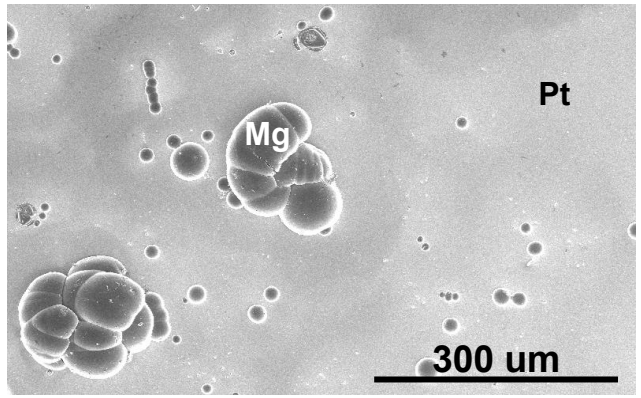


$Mg(TFSI)_2$ + 2G2 in BTFE



Mg Deposit SEM:
(2 mA/cm^2)

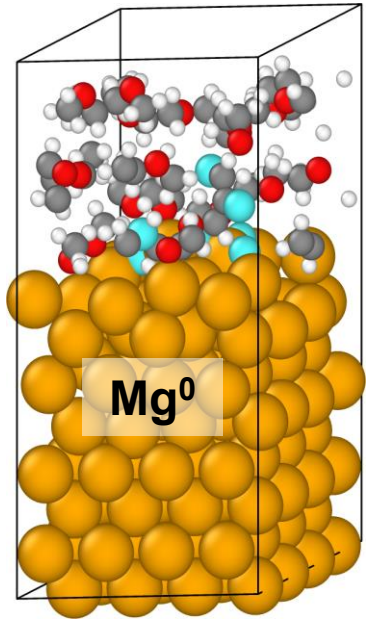


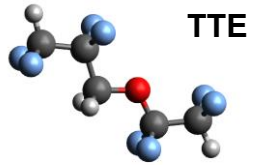


Predicted Impact of HFE on Reductive Stability

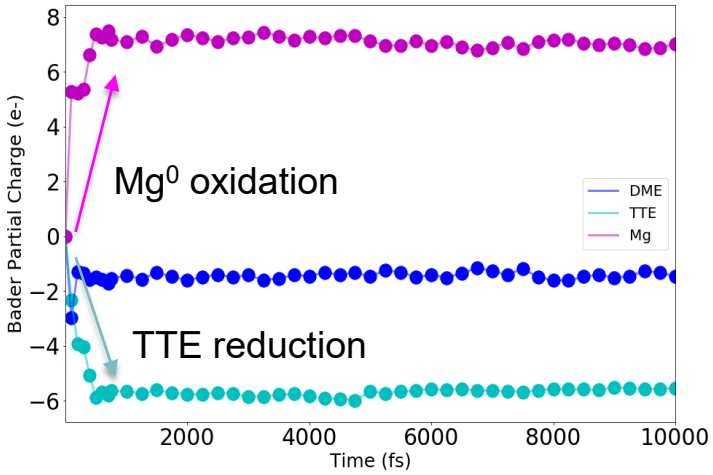
AIMD Simulations
Lei Cheng grp

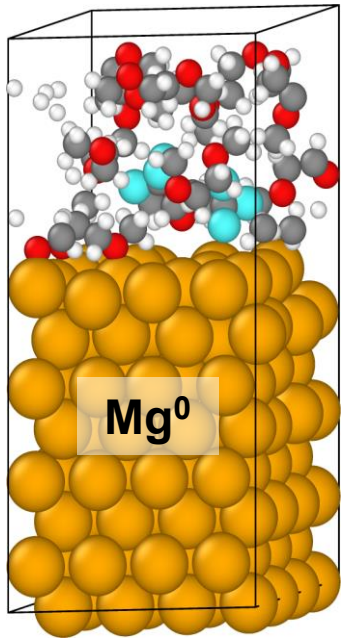
Argonne NATIONAL LABORATORY

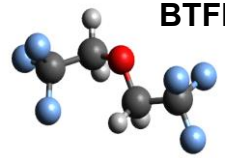




TTE







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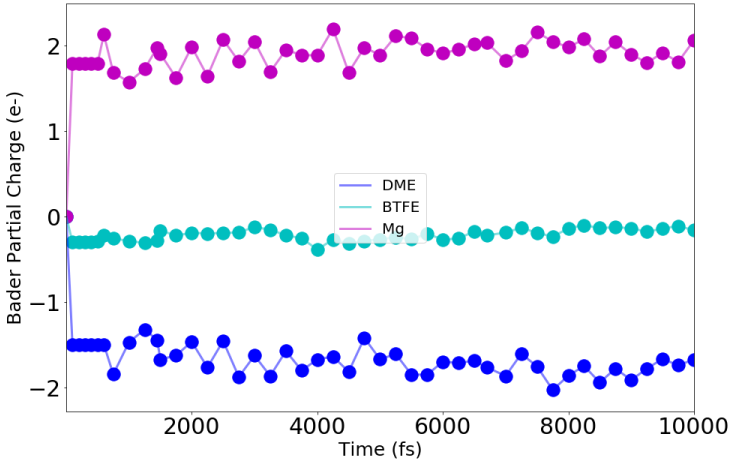
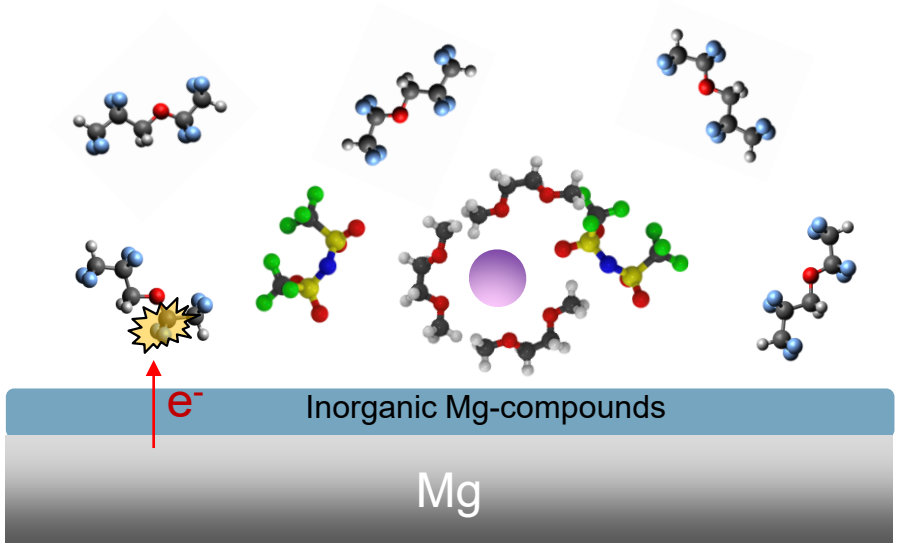


- TTE reduction <u>is</u> a significant driver of parasitic chemistry
- BTFE reduction <u>is not</u> a significant driver of parasitic chemistry

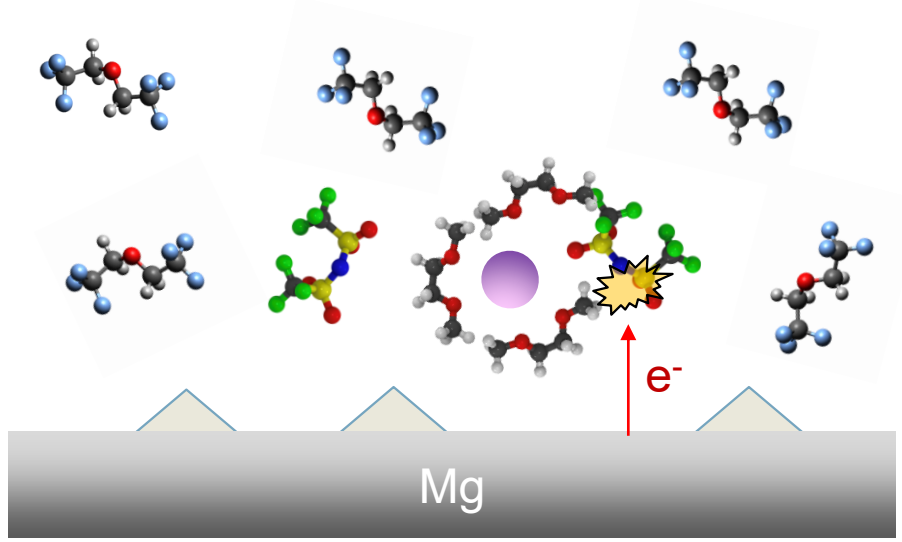
Impact of HFE on Mg Deposition/Reactivity

TTE Electrolyte



Limited by HFE Reduction

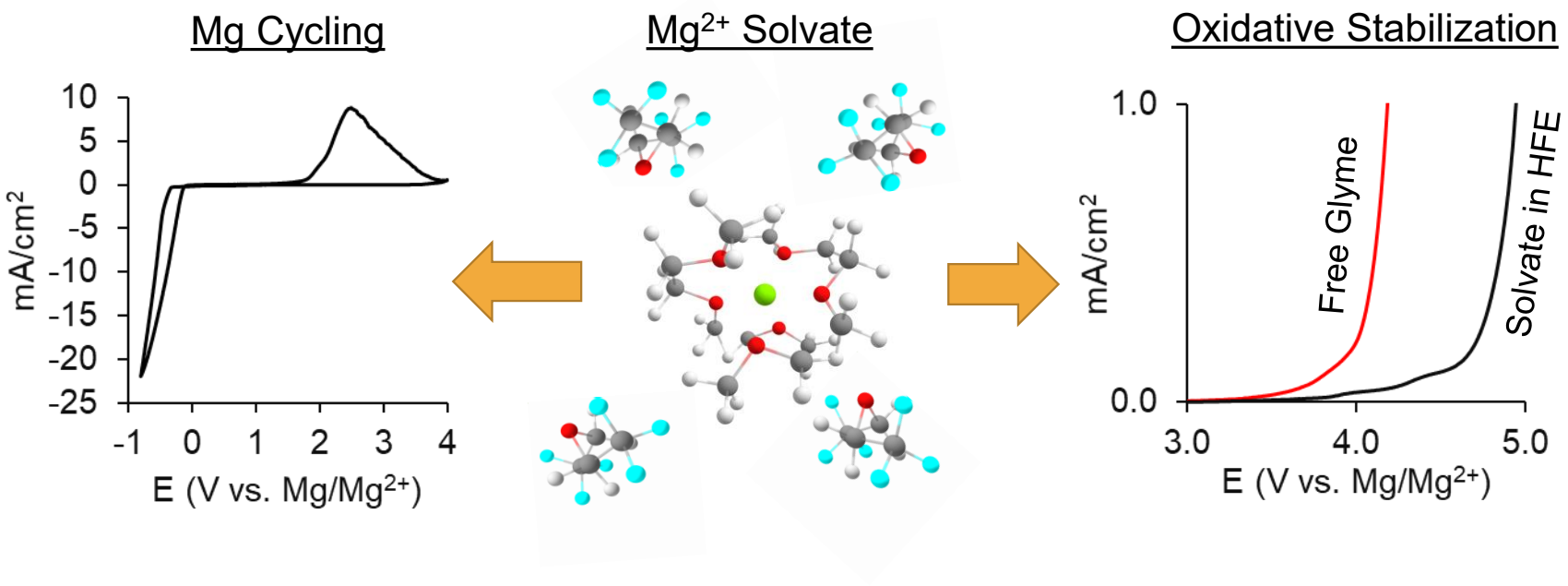
BTFE Electrolyte



Limited by Mg-TFSI- Reduction

Key Takeaways

- Selective solvation enables HFE-based Mg^{2+} electrolytes for higher voltage batteries
- Coordination selectivity is sensitive to glyme structure but not HFE structure
- Reductive stability is sensitive to HFE structure: BTFE more stable than TTE
- $TFSI^-$ salt becomes the limiting factor in BTFE: better salts needed



Acknowledgement

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