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MANAGING MAGNESIUM ELECTROLYTE/ELECTRODE INTERACTIONS AND REACTIONS

Connecting solvation and interfaces for high voltage Mg electrolytes

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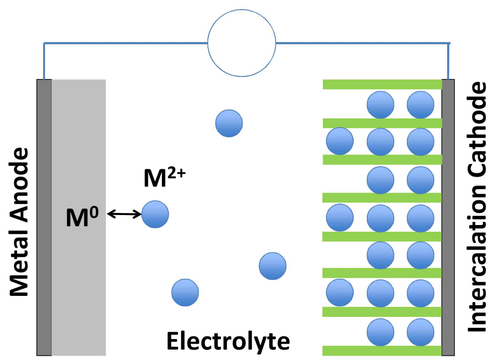
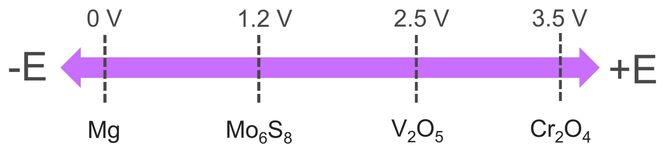
HIGH VOLTAGE DIVALENT BATTERIES

- High voltage Mg batteries offer significant potential for energy storage applications.
- Fundamental understanding concerning the roles of solvation and interface environments is critical for driving key advancements in divalent electrolyte design.
- Electrochemical stability is a critical electrolyte property supporting high efficiency metal plating and high voltage cathode insertion.

HV Divalent Energy Storage



Stability Demands

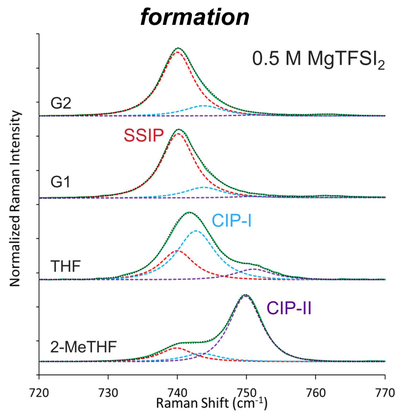


- What species are susceptible at potential extremes?
- What interphases are formed through electrochemical reaction?
- How can we rationally design new electrolytes or interphases?

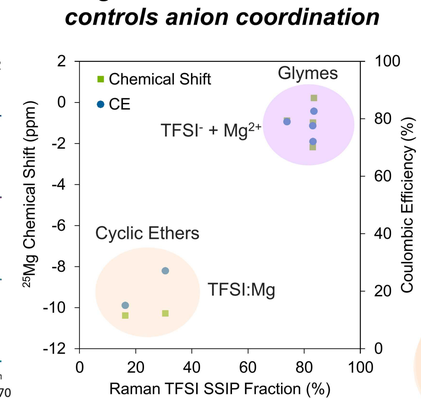
SOLVENT LINKS COORDINATION TO EFFICIENCY[2]

- Theory points to TFSI:Mg^{2+} CIPs as precursors for TFSI decomposition.[3]
- Cyclic ethers allow significant TFSI:Mg^{2+} interactions whereas glymes do not.
- Solvent regulation of these interactions is critical to facilitate high coulombic efficiency for Mg deposition.

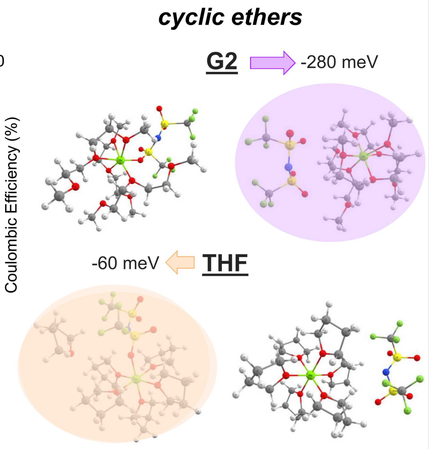
Raman: Solvent controls CIP formation



25Mg NMR: Solvent structure controls anion coordination



DFT: CIP more favorable in cyclic ethers

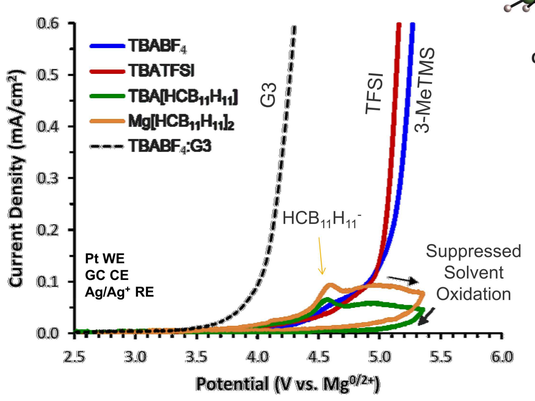


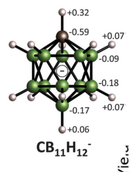
➢ ***First generalized experimental causal relationship between TFSI:Mg^{2+} coordination and Mg deposition efficiency***

ANION STABILIZATION AT CATHODE INTERFACES[1]

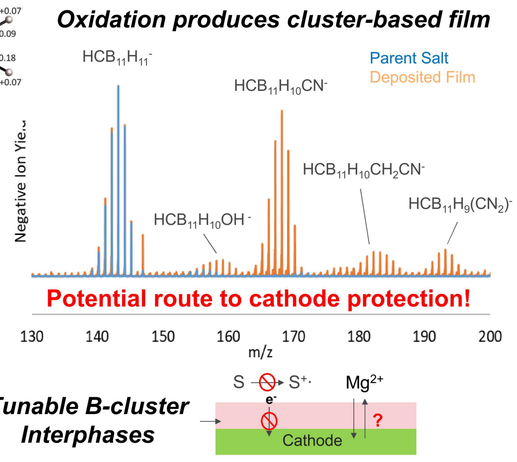
- Oxidative stability/behavior of $Mg(HCB_{11}H_{11})_2$ electrolytes is not well understood
- Previous claims of extreme anion stability masked by unique $CB_{11}H_{12}^-$ film protection process

$HCB_{11}H_{11}^-$ less stable than TFSI, BF_4





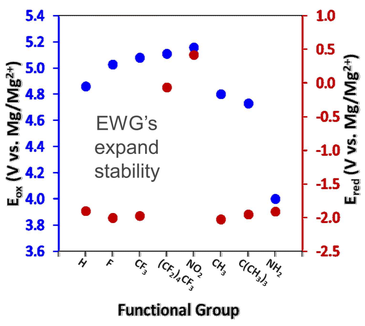
Oxidation produces cluster-based film



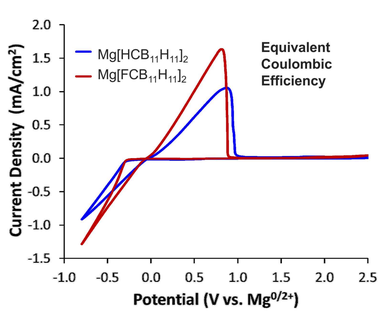
Tunable B-cluster Interphases

- Integrated computational/experimental approach promises route to expansion of anion stability
- Synthesis and electrochemical testing validates the predicted stability gain

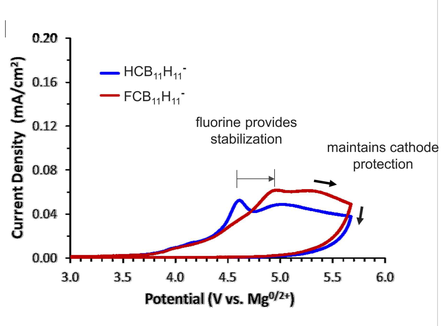
Computational Prediction



Maintenance of Reductive Stability



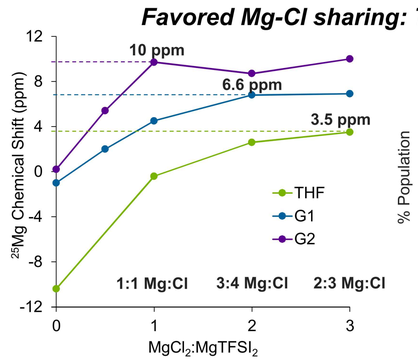
Increase in Oxidative Stability

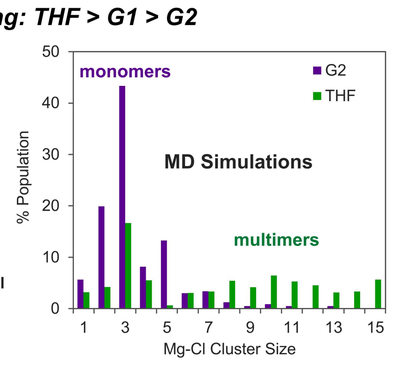


REGULATION OF MAGNESIUM SPECIATION[2]

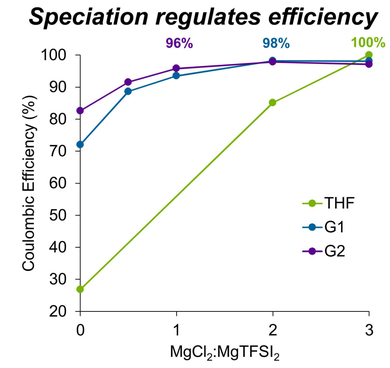
- Cationic chloride clusters in mixed salt systems ($MgCl_2$:$MgTFSI_2$) are dictated by solvent structure: longer glymes favor monomeric species

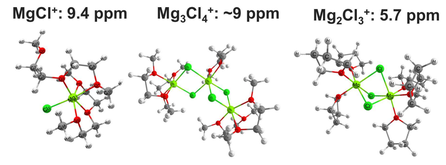
Favored Mg-Cl sharing: THF > G1 > G2





Speciation regulates efficiency



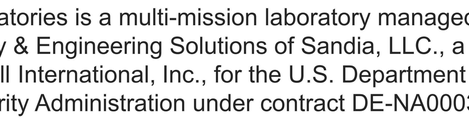


Face-shared dimers (μ_3-Cl) energetically favored only in THF

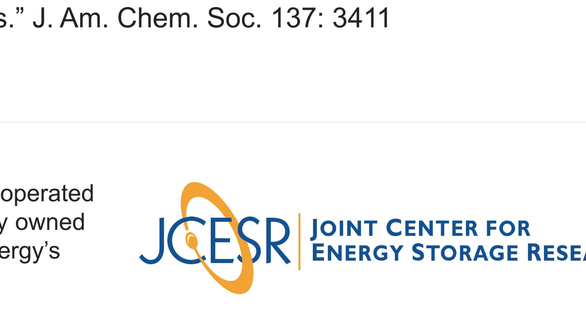
Reaction	ΔG (eV)
$MgCl{\cdot}THF^+ + MgCl_2{\cdot}THF \rightarrow Mg_2Cl_3{\cdot}THF^+$ (μ_3)	-0.60
$MgCl{\cdot}G1^+ + MgCl_2{\cdot}G1 \rightarrow Mg_2Cl_3{\cdot}G1^+$ (μ_3)	0.40
$MgCl{\cdot}G2^+ + MgCl_2{\cdot}G2 \rightarrow Mg_2Cl_3{\cdot}G2^+$ (μ_2)	0.67

- Interfacial spectroscopy bridges the gap between bulk speciation and metal deposition efficiency

100% CE despite 22% TFSI CIP?



XAS: Species in Bulk ≠ Species at Interface



TFSI-species are displaced from the electrode

CONCLUSIONS

- Functionalization is a viable strategy for tuning electrolyte stability and transport properties.
- Facile carborane anion oxidation could offer a route to protective solid electrolyte interphases by tuning film structure and composition.
- Displacement of TFSI from either Mg^{2+} coordination or from the electrode interface decreases parasitic cathodic reaction.
- Mg-Cl coordination structure varies dramatically with ether – the key to zero parasitic charge is creation of the μ_3-Cl face-shared dimer.

NEXT STEPS

- Design and characterization of boron cluster anion derived surface films to establish Mg^{2+} transmission while sparing solvent oxidation
- Determination of competitive solvent/anion/cation interactions across diverse weakly coordinating anion and solvent space to link divalent cation solvation environments to stability and transport
- Deeper understanding of how the solvation environment is perturbed by the electrified interface facilitating metal cation delivery vs. parasitic pathways

REFERENCES

[1]Hahn, N., et al. (2018). "Enhanced Stability of the Carba-closo-dodecaborate Anion for High-Voltage Battery Electrolytes through Rational Design" J. Am. Chem. Soc. 140: 11076.

[2]Hahn, N., et al. (2018). "Solvation Environment Regulation of Magnesium Speciation and Deposition." *in preparation*

[3]Rajput, N., et al. (2015). "The Coupling between Stability and Ion Pair Formation in Magnesium Electrolytes from First-Principles Quantum Mechanics and Classical Molecular Dynamics." J. Am. Chem. Soc. 137: 3411

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