SAND2020-11881C

2020 VIRTUAL MRS® SPRING/FALL MEETING & EXHIBIT

November 27 – December 4, 2020

mrs.org/spring-fall-2020

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2020 VIRTUAL MRS® SPRING/FALL MEETING & EXHIBIT

JCESR

Divalent Electrolytes: From Mg^{2+} to Ca^{2+}

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Presentation No. S.EN08.02.05

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Sandia National Laboratories

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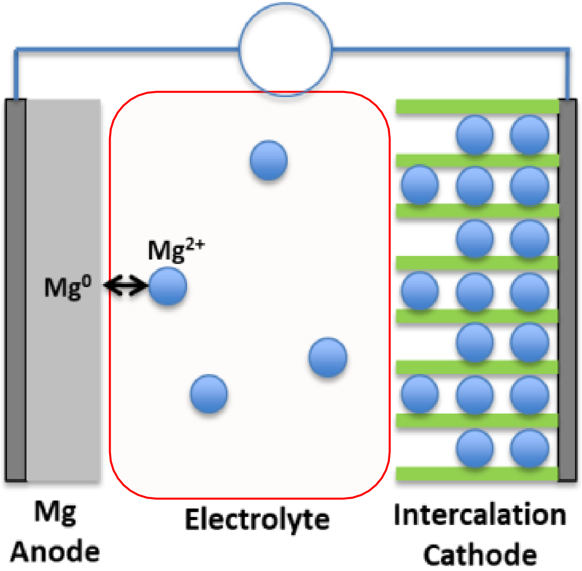
Opportunities for Divalent Electrolytes

- Mg^{2+} and Ca^{2+} both offer potential paths to ≥ 400 Wh/l batteries

Mg: 3800 mAh/l

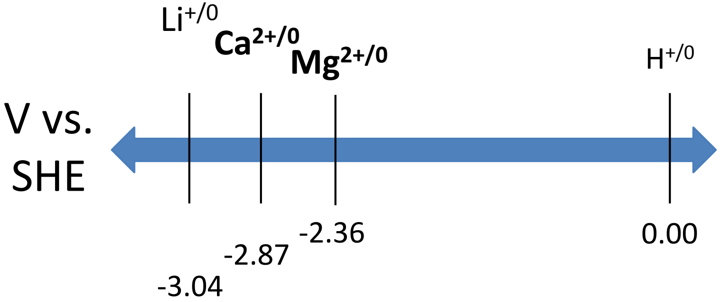
Ca: 2100 mAh/l



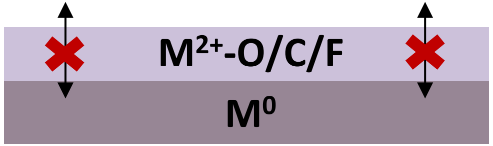
> 99.9% CE

> 3.0 V

Stability Challenges



Interfacial Passivation



Parallel Development Pathways

Ethereal solvents

Mg^{2+}

Reducing Agents, Chloro-complexes	Weakly Coordinating Salts	Solvent Oxidation?
PhMgCl, $MgCl_2$, $AlCl_3$, **$Mg(BH_4)_2$**	$Mg(TFSI)_2$, $Mg(CB_{11}H_{12})_2$ $Mg(BHFIP)_2$	**?**

Ca^{2+}

Reducing Agents	Weakly Coordinating Salts	Anion vs. Solvent Reduction?
$Ca(BH_4)_2$	$Ca(BHFIP)_2$	**?**

Solvation is Cation Dependent

Why Calcium? How Calcium Became the Best Communicator*

Published, JBC Papers in Press, July 26, 2016, DOI 10.1074/jbc.R116.735894

Ernesto Carafoli[‡1] and Joachim Krebs[§]

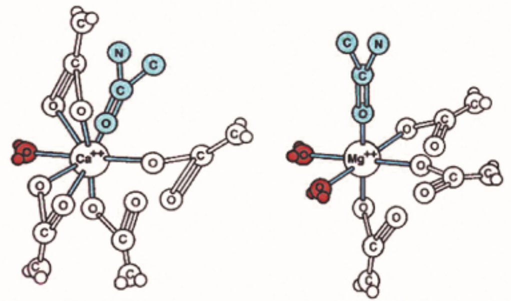
Designing successful multivalent battery electrolytes requires understanding and controlling ion interactions

- Formation and delivery of active species
- Stabilization of the supporting electrolyte

These features depend on the cation →

Properties of un-hydrated and hydrated Ca^{2+} and Mg^{2+}:

	Ionic radius Å	Polarizability $\alpha_0 \times 10^{24}$ cm^3	Hydration energy kcal/g ion	Hydrated ions Å
Ca^{2+}	0.99	0.531	410	4.5
Mg^{2+}	0.65	0.012	495	5.9

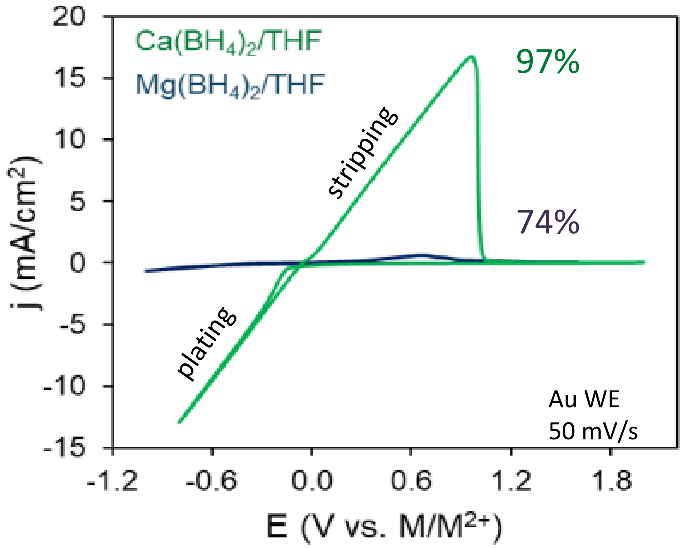


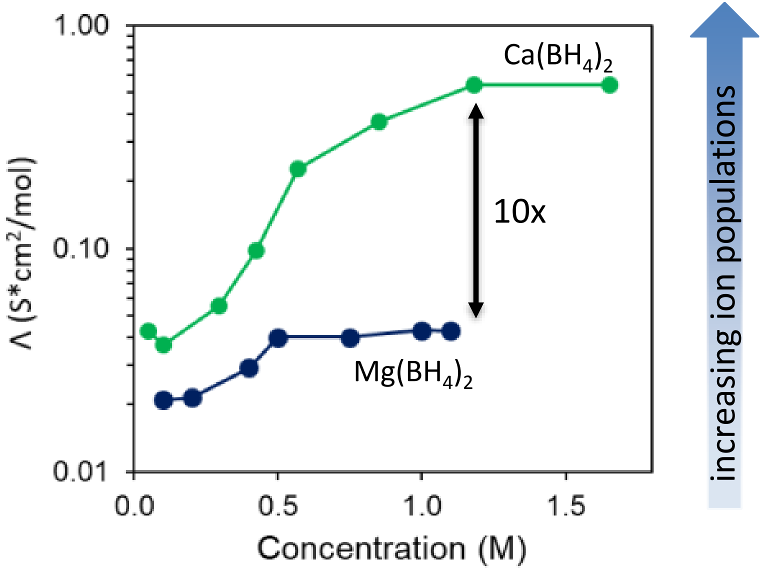
Range of Ca-O distances 0.230-0.282 nm

Range of Mg-O distances 0.200- 0.212 nm

Cation Size Determines Coordination Flexibility

Differences in BH_4 electrolytes





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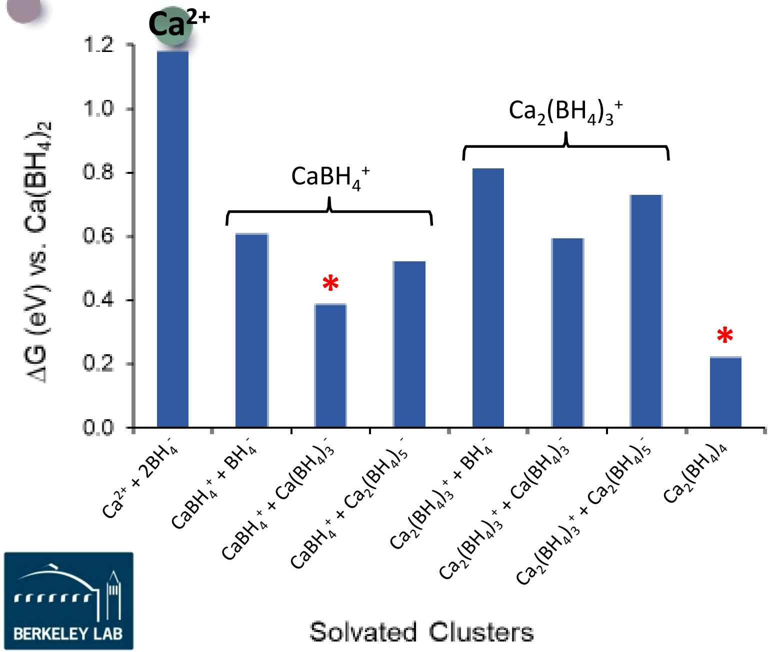
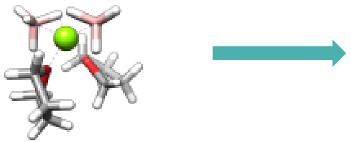
Flexibility Determines Speciation



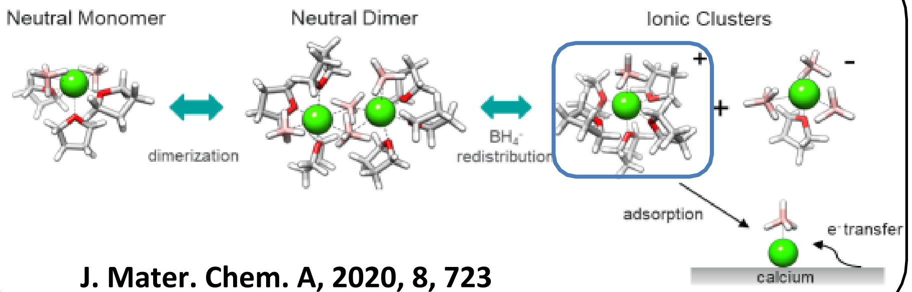
Mg^{2+}

Neutral Monomer



Insufficient active species formation and delivery

Ca^{2+}



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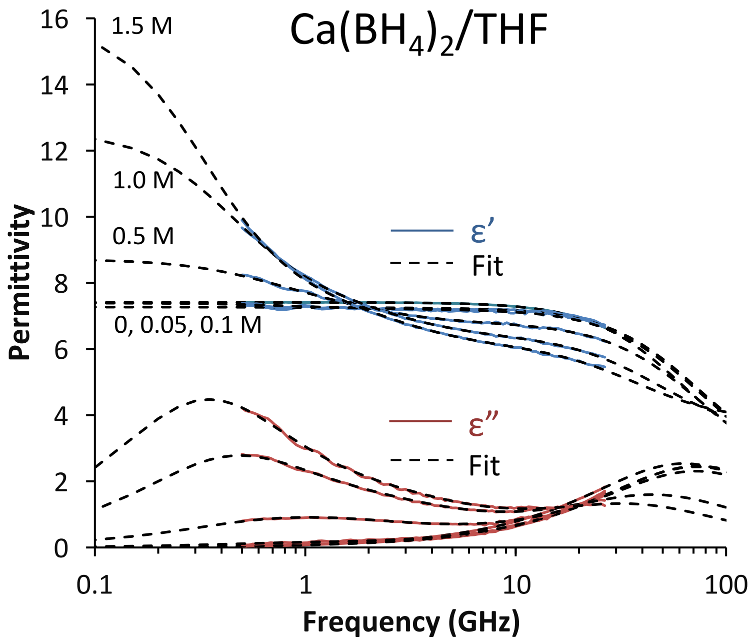
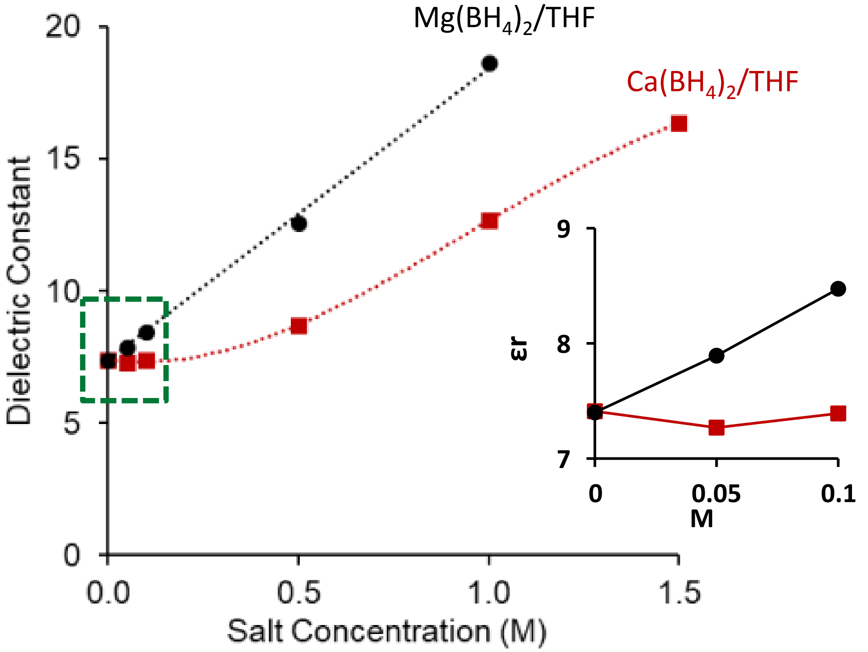
Differences in M^{2+} size produce important differences in speciation

Insight into Divergent Trends

Solution Dipoles Evolve Differently with Concentration

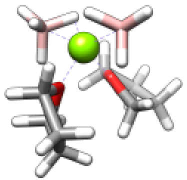




Insight into Divergent Trends

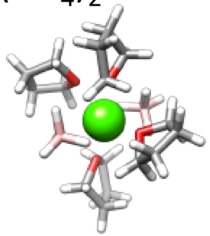
Dielectric Modeling Confirms Dipole Contributions

$Mg(BH_4)_2^0$



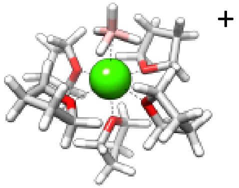
Δε = 8.9 M⁻¹

$Ca(BH_4)_2^0$



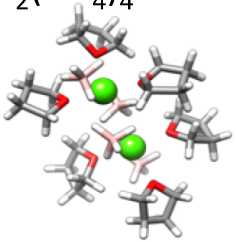
Δε = -2.1 M⁻¹

$CaBH_4^+$

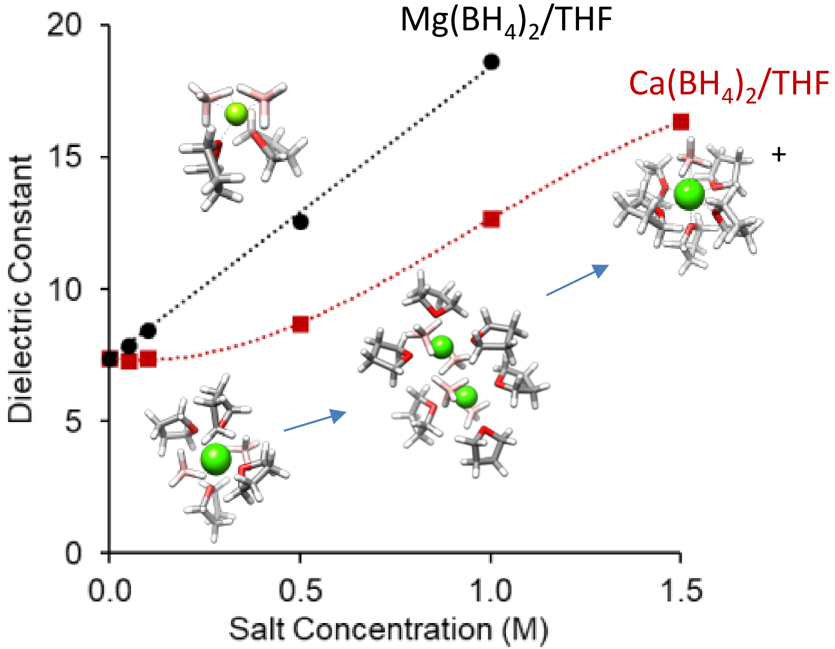


Δε = 20.5 M⁻¹

$Ca_2(BH_4)_4^0$



Δε = 16.3 M⁻¹



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Conclusions

- Despite their similarities, Mg^{2+} and Ca^{2+} exhibit different coordination tendencies, which influence their electrochemical behavior
- The larger size of Ca^{2+} increases the diversity of potential solvation motifs and/or reconfigurability in solution, and presumably at electrified interfaces

Acknowledgements

JCESR Joint Center for Energy Storage Research

Sandia National Laboratories

Kevin Zavadil
Scott McClary

BERKELEY LAB

Kristin Persson
Trevor Seguin
Julian Self

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