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Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance

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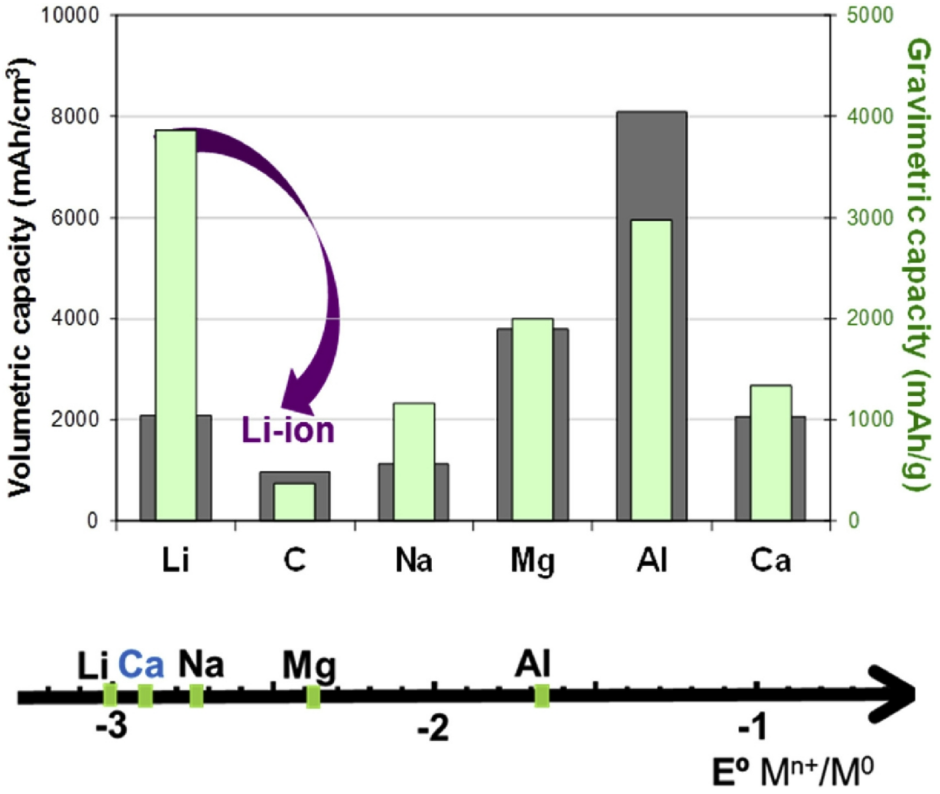
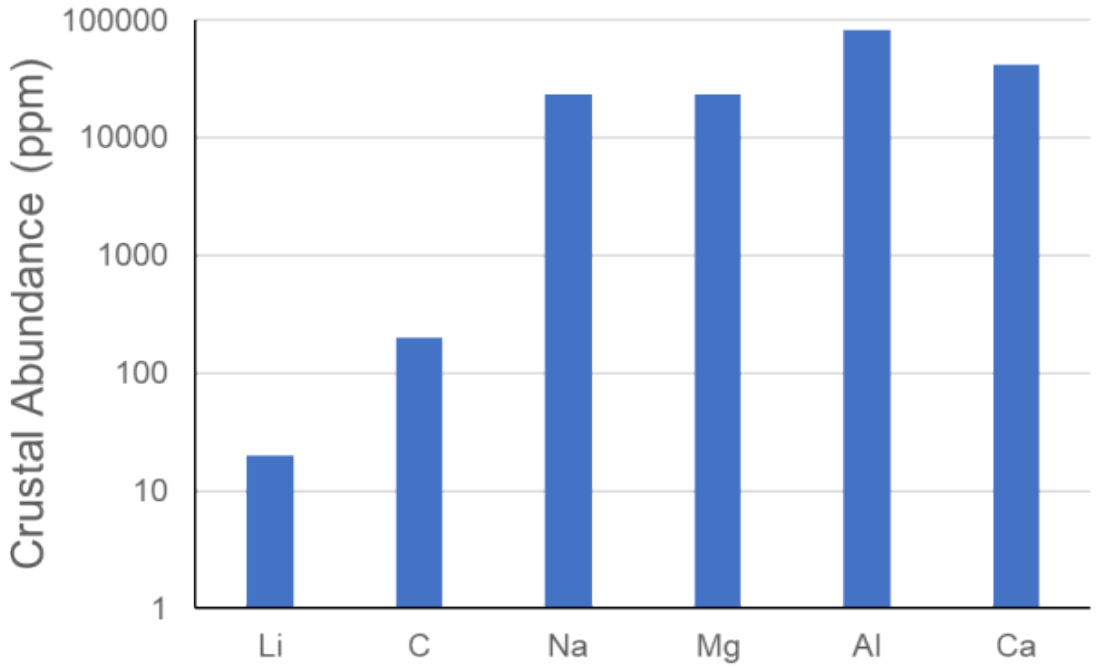
Beyond lithium-ion batteries are needed for emerging energy storage applications



Ponrouch, A., et. al., *Energy Storage Mater.*, **2019**, 20, 253.

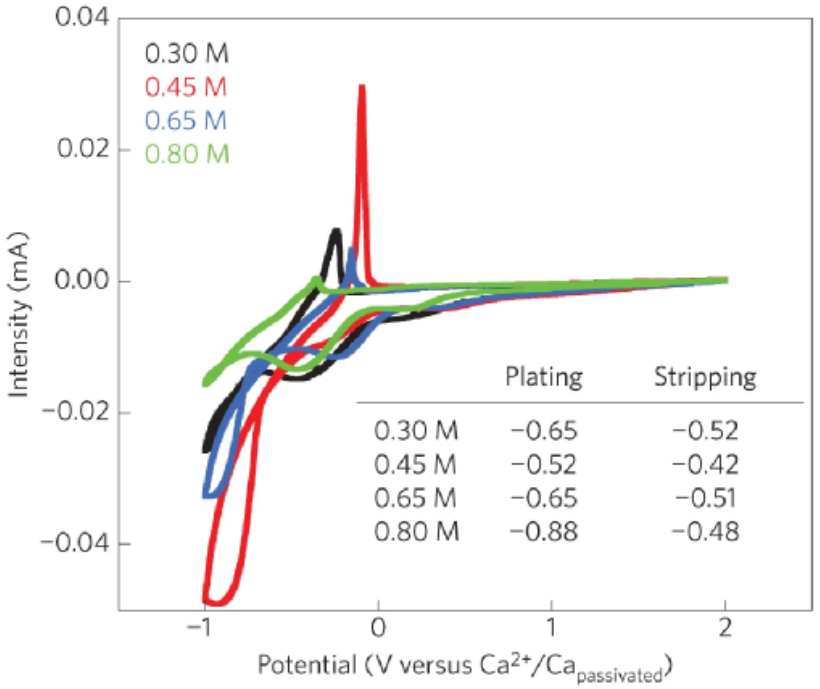


Data from: *CRC Handbook of Chemistry and Physics*, 97th ed. 2016-2017.

Ca metal batteries could provide higher energy densities at lower costs and fewer supply chain limitations than Li-ion batteries

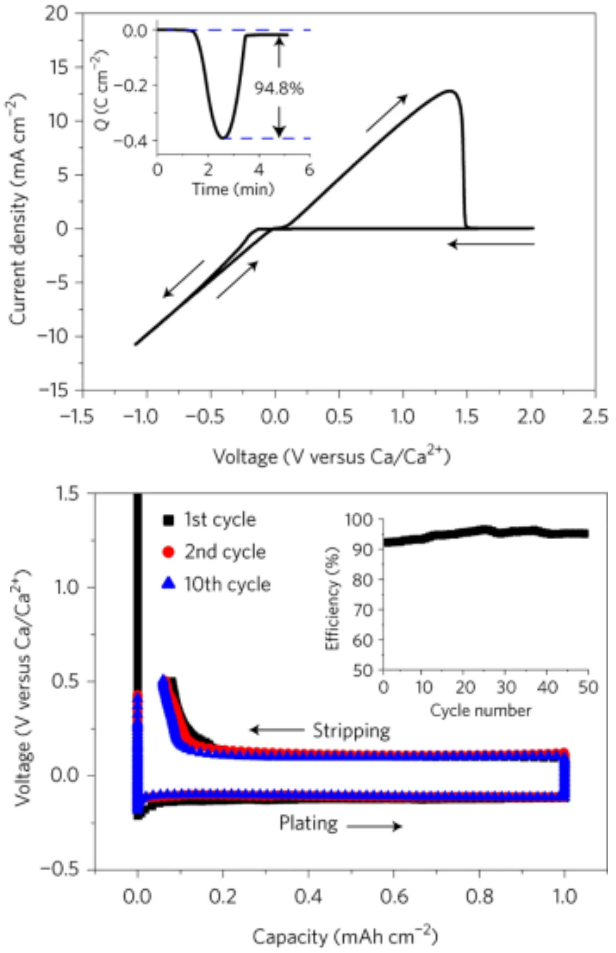
Development of practical calcium-ion electrolytes has been limited

High temperature Ca plating and stripping from carbonate electrolytes



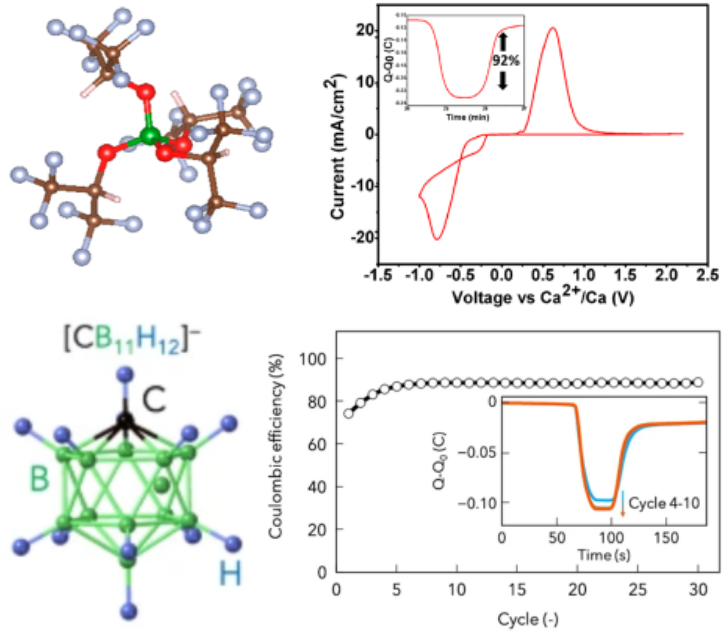
Ponrouch, A., et. al., *Nat. Mater.*, **2016**, *15*, 169.

Room temperature Ca plating and stripping from $Ca(BH_4)_2$/THF



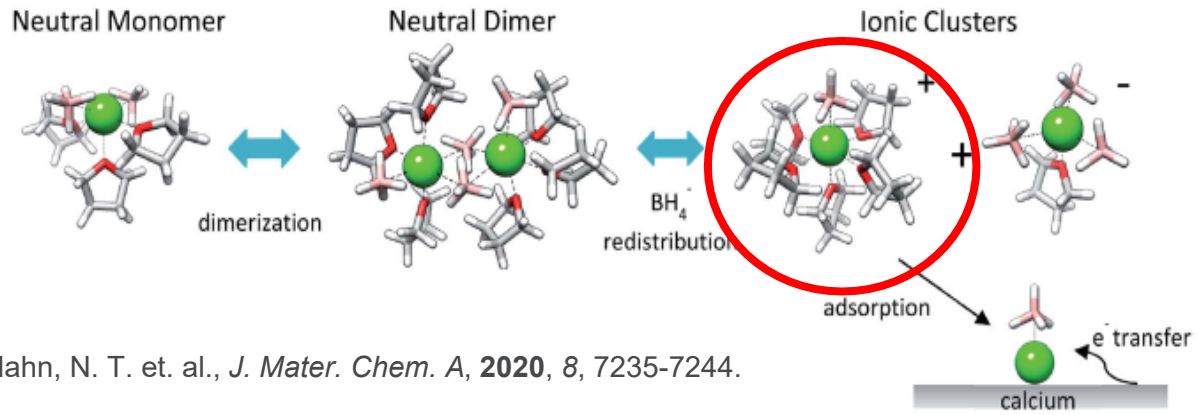
Wang, D., et. al., *Nat. Mater.*, **2018**, *17*, 16.

Weakly Coordinating Ca Salts

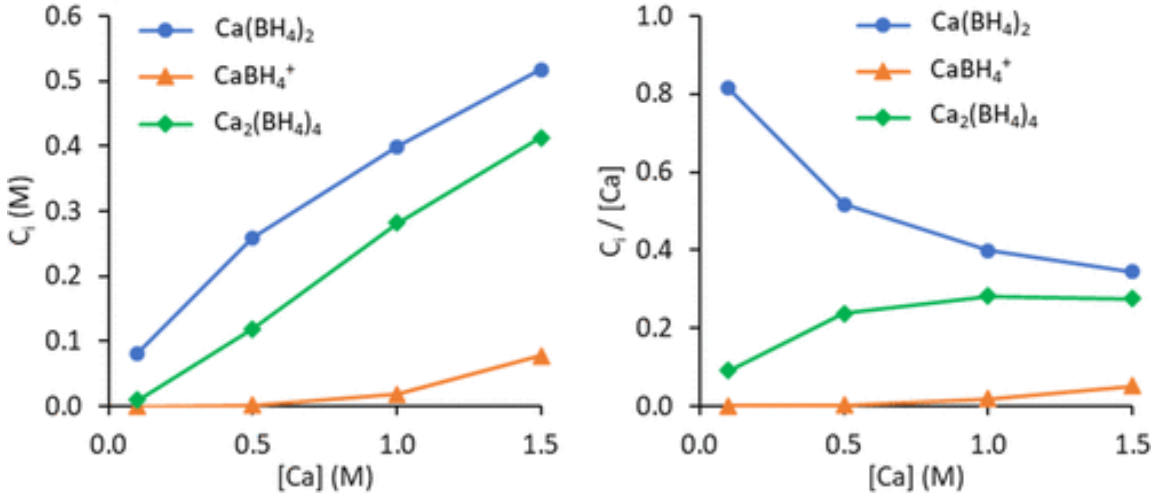


$Ca(BHFIP)_2$
Shyamsunder, A., et. al., *ACS Energy Lett.*, **2019**, *4*, 2271
Li, Z., et. al., *Energy Environ. Sci.*, **2019**, *12*, 3496.
$Ca(CB_{11}H_{12})_2$
Kisu, K., et. al., *Sci. Reports.*, **2021**, *11*, 7563.
$Ca(TPFA)_2$
Leon, N., et. al., *J Phys. Chem. C.*, **2022**, *Article ASAP*.

A minority species is responsible for reversible Ca cycling in $Ca(BH_4)_2$/THF



Hahn, N. T. et. al., *J. Mater. Chem. A*, **2020**, *8*, 7235-7244.

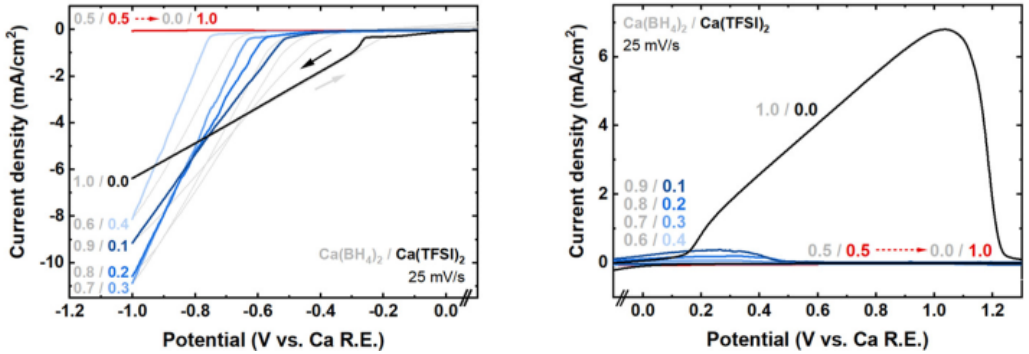


Hahn, N. T. et. al., *J. Phys. Chem. B*, **2021**, *125*, 3644-3652.

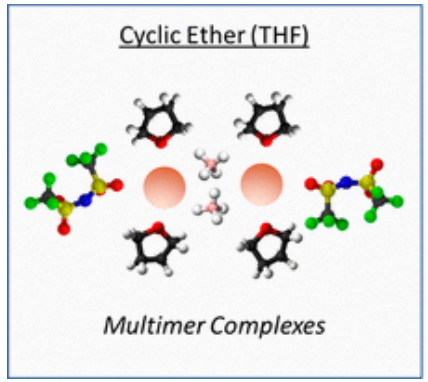
Hypothesis 1: Increasing concentration of active species improves electrochemical performance

Hypothesis 2: Addition of weakly coordinating Ca salt to $Ca(BH_4)_2$/THF increases active species concentration

$$Ca(BH_4)_2 + CaWCA_2 \leftrightarrow 2CaBH_4^+ + 2WCA^-$$



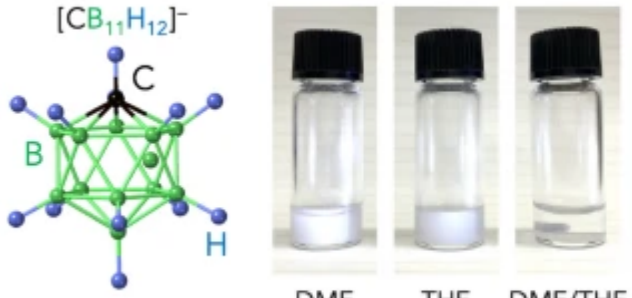
Gallant, B. M., et. al., *J. Phys. Chem. C*, **2022**, *126*, 892-902.

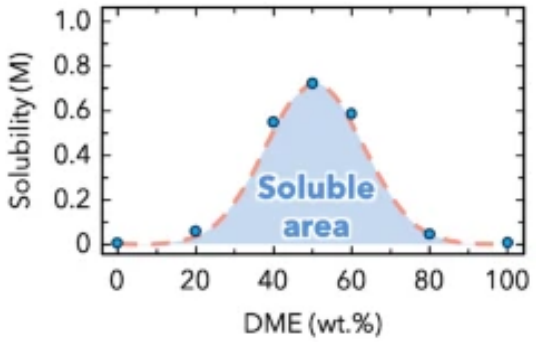


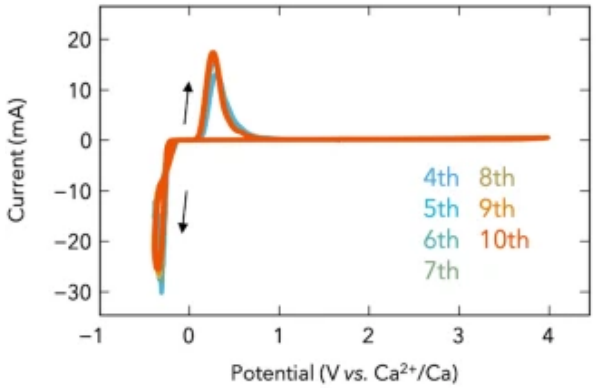
Hahn, N. T., et. al., *J. Phys. Chem. C*, **2022**, *126*, 10335-10345.

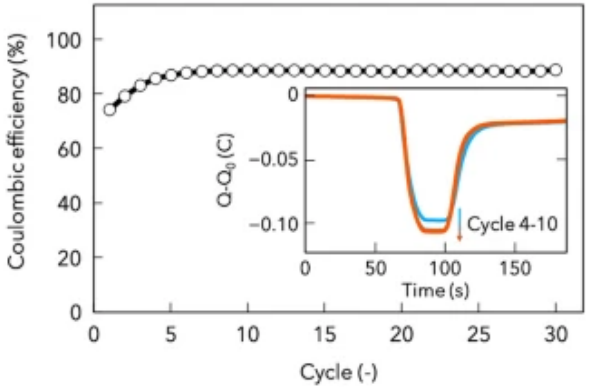
Attempts to use $Ca(TFSI)_2$ as weakly coordinating salt prevent Ca stripping and show complex speciation

$Ca(CB_{11}H_{12})_2$ serves as a model weakly coordinating salt









Kisu, K., et. al., *Sci. Reports,* **2021**, *11*, 7563.

New Synthesis Route

$$2TMAHCB_{11}H_{12} + Ca(BH_4)_2 \rightarrow 2TMA(g) + 2H_2(g) + 2BH_3(g) + Ca(CB_{11}H_{12})_2\ (s)$$

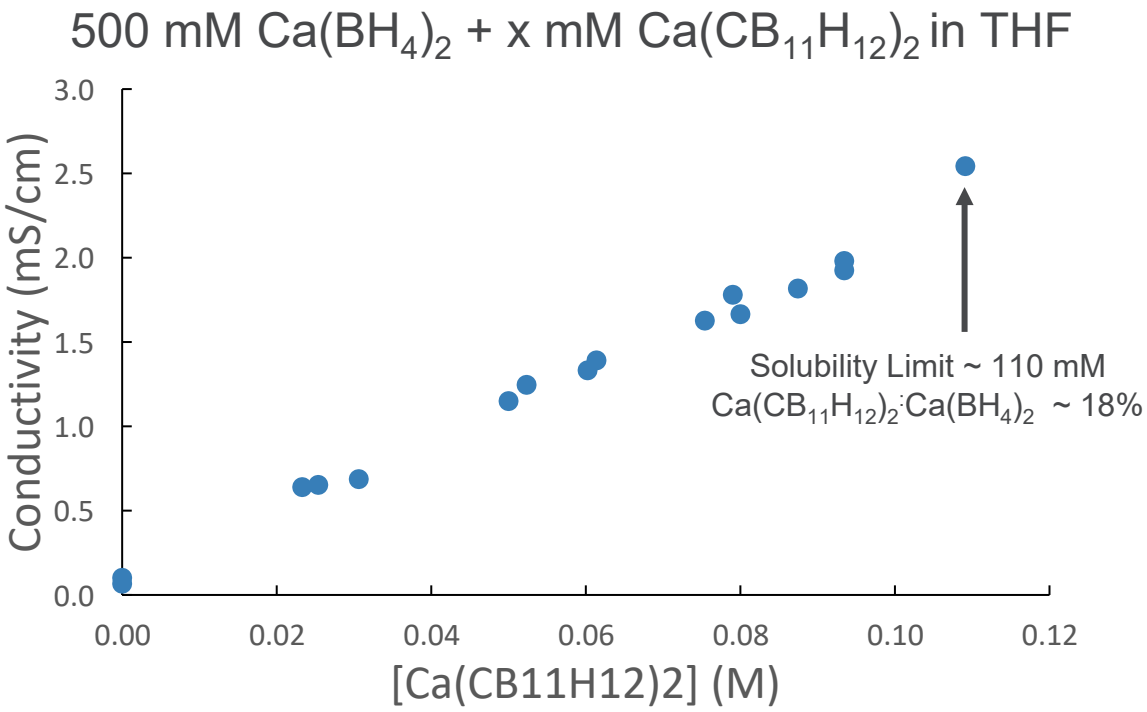
Proposed Speciation Reaction

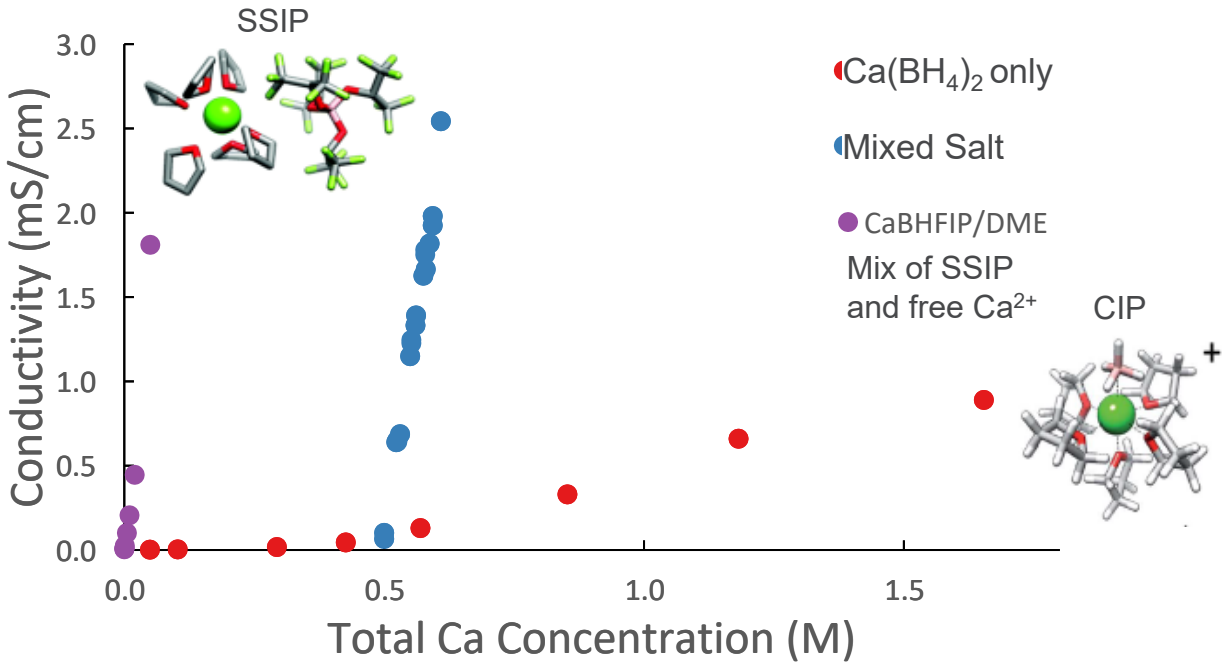
$$Ca(BH_4)_2 + Ca(CB_{11}H_{12})_2 \leftrightarrow 2CaBH_4^{+} + 2CB_{11}H_{12}^{-}$$

Reductive stability of $CB_{11}H_{12}^-$ anion enables wider range of electrochemical experiments

Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

Large changes in apparent ionicity signal speciation change





$Ca(BHFIP)_2$/DME data from Hahn, N. T., et. al., *Phys. Chem. Chem. Phys.*, **2022**, *24*, 674.

Conductivity comparison suggests possibility of SSIPs or free Ca^{2+} in solution

Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

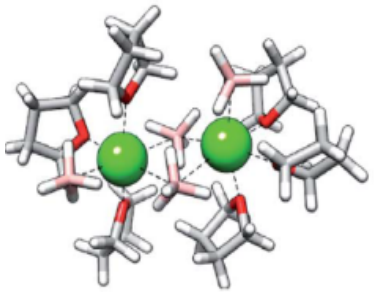
Added $Ca(CB_{11}H_{12})_2$ produces predominantly solvent coordinated Ca

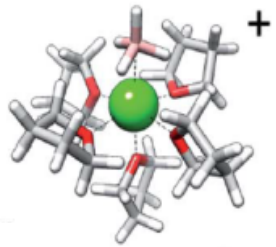
Downfield shift with added $Ca(BH_4)_2$

Upfield shift with added $Ca(CB_{11}H_{12})_2$

Upfield shift expected for non-BH_4^--coordinated Ca

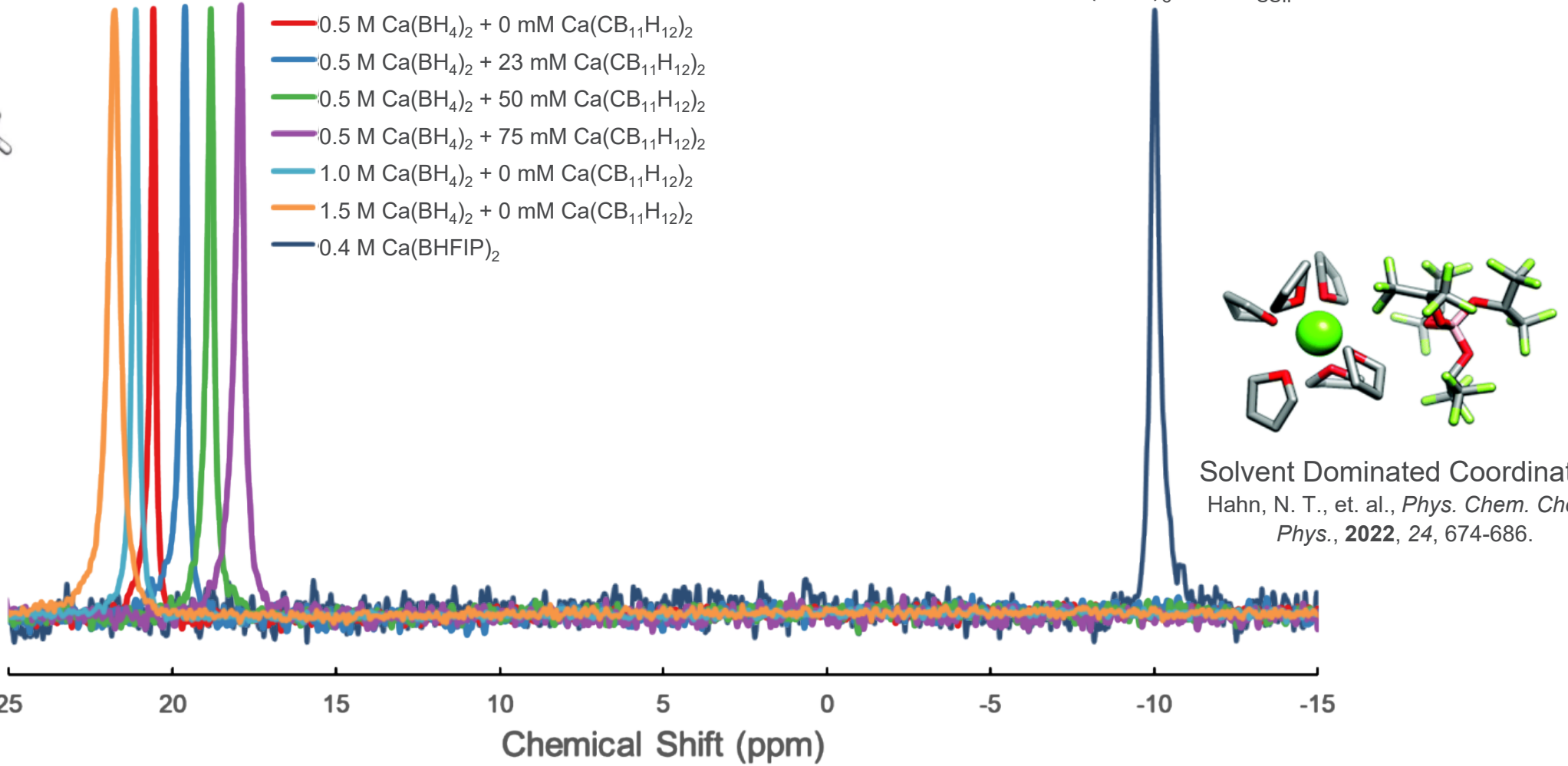
90% $Ca(THF)_6^{2+}$
10% $Ca(THF)_6BHFIP_{SSIP}^+$





BH_4^- Dominated Coordination

Hahn, N. T. et. al., *J. Mater. Chem. A*, **2020**, *8*, 7235-7244.

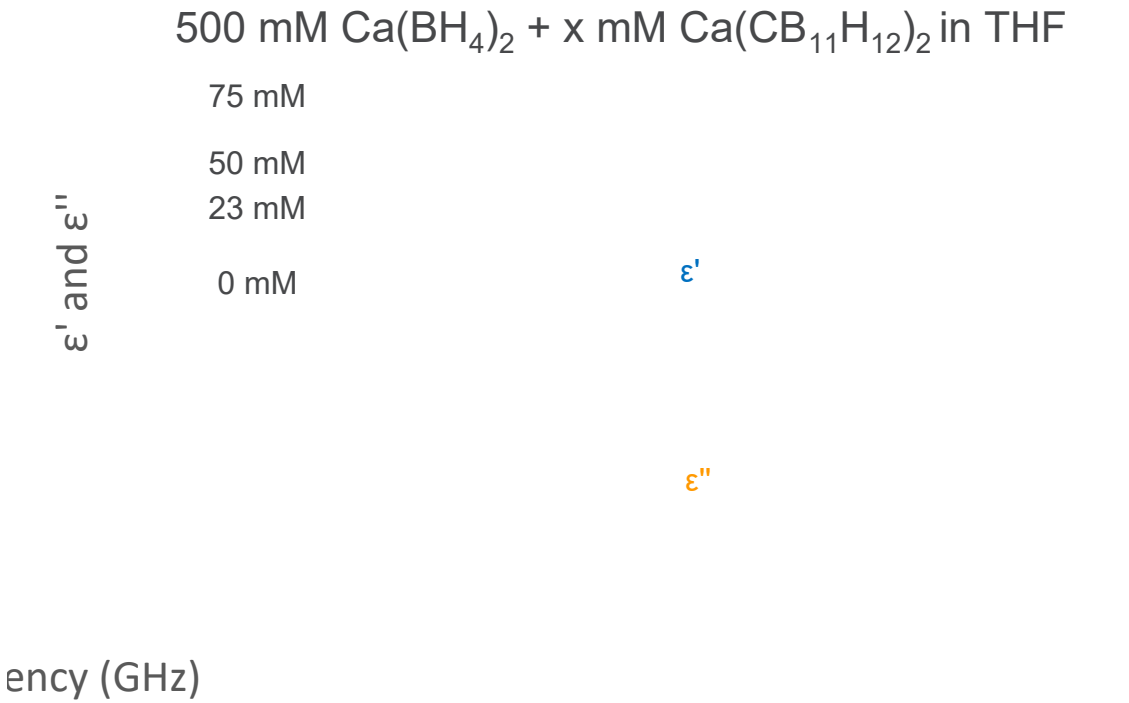


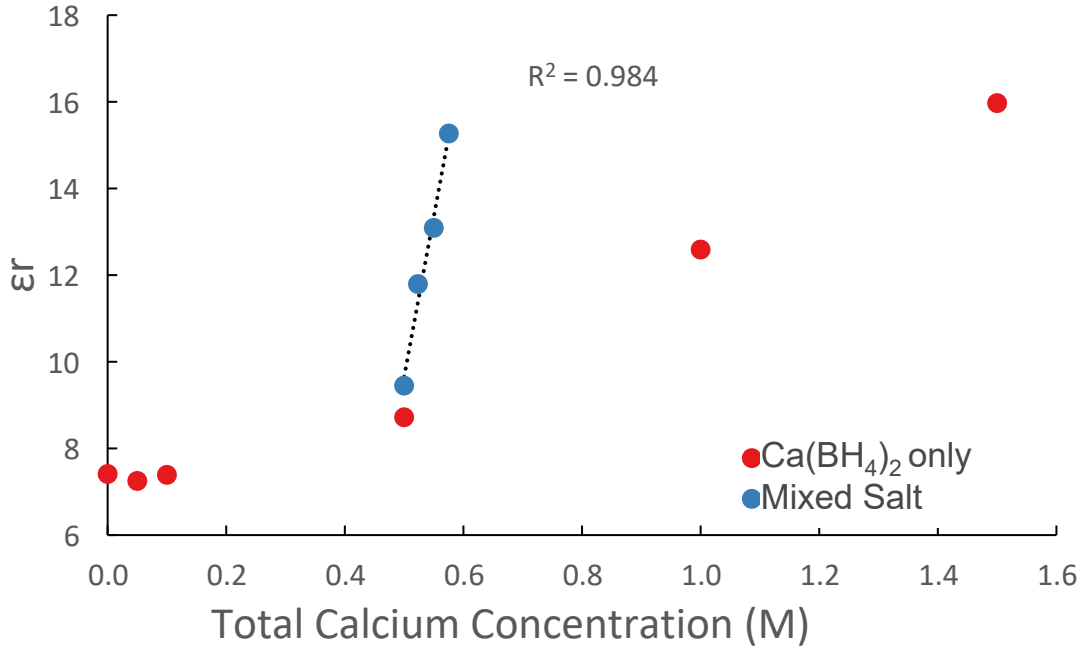
Solvent Dominated Coordination

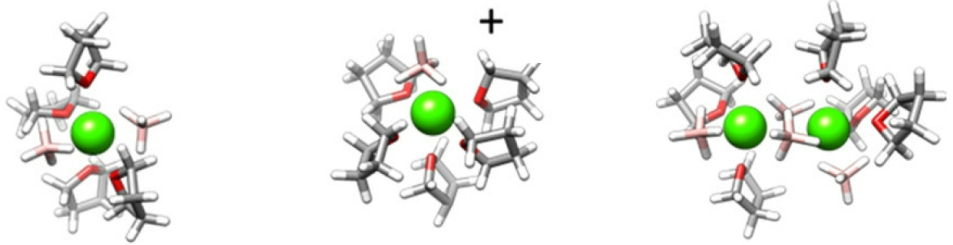
Hahn, N. T., et. al., *Phys. Chem. Chem. Phys.*, **2022**, *24*, 674-686.

Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

A large fraction of added $Ca(CB_{11}H_{12})_2$ exists as SSIPs

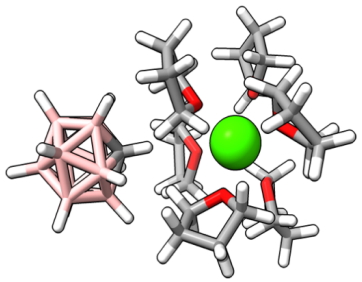






$\Delta\varepsilon = -2.1\ M^{-1}$ $\Delta\varepsilon = 20.5\ M^{-1}$ $\Delta\varepsilon = 16.3\ M^{-1}$

Hahn, N. T. et. al., *J. Mater. Chem. A*, **2020**, *8*, 7235-7244.

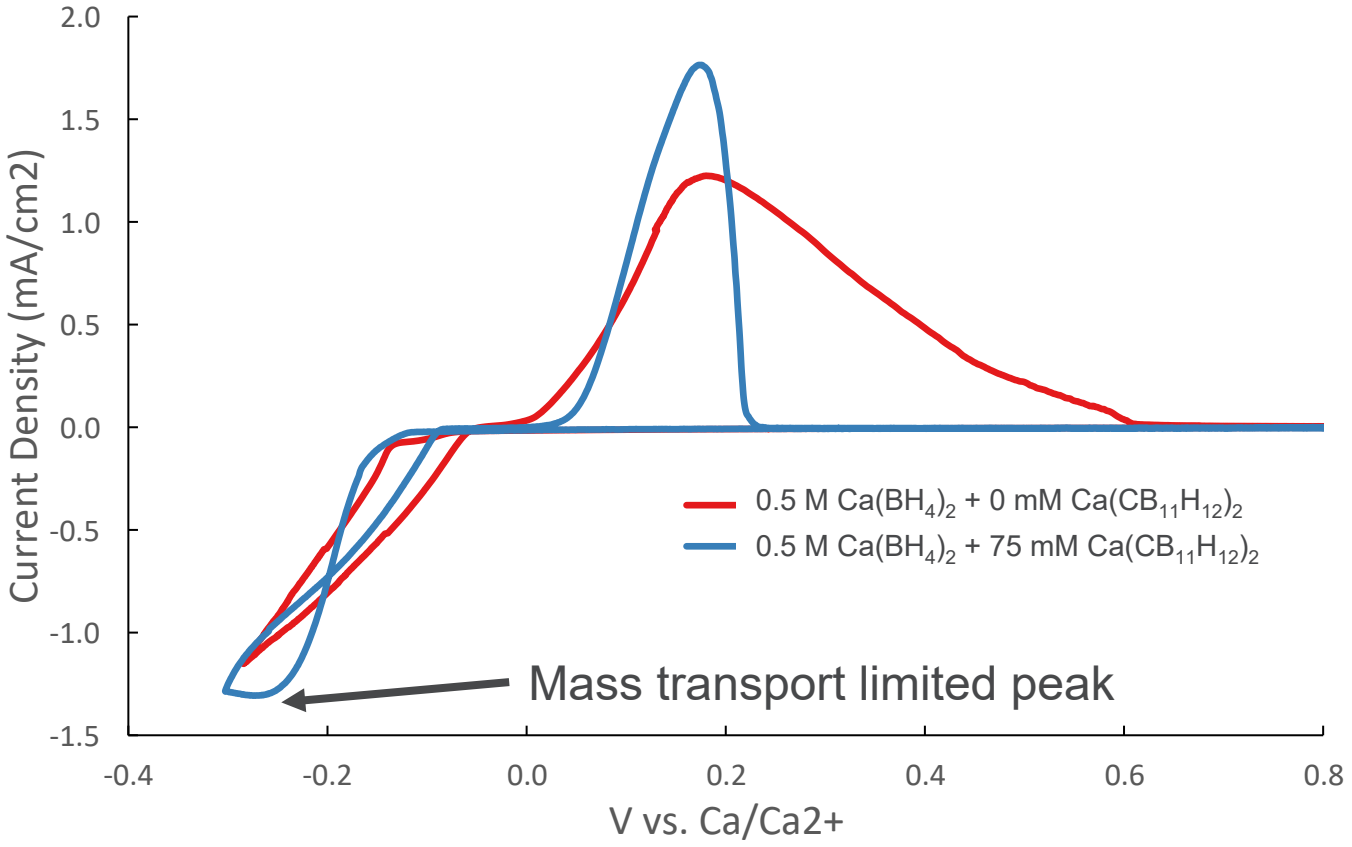


$\Delta\varepsilon = 108\ M^{-1}$

Magnitude of dielectric increment implies SSIP formation

Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

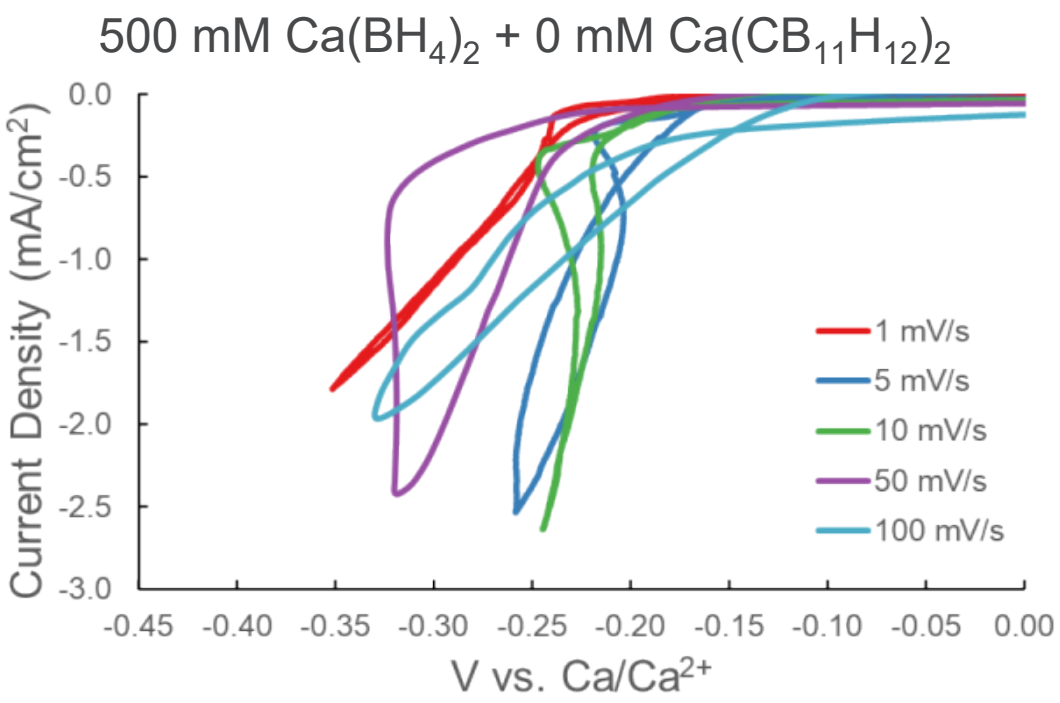
$Ca(CB_{11}H_{12})^+$ SSIP yields a distinct mass transport limited response



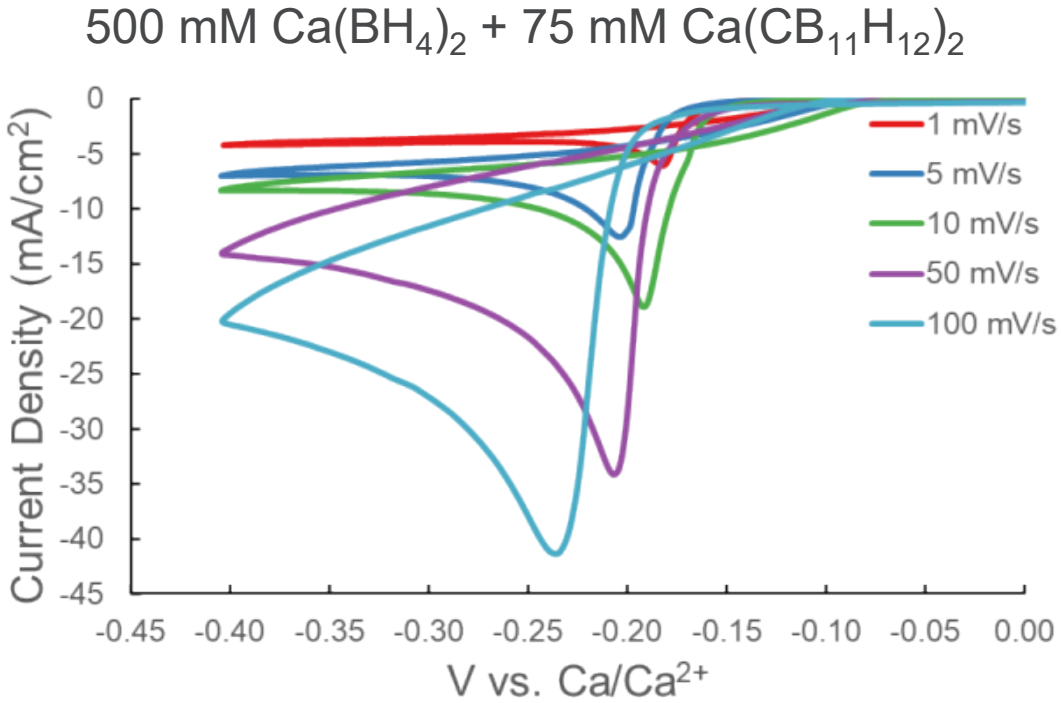
$[Ca(CB_{11}H_{12})_2]$ (M)	Conductivity (mS/cm)
0	0.07
75	1.74

Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

Reduction of $Ca(CB_{11}H_{12})^+$ SSIP is kinetically more facile than reduction of $CaBH_4^+$ CIP



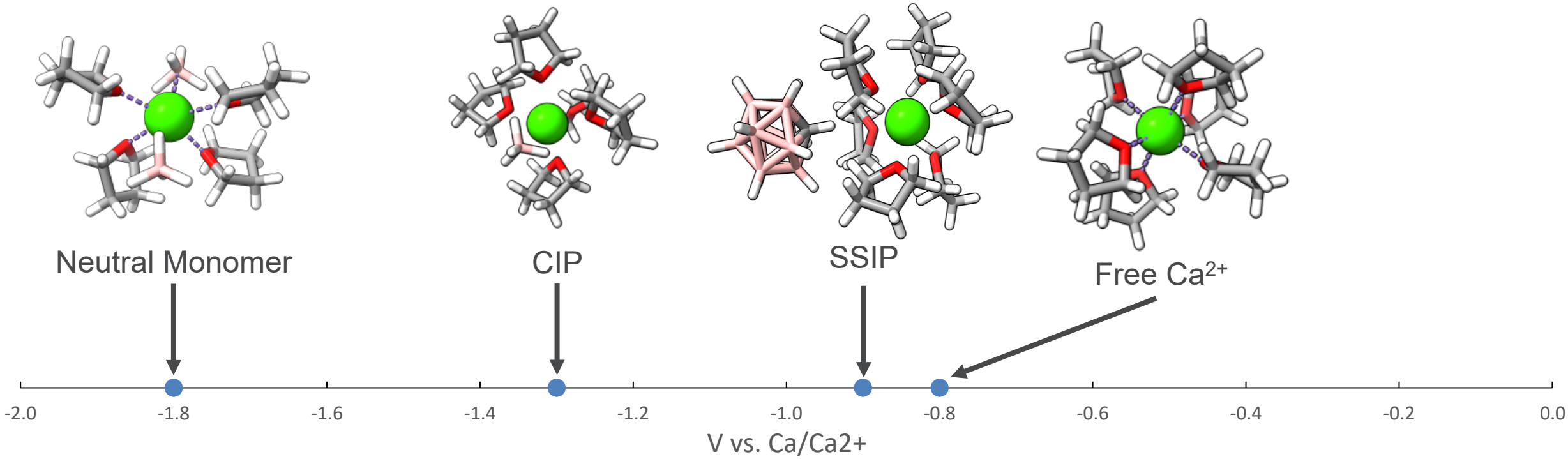
No scan rate dependence - deposition is kinetically limited



Current varies with scan rate - deposition is mass transport limited

Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

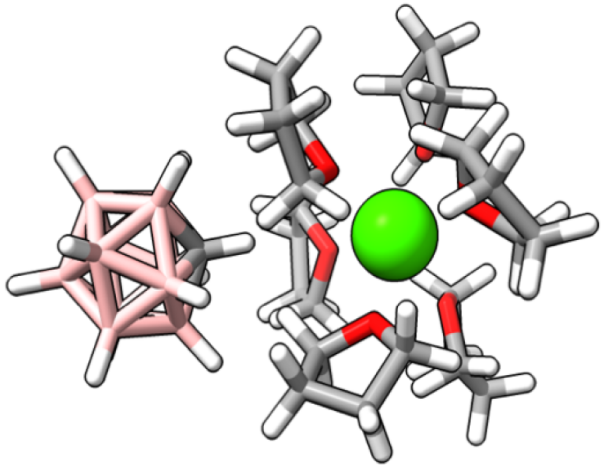
Lower BH_4^- coordination reduces thermodynamic potential for deposition

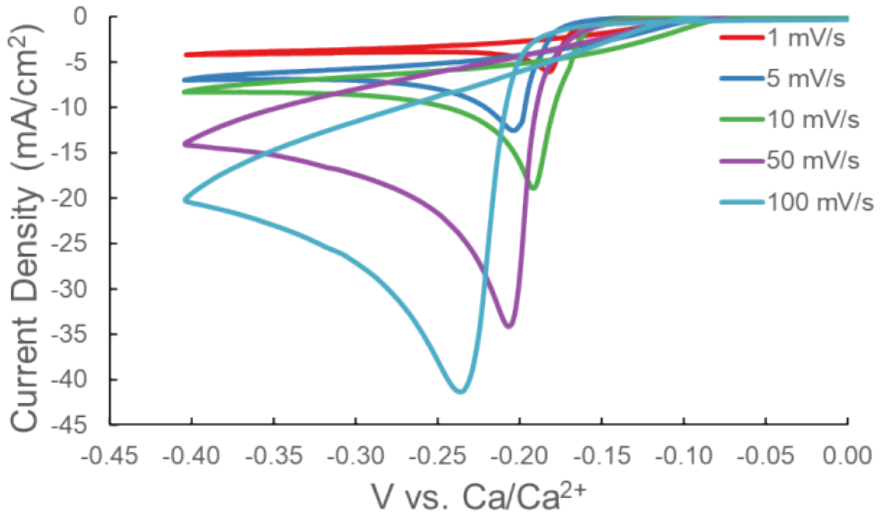


Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

Speciation Drives Electrochemical Performance

- $Ca(CB_{11}H_{12})_2$ added to $Ca(BH_4)_2$/THF produces $Ca(CB_{11}H_{12})^+$ SSIPs as an alternate active species
- Ca^{2+} reduction from $Ca(CB_{11}H_{12})^+$ SSIP is more facile than $CaBH_4^+$ CIP
- Hypothesis: SSIPs can deliver Ca more effectively than CIPs by better balancing charge screening and desolvation penalties
- Altering solvation shell through co-salts or co-solvents enables electrolyte design





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Acknowledgements

Julian Self (DRS computation)

Scott McClary (electrolyte preparation, interphase characterization)

David Bazak (NMR computation)

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Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

Backup Slides

Addition of $Ca(CB_{11}H_{12})_2$ to $Ca(BH_4)_2$/THF leads to complex speciation

$Ca(BH_4)_2$ Equilibria

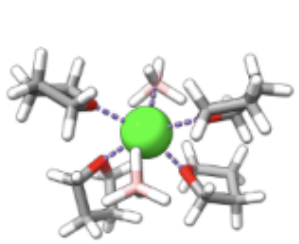
$$2Ca(BH_4)_2 \leftrightarrow Ca_2(BH_4)_4$$
$$Ca_2(BH_4)_4 \leftrightarrow CaBH_4^+ + Ca(BH_4)_3^-$$

$Ca(CB_{11}H_{12})_2$ Equilibria

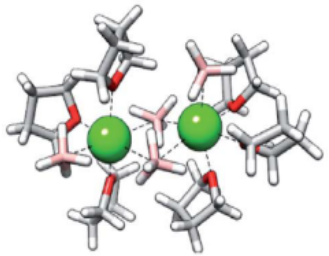
$$Ca(CB_{11}H_{12})_2 \leftrightarrow Ca^{2+} + 2CB_{11}H_{12}^-$$
$$Ca(CB_{11}H_{12})_2 \leftrightarrow Ca(CB_{11}H_{12})_{SSIP}^+ + CB_{11}H_{12}^-$$

Interaction Between $Ca(BH_4)_2$ and $Ca(CB_{11}H_{12})_2$

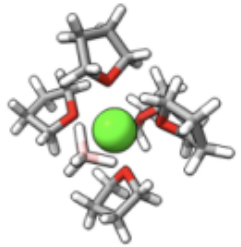
$$Ca(BH_4)_2 + Ca(CB_{11}H_{12})_2 \leftrightarrow 2CaBH_4^+ + 2CB_{11}H_{12}^-$$
$$Ca(BH_4)_2 + Ca(CB_{11}H_{12})_{SSIP}^+ \leftrightarrow CaBH_4^+ + (CaBH_4)(CB_{11}H_{12})_{SSIP}$$



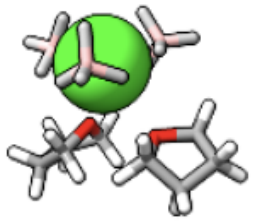
$Ca(BH_4)_2$



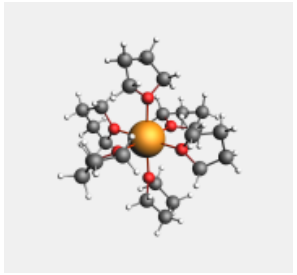
$Ca_2(BH_4)_4$



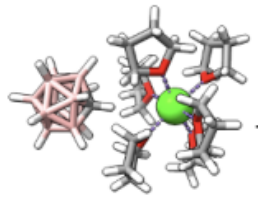
$CaBH_4^+$



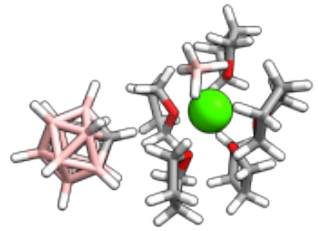
$Ca(BH_4)_3^-$



Ca^{2+}



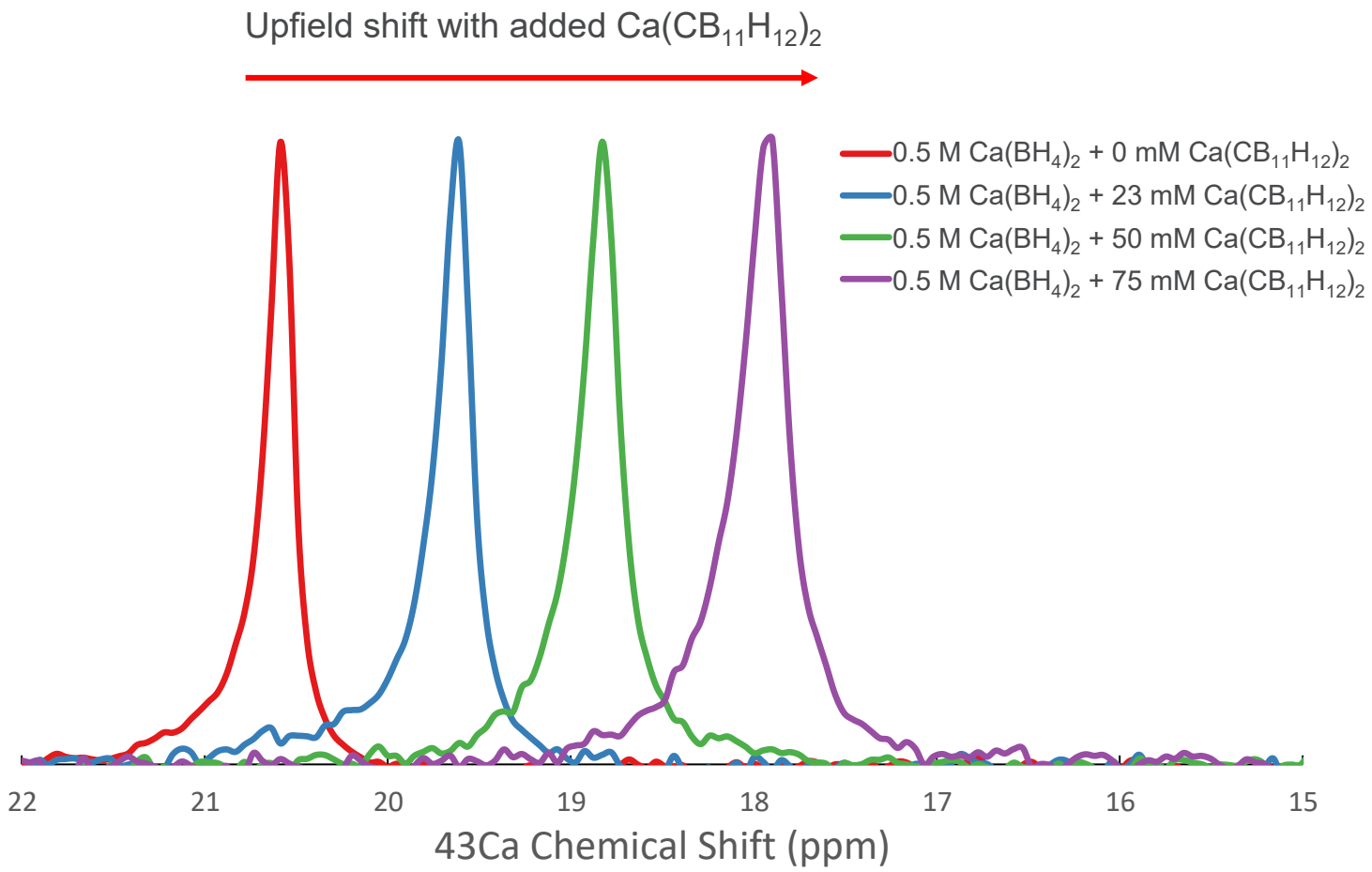
$Ca(CB_{11}H_{12})_{SSIP}^+$

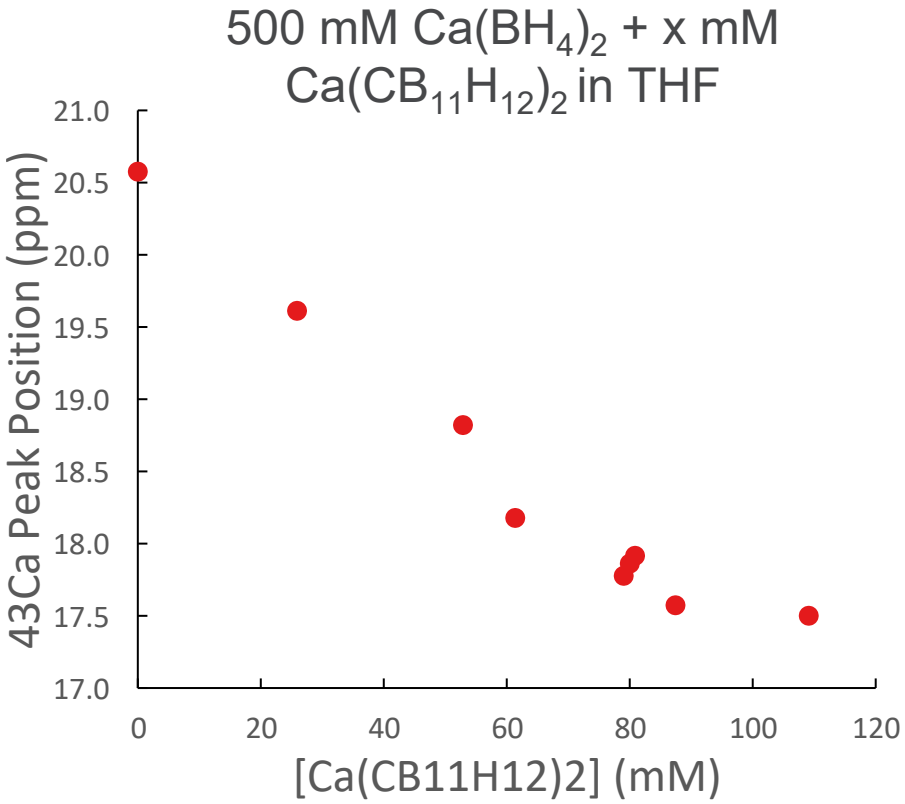


$(CaBH_4)(CB_{11}H_{12})_{SSIP}$

As many as 7 Ca species in solution!

Added $Ca(CB_{11}H_{12})_2$ alters local Ca coordination





Linear upfield shift in ^{43}Ca NMR peak with added $Ca(CB_{11}H_{12})_2$

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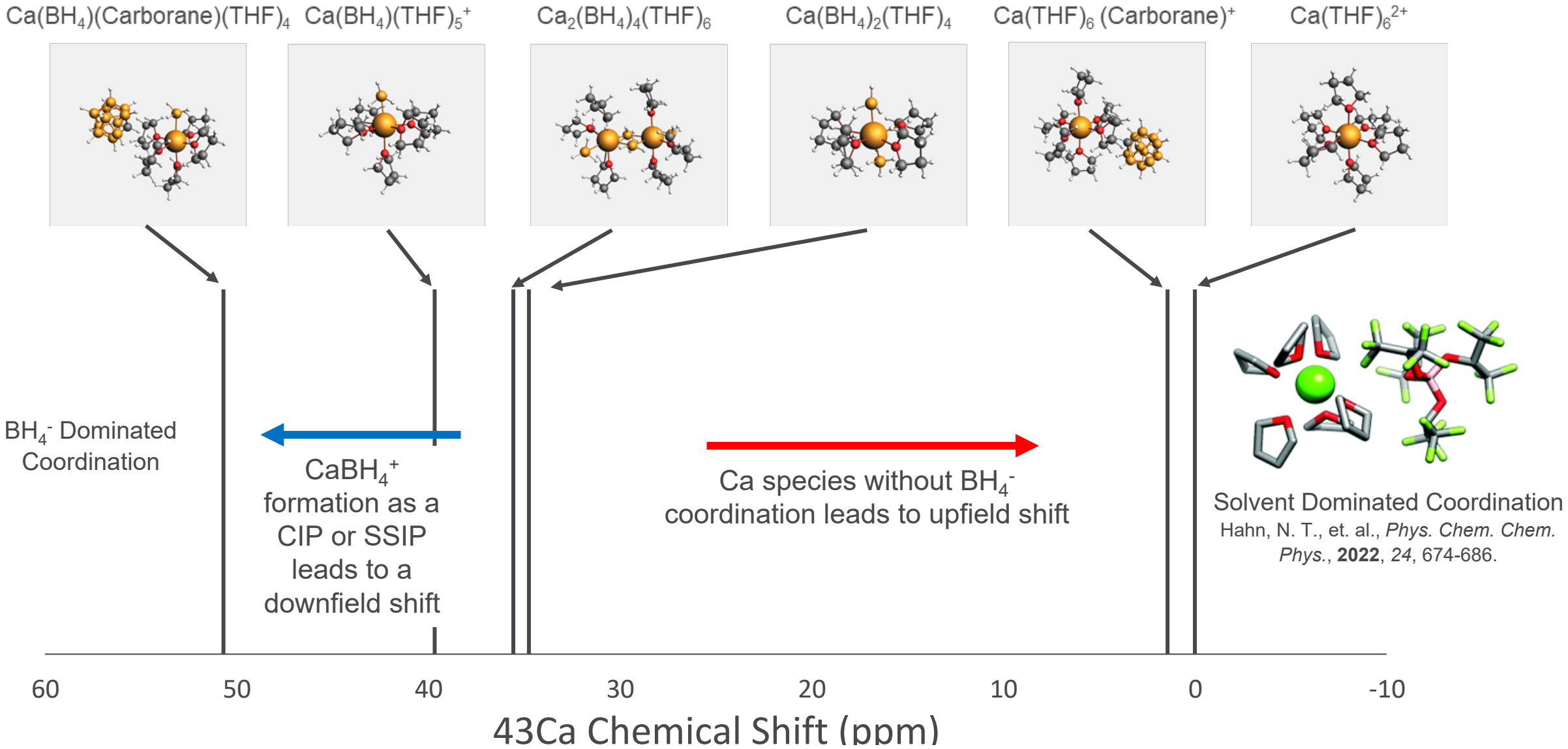
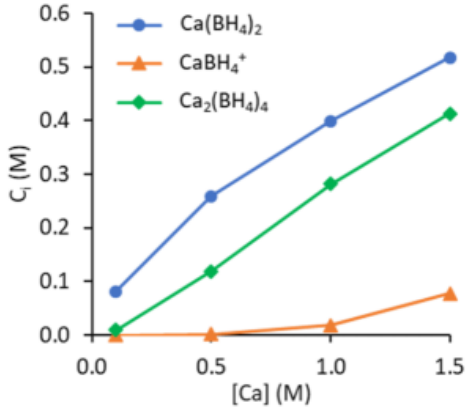
Computational NMR validates SSIPs without BH_4^- as critical component of speciation



Hahn, N. T., et. al., *Phys. Chem. Chem. Phys.*, **2022**, *24*, 674-686.

Determining Speciation Through ^{43}Ca NMR



Hahn, N. T. et. al., *J. Phys. Chem. B*, **2021**, *125*, 3644-3652.

1500 mM $Ca(BH_4)_2$

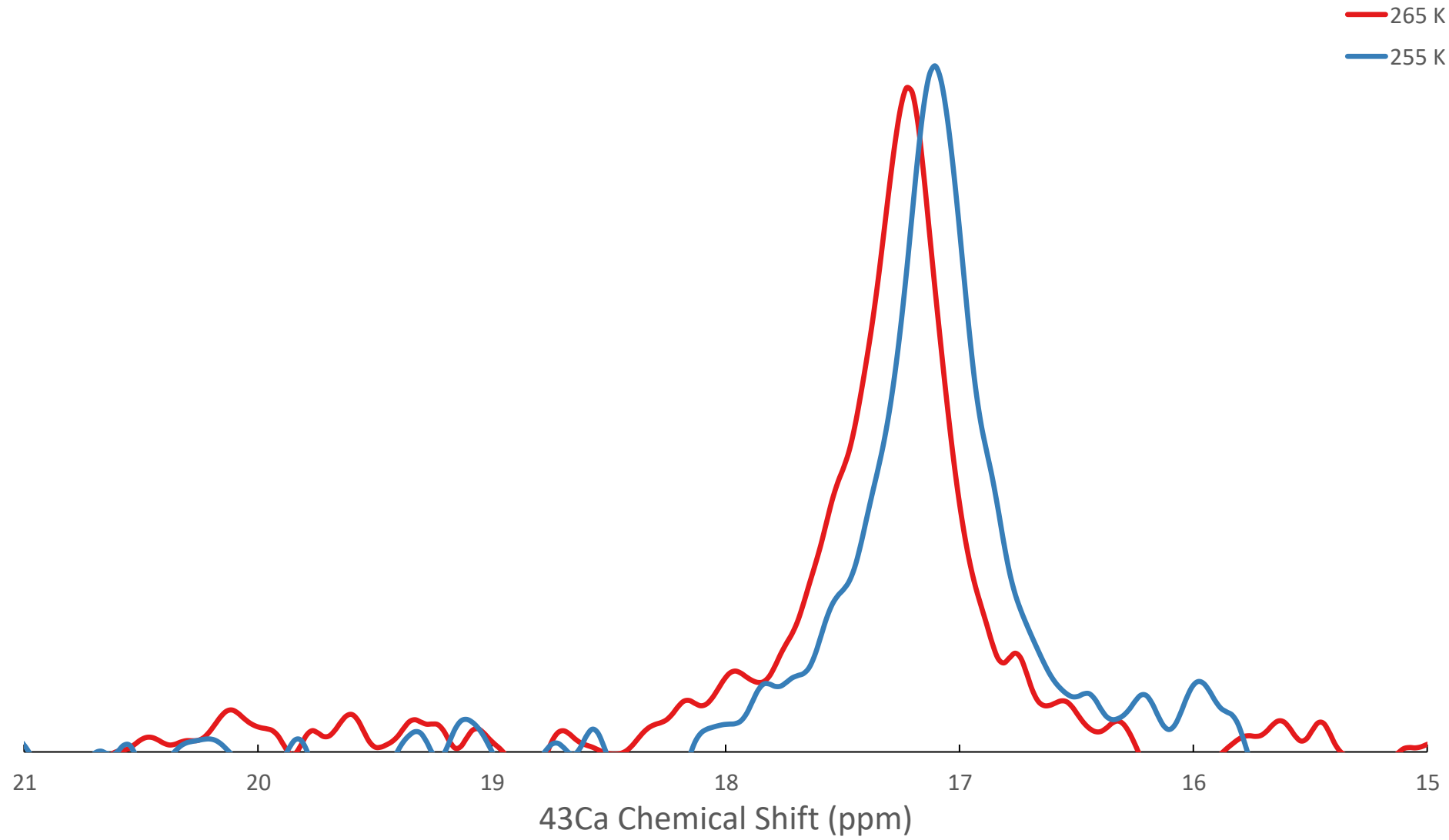
1000 mM $Ca(BH_4)_2$

500 mM $Ca(BH_4)_2$

100 mM $Ca(BH_4)_2$

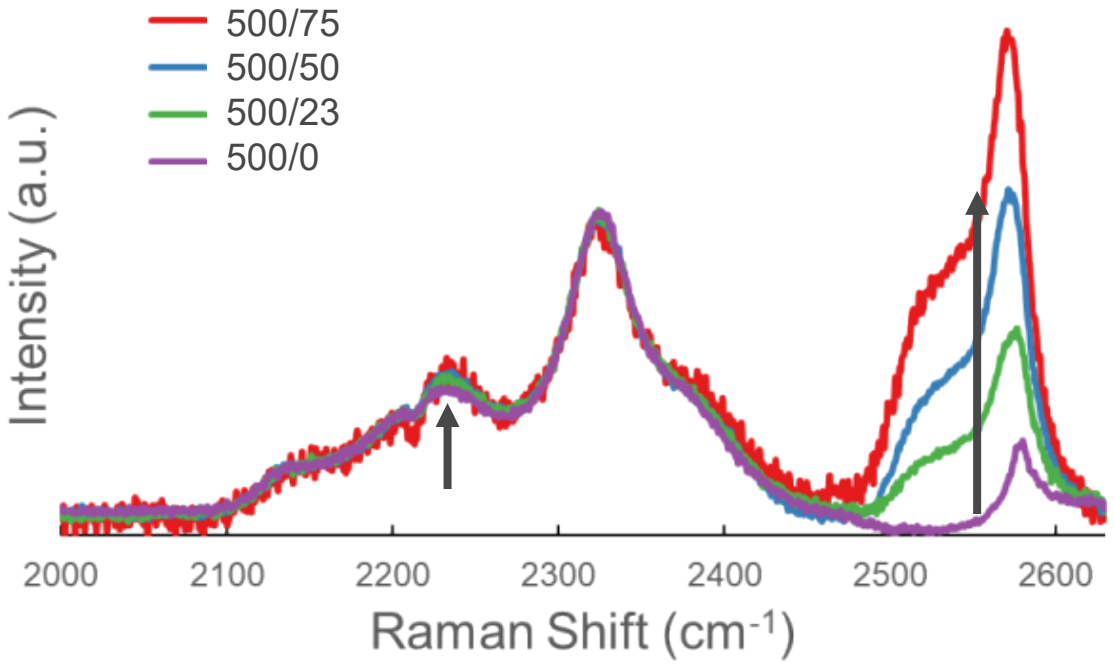
- Downfield shift in ^{43}Ca peak position suggests increasing average BH_4 CN
- Broadening of peak suggests wider range of coordination environments

Low Temperature NMR

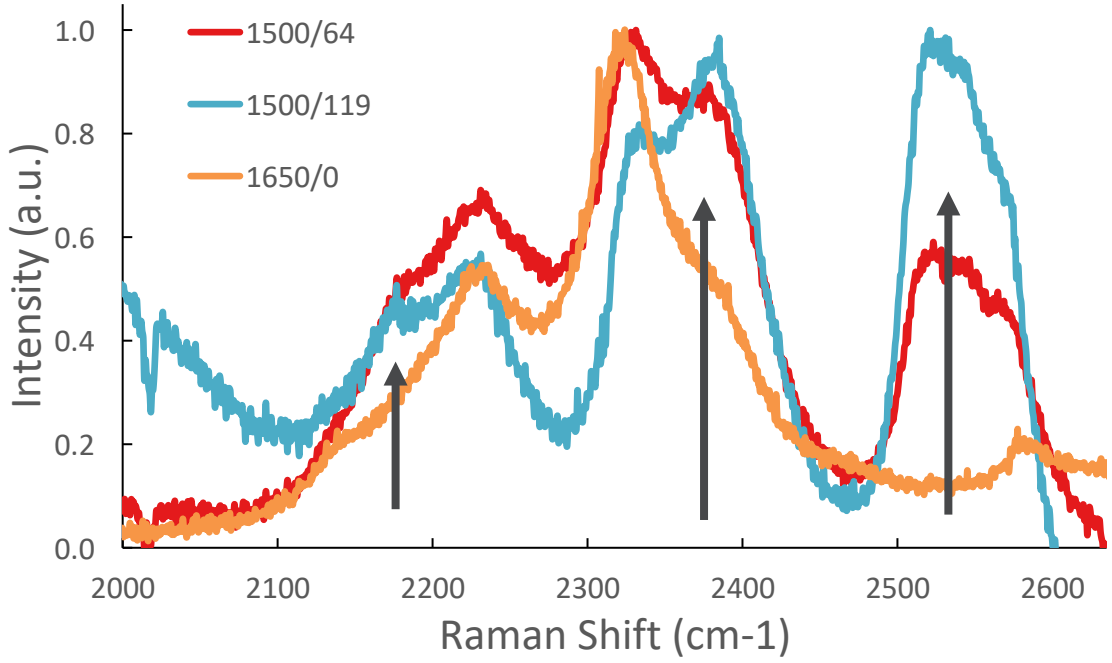


No obvious splitting at low temperature - exchange must be very fast

$Ca(BH_4)_2$ concentration dictates change in speciation with added $Ca(CB_{11}H_{12})_2$



$Ca(CB_{11}H_{12})^+$ SSIPs are formed at low $[Ca(BH_4)_2]$



$Ca(CB_{11}H_{12})^+$ CIPs are formed at high $[Ca(BH_4)_2]$

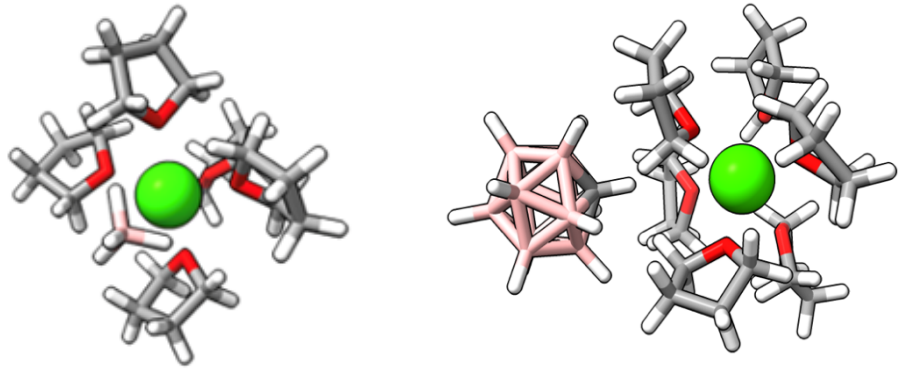
$[Ca(BH_4)_2]$ (mM)/$[Ca(CB_{11}H_{12})_2]$ (mM)

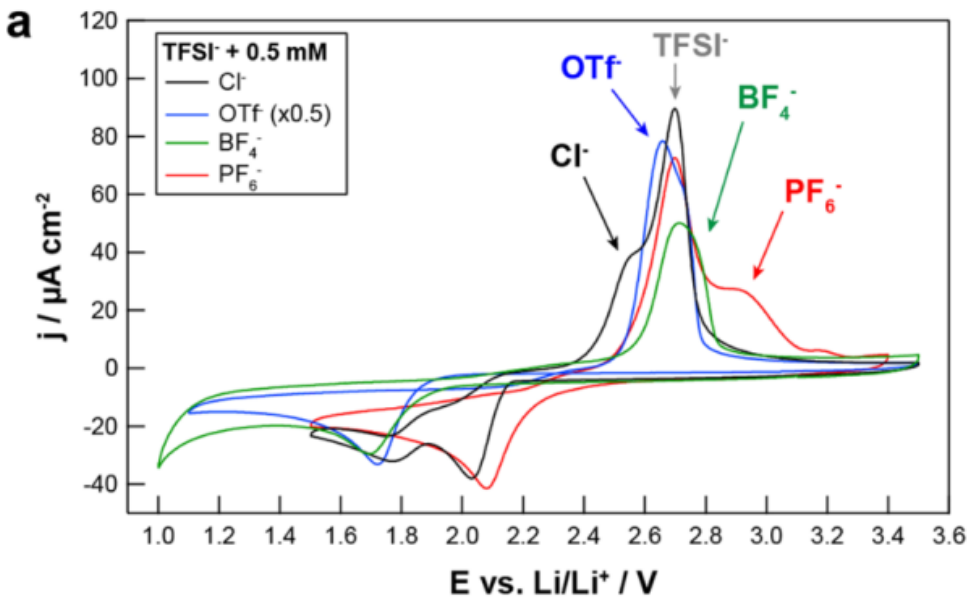
Addition of $Ca(CB_{11}H_{12})_2$ to $Ca(BH_4)_2$/THF leads to significant population of $Ca(CB_{11}H_{12})^+$ SSIP

- We hypothesized enhanced $CaBH_4^+$ with non-interacting $CB_{11}H_{12}^-$ but found $Ca(CB_{11}H_{12})^+$ SSIP
- Refined speciation description underway

- We have two Ca delivery species: $CaBH_4^+$ and $Ca(CB_{11}H_{12})_{SSIP}^+$

- Implications
  - New features in voltammetry
  - Decreased deposition overpotential
  - Improved Ca delivery at high current densities

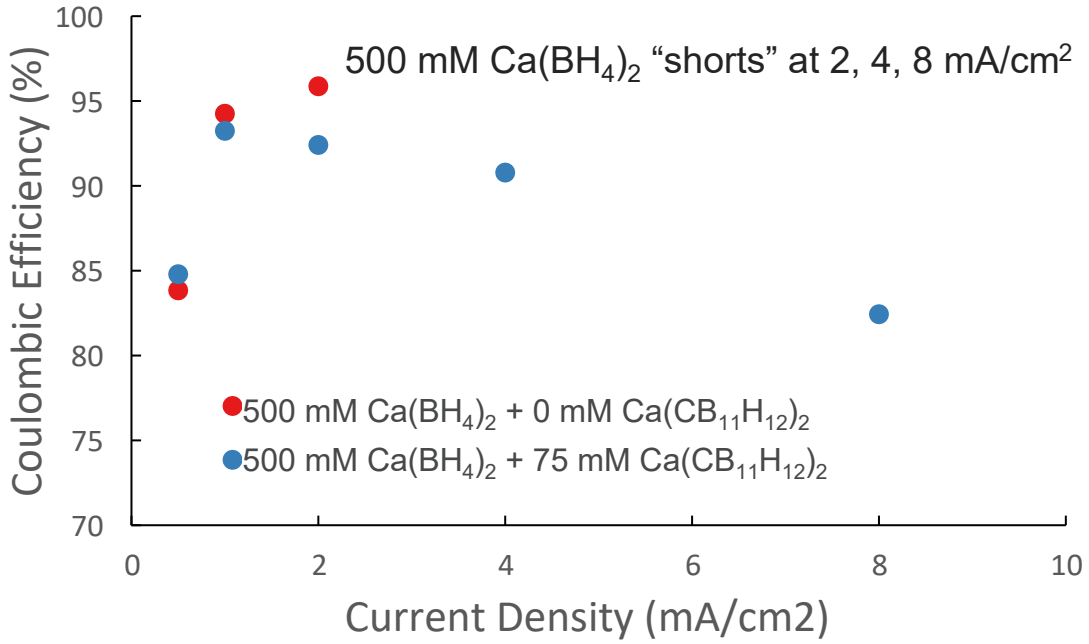


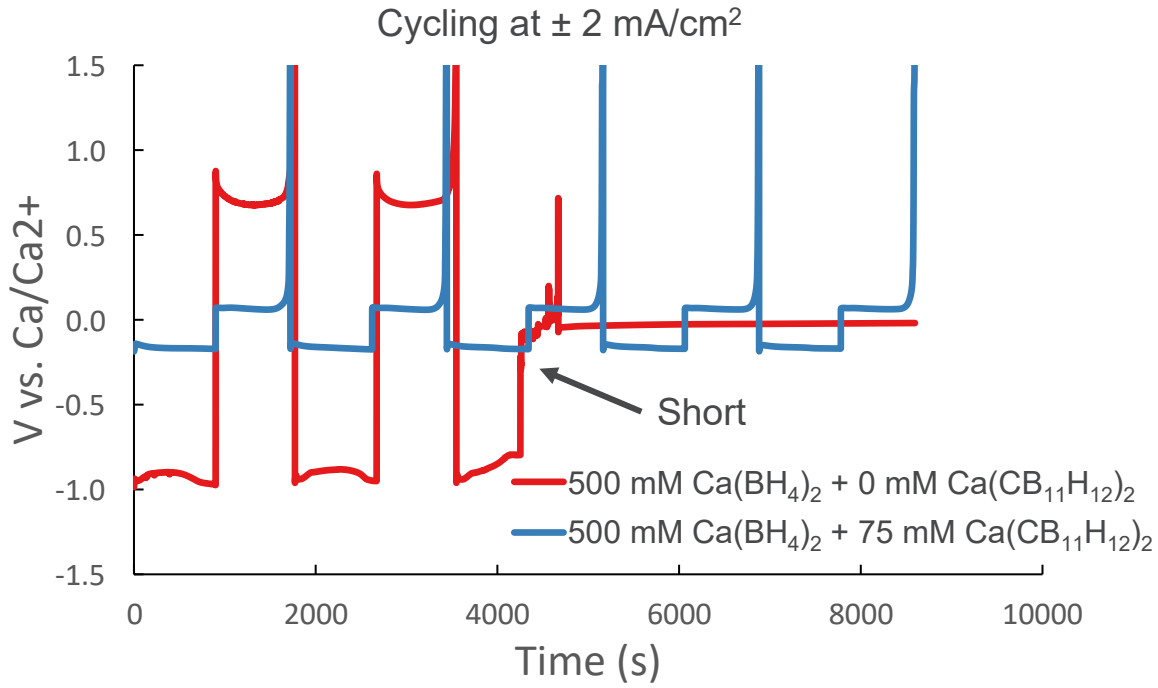


Connell, J. G., et. al., *ACS Appl. Mater. Interfaces*, **2020**, *12*, 36137.

Relieving kinetic constraints enables cycling at higher current densities

Au Substrate
500 mM $Ca(BH_4)_2$ + x mM $Ca(CB_{11}H_{12})_2$ in THF
~1380 ppm by mass Na:Ca
0.5 mAh/cm^2 capacity - ~ 2.4 µm Ca
Average of 5 cycles

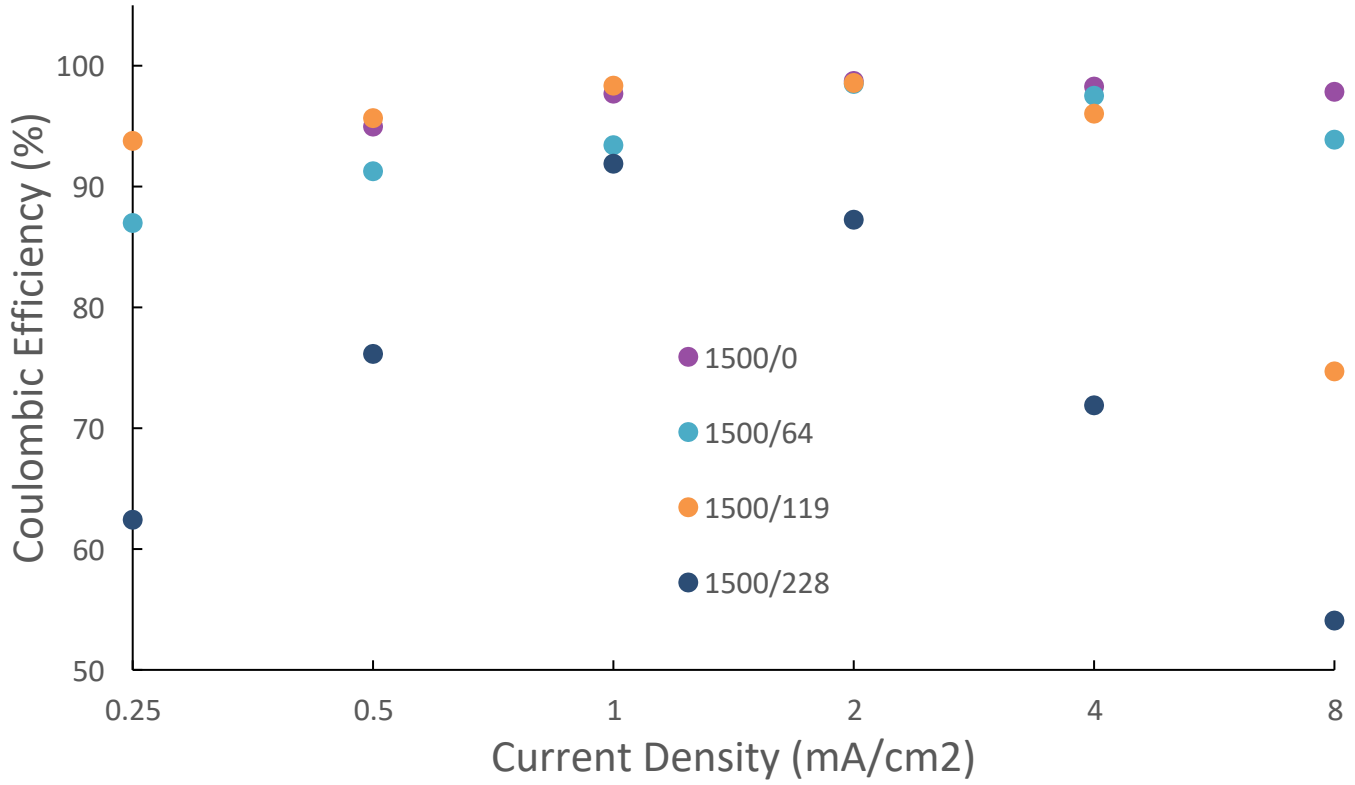




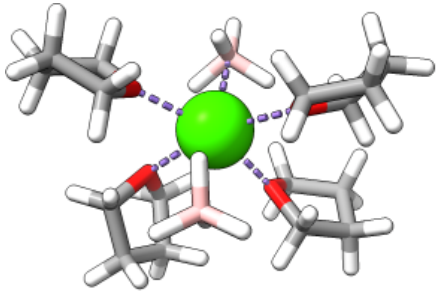
Pushing beyond kinetic constraints results in current localization and dendrite formation

Presence of $Ca(CB_{11}H_{12})^+$ CIP reduces Coulombic efficiency

Au Substrate
500 mM $Ca(BH_4)_2$ + x mM $Ca(CB_{11}H_{12})_2$ in THF
~1380 ppm by mass Na:Ca
0.5 mAh/cm^2 capacity - ~ 2.4 µm Ca
Average of 5 cycles

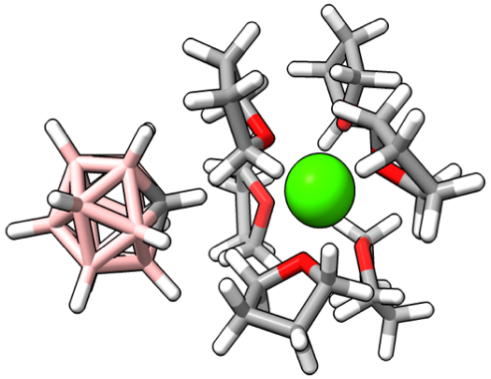


Lower BH_4^- coordination reduces thermodynamic potential for deposition



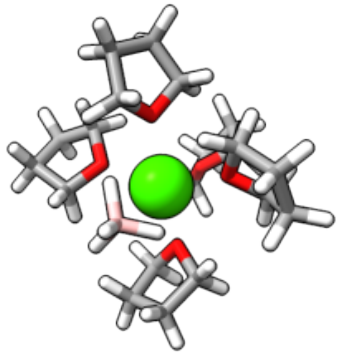
$Ca(BH_4)_2(THF)_4 + e^- \leftrightarrow Ca(BH_4)_2(THF)_3^- + THF$

E^0_{red} = -1.8 V vs Ca/Ca^{2+}



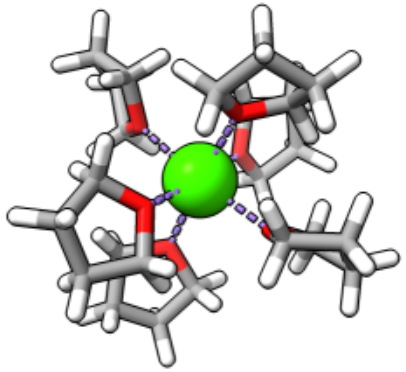
$Ca(THF)_6(CB_{11}H_{12})^+ + e^- \leftrightarrow Ca(THF)_5(CB_{11}H_{12}) + THF$

E^0_{red}= -0.9 V vs Ca/Ca^{2+}



$Ca(BH_4)(THF)_5^+ + e^- \leftrightarrow Ca(BH_4)(THF)_4 + THF$

E^0_{red}= -1.3 V vs Ca/Ca^{2+}



$Ca(THF)_6^{2+} + e^- \leftrightarrow Ca(THF)_5^+ + THF$

E^0_{red}= -0.8 V vs Ca/Ca^{2+}

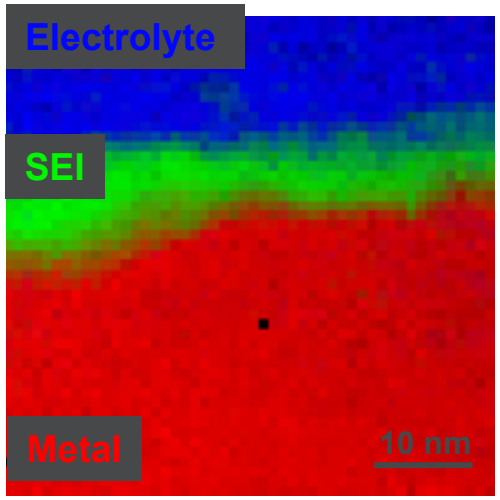
Landers, A., et al., Manipulating the Speciation of Ca-Ion Electrolytes through the Addition of a Weakly Coordinating Calcium Salt to Enhance Calcium Metal Anode Performance, *in preparation.*

Changes in speciation affect SEI heterogeneity and functionality

Au Substrate
x mM $Ca(BH_4)_2$ + y mM $Ca(CB_{11}H_{12})_2$ in THF
~1380 ppm by mass Na:Ca
~ 640 nm Ca
±1 mA/cm^2

Cryo-EELS mapping of SEI composition

500/75



C K-edge
500/75: organics

1650/0: $CaCO_3$

O K-edge – CaO

500/75

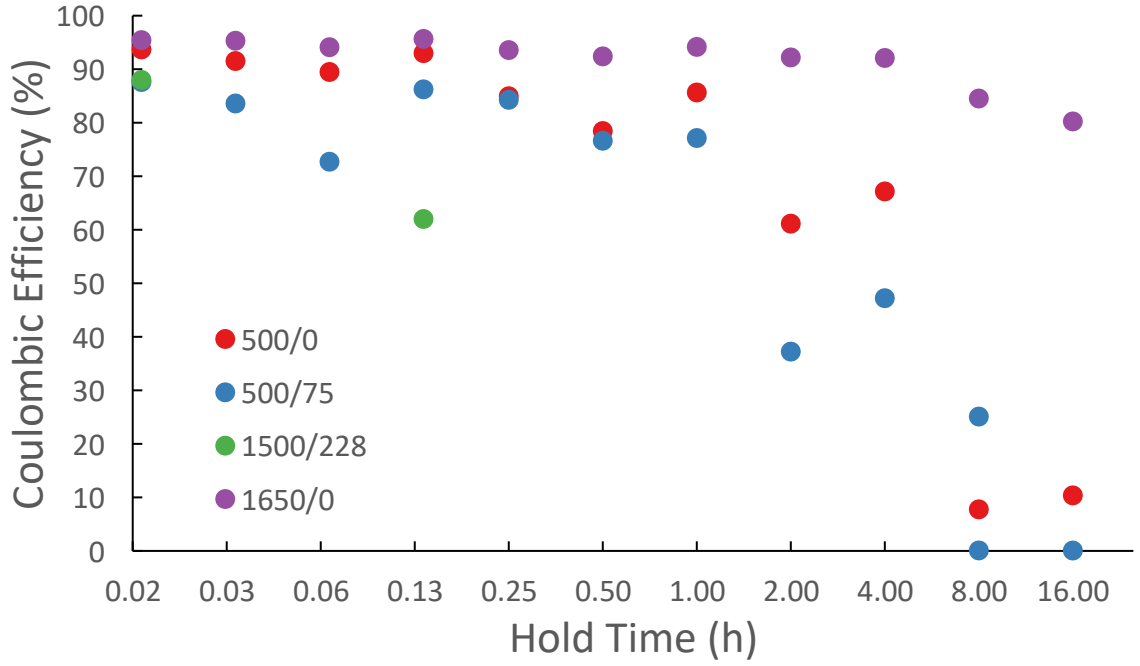
1650/0

B K-edge – Ca Borates
500/75

1650/0

Figures provided by Scott McClary

Deposit – Hold – Strip



Planning to characterize SEI composition for mixed anions at high and low [$Ca(BH_4)_2$]