Manipulating Ca-Ion Electrolyte Speciation to Enhance Ca Metal Anode Performance through Addition of Free Ca^{2+}

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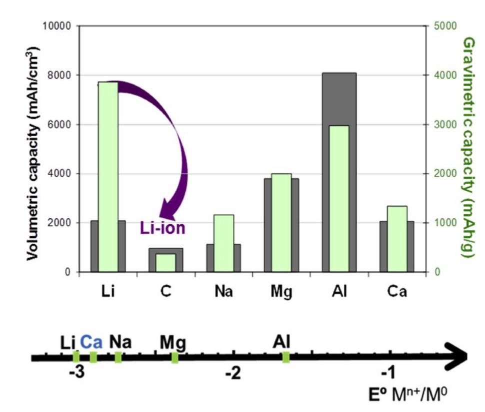
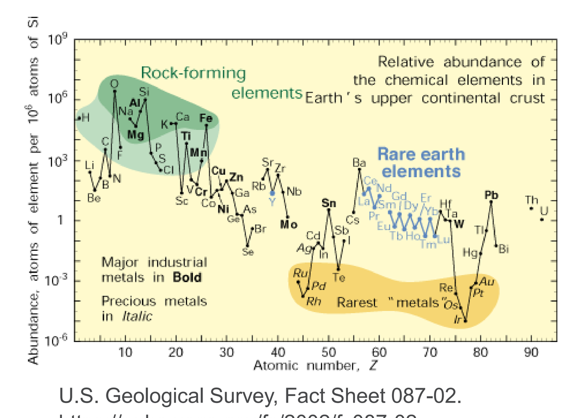
Speciation of Ca-Ion Electrolytes



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



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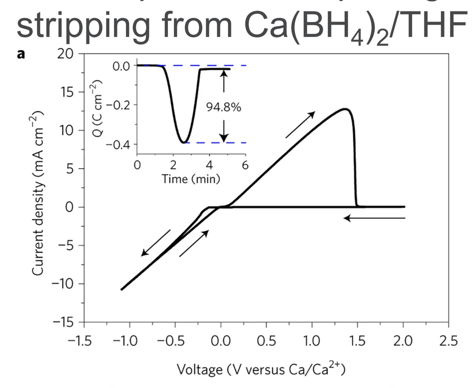
Room temperature Ca plating and stripping from $Ca(BH_4)_2$/THF



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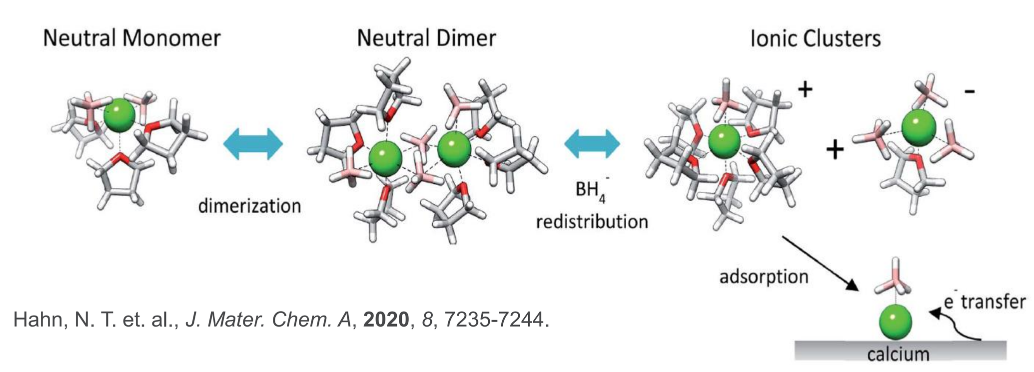
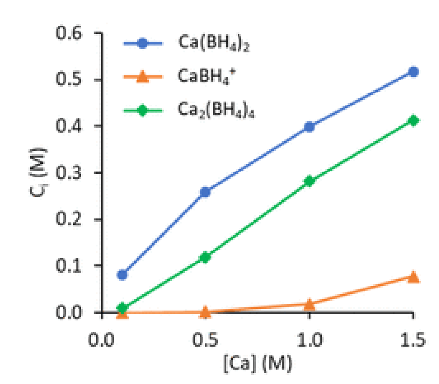
Calcium metal batteries could provide higher energy density and lower cost than Li-ion batteries, but improved electrolytes need to be developed



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



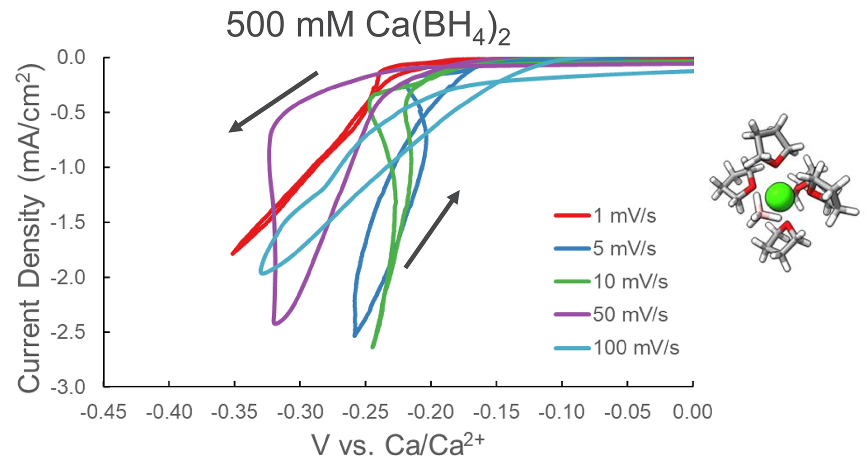
Hahn, N. T. et. al., *J. Phys. Chem. B*, **2021**, 125, 3644-3652.

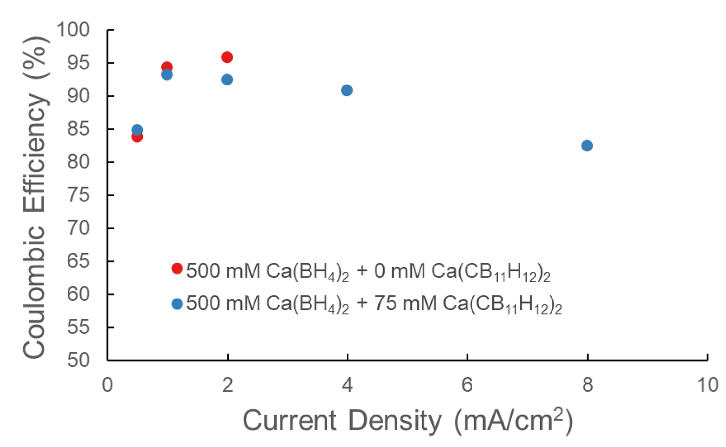
Hypothesis 1: Increasing concentration of active species improves electrochemical performance
Hypothesis 2: Addition of weakly coordinating Ca salt to $Ca(BH_4)_2$/THF increases active species concentration

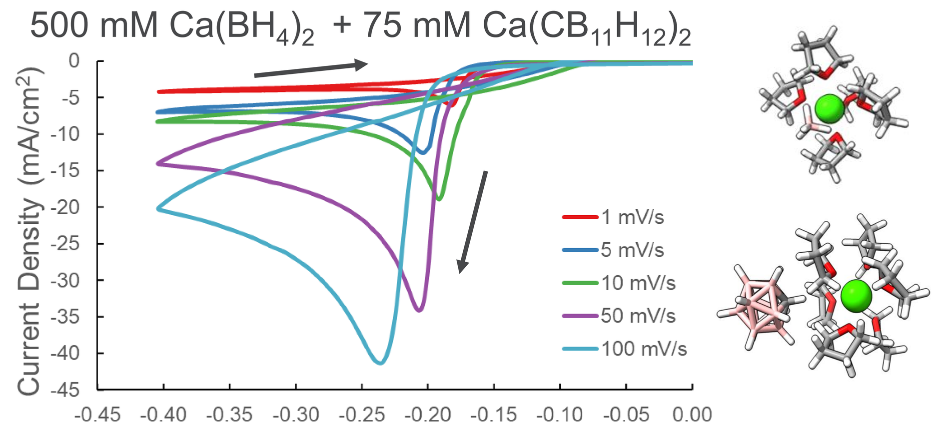
Proposed Speciation Reaction

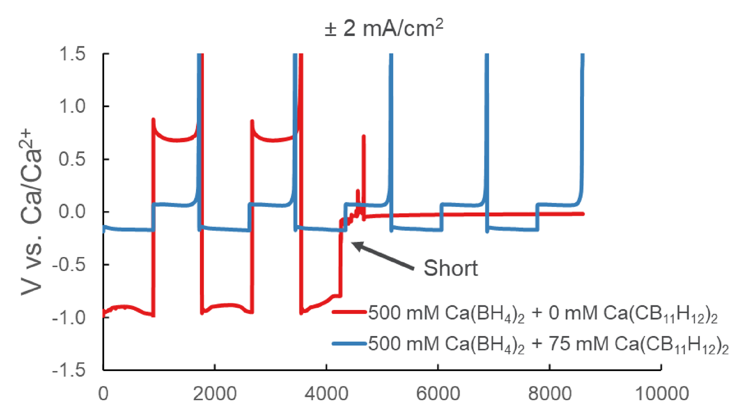
$$Ca(BH_4)_2 + Ca(CB_{11}H_{12})_2 \leftrightarrow 2CaBH_4^+ + 2CB_{11}H_{12}^-$$

Speciation Controls Deposition

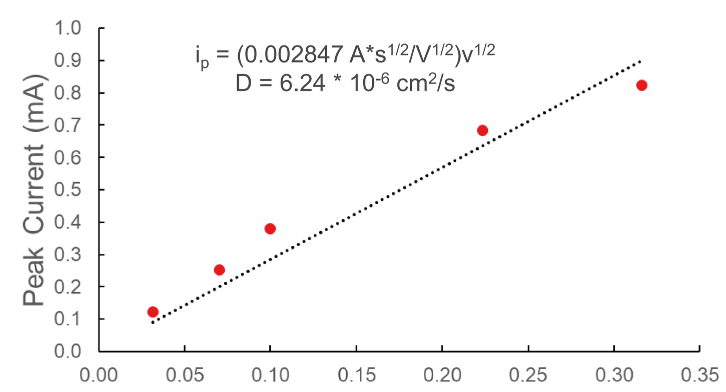






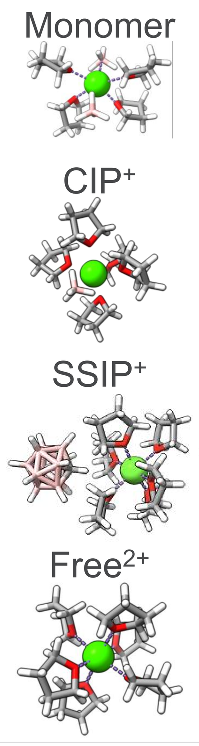


Mixed salt electrolyte enables cycling at higher current densities



Calcium deposition transitions from kinetic to mass transport limitations with added $Ca(CB_{11}H_{12})_2$

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



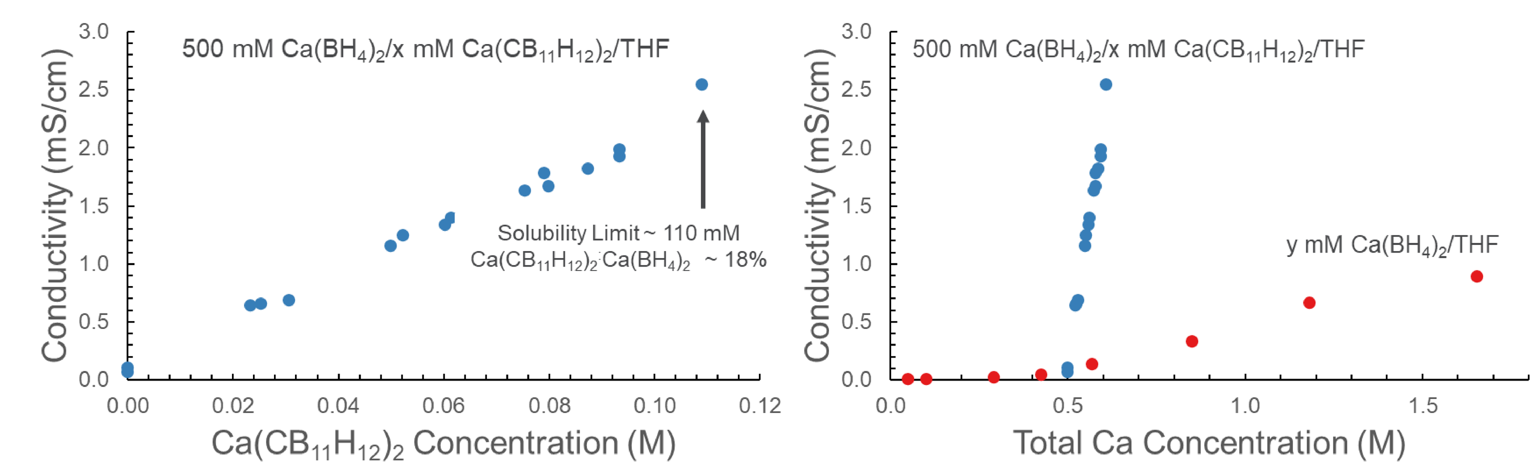
$Ca(BH_4)_2(THF)_4 + e^- \rightarrow Ca(BH_4)_2(THF)_3^- +$ THF
E^0_{red} = -1.8 V vs Ca/Ca^{2+}

$CaBH_4(THF)_5^+ + e^- \rightarrow CaBH_4(THF)_4 +$ THF
E^0_{red} = -1.4 V vs Ca/Ca^{2+}

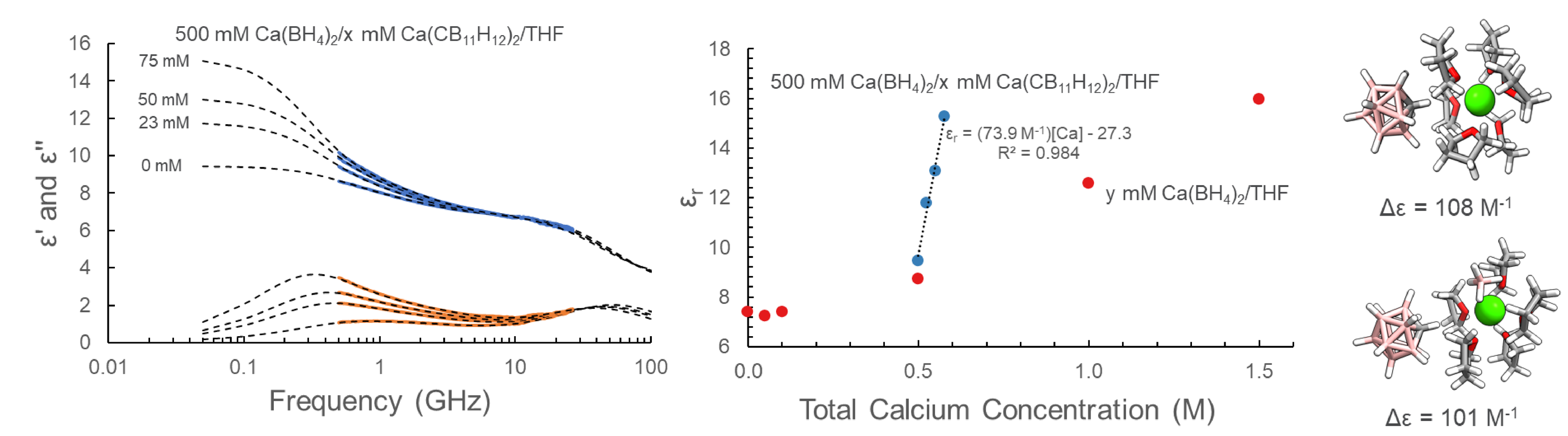
$Ca(THF)_6(CB_{11}H_{12})^{2+} + e^- \rightarrow Ca(THF)_5(CB_{11}H_{12})^+ +$ THF
E^0_{red} = -0.9 V vs Ca/Ca^{2+}

$Ca(THF)_6^{2+} + e^- \rightarrow Ca(THF)_5^+ +$ THF
E^0_{red} = -0.8 V vs Ca/Ca^{2+}

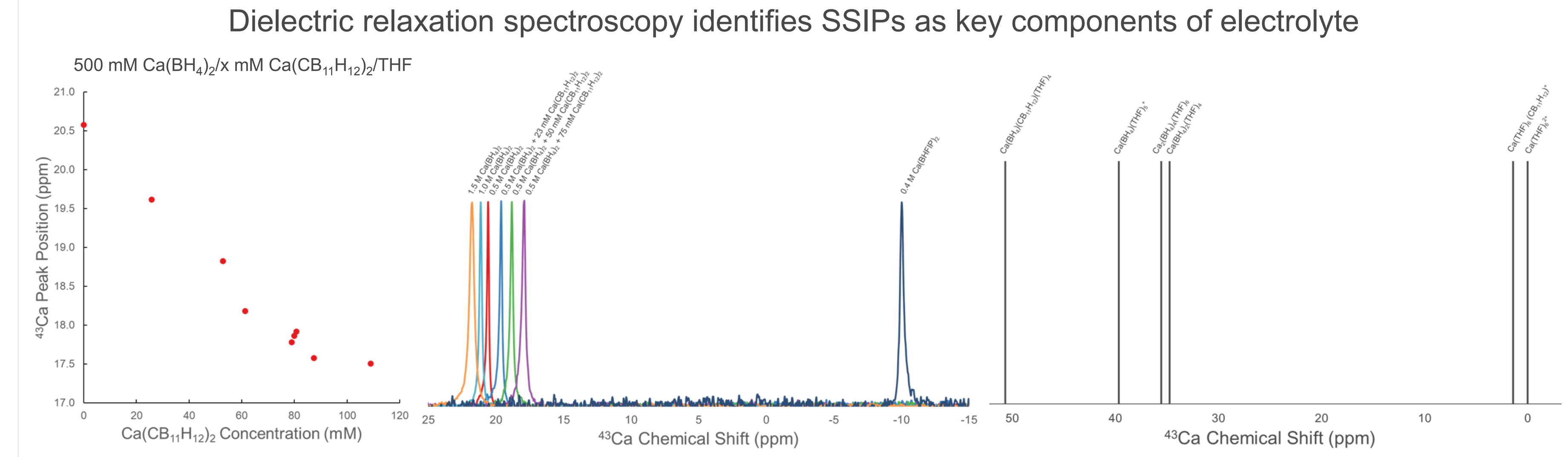
Manipulating Electrolyte Speciation



Conductivity trends suggest possibility of SSIPs or free Ca^{2+} in solution

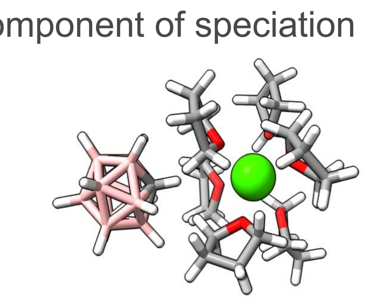


Dielectric relaxation spectroscopy identifies SSIPs as key components of electrolyte



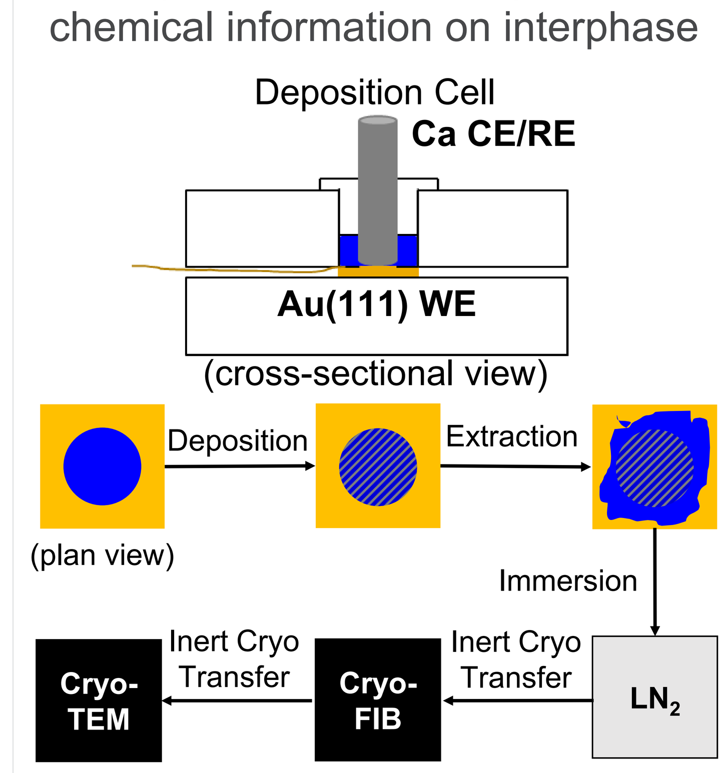
^{43}Ca NMR validates SSIPs without BH_4^- as critical component of speciation

➤ ***Addition of $Ca(CB_{11}H_{12})_2$ to $Ca(BH_4)_2$/THF produces $Ca(CB_{11}H_{12})^+$ SSIPs as alternative Ca^{2+} delivery species***



Speciation Modulates Interphase

Cryo-FIB and Cryo-TEM preserve interphase while EELS provides chemical information on interphase



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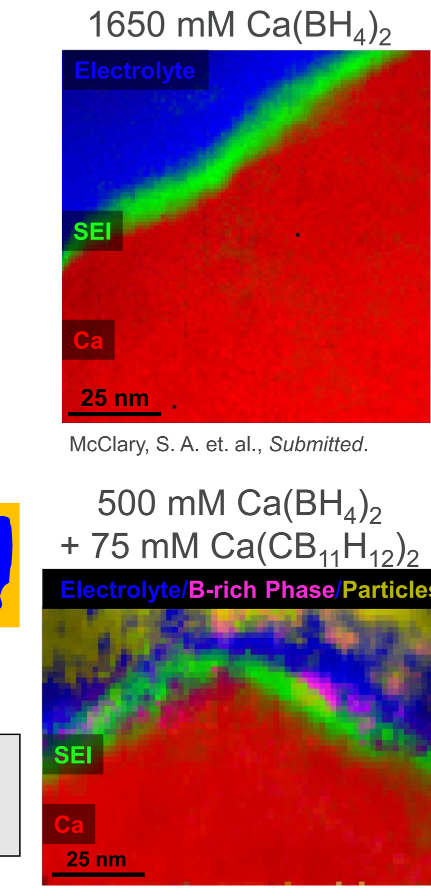
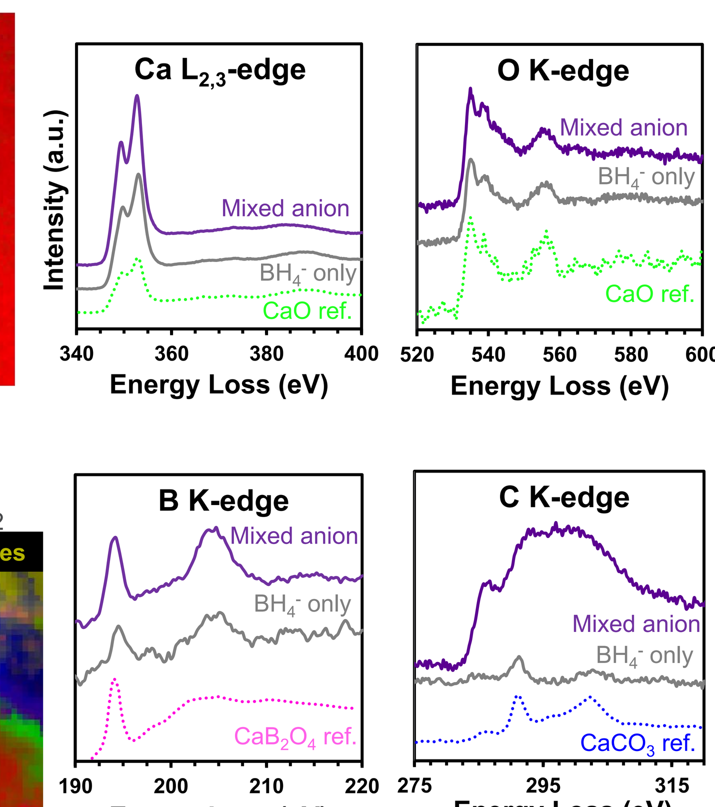


McClary, S. A. et. al., *Submitted.*



➤ ***Mixed $Ca(BH_4)_2/Ca(CB_{11}H_{12})_2$/THF electrolytes exhibit increased organic content in SEI***

Lessons Learned

- Design of effective Ca-ion electrolytes must balance charge screening with desolvation penalties at the interface
- Mixed salts can provide a design pathway for creating alternate Ca delivery species
- $Ca(CB_{11}H_{12})_2$ added to $Ca(BH_4)_2$/THF produces $Ca(CB_{11}H_{12})^+$ SSIP as an alternate Ca delivery species
- Ca^{2+} reduction from $Ca(CB_{11}H_{12})^+$ SSIP is more facile than from $CaBH_4^+$ CIP
- Organic content of SEI is significantly increased in mixed salt electrolyte

Next Steps

Hypothesis: SSIPs can deliver Ca more effectively than CIPs by reducing the desolvation barrier while still allowing close approach of the Ca coordination complex

- Determine desolvation barriers through combined electrochemical and computational measurements
- Compare approach distances of CIPs and SSIPs using interfacial characterization techniques
- Generalize SSIP formation and reactivity across multivalent electrolytes
- Correlate intentional interphase modulation with electrochemical performance

Key References

- Landers, A., et al. (2022). "Manipulating Ca-Ion Electrolyte Speciation to Enhance Ca Metal Anode Performance through Addition of Free Ca^{2+}" *in preparation*
- McClary, S. A., et al. (2022). "A Heterogeneous Calcium Oxide Enables Reversible Calcium Electrodeposition for a Calcium Battery" *in review*
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