SAND2022-6329C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Sandia National Laboratories

Solid Electrolyte Interphase Engineering for Calcium Metal Anodes

Scott A. McClary,[1,2] Daniel M. Long,[1,2] Ana Sanz Matias,[2,3] Alan T. Landers,[1,2] Kathryn A. Small,[1] Paul G. Kotula,[1] David Prendergast,[2,3] Katherine L. Jungjohann,[1,2] and Kevin R. Zavadil[1,2]

scott.mcclary@sandia.gov

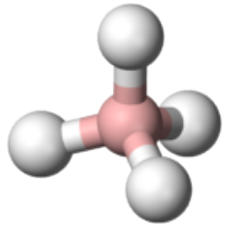
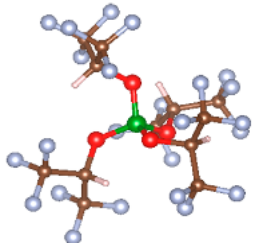
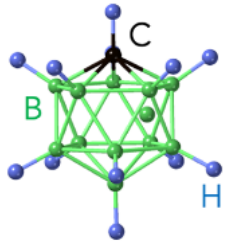
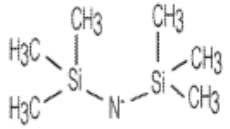
1 – Material, Physical, and Chemical Sciences Center, Sandia National Laboratories, Albuquerque, NM
2 – Joint Center for Energy Storage Research (JCESR), Lemont, IL
3 – The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA

2022 MRS Spring Meeting & Exhibit
May 12, 2022

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. Any subjective views expressed in this presentation do not necessarily represent the views of the U.S. Department of Energy or United States Government. This work was performed, in part, at the Center for Integrated Nanotechnologies (CINT), an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science.

Calcium metal anodes are a promising component of innovative batteries

Graphite	Calcium
-2.84 V	-2.87 V
850 mAh/mL	2072 mAh/mL
372 mAh/g	1337 mAh/g
20 ppm (Li)	41500 ppm

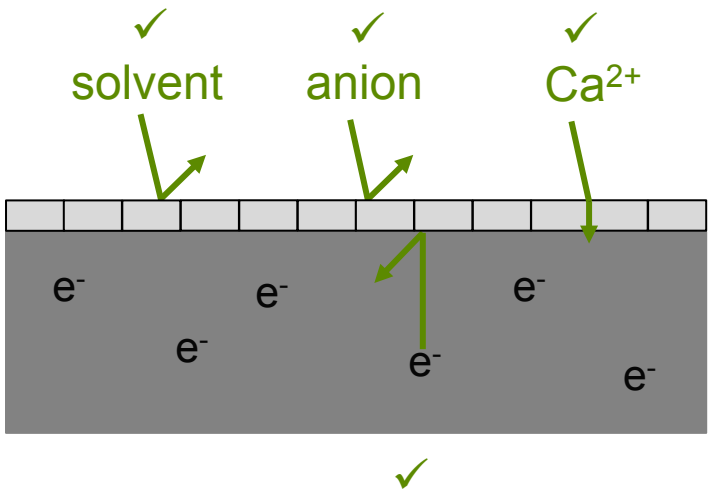
$Ca(BF_4)_2$		Ponrouch et al. *Nat. Mat.* 2016
$Ca(BH_4)_2$		Wang et al. *Nat. Mat.* 2018
$Ca(B(Ohfip)_4)_2$		Shyamsunder et al. *ACS Energy Lett*. 2019 Li et al. *Energy Env. Sci.* 2019
$Ca(CB_{11}H_{12})_2$		Kisu et al. *Sci. Rep.* 2021
$Ca(HMDS)_2$		Buttry and Rheinhardt. U.S. Patent Application, 2020

The Grand Challenge: Selectively Protecting Ca Metal

-2.87 V vs. SHE

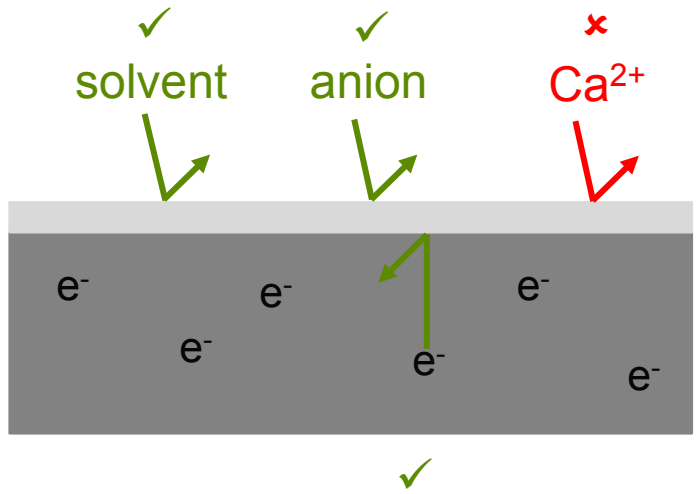
Ideal case

Solid Electrolyte Interphase (SEI)



Typical case

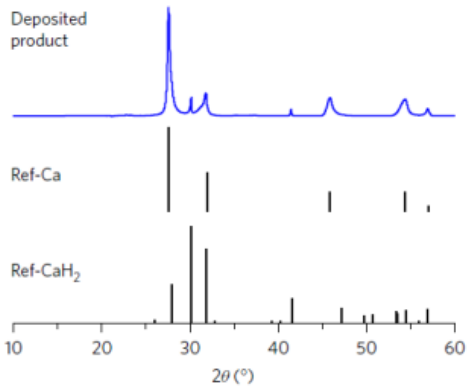
Passivating surface layer

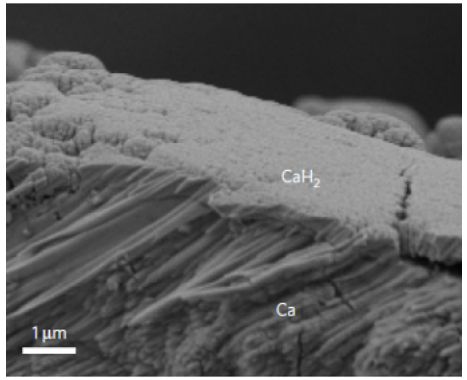


"In contrast to lithium systems, however, calcium deposition in these solvent systems … is impossible, due to the nature of the surface films formed." – Aurbach et al, *J. Electrochem. Soc.* 1991

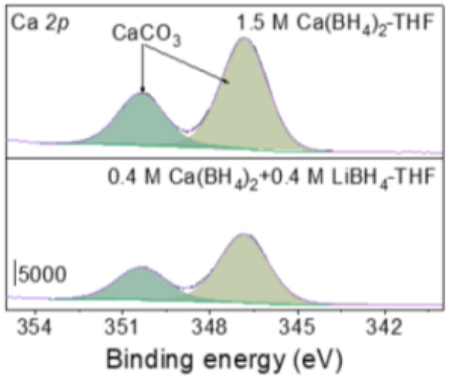
Characterizing Ca interphases is challenging and often inconsistent

Current: *ex situ*, **micro**scale characterization

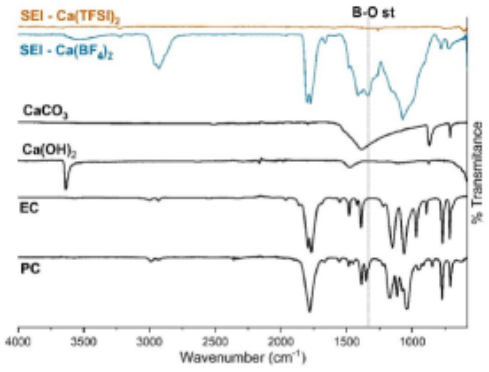




Wang et al. *Nat. Mat.* 2018



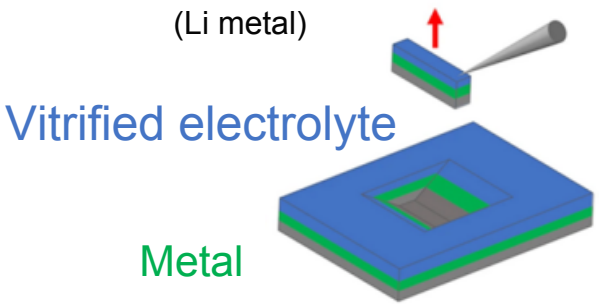
Jie et al. *Angew. Chem. Int. Ed.* 2020



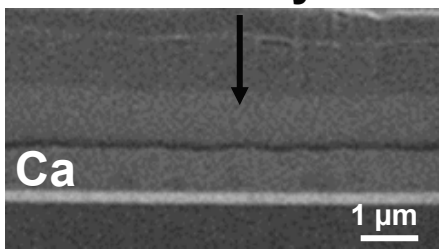
Forero-Saboya et al. *Energy Env. Sci.* 2020

Needed: *in situ*, **nano**scale characterization

Cryo FIB and liftout

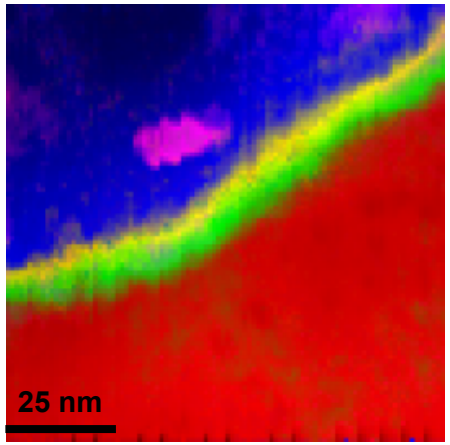


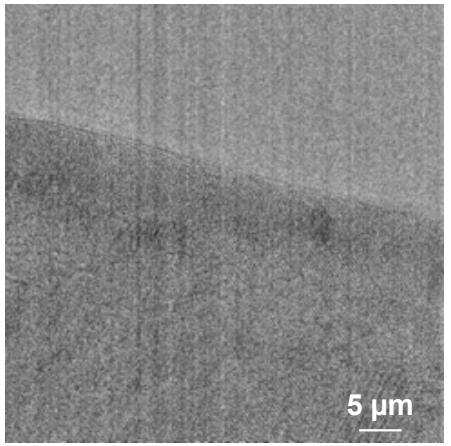
Zachman et al. *Nature.* 2018



McClary et al. *Submitted*

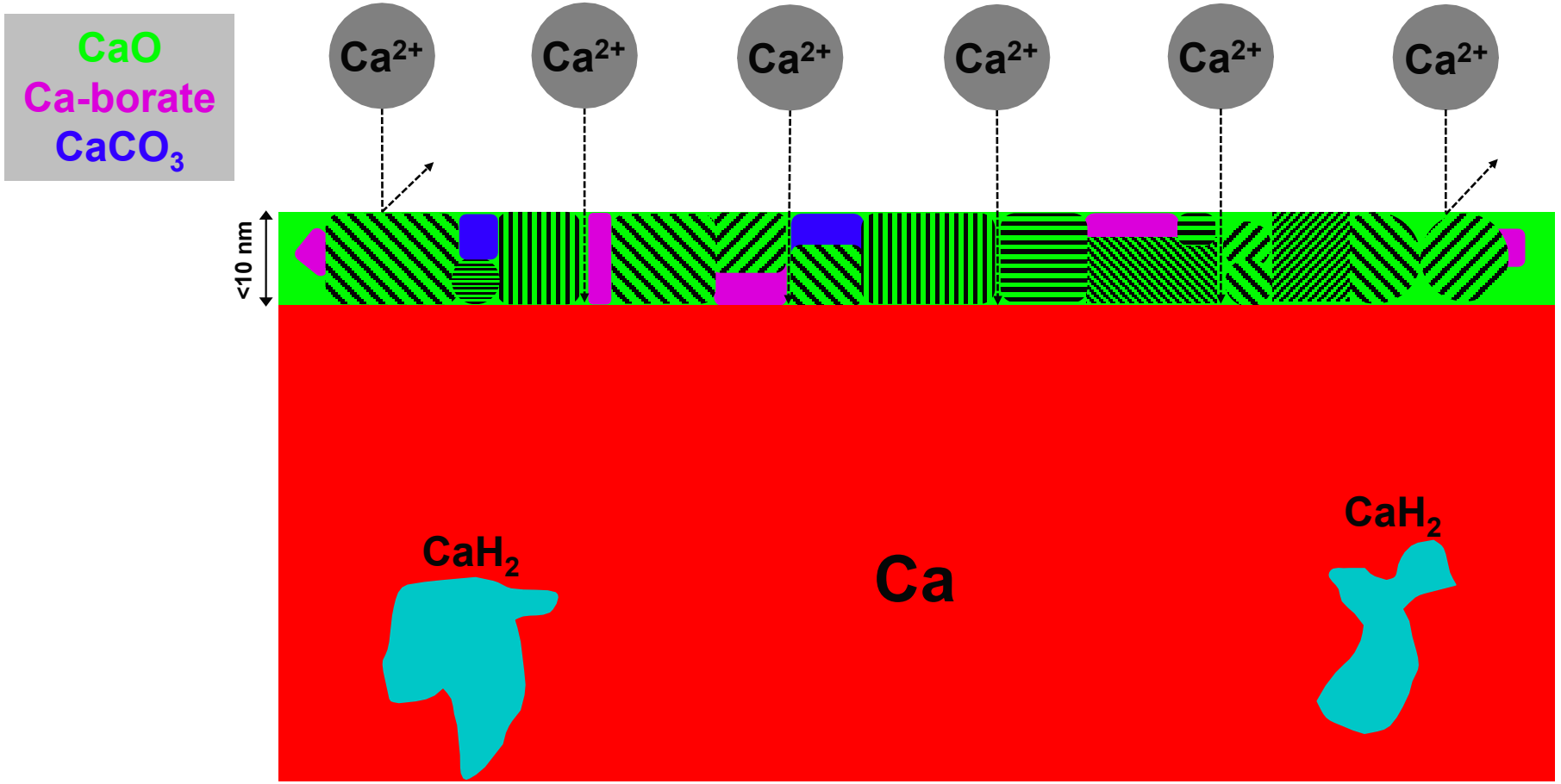
Cryo chemical mapping and imaging





McClary et al. *Under revision*

A nanometric, heterogeneous CaO is an effective SEI for Ca



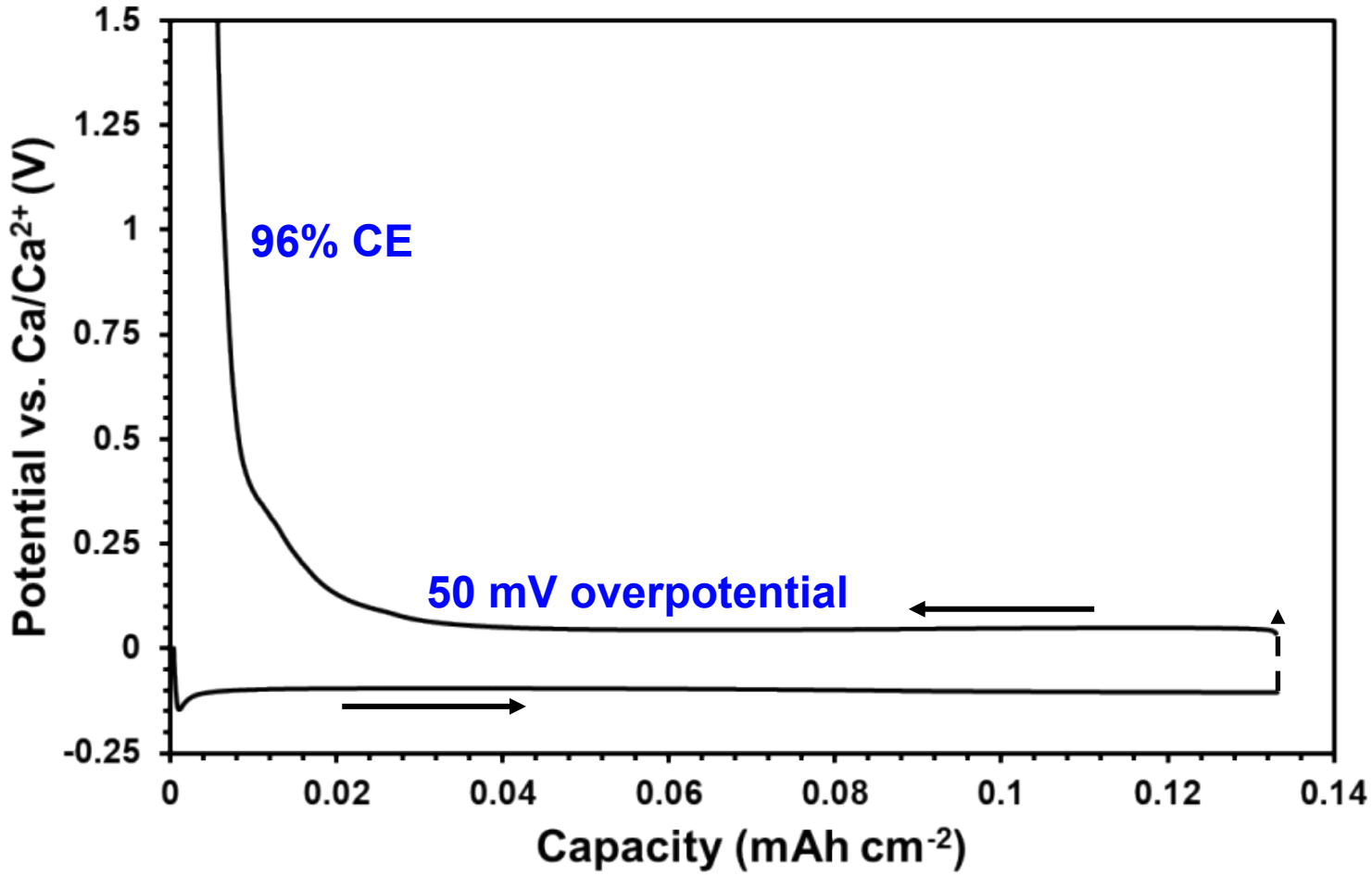
Why $Ca(BH_4)_2$-THF? **Why** does this SEI work? **How** does this SEI form? **How** do we control the SEI?

McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

$Ca(BH_4)_2$:THF is a model system with a functional SEI

Only Ca electrolyte with high efficiency, low self-discharge, and dimensional control

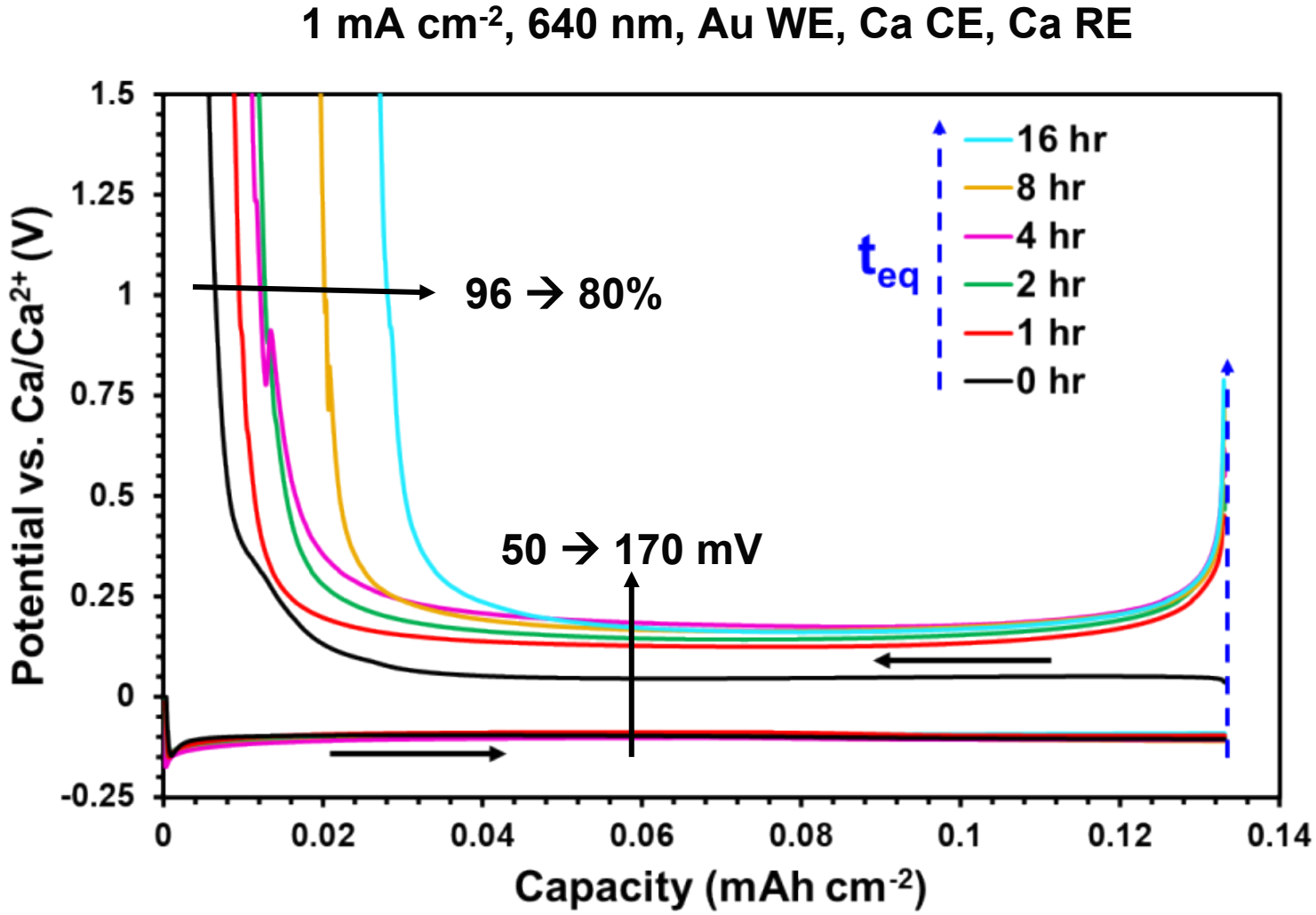
1 mA cm^{-2}, 640 nm, Au WE, Ca CE, Ca RE



McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

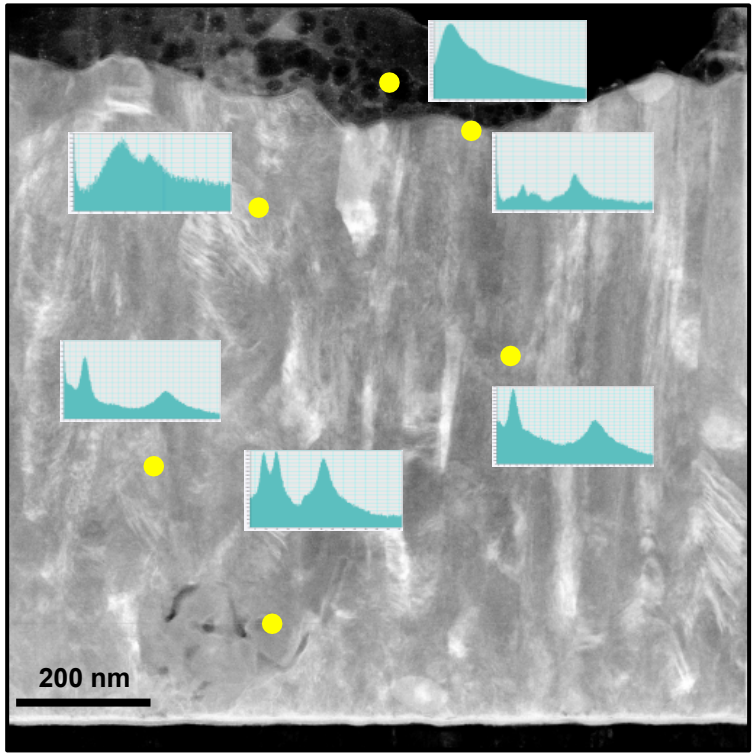
$Ca(BH_4)_2$:THF is a model system with a functional SEI

Only Ca electrolyte with high efficiency, low self-discharge, and dimensional control



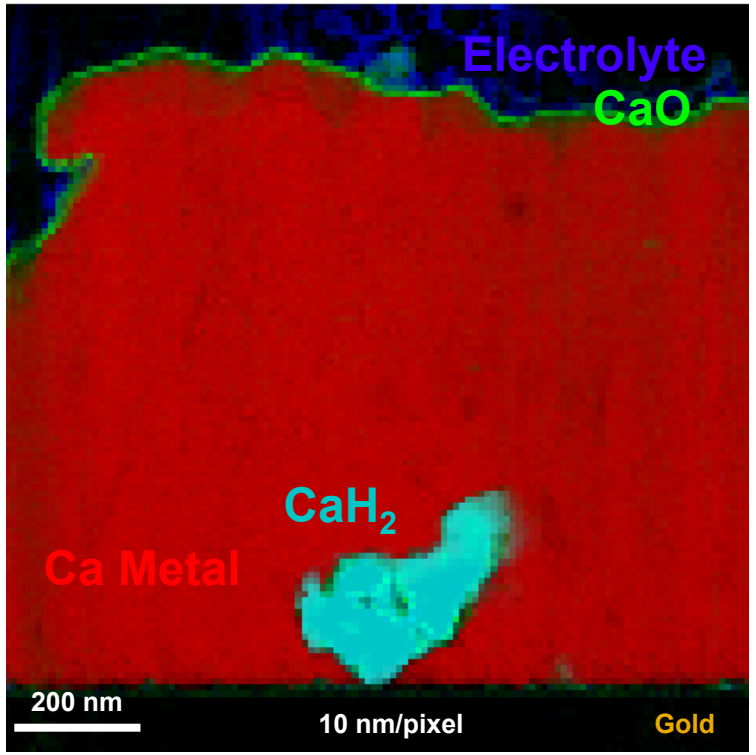
McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

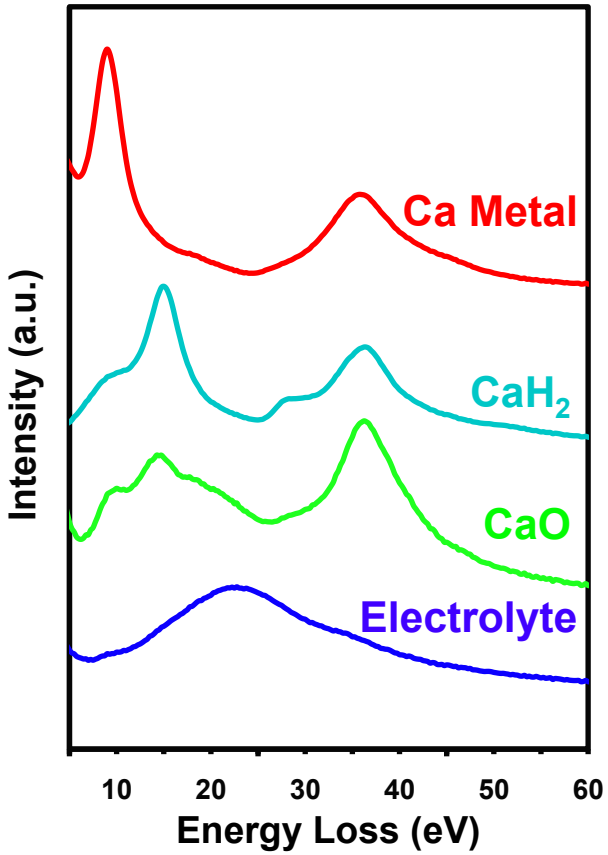
The $Ca(BH_4)_2$:THF SEI is primarily CaO



(~50 nm lamella thickness)

EELS Map

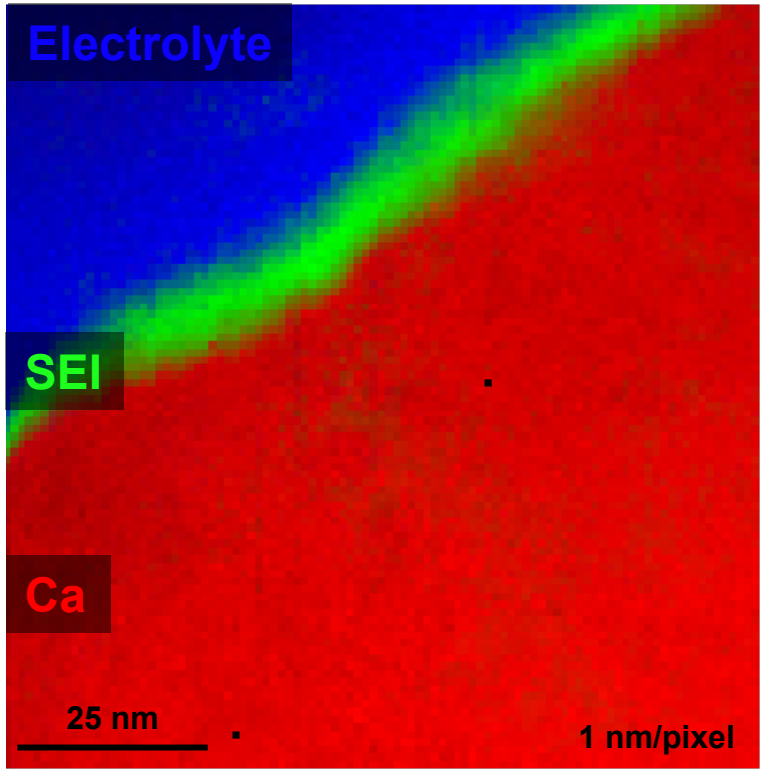




CaO: ~1 eV migration barrier!

(Forero-Saboya et al, Energy Env. Sci. 2020)

Chemical heterogeneity enhances Ca^{2+} transport



Ca $L_{2,3}$-edge

CaO ref.

O K-edge

CaO ref.

B K-edge

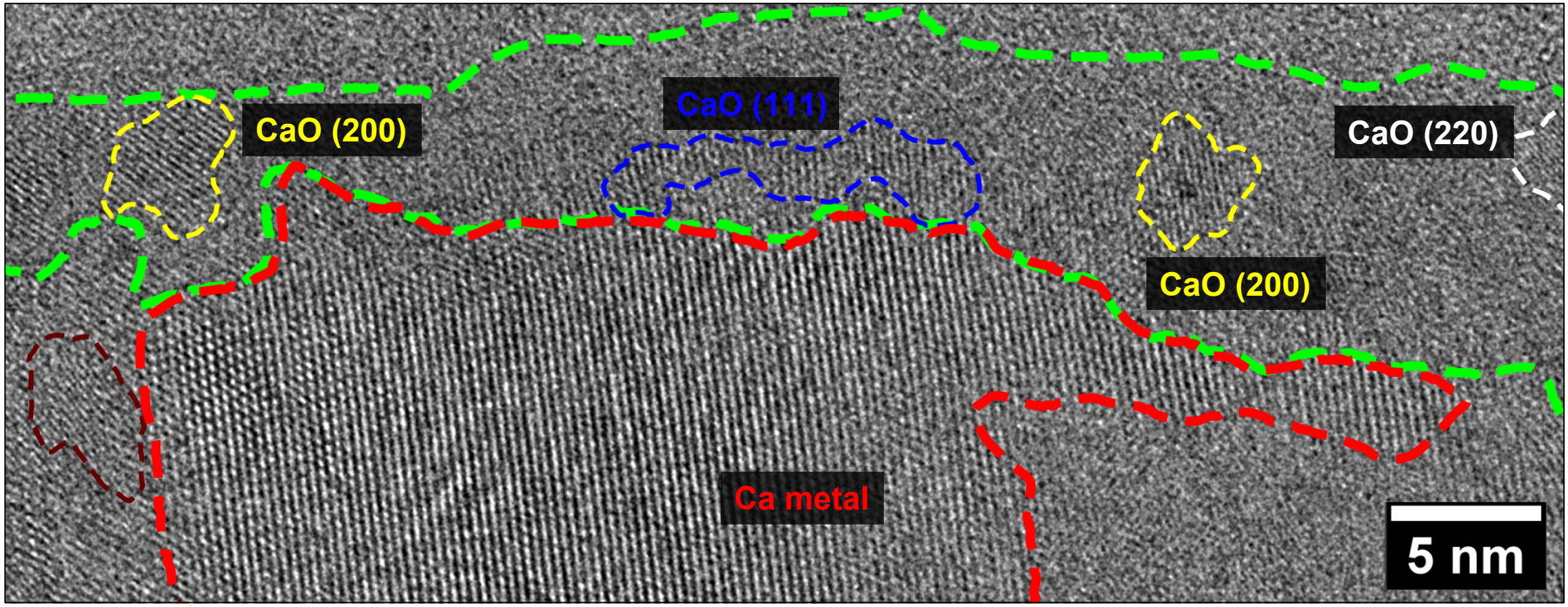
CaB_2O_4 ref.

C K-edge

$CaCO_3$ ref.

Transport enhanced at **<u>phase boundaries</u>**

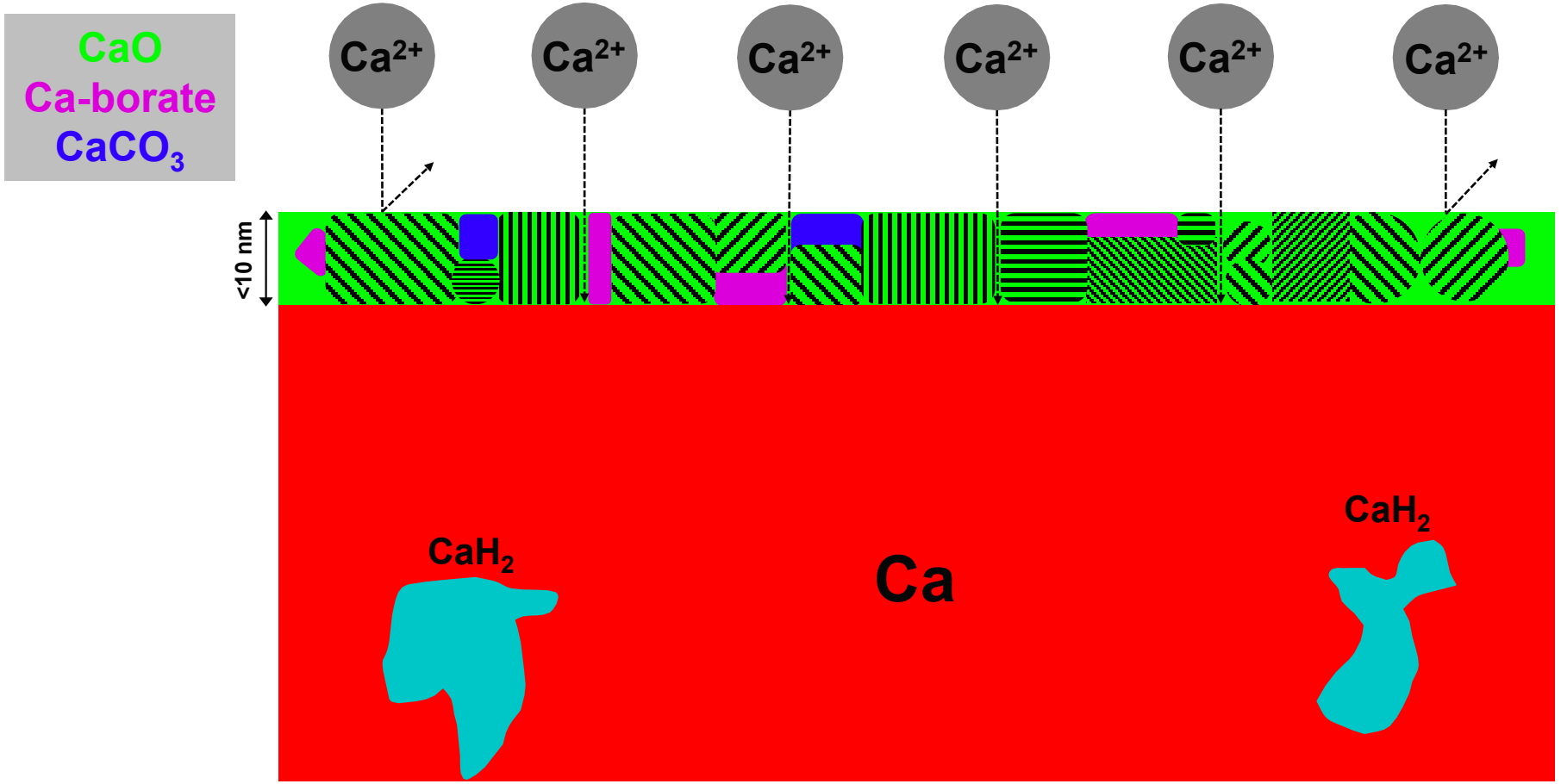
Structural heterogeneity enhances Ca^{2+} transport



Transport enhanced at **grain boundaries**

McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

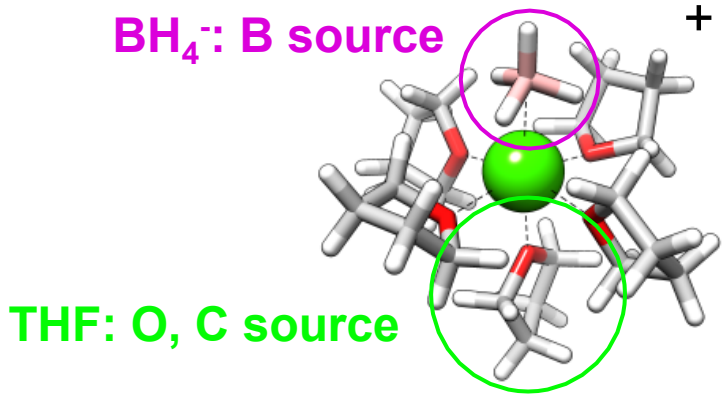
A nanometric, heterogeneous CaO is an effective SEI for Ca



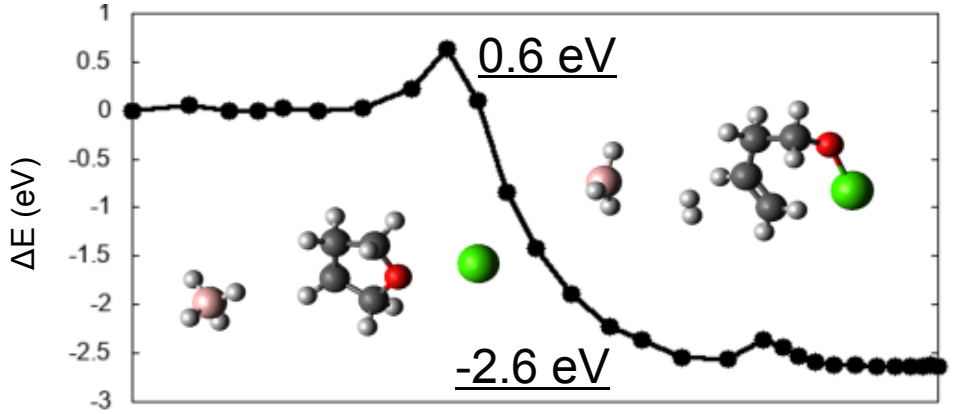
Why $Ca(BH_4)_2$-THF? **Why** does this SEI work? **How** does this SEI form? **How** do we control the SEI?

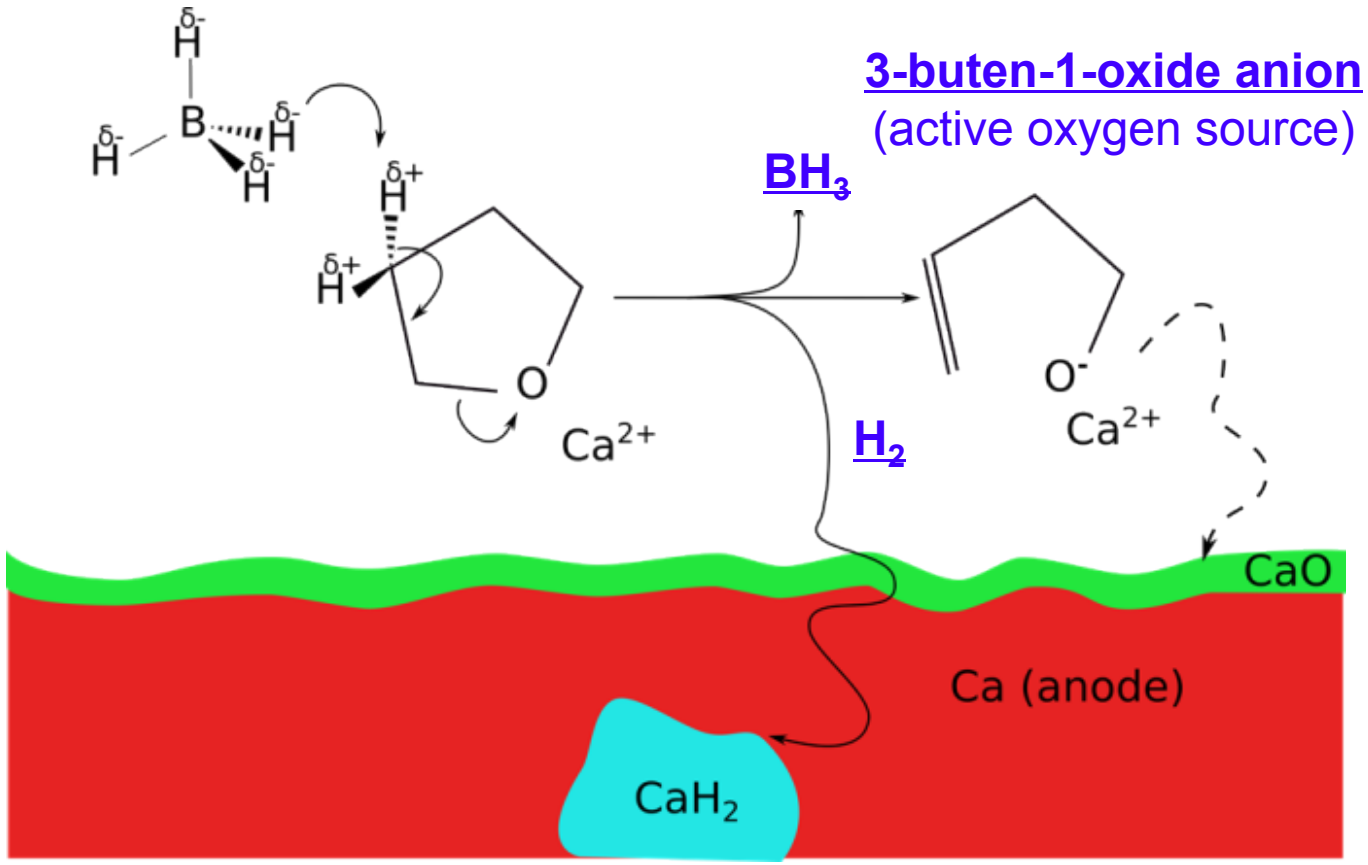
McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

SEI components are dictated by Ca^{2+} solvation structure



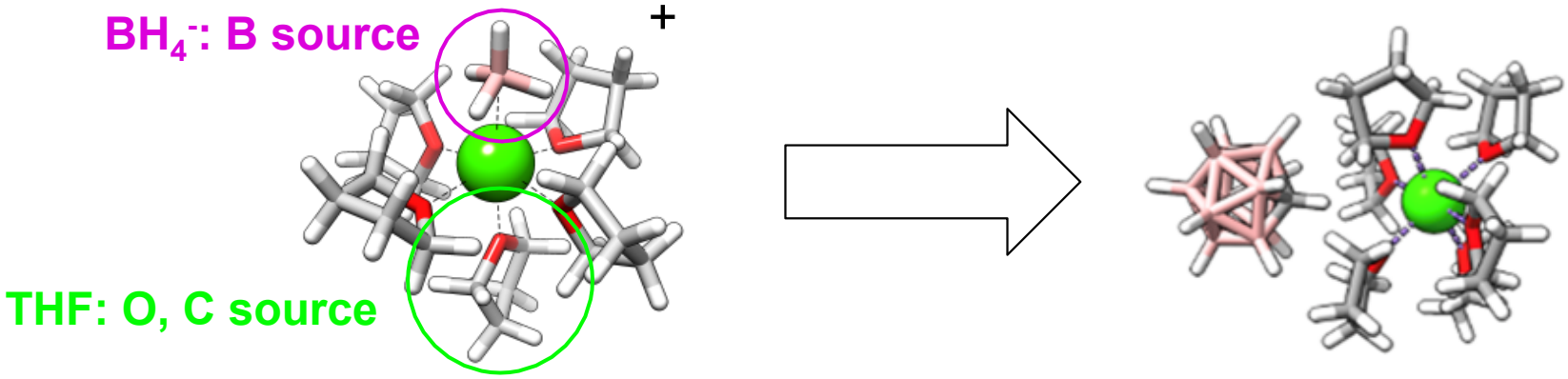
Hahn et al. *J. Mat. Chem A.* 2020
Hahn et al. *J. Phys. Chem. B.* 2021





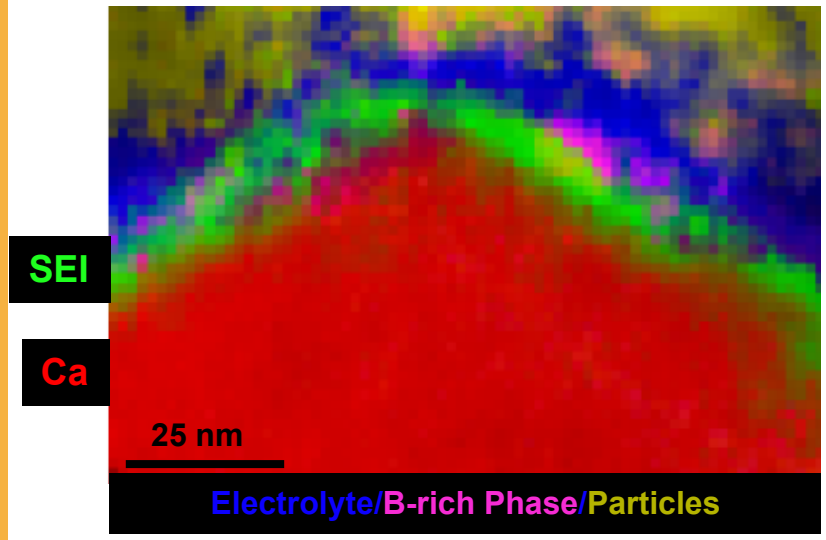
SEI components are dictated by Ca^{2+} solvation structure

Example: $CaBH_4^+$ (contact ion pairs) → $CaCB_{11}H_{12}^+$ (solvent-separated ion pairs)



Hahn et al. *J. Mat. Chem A.* 2020
Hahn et al. *J. Phys. Chem. B.* 2021

Landers, Self, **McClary**, et al. *In preparation*



O K-edge

Mixed anion SEI

BH_4^- only

CaO ref.

B K-edge

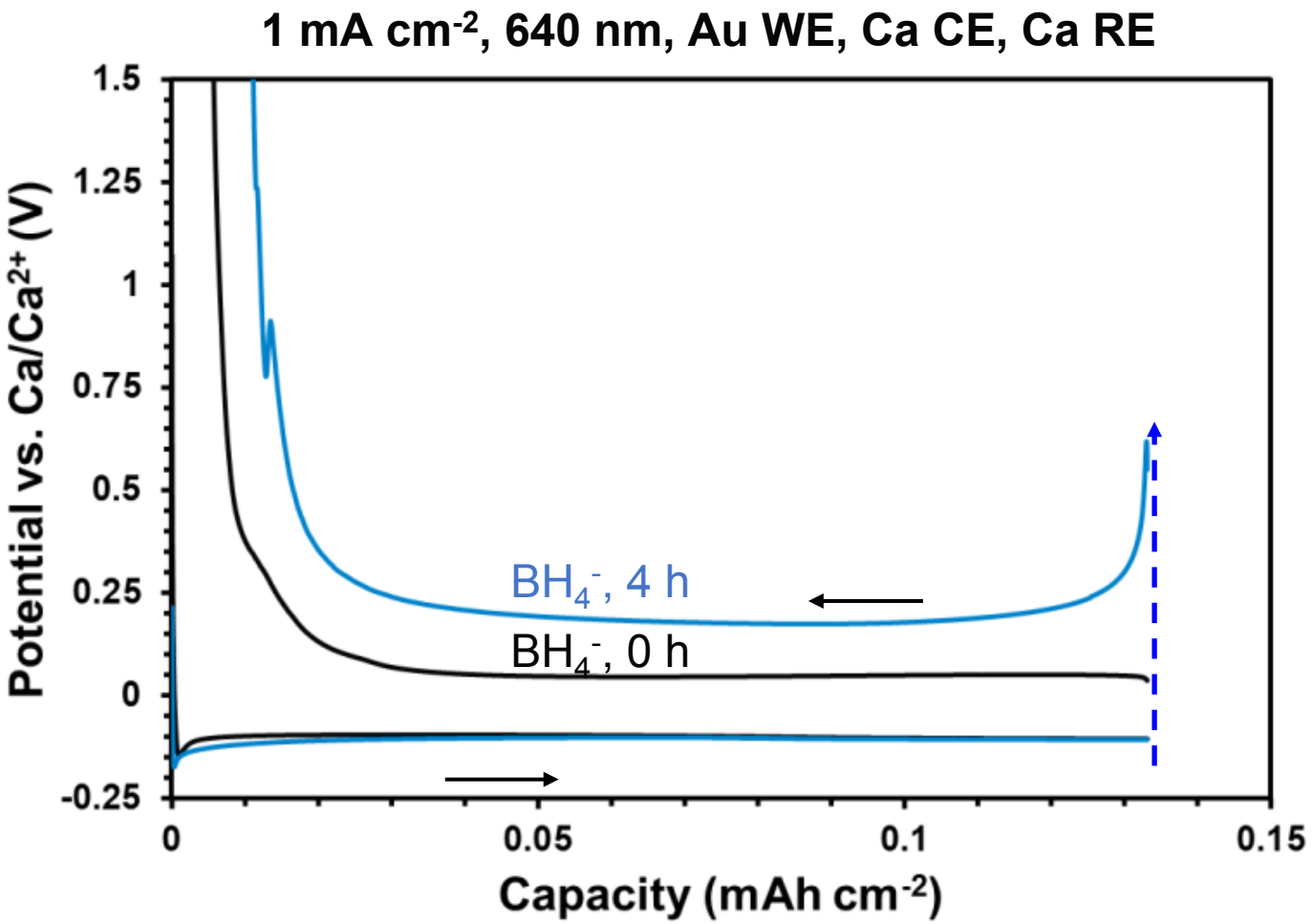
CaB_2O_4 ref.

C K-edge

$CaCO_3$ ref.

McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

SEI heterogeneity and functionality are directly linked

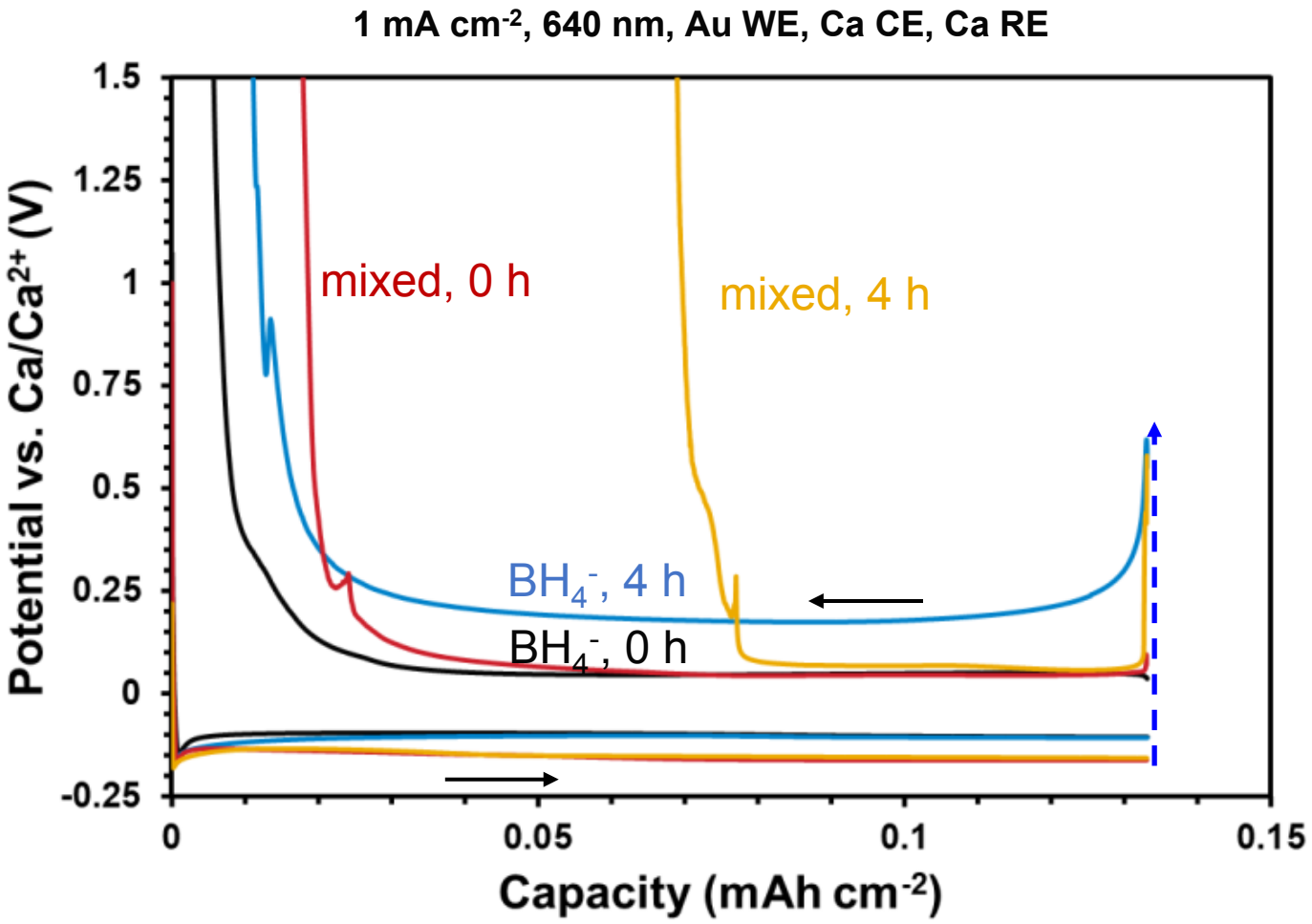


C K-edge

$CaCO_3$ ref.

Landers, McClary, et al. *In preparation*

SEI heterogeneity and functionality are directly linked

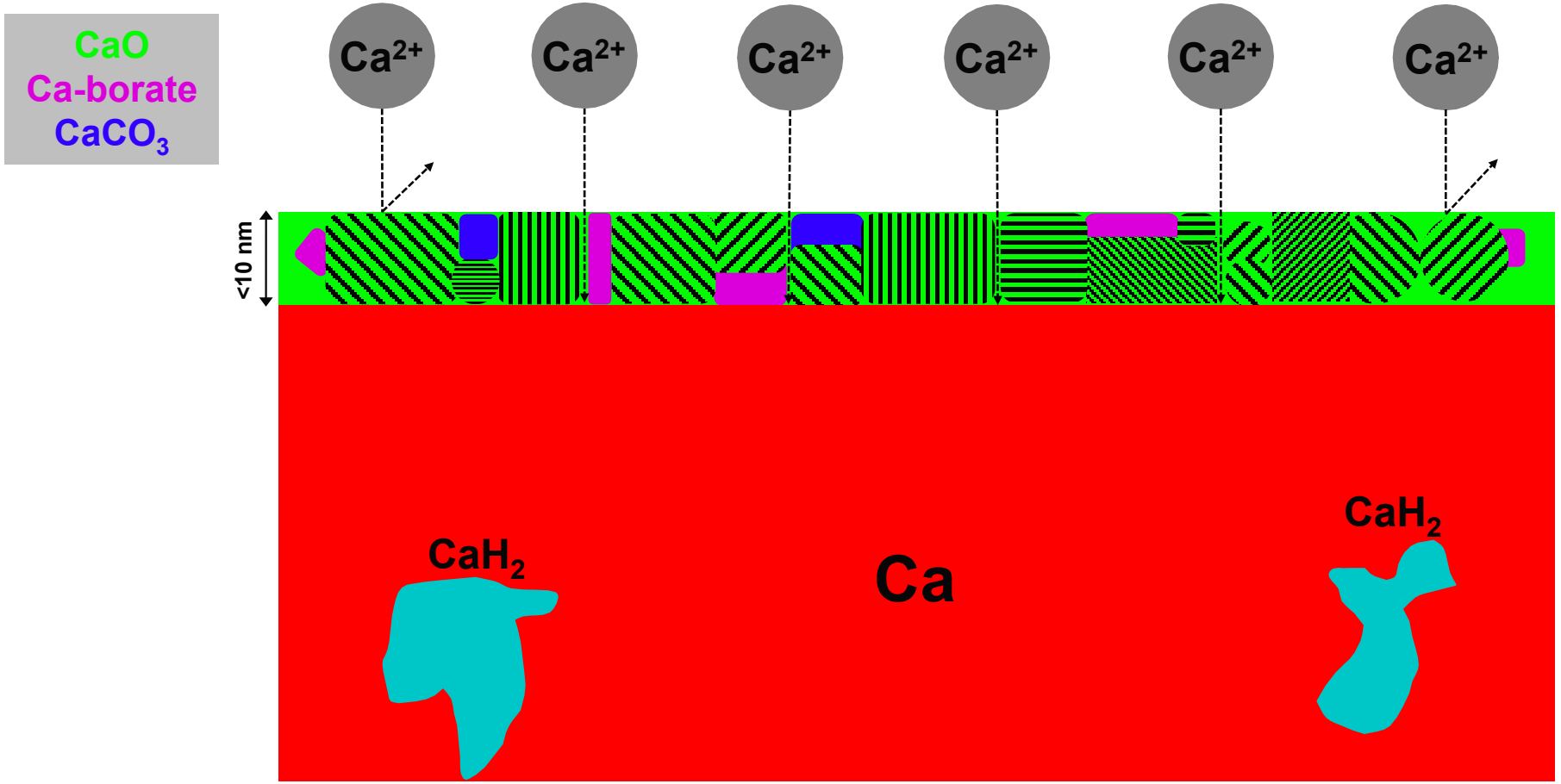


C K-edge

$CaCO_3$ ref.

Landers, McClary, et al. *In preparation*

A nanometric, heterogeneous CaO is an effective SEI for Ca



By rationally designing solvation structure, one can modulate SEI heterogeneity and hence its properties!

McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

Acknowledgements

Daniel Long (cryo-FIB and -TEM)

Ana Sanz Matias (DFT calculations)

Alan Landers (electrolyte synthesis, deposition)

Kathryn Small (cryo-FIB)

Paul Kotula (cryo-TEM)

Nathan Hahn (electrochemistry, solvation)

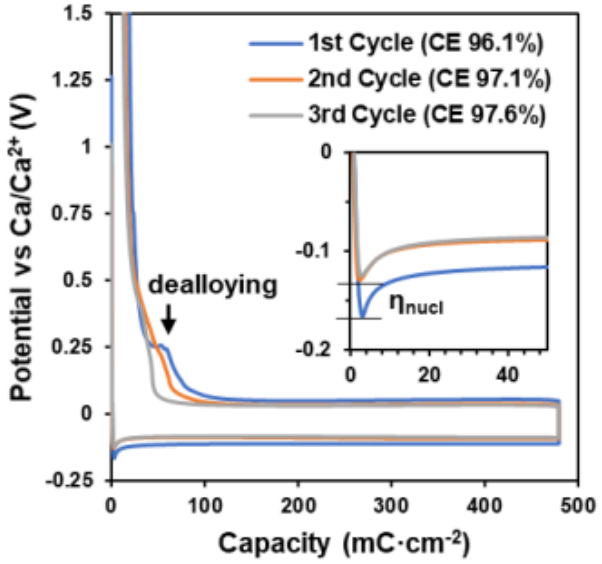
David Prendergast (DFT calculations, PI)

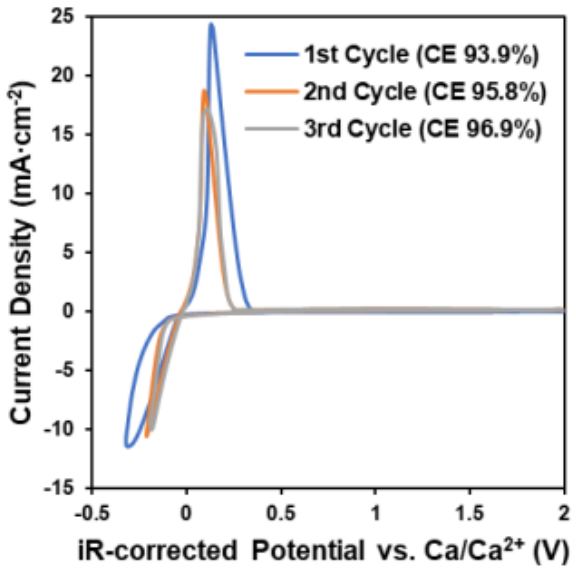
Katherine Jungjohann (FIB and TEM, PI)

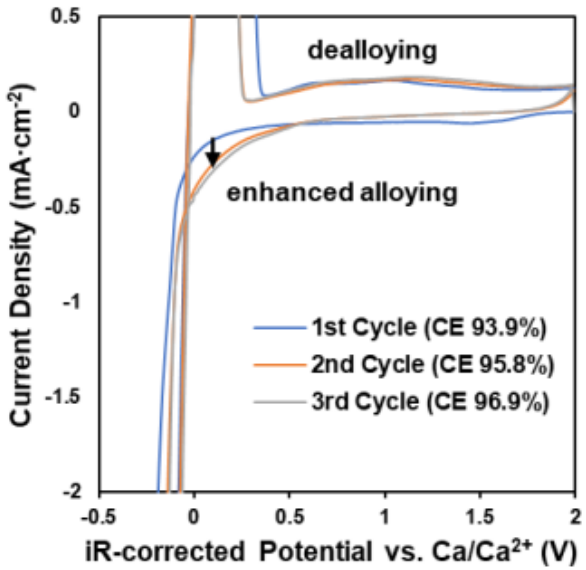
Kevin Zavadil (electrochemistry, PI)

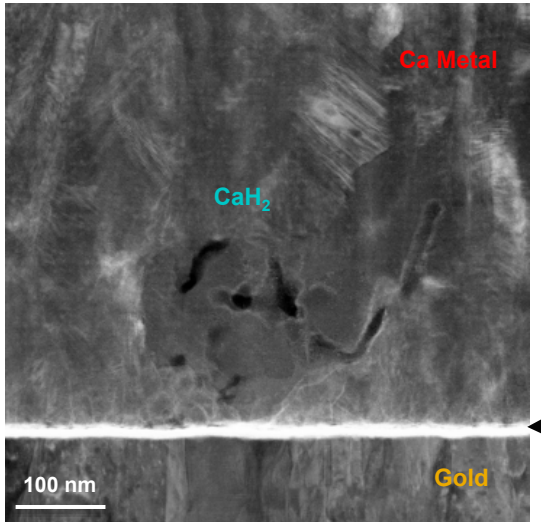
scott.mcclary@sandia.gov

Ca-Au alloying reduces nucleation overpotential







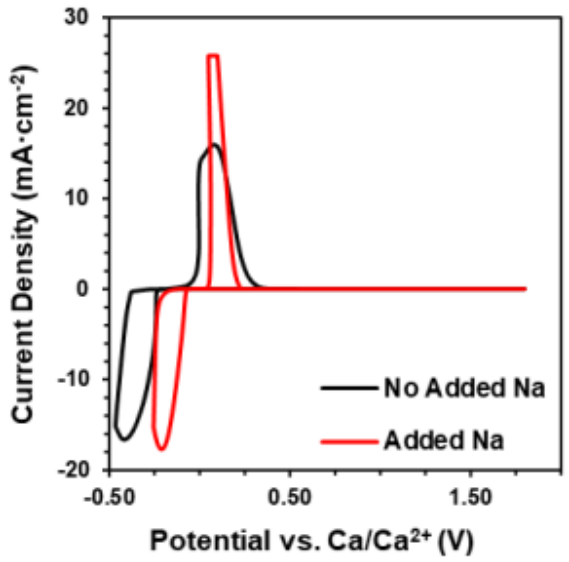


Ca-Au alloy

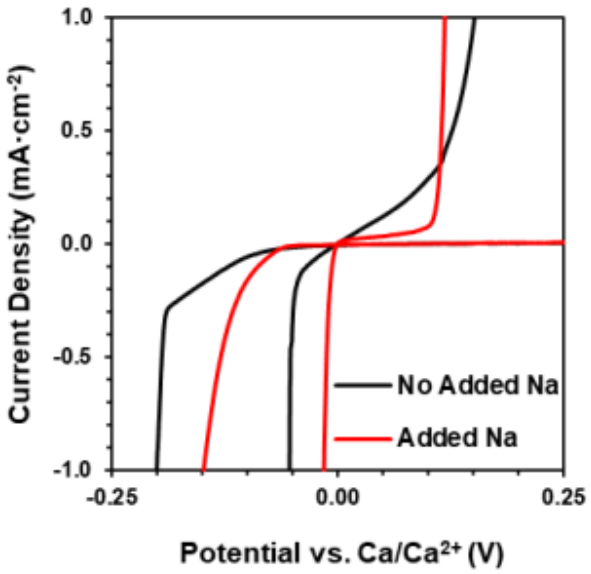
McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*

Na additives are critical for Ca electrodeposition

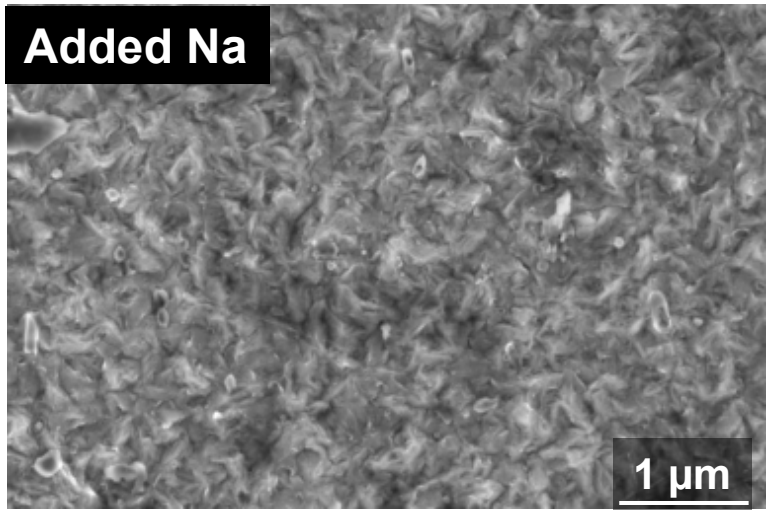
Impurity is present in commercial $Ca(BH_4)_2$ at widely variable concentrations



(iR-corrected)



(iR- and E_0-corrected)



"Ideal" Electrolyte: ~1650 mM $Ca(BH_4)_2$, ~4 mM $NaBH_4$, THF

McClary, Long, Sanz Matias, Kotula, Prendergast, Jungjohann, Zavadil. *Under Revision*