SAND2018-3302C

Improving Solid State Sodium Ion Conductors for Next Generation Energy Storage

Materials Research Society

Symposium EN21: Next Generation Solid-State Super Ion Conductors

4 April 2018

PRESENTED BY

Leo J. Small, Stephen J. Percival, Erik D. Spoerke

Ljsmall@sandia.gov

OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

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Acknowledgements

Sandia National Labs

Dr. Erik Spoerke

Dr. Stephen Percival

Dr. Paul Clem

Dr. Joshua Lamb

Dr. Eric Allcorn

Harry Pratt

Jill Wheeler

Ceramatec, Inc.

Dr. Sai Bhavaraju

Alexis Eccleston

Andrew Reed

University of Virginia

Prof. Jon Ihlefeld

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ENERGY RELIABILITY

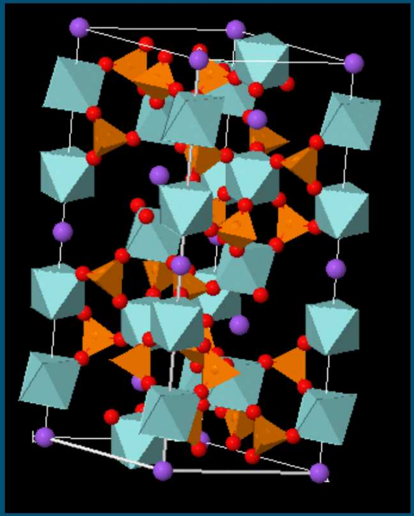
Dr. Imre Gyuk
DOE Energy Storage Program

Overview

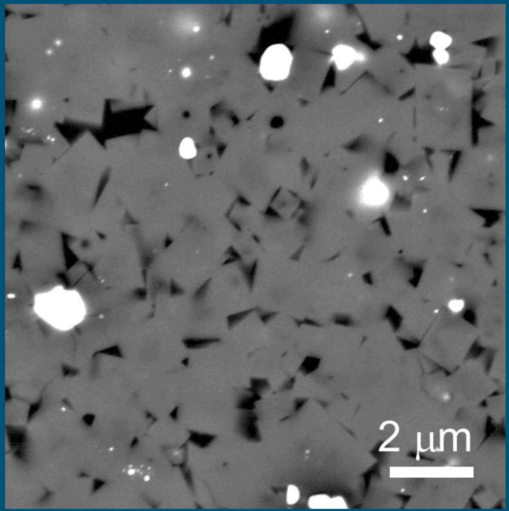
- NaSICON: Na^+ Ion Super CONductor
  - What is NaSICON?
  - Why NaSICON?
- Intermediate temperature (150-180 °C) molten sodium batteries enabled by NaSICON
- Stabilizing "weak links" in NaSICON phase stability via Hf-substitution
- Zero-crossover redox flow batteries enabled by NaSICON

NaSICON: Na^+ Ion Super CONductor

- NaSICON: Na^+ Ion Super CONductor
  - $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$
  - Highest Na^+ conductivity near x=3, $Na_3Zr_2Si_2PO_{12}$
- First reported by Goodenough, Hong, and Kafalas (Mat. Res. Bull. 1976)
- "Skeleton structure" of ZrO_6 octahedra and PO_4, SiO_4 tetrahedra enable fast Na^+ transport

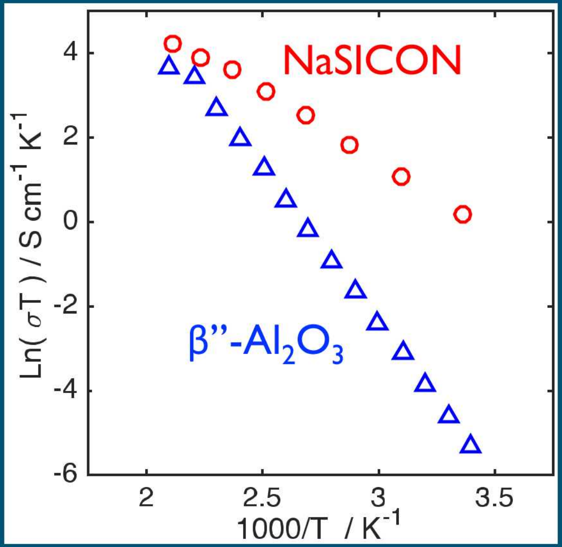


Microstructure



Why NaSICON?

- Tunable crystal structure, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$
- Dopants enable conductivities as high as 4 mS/cm at 25 °C.
- Chemical stability over 20 -180 °C
  - molten sodium
  - inorganic molten salts with $AlCl_3$
- Can be synthesized in a variety of form factors
  - sheets, discs
  - tubes, open or close-ended
  - thin films



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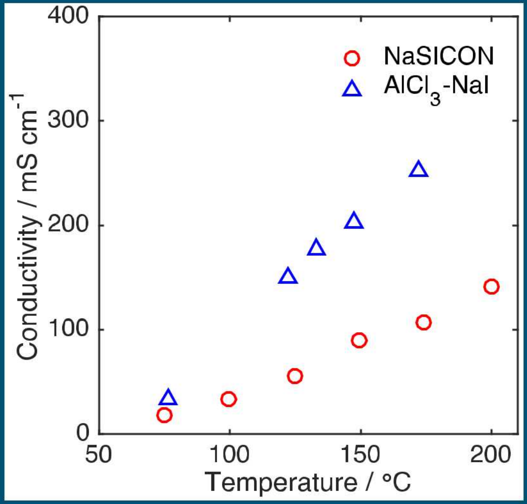
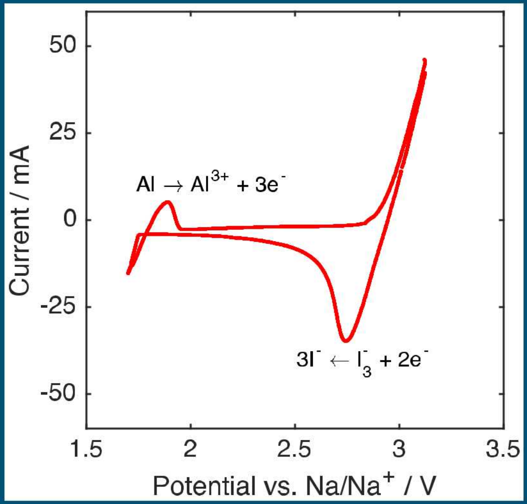
NaSICON Enables Intermediate Temperature Na Batteries

- High conductivity at 180 °C: 110 mS cm^{-1}
  - minimize IR losses in battery

- NaSICON chemically stable at 180 °C
  - molten sodium
  - inorganic molten salts with $AlCl_3$
  - iodine species: I^- / I_3^- / I_2

- NaI-$AlCl_3$ molten salt catholyte
  - charge reaction: $3I^- \rightarrow I_3^- + 2e^-$
  - discharge reaction: $I_3^- + 2e^- \rightarrow 3I^-$
  - concentration of I^-: ~11 M





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NaI Prototype Battery Assembly

- Up to 28 Wh (10 Ah) cell
- Graphite felt + tungsten wire current collectors
- NaI-$AlCl_3$ based molten salt catholyte
- 1” NaSICON tube glass-sealed to α-alumina
- T = 150-180 °C

Anode:

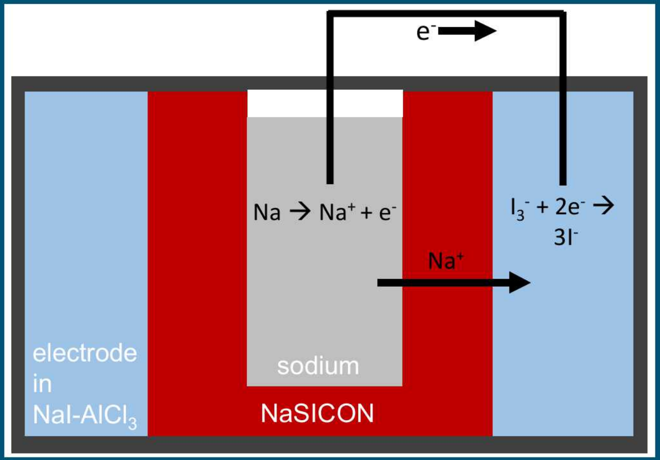
$Na \rightarrow Na^+ + e^-$ $E^0 = 0.00\ V$ vs. Na/Na^+

Cathode:

$I_3^- + 2e^- \rightarrow 3I^-$ $E^0 = 3.24\ V$ vs. Na/Na^+

Overall:

$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$ $E^0 = 3.24\ V$



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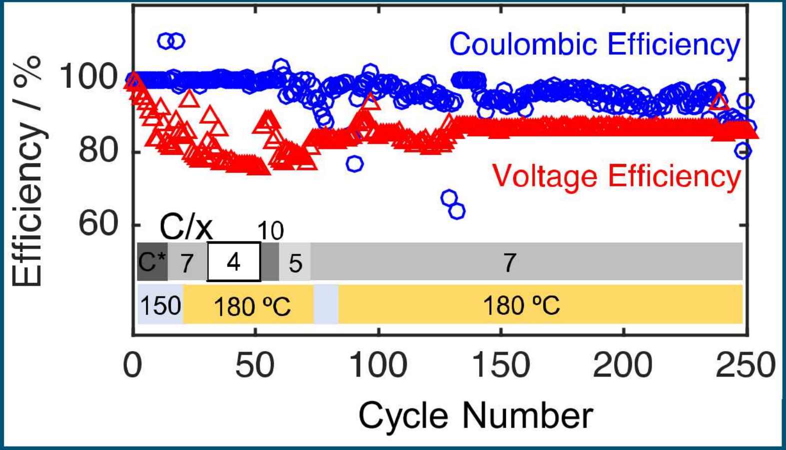
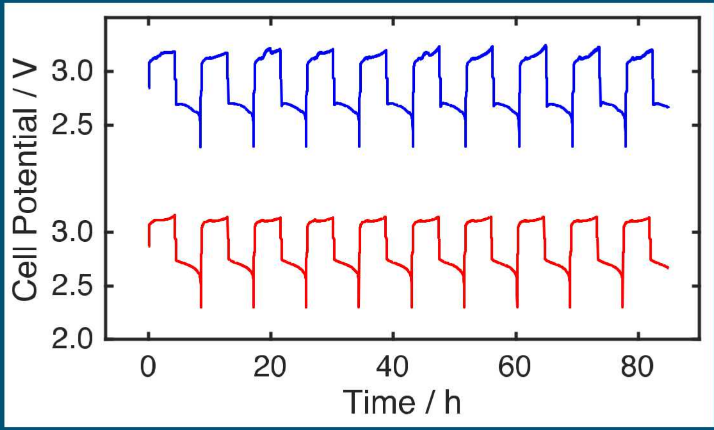
Demonstrated Long Term Battery Performance

- 0.75, 3, 10 Ah battery sizes
- Functional C-rates: C/4 - C/14
- Up to 50 mA cm^{-2}
- High energy efficiency of ~80%

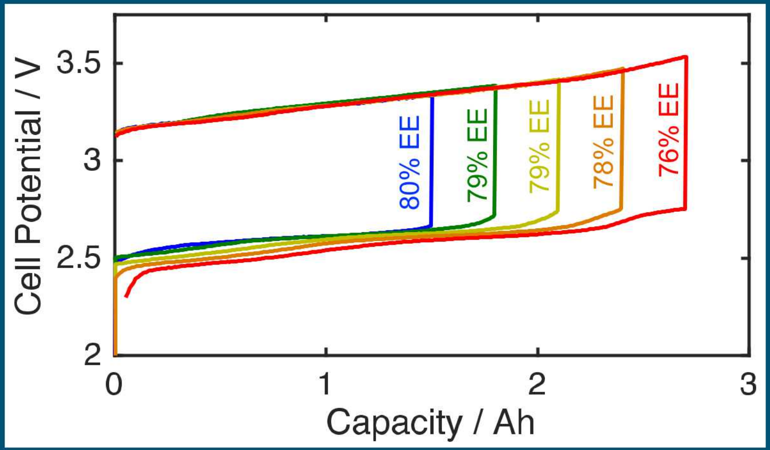
>80% energy efficiency over 3,000 h



Consistent cycling **before** and **after** rest at room temperature for 1 week.



High energy efficiency at deep discharge



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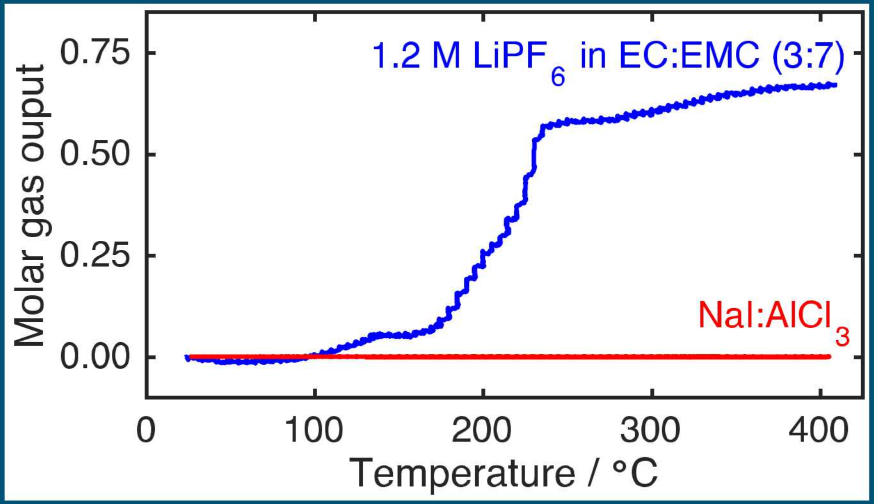
Inorganic Molten Salt Electrolytes Minimize Safety Concerns

- Typical Li-ion battery organic electrolyte can release much gas and heat during failure → potential fire and explosion hazard
- $NaI\text{-}AlCl_3$ molten salt electrolytes release no detectable gas upon simulated internal failure



Dr. Joshua Lamb (Sandia)

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- **Stabilizing "weak links" in NaSICON phase stability via Hf-substitution**

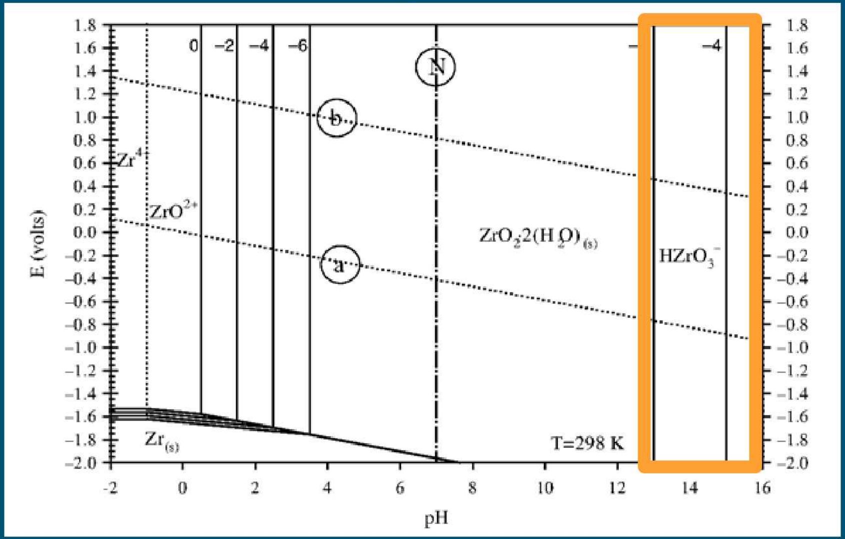
- Zero-crossover redox flow batteries enabled by NaSICON

Weak Links in NaSICON Phase Stability

- $Na_3Zr_2Si_2PO_{12}$ is susceptible to attack at high (aqueous) pH.
  - Zr-O and Si-O bonds are vulnerable.

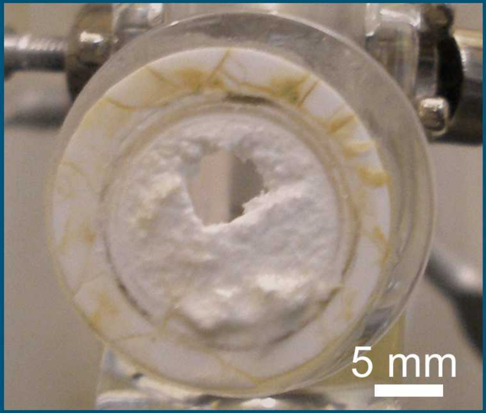
- Examine $Na_{1+x}\,Zr_2Si_xP_{3-x}O_{12}$ phase space to find chemically stable composition.
  - Avoid Si → choose x=0, $NaZr_2P_3O_{12}$
  - Examine Pourbaix diagrams to find substitute for Zr

ZrO_2 dissolution, pH>13



Zr Pourbaix Diagram (Uhlig's Corrosion Handbook)

$Na_3Zr_2Si_2PO_{12}$



NaSICON in 10M KOH
for 24 h at 80 °C

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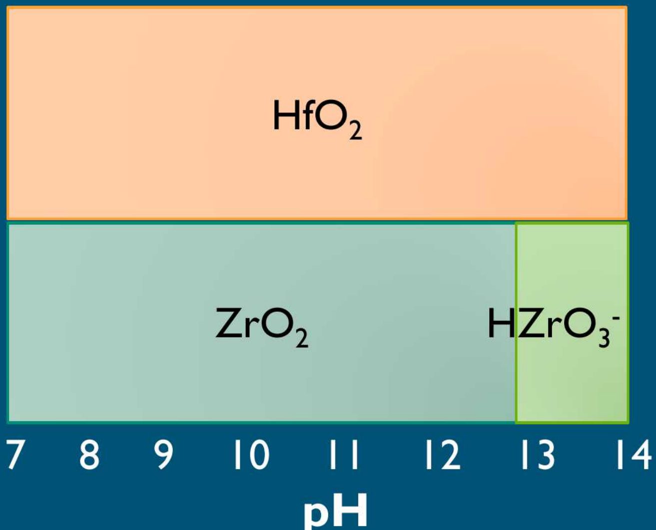
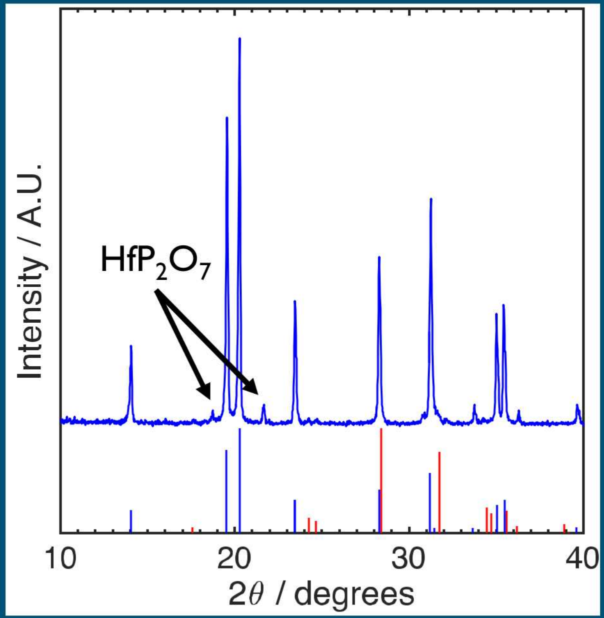
Hf Substitution in NaSICON

- Pourbaix diagram of Hf suggests increased stability at high pH
- Hf^{4+} isoelectric with Zr^{4+}: direct substitution possible
  - Aono and Sugimoto (JACerS, 1996) demonstrate synthesis of $NaHf_2P_3O_{12}$
- $NaHf_2P_3O_{12}$ successfully synthesized
  - HfO_2, P_2O_5, $NaH_2PO_4 \cdot H_2O$ mixed
  - Fired at 1050 °C for 12 h in air
  - Trace HfP_2O_7 and HfO_2 observed in XRD

Stable Phases of Zr or Hf



$NaHf_2P_3O_{12}$



L.J. Small, E.D. Spoerke et al, *J. Mater. Chem. A* (accepted) 2018.

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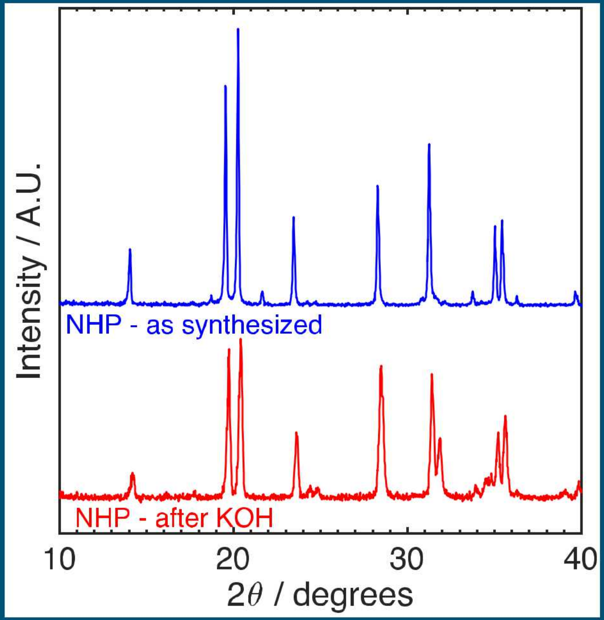
Hf Substitution in NaSICON Enhances Alkaline Stability

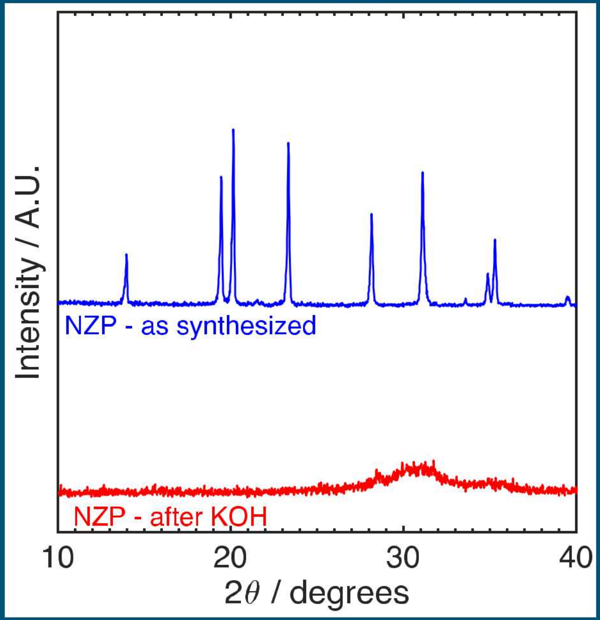
- Compare stability of $NaHf_2P_3O_{12}$ (NHP) and $NaZr_2P_3O_{12}$ (NZP) powders in 10 M KOH at 80 °C for 72 h.

- Powder X-ray diffraction analysis:
  NHP powder survived with trace HfO_2; NZP turned amorphous.

$NaHf_2P_3O_{12}$ (NHP)



$NaZr_2P_3O_{12}$ (NZP)



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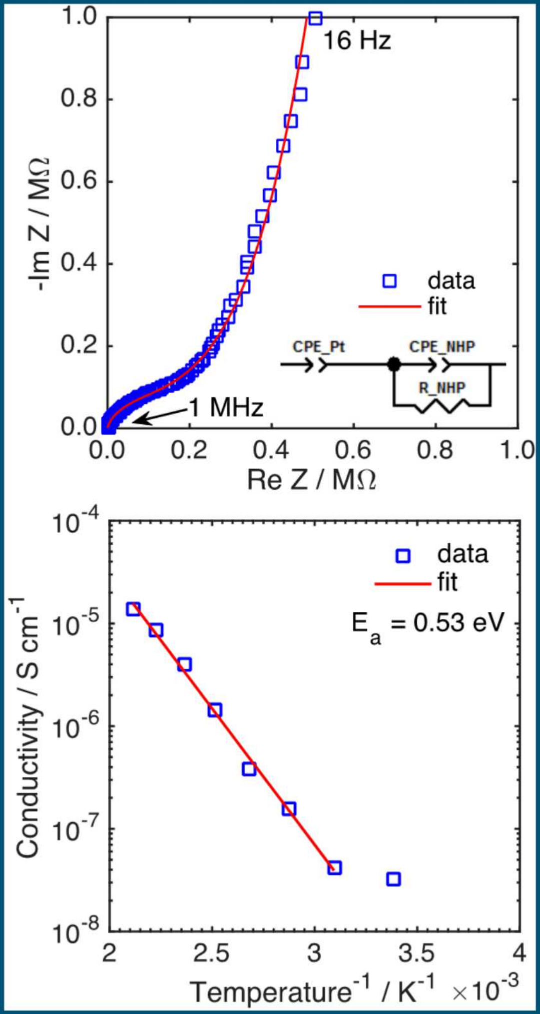
Low Ionic Conductivity in Hf-Substituted NaSICON

- Use impedance spectroscopy to measure ionic conductivity of different NaSICONs.
- Na^+ conductivity of $NaHf_2P_3O_{12}$ (NHP) is 1,000× less than that of $Na_3Zr_2Si_2PO_{12}$.
- ***How can we retain the alkaline stability of NHP without harming ionic conductance of system?***



Prof. Jon Ihlefeld (UVA)

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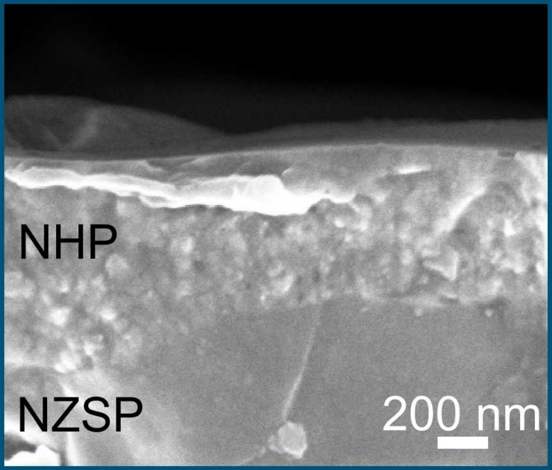
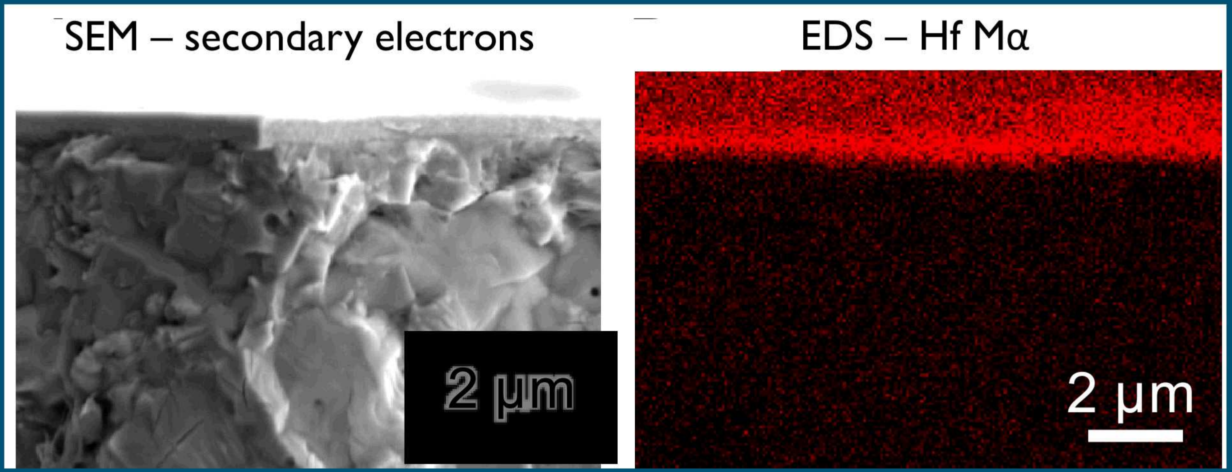
Thin Films of Hf-Substituted NaSICON

- Sol-gel process developed to create thin films of $NaHf_2P_3O_{12}$ (NHP)

- Coat bulk NaSICON pellets or Si wafers
  - Spin-coat 3000 rpm 30s
  - Pyrolyze 300 °C in air 5 min
  - Crystallize 775 °C in air 10 min

- Maintain high Na^+ conductance: $Na_3Zr_2Si_2PO_{12}$ pellet conductance decreased from 26.8 to 26.1 mS cm^{-2} (80 °C)





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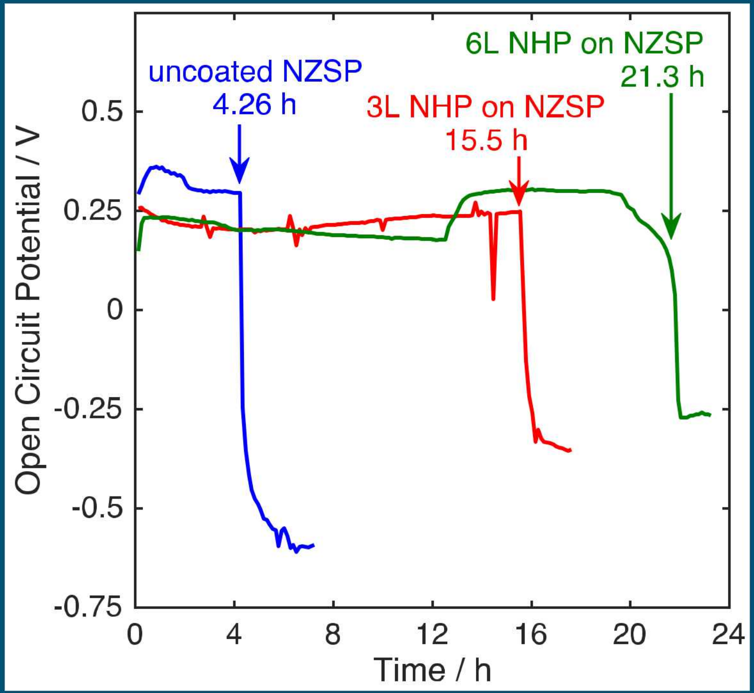
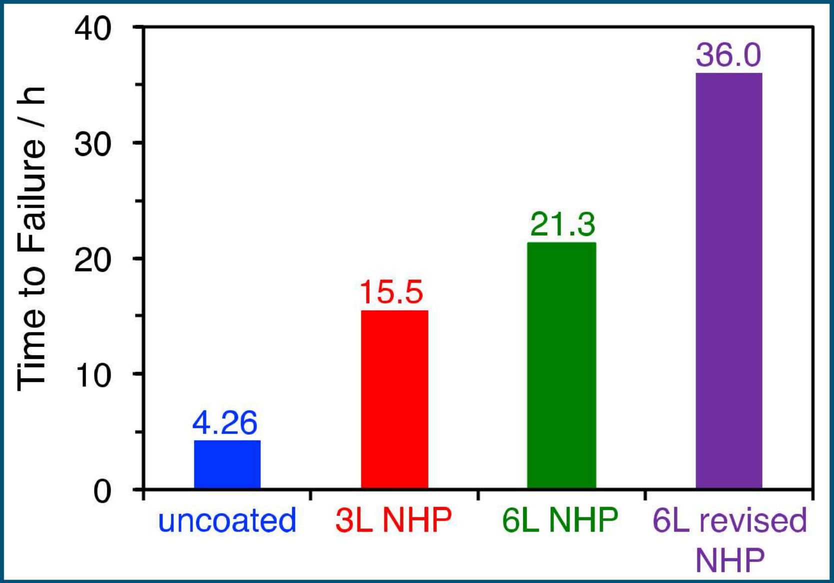
Thin Films of Hf-Substituted NaSICON Protect Bulk NaSICON

- $NaHf_2P_3O_{12}$ (NHP) thin films extend bulk $Na_3Zr_2Si_2PO_{12}$ (NZSP) lifetime from 4 to 36 hours in 10 M KOH at 80 °C
- Film quality (cracks, pinholes) very important





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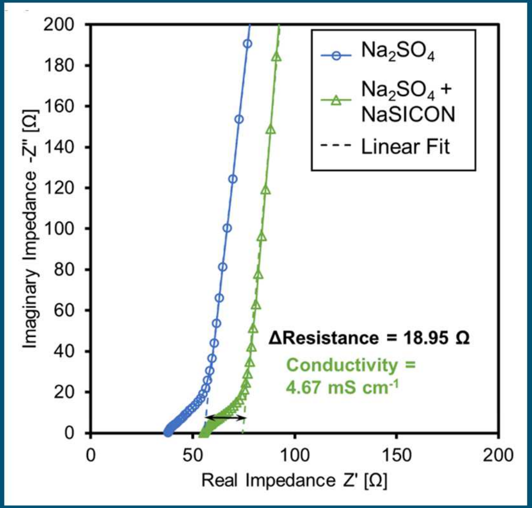
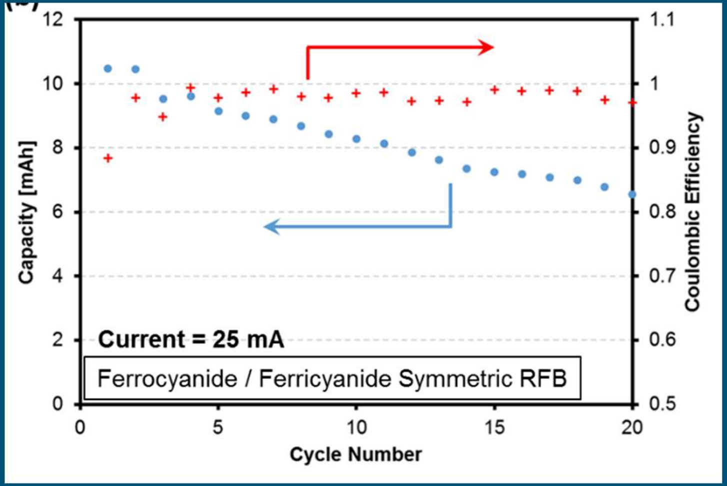
- **Zero-crossover redox flow batteries enabled by NaSICON**

Zero-Crossover Redox Flow Batteries

- Crossover of redox-active species is major source of capacity fade in RFB.
- Most polymeric membranes allow solvent through them.
- High Na^+ conductivity NaSICON was used as a separator in a RFB with Fe-based redox couples in Na_2SO_4.
- >95% Coulombic efficiency

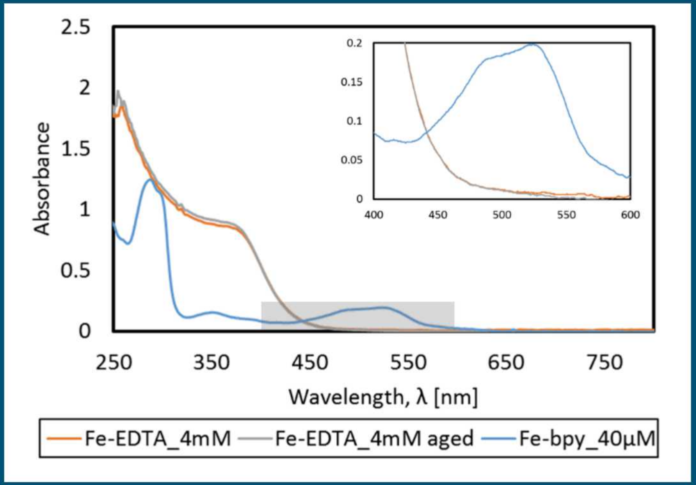


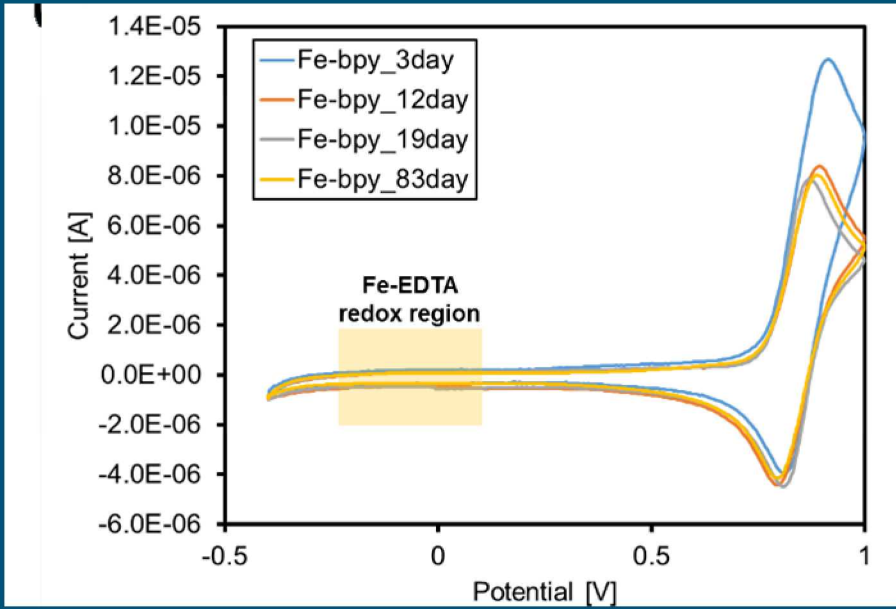


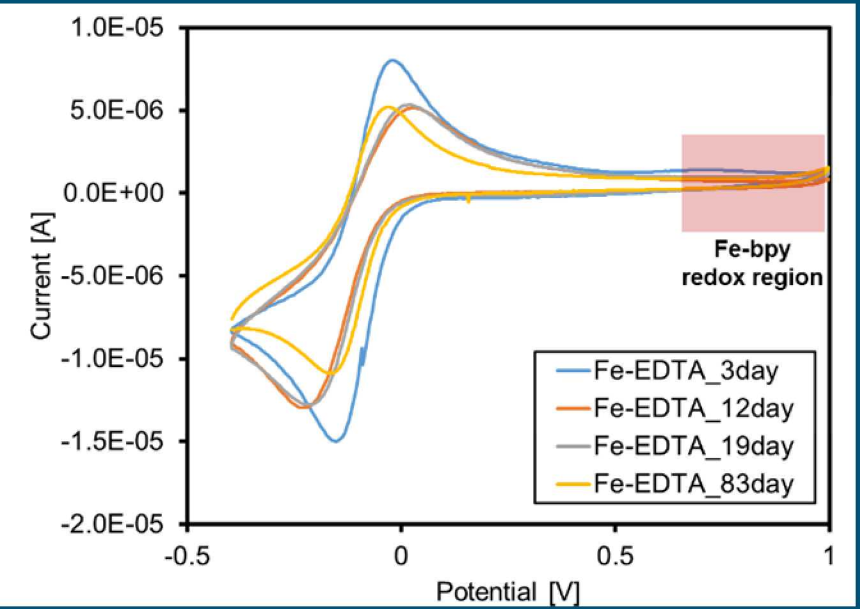
Dr. Eric Allcorn, Harry Pratt (Sandia)

Zero-Crossover Redox Flow Batteries II

- No crossover of Fe-bpy or Fe-EDTA detected in post cycled solutions
  - Cycling voltammetry (CV)
  - UV-Vis spectroscopy







E.A. Allcorn, E.D. Spoerke et al, *J. Power Sources* 37 (2018) 353-361.

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Dr. Eric Allcorn (Sandia)

Moving Forward

Driving Na-battery operating temperatures down to 100 °C

- Low temperatures allow plastic seals for decreased materials cost
- Decreased aging on full assembly → increased reliability and lifetimes
- Optimization of molten salt catholyte for decreased temperatures

Leveraging enhanced NaSICON to other applications

- Alkaline Zn/MnO_2 batteries – see Dr. Jonathon Duay's talk up next!
- Redox flow batteries

Advanced form factors

- Integration of thin film NaSICON

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