Ambient Temperature All-Solid Sodium-Sulfur Batteries

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Molten Sodium Batteries

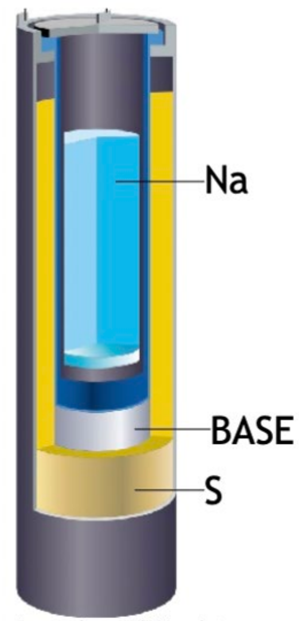


Image from NGK Insulators

High-temperature sodium batteries

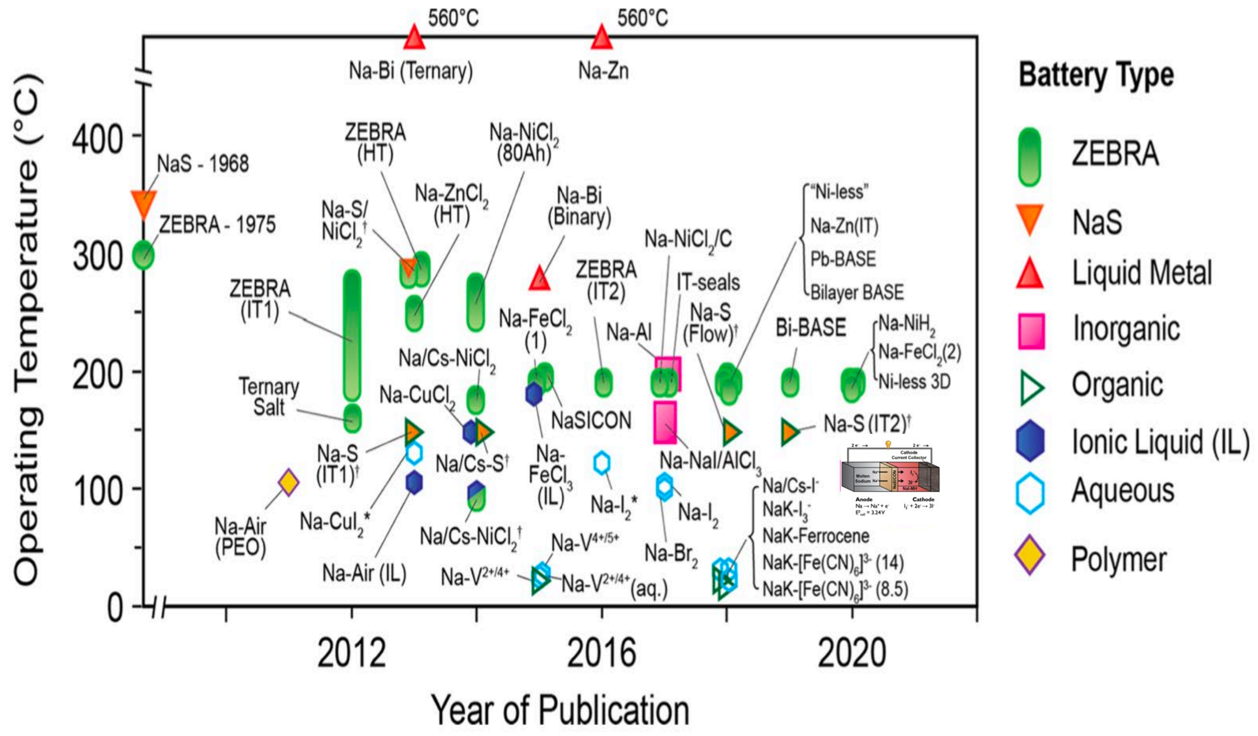
- operate at high temperatures (~300 °C)
- “mature” technology that supports
- renewables integration
- microgrids
- behind-the-meter applications

Emerging systems show promise

- intermediate or low-temperature
- molten Na flow batteries

NGK BASF We create chemistry INLYTE ENERGY ADENA POWER

Erik D. Spoerke, DOE Office of Electricity Peer Review 2023



Erik D. Spoerke et al. ACS Appl. Energy Mater. 2020, 3, 11456

Ambient Temperature All-Solid Sodium-Sulfur Batteries

Ambient temp. (~ 60 ℃) all-solid Na-S batteries

- Strong motivation to lower temperature to
  - Increase lifetime
  - Reduce materials and operation cost
  - Improve safety of systems
- Full conversion of sulfur overcomes the discharge limit at molten state

$S_8 + 4\ Na^+ + 4\ e^- \leftrightarrow 2\ Na_2S_4$: 419 mAh g^{-1} (molten)

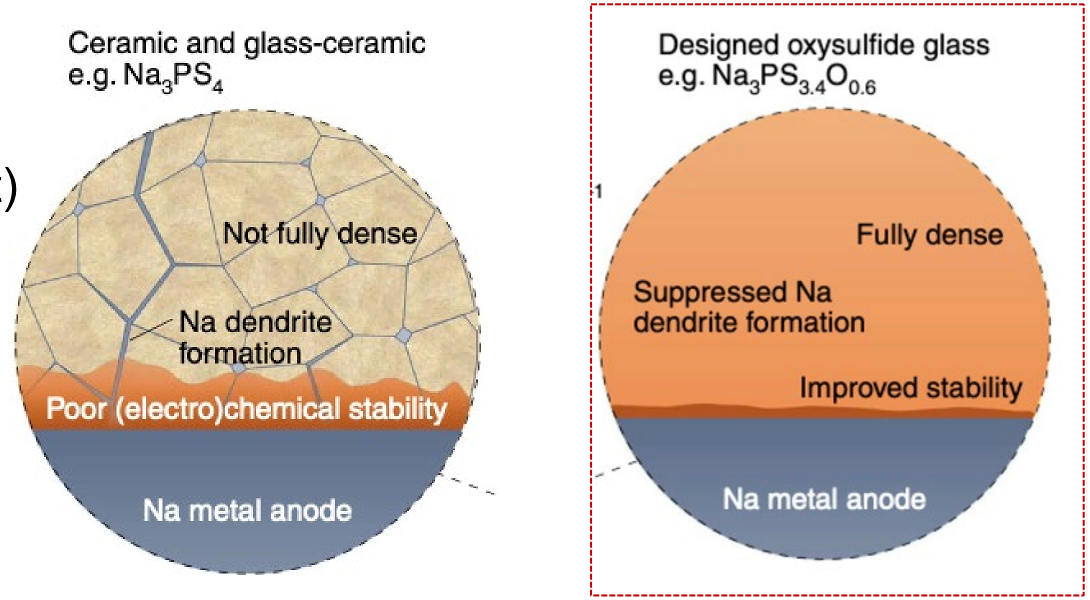
$S_8 + 16\ Na^+ + 16\ e^- \leftrightarrow 8\ Na_2S$: 1675 mAh g^{-1} (ambient)

Challenges of sulfide-based Na-ion conductors

- Poor electrochemical stability
- Solid electrolyte not full dense
- Na dendrites
- Slow kinetics of sulfur reaction

Composition control of phosphorous oxysulfide $Na_3PS_{4-x}O_x$

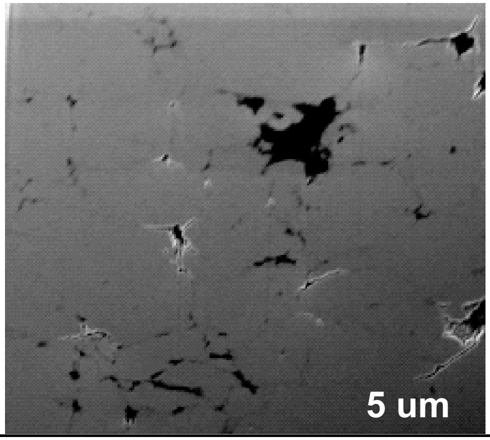
- Improved electrochemically stability with Na metal, forming thin, dense, self-limiting interphase
- Fully dense microstructure

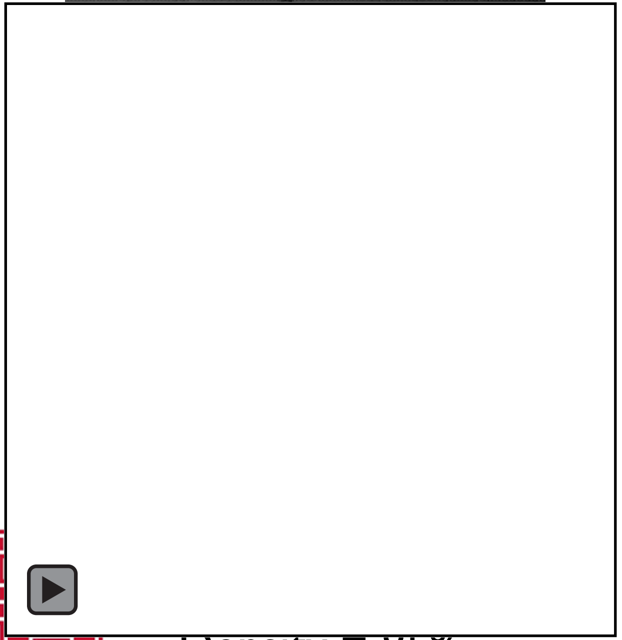


Chi, Zhang, Hao, Kmiec … Martin* and Yao*, *Nature Comm.* 13, 2854 (2022)
News & Views, Ohno, Zeier, *Nature Energy*, 7, 686 (2022)

Mechanochemical Synthesis of Oxysulfide with Composition Control

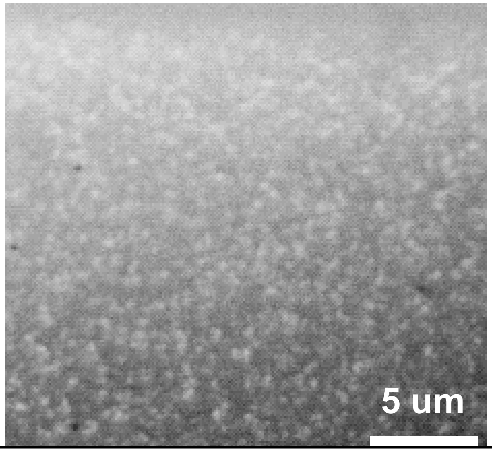
Na_3PS_4 glass

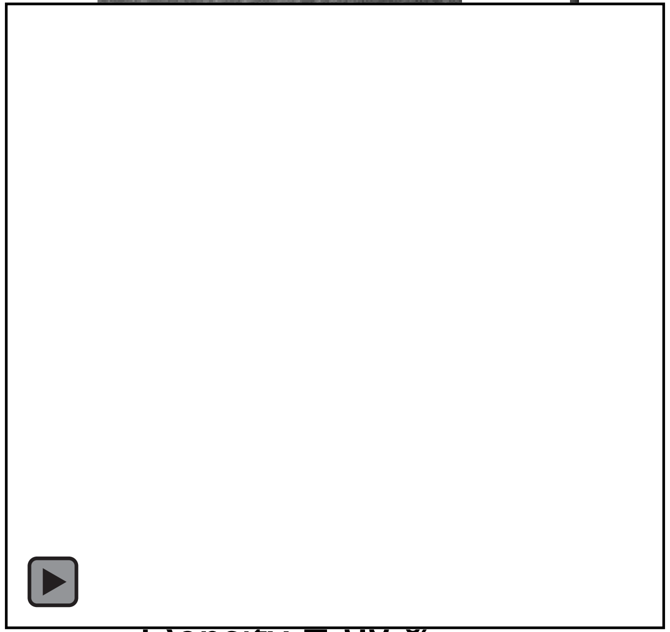




Density = 85%

$Na_3PS_{3.4}O_{0.6}$ glass

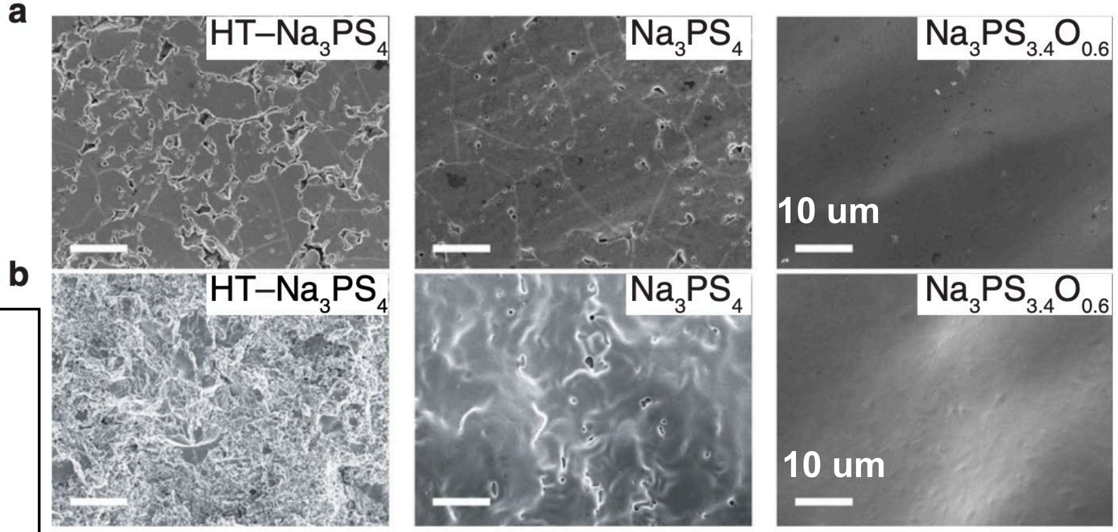


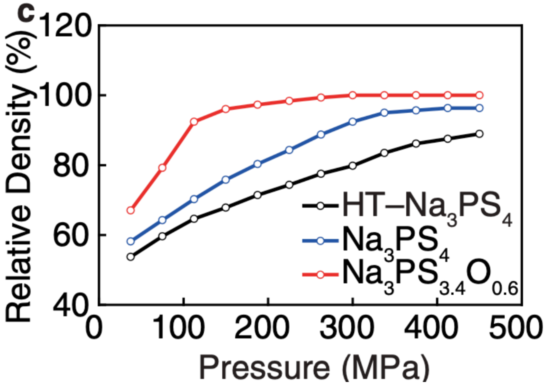


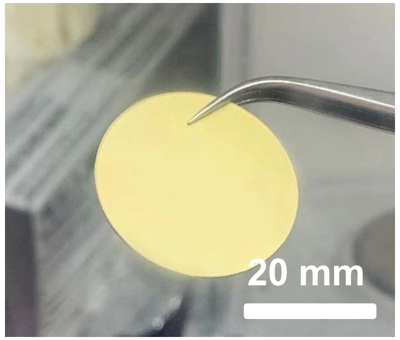
Density = 98 %

Room temperature synthesis of $Na_3PS_{4-x}O_x$

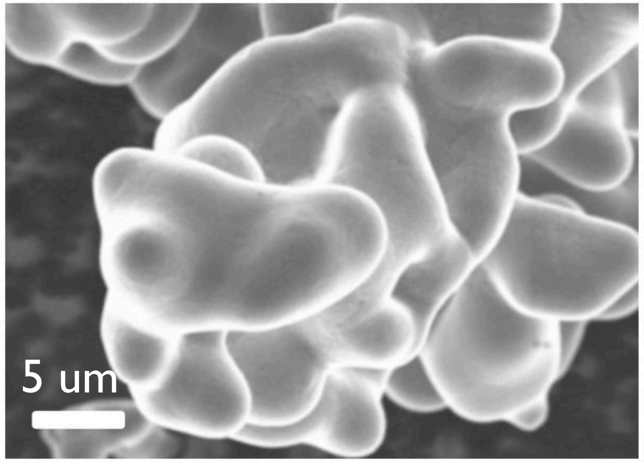
ball milling (Na_2S, P_2S_5, P_2O_5) and cold pressing

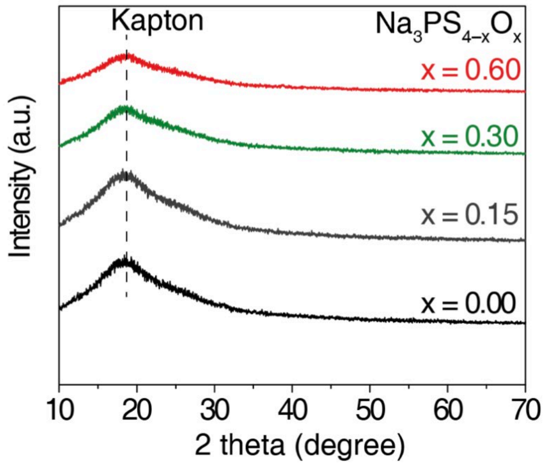




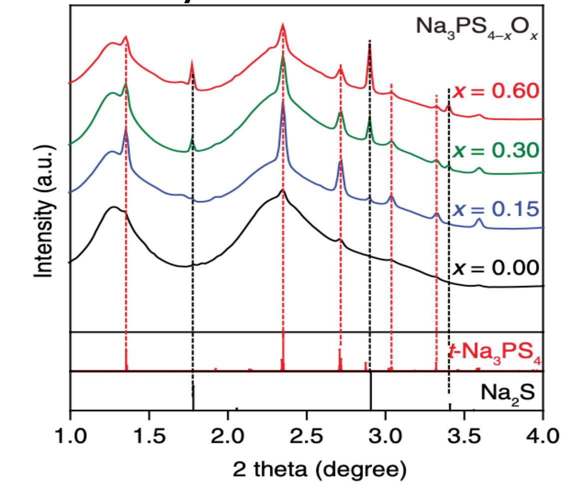


Mechanochemical Synthesis and Chemical Short-range Order

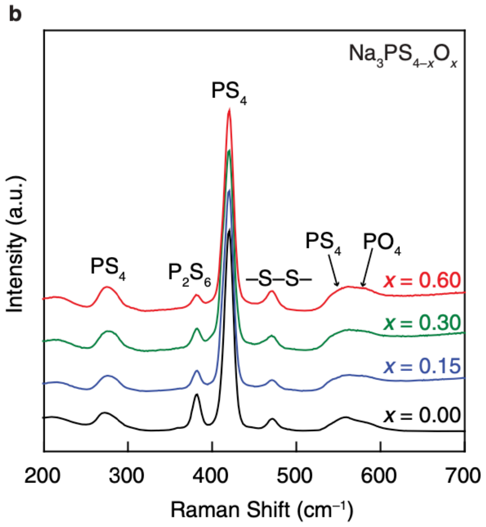


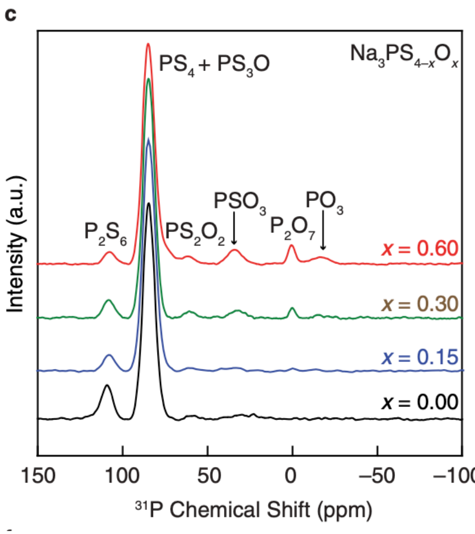


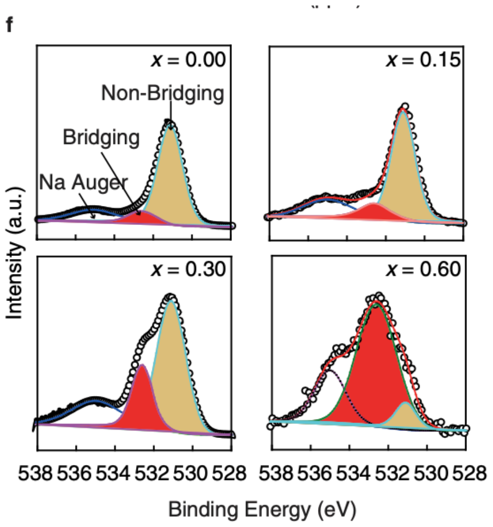
Synchrotron XRD

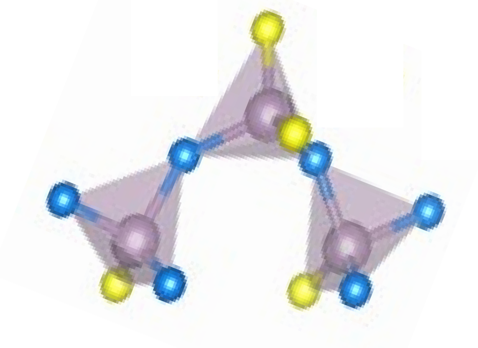


Amorphous NPSO powders with a small amount of crystalline phase < 5 mol.%,



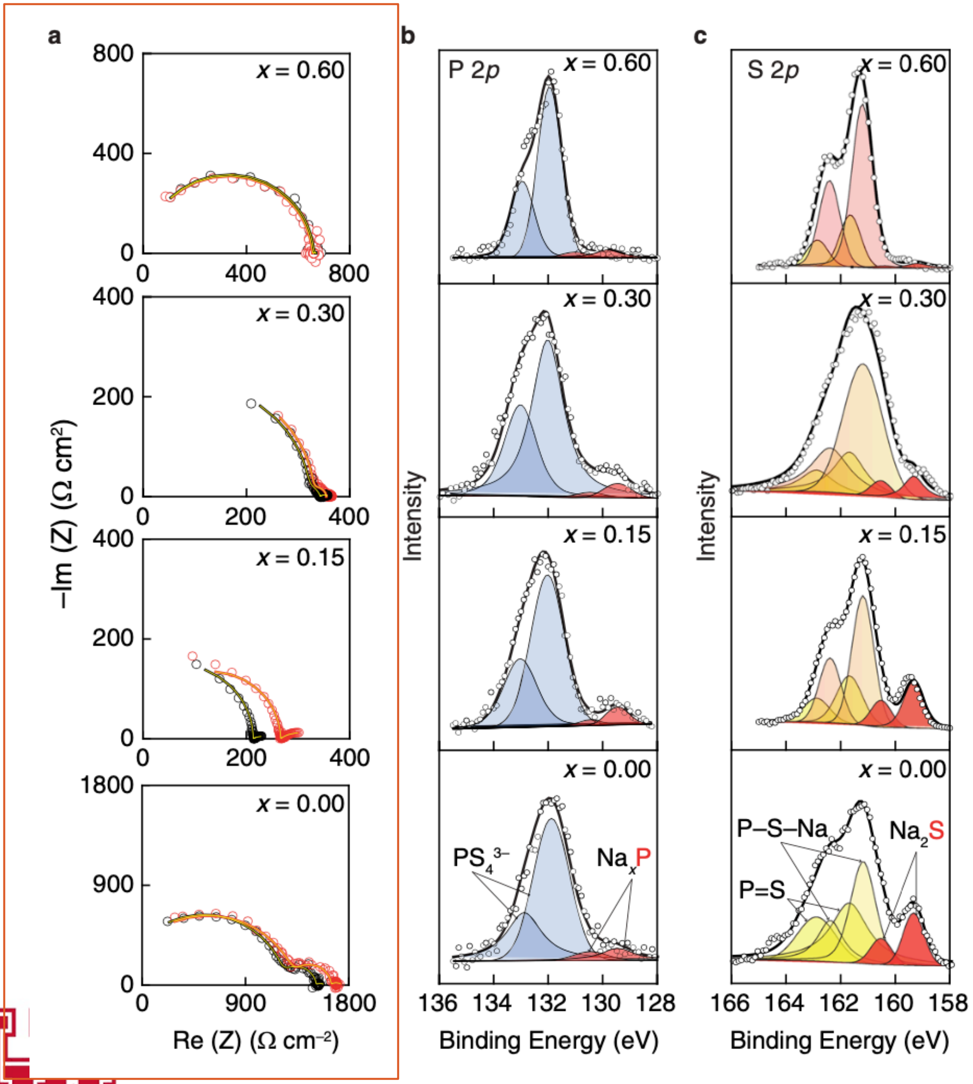




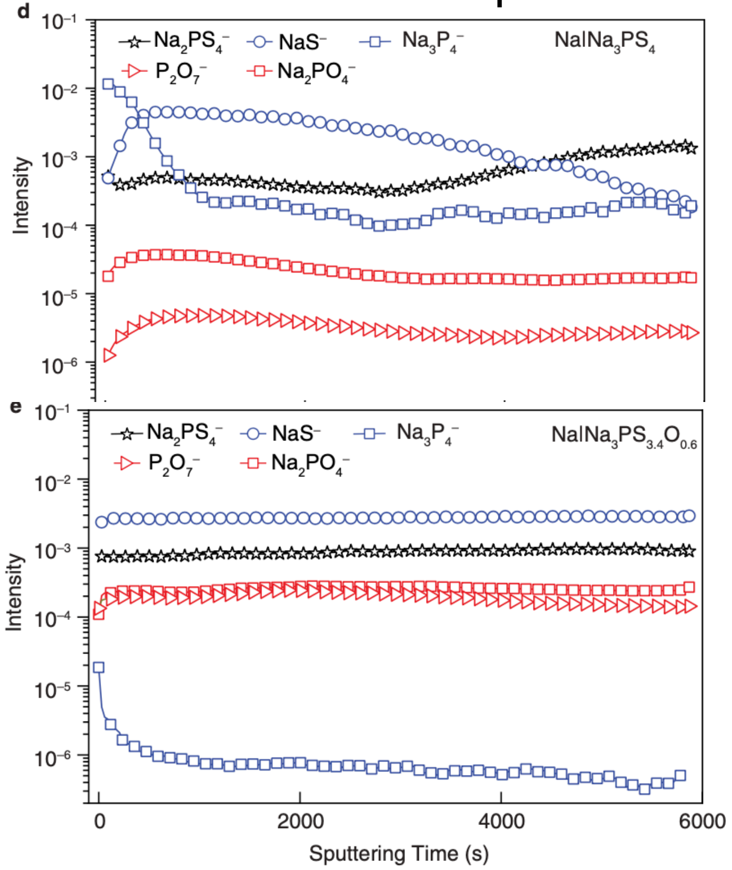


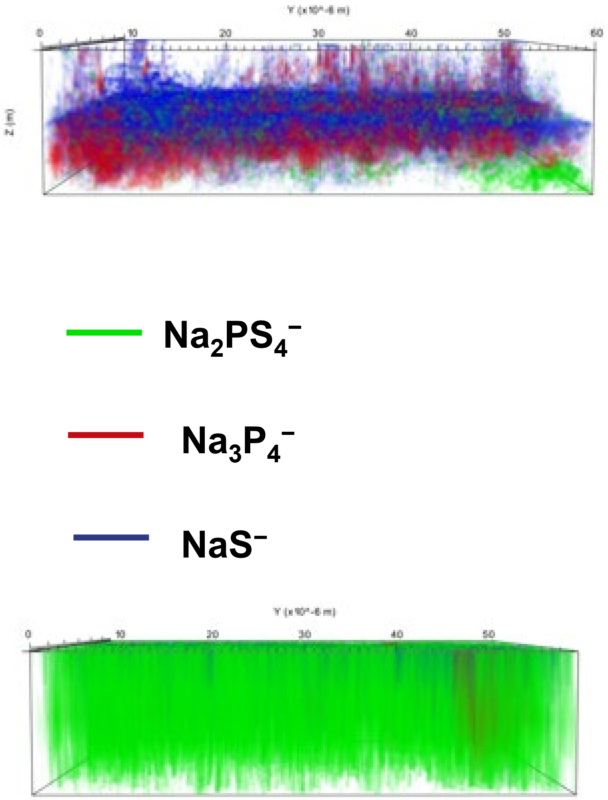
90% O atoms in NPSO are present as bridging oxygen

Chemical Stability towards Na Metal at 60 ℃



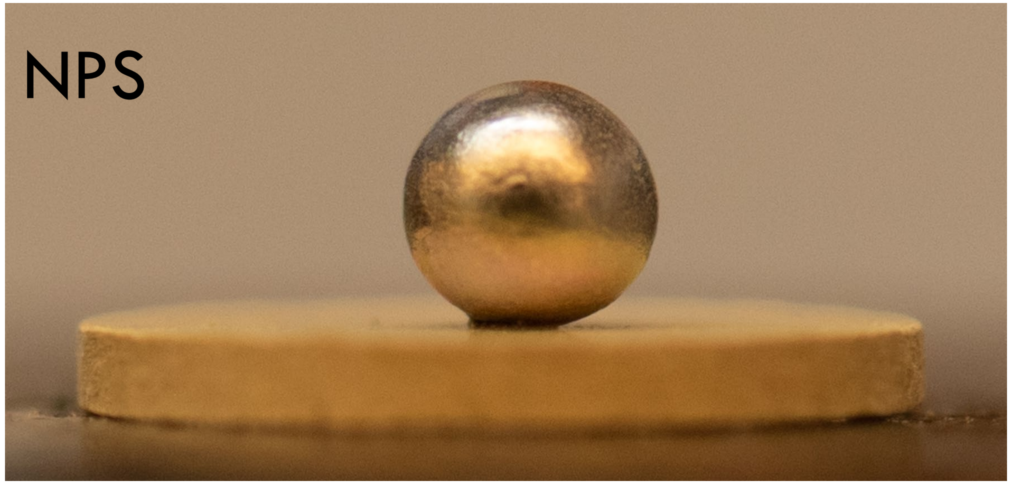
TOF-SIMS Depth Profile

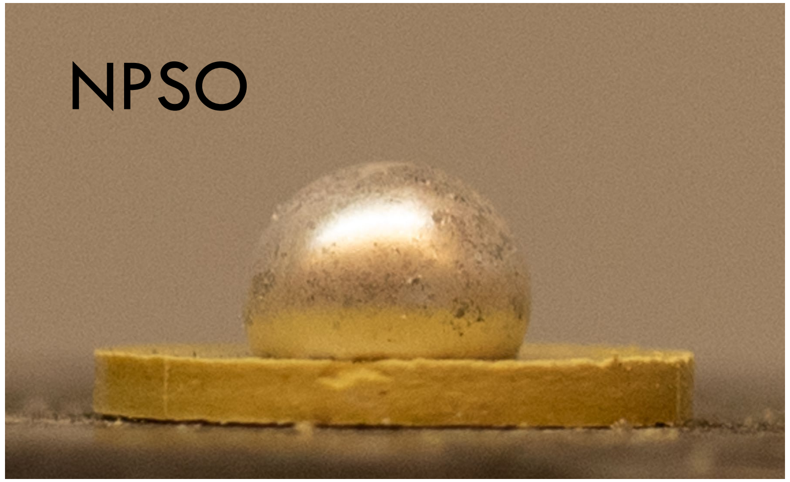


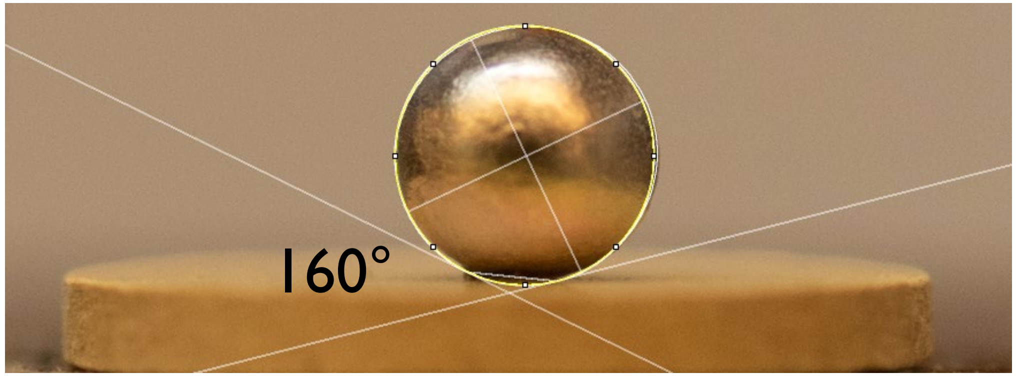


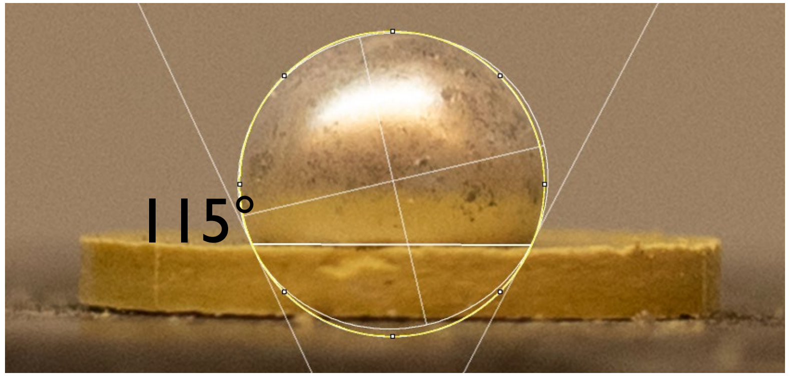
- Suppressed NPSO decomposition by 1000x and thickness by 10x, based on $Na_3P_4^-$ because Na_3P is electronically conductive.
- Thin, self-passivating interphase is formed, most likely due to the decomposed product of insulating Na_2O.

Chemical Stability with Molten Na Metal



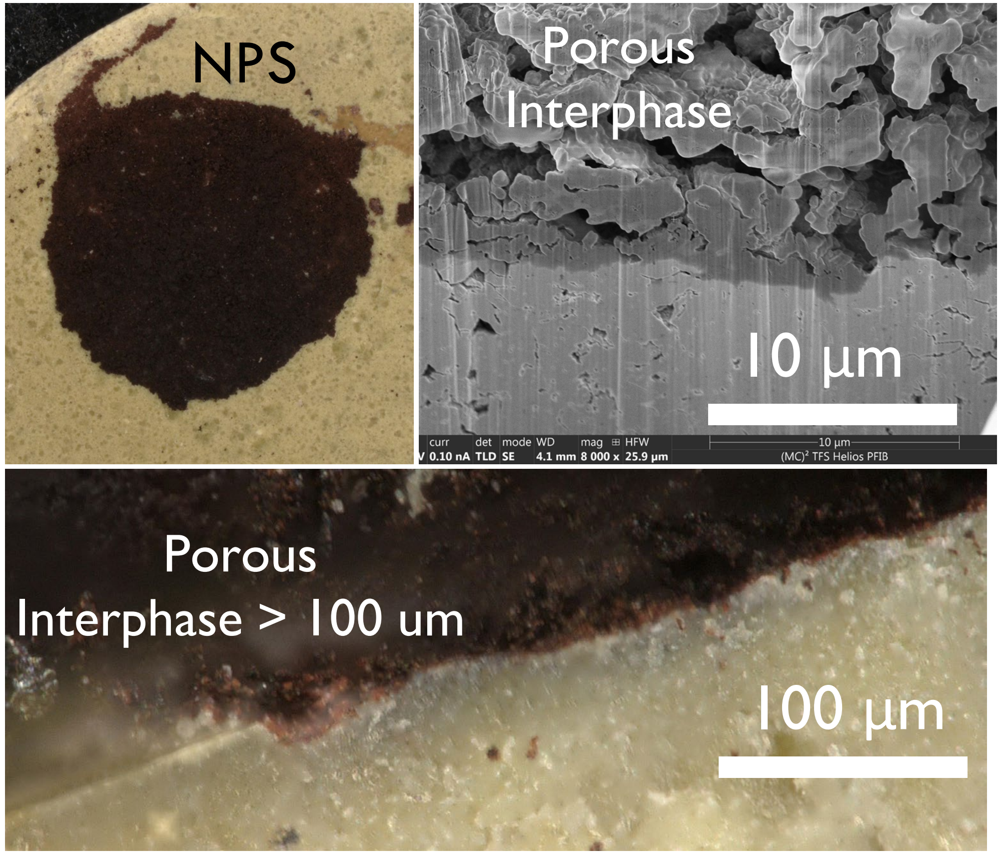




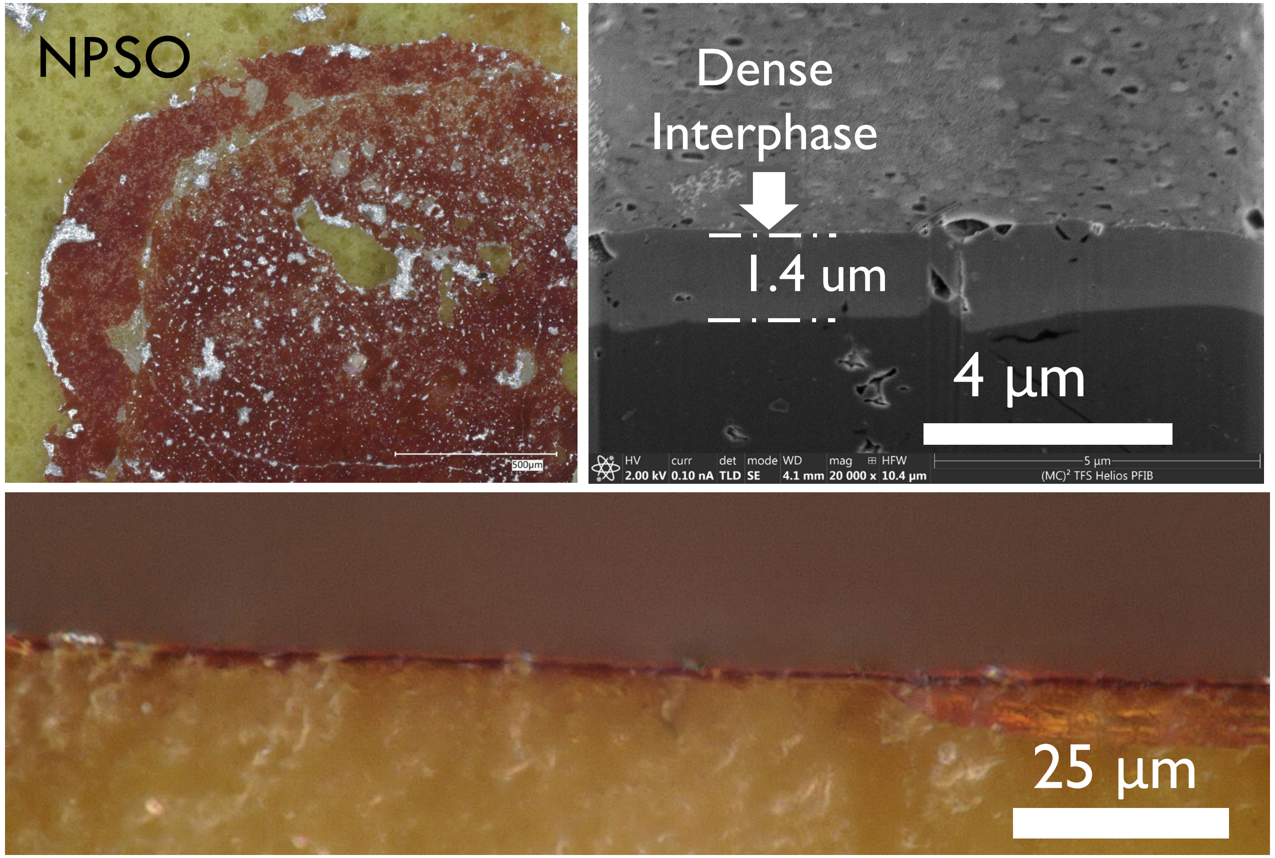


Eric Kazyak, Neil Dasgupta (U Michigan)

NPSO Forms Thin, Dense Interphase with Molten Na



Residual sodium reacted and turned into a thick porous black layer



Sodium mostly came off, but only a thin layer reacted, interphase was reddish and appears dense

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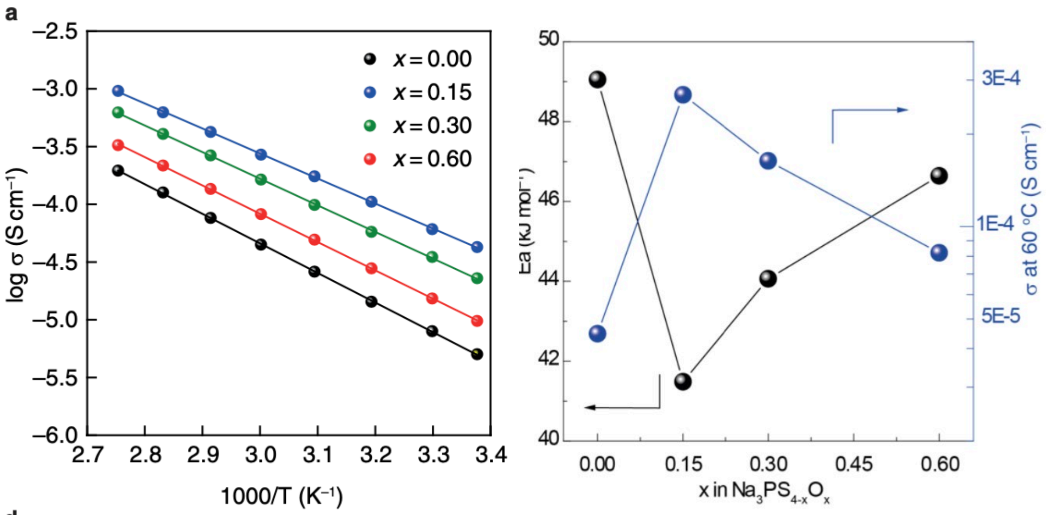
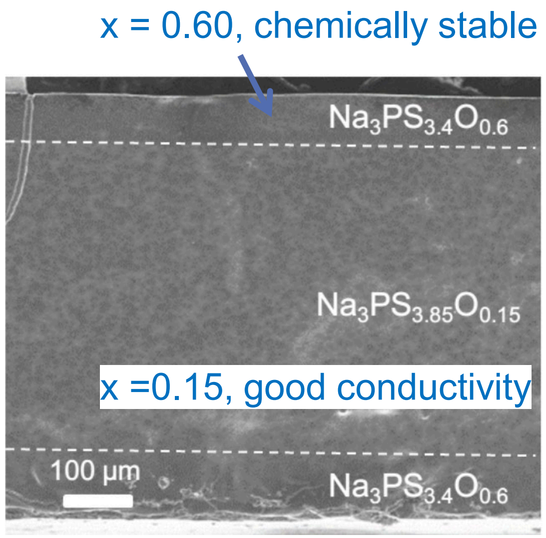
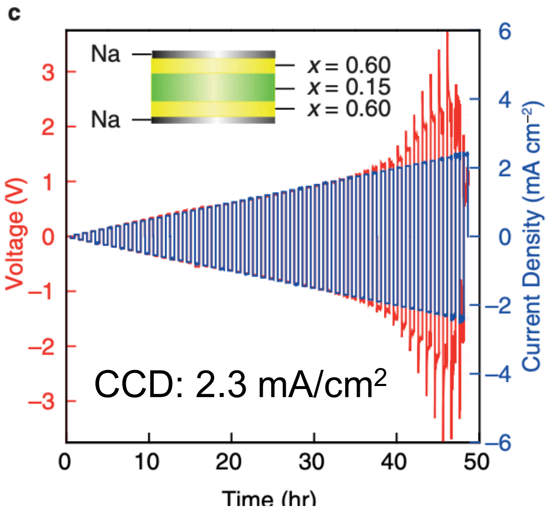
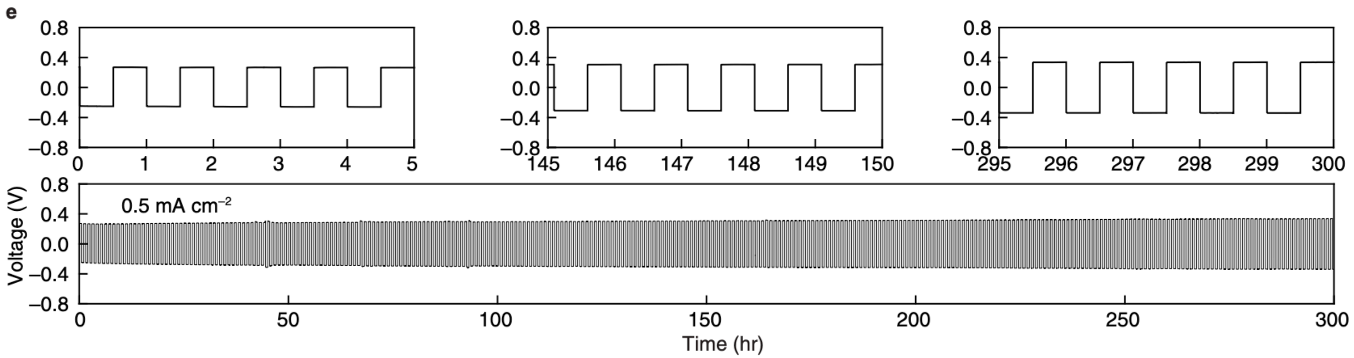
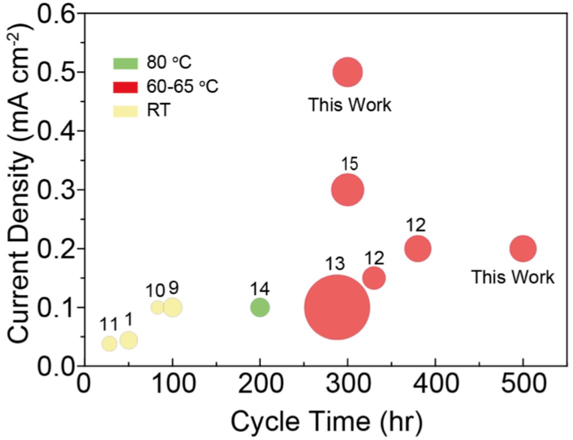
Tri-layer Electrolyte Separator and Na Symmetrical Cells



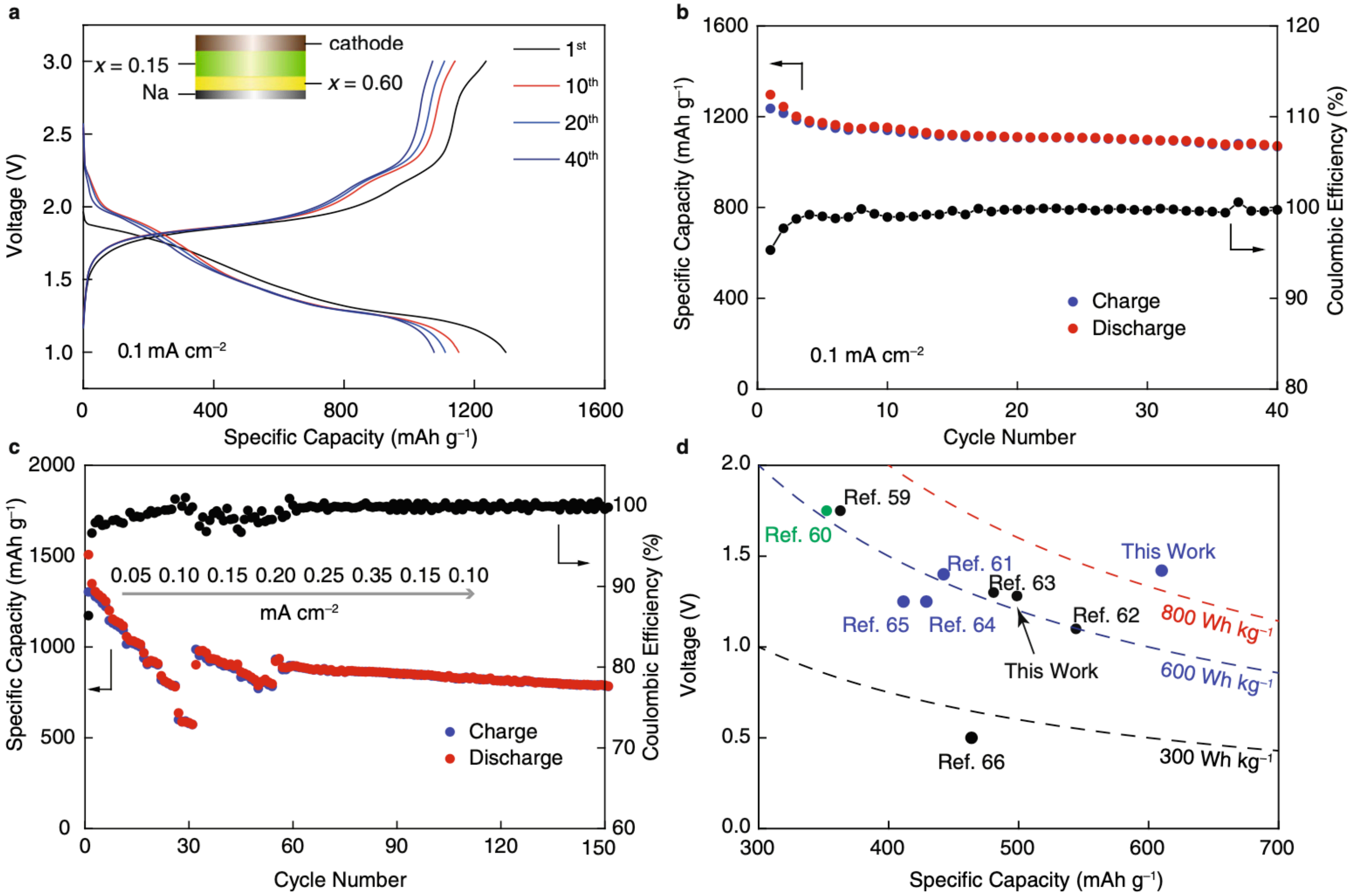








All-solid-state Na–S Full Cells at 60 °C



- High initial discharge capacity of 1280 mAh/g, 76% of theoretical capacity, overcoming the discharge limit Na_2S_4
- The cell cycled stably for 150 cycles.
- The cell shows highest material-level specific energy.

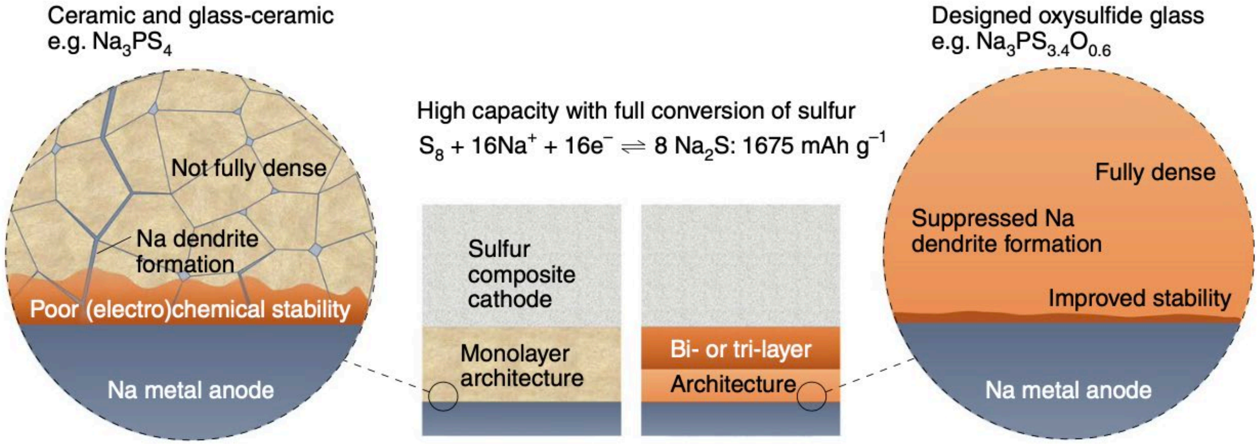
Summary

- All-solid Na-S batteries make it potentially possible to eliminate scarce materials such as lithium and transition metals.

- This work shows how minor compositional differences can affect the overall local chemical composition, decomposition kinetics at the interface, and the resulting properties of the formed decomposition interphases.

- This work extends previous work on oxysulfides in Li solid electrolyte, and opens the door for developing all-solid sodium-sulfur batteries.

- Faster ionic conductor catholyte should be used. Further improve areal loading of sulfur, higher current density,



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