

NASICON Electrolytes for Room-Temperature Sodium-Sulfur Batteries: from Material Synthesis to Cell Testing

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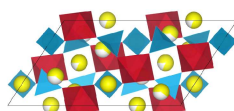
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Background and Motivation

Solid electrolytes (SE) allow to employ alkali-metal negative electrodes (NE) in new cell concepts, increasing energy density and safety of batteries for stationary and portable applications. The aim of this research is to develop a novel NASICON (NA Super Ionic CONductor) electrolyte for room-temperature (RT) sodium-sulfur (Na-S) cells employing a liquid sodium-potassium (Na-K) alloy at the SE/NE interface. The Na-K alloy can improve the interfacial contact between the sodium-metal NE and the SE.

- NASICON ceramics offer 3-dimensional migration pathways for Na⁺ migration.
- Ionic conductivity is typically in the range of ~1 mS/cm.
- Wide electrochemical window, high stability against air and moisture.
- Good interfacial contact with alkali-metal electrodes is difficult to achieve.



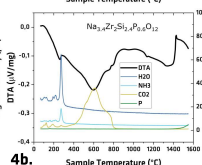
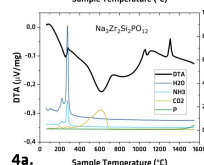
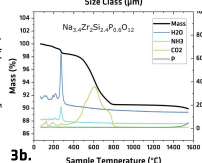
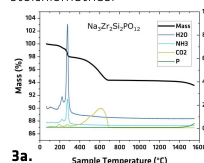
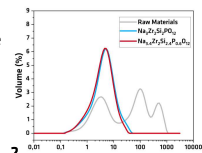
1. Monoclinic Na₃Zr₂Si₂P₂O₁₂ structure, with ZrO₆ octahedra and (Si/P)O₄ tetrahedra forming 3-dimensional Na⁺ migration pathways.

- NASICON stoichiometries produced and tested at BAM: Na_{3+x}Zr₂Si_{2+x}P_{1-x}O₁₂ (x = 0.0, 0.2, 0.4).
- Tuning Si/P ratio allows to increase Na content in lattice.
- Synthesis routes: Solid-state reaction (SSR) and solution-assisted solid-state reaction (SA-SSR).

Production and study of NASICON Solid Electrolytes at BAM

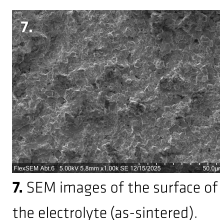
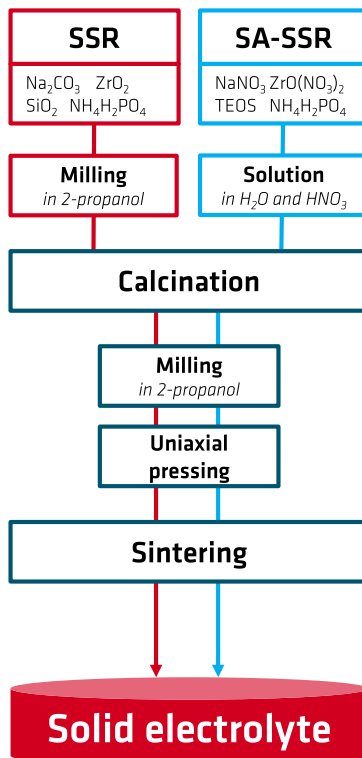
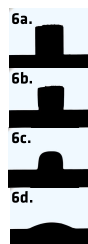
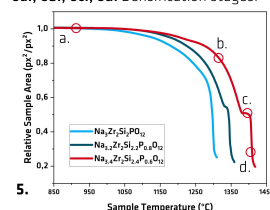
NASICON phase formation:

2. Particle size distribution before calcination (laser diffraction). 3a., 3b TG curves with MS results for two different stoichiometries. 4a., 4b. DTA curves with MS results for two different stoichiometries.

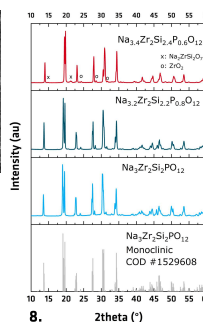


Densification during sintering:

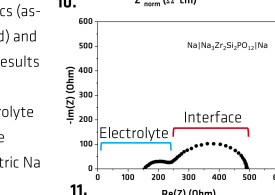
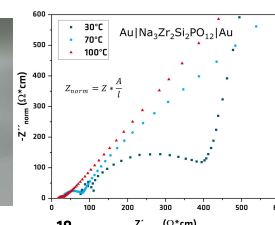
5. Dilatometry curves for densification of discs for different stoichiometries. 6a., 6b., 6c., 6d. Densification stages.



7. SEM images of the surface of the electrolyte (as-sintered). 8. XRD reflections of sintered discs with different Si/P ratios. Peaks related to secondary phases (zirconia and parakeldyshite) are highlighted.



9. NASICON powder, discs (as-sintered and gold-plated) and solid-state cell. 10. EIS results for ionic conductivity measurement. 11. Electrolyte and interface impedance contributions in symmetric Na cell (PEIS).

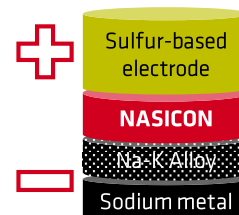


Conclusions

- NASICON electrolytes are produced at BAM through two different synthesis routes.
- Thermal analyses confirm that changes in stoichiometry significantly affect the material's thermal behavior and densification curves.
- Improvement of the interface at the NE is needed to ensure long-term cycling and stable operation.

Next steps

- Long term cycling tests.
- Interface improvement with Na-K alloy and sodiophilic coatings.
- Assembly of full cells.
- Safety of solid-state sodium batteries, abuse tests.



Sicherheit in Technik und Chemie

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D. Nicolaides - dilatometry
A. Seidel - assistance during EC measurements and synthesis

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