Synthesis and Stability of NaSICON for Sodium-Based Batteries

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Dr. S. Bhavaraj, Ceramatec – prototype development and ceramic supplier

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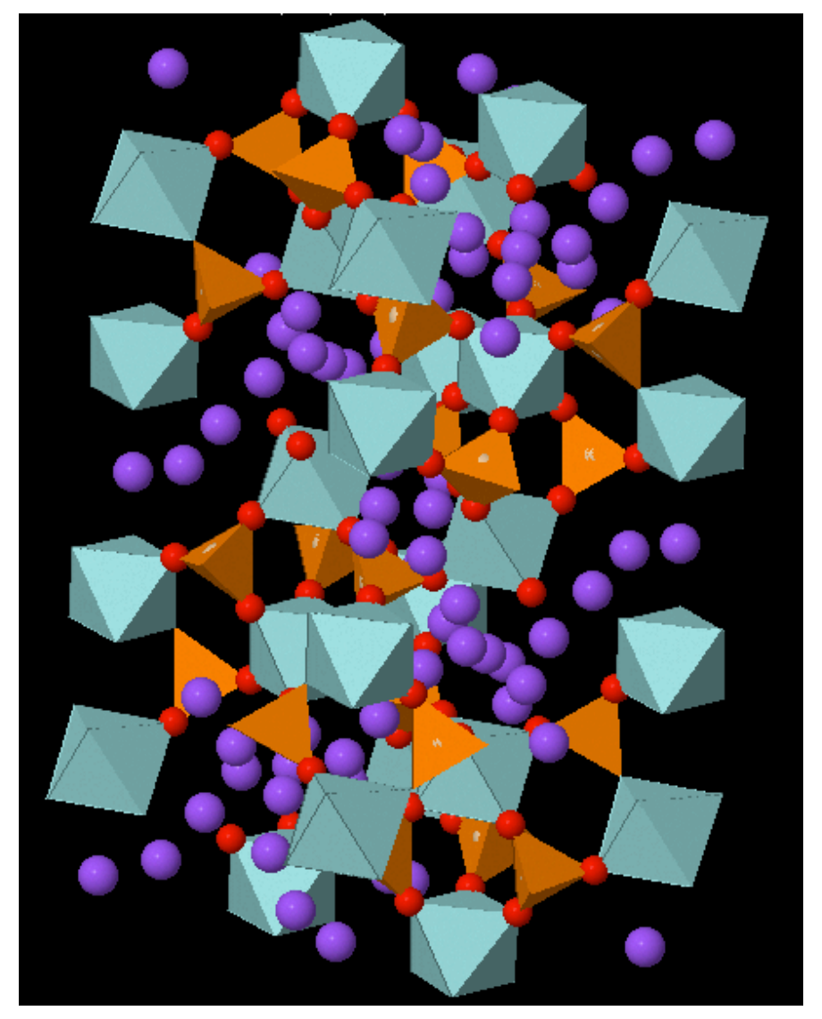
Why NaSICON?

(Sodium (**Na**) **S**uper **I**onic **Con**ductor)

$$Na_{1+x}Zr_2P_{3-x}Si_xO_{12} \xrightarrow{x = 2} Na_3Zr_2PSi_2O_{12}$$



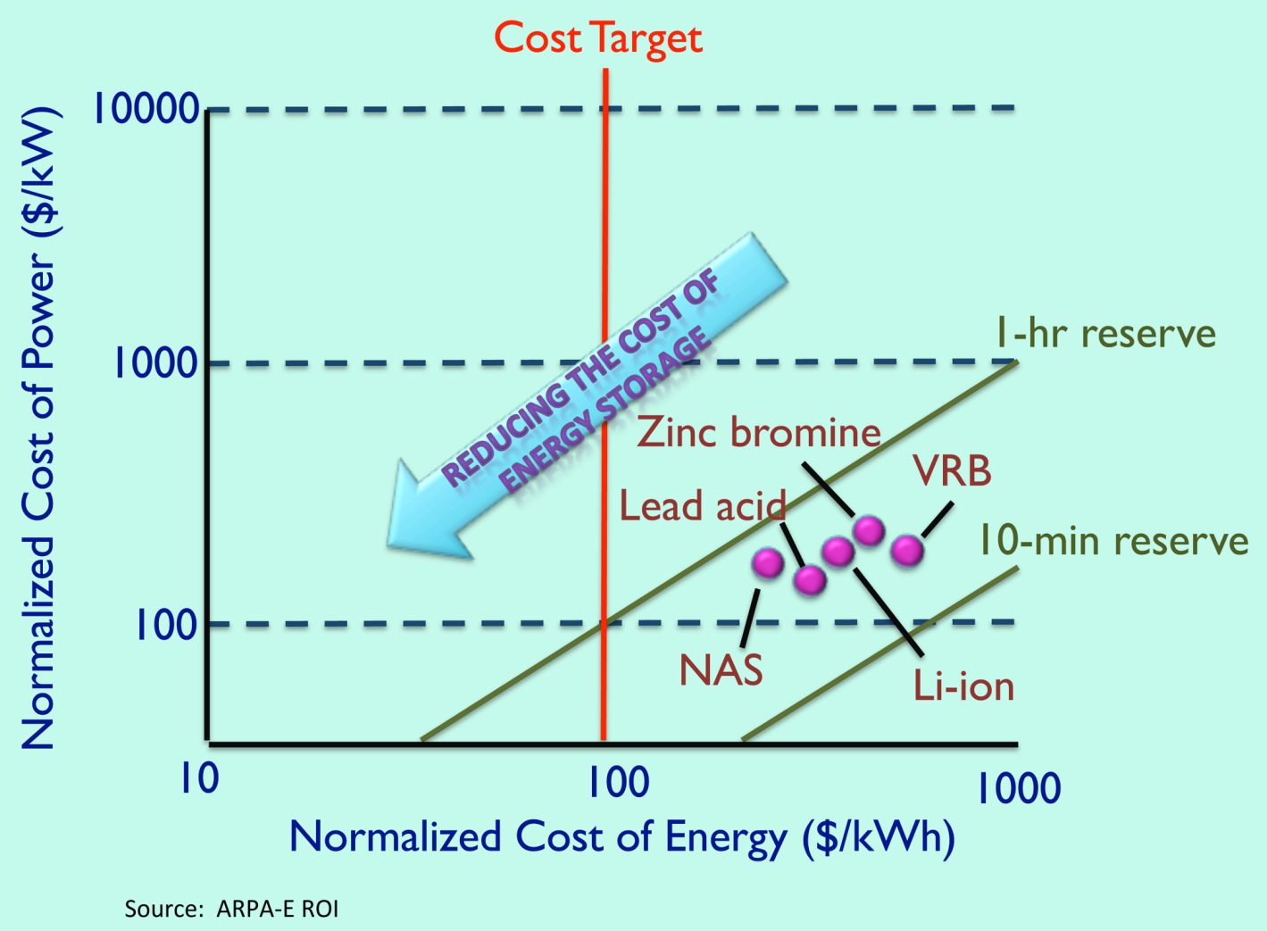
NaSICON is a high conductivity (up to 10^{-2} S/cm at room T°C) solid state electrolyte that is stable against molten sodium and which we are using in development of a family of sodium-based battery technologies.

Select batteries under development

1. Sodium-air
2. Sodium-ion
3. Low temperature sodium-sulfur
4. Sodium-bromine: $Na + ½ Br_2 \leftrightarrow Na^+ + Br^-$
   3.79 V 987 Wh/kg
5. Sodium-iodine: $Na + ½ I_2 \leftrightarrow Na^+ + I^-$
   3.25 V 581 Wh/kg

Programmatic Goals and Objectives

- Reduce the cost of energy to < 100 $/kWh
- Develop a suite of sodium-based battery solutions to fill the multiple application needs for stationary storage
- Facilitate short development timeframe



Source: ARPA-E ROI

Fully realizing sodium battery potential will require stable, high conductivity NaSICON.

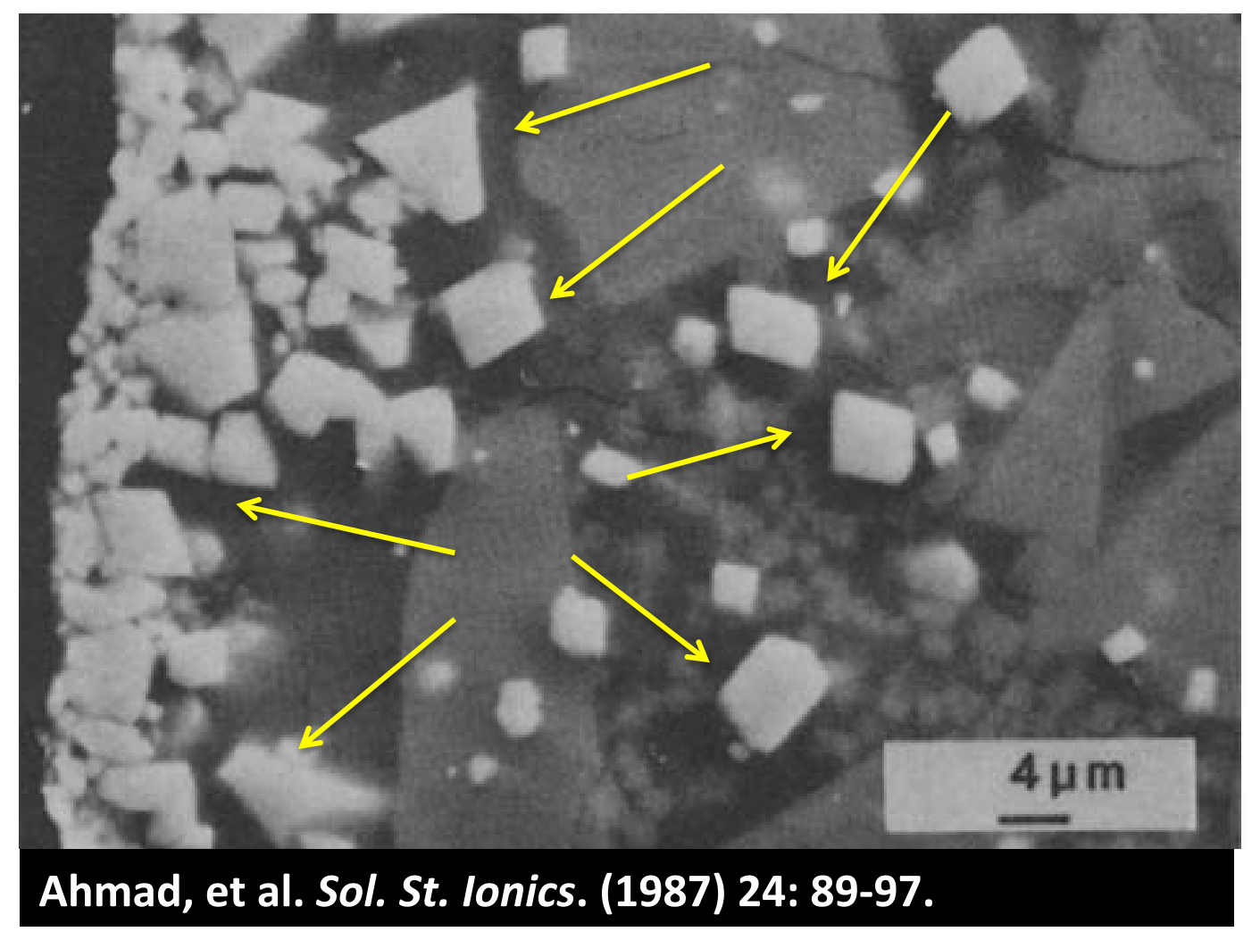
The Chemistry of NaSICON – Toward understanding and optimizing behavior

- NaSICON is a multi-component material having complex chemistry.
- High temperature synthetic routes often produce secondary "contaminant" phases.
- These secondary phases can and do dramatically affect *performance and stability.*

Our approach:

1) study the effects that secondary phases have on performance
2) determine how to tailor the phase composition in order to control performance
3) prepare improved materials based on this increased understanding of NaSICON's complex chemistry

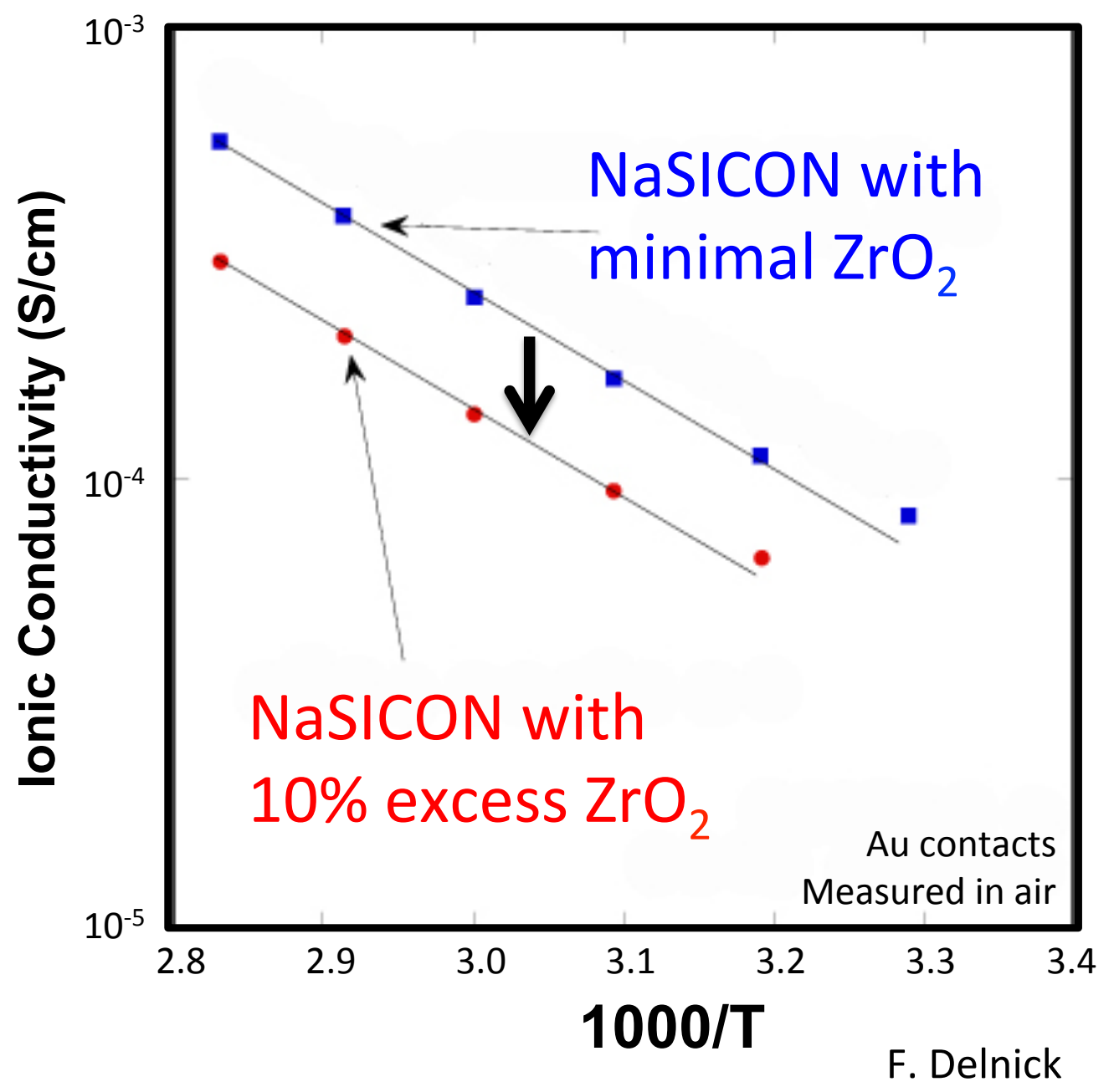
ZrO_2 Phase Leads to Reduced Conductivity



Ahmad, et al. *Sol. St. Ionics*. (1987) 24: 89-97.

Scanning electron micrograph of monoclinic ZrO_2 in NaSICON produced at 1300°C sintering temperature.

Ionic conductivity decreases with excess ZrO_2.

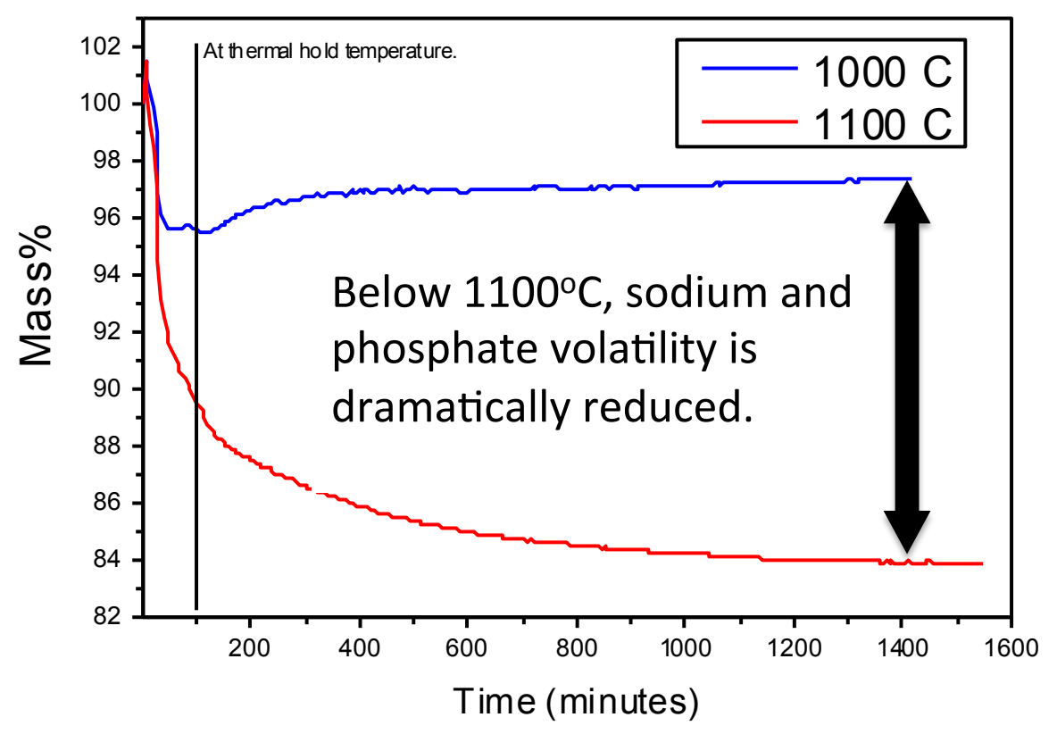


F. Delnick

Decreased ionic conductivity leads to decreased battery performance.
How can we address excess ZrO_2?

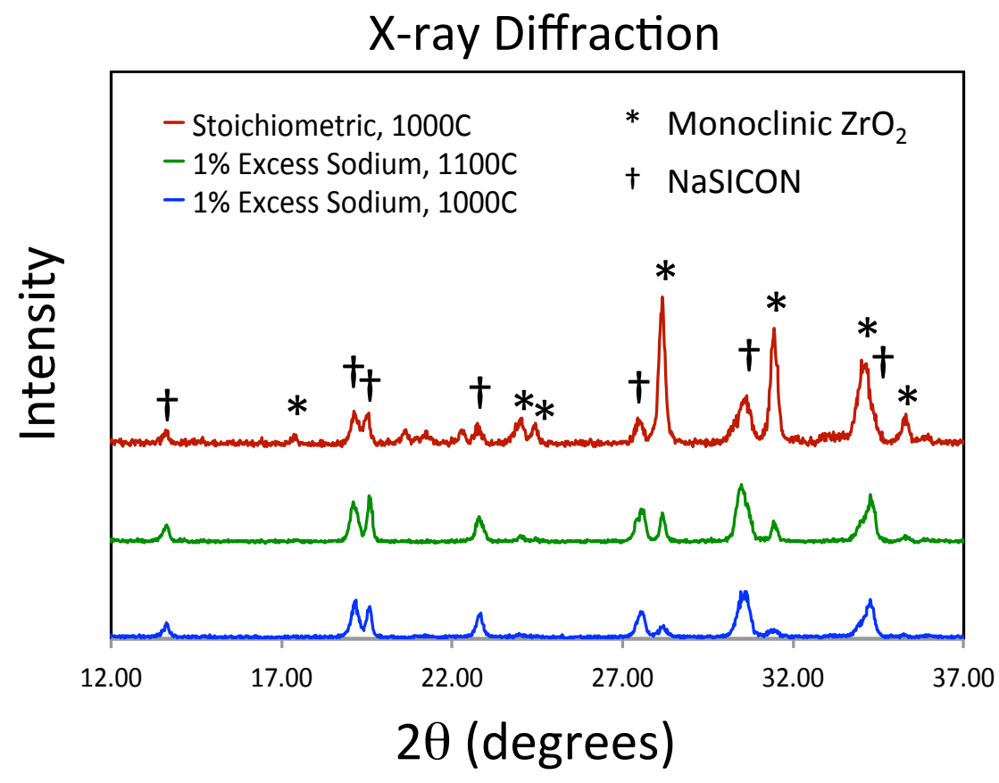
Engineered sol-gel processing allows for lower temperature processing and tailoring of NaSICON composition to address secondary ZrO_2 formation.

Thermogravimetric Analysis



Reducing firing temperature below 1100°C or introducing a small excess of sodium to the sol-gel precursors dramatically reduces ZrO_2 formation.

X-ray Diffraction

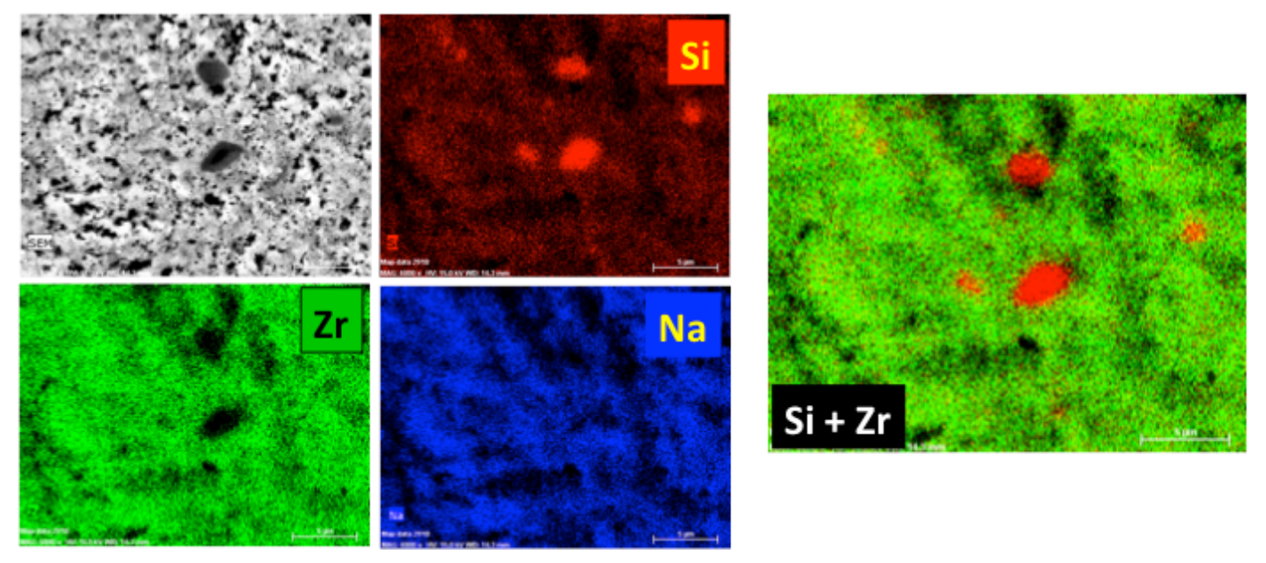


Glassy Phases Reduce Stability

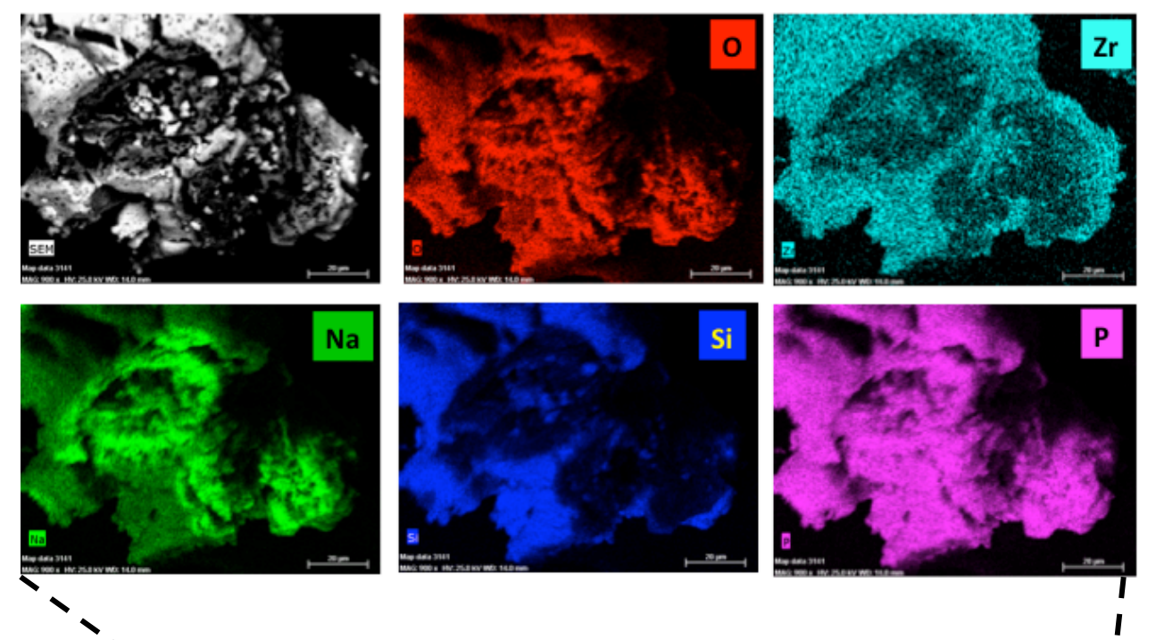
Glassy silicate and phosphate phases reduce NaSICON stability, thereby compromising reliability.

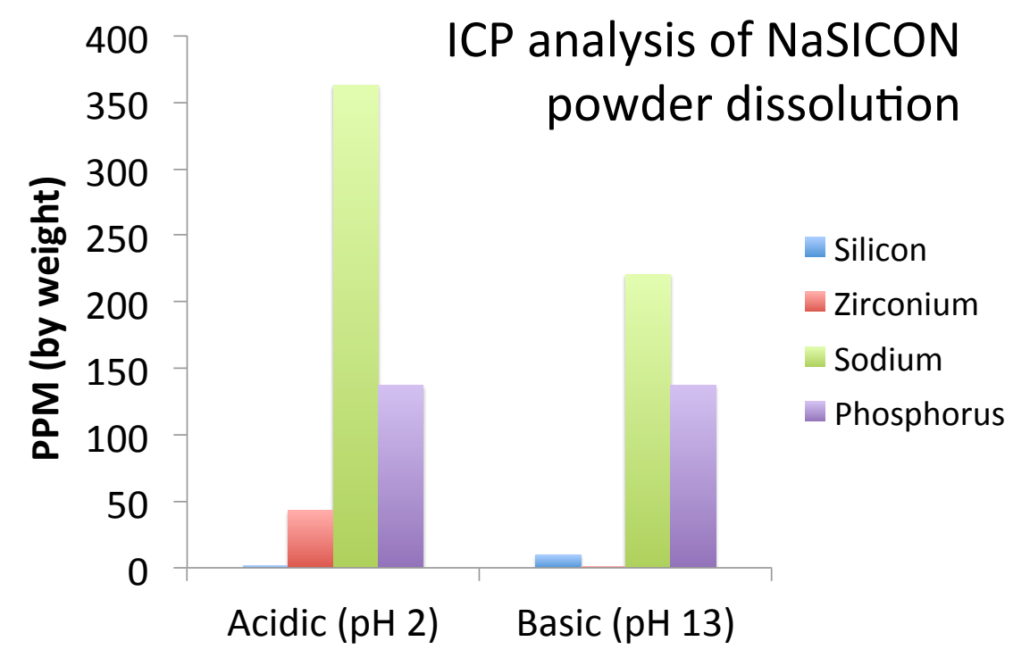
Glassy phases, particularly sodium phosphates, decrease stability in alkaline electrolytes.

Silicate Glasses



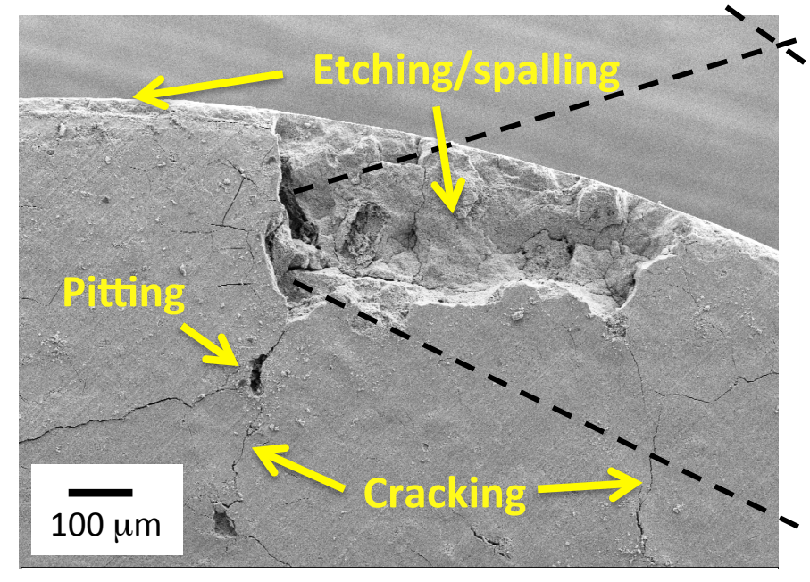
Phosphate Glasses



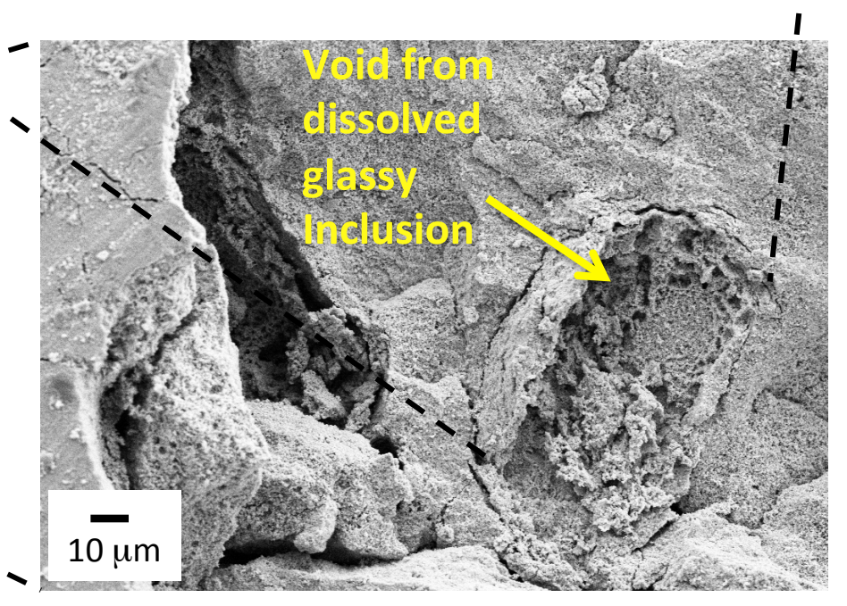


Aqueous powder dissolution studies (7 days, RT):

- Zr-solubility in acid
- Si-solubility in base
- Na, PO_4 solubility under all conditions

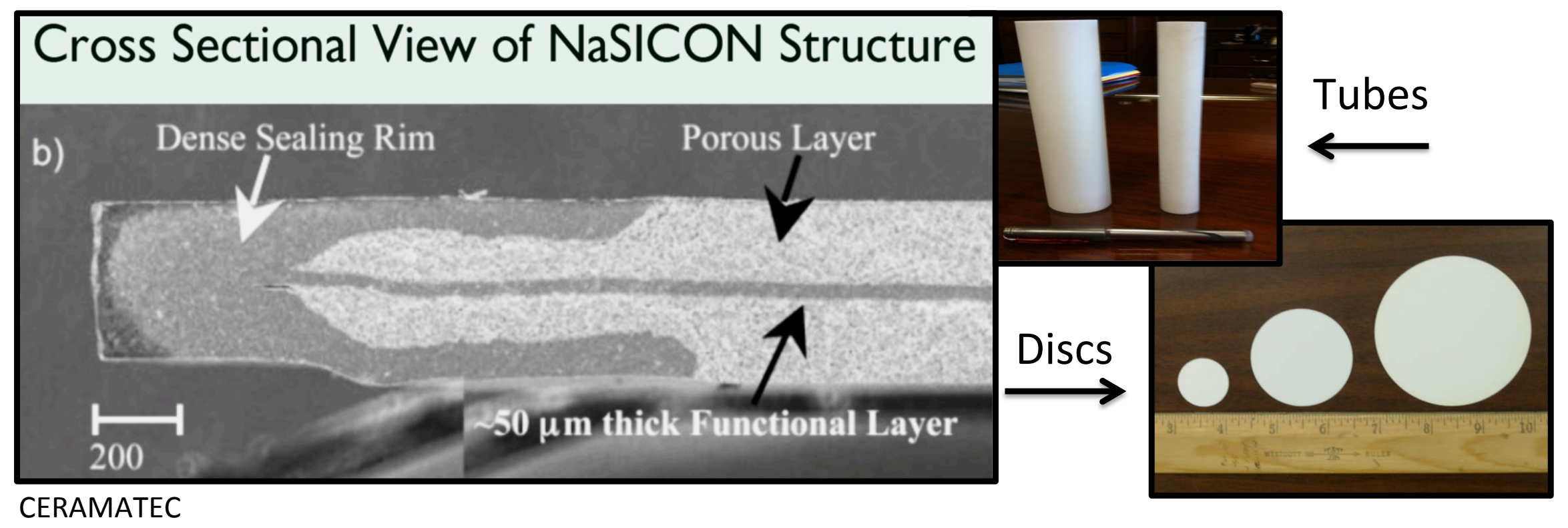


Under alkaline conditions (14 days, RT) NaSICON pellets show signs of physical degradation.



Dissolution of phosphate glassy particles is implicated in the degradation of NaSICON.

Refinement of NaSICON conversion chemistry and sintering conditions are expected to address deleterious glass formation.



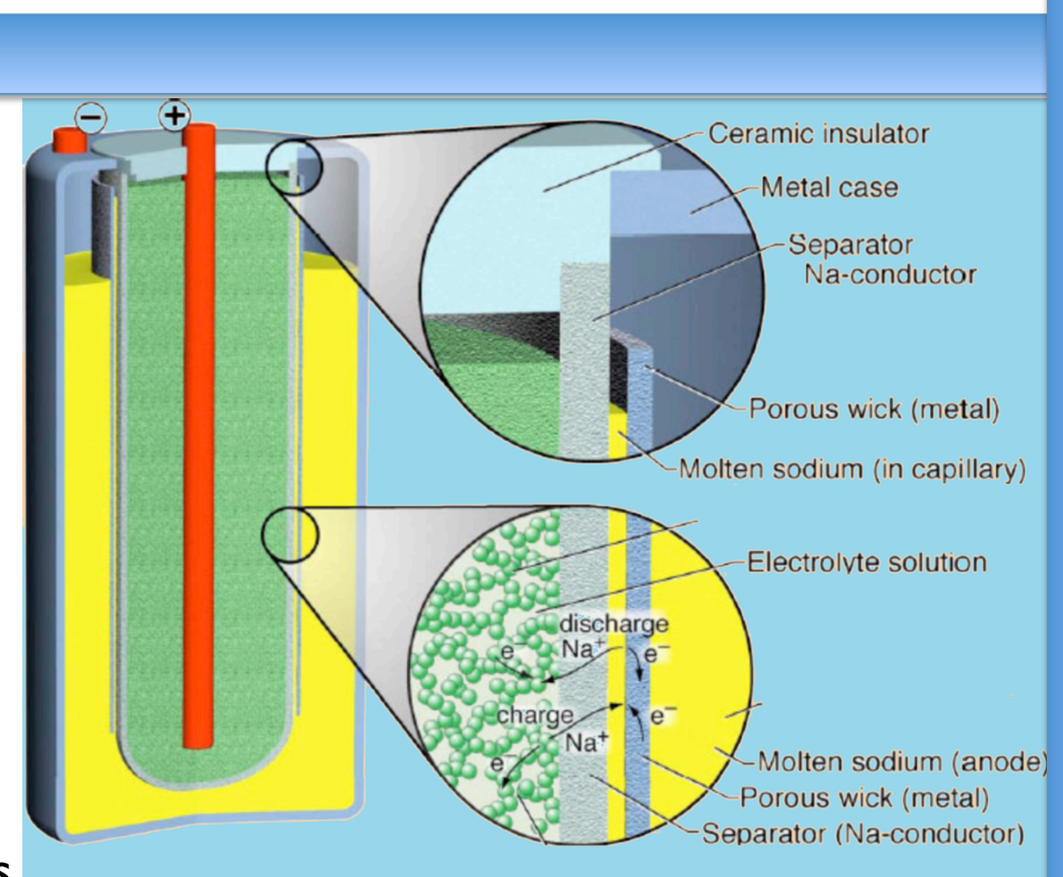
CERAMATEC

Enabling Prototype Development

Optimized NaSICON conductivity and stability will enable advanced ceramic structures for versatile, efficient battery development.

- No crossover, eliminates cathode-anode materials compatibility issues
- Planar bipolar stacks & flow designs are possible

R. Kee, conceptual designs



OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

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