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Relating NaSICON Chemistry and Microstructure to Ion Conducting Ceramic Separator Performance

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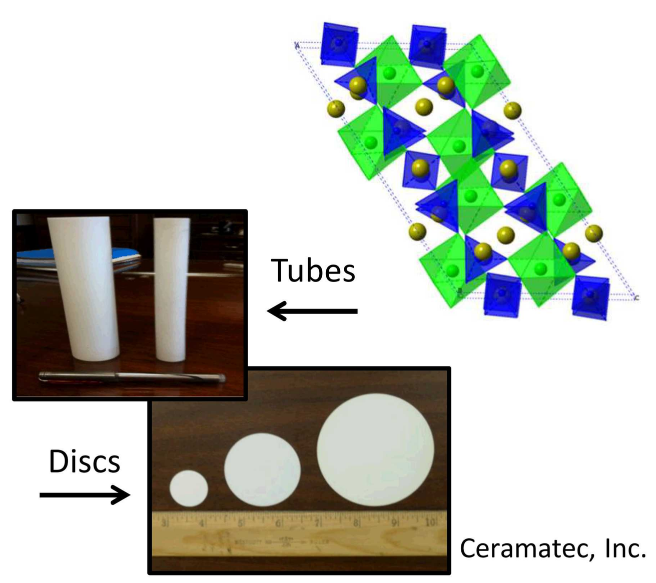
What is NaSICON?

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

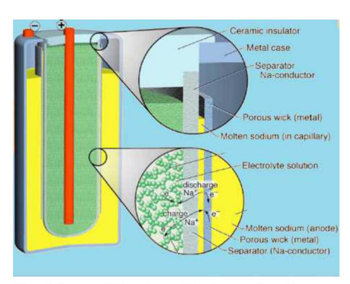
$$Na_{1+x}Zr_2P_{3-x}Si_xO_{12} \xrightarrow{x=2} Na_3Zr_2PSi_2O_{12}$$

NaSICON is a high conductivity (> 10^{-3} S/cm at 25°C) solid state electrolyte. High conductivity, good chemical stability, and robust structural integrity stand to make this a zero-crossover separator to enable a number of new sodium batteries:



Ceramatec, Inc.

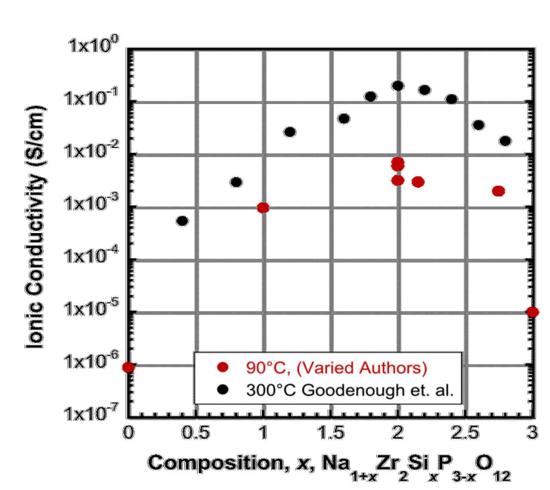
- Sodium-air
- Sodium-ion
- Aqueous Redox Flow
- Low temperature sodium-sulfur
- Sodium-bromine: Na + ½ Br_2 ⟷ Na^+ + Br^-
- Sodium-iodine: Na + ½ I_2 ⟷ Na^+ + I^-
- Sodium-nickel chloride: Na + ½ $NiCl_2$ ⟷ Na^+ + Cl^- + Ni(s)
- Sodium-copper iodide: Na + CuI_2^- ⟷ Na^+ +2I^- + Cu(*s*)


R. Kee (Colo. School of Mines)

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

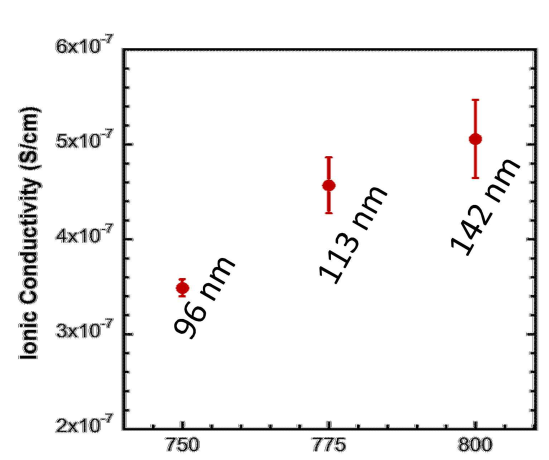
Structural Effects on Conductivity

Atomic Structure:
NaSICON composition affects ionic conductivity, frequently mediated through changes in atomic structure.



90°C data from Breval, *et. al., Brit. Cer. Trans.*, **93** (76), 239-251 (1994)
300°C data from Goodenough, *et. al., Mater. Res. Bull.*, **11** (2), 203-220 (1976)

Microstructure:
In thin film NaSICON structures, grain size (controlled with processing temperature) affects ionic conductivity.



W. Meier and J.F. Ihlefeld, *et. al.*, *J. Electrochem. Soc.*, **161** (3), A364-A367 (2014)

Complex Phase Chemistry of NaSICON

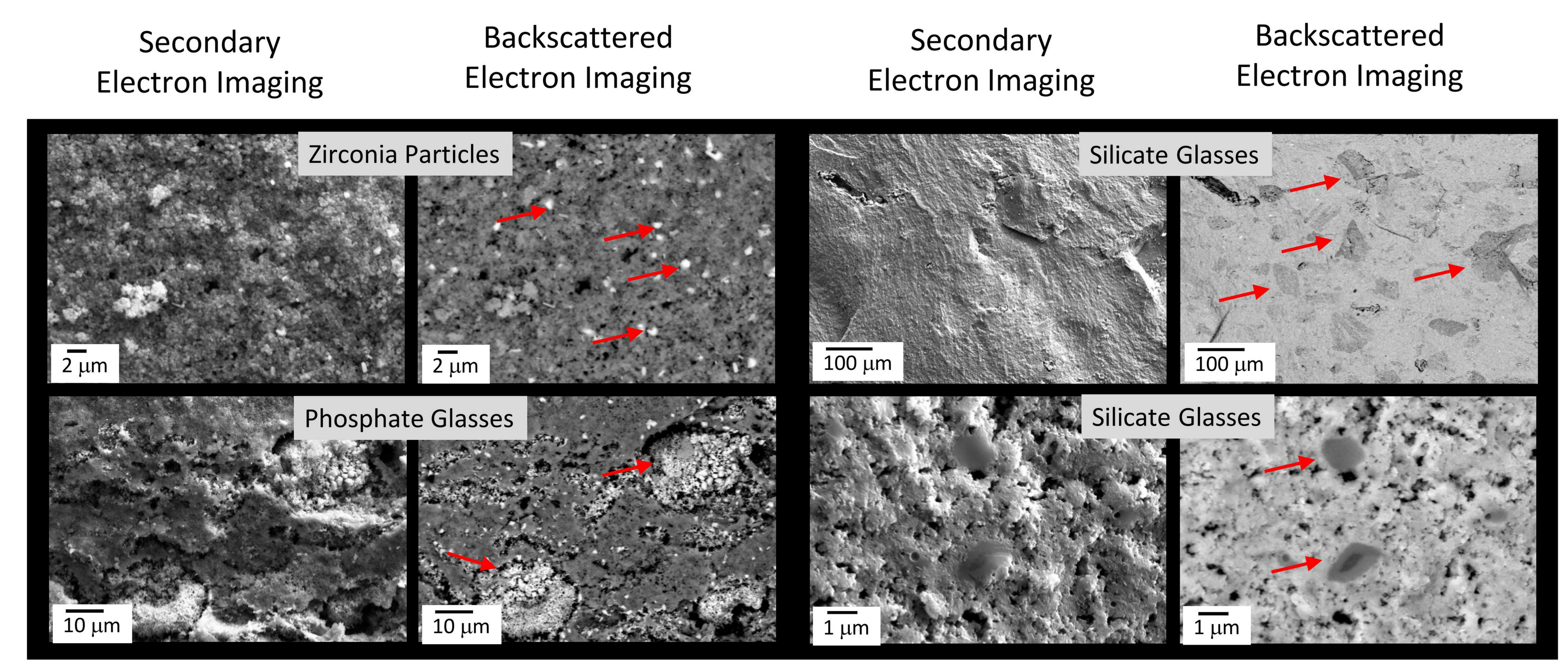
NaSICON is not a single phase material!

- 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.*

Identifying Secondary Phases in NaSICON

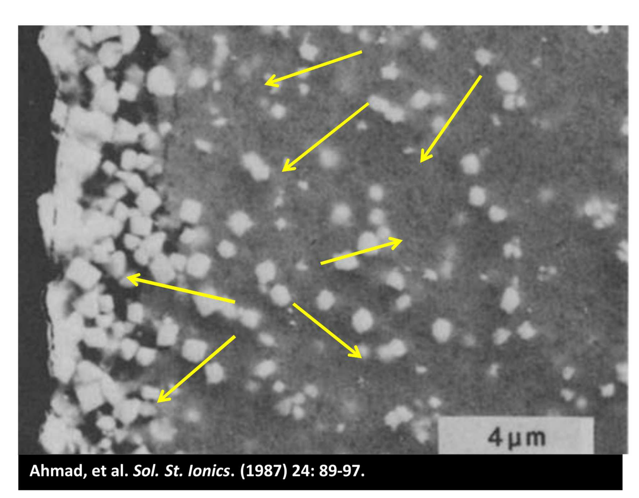
- X-ray diffraction is commonly used to characterize phase purity in NaSICON, *but not all secondary phases are crystalline*!
- Backscattered scanning electron microscopy reveals secondary phases.
- Energy dispersive x-ray mapping can reveal chemical composition of secondary phases.

Backscattered Electron Imaging: In scanning electron microscopy, backscattered electron (BSE) imaging is more sensitive to differences in atomic mass (and therefore composition variation) than secondary electron (SE) imaging. Below, identical sample areas imaged with each technique reveal how BSE imaging can reveal secondary phase formation in NaSICON.



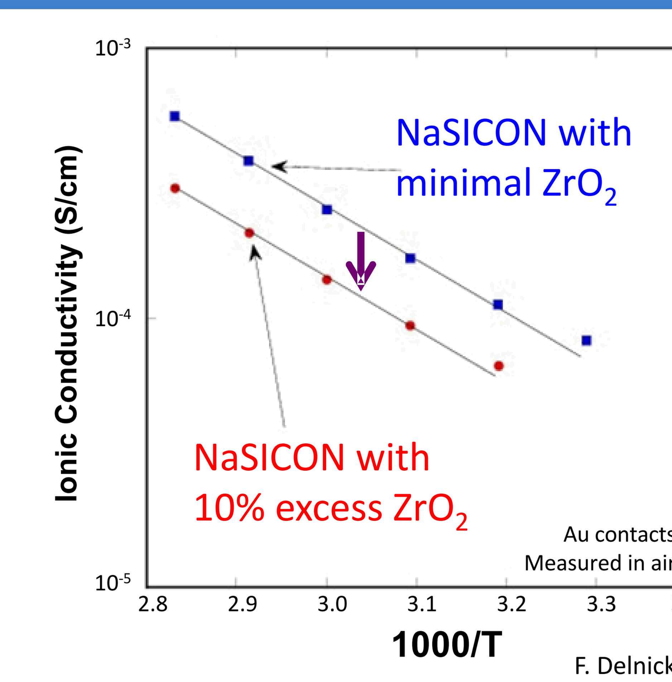
*Compositions identified by energy dispersive x-ray spectroscopy (see below).

ZrO_2 Phase Leads to Reduced Conductivity



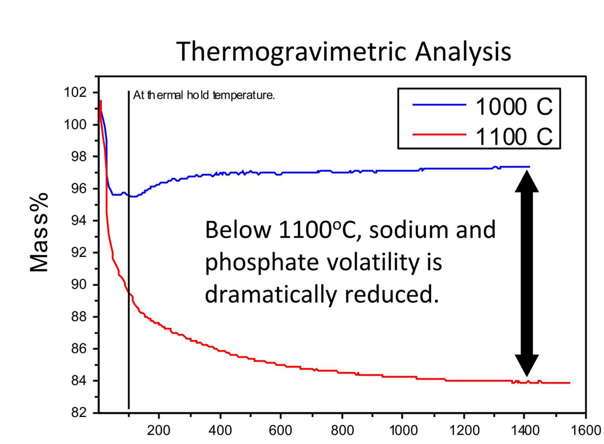
Scanning electron micrograph of monoclinic ZrO_2 produced at 1300°C sintering temperature.

Ionic conductivity decreases with excess ZrO_2.

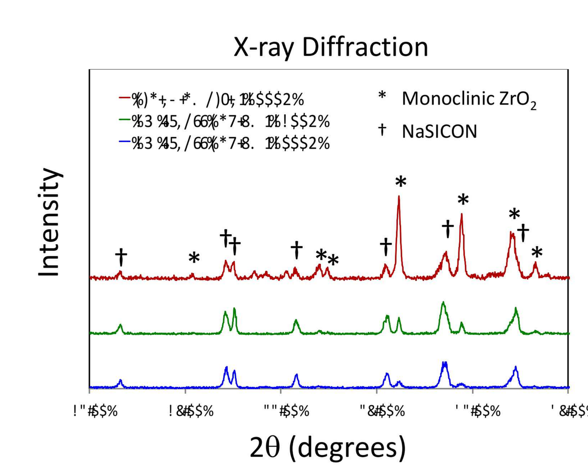


Decreased ionic conductivity leads to decreased battery performance. How can we address excess ZrO_2?

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



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

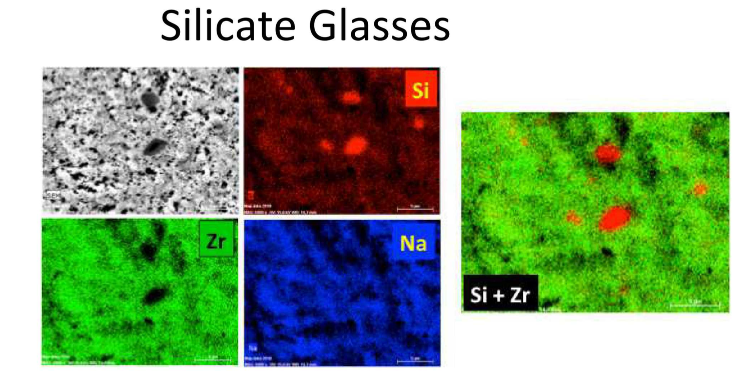


Glassy Phases Reduce Stability

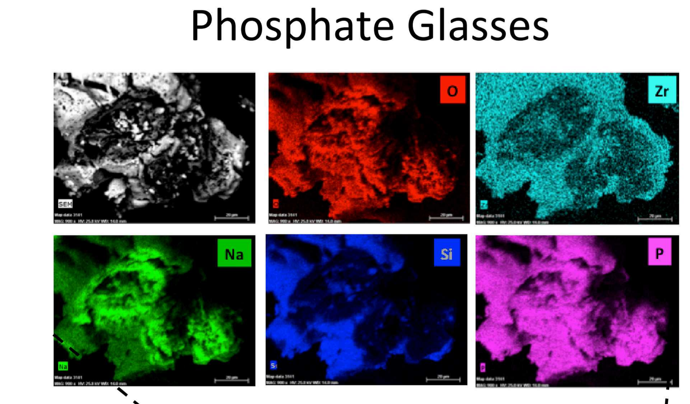
Glassy silicate and phosphate phases affect NaSICON stability, thereby compromising reliability.

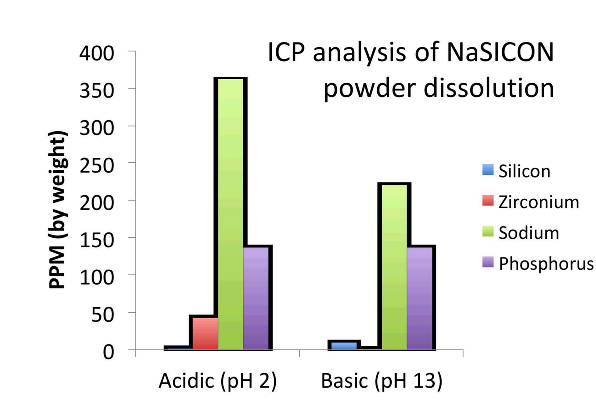
Glassy phases, particularly sodium phosphates, decrease stability toward aqueous electrolytes.

Silicate Glasses

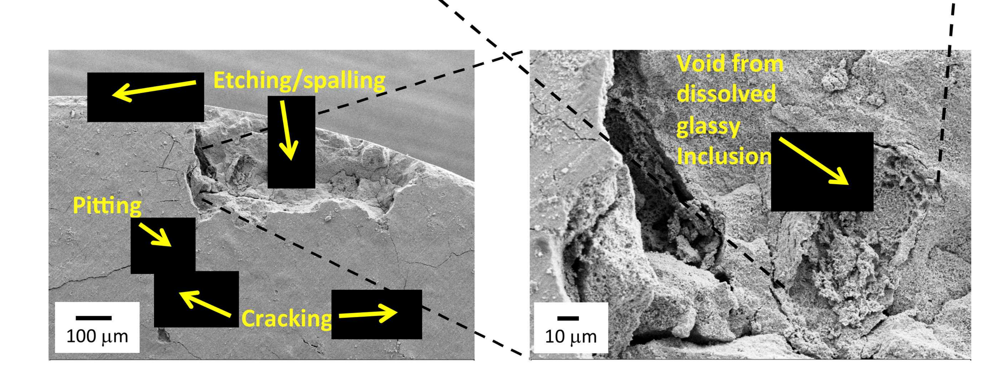


Phosphate Glasses





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 improve deleterious glass formation.

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