Investigate the Impact of Doping on the Structural Stability and Conductivity of Solid Electrolytes

Zonghai Chen (PI)

Argonne National Laboratory

2019 DOE VTO Annual Merit Review

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Project ID: bat418

Overview

Timeline

- Start: 10/01/2018
- End: 09/30/2021
- 10% completed

Budget

- Total project funding
  - DOE - $433K (FY19)
  - Contractor - $ 0
- Funding received in FY18
  - N/A
- Funding for FY19
  - DOE - $433K

Barriers

- Barriers addressed
  - Performance: to achieve a high energy density by enabling lithium metal
  - Abuse tolerance: to improve the safety characteristics by reducing or illuminating the use of volatile solvents

Partners

- Dr. Anh T. Ngo (MSD, ANL)
- Dr. Larry Curtiss (MSD, ANL)
- Dr. Venkat Srinivasan (ANL)
- Dr. Yang Ren (APS, ANL)
- Dr. Joseph A. Libera (MERF, ANL)
- Dr. Tao Li (NIU)
- Dr. Di Chen (U. Houston)

Relevance

Impact

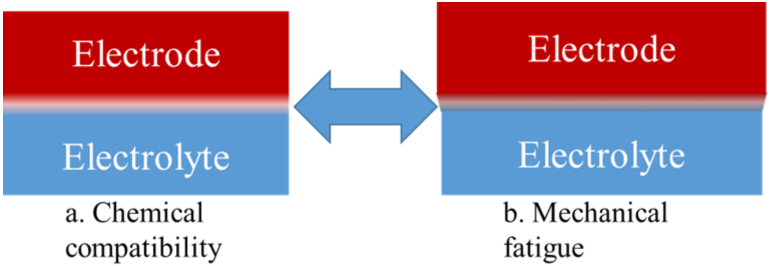
Development of structurally, chemically and electrochemically stable high conductivity solid electrolytes can significantly improve

- **Volumetric energy density; and**
- **Safety characteristics of lithium batteries**

and to accelerate the penetration of electric vehicles.

Objectives

- Developing high conductivity ceramic electrolyte through cation doping.



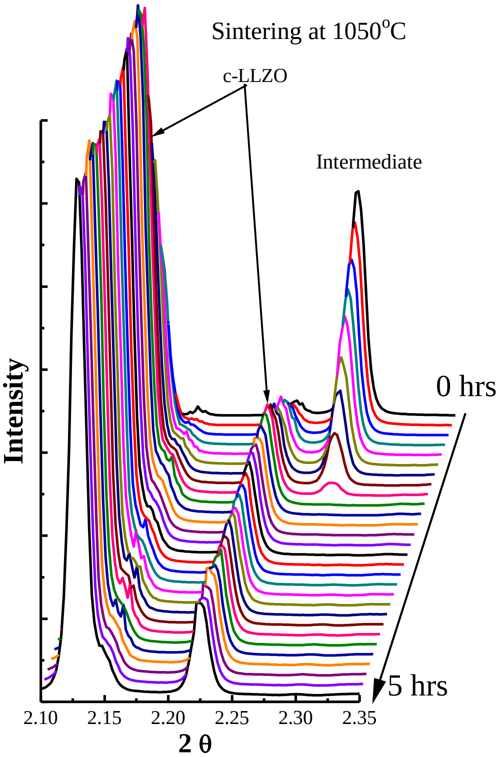
- Stabilizing the structure and cathode/electrolyte interface through cation doping and co-sintering between electrolyte and cathode.

Milestones

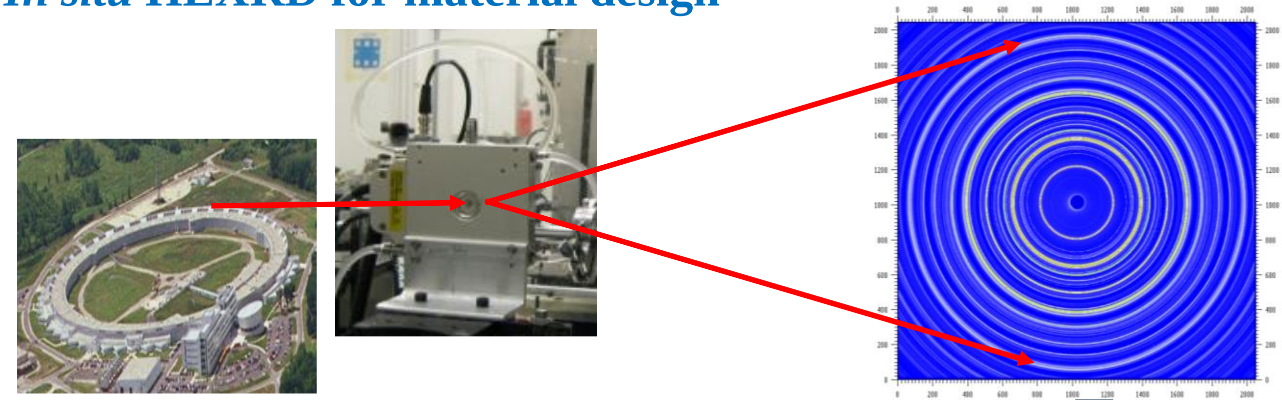
Date	Milestones	Status
12/2018	Developing in situ high energy X-ray diffraction capability to investigate the phase transformation of ceramic electrolytes.	Completed.
03/3019	Investigating the tetragonal/cubic phase transformation of LLZO.	Completed.
06/2019	Investigating the impact of bonding between LLZO and cathode materials.	On going.
09/2019	Synthesizing W-doped LLZO for investigation on structural stability and mechanical stability.	On track.

Approach/Strategy

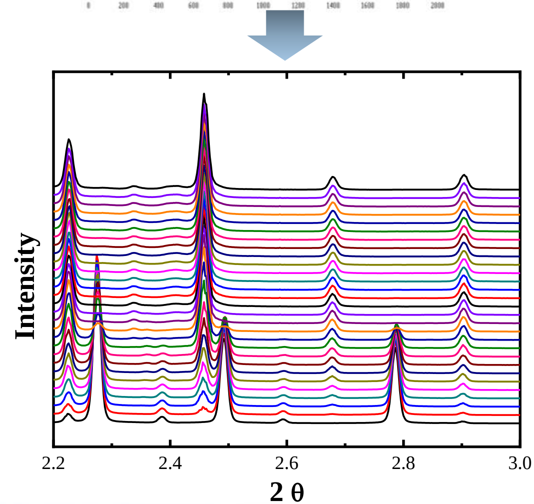
- Understanding the physics behind the transformation between the low conductivity phase and the high conductivity phase.
- Investigating the bonding strength of the cathode/electrolyte interface using model systems.
- Developing electrolytes with high ionic conductivity and good bonding to cathodes through cation doping.
- Crosschecking the findings with multi-scale modelling team (Anh T. Ngo and Venkat Srinivasan).



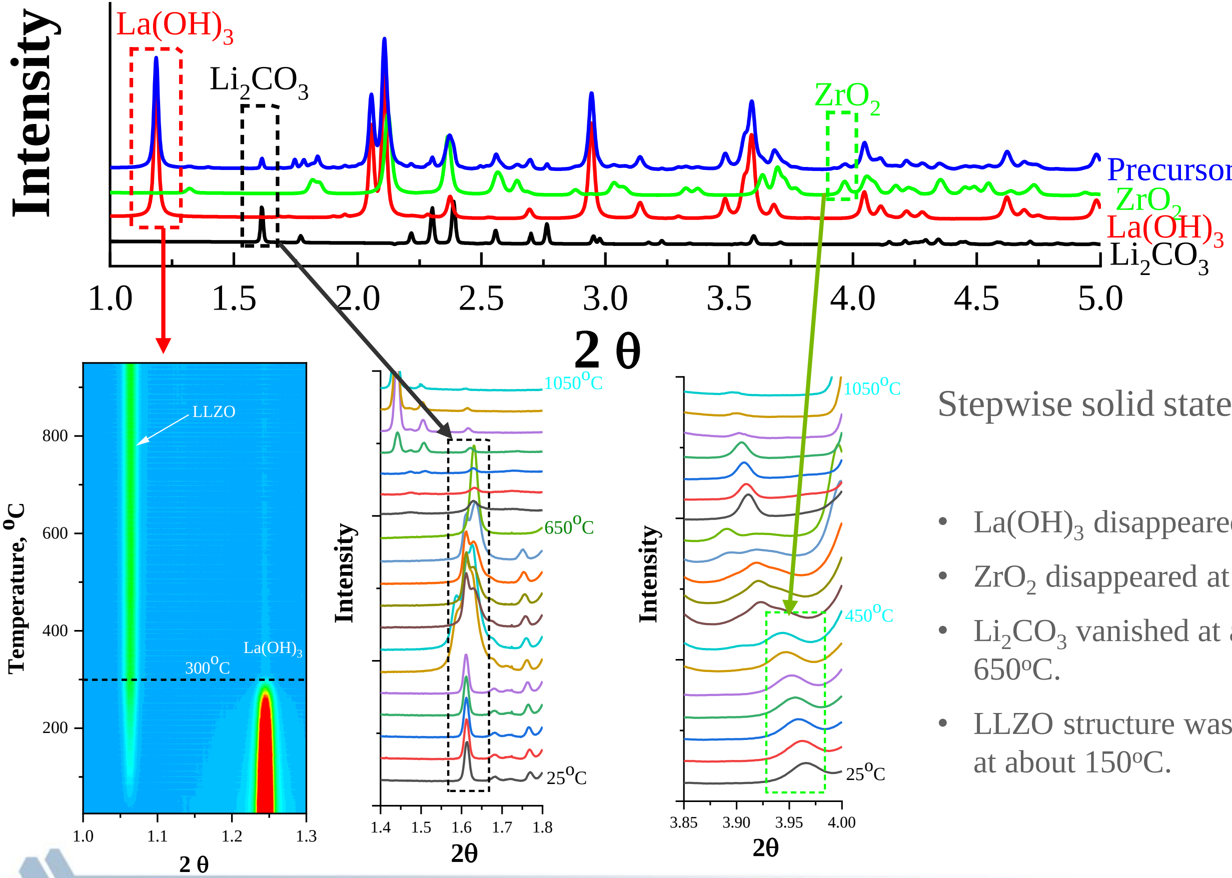
Technical accomplishments and Progress
In situ HEXRD for material design



- HEXRD=high energy X-ray diffraction
- *In situ* HEXRD was used to study the phase transformation during the solid state synthesis of LLZO.
- *In situ* HEXRD will also be used to investigate the bonding stability between the cathode and LLZO.



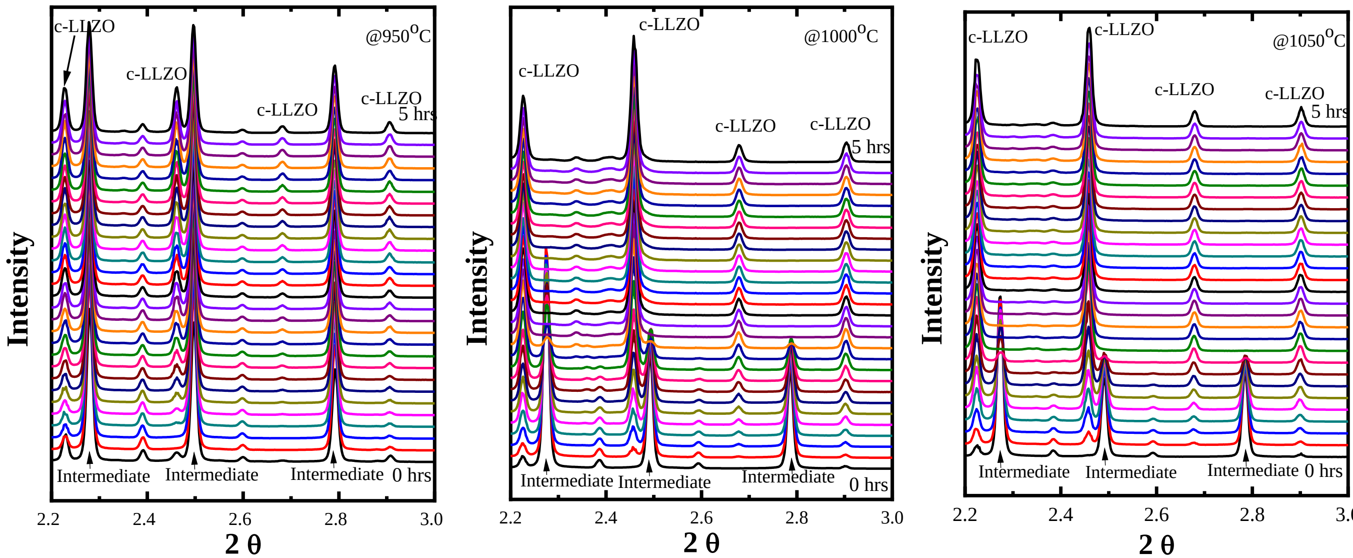
Technical accomplishments and Progress
Solid State Synthesis of $Li_7La_3Zr_2O_{12}$ (LLZO)



Stepwise solid state reaction.

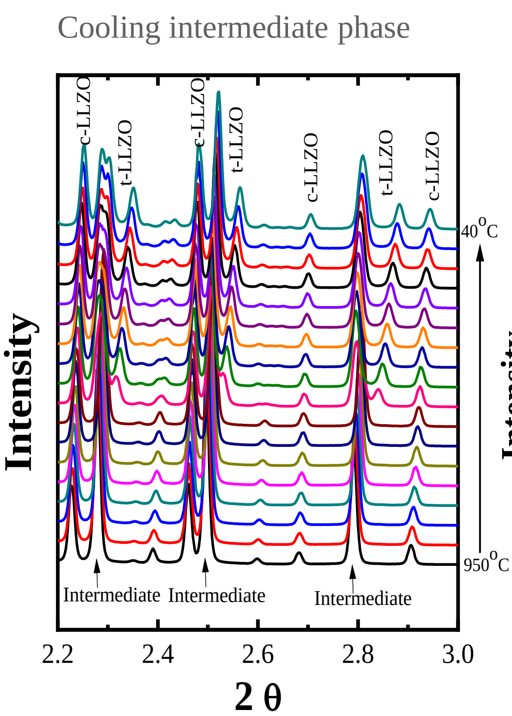
- $La(OH)_3$ disappeared at 300°C.
- ZrO_2 disappeared at 450°C.
- Li_2CO_3 vanished at about 650°C.
- LLZO structure was observed at about 150°C.

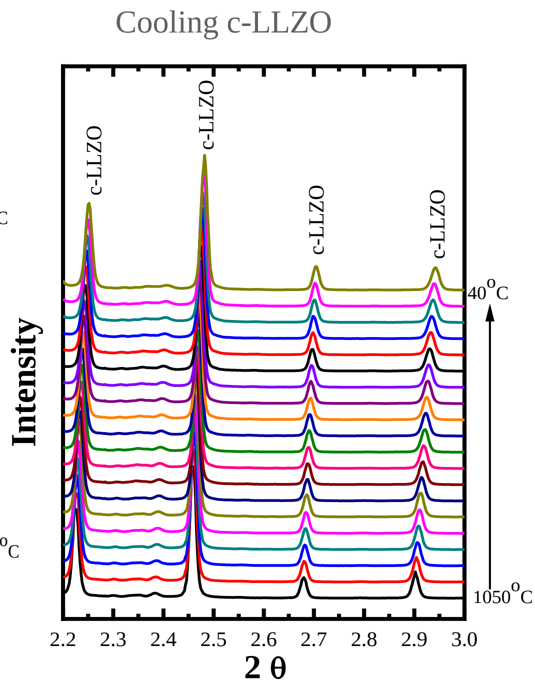
Technical accomplishments and Progress
Sintering of $Li_7La_3Zr_2O_{12}$ (LLZO)



- An intermediate phase, probably cubic, is formed at low temperature.
- The intermediate phase slowly convers to thermodynamically stable cubic $Li_7La_3Zr_2O_{12}$ (*c*-LLZO) at high temperatures (>950°C).
- A quick conversion was observed at >1000°C.

Technical accomplishments and Progress
Formation of tetragonal $Li_7La_3Zr_2O_{12}$ (*t*-LLZO)



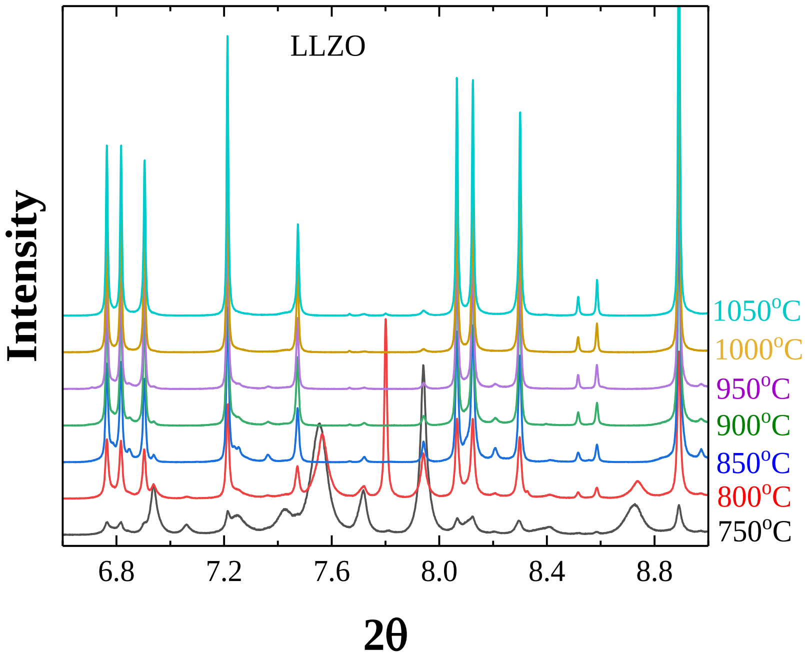


- *c*-LLZO is thermodynamically stable within the range of solid state synthesis. It remains cubic phase during the cooling process.
- The intermediate phase is thermodynamically unstable; it partially converts to a tetragonal phase (*t*-LLZO) during the cooling process.
- A complete conversion of intermediate phase to *c*-LLZO at high temperatures is crucial.

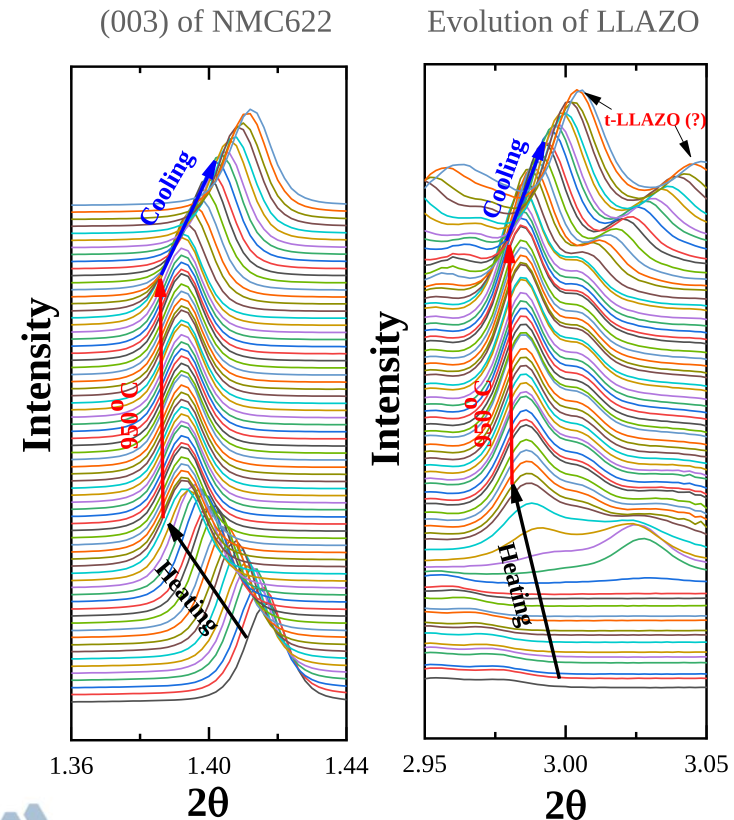
Technical accomplishments and Progress
Slow kinetics for the formation of *c*-LLZO

- To validate the slow kinetics of *c*-LLZO formation:
  - Samples were sintered overnight (15 hrs) at various temperatures.
  - Pure *c*-LLZO was obtained at temperature above 950ºC.
  - Small amount of *t*-LLZO was observed for samples sintered between 800ºC and 950ºC.
  - Small amount *c*-LLZO was observed at 750ºC
- A reduction of the critical temperature to **800ºC** range is ideal for **co-sintering** with nickel-rich cathodes.

High resolution X-ray diffraction



Technical accomplishments and Progress
Preliminary result on co-sintering



- Al-doped LLZO precursor (green powder) was provided by MERF (Dr. Joseph Libera).
- The green power converts to a cubic phase when sintered individually.
- NMC622 powder was mixed with the green powder (50:50 by weight).
- **Co-sintering process didn't change the structure of NMC622.**
- *c*-LLAZO was not formed after the co-sintering.
- More work is needed to investigate the sintering of Al-doped LLZO.
- The bonding strength between NMC and LLZO also deserves investigation.

Responses to Previous Year Reviewers' Comments

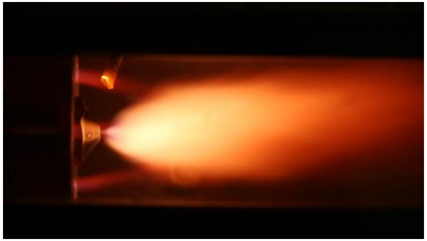
This project was started FY19. It has not been reviewed yet.

Partners/Collaborators

Internal collaboration:

- Dr. Joseph A. Libera
  Flame Spray Pyrolysis synthesis of ceramic electrolyte

- Dr. Anh T. Ngo, Dr. Larry Curtiss, Dr. Venkat Srinivasan
  Theory-experiment cross validation of material design.



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- Ion implantation to modify the chemistry of ceramic electrolytes.

Northern Illinois University

- Advanced characterization of solid/solid interface.

Remaining Challenges and Barriers

- The bulk Li^+ conductivity was intrinsically determined by the structure of the electrolyte. The kinetics of the phase transformation from the cubic intermediate to c-LLZO is crucial for the synthesis of high conductivity electrolyte. The impact of cation doping on the kinetics of the phase transformation needs to be investigated.
- A mechanically stable electrode/electrolyte interface is crucial for efficient Li^+ transport across the interface. Co-sintering of cathode and electrolyte is needed to create effective bonding, but without scarifying the functionality of each components. Establishing a chemical route to build a robust solid/solid interface holds the key for high performance lithium batteries.

Proposed Future Research

In the coming year, we will be focusing on following tasks.

1. Investigating the impact of cation doping (Al or W) on the kinetics of intermediate/c-LLZO phase transformation.
2. Investigating the impact of cation doping on the Li^+ conductivity.
3. Understanding the interaction between NMC622 and LLZO electrolyte.
4. Electrochemically quantifying the strength and effectiveness of solid/solid interface using model lithium-ion cells. NMC622 will used as the model cathode, and LLZO will be used the model electrolyte.

Summary

- A direct transformation between *c*-LLZO and *t*-LLZO was not observed.
- A cubic intermediate phase is the link between the *c*-LLZO and *t*-LLZO.
- The conversion from the intermediate phase to *c*-LLZO is kinetically slow, needing high temperature and sintering time.
- The intermediate phase converts to *t*-LLZO during the cooling process.
- *c*-LLZO is globally stable; it doesn't convert to *t*-LLZO once formed.
- Doping chemistries to reduce the energy barrier of intermediate/*c*-LLZO transformation is actively pursued for effective co-sintering between NMC and LLZO.