INVESTIGATING THE STABILITY OF SOLID-SOLID INTERFACE

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Argonne National Laboratory

2019 DOE VTO Annual Merit Review

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Project ID: bat418

OVERVIEW

Timeline

- Start: 10/01/2019
- End: 09/30/2022
- 30% completed

Budget

- Total project funding
  - DOE - $410K (FY20)
  - Contractor - $ 0
- Funding received in FY19
  - N/A
- Funding for FY20
  - DOE - $410K

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

- University of Arkansas
- Northern Illinois University
- Brookhaven National Laboratory

RELEVANCE

Objective:

- To characterize the physical/chemical properties of species at the solid/solid interfaces, and to fundamental understand the critic issues that limit the mechanical, chemical and electrochemical stability of solid/solid interfaces at the cathode and the anode.

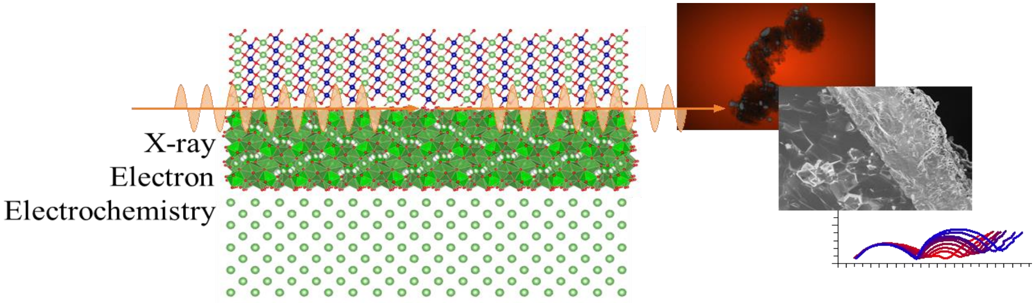
Impact:

- To generate knowledge that supports the rational design of materials and process development;
- To establish structure-properties relationship of the interface;
- To understand the formation mechanism of lithium dendrite, and to predict potential solutions.

MILESTONES

Month/Year	Description of Milestone or Go/No-Go Decision	Status
December, 2020	Forming model Ta-LLZO/NMC622 interface for physical diagnosis	**Completed**
March, 2020	Investigating the interaction between Ta-LLZO and NMC622 at the interface upon cycling	On going
June, 202	Investigating the chemical reactions of Ta-LLZO at the reducing environment	On going
September, 2020	Investigating the chemical/mechanical stability of LI/Ta-LLZO interface	On schedule

APPROACH

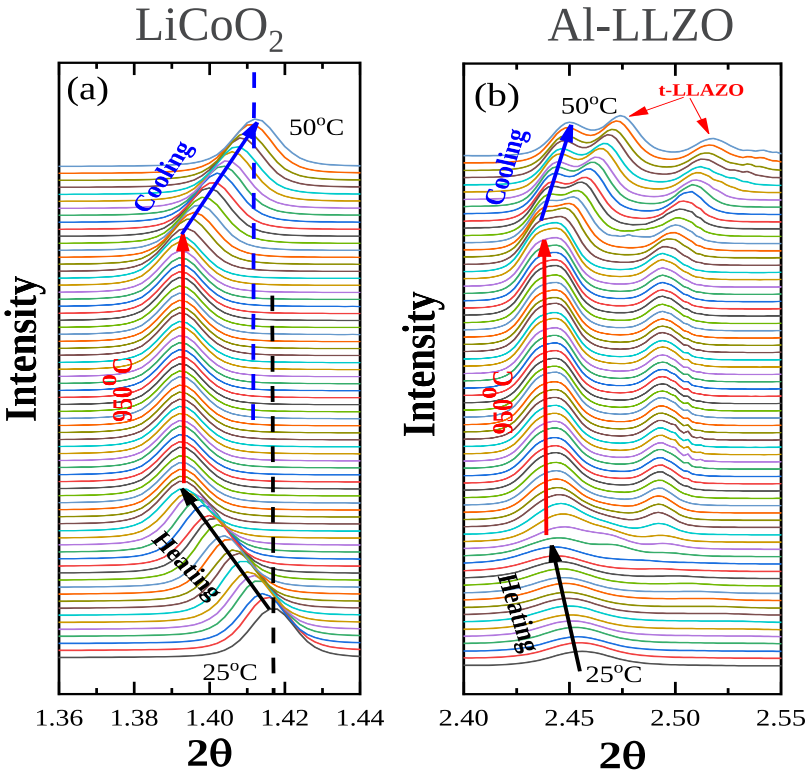


- Multiple excitation sources will be utilized to probe the structure and properties of materials at the solid-solid interface.
  - X-ray probes for local structure and chemical environment at the interface
  - Electron probes for local morphology characterization
  - Electrochemical probes for transport properties and chemical stability of the interface
  - *In situ* probes for dynamic properties of the interface

- Providing data feed to multiscale modelling team to extract physics behind the observation.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

Interaction between electrolyte and cathode during co-sintering

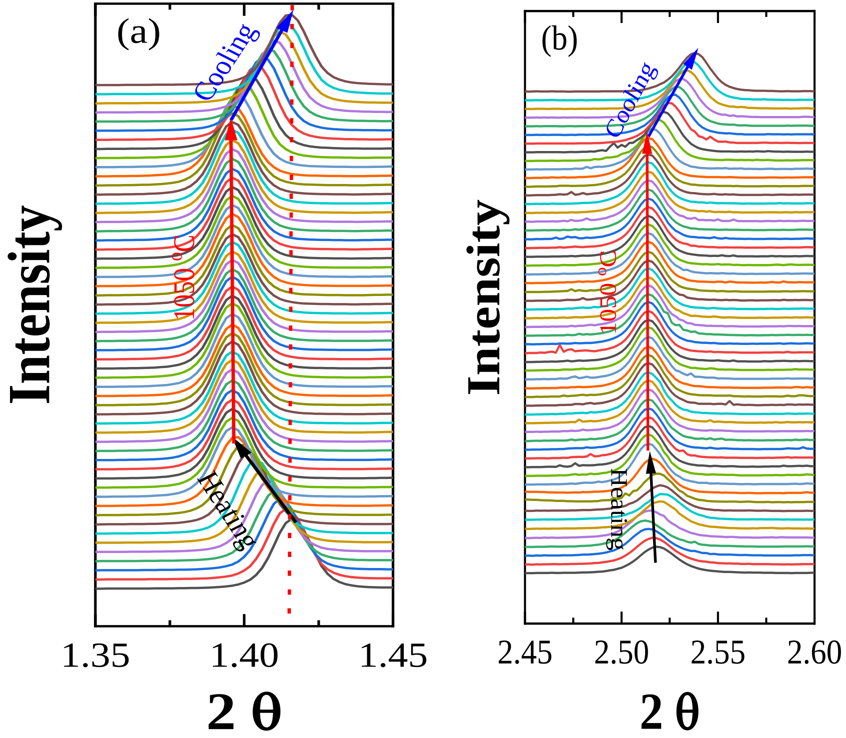


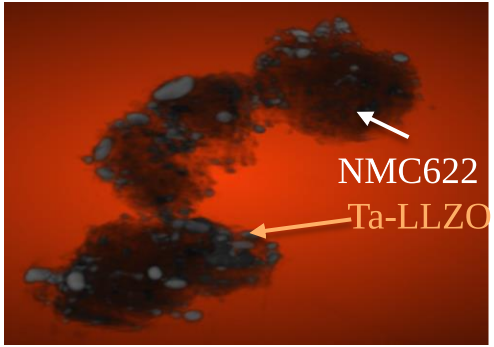
***In situ* high-energy X-ray diffraction during the co-sintering between $LiCoO_2$ and precursor for Al-doped LLZO**

- Al-doped LLZO precursor (green powder) was provided by MERF (Dr. Joseph Libera).
- The green power converts to a cubic phase when sintered individually.
- $LiCoO_2$ powder was mixed with the green powder (50:50 by weight).
- Co-sintering process didn't change the structure of $LiCoO_2$, but a clear lattice expansion was observed.
- *c*-LLAZO was not formed after the co-sintering.
- The adverse phase change can be originated from the uptake of Al-species by $LiCoO_2$.
- **Potential solution:** (1) using an alternative dopant, and (2) using cubic LLZO instead of precursor.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Co-sintering between Ta-LLZO and $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622)

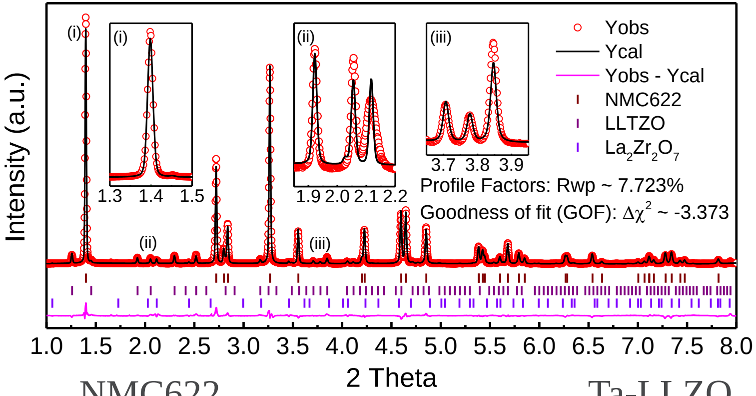


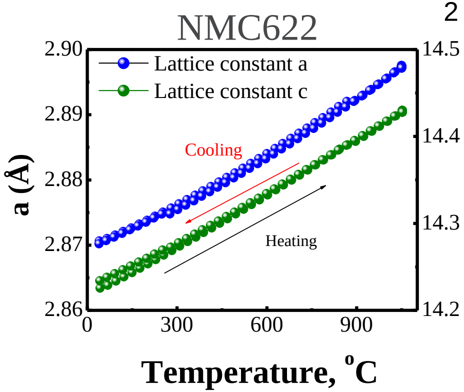


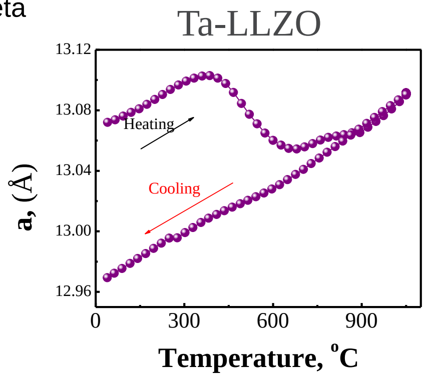
- The structures of both materials were well maintained after co-sintering.
- Ta-LLZO particles were physically attached to NMC622 particle.
- No change on the NMC622 lattice parameters was visually observed.
- Ta-LLZO experienced unusual phase transformation at early stage, but maintained cubic phase after co-sintering.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Structure evolution of materials during co-sintering







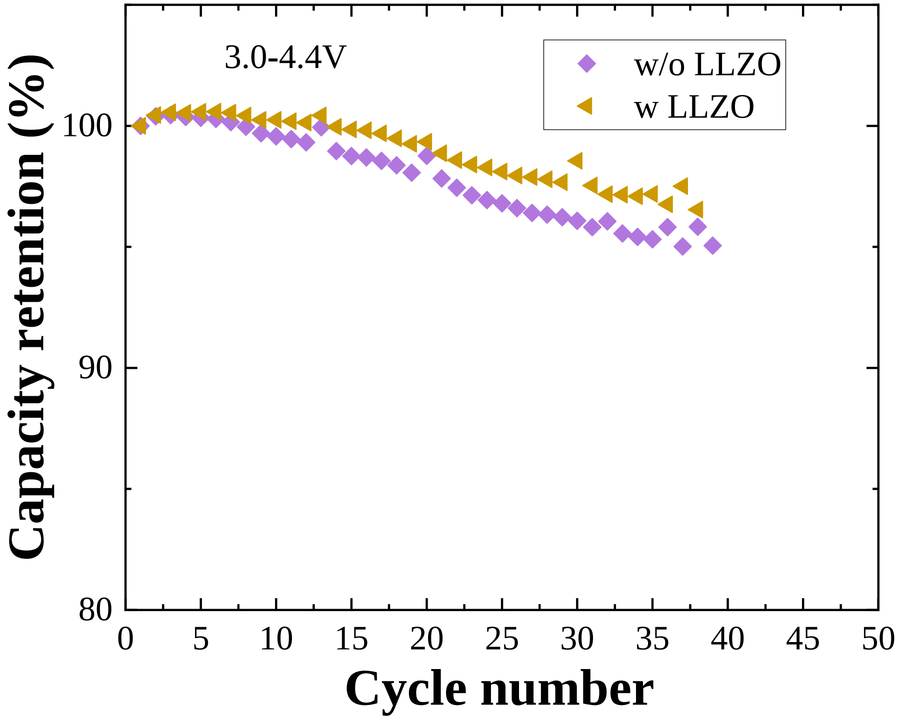
During the co-sintering process,

- NMC622 experienced reversible thermal expansion/contraction during the co-sintering.
- TA-LLZO experienced irreversible phase transformation during the initial heating process (the big hysteresis loop below 700°C).
- Rietveld refinement showed Ta-LLZO was in cubic phase both before and after thermal treatment.
- A small amount of $La_2Zr_2O_7$ was observed after the thermal treatment.

- The origin of irreversible phase transformation and formation of $La_2Zr_2O_7$ deserves further investigation.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Electrochemical properties of Ta-LLZO decorated NMC622

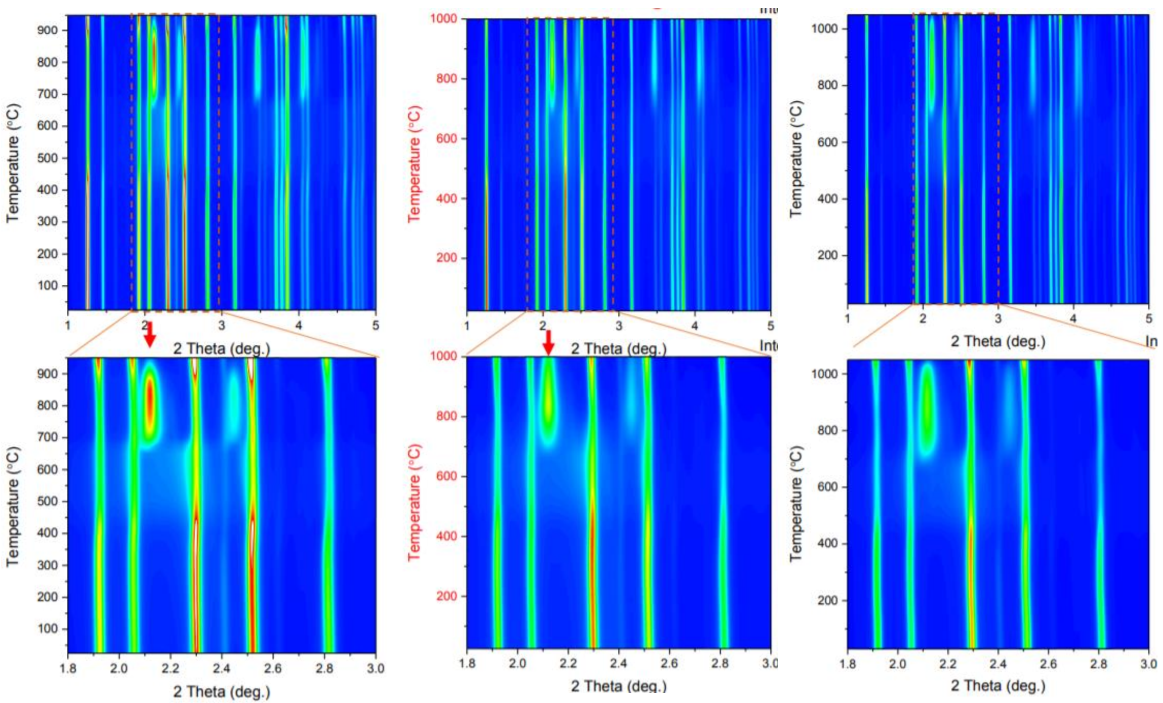


- The assembling of all solid-state cell using the co-sintered cathode and LLZO electrolyte was not successful. (The cell was electrochemically inactive.)
- The co-sintered pallet was grinded and used as a regular cathode materials, and then tested in liquid cells. The material with LLZO showed marginally improvement on the capacity retention.
- The decoration of LLZO on NMC622 doesn't hurt the electrochemical properties of NMC622.
- The failure mechanism of the solid-state cell is further investigated.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Common phase transformation for various doped LLZO

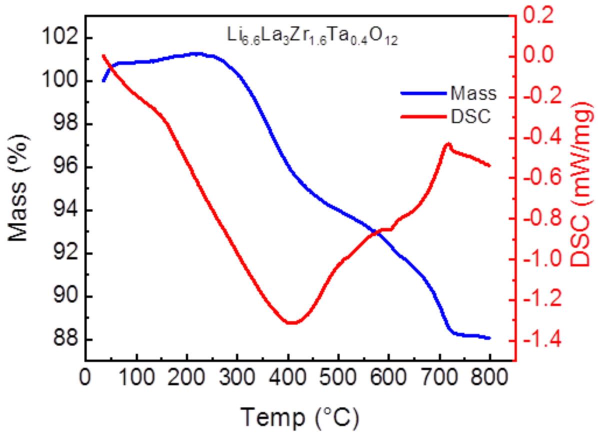
Ta-LLZO Al-LLZO Ga-LLZO

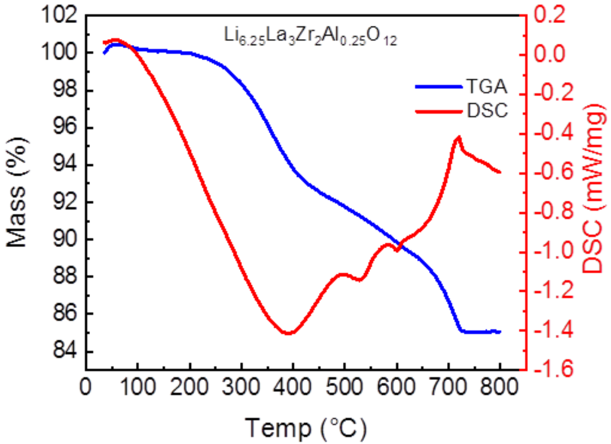


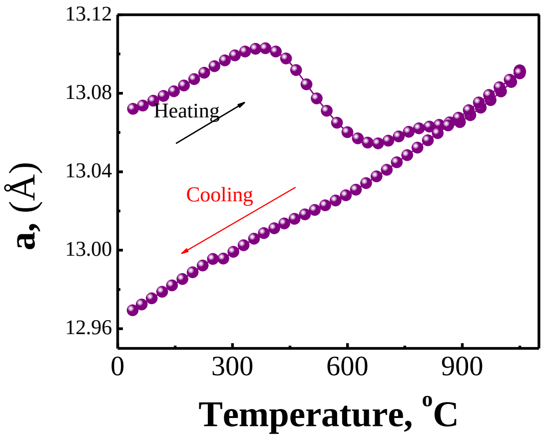
- *In situ* HEXRD was carried out different LLZO with Ta, Al, and Ga doping.
- All materials exhibited irreversible phase transformation below 700 ^{o}C.
- All materials generated $La_2Zr_2O_7$ impurity after thermal processing.
- These observation was attributed to the uptake of proton and generation of $LiOH/Li_2CO_3$ at the surface. (Supported by TGA data in next slide.)

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Substantial mass loss during the thermal processing



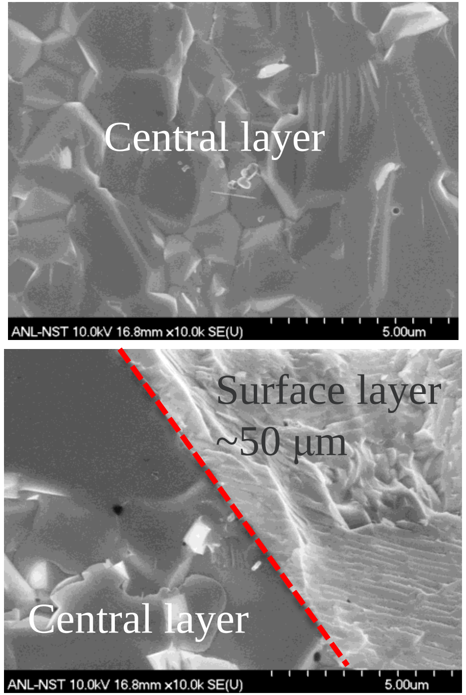




- Strong correlation between the mass loss and the phase transformation was observed.
- About 12-14% mass loss was observed for stored LLZO samples.
- It is speculated that proton-lithium exchange occurred during the storing period.
- Two-step reaction was observed, 1) reaction of H-bearing LLZO with LiOH (at ~400 ^oC), releasing H_2O;
- 2) reaction between oxides and Li_2CO_3 (at ~700^{o}C), releasing CO_2.
- **All aged LLZO need thermal processing before direct use.**

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

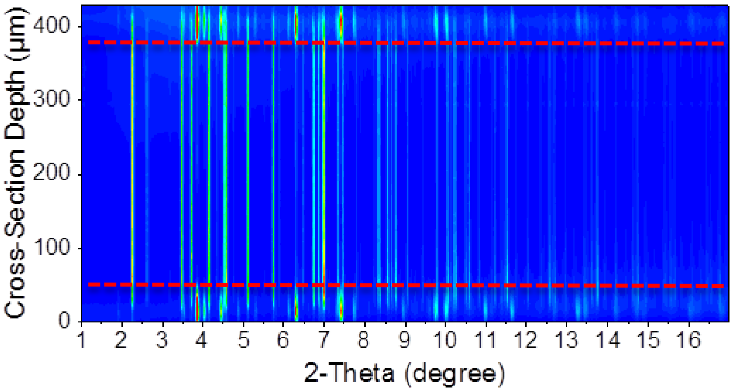
Hot-pressing LLZO pallets for use as separator

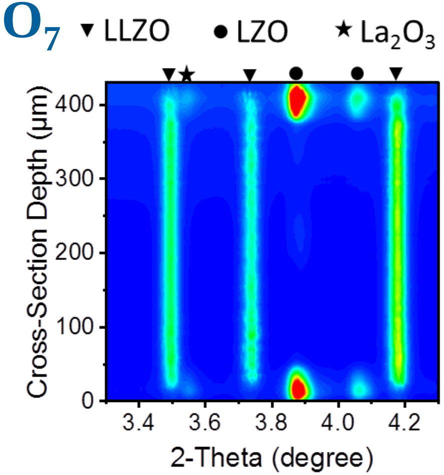


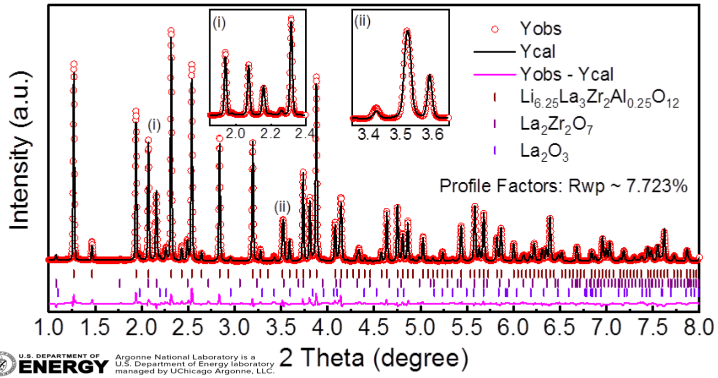
- A solid and mechanically strong pallet was obtained after hot-pressing (1000^{o}C & 1000lb).
- The pallet showed a tri-layer structure, a thick dense and well crystallized layer in the middle; both sides are covered with a layer of different materials (~50 µm each).

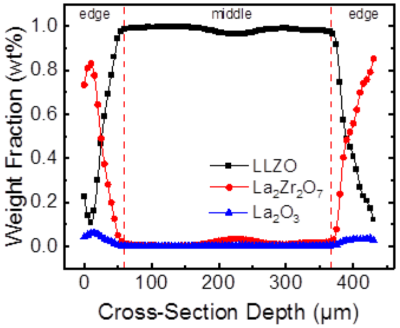
TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

The interface layers were $La_2Zr_2O_7$





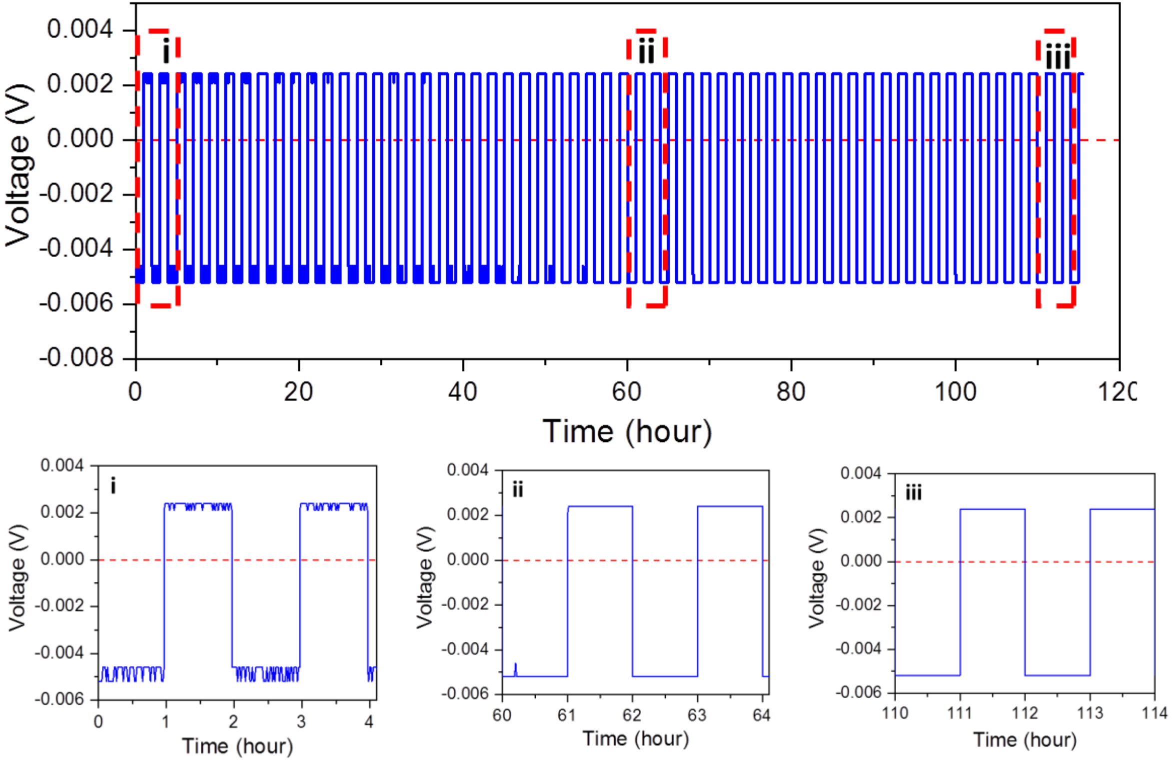




- ➢ The interface layer after hot-press is dominated by $La_2Zr_2O_7$ with a small amount of La_2O_3.
- ➢ The central layer remains cubic LLZO.
- ➢ The mechanism of Li_2O at the interface is not clear yet.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

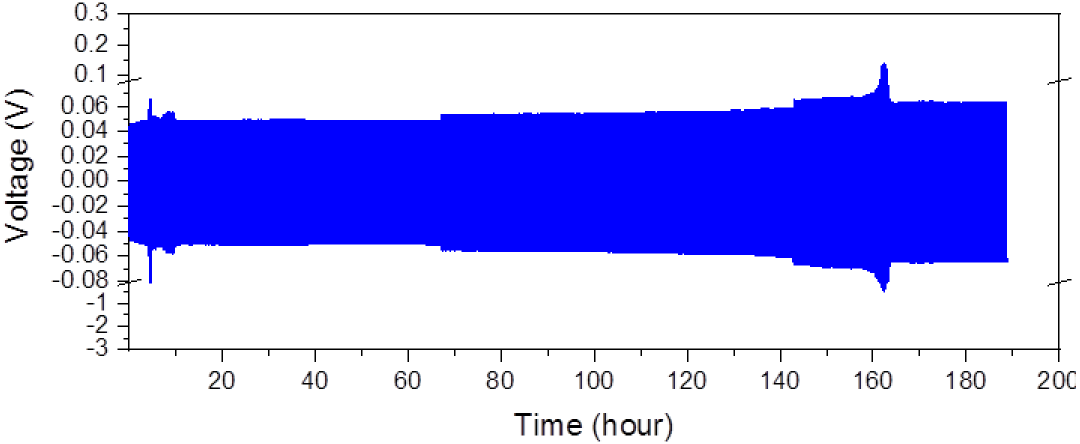
Stable lithium plating/stripping using Ta-LLZO electrolyte

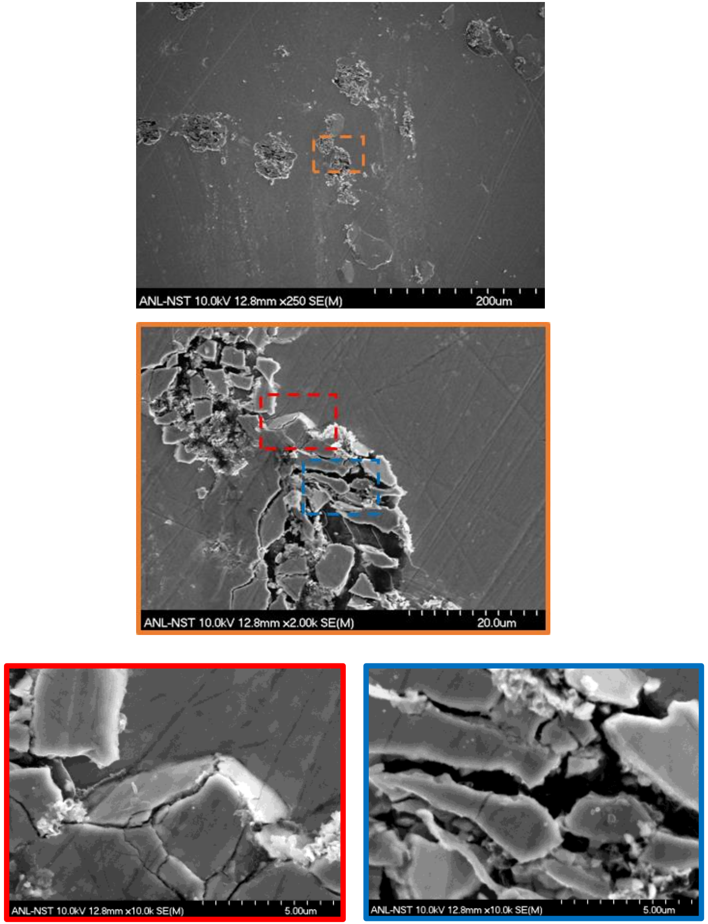


- Ta-LLZO powder was hot-pressed into a pallet.
- The surface layers were polished off before assembling symmetrical cells.
- The cell was cycled at a low current density of 0.1 mA/cm^2.
- Stable lithium plating/stripping was achieved.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Dendrite formed at a high current density





- Severe lithium dendrite formation was observed when plating/stripping at a high current density, 2 mA/cm^2.
- Preliminary results from *ex situ* SEM study showed that lithium dendrite could grow inside the LLZO pallet.
- This observation needs to be reproduced.
- Measurement of critic current density is also important.

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This is the first year that the project is reviewed.

COLLABORATION S

- University of Arkansas (Prof. Xiangbo Meng)
  - Surface modification using atomic layer deposition (ALD) and molecular layer deposition (MLD)

- Northern Illinois University (Prof. Tao Li)
  - Powder characterizing using small angle X-ray scattering (SAXS)

- Brookhaven National Laboratory (Dr. Feng Wang, Dr. Xianghui Xiao)
  - Morphology characterization using *in situ* and *ex situ* transmission X-ray microscopy (TXM)

- Argonne National Laboratory (Dr. Anh Ngo, Dr. Larry Curtiss, Dr. Venkat Srinivasan, Dr. Nenad Markovic, Dr. Yang Ren, Dr. Yuzi Liu, Dr. Bryant Polzin, Dr. Joseph Libera)
  - Providing data feed for theory and modeling team (A.N., L.C., V.S., and N.M.)
  - Structure characterization using high energy X-ray diffraction (HEXRD) (Y.R.)
  - Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Y.L.)
  - Material processing (CAMPS, BP)
  - Material processing (MERF, JL)

REMAINING CHALLENGES AND BARRIERS

- **Degradation mechanism of aged LLZO powder during storage**
  - Specialization of aged samples
  - Elucidating the impact of doping chemistry on degradation mechanism
  - Exploring possibility to reverse the degradation process of aged LLZO powder

- **Chemical stability of LLZO at reducing environment**
  - Illustrating the decomposition mechanism of LLZO exposed to both reducing environment and high temperature
  - Fundamental understanding and specialization of the reaction between lithium and LLZO electrolyte
- **Rooting the cause of lithium dendrite formation against LLZO**
  - Understanding the lithium plating/stripping behaviors below and above the critic current density
  - Quantifying the role of electronic conductivity to the formation of lithium dendrite

PROPOSED FUTURE RESEARCH

- FY20: lithium plating/stripping behavior at high current density
  - *In situ* SEM/TEM to observe the rapid growth of lithium whiskers
  - Exploring the impact of doping chemistry on the formation of lithium whiskers

- FY21: quantifying structural and chemical stability of LLZO in adverse environments
  - *In situ* HEXRD to investigate the recovery of degraded LLZO
  - *Focused beam* HEXRD to investigate the structural heterogeneity at the solid/solid interface
  - *Ex situ* TXM to investigate the morphological change at the interface after lithium plating/stripping
  - Accessing the critic current density of LLZO electrolytes and the potential impact of doping chemistry

SUMMARY

- A physical interface between LLZO and NMC cathode can be formed by co-sintering.

- The creation of functional solid-solid interface is influenced by:
- 1) chemical reaction between LLZO and ambient air at the surface of LLZO;
- 2) decomposition of LLZO during thermal process of LLZO pallet;

- The lithium plating/stripping behavior shows strong dependence on the applied current density. Plating/stripping at high current density shows preliminary clue of outward dendrite formation (from electrolyte towards lithium foil). *In situ* SEM/TEM will be carried out to validate the observation.