INVESTIGATING THE STABILITY OF SOLID-SOLID INTERFACE

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Argonne National Laboratory

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Project ID: bat418

U.S. DEPARTMENT OF ENERGY

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OVERVIEW

Timeline

- Start: 10/01/2019
- End: 09/30/2022
- 60% completed

Budget

- Total project funding
  - DOE - $1,380K
  - Contractor - $ 0
- Funding received in FY21
  - $325.4K
- Funding for FY21
  - DOE - $380K

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
- 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.

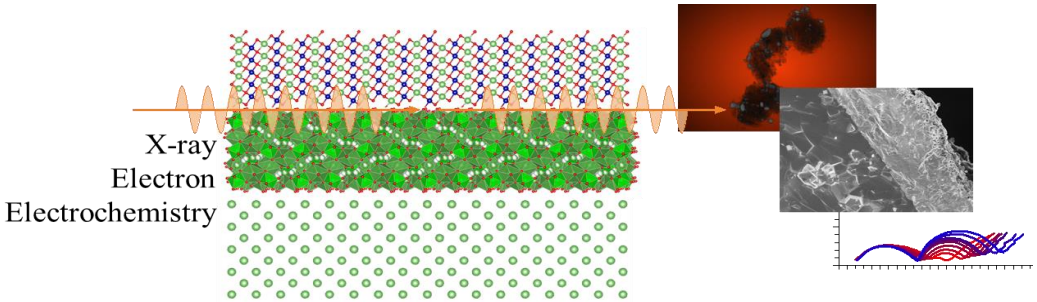
Impact:

- 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	In situ electron microscopic characterization of the dendrite formation on LLZO.	**Completed**
March, 2021	Investigation of electronic conducting path in LLZO pallet.	**Completed**
June, 2021	Investigation of the mechanical stability of cathode/LLZO interface using model system .	On going
September, 2021	Microscopic study of the mechanical stability of cathode/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.

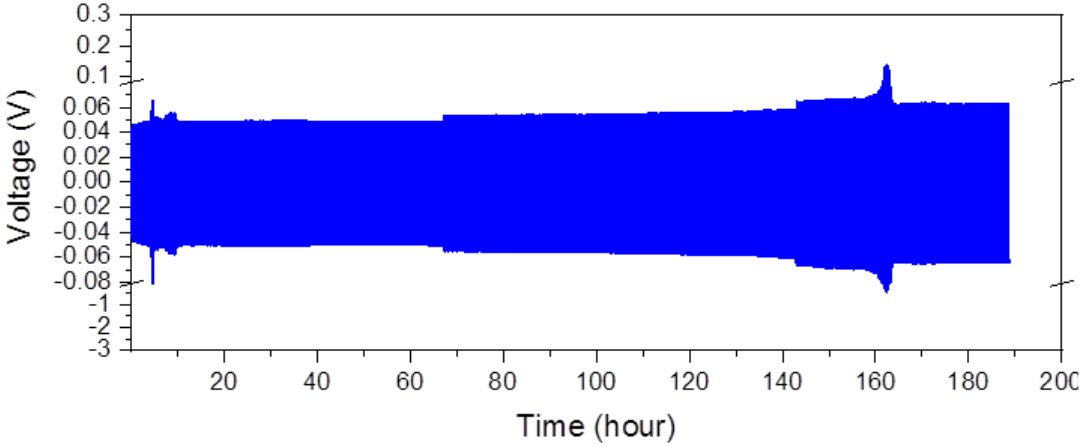
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

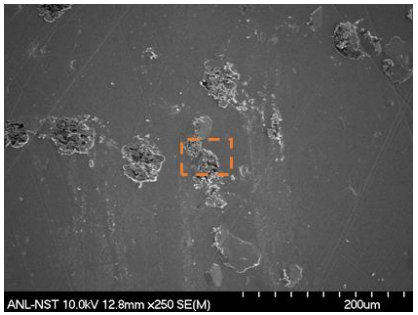
- Lithium/LLZO interface
  - ✓ Lithium dendrite formation at high current density (~2mA/cm^2)
  - ✓ In situ SEM visualization of lithium plating on LLZO
  - ✓ Confirmed two lithium dendrite formation mechanisms
    1. Dendrite grows from lithium towards LLZO (outside in, conventional)
    2. Dendrite grows from LLZO towards lithium (inside out, newly discovered)

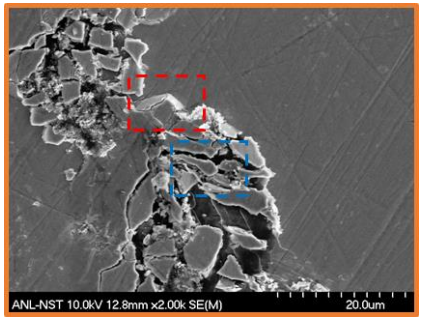
- LLZO/NMC interface
  - ✓ NMC/LLZO bonding can be formed through co-sintering and dry coating process
  - ✓ The interaction between LLZO and NMC was confirmed with model cells using a liquid electrolyte.
  - ✓ In situ cell for solid interface study was implemented.
  - ✓ Making liquid-free cells remains a big challenge.

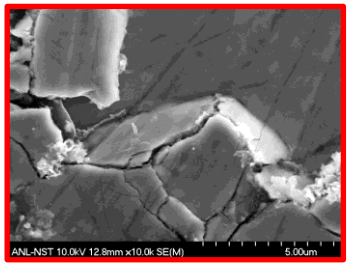
TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

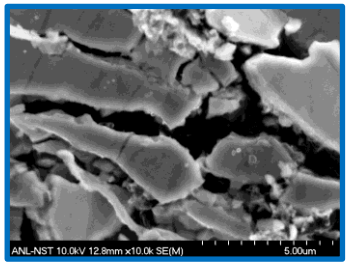
Dendrite formed at a high current density







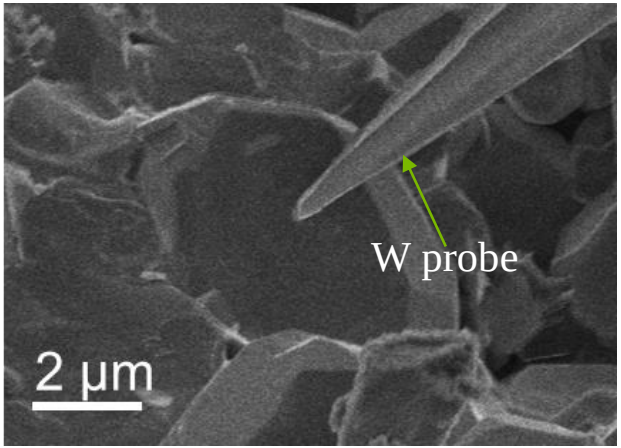


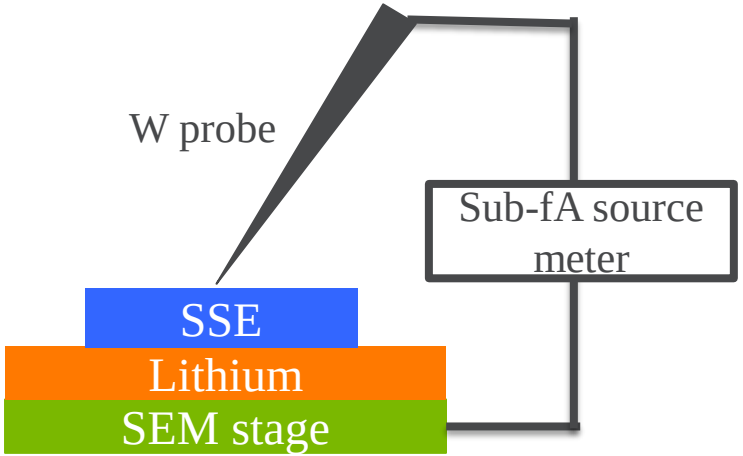


- Severe lithium dendrite formation was observed when plating/ stripping at a high current density, 2 mA/cm^2.
- Preliminary results from *ex situ* SEM study showed that lithium dendrite could grow from inside out of LLZO pellet.
- This observation implies the existence of electronic conducting pathway to transport electrons into the bulk part of LLZO pellet.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

In situ Scanning Electron Microscopy to visualize lithium plating

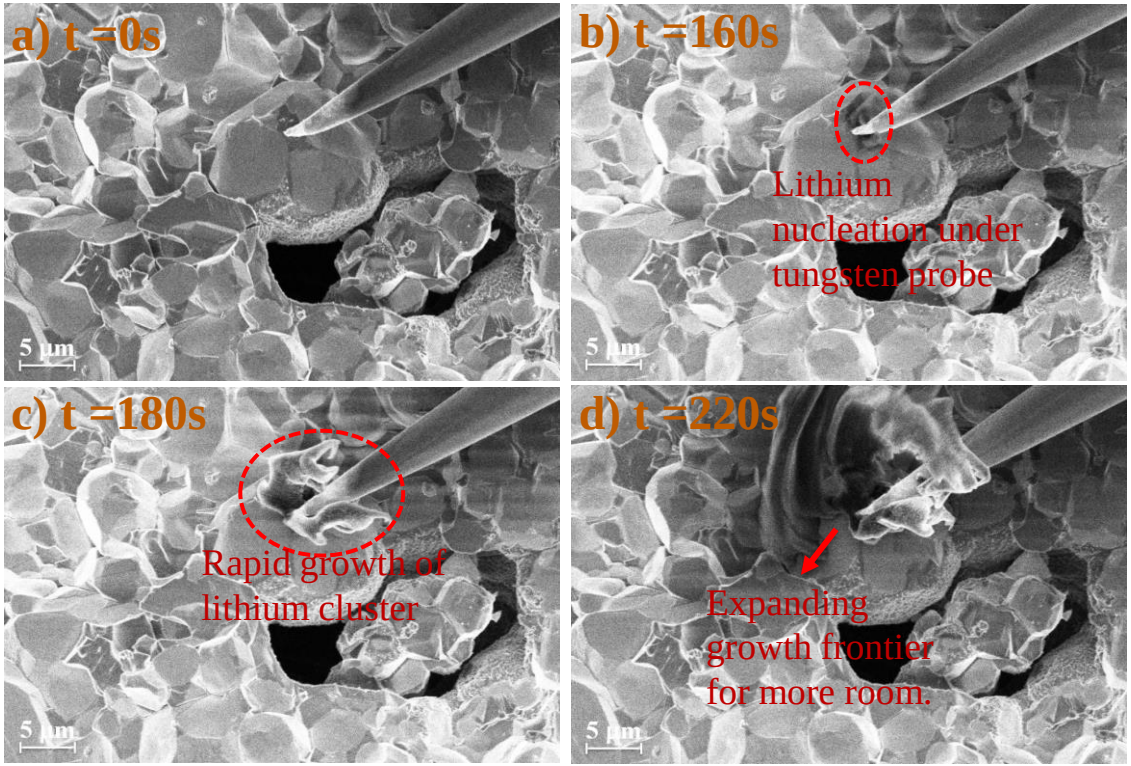




- Negative potential is applied on tungsten probe to "draw" lithium out of electrolyte.
- Tungsten probe acts as an electron source to reduce Li^+ into Li.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Visualizing the normal growth of lithium clusters

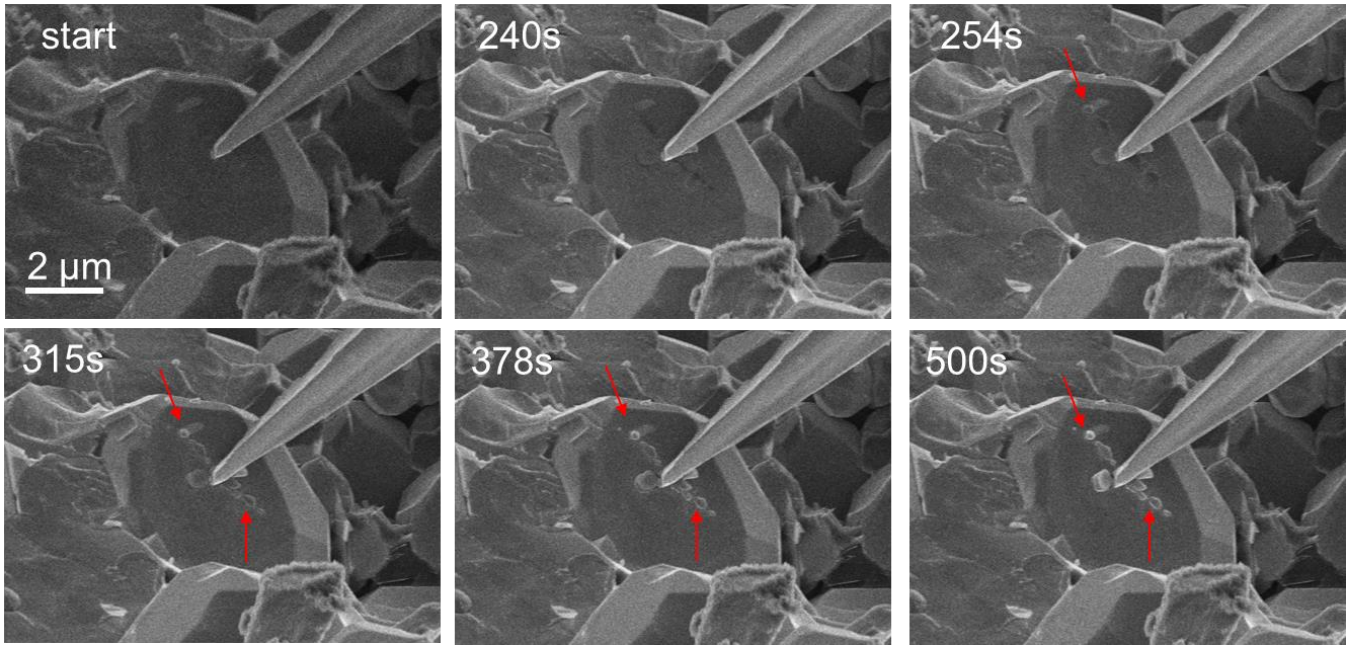


10 out of 12 cases, the normal lithium nucleation pattern was observed:

- Lithium nucleation starts below the tungsten probe that acts as the electron sources.
- The frontier for lithium growth expands with time get more room for lithium to grow into.
- When no room is preserved, lithium can grow into the electrolyte, growing dendrites into the electrolyte as well conventionally believed.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Visualizing the remote nucleation of lithium clusters at single LLZO particle

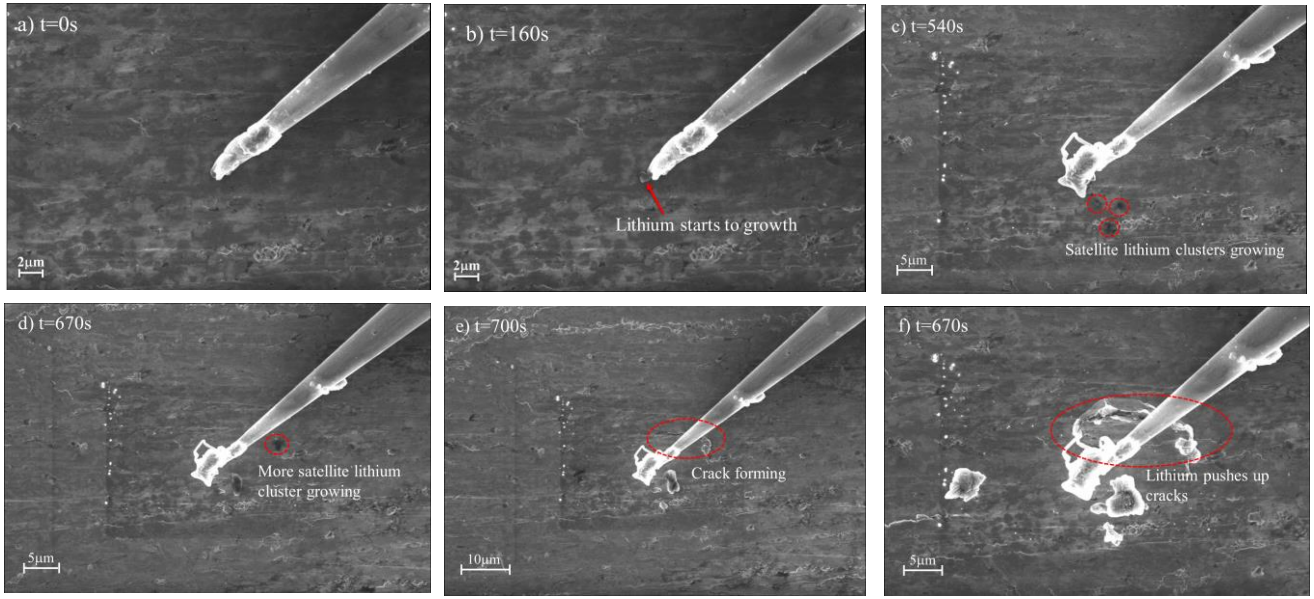


- Cold-pressed pellet was used to maintained the particle morphology.
- Remote growth of lithium clusters was observed at the single particle, not the boundary.
- The observation implies the electronic conducting path exists at the particle level.

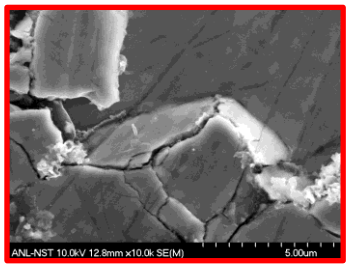
- Only 2 out of 12 cases show the remote growth of lithium clusters.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Remote nucleation of lithium clusters and cracking of hot pressed LLZO pellet



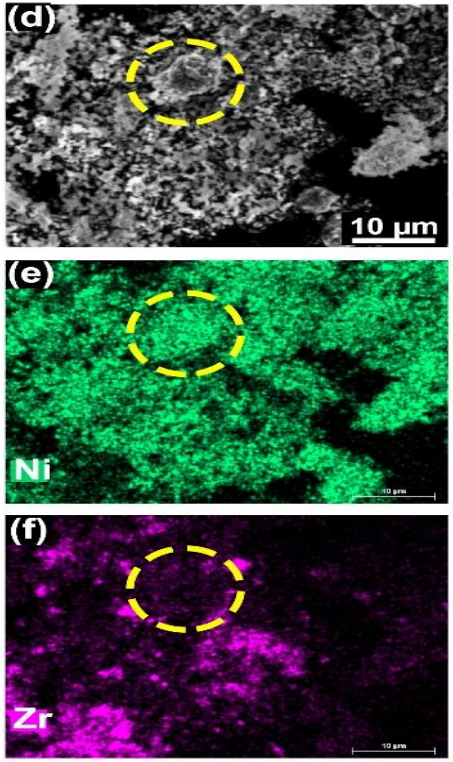
- Growth of satellite lithium dendrite was observed.
- A clear pushing-out crack pattern was observed.

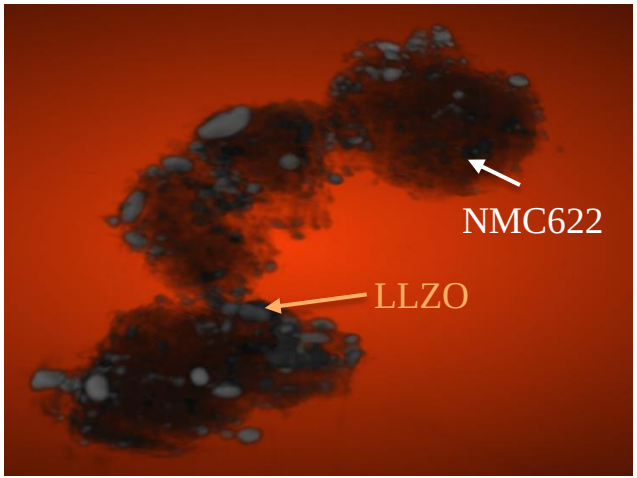


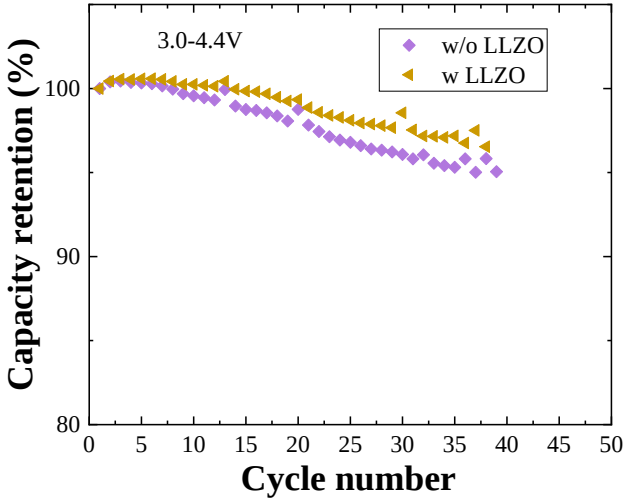
- Hot press was used to prepare a dense LLZO pellet.
- The results imply the existence of electronic conducting path in LLZO.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Creating bonding between LLZO and NMC





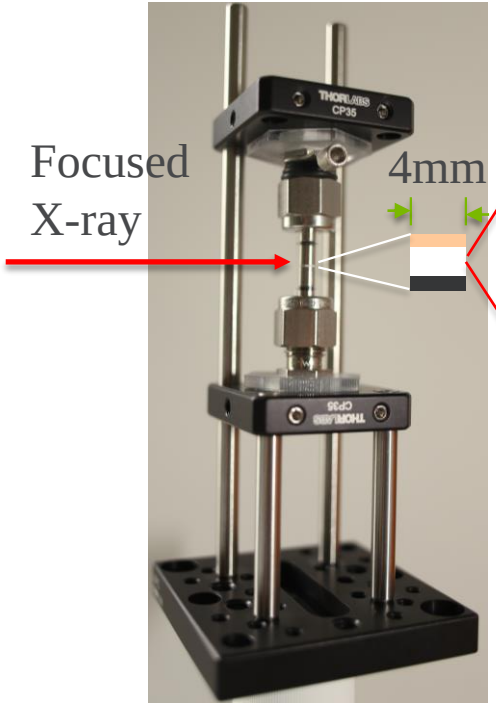


- Creating NMC/LLZO interface can be achieved via either co-sintering or dry coating process.
- A stable bonding between LLZO and NMC was confirmed by model cells using a liquid electrolyte
  - LLZO reduces exposed NMC surface for a slightly better capacity retention.

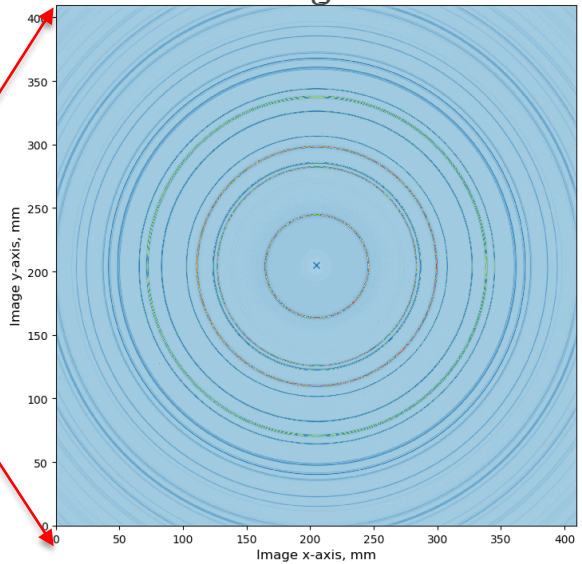
TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

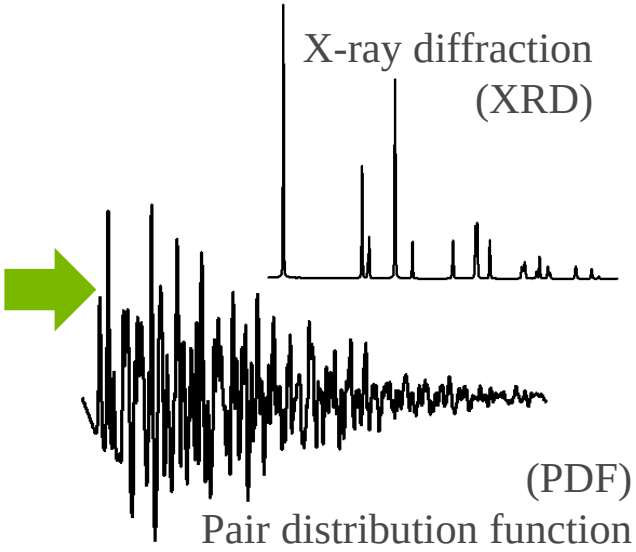
Developing spatial resolved X-ray probes for interface study

In situ electrochemical cell



2d image





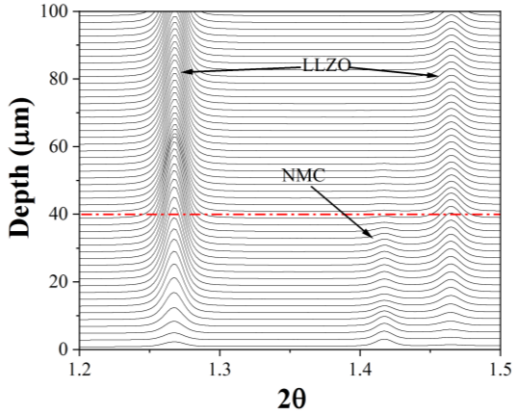
Development focus:

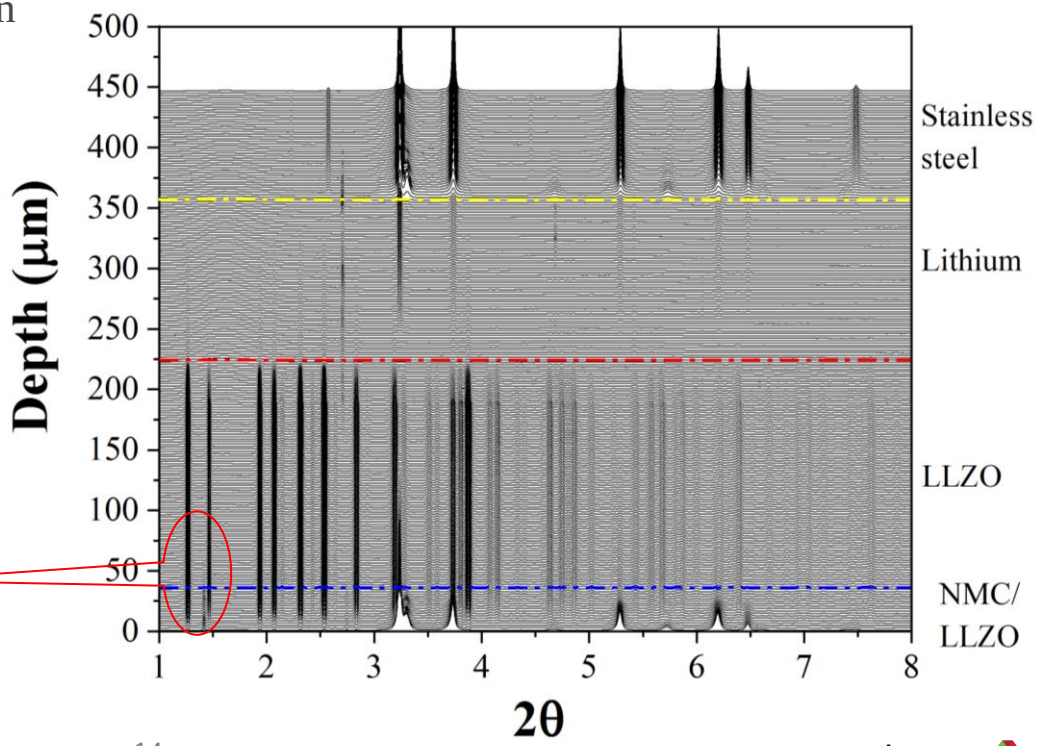
1) X-ray transparent in situ cell for high quality data
2) Focused X-ray beam to ~3 μm for spatial resolution
3) Improving X-ray flux for temporal resolution

TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Probing the solid/solid interface using spatial resolved HEXRD

- HEXRD=High energy X-ray diffraction
- Wavelength: 0.1173Å for optima penetration
- Beam size: ~3 μm
- Layer-by-layer structure can be easily visualized.

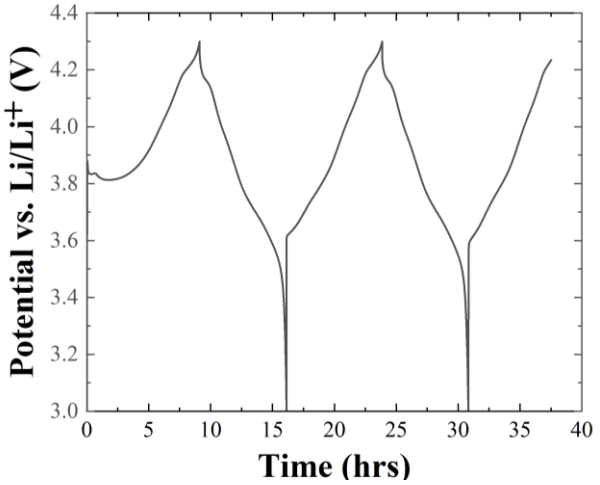




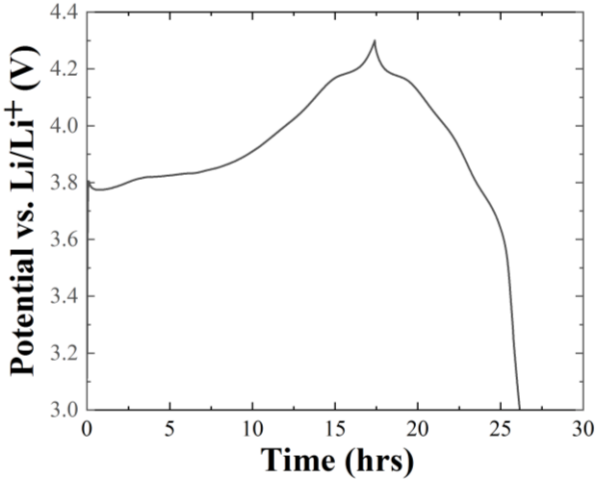
TECHNICAL ACCOMPLISHMENTS AND PROGRESS (CONTINUED)

Challenge in fabricating liquid free cells

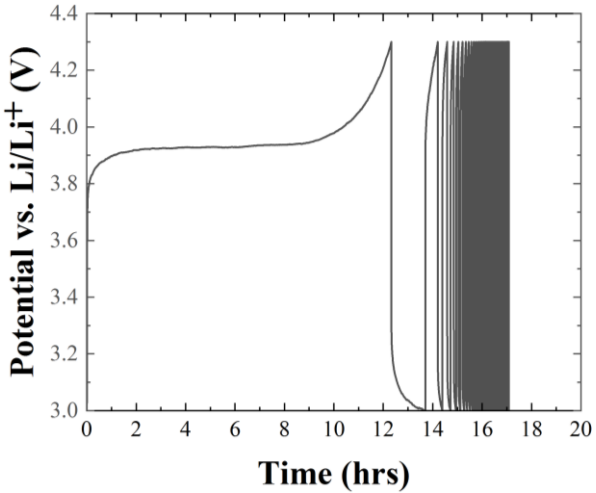
- Button cell
- LLZO separator
- NMC/Carbon black/PVDF
- with liquid electrolyte



- In situ cell
- LLZO separator
- NMC/Carbon black/PVDF
- with liquid electrolyte



- In situ cell
- LLZO separator
- NMC/LLZO
- with liquid electrolyte



- Making liquid-free cell remains a challenge.
- Carbon black is needed in cathode to conduct electrons.
- Alternative approach to co-sintering is needed to allow the survival of carbon black.

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This project was not reviewed in the previous year.

COLLABORATION S

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

- 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)
  - 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)

REMAINING CHALLENGES AND BARRIERS

- **Developing solutions to suppress the formation of lithium dendrite**
  - Two lithium dendrite growth mechanisms
    - Lithium dendrite outside in to LLZO
    - Lithium dendrite inside out of LLZO
  - Strong mechanical strength of LLZO can be sufficient to stop outside-in growth mode
  - An electronically insulating layer is needed to block the inside-out growth mode

- **Fabrication of cathode architecture to enable liquid free design**
  - Carbon black, or alternative conducting fillers, is needed for electron transport in cathode layer
  - A “soft” electrolyte, alternative to LLZO, is needed to enable processing with the existence of carbon black

- **Investigating the stability of electrolyte/cathode interface**
  - Spatial resolved characterization techniques are needed to localize the chemical/electrochemical/mechanical degradation of solid/solid interface

PROPOSED FUTURE RESEARCH

- FY21: X-ray technique development for solid/solid interface characterization
  - Continuing development of in situ cell and focused X-ray beam
  - Technical demonstration of in situ capability using model cells with liquid electrolyte to facilitate Li^+ transport in cathode.

- FY22
  - ➢ Blocking electron transfer between Li and LLZO
    - Molecular layer deposition (MLD) of a polymer layer in between Li and LZZO
    - Inorganic coating on the LLZO surface to avoid direct contact with lithium
  - ➢ Developing cathode architecture for liquid free design
    - Developing Li_3InCl_6 as a soft catholyte
    - Developing a warn process for fabricating dry cathode using NMC, Li_3InCl_6, and carbon black
    - In situ study on the structural/chemical/mechanical stability at solid/solid interface

SUMMARY

- In situ scanning electron microscopy (SEM) was deployed to visualize the lithium plating on LLZO.
- A new lithium dendrite mechanism, growing from inside out of LLZO, was visually demonstrated.
- A new electrochemical cell was developed for spatially resolved synchrotron study of solid/solid interface.
- Electron conducting filler is crucial for enabling the design of liquid free cells.
- “Soft” catholytes are needed to avoid co-sintering for a liquid free design.