Developing an In-Situ Formed Dynamic Protection Layer to Mitigate Lithium Interface Shifting: Preventing Dendrite Formation on Metallic Lithium Surface to Facilitate Long Cycle Life of Lithium Solid State Batteries

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Project ID: BAT484

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Overview

Timeline

- Start: 10/01/2019
- Finish: 09/30/2022
- Percentage Complete:50%

Budget

- Funding received in FY19/20:
  DOE: $330k; Non-Federal: $83K
- Funding received in FY 20/21:
  DOE: $340K; Non-Federal:$85K

Barriers addressed

- Performance of beyond Li-ion cells with metallic Li anode and solid-state-electrolyte.
  - Long cycle life Li anode was achieved in solid state electrolytes with dynamic surface protections.
  - Long cycle life full cells with metallic Li, adequate cathode and solid state electrolyte were achieved.
  - *In-site* diagnostic tools are validated for real time observation of metal Li anode surface during operation.

Collaborators

- Millipore Aldrich.
- University of Washington Seattle.
- Pacific Northwest National Laboratory (PNNL)
- Brookhaven National Laboratory (BNL)
- Cornell University.

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Relevance and Project Objectives

- ***Overall Objectives:***
  - ✓*Gain new knowledge about dendrite formation and growth.*
  - ✓*Establish Dynamic protection layer to tackle the Li interface shift during operation.*
  - ✓*A Li anode with ≥2 Ah/g energy density at ≥5 mA/cm^2 rate discharge for over 1000 cycles*
  - ✓*A pouch cell of Li anode with adequate electrolyte and cathode, achieving over 400 Wh/Kg at C/3 rate over 200 cycles*

- ***Objectives this period:***
  - ✓*Redesign the cell for Li/solid electrolyte interface observation and image dendrite growth during operation.*
  - ✓*Forming a surface layer with homogenous activity. The optimal compounds will form a layer of coating which will make the surface homogenized, thus forming a uniform deposition of Li.*
  - ✓*Forming a dynamic protection layer by in-situ alloying Li dendrites.*
  - ✓*Dissolving and re-depositing Li through re-distribution of a Li-carrier complex.*
  - ✓*Controlling local Li$^+$ concentration on the Li electrode surface.*

Milestones

Milestone Name/Description	End Date	Status
Lithium anode electrochemical performance evaluation. Synthesis n-type polymer materials and evaluation of the electrochemical performance.	12/31/2020	Completed
Roll-press coating development. Complete the process development of roll-press coating.	3/31/2021	Completed
PAH derivative structure identified. Identification of the synergy of the parameters and their impact on dendrite growth.	6/30/2021	On schedule
Synthesis and test of PE with PAHs. Synthesis of PE with various PAH functionality and test with lithium anode in a half cell. Dendrite suppression demonstrated / interim cell performance verified. Dendrite suppression on coated lithium anode demonstrated, and analysis indicates technical approach capable of achieving performance targets.	9/30/2021	On schedule
FY 2021 GO/NO GO: Dendrite suppression demonstrated/interim Cell Performance Verified.	9/30/2021	On schedule

Approaches

The novelty of our approach is that we intend to mitigate the dendrite problem by creating a dynamic protection layer during the interface shift to prevent dendrite formation throughout the battery operation.

- *Design and use In-situ diagnostic tools, MS-Electrochemical cells and Optical-Electrochemical cells,* to investigate the protective layer formation and dendrite growth real-time.
- Determination of stable and reliable test vehicles for Li anode, including both Li_6PS_5Cl and Li_3YCl_6.
- Dendrite growth prevention with dynamic surface protective layers.
- Demonstration of full cell performance in a prove-of-concept lab cells.
- Extended collaboration with other US academic institutions and US industrial partners.

Technical Accomplishments and Progress

- **Designed and optimized *in-situ* electrochemical cells to observe a Li dendrite growth and real-time protective layer formation during a cell operation, and to monitor the generation of gases during a cell formation.**

- **Set up a dedicated infrastructure for the solid-state-electrolyte research including materials synthesis, an Ar-filled glove box in a dry room, a double workspace glove box with temperature control chamber and static removal capability etc.**

- **Successfully formed the dynamic interfacial protective layers on metallic anode surface.**

- **Designed and optimized solid-state FULL cells for cycling test (organic active material/*sulfide SSE/protected Li* and *NMC811/Halide SSE/protected Li*).**

- **Demonstrated long cycle Li solid state cells for both sulfide and halide electrolytes.**

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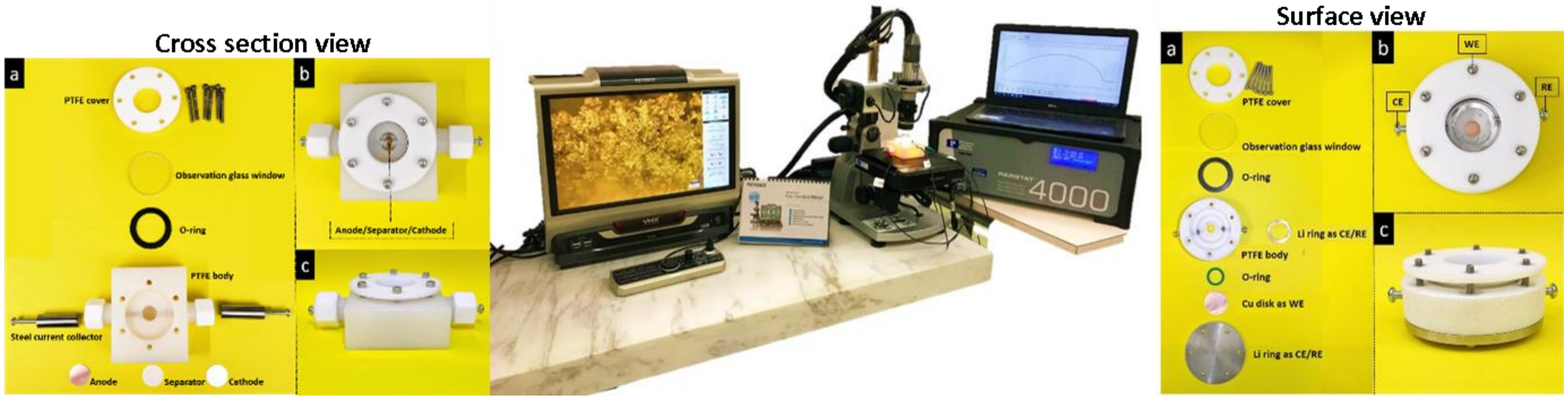
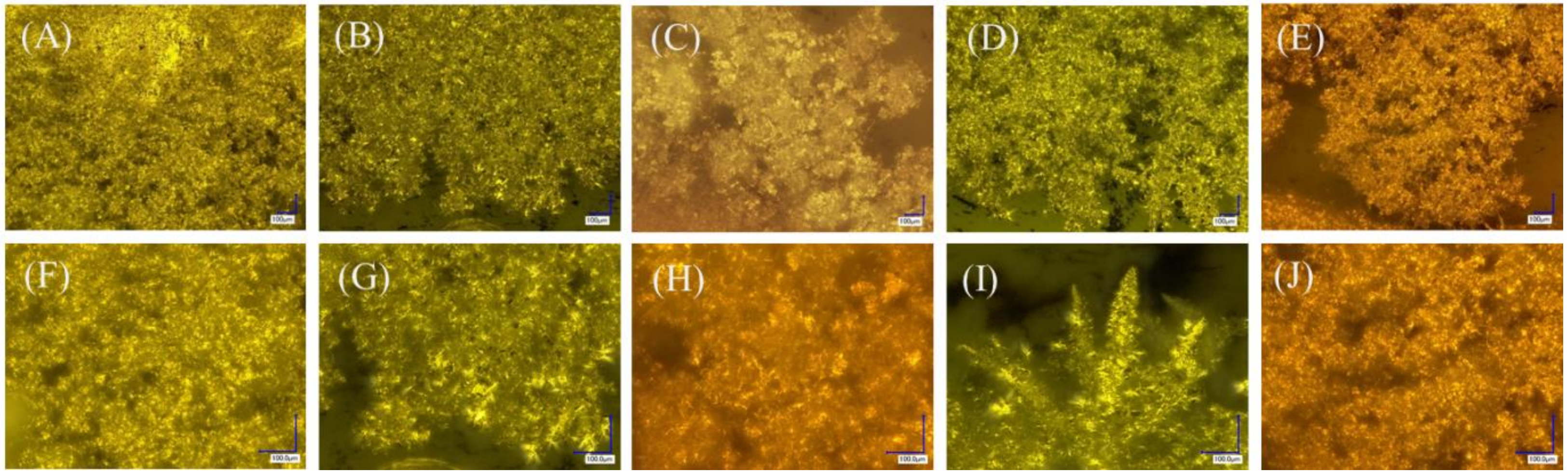
Formation of dynamic Li protective layer and dendrite growth can be observed in an *in-Situ* optical electrochemical cell



In-situ optical electrochemical cells (left: cross section view; right: surface view) and apparatus (center)



Examples of Li dendrite growth under different conditions

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The electrochemical-synthesis of organic dynamic protective layer growth can be observed in real-time

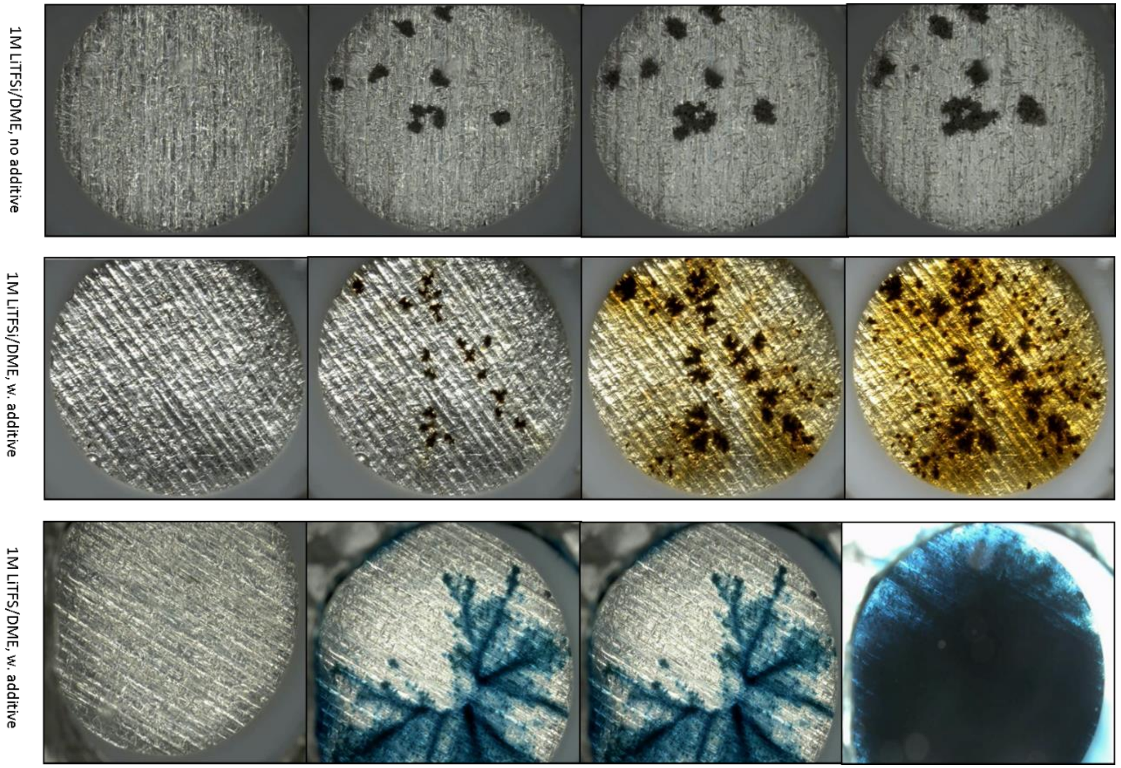
<u>The dendrite growth can be prevented with a surface self-assembled interfacial layer</u>. The dynamic interfacial layer was elastic, liquid electrolyte can be trapped in the layer through a strong bonding. The size of the layer can self-adjust to compensate the volume change of the Li anode during cycling to maintain a stable electrochemical interface.

0 min | 5 min | 10 min | 15 min

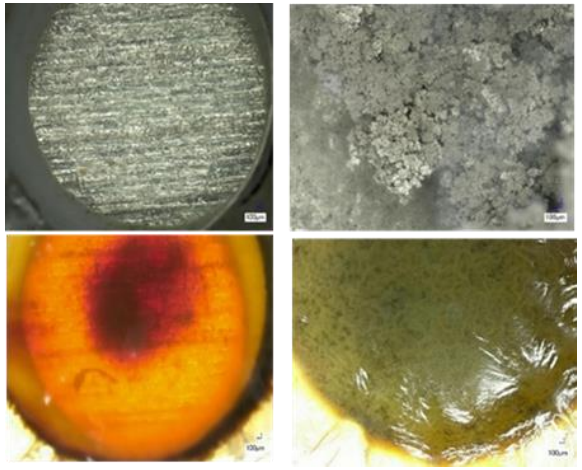
Pristine Li anode surface.

Li anode surface with addition of *monomer 1*.

Li anode surface with addition of *monomer 2.*

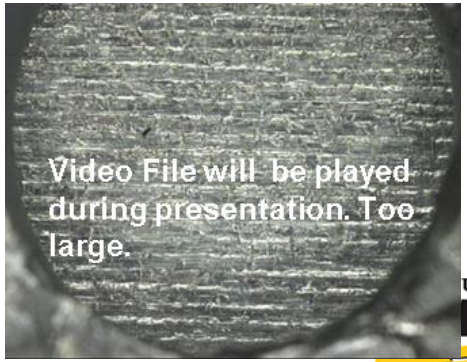


0 cycle | 6 deep cycle



Pristine Li anode surface.

Li anode surface with addition of *monomer 1*.



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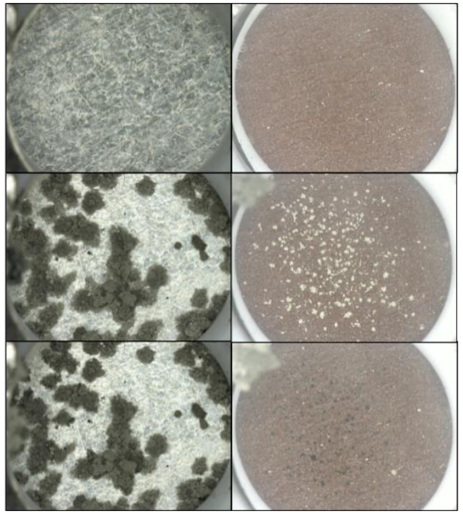
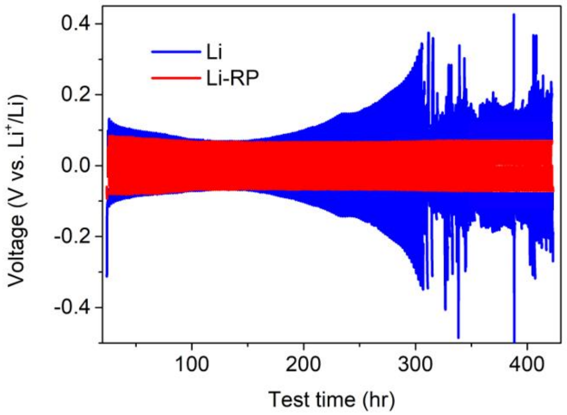
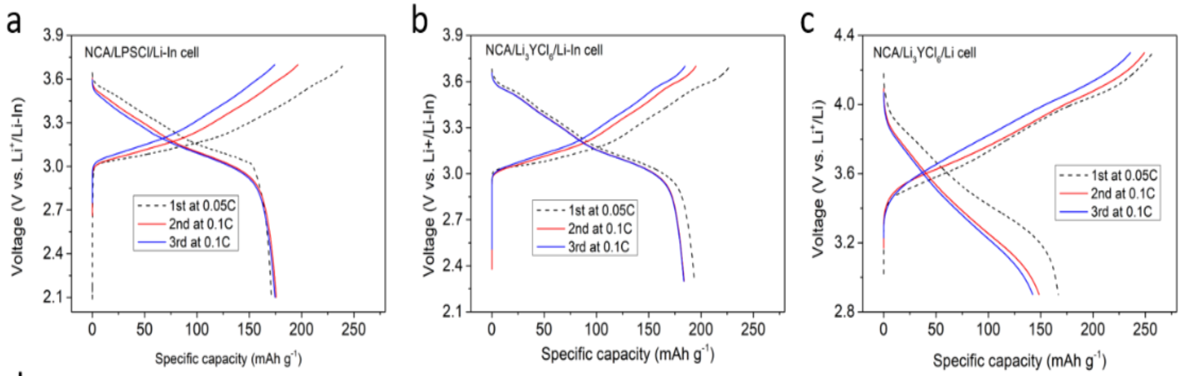
The inorganic dynamic protective layer can be laminated through roller coating and the dendrite growth prevention can be observed in real-time

The inorganic coating of the materials that could form "alloy" with the surface Li. Therefore, Li stripping and deposition occur through the thin "alloy", not directly on metallic Li.





Red P laminated Li surface



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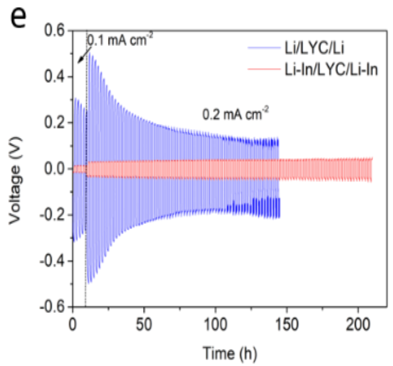
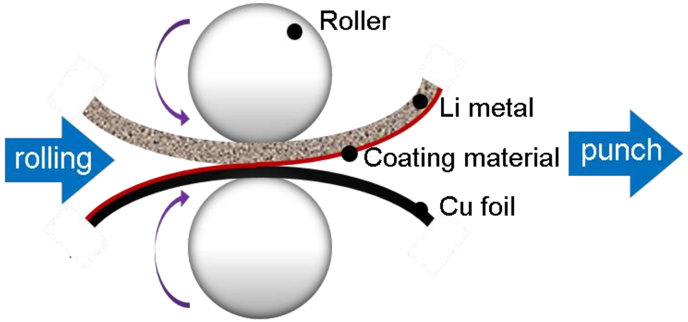
	1st Dis.cap/C.E.	2nd Dis.Cap/C.E.	3rd Dis.Cap/C.E.
NCA/Li_3YCl_6/Li	167mAh g^{-1}/65%	149mAh g^{-1}/65%	142mAh g^{-1}/65%
NCA/Li_3YCl_6/Li-In	194mAh g^{-1}/85%	184mAh g^{-1}/94%	184mAh g^{-1}/99%
NCA/PSCl/Li-In	171 mAh g^{-1}/71%	175mAh g^{-1}/89%	173.5mAh g^{-1}/96%





Comparison of NCA 811/halide cells with pristine Li and In laminated Li

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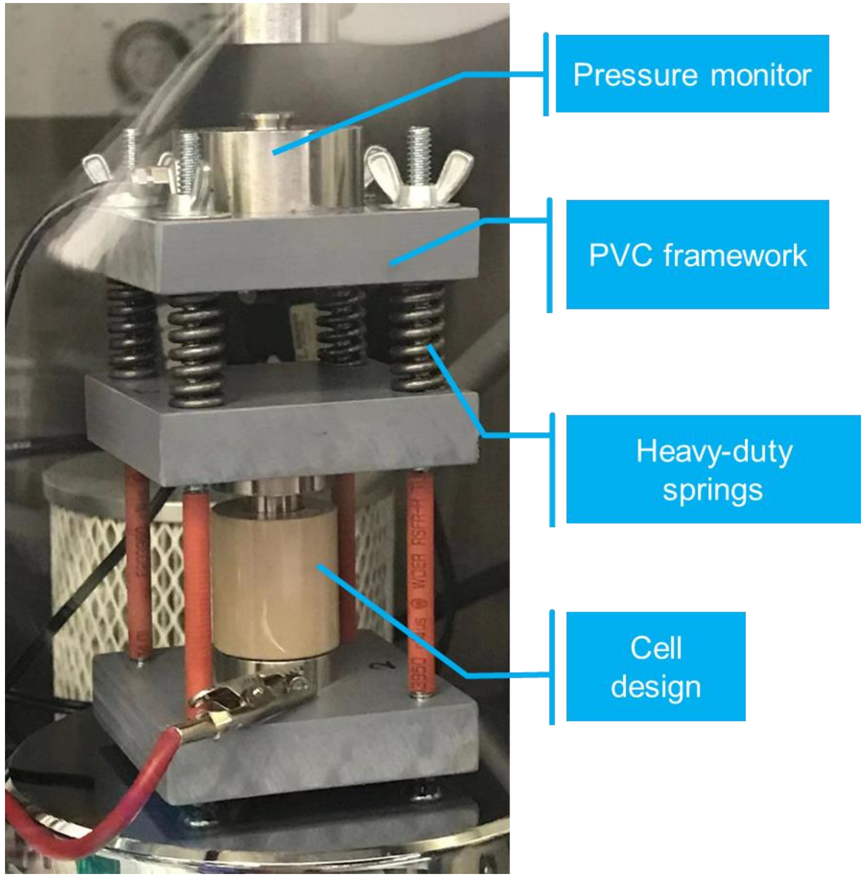
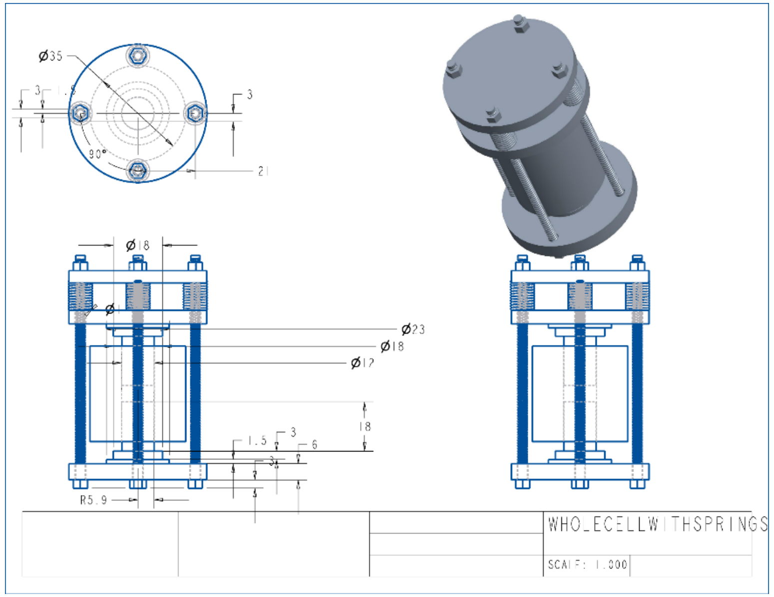
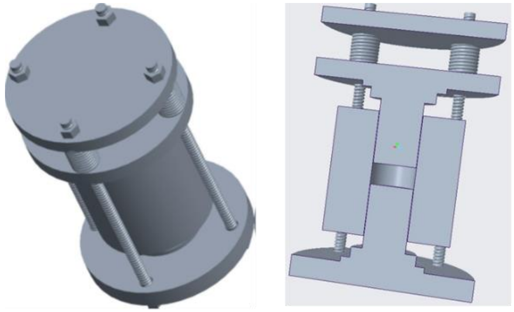
A electrochemical cell (G-4) was designed and validated for both Li/SSE/Li symmetric and NMC811/SSE/Li full cell testing

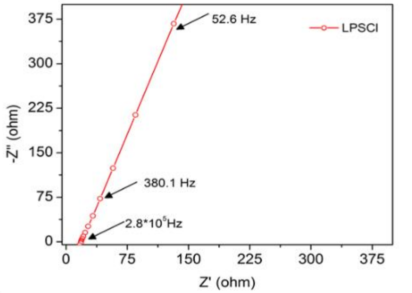
The final design of electrochemical cell: stand alone, pressure adjustment, uniform pressure on the electrode/SSE assemble, strong body so the SSE can be formed inside the cell (easy to handle in glovebox)







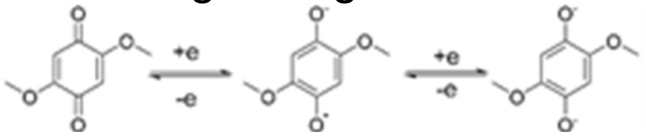
(i)

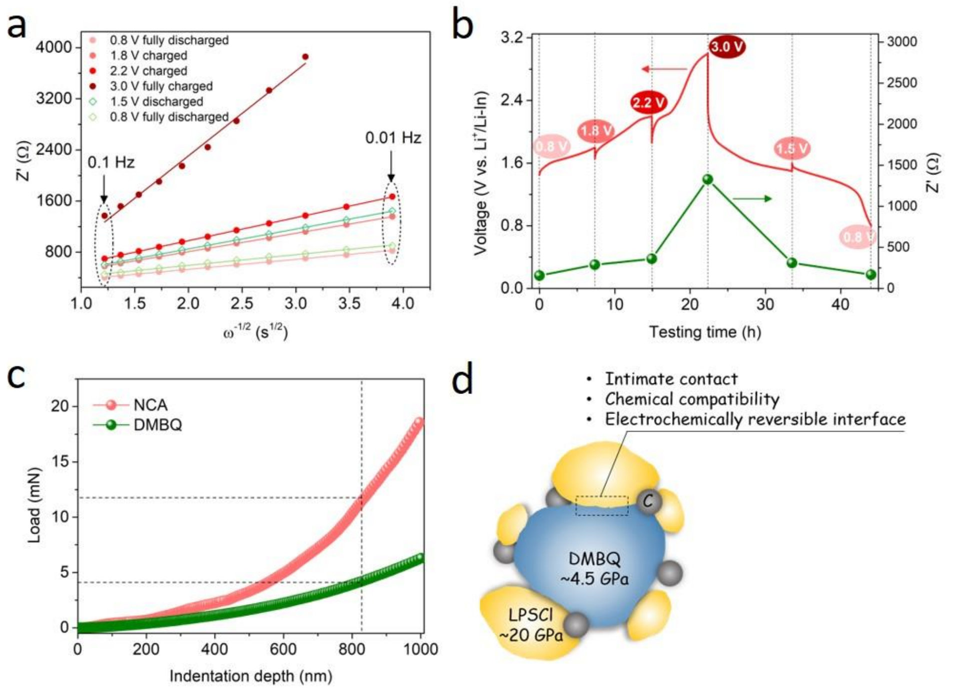


(ii)

Determination of a reliable cathode/SSE/metallic Li system for Li anode study

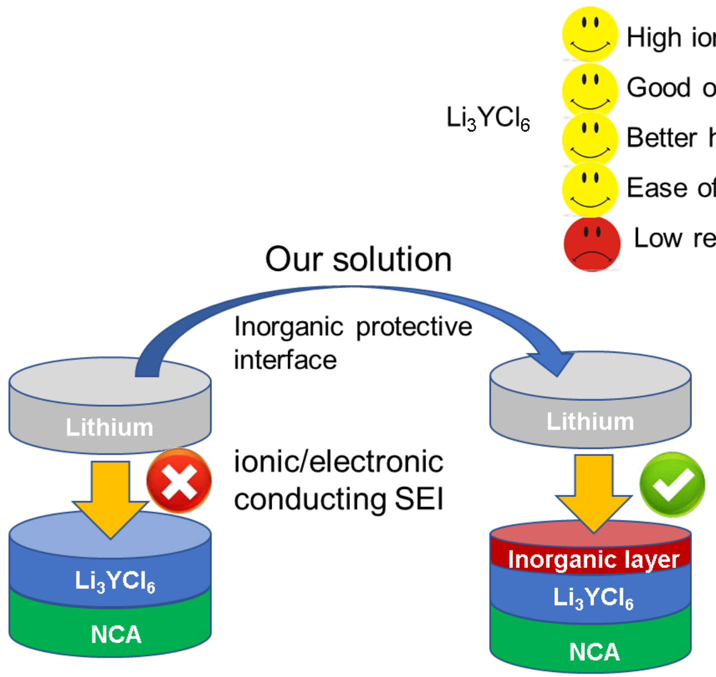
Challenges: LPSCL (sulfide) SSE does not work with NMC811 well.
Solution: Found an organic cathode with moderate working voltage work with sulfide SSE.





DMBQ Young's modulus : 4.2GPa vs. Sulfide Young's modulus ~20 GPa
DMBQ Hardness: 0.34 GPa

Challenges: Li_3YCl_6 (halide) SSE does not work with metallic Li.
Solution: Formation an surface protective layer on Li anode.



- Ionic conducting, electronic blocking SEI
- Kinetically stable SEI like the case in liquid EL

$$Li_3YCl_6 + 3Li \rightarrow Y^0 + 6LiCl$$

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Performance of organic cathode/sulfide SSE/protected Li full cell

All-solid-state lithium batteries: DMBQ/LPSCl/Li cell

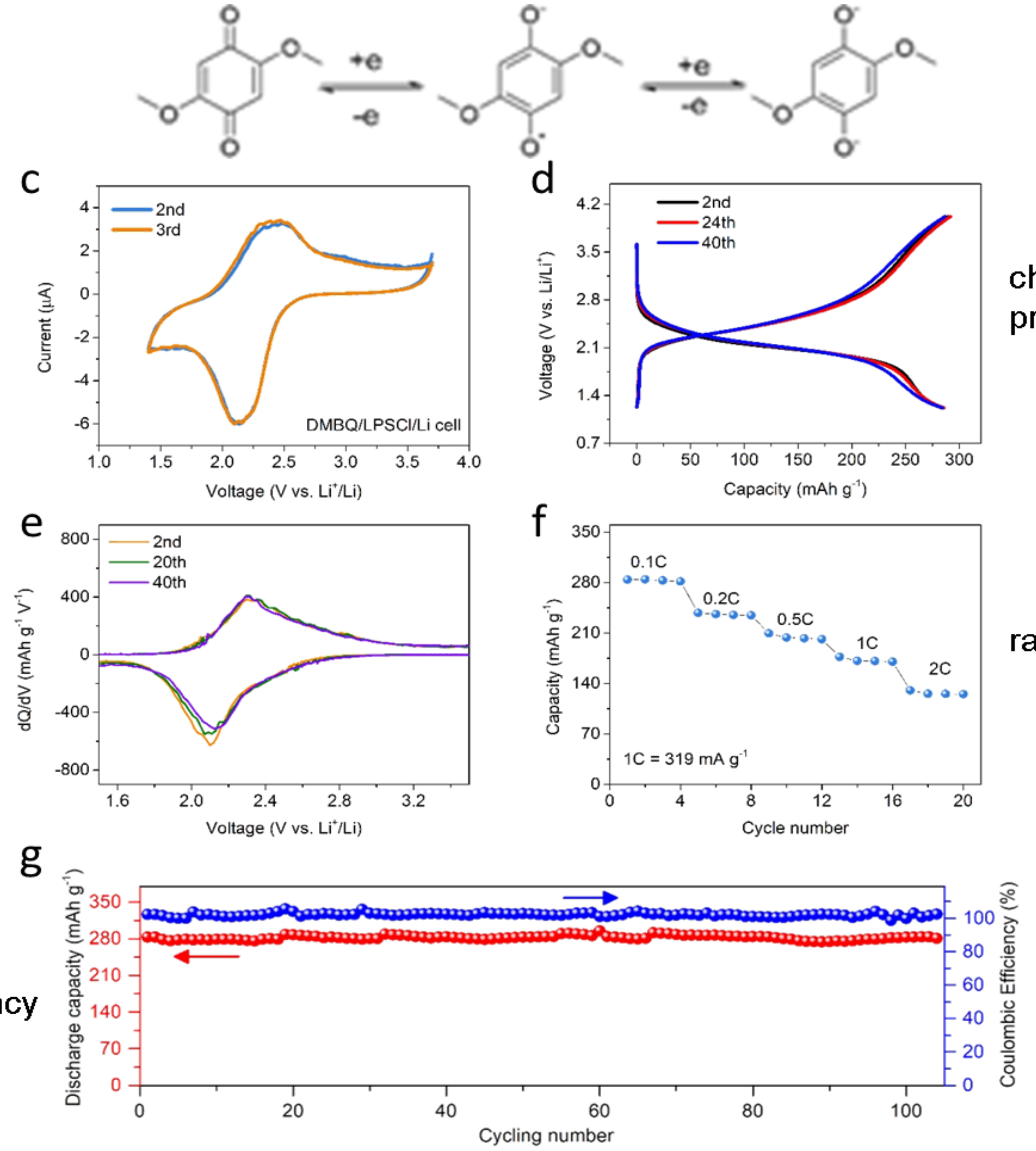
cyclic voltammetry

charge-discharge profiles at 0.1 C

dQ/dV curves at different cycles

rate performance

cycling performance and Coulombic efficiency at 0.1 C



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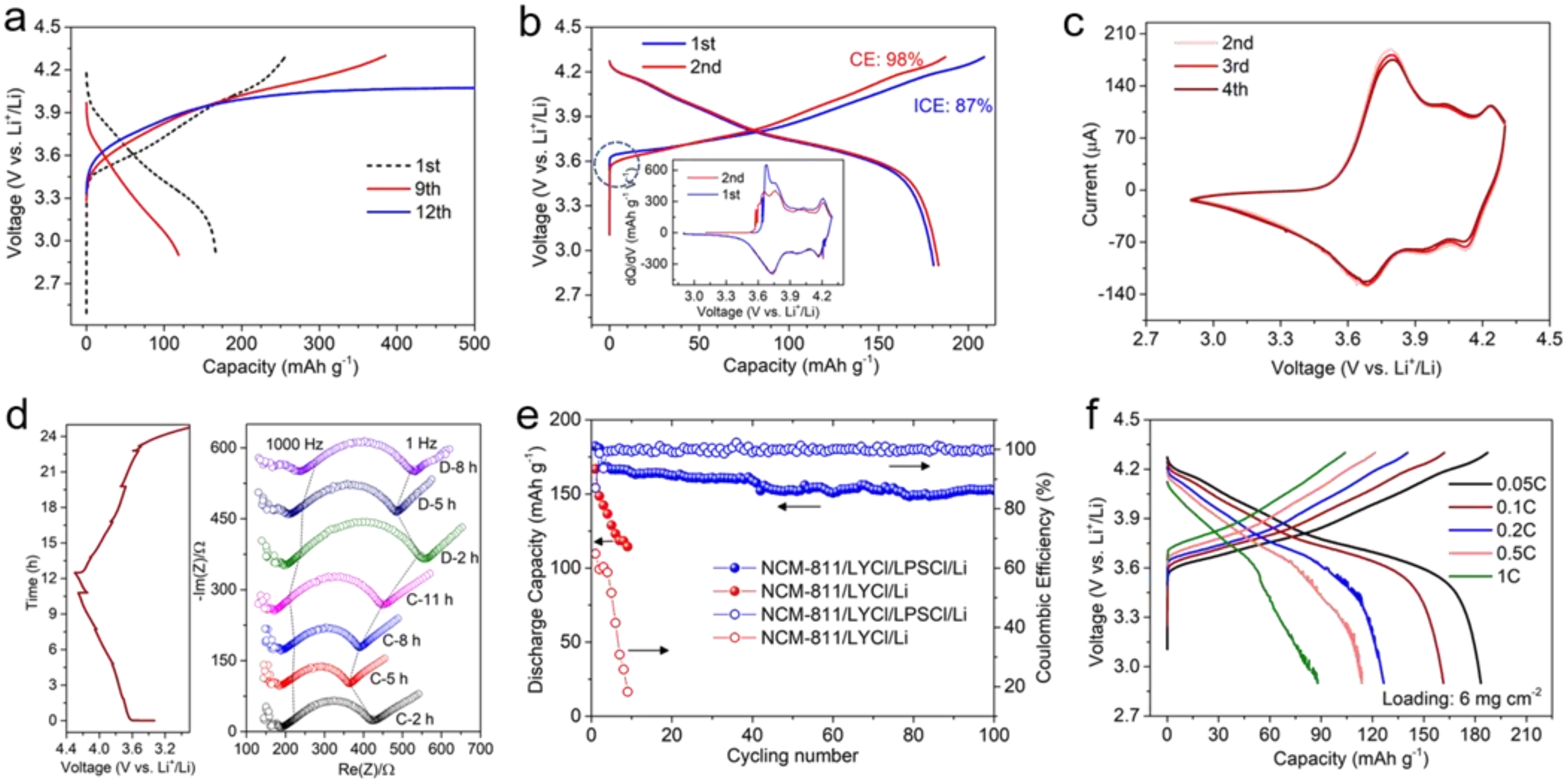
Performance of NMC811/Halide SSE/protected Li full cell

For the first time, protected metallic Li was employed as anode in a halide-based all-solid-state battery.



a) Charge/discharge profiles of NCM-811/LYCl/Li cell at 0.1 mA cm^{-2}
b) Electrochemical performance of NCM-811/LYCl/ protected Li cell:
b) initial two charge/discharge profiles at 0.1 mA cm^{-2} (corresponding dQ/dV curves shown insert);
c) CV profiles at 0.02 mV s^{-1};
d) impedance evolution during one charge/discharge cycle.
e) cycling performance at 0.1 mA cm-2; f) rate capability from 0.1 C to 1 C.

Response to last year reviewer's comments

The Project was not reviewed in FY 2020

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Collaborations with other institutions and companies

- **University of Washington Seattle**
  Solid state electrolyte synthesis.
- ***Cornell University***
  Organic material synthesis,
- **Pacific Northwest National Laboratory (PNNL)**
  Material synthesis and cell configuration.
- **Brookhaven National Laboratory (BNL)**
  Diagnosis
- **Millipore Aldrich**
  Organic cathode materials.

- **Department of Chemistry, Wuhan University**
  In situ electrochemistry – spectroscopy technique development.

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Remaining Challenges and Barriers

- **The major challenges are material process engineering and cell engineering to build a pouch cell:**
  - **In which to fabricate a large (min 1'x1') and thin (<50 μm) SSE is the top challenge.**
  - **To prevent shorting between elastic protective coating and cathode during cell assembling with stacking pressure remains No. 2 challenge.**
  - **To seal the pouch and maintain adequate and constant stacking pressure during operation.**

- **With the promising initial results for both sulfide and halide SSE, the cells need to be optimized to reach high active material utilizations**

- **The reaction mechanisms and fundamental science need to be better investigated and understood, e.g. need to overcome the problem of static electric in the in-situ optical cell.**

Any proposed future work is subject to change based on funding levels

Proposed Future Work for *FY 2021* and *FY2022*

- FY2021 Q3 Milestone:

PAH derivative structure identified. Identification of the synergy of the parameters and their impact on dendrite growth.

- FY2021 Q4 Milestone:

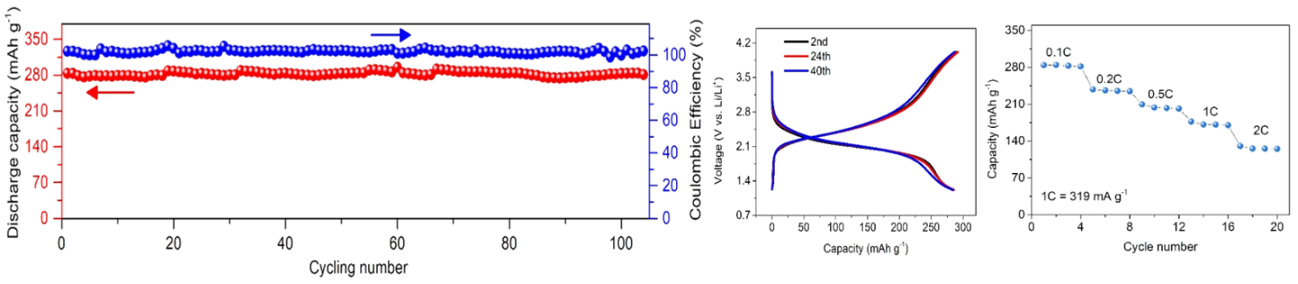
Synthesis and test of PE with PAHs. Synthesis of PE with various PAH functionality and test with lithium anode in a half cell.

- FY2021 work:
  - Demonstrate the effectiveness of the inorganic artificial protective layer for dendrite suppression.
  - Complete down select active materials and SSE, optimal Li protective layer chemistry.
  - Optimize material processes and cell fabrication processes.
  - Fabricate and teste 1 Ah pouch cells for final deliverables.
  - Continuing and enhancing the collaborative research with academic research institutions and industrial partners.

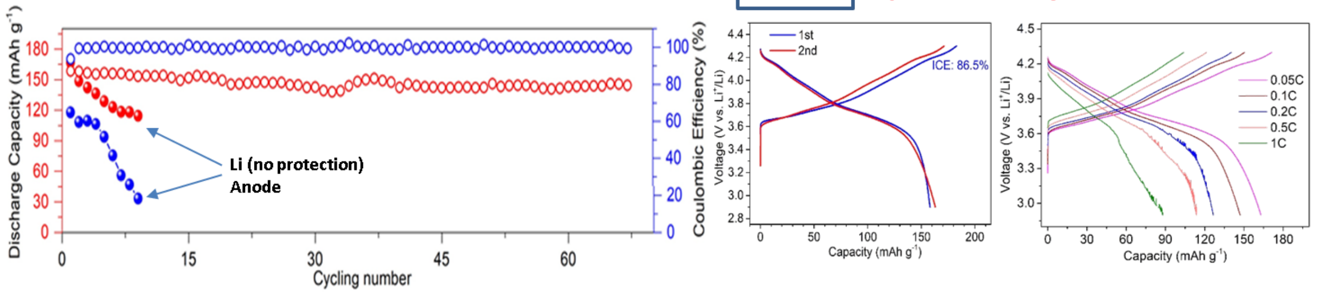
Any proposed future work is subject to change based on funding levels

Summary

All-solid-state lithium batteries: ***DMBQ/LPSCl/Li (Protected) cell***



All-solid-state lithium batteries: ***NCM811/LYCL/Li (Protected) cell***



➢Accomplishments:

- ➢**Demonstrated a good cycle performance at high rate in a All-Solid-State Li batteries with dynamic protective layers.**
- ➢**For the first time, protected metallic Li was employed as anode in a halide-based all-solid-state battery.**
- ➢**Both organic and inorganic dynamic protective layers were proven to be effective.**
- ➢**In-situ diagnostic tools were designed and built for the fundamental investigation.**

➢ Future work:

- ➢ **Optimizing Li protective layer, SSE/protected Li interface and cathode/SSE interface.**
- ➢ **Down selecting Li protective chemistry.**
- ➢ **Overcoming engineering barriers for the fabrication of 1’ x 1’ pouch cell with thin SSE layer.**
- ➢ **Building and testing deliverable cells.**
- ➢ **Continuing fundamental investigation on Li dendrite prevention and SSE interface.**

Any proposed future work is subject to change based on funding levels

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