Hot Pressing of Reinforced Lithium Nickel Manganese Cobalt Oxide (Li-NMC) All-Solid-State Batteries with Sulfide Glass Electrolyte

Project ID: BAT482

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General Motors LLC

2021 DOE Vehicle Technologies Office Annual Merit Review
June 24, 2021

GENERAL MOTORS

Overview

Timeline

- ❑ Project Start: October 1, 2019
- ❑ Project End: June 30, 2023
- ❑ Percent Complete: 33%

Budget

- ❑ Total project funding
  - DOE: $1,000,000
  - Industrial cost share: $250,000
- ❑ FY2020 funding: $388k
- ❑ FY2021 funding: $299k

Partners

- ❑ Project lead: General Motors LLC

Barriers

- ❑ All-solid-state batteries should achieve a useable specific energy @ C/3 of ≥ 350 Wh/kg with similar operational specifications as those of conventional Li-ion batteries.

- ❑ All-solid-state batteries (ASSBs) are stuck in a paradigm of low energy density or limited functionality:
  - ❑ Li-ion configurations typically have energy density < 170 Wh/kg.
  - ❑ Li metal configurations may require slow charging at elevated temperature and high stack pressure.

- ❑ The performance of ASSBs with sulfide solid-state electrolyte (SSE) is limited by the fact that they are essentially green tapes with 10 – 20 % porosity.
  - ❑ Porosity provides a conduit for Li deposits in the separator.
  - ❑ Porosity limits the energy density of the composite cathode.

Relevance

Objectives

- Eliminate porosity in both the separator and the cathode by assembling ASSB using a hot-pressing process and appropriately formulated sulfide glass solid-state electrolytes.

- Demonstrate a hot-pressed cathode with a reversible capacity of > 120 mAh/g (June 2021 Go/No-Go).
  - Eliminate porosity in the composite cathode to increase cell energy density.
  - Demonstrate the feasibility of cathode-supported hot-pressed glass separator.

Impact

- Elimination of porosity may allow ASSB to escape the paradigm of low energy or limited functionality to help achieve program goals of:
  - ≥ 350 Wh/kg useable specific energy @ C/3
  - 15 year calendar life
  - 1000 cycle life (C/3 deep discharge with <20% energy fade)
  - ≤ $100/kWh cost

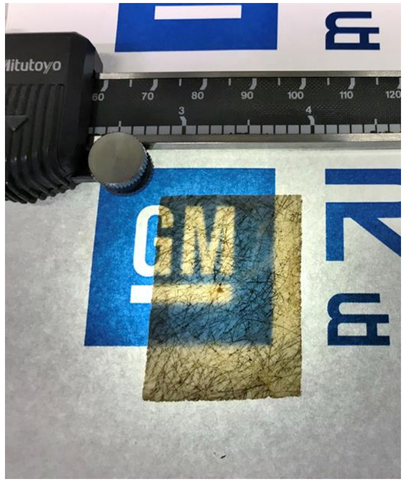
Milestones

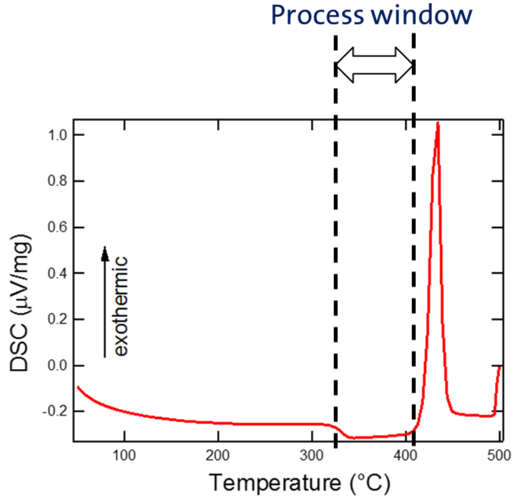
Month/Year	Milestone Type	Description of Milestone or Go/No-Go Decision
March 2020 (FY20)	Milestone	*Baseline cathode performance metric:* Develop a suitable baseline system with a reversible capacity of about 120 mAh/g.
June 2020 (FY20)	Milestone	*Establish protective coating on cathode:* Select the best coating method and coating chemistry.
March 2021 (FY21)	Milestone	*Interfacial characterization:* Determine the parameters required to prepare cathode samples via FIB/SEM lift-out and to analyze samples via HRTEM. (**completed**)
June 2021 (FY21)	Milestone	*Catholyte candidate selected:* Performing catholytes will be identified. (**completed**)
June 2021 (FY21)	**Go/No-Go Decision Point**	***Design capable of meeting performance requirements:*** **Demonstrate a hot pressed cathode with a reversible capacity of > 120 mAh/g. Analysis indicates technical approach capable of achieving performance targets. (Go decision)**

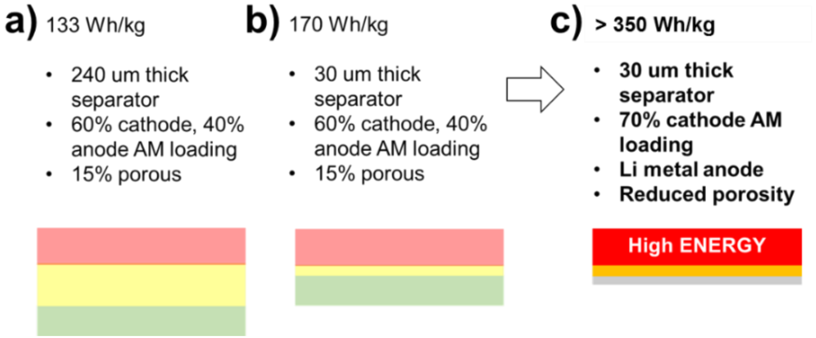
Approach

1) Apply GM's hot-pressed, reinforced glass separator technology to ASSB.[1] Cathode support provides pathway towards thinner separator for increased energy density.

2) Elucidate the mechanisms that promote NCM-catholyte thermal stability to enable hot pressing of cathode composites.

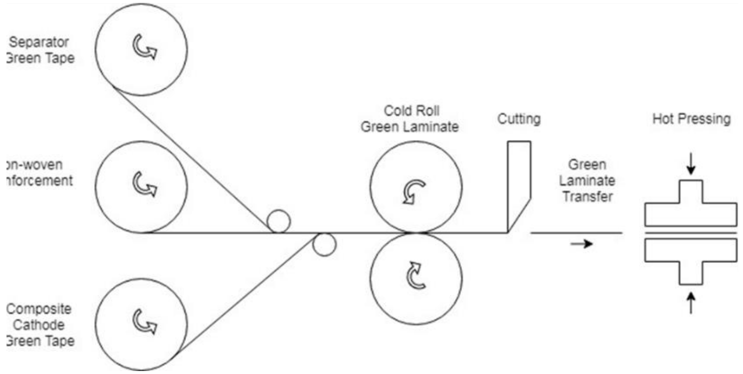






Phenomena to assess during hot pressing:

- ❑ Consolidation of softened glass SSE by viscoplastic flow
- ❑ Devitrification of glass SSE
- ❑ NCM/SSE interfacial reaction
- ❑ NCM microcracking (especially important for high Ni-content CAM).



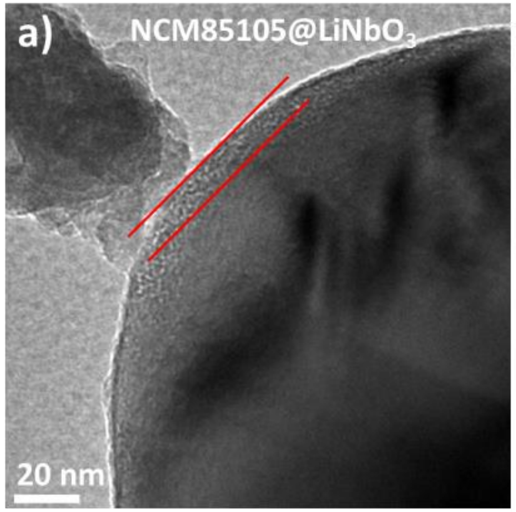
[1] T. Yersak et al., *Int'l J. of Applied Glass Science,* 12, 1, (2021): 124 – 134.
[2] Y. J. Nam et al., *Nano Letters,* 15, (2015): 3317 – 3323.

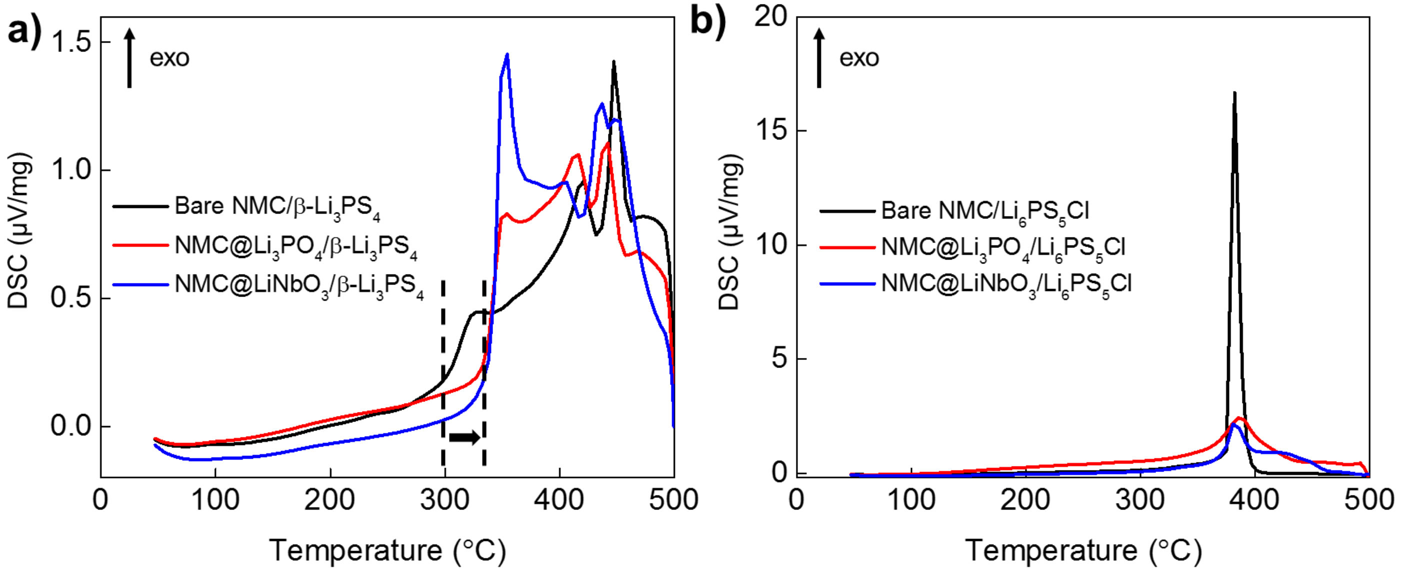
GM RESEARCH & DEVELOPMENT

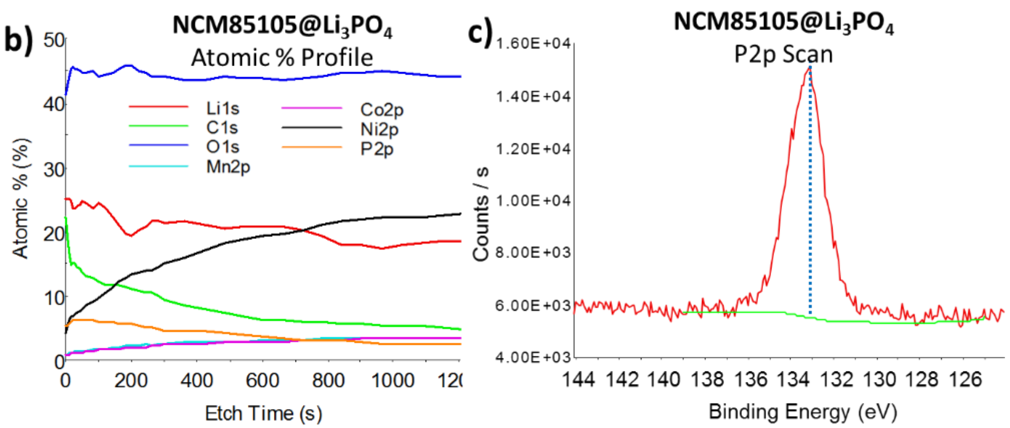
Technical Accomplishments and Progress

Milestone (March FY20) – *Establish protective coating on cathode:* Select the best coating method and coating chemistry.

- ❑ $LiNbO_3$ is the dominant cathode active material (CAM) coating material for sulfide SSE-based ASSB, but it may not be the optimal choice to promote thermal stability.
- ❑ Three coatings investigated: $LiNbO_3$,[3] Li_3PO_4,[4] and Li_2O-ZrO_2 (LZO)[5]
- ❑ Coatings characterized by differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS), and/or high-resolution transmission electron microscopy (HR-TEM)







[3] N. Ohta et al., *Electrochemistry Communications,* 9, (2007): 1486 – 1490.
[4] Y. -G Lee et al., *Nature Energy*, 5, (2020): 299 – 308.
[5] S. Deng et al., *Energy Storage Mater.,* 27, (2020): 117-123.

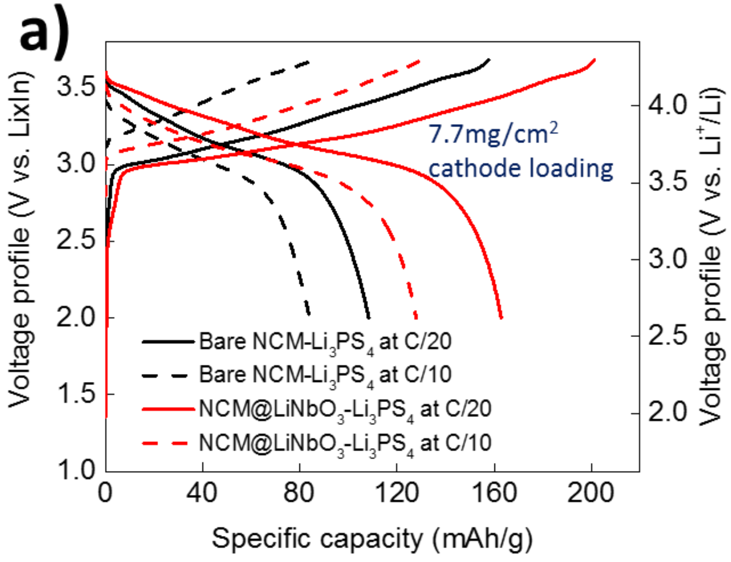
GM RESEARCH & DEVELOPMENT

Technical Accomplishments and Progress

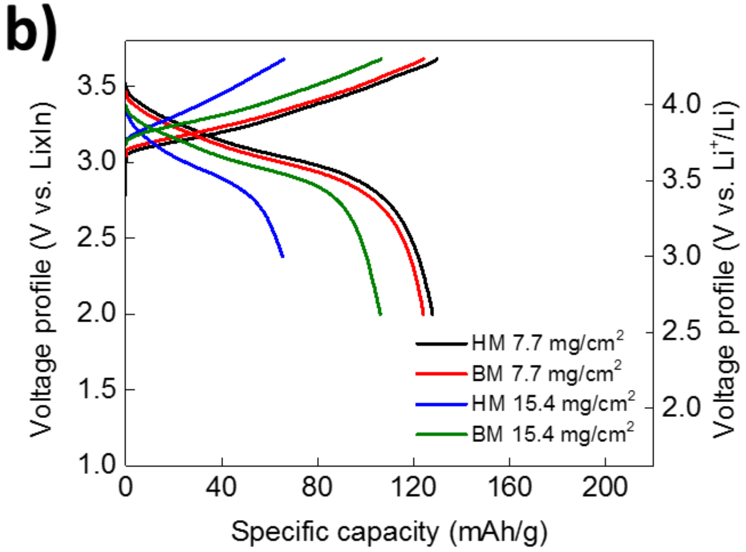
Milestone (June FY20) – *Baseline cathode performance metric:* Develop a suitable baseline system with a reversible capacity of about 120 mAh/g.

- Hot-pressing technology should be evaluated using commercially relevant cathode.
- Three considerations: NCM coating, composite preparation method (HM = hand mixing vs. BM = ball milling), and electrode loading.
- Cell description:
  - Cathode: 7:3 (w/w) NCM85105@$LiNbO_3$:β-Li_3PS_4
  - Separator: 3wt.% Kevlar fiber pulp in β-Li_3PS_4
  - Anode: Indium

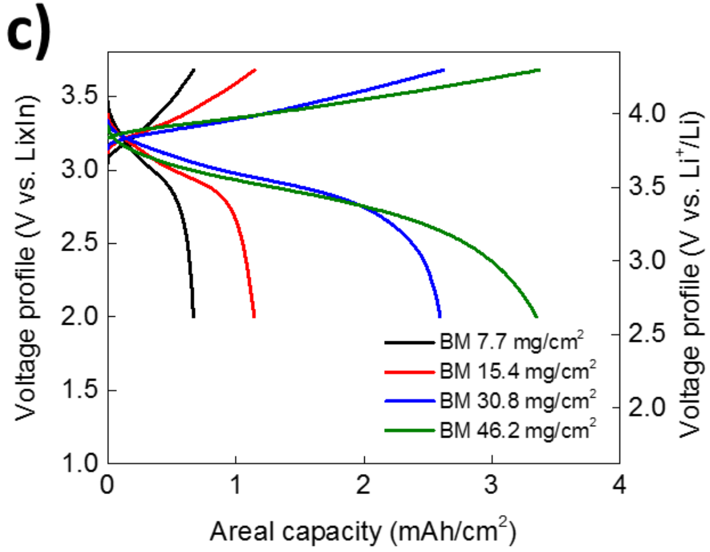
NCM coating



Composite preparation method



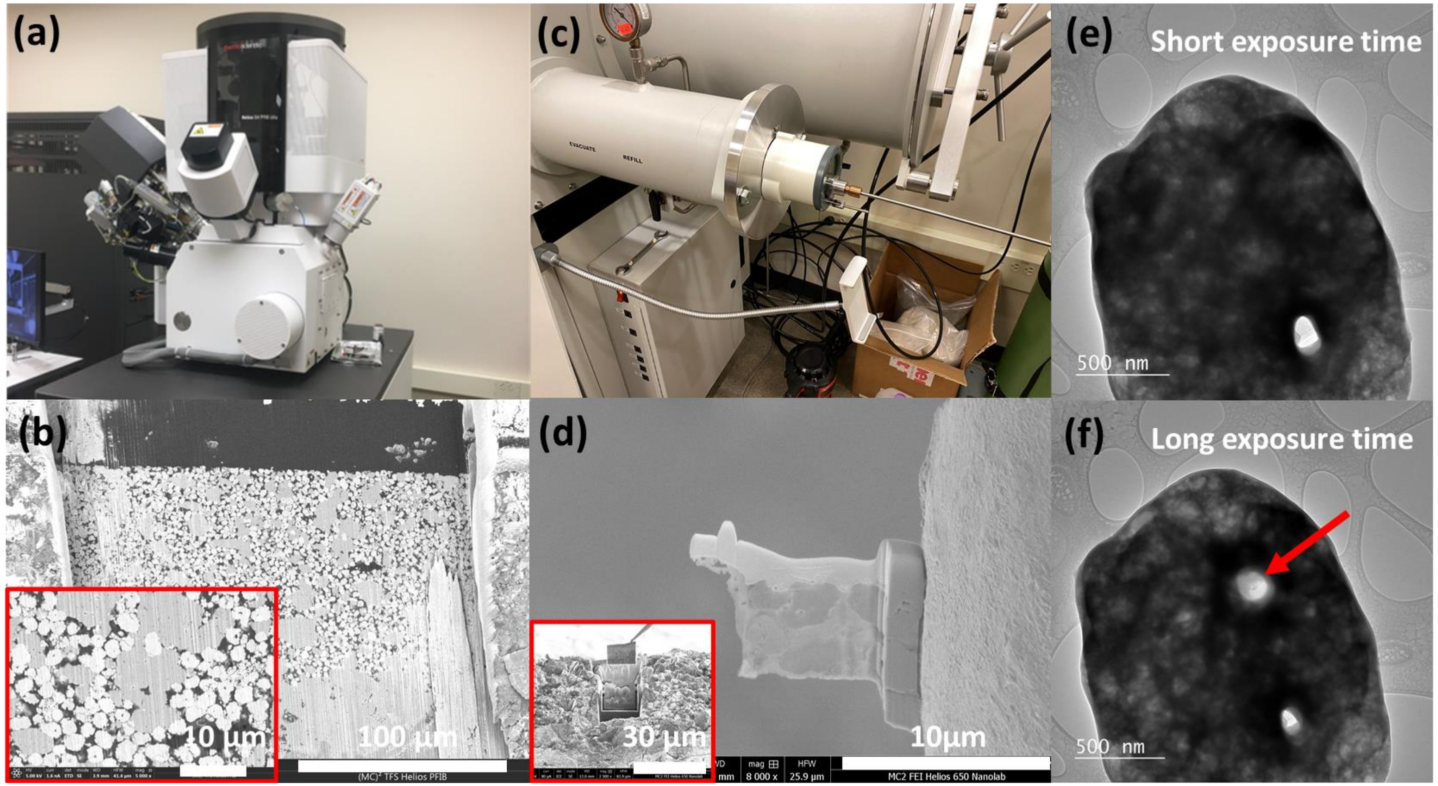
Electrode loading



Technical Accomplishments and Progress

Milestone (March FY21) – *Interfacial characterization:* Determine the parameters required to prepare cathode/catholyte samples via FIB/SEM lift-out and to analyze samples via HRTEM.

- HR-TEM samples successfully prepared by focused ion beam (FIB) lift-out technique; however, samples were beam damaged despite cyrogenic temperature (-170 °C) and utilization of beam dose control.



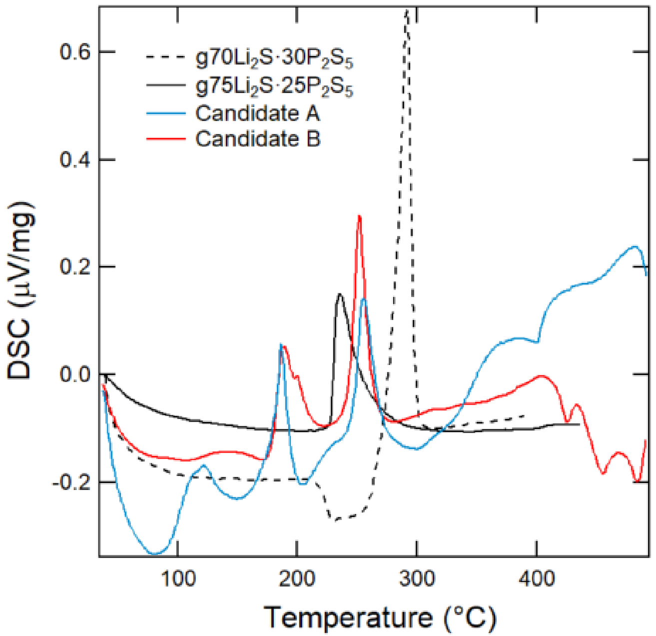
Alternative methods to study the buried NCM/SSE interface:
- Electrochemical evaluation
- XPS
- DSC – reaction kinetics
- Cyclic voltammetry (CV)

Technical Accomplishments and Progress

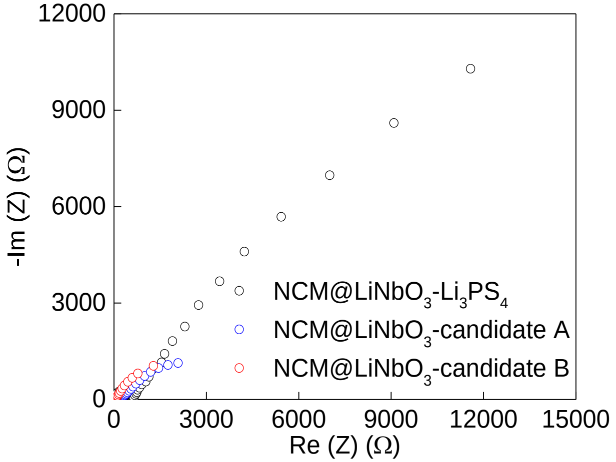
Milestone (June FY21) – *Catholyte candidate selected:* Best performing catholytes will be identified.
Go/No-Go (June FY21) – *Design capable of meeting performance requirements:* Demonstrate a hot-pressed cathode with a reversible capacity of > 120 mAh/g.

- Three catholytes evaluated in trials:
  - Baseline: β-Li_3PS_4
  - Candidate A: Li_3PS_4 + ½LiI
  - Candidate B: Li_3PS_4 + ½LiBr (may also be expressed as "$75Li_2S{\cdot}25P_2S_5$ + 20 mol% LiBr," or "$60Li_2S{\cdot}20P_2S_5{\cdot}20LiBr$")

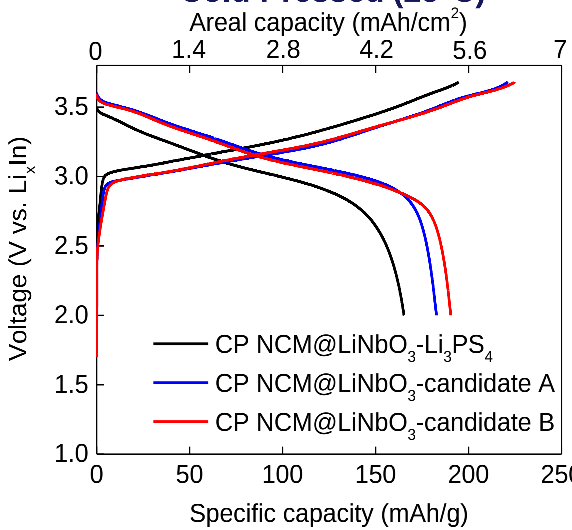
Material System	Cold Press density (g/cc)	Hot Press density (g/cc)	True density (g/cc)	Cold Press porosity (%)	Hot Press porosity (%)
7:3 (w/w) NCM85105@$LiNbO_3$:β-Li_3PS_4	2.36	2.47	3.36	29.7	26.7
7:3 (w/w) NCM85105@$LiNbO_3$:Candidate A	2.63	2.95	3.69	28.8	20
7:3 (w/w) NCM85105@$LiNbO_3$:Candidate B	2.63	2.95	3.55	26.1	16.9



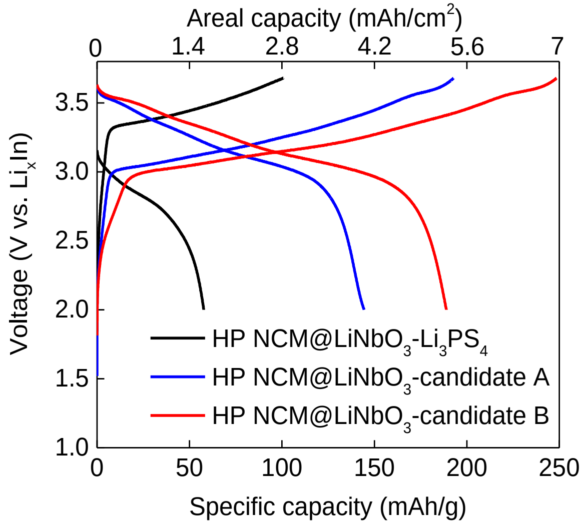
Electrochemical Impedance Spectroscopy (EIS)



Cold Pressed (25°C)



Hot Pressed (200°C)

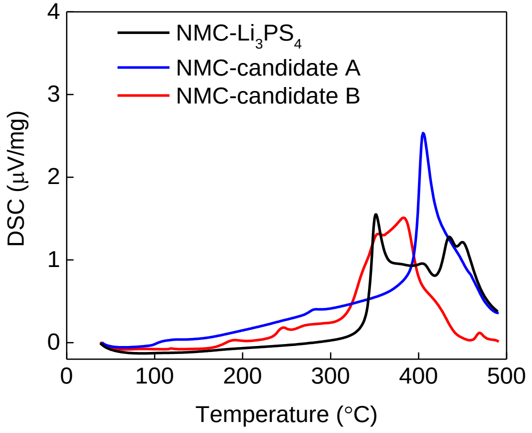


Technical Accomplishments and Progress

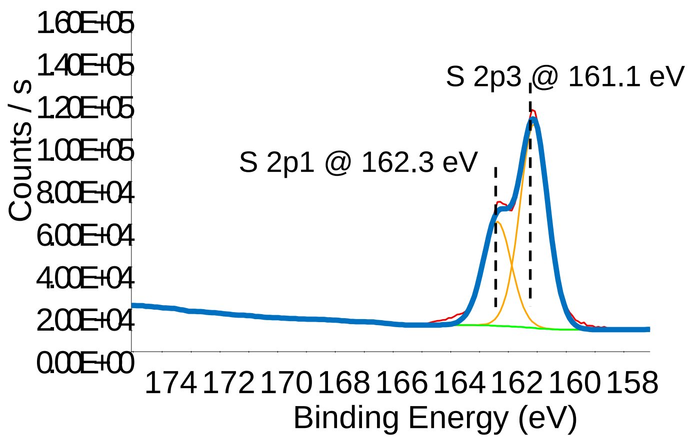
- Stability of the buried NCM/SSE interface evaluated using DSC, CV, and XPS.
- Energy of activation for β-Li_3PS_4/NCM exothermic reaction calculated to be 259 kJ/mol whereas for Candidate B/NCM exothermic reaction it's closer to 264 kJ/mol. Used Kissinger method.
- XPS data show interfacial thermal SSE decomposition is similar to that of interfacial anodic SSE decomposition.[6]

DSC
(10 K/min data shown here)

(a)



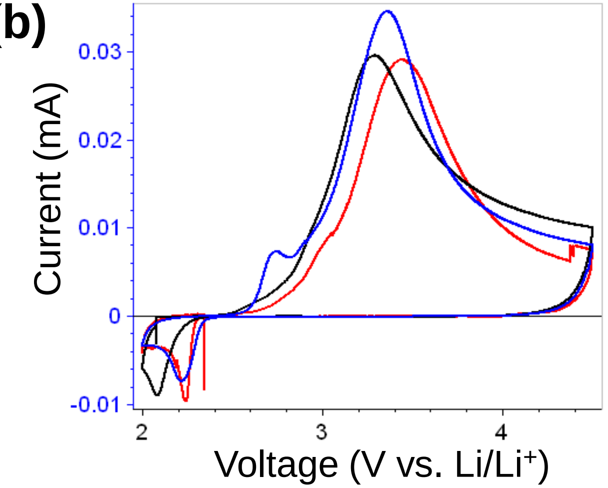
(c)



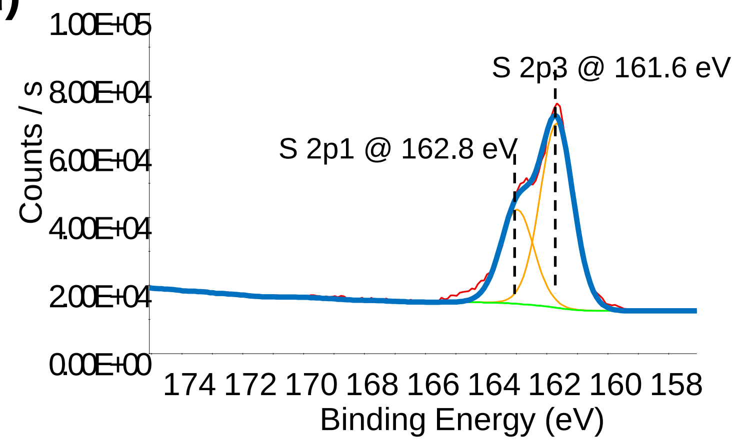
XPS
Cold pressed baseline composite

CV
(working electrode = 9:1 (w/w) SSE:carbon black, counter electrode = Li)

(b)



(d)



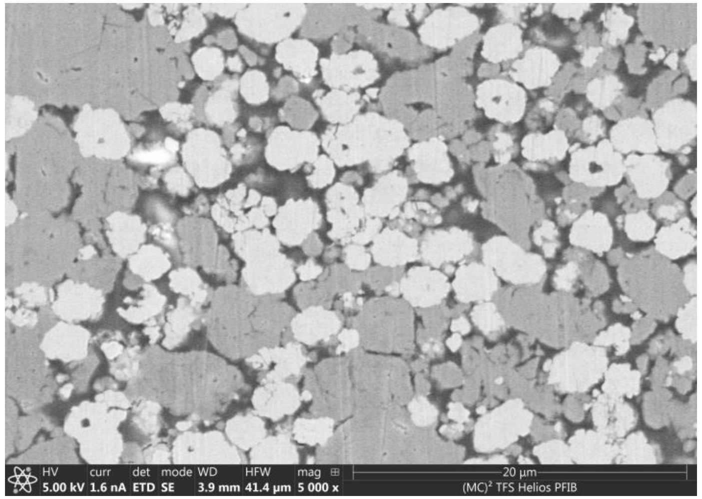
XPS
Hot pressed (200°C) baseline composite

[6] H. Tsukasaki et al., *J. Power Sources*, 367, (2017): 42-48.

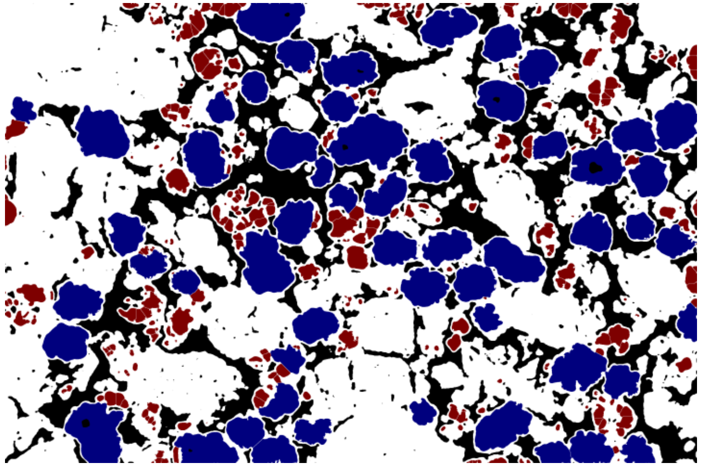
Technical Accomplishments and Progress

- ❑ NCM microcracking quantified using digital image analysis.
- ❑ High Ni content CAM are susceptible to microcracking[7] under the compressive stress applied during ASSB fabrication (370 MPa). In some cases, hot-pressing exacerbates micro-cracking.

PFIB cross section image of NCM85105/β-LI_3PS_4 composite



Processed image



White = SSE particle
Black = pore
Blue = intact NCM particle
Red = damage NCM particle

		% of damaged particles	% of intact particles
NCM85105/β-Li_3PS_4	CP	20.50%	79.50%
	HP	31.25%	68.75%
NCM85105/ Candidate B	CP	20.00%	80.00%
	HP	15.40%	84.60%

[7] G. W. Nam et al., *ACS Energy Letters*, 4, (2019): 2995 - 3001.

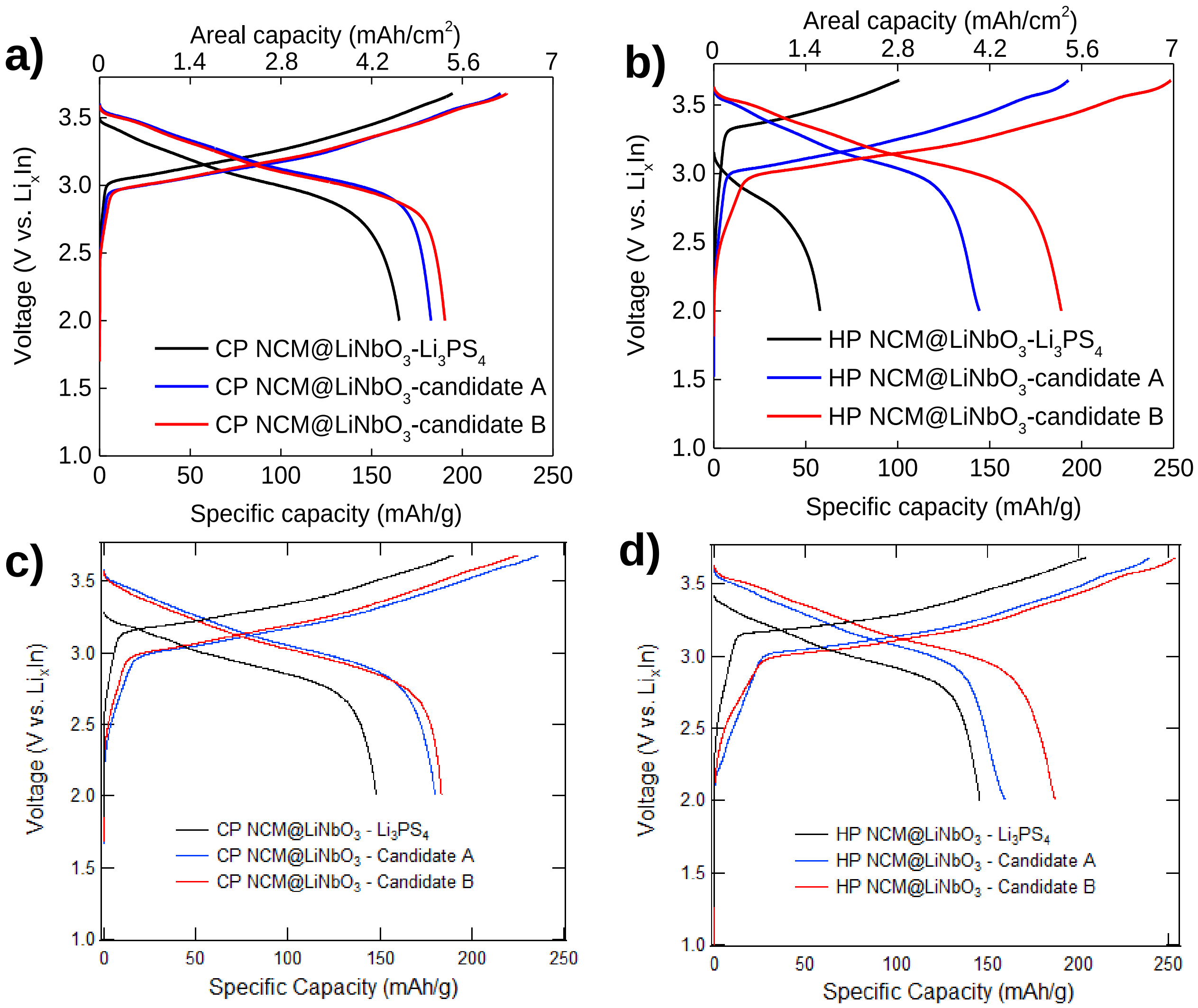
Technical Accomplishments and Progress

- ❑ Addition of 2 wt.% carbon black mitigates the effects of NCM 85-10-5 microcracking.
- ❑ Carbon black does increase the initial side reaction.

Cold Pressed | Hot Pressed (200 °C)

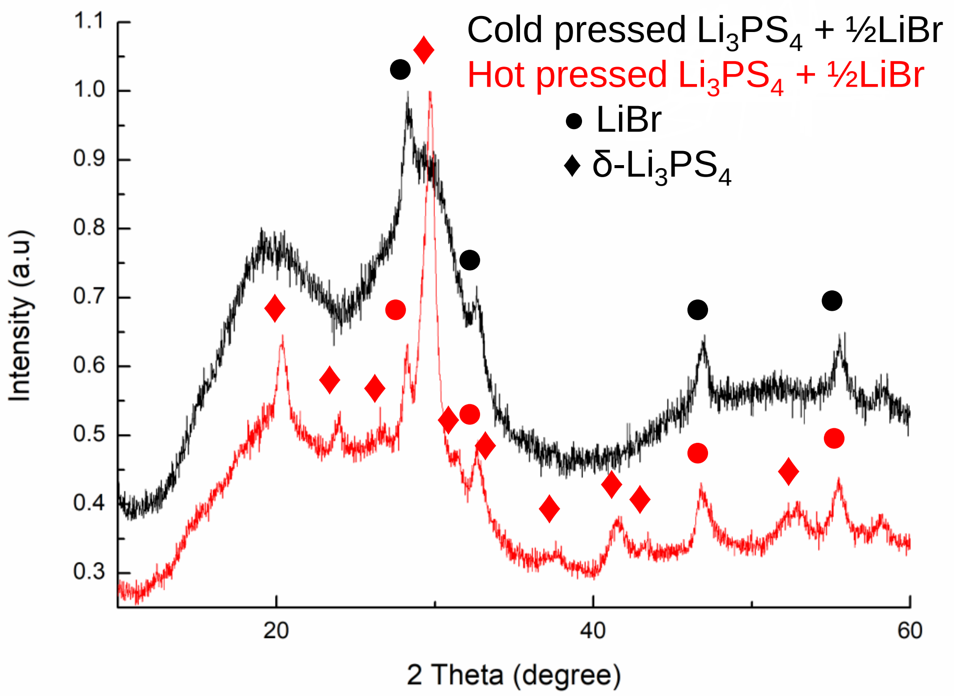
No carbon black

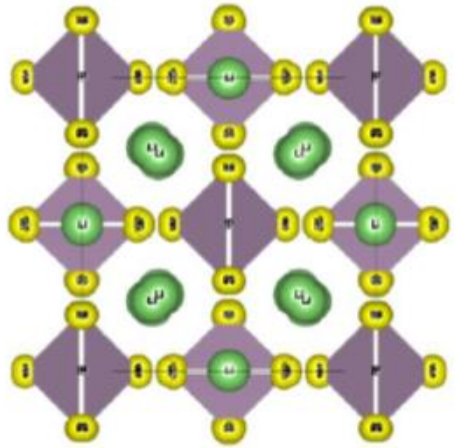
2 wt.% carbon black



Technical Accomplishments and Progress

❑ During hot pressing the glassy catholyte may devitrify. In some cases, ceramic precipitates may have higher ionic conductivity than the mother glass.
❑ The newly reported superionically conductive δ-Li_3PS_4 phase,[8] precipitated from the LiBr-doped Li_3PS_4 glass, may compensate for thermal degradation of NCM/SSE interface.





δ-Li_3PS_4 crystal structure[8]

SSE system	Phase	Ionic conductivity (mS/cm)
Li_3PS_4	glass	0.25
	β-Li_3PS_4	0.29
Li_3PS_4 + ½LiI	glass	1.2
	$Li_7P_2S_8I$ [ref 9]	0.63
Li_3PS_4 + ½LiBr	glass	0.54
	δ-Li_3PS_4	1.77

[8] A. D. Bui et al., *ACS Applied Energy Materials*, 4, (2021): 1-8.
[9] E. Rangasamy et al., *J. of the American Chemical Society*, 137, (2015), 1384 – 1387.

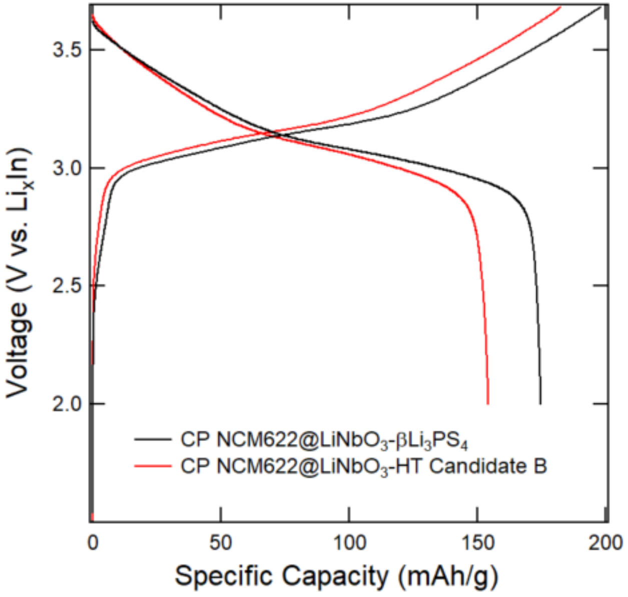
Technical Accomplishments and Progress

Milestone (June FY21) – *Catholyte candidate selected:* Performing catholytes will be identified.
Go/No-Go (June FY21) – *Design capable of meeting performance requirements:* Demonstrate a hot-pressed cathode with a reversible capacity of > 120 mAh/g.

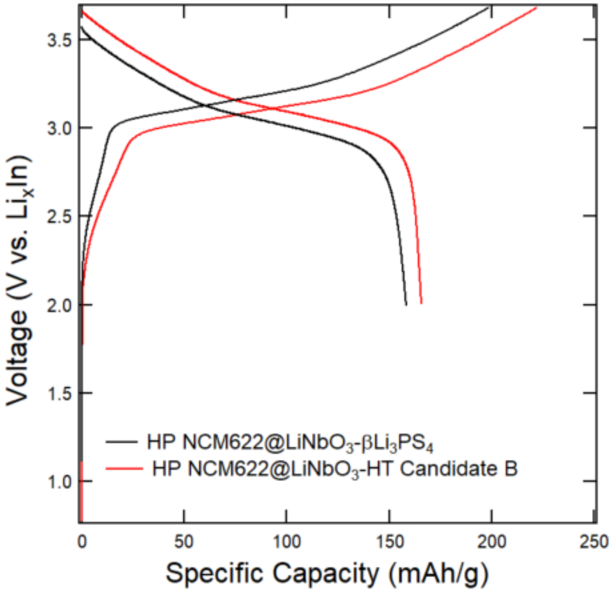
❑Electrochemical performance of NCM622 cells meets performance criteria.

Cathode composite	% damaged particles	% intact particles
HP NCM622/β-Li_3PS_4	8.42%	91.58%
HP NCM622/ Candidate B	14.50%	85.50%

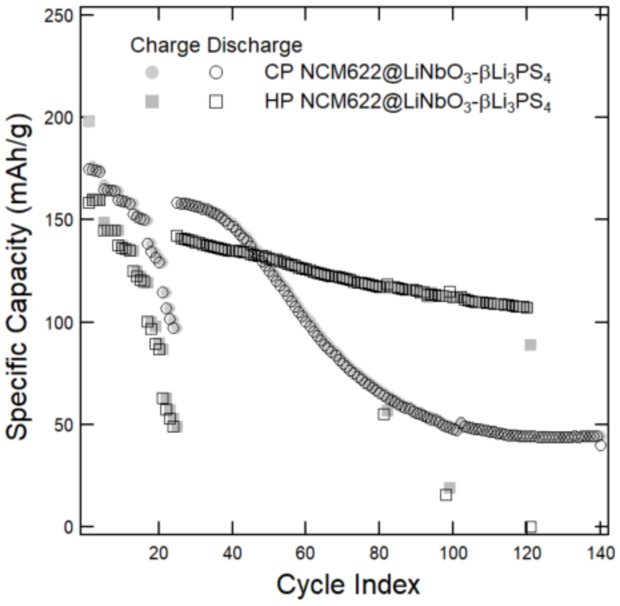
Cold Pressed (25°C)



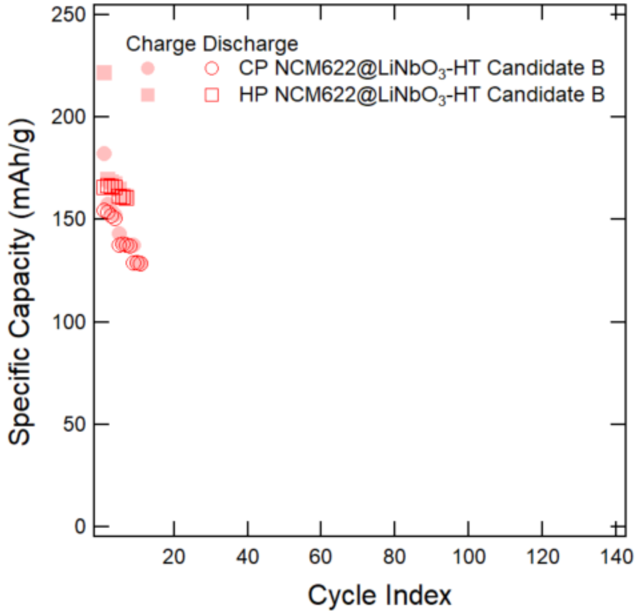
Hot Pressed (200°C)



Cyclic Stability: β-Li_3PS_4



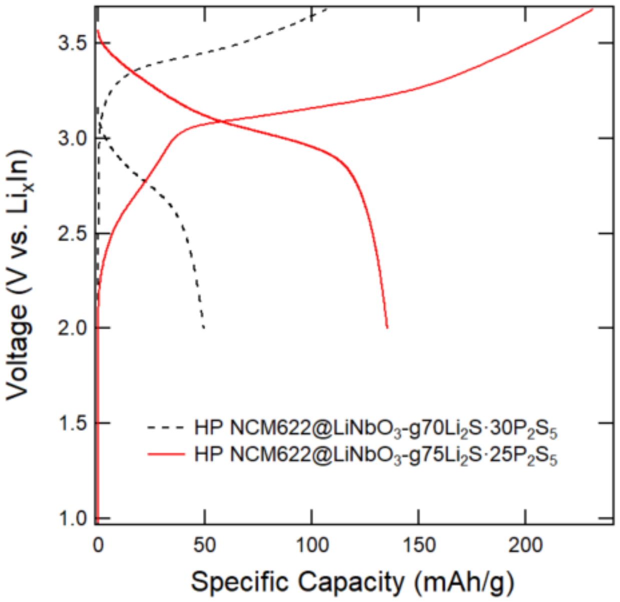
Cyclic Stability: HT (1hr 200°C) Li_3PS_4 + ½LiBr

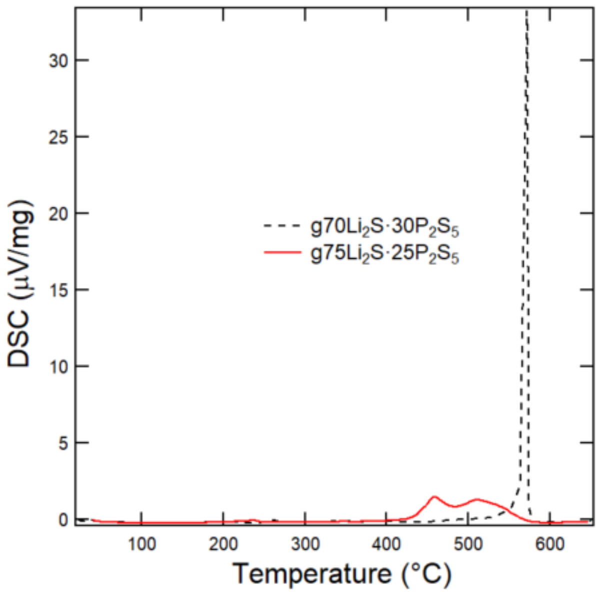


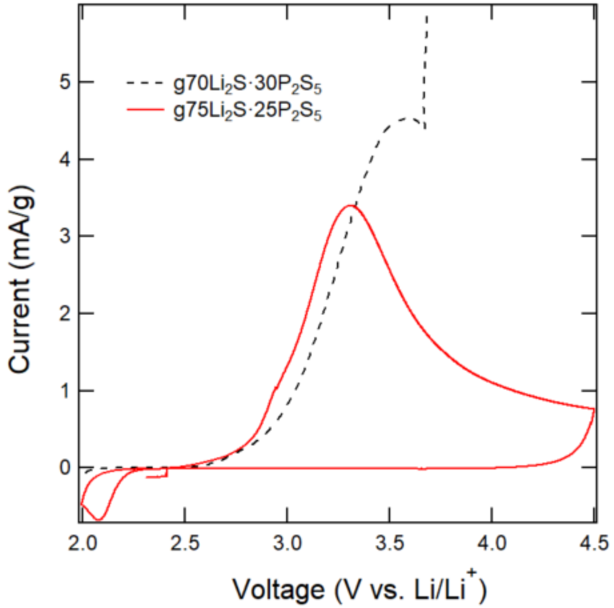
Technical Accomplishments and Progress

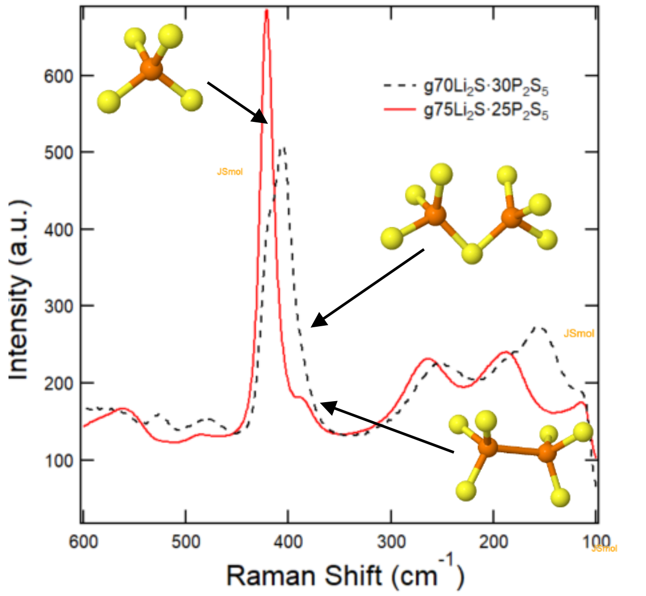
- ❑ Thermal stability is predicted by a glass' short range structure and not by presence of halide dopants.
    - ❑ Li_3PS_4, otherwise known as $75Li_2S{\cdot}25P_2S_5$, is a fully de-networked glass composed predominantly of stable PS_4^{3-} tetrahedra.
    - ❑ $70Li_2S{\cdot}30P_2S_5$ consolidates most effectively by hot pressing, however, it has poor thermal stability versus NCM CAM since it contains labile $P_2S_7^{4-}$ and $P_2S_6^{4-}$ structural units.

Material System	Cold Press density (g/cc)	Hot Press density (g/cc)	True density (g/cc)	Cold Press porosity (%)	Hot Press porosity (%)
NCM622 + g-$70Li_2S{\cdot}30P_2S_5$	2.863	3.499	3.483	17.8	0
NCM622 + g-$75Li_2S{\cdot}25P_2S_5$	2.863	3.149	3.455	17.1	8.86









Responses to Previous Year Reviewers' Comments

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

Collaboration and Coordination

- Michigan Technological University – Prof. Erik Herbert
  - Agreement in place for MTU to measure mechanical properties of sulfide separator glasses with nano-indentation.

- The Iowa State University – Prof. Steven W. Martin
  - Material transfer agreement to be executed to evaluate processability of Iowa State's glass electrolyte formulations.

- Participation in 2020 Oak Ridge National Lab SSE virtual workshop (5/15/20)
  - Led session: "[Solid-state battery] Architecture – Design for Strength"
  - Workshop findings reported in recent *ACS Applied Energy Materials Paper* (see Publications and Presentations)

Remaining Challenges and Barriers

- Scale up challenge: Translation of technology to a high throughput roll-to-roll process
    - Process specifications (T, t, P) require optimization
        - Reduction of pressure (370 MPa)
        - Reduction of time (10 minutes)
    - Binder, reinforcement, and solvent system design requires explication
    - Tolerance of hot-pressing process to dry room conditions currently unknown

- Integration of cathode support with separator to be addressed in the following budget period.

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

Proposed Future Research

- ❑ Design of a supported separator with process specifications matching that of the cathode support developed in this first budget period.
- ❑ Verifying separator performance (*e.g.*, critical current density, capacity, and cycle stability)
- ❑ Ensuring that separator performance is maintained at target thickness of < 40 µm. Management of defects by interlayer technology is crucial.

Month/Year	Milestone Type	Description of Milestone or Go/No-Go Decision
Sept. 2021 (FY21)	Milestone	*Test cell implemented:* Implementation of a 3-electrode test cell. (**in progress**)
Dec. 2021 (FY22)	Milestone	*Multifunctional reinforcement:* Decision regarding use of multifunctional reinforcement. (**not started**)
March 2022 (FY22)	Milestone	*Moisture stability demonstrated:* Demonstrate that H_2S generation of target separator glasses and catholytes can be cut by 50% in a -40 °C dewpoint dry room. (**not started**)
June 2022 (FY22)	Milestone	*Separator glass candidates selected:* Selection of separator glass candidates. (**not started**)
June 2022 (FY22)	**Go/No-Go Decision Point**	*Design capable of meeting performance requirements:* Establish a critical current density of 1 mA/cm^2 and a capacity of 4 mAh/g for > 100 cycles for a separator. Analysis indicates technical approach capable of achieving performance targets. (**not started**)

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

Summary

- ❑ Our work verifies the possibility of utilizing cathode support for GM's hot-pressed, reinforced sulfide glass separators.

- ❑ The thermal stability of the buried NCM/SSE interface was studied as a function of catholyte SSE composition: $(1\text{-}y)[xLi_2S\cdot(1\text{-}x)P_2S_5]\cdot yLiM$ (M = Br, I).

- ❑ Thermal degradation of the buried NCM/SSE interface is analogous to anodic degradation of the same interface during extended cycling

- ❑ LiBr halide dopant promotes the formation of a new metastable δLi_3PS_4 phase with superionic conductivity (1.77 mS/cm at 25 °C). The formation of this new phase compensates for thermal degradation of the buried NCM/SSE interface.

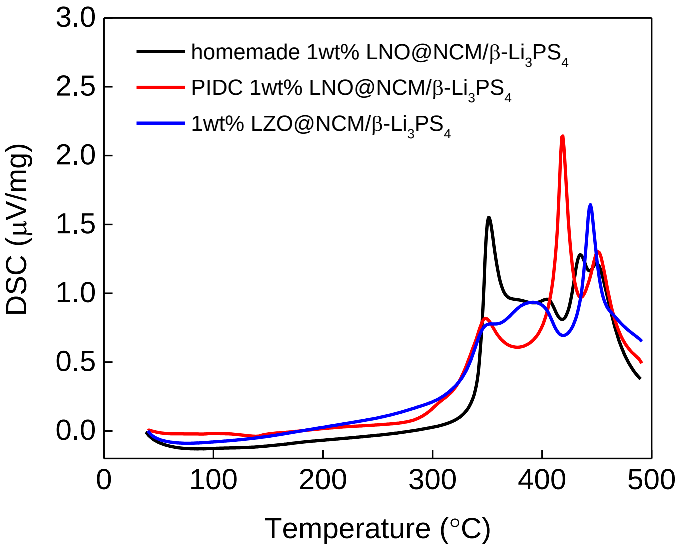
- ❑ Prevention of CAM microcracking during cell manufacture should be a universal consideration for ASSB.

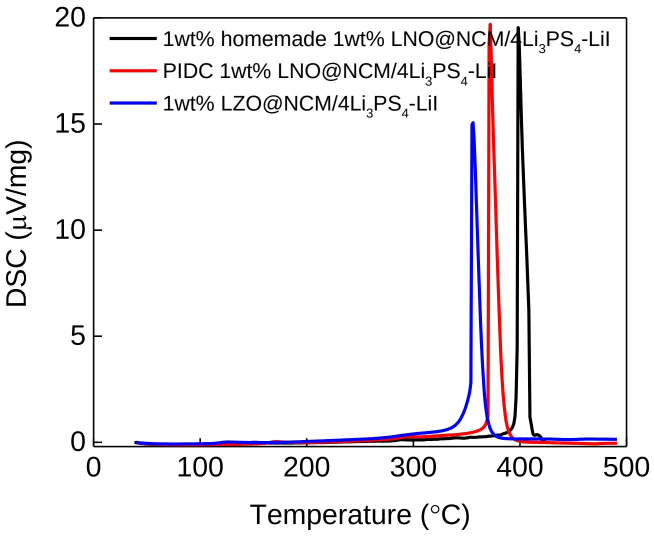
Technical Back-Up Slides

Technical Back-Up Slides

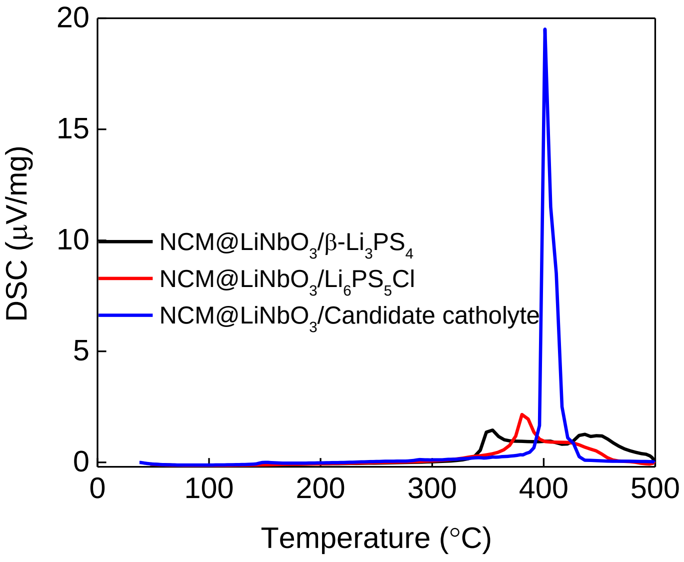
Additional DSC data

- Why did we choose not to use LZO coating? Because it consistently showed lowest exothermic onset temperature.





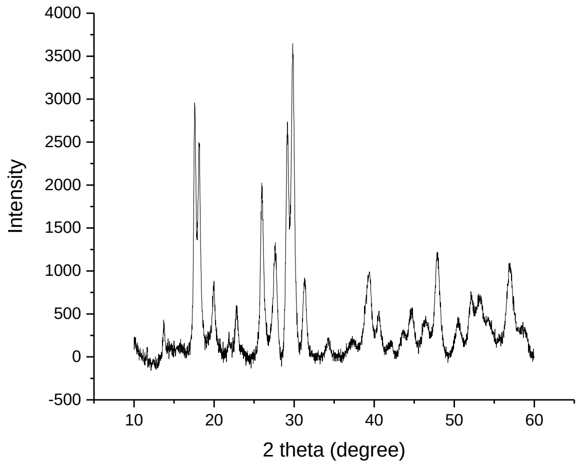
- While DSC shows higher onset for Candidate A catholyte, it does have a higher peak response.



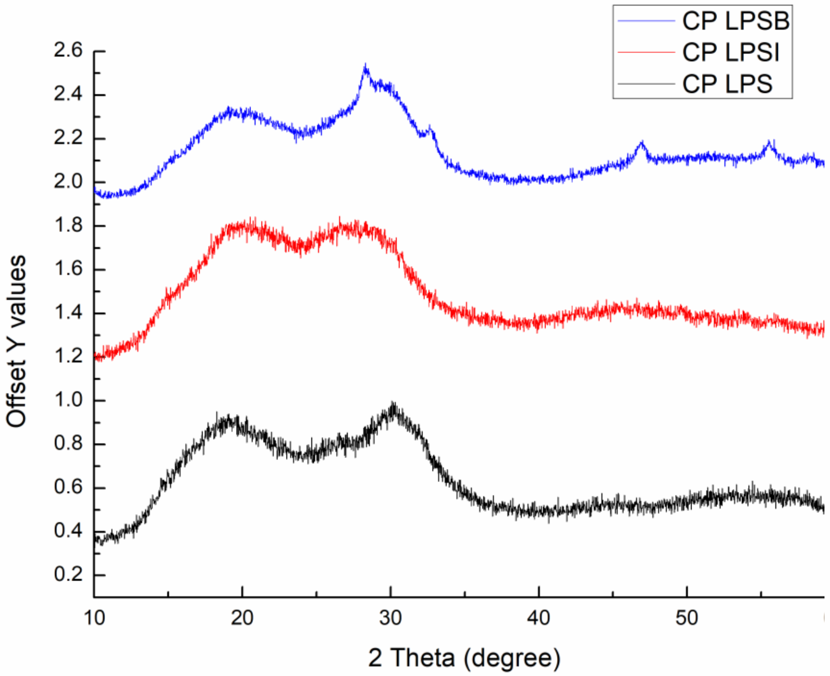
Technical Back-Up Slides

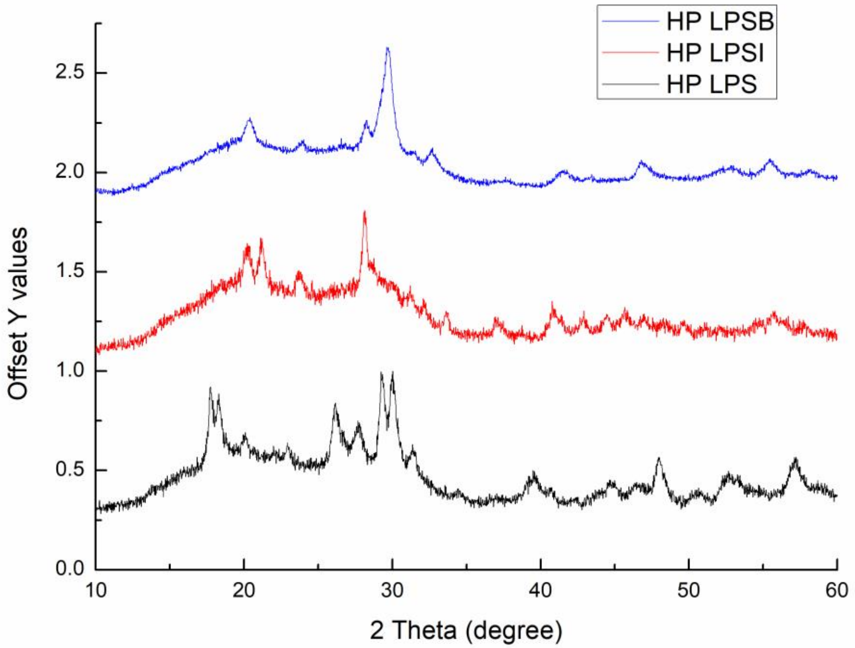
Additional XRD data

β-Li_3PS_4
(HT 2 hours, 240°C)



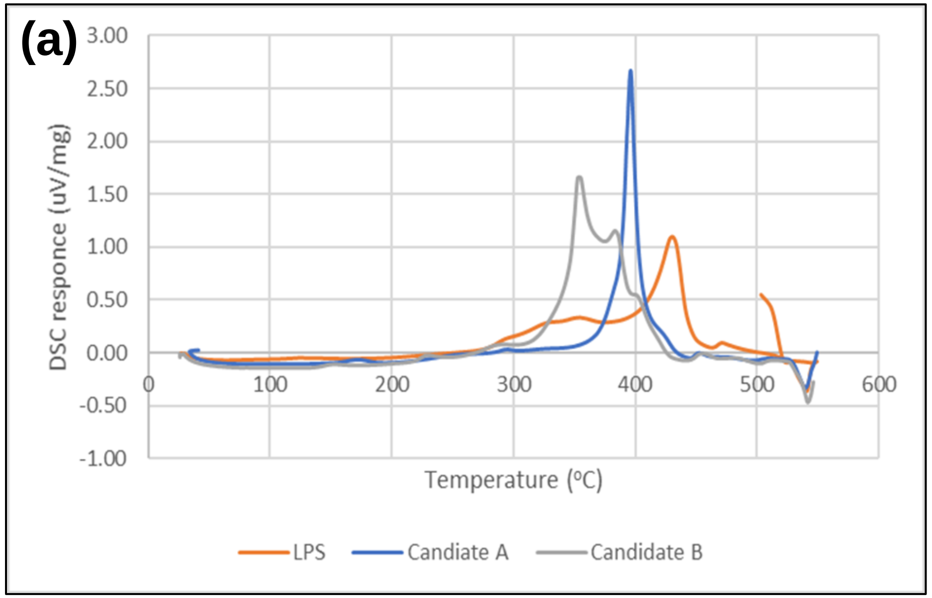
- Primary ceramic phases present after hot pressing are δ-Li_3PS_4, $Li_7P_2S_8I$, and β-Li_3PS_4 for LPSB, LPSI, and LPS mother glasses, respectively.

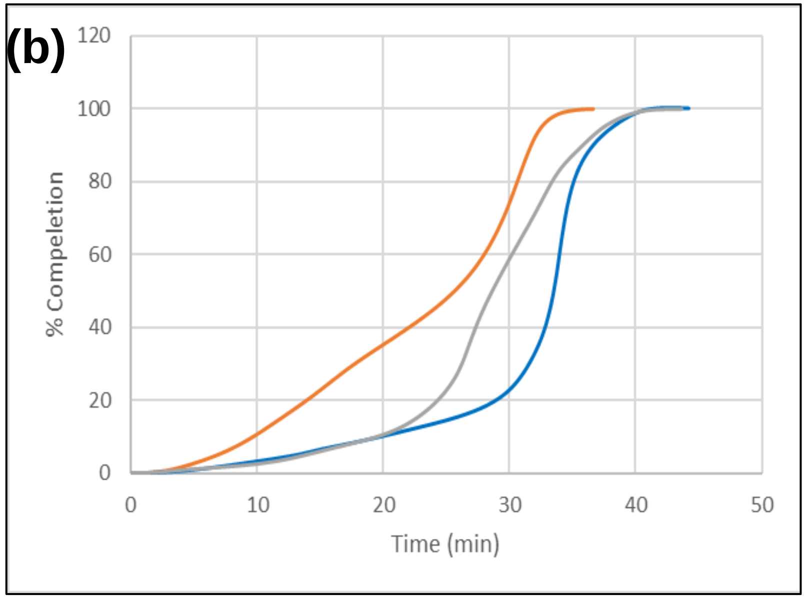


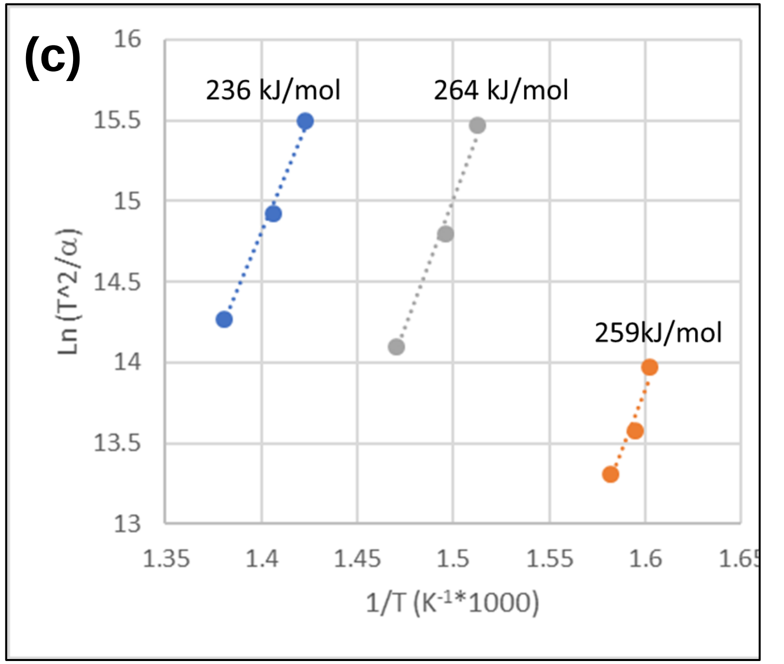


Technical Back-Up Slides

DSC reaction kinetics study



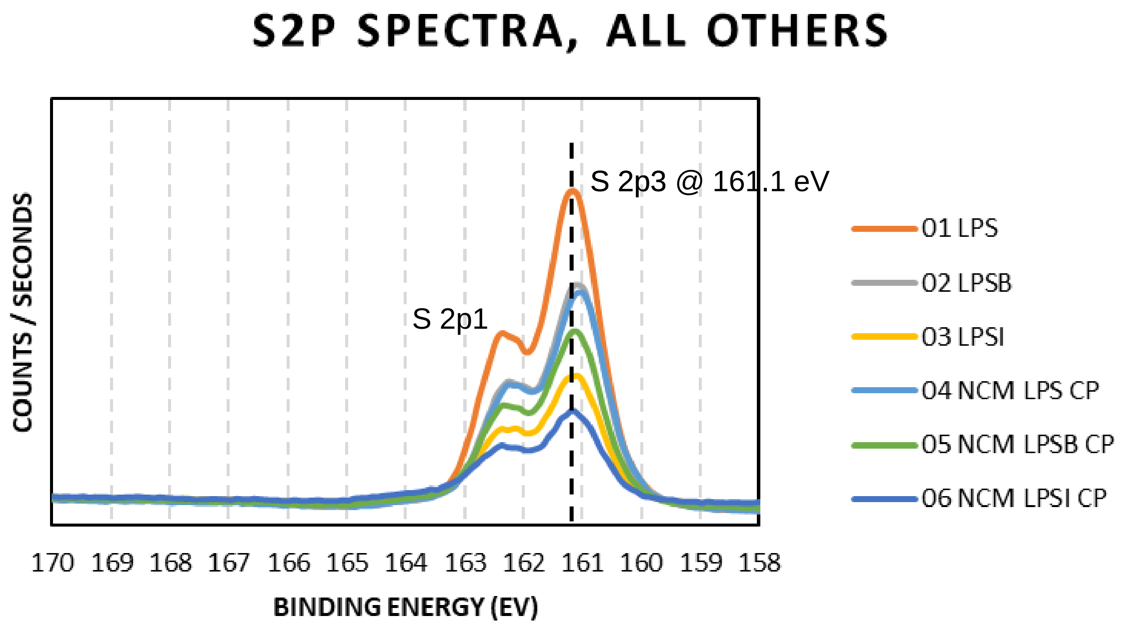


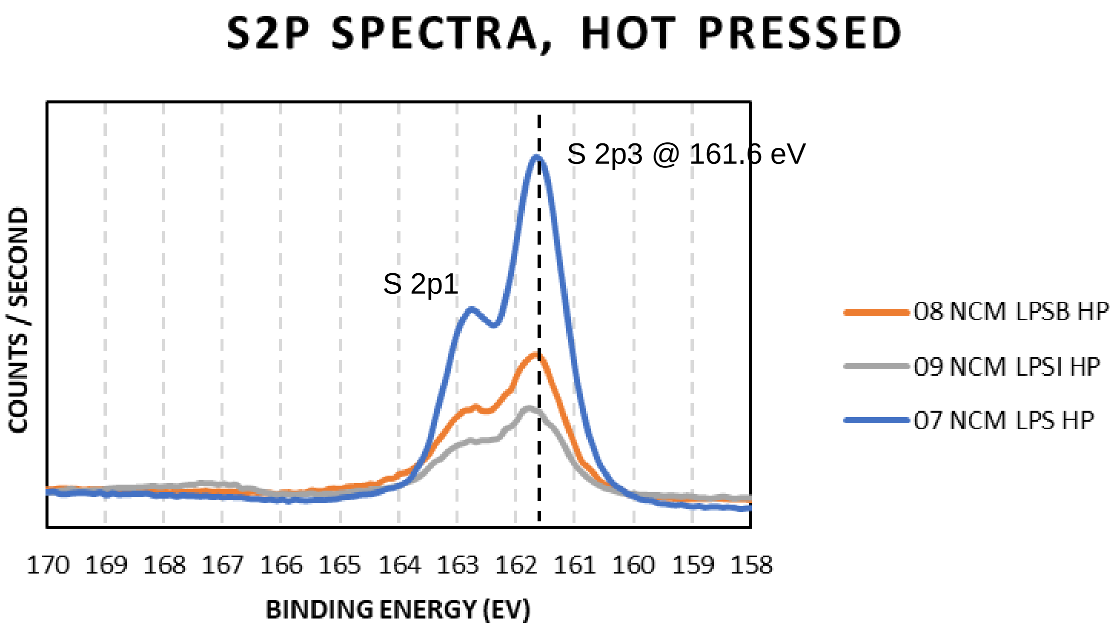


- DSC response for LPS/NCM, LPSI/NCM, and LPSB/NCM composites when heated at 5K/min.
- Fractional reaction completion as a function of time for cathode composites. Legend same as for (a).
- Kissinger plot of cathode composites and the energy of reaction computed at 33% of reaction completion. Legend same as for (a).

Technical Back-Up Slides

Additional XPS data





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