Project ID: bat416

Cobalt-Free Cathode Materials and Their Novel Architectures

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Overview

Timeline

- October 1st, 2018
- September 30th, 2021
- Percent complete: 50%

Budget

- Total project funding
  - US$ 2,500,000 (20% non-federal matching)
- Funding received in FY19
  - US$ 834,000
- Funding for FY20
  - US$ 834,000 (matching non-federal US$ 209,000)

Barriers

- Barriers addressed
  - electrolyte decomposition at high voltage
  - LNMO/graphite surface instability
  - poor rate performance for thick electrodes

Partners

- Interactions/ collaborations
  - University of Texas, Austin
  - Lawrence Berkeley National Lab
  - Tesla, Inc.
  - Army Research Laboratory

Relevance and Project Objectives

Overall Objectives:

- The objective of this project to research, develop, and demonstrate a spinel type $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) electrode and novel electrolyte formulation for use in next-generation Li-ion batteries (LIB).

Objectives in this Period:

- Baseline electrochemistry of LNMO cathode;
- LNMO and graphite surface chemistry evaluation;
- Dry coated LNMO electrochemical performance optimization;
- LNMO thick electrode (at least $3mAh/cm^2$ per side) delivers 600Wh/kg (cathode level) with capacity retention >80% at C/3 rate for 300 cycles in full cell with graphite anodes.

Project Impact:

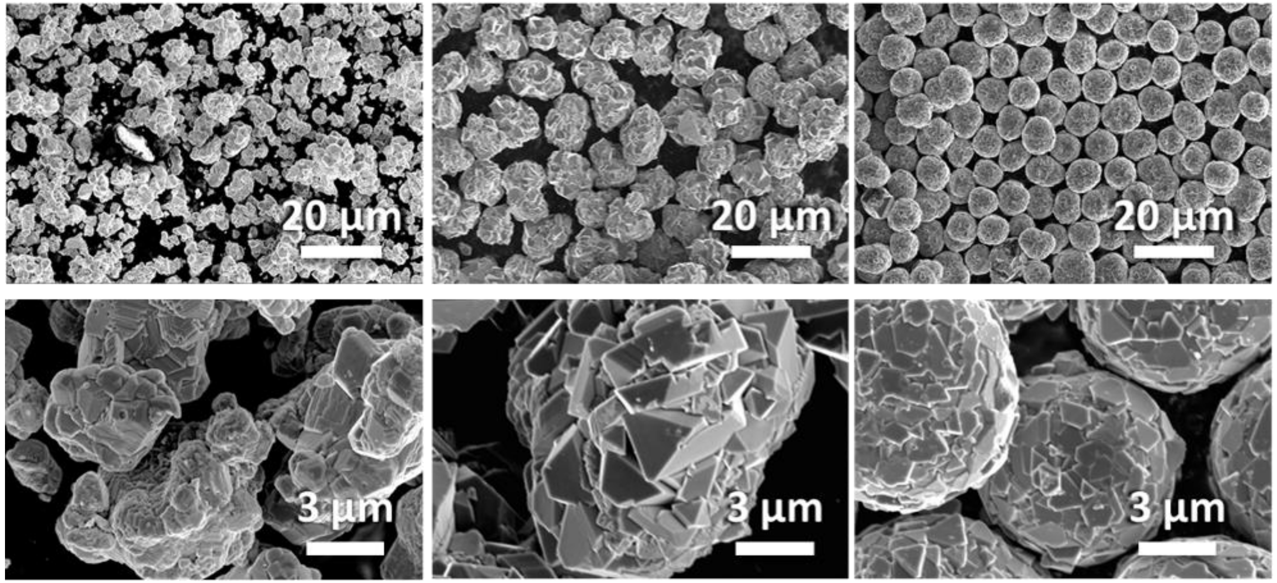
- Our proposed cathode is 100% free of cobalt and its novel architecture will have porosity less than 20% and designed tortuosity for high rate capability. Our innovative, solvent-free, dry- electrode process will be applied. At the cathode level we will reach more than 600Wh/kg at the cathode level with the possibility of reaching an areal loading of at least $4mAh/cm^2$ for the delivered pouch cells.

Approach

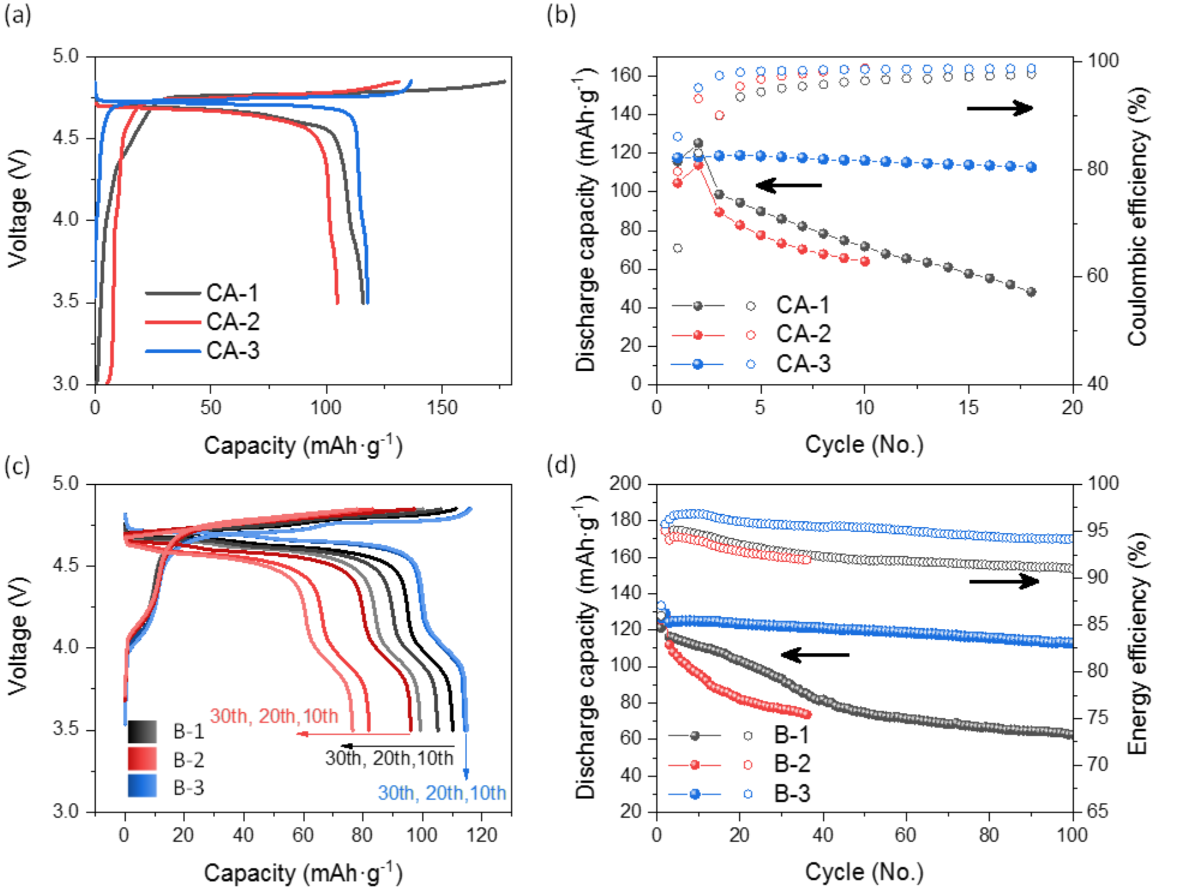
- Innovative synthesis of high tap density LNMO; Various approaches for the high-voltage spinel cathode materials, such as TM ratio control, and elemental doping, which will be applied in this project.
- Novel electrolytes screening from ARL; As an un-funded partner of this proposal, the ARL team led by Dr. Kang Xu will provide support in electrolyte and additive materials.
- Thick electrode architecture cell prototyping; Tesla's dry coated battery electrode offers extraordinary benefits particularly at high loading weights.
- In addition, we will develop a series of characterization techniques such as ex-situ X-ray photoelectron spectroscopy (XPS), ex-situ cryogenic transmission electron microscopy (cryo-TEM), ex-situ cryogenic focused ion beam microscope (cryo-FIB) and in situ time-of-flight secondary-ion mass spectrometry (TOF-SIMS).

Accomplishment to Date FY 20

Baseline electrochemistry of LNMO cathode materials



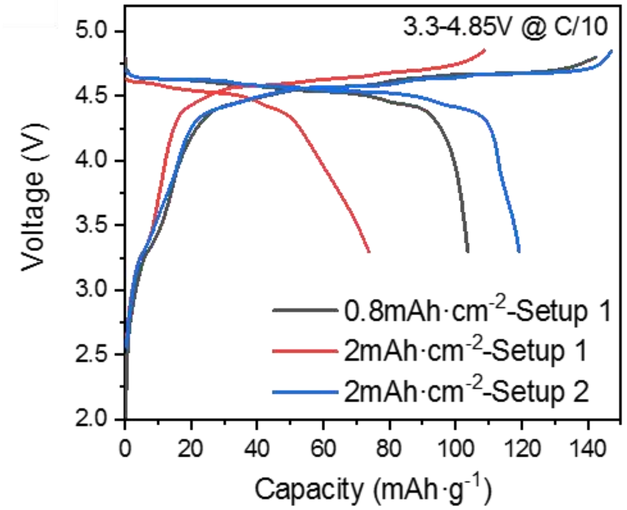
NEI	UT-Austin	Haldor Topsoe
Commercial available	>1kg per batch	Commercial available
No well defined secondary particle	~10µm	~8µm

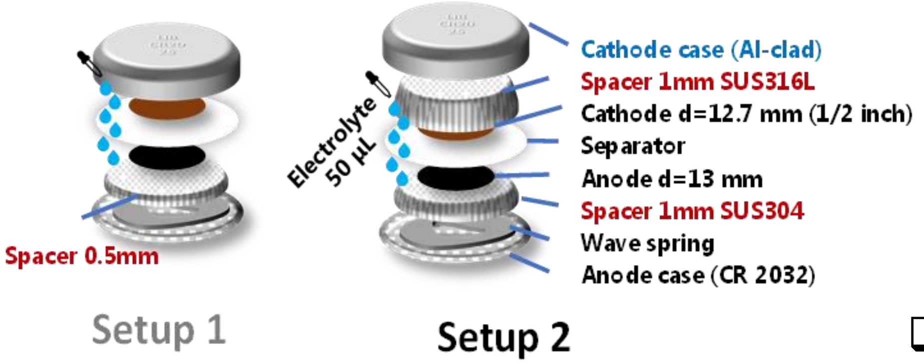


- ❑ All the performances are tested using coin cell half cell with electrode loading around $1mAh/cm^2$ using 50µl Gen 2 electrolyte (EC: EMC = 3: 7 wt.% with 1 mol/L $LiPF_6$).
- ❑ Every single component in the cell can have a significant influence on long-term cycling stability including conductive agent, binder, coin cell cases, etc.

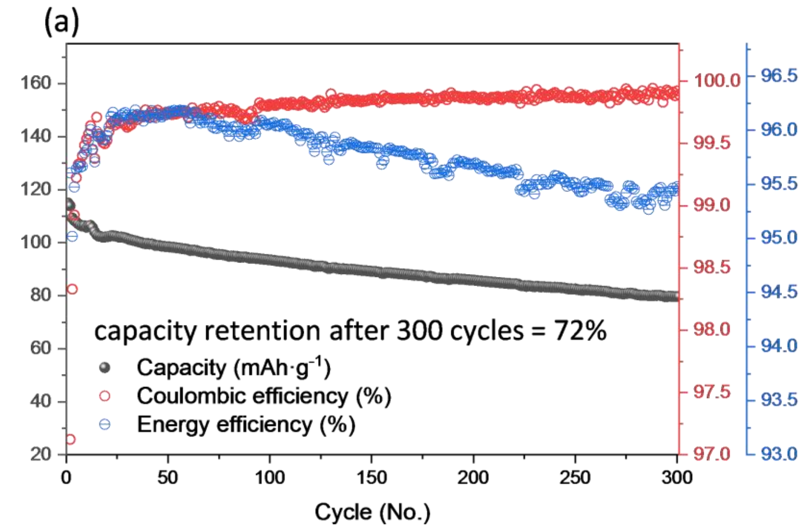
Accomplishment to Date FY 20

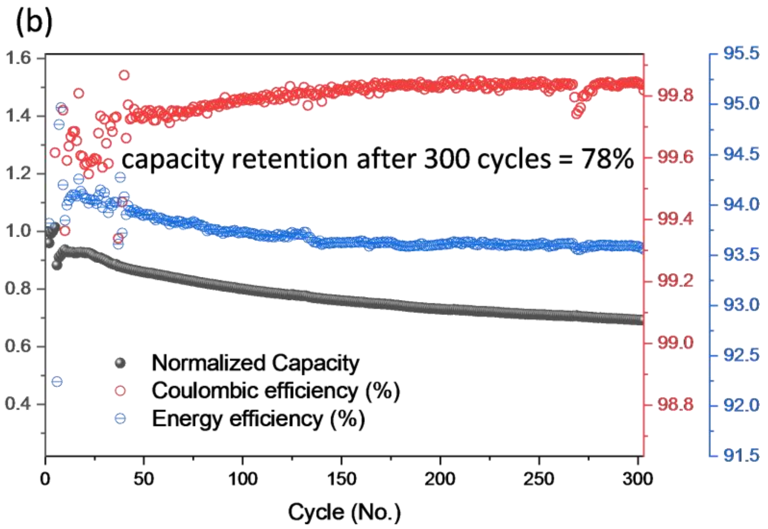
LNMO thick electrode full cell performance with stacking pressure control





Coin cell with 3mAh/cm^2 electrodes   Pouch cell with 3mAh/cm^2 electrodes



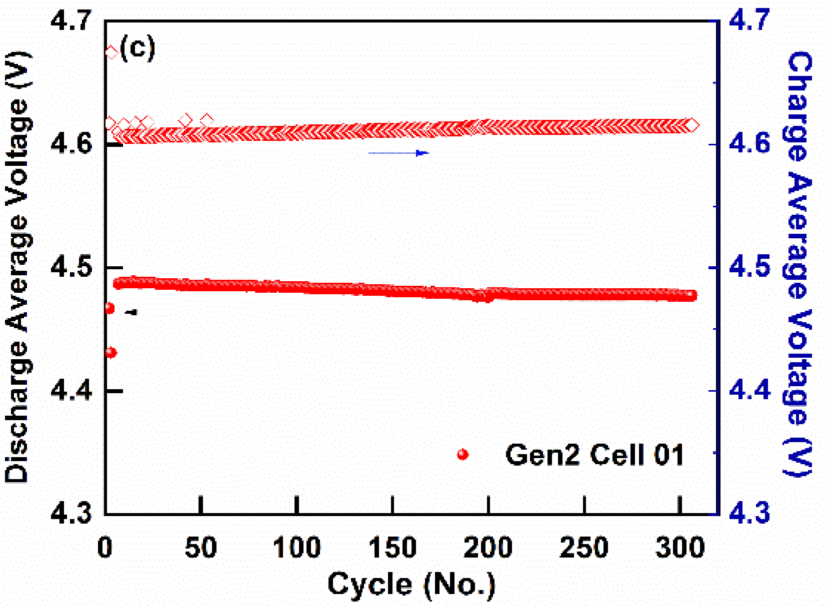


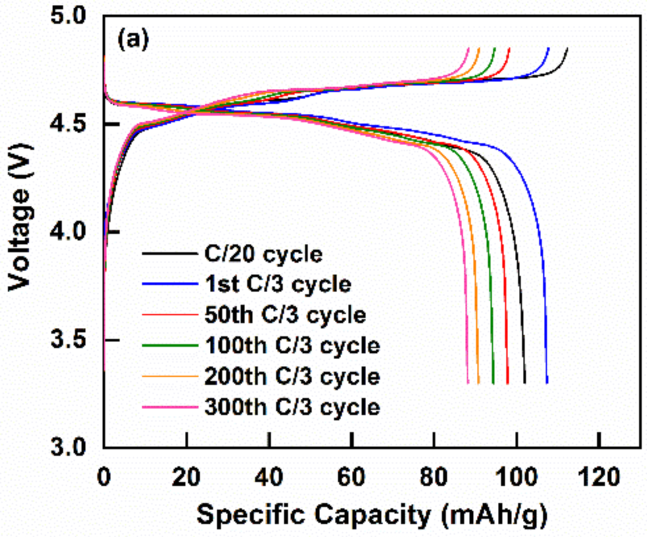
- The thicker electrode with the optimized cell setup2 delivers even better initial cycling performance than the thinner electrode with the conventional setup1 due to stacking pressure increase.
- However, the stacking pressure of the coin cell after crimping can be hardly monitored so that large-format pouch cell is recommended for this system to obtain more consistent testing results.
- After optimization, cycle retention 78% has been achieved after 300 cycles of the pouch cell with the thick LNMO electrode (~3mAh/cm^2) using Gen 2 electrolyte. Note the pouch cell cycling stability is always better than coin cell using the same material due to delicate pressure control.

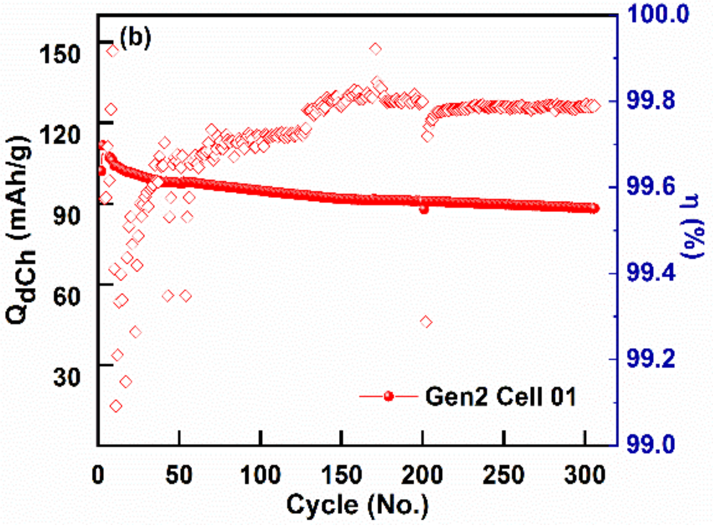
Accomplishment to Date FY 20

LNMO/graphite multilayer pouch cell performance testing

3.5Ah multilayer pouch cell with LNMO/graphite electrode





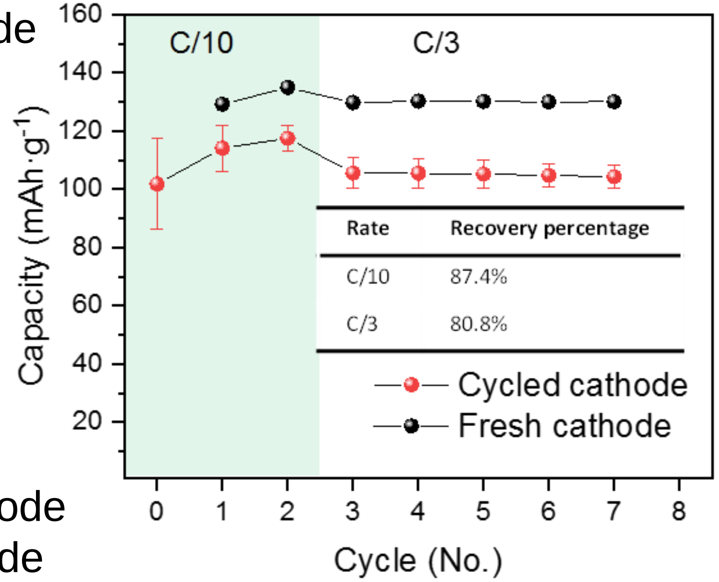


- The designed multilayer LNMO/graphite pouch cell (~3Ah actual capacity) delivers 82.2% capacity retention after 300 cycles at C/3 rate cycling.

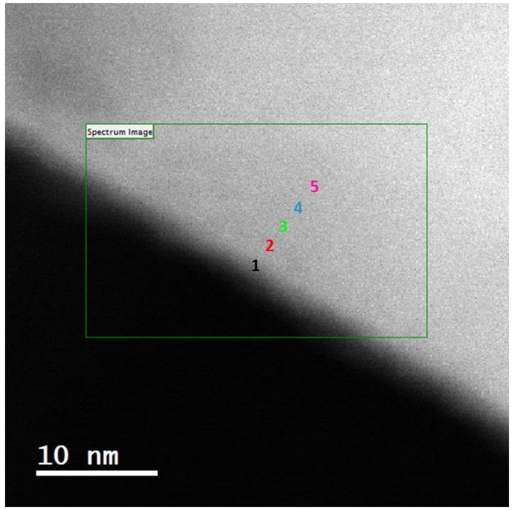
Accomplishment to Date FY 20

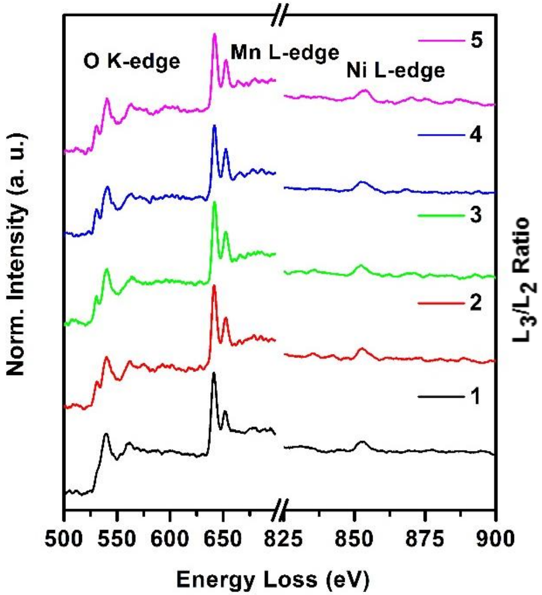
LNMO/graphite full cell performance degradation analysis

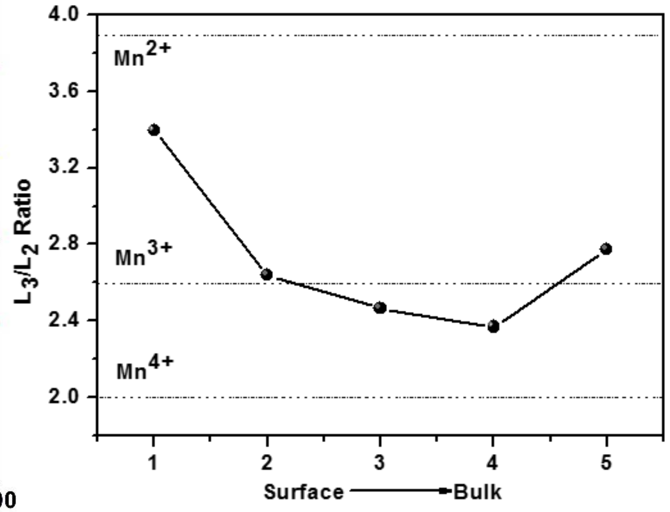
Cathode side



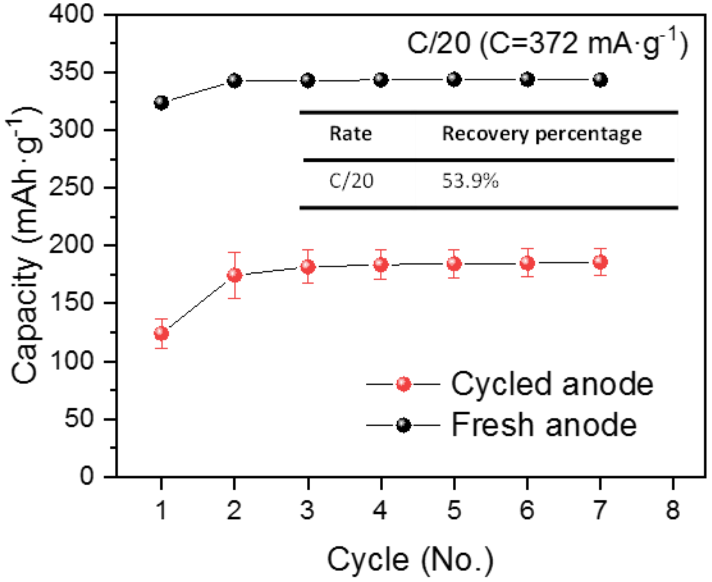
Rate	Recovery percentage
C/10	87.4%
C/3	80.8%



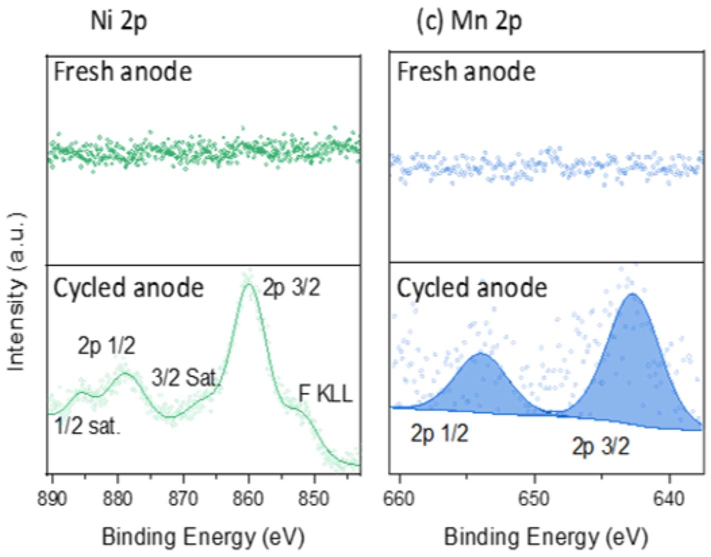


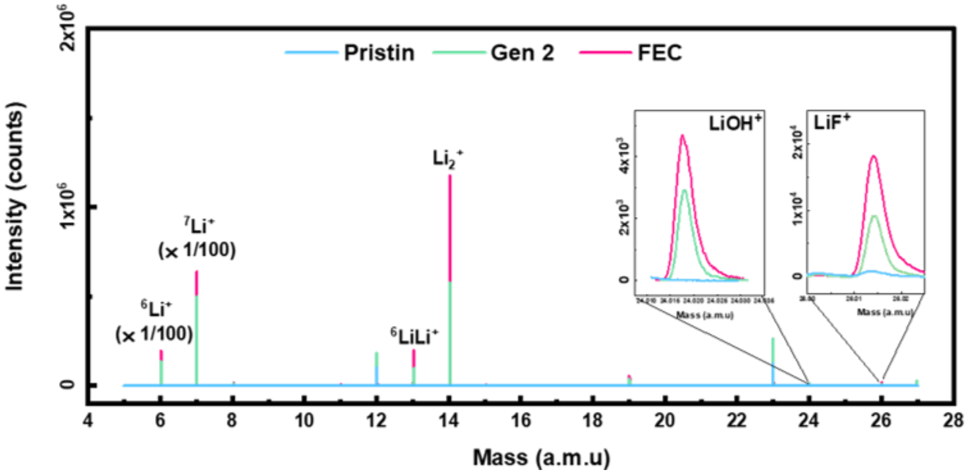


Anode side



Rate	Recovery percentage
C/20	53.9%





- ❑ Both electrode degrades after cycling, graphite anode becomes more inactive due to TM redeposition and active lithium loss.

Collaboration and Coordination with Other Institutions

Dr. Arumugam Manthiram
University of Texas, Austin

Dr. Vincent Battaglia
Lawrence Berkeley National Lab

Dr. Hieu Duong
(Tesla, Inc.)

Dr. Kang Xu
(Army Research Lab)

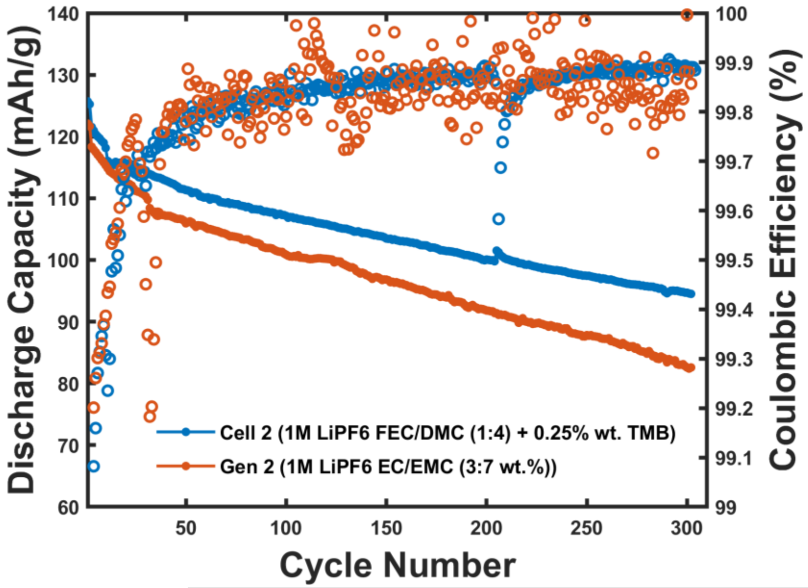
San Diego Nanotechnology Infrastructure (SDNI)
Irvine Materials Research Institute (IMRI)

Our Appreciation for Guidance from VTO Program Manager (Dr. Peter Faguy), NTEL and TARDEC Managers

Proposed Future Research

Future Research:

- Surface chemistry evaluation for modified LNMO and graphite through XPS and TOF-SIMS.
- Performance testing with different novel electrolytes and cut off voltage using LNMO thick electrode pouch cell.
- Dry coated LNMO single layer pouch cell investigation.

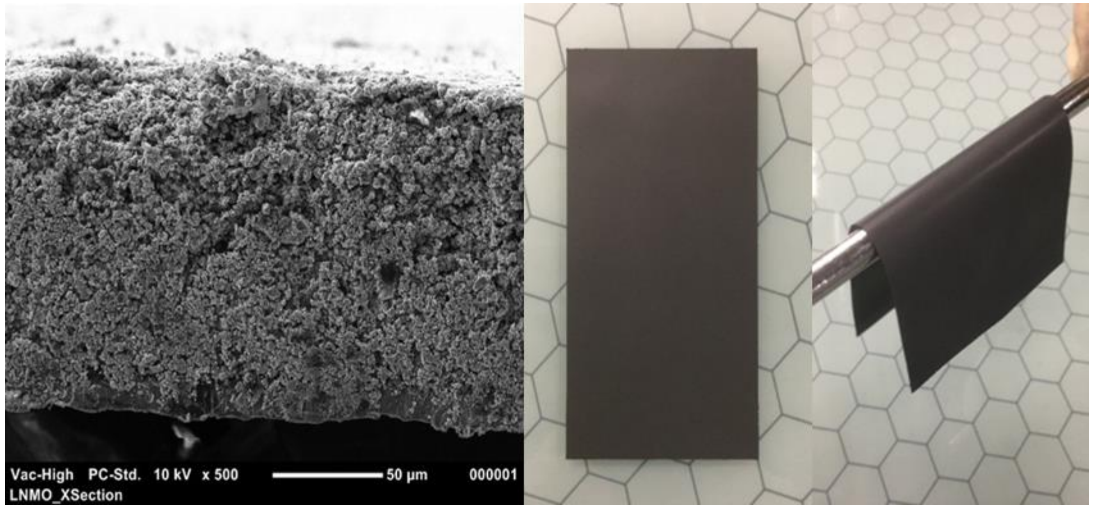


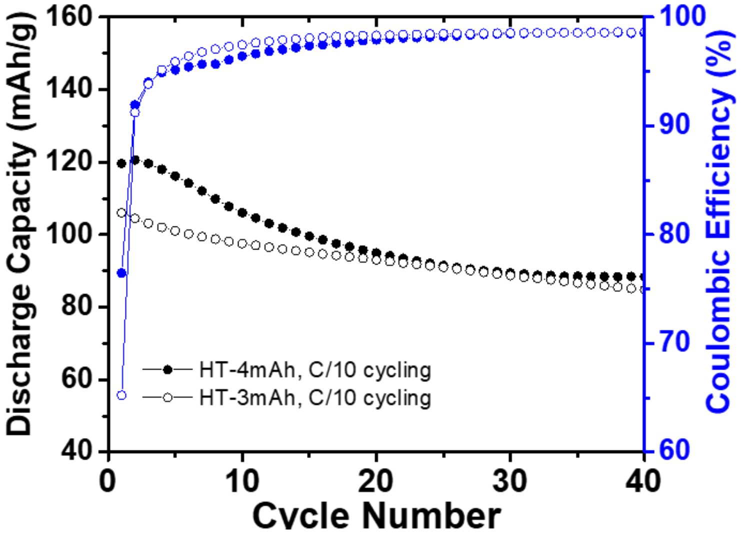
- FEC based electrolyte with TMB additive has shown promising electrochemical result compared with Gen 2 baseline at coin cell level for thick electrode ($3 mAh/cm^2$ loading)

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

Summary

- LNMO baseline performance has been obtained after optimizing components in the testing cell including conductive agent, binder, coin cell cases, etc.
- Stacking pressure has critical impact on the full cell cycling with thick electrode.
- The designed multilayer LNMO/graphite pouch cell (~3.5Ah designed capacity) delivers 82.2% capacity retention after 300 cycles at C/3 rate cycling.
- The degradation of LNMO/graphite full cell can be due to active Li loss other than transition metal dissolution/redeposition.
- Dry coated thick electrodes with areal loading larger than 3mAh/cm^2 have been prepared and their electrochemical performance has been improved.





Technical Back-Up Slides

Technical Back-Up Slide

Different cell components information used in this work

Different binder information used in this work

Sample	Vendor	Type	Melting point (℃)	Melt Viscosity (kp)
B-1	\	\	160-168	30 - 40
B-2	\	\	161-167	40 - 46
B-3	Arkema	Kynar HSV 900	160-169	44 - 54

Different conductive agent information used in this work

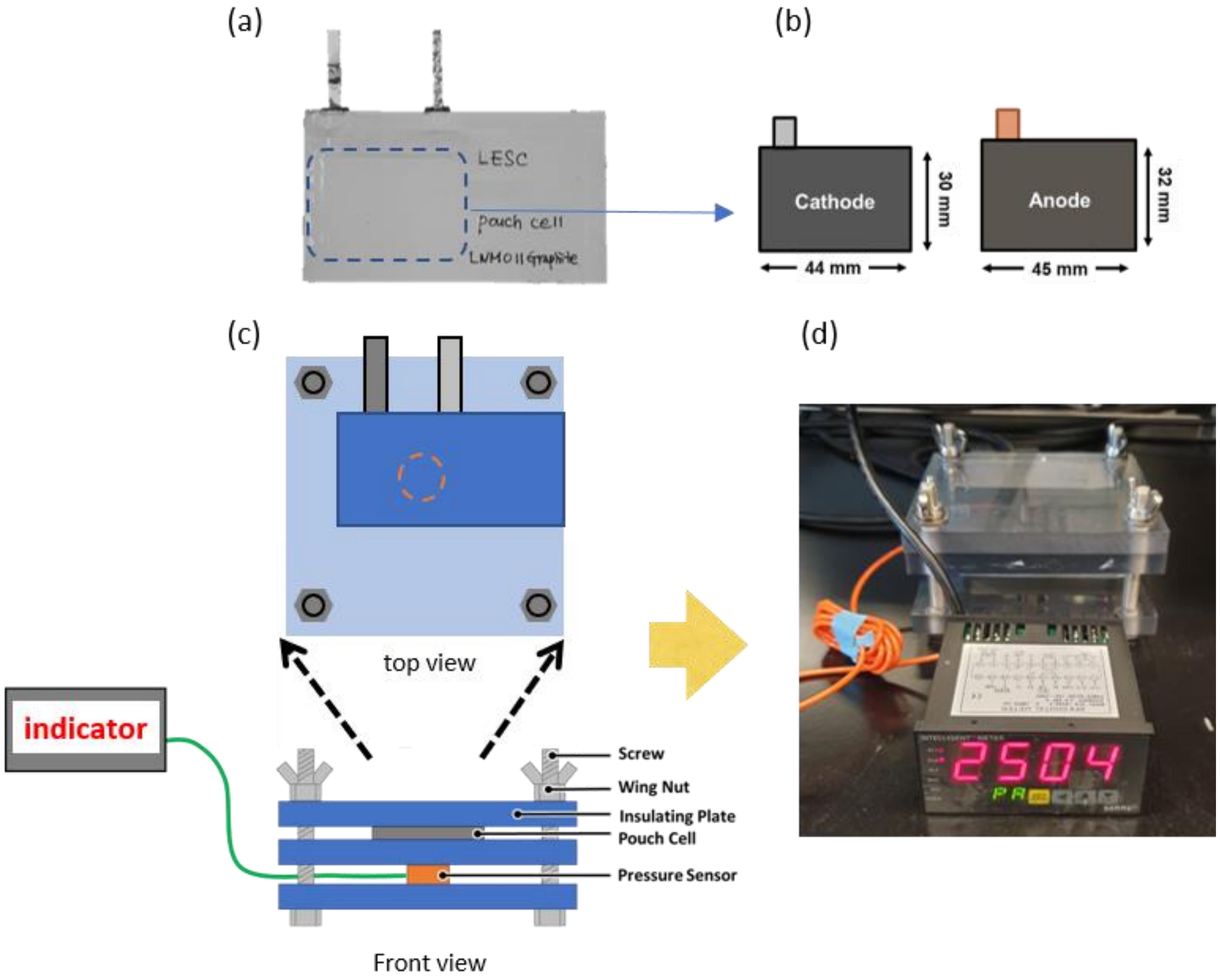
Sample	Vendor	Type	Surface area ($m^2 \cdot g^{-1}$)	Volume ($cm^3 \cdot g^{-1}$)
CA-1	\	\	1320	1.78
CA-2	\	\	74.34	0.15
CA-3	TIMICAL	Super C65	53.5	0.10

Coin cell case information

Type	Vendor	Stainless steel type (Japanese Standards)	Clad substance
SS304	\	SUS304	\
Al-clad	Hohsen	SUS316L	Al_2O_3

Technical Back-Up Slide

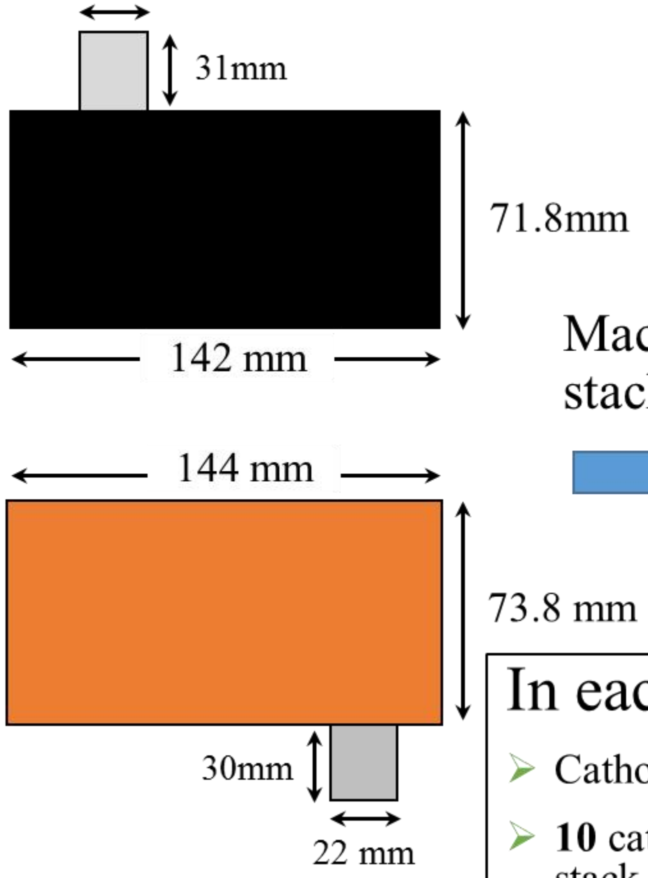
Stacking pressure control fixture for single layer pouch cell



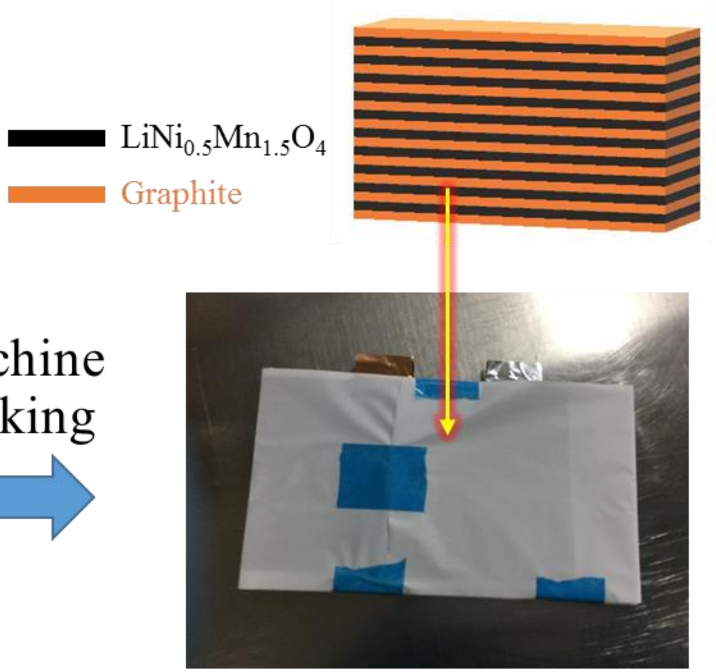
- To achieve the enhanced performance, the pouch cell was highly pressed with pressure controller. We have designed and set up the pressure device by sandwiching the pouch cell between insulating plates to uniformly press the pouch cell;
- The pressure sensor was plated on the bottom place with one more insulating plate, and sensor indicator was connected to sensor to monitor the pressure change;
- The pressure has been controlling around 1100kPa before testing the pouch cells.

Technical Back-Up Slide

Fabrication process of multi-layer pouch cells



Machine stacking



Tab welding and hot sealing without electrolyte injection

After electrolyte injection

+ pressure

In each dry pouch cell,

- Cathode size = 71.8 x 142 ; anode size = 73.8 x 144 (all in mm);
- **10** cathode stack layers (~12-13 mg/cm^2 active loading), **11** anode stack layers (5.5-6.0 mg/cm^2 active loading), **N/P ~ 1.15**;
- Approximately **3.5 Ah** per pouch cell, **more than 30** pouch cells will be fabricated;
- Separator = single-sided coated ceramic separator (Asahi Kasai)