MATERIALS BENCHMARKING ACTIVITIES FOR CAMP FACILITY

Project ID: BAT028

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ANNUAL MERIT REVIEW AND PEER
EVALUATION MEETING
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OVERVIEW

Timeline

- Start – Oct. 1st 2014
- Finish – Sep. 30th 2020

Barriers

- Development of EV batteries that meet or exceed DOE/USABC goals
  - Cost
  - Performance
- High energy active material identification and evaluation

Budget

- Total project funding in FY2019: $350K (as part of CAMP effort)
- 100% DOE

Partners and Collaborators

- The Cell Analysis, Modeling, and Prototyping (CAMP) Facility (Argonne)
- Battery Manufacturing Facility (ORNL)
- Materials Engineering Research Facility (MERF) (Argonne)
- Post Test Facility (Argonne)
- Industrial partners are listed at the end

RELEVANCE

- An overwhelming number of materials are being marketed/reported to improve Lithium-ion batteries, which need to be validated for their impact on EV applications.
- CAMP Facility was established at Argonne to provide a realistic and consistent evaluation of candidate materials. In order to utilize the facility more efficiently and economically, cell materials need to be validated internally to determine if they warrant further consideration.
- The benchmarking (validation) activities will not only benefit the CAMP Facility, but also provide an objective opinion to material developers. Moreover, the better understanding of the active materials at cell level will speed up material development efforts.

TECHNICAL ACCOMPLISHMENTS

- The capacity fading phenomenon of silicon monoxide (SiO) anode
  - NMC532 was used as cathode and Li_4FeO_5 (LFO) was used to compensate the irreversible capacity loss of SiO
- Electrochemical characterization of nickel-rich high energy cathode materials (BTR) were completed.
  - $LiNi_xMn_yCo_zO_2$ ($x \approx 0.9$)
  - $LiNi_xCo_yAl_zO_2$ ($x \approx 0.9$)
- High voltage electrolyte (Shenzhen Capchem Technology) for NMC532 cathode

MILESTONES

- Develop methods to fabricate pre-lithiated high-energy electrode couples on pilot-scale coater in dry room

APPROACH AND STRATEGY

- Collaborate with material developers and leverage Argonne's expertise in electrode design and cell testing.
- Cell materials which have impact on the cell performance will be considered for testing, mainly in terms of
  - Electrochemical performance
  - Electrode optimization
  - Thermal stability
- The electrochemical performance will be validated using 2032 coin type cells under test protocol derived from USABC EV requirements.

Energy Storage Systems Performance Target for Electric Vehicle by USABC

USABC Requirements of Energy Storage Systems for EV

Characteristics at EOL	Unit	System level	Cell level
Peak discharge Power Density (30 Sec)	W/L	1000	1500
Peak Specific discharge Power (30 Sec)	W/kg	470	700
Peak Specific Regen Power (10 sec)	W/kg	200	300
Available Energy Density @ C/3 discharge rate	Wh/L	500	750
Available Energy @ C/3 discharge rate	kWh	45	N/A
Calendar Life	Years	15	15
DST Cycle Life	Cycles	1000	1000
Normal Recharge Time	hours	<7	<7
High Rate Charge	min	80% DSOC in 15 min	
Selling price @ 1000 units	$/kWh	125	100

United States Advanced Battery Consortium Battery Test Manual For Electric Vehicles, U.S. Department of Energy Vehicle Technologies Program, Revision 3, INL, June 2015

Test Protocol development

In order to conduct the electrochemical characterization of the battery chemistries for Applied Battery Research for Transportation (ABR) program, C-rate and pulse current was calculated for coin cells according to EV requirements.

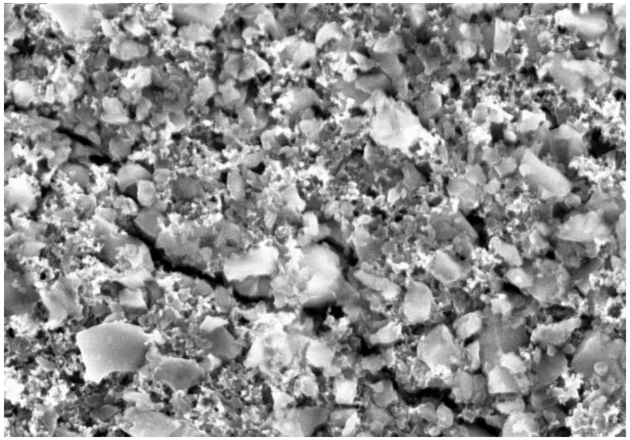
OBJECTIVES

- To identify and evaluate low-cost cell chemistries that can simultaneously meet the following criteria for EV applications.
    - Electrochemical performance
    - Abuse tolerance
    - Cost
- To enhance the understanding of advanced cell components on the electrochemical performance and safety of LIB.
- To support the CAMP Facility for prototyping cells and electrode library development.

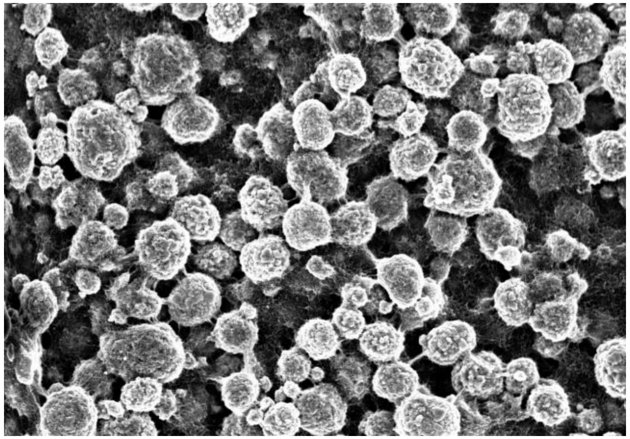
CALENDAR AND CYCLE LIFE OF SiO ELECTRODE

- Silicon monoxide (SiO) has been investigated as the next-generation anode material for lithium-ion batteries due to its high energy density. Compared to commercially used graphite, SiO has a theoretical gravimetric capacity of 1710 mAh/g and volumetric capacity of 1547 Ah/L and can offer an 18% increase in volumetric energy density on the cell stack level.
- In order to replace graphite with SiO as the anode, its lifetime, as one of the most important characteristics of LIBs, should be investigated. In this work, we study the calendar life and cycle life of LIBs, using SiO as the anode and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) as the cathode.

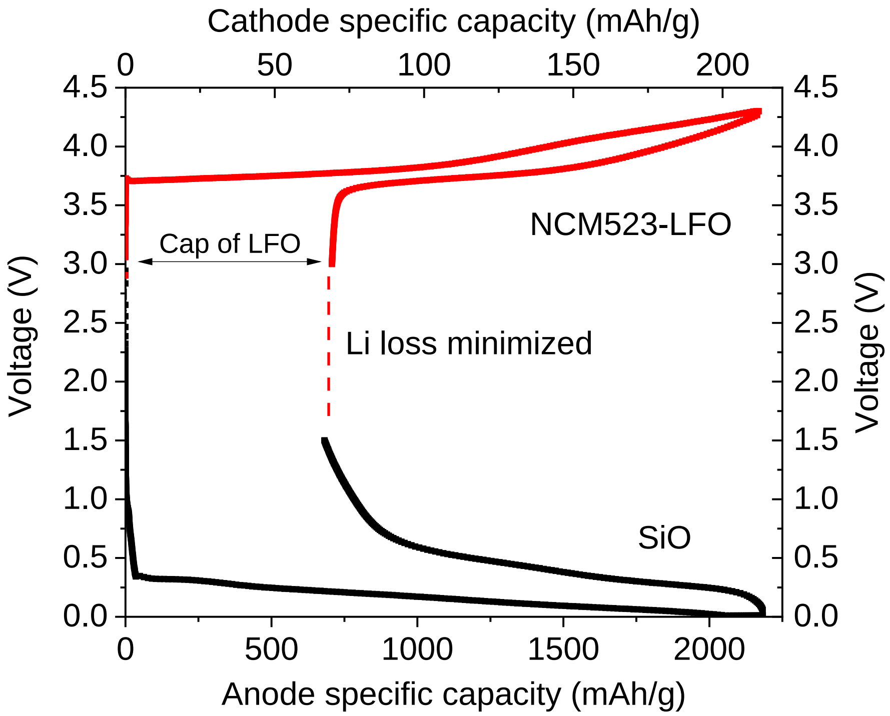
SiO anode



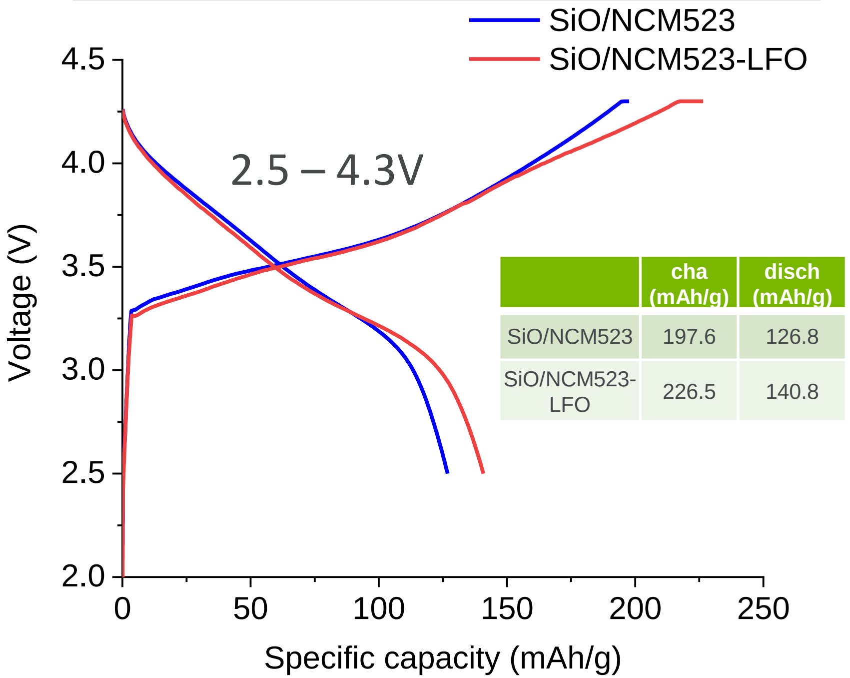
NMC532-LFO cathode



SiO/NMC532-LFO FULL CELL MATCHING



NMC532-LFO (10wt.%):C45:PVDF=90:5:5



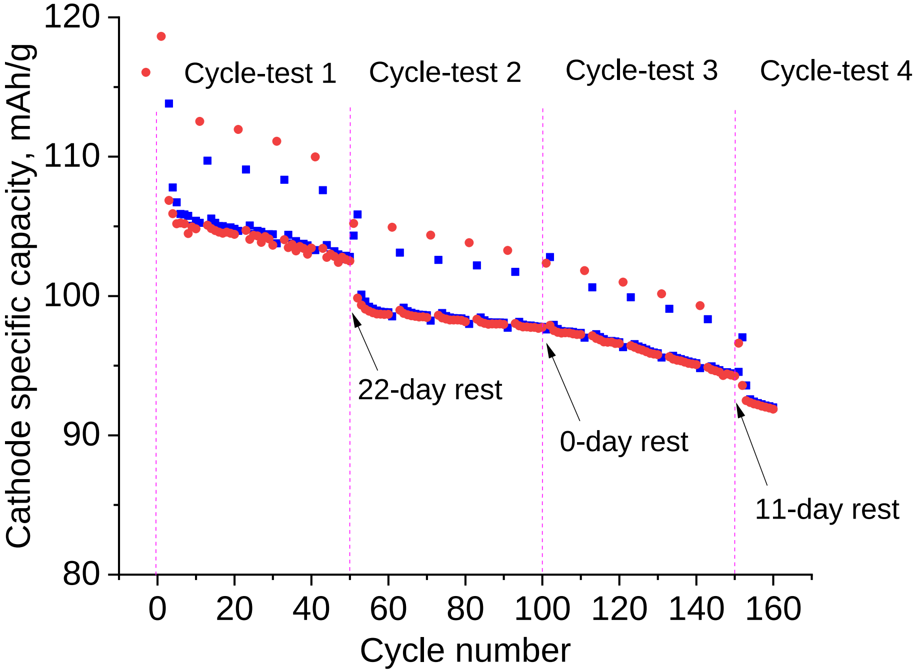
	cha (mAh/g)	disch (mAh/g)
SiO/NCM523	197.6	126.8
SiO/NCM523-LFO	226.5	140.8

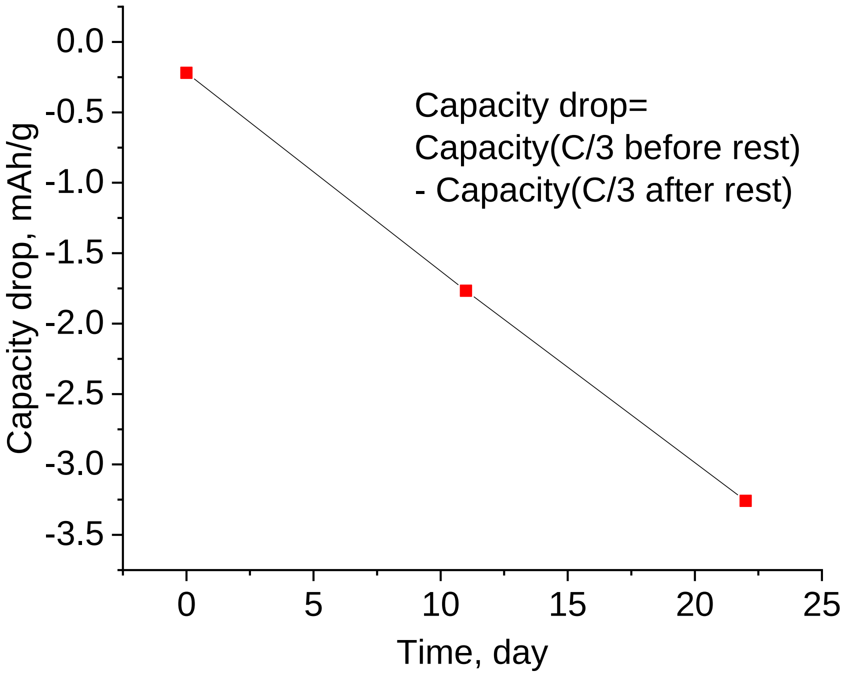
- The 1st cycle coulombic efficiency of silicon monoxide is usually lower than 70% due to the parasitic reactions. To address the problem, Li_5FeO_4 (LFO) was mixed with NMC532 to compensate the irreversible capacity loss of SiO.

- First formation cycle of full cell shows that the cathode discharge capacity increased from 126.8 mAh/g to 140.8 mAh/g based on the weight of NMC523/LFO blend, or 154.9 mAh/g based on the weight of NMC532 alone.

REST EFFECT ON SiO/NMC532-LFO FULL CELL

Cycling test includes 1 C/10, 1 HPPC, and 8 C/3, which will repeat 5 times.

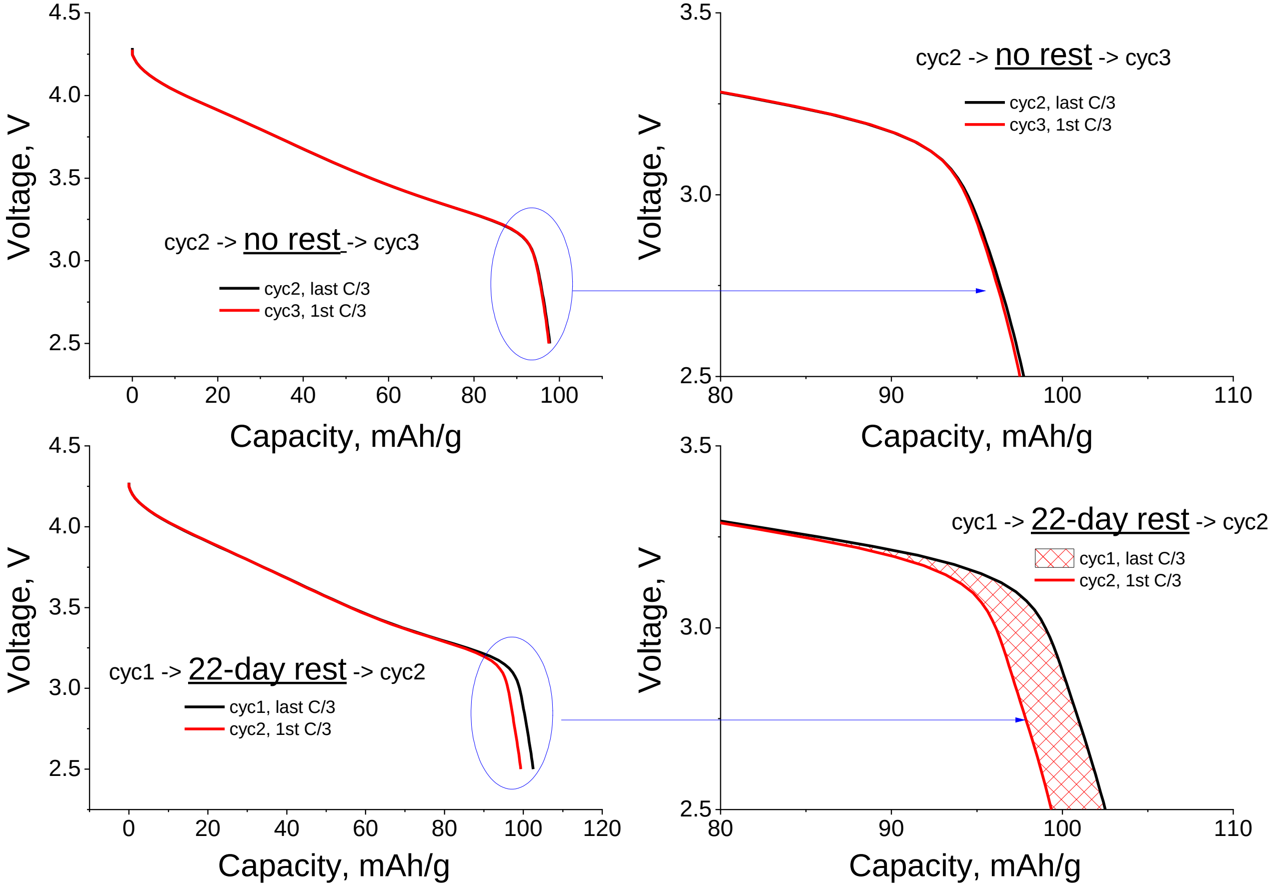




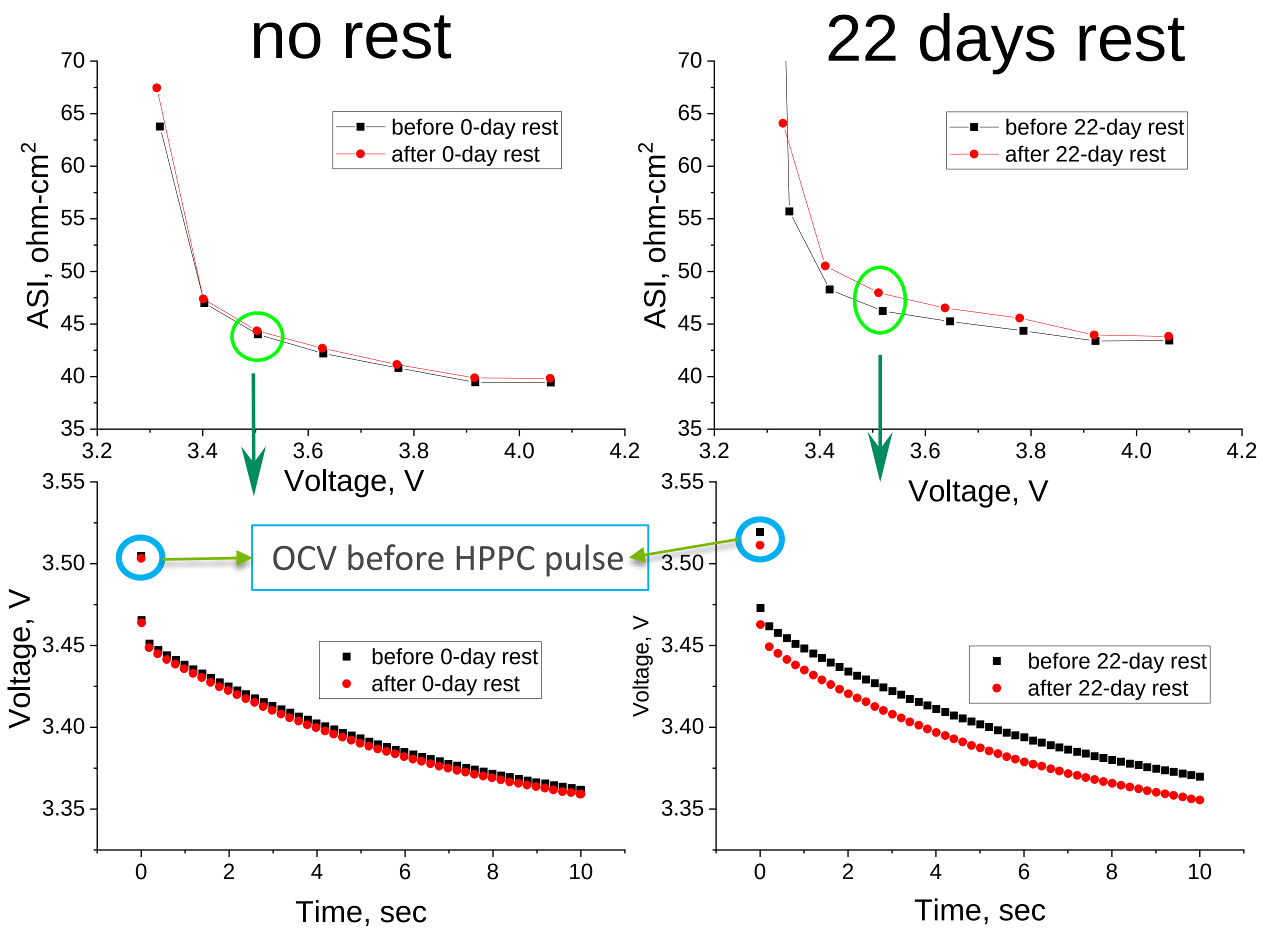
- High capacity retention of 96% for cycle-test 1, 98% for cycle-test 2, and 97% for cycle-test 3, respectively, during cycling test.
- However, we noticed that there is small, but noticeable capacity drop between cycle-tests when the rest time is not short.
- It is observed that the capacity drop linearly with resting time.

VOLTAGE PROFILES BEFORE AND AFTER REST

- According to the detailed analysis of voltage profiles before and after rest between the cycle-tests, the capacity loss only appeared at the end of discharge when there were 22 days rest between cycles.



AREA SPECIFIC IMPEDANCE (ASI)



no rest

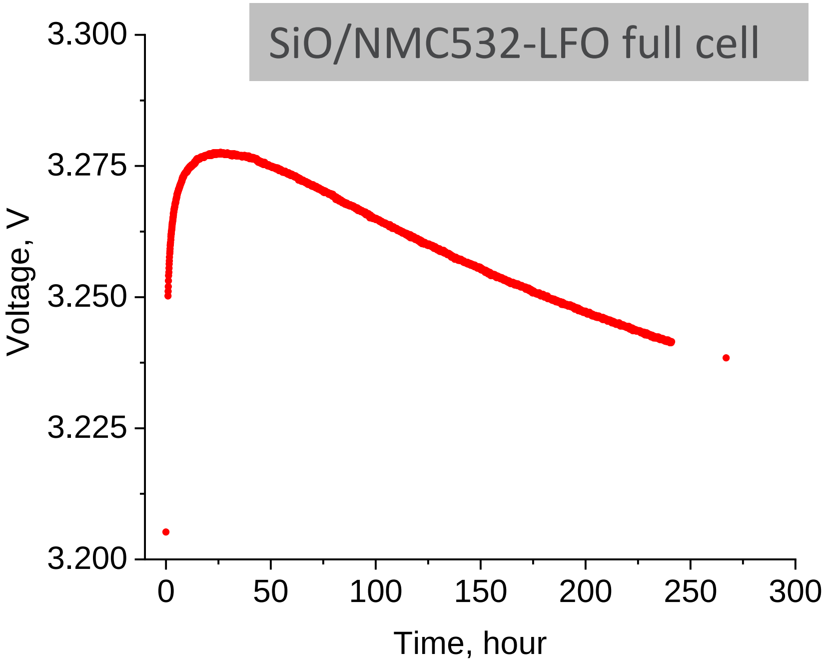
22 days rest

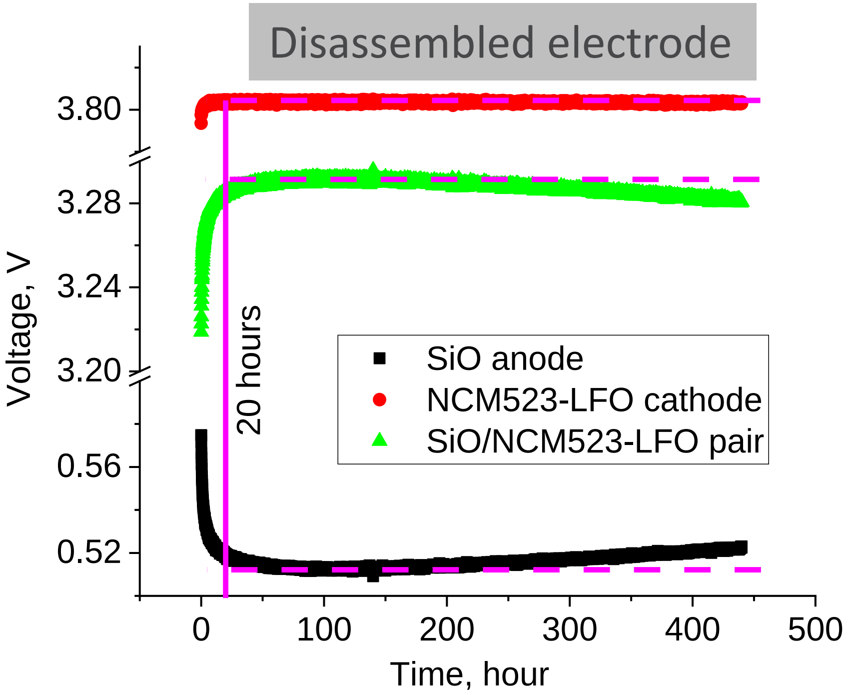
OCV before HPPC pulse

- The ASI values before 0-day rest are almost same to that after 0-day rest.
- However, obvious impedance rise was observed when the cell experienced 22-day rest.
- By examining the voltage response during HPPC (lower 2 figures), the impedance rise is caused by the voltage slippage.

- The capacity loss during the rest can be attributed to the loss of lithium inventory.

OPEN CIRCUIT VOLTAGE OF SiO/NCM ANODE AND CATHODE



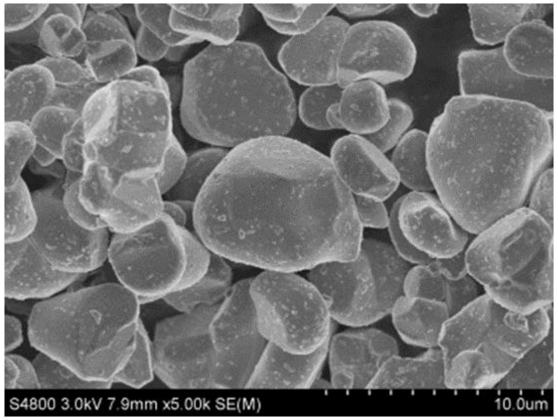


- After discharge, the open circuit voltage (OCV) of SiO/NMC532-LFO full cell is found to increase and then decrease during the rest.
- By monitoring the OCV of disassembled SiO and NMM532-LFO, it is found that the OCV drop of full cell is caused by OCV rise of anode, which can be attributed to the loss of lithium ion due to parasitic reactions.

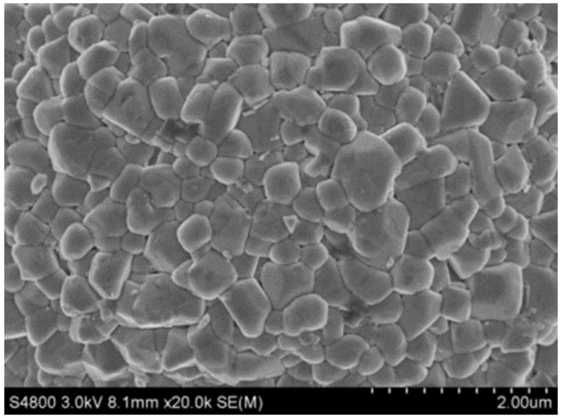
HIGH ENERGY CATHODE MATERIALS

- Nickel-rich $LiNi_xMn_yCo_zO_2$ (NMC) is becoming as high energy cathode materials for electric vehicle applications due to its high performance and low cost.
  - NMC532 and NMC622 are adopted by the market, and
  - NMC811 is expected to be next generation high energy cathode material, which were tested and reported last year.
- Even higher nickel content (Ni ≈ 0.9) NMC and NCA (BTR) was obtained and investigated in this study.

NMC



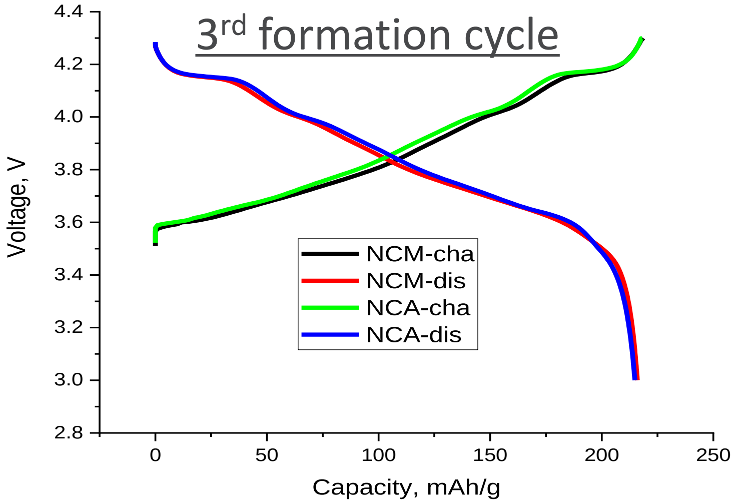
NCA



HALF CELL PERFORMANCE

	NMC **Ni ≈ 0.9**	**NCA** **Ni ≈ 0.9**
Active	90%	90%
C45	5%	5%
Binder (PVDF)	5%	5%
Electrolyte (flooded)	Gen2	Gen2
Laminate Mass	~7 mg/cm²	~7 mg/cm²
Laminate Thickness	26 µm	28 µm
Porosity	~35%	~35%

Cycling 3.0–4.3 V vs $Li^{+/0}$, 30°C,
3 formation cycles at C/10
3 rate cycles each with lithiation at C/5, delithiation at C/5, C/3, C/2, 1C, 2C
50 cycles with HPPC every 10 cycles (1 x C/10 slow; HPPC; 8 x C/3) x 5



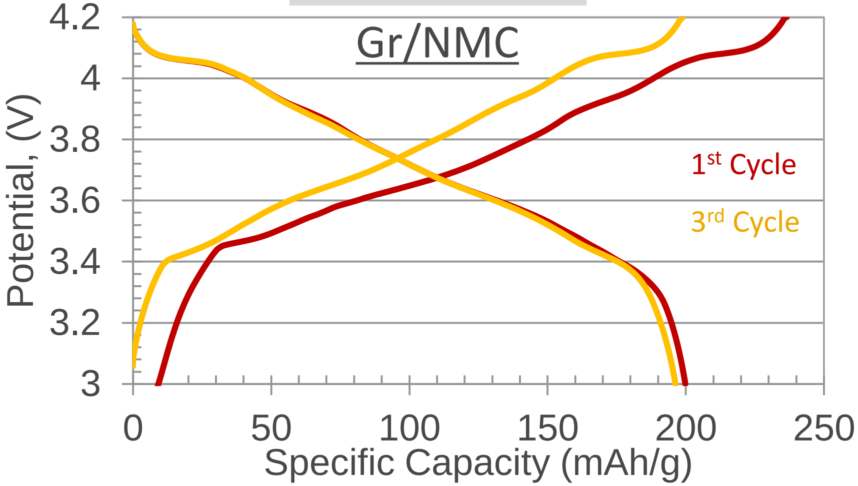
1st Cycle, Specific Cap (mAh/g)

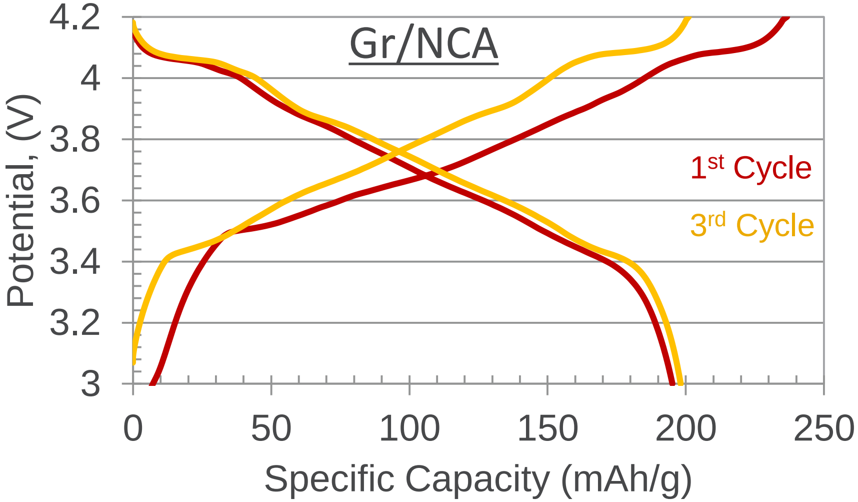
	Delith. Cap	**Lith. Cap.**	**CE (%)**
NMC	223 ± 2	215 ± 2	92.3
NCA	240 ± 6	213 ± 3	88.7

- Both Ni-rich materials showed similar voltage profiles, which suggest similar redox reactions.
- Both materials also deliver about same amount of specific capacity, above 210 mAh/g.

FULL CELL FORMATION

30°C; 3.0–4.2V

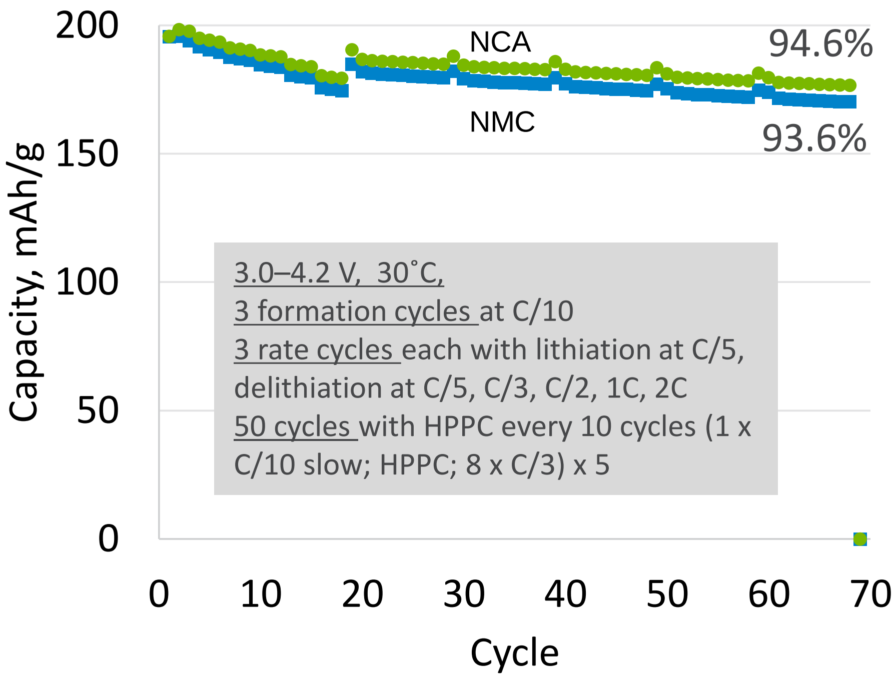




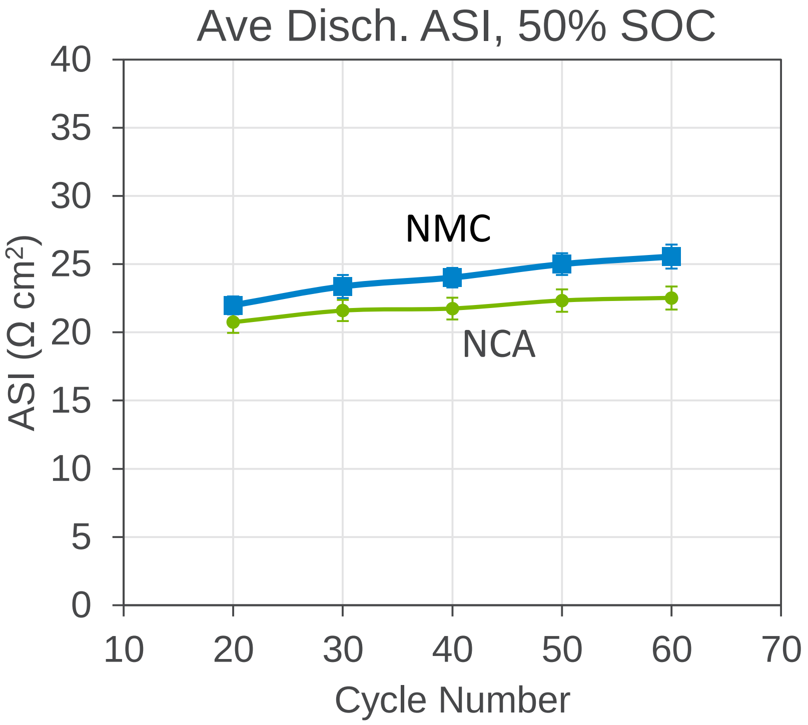
Anode	**CAMP A002B (A12 Gr)**
Active	92%
C45	2%
Binder (PVDF)	6%
Electrolyte (flooded)	Gen2
Laminate Mass	~6.1 mg/cm²
Laminate Thickness	~43 µm
Porosity	~35%

- Full cells for these two Ni-rich materials were fabricated using same graphite anode from the CAMP Facility (BAT030) and electrochemically tested.
- Again, similar electrochemical behavior was obtained during formation cycles with 200 mAh/g reversible capacity regarding to cathode material.

FULL CELL CYCLING PERFORMANCE



3.0–4.2 V, 30˚C,
3 formation cycles at C/10
3 rate cycles each with lithiation at C/5, delithiation at C/5, C/3, C/2, 1C, 2C
50 cycles with HPPC every 10 cycles (1 x C/10 slow; HPPC; 8 x C/3) x 5



- Very good cycle performance was obtained for both Ni-rich cathode materials with around 94% capacity retention during 50 cycle life test.
- The calculated area specific impedance (ASI) showed that the full cells using NMC have slightly higher impedance rise.

THERMAL ANALYSIS BY DSC

Cycling

Half-Cells were cycled 3.0–4.2 V vs $Li^{+/0}$, 30˚C

2 formation cycles at C/10

C/10 capacity-limited charge to **$Li_{0.25}MO_2$**

DSC Sample Preparation

Cell disassembled in glove box.

Cathode rinsed 2x60s in 1 mL EMC, vacuum dried.

Cathode laminate powder scraped from Al.

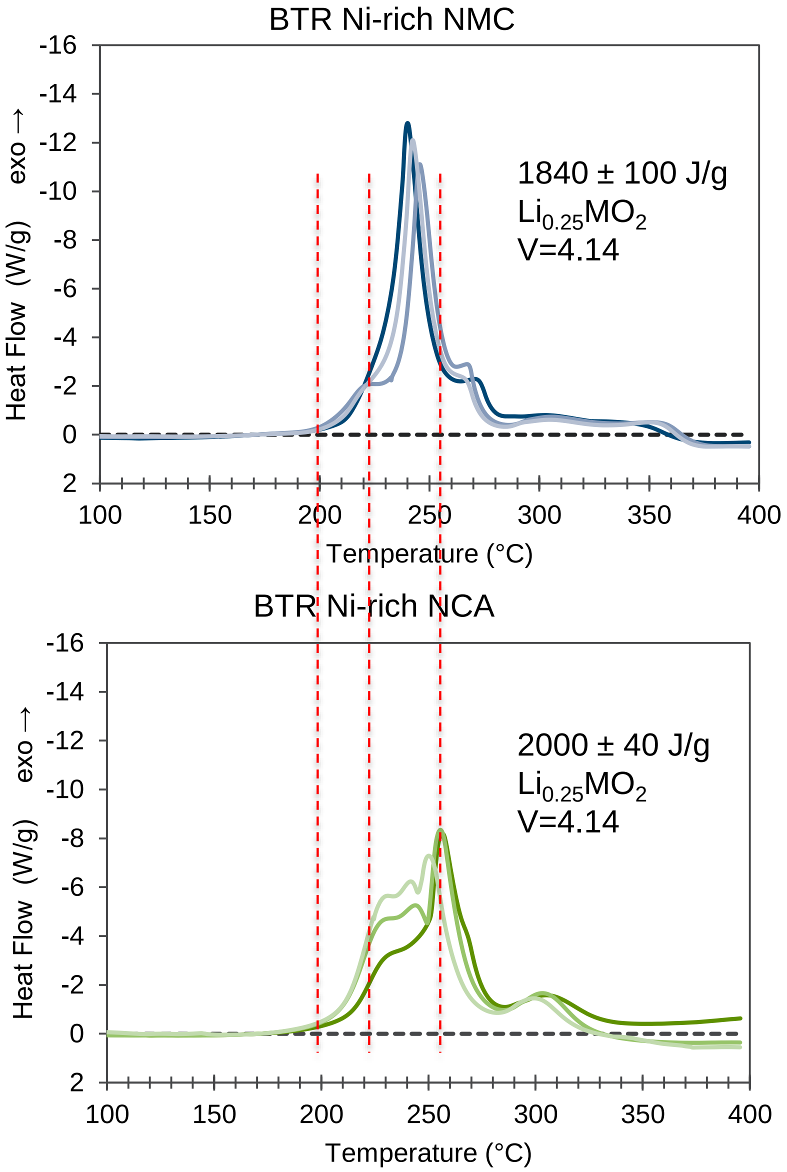
2–3 mg cathode powder added to DSC capsule with Gen2 electrolyte (1 µL : 1 mg powder).

2 cell x 2 samples tested per chemistry.

DSC Testing

30–400 ºC, 10 ºC /min.

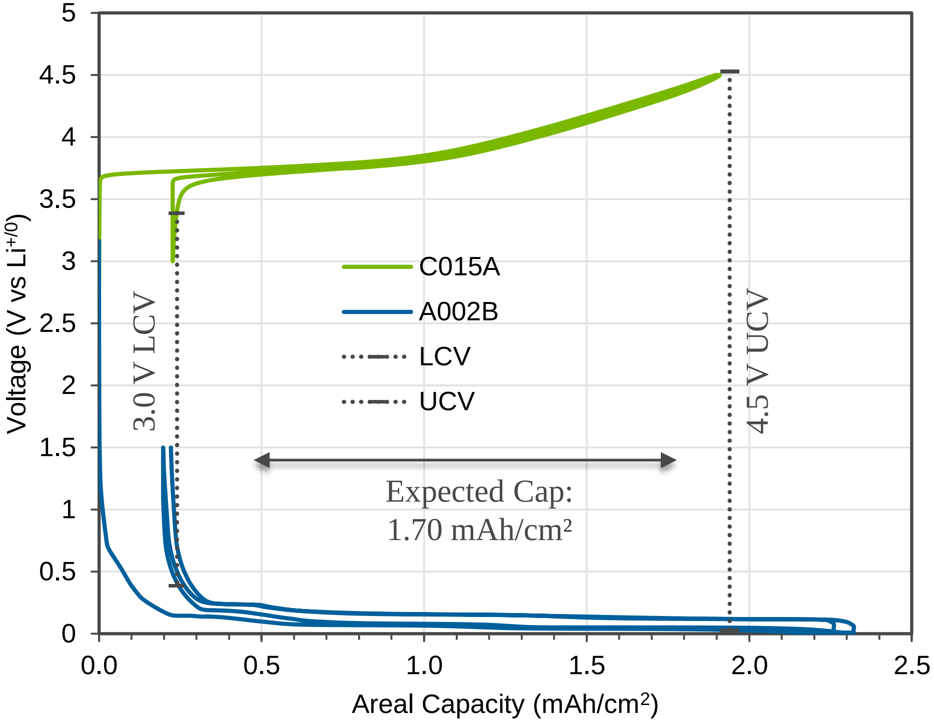
- All materials show similar decomposition onset temperature ~200 ºC
- The first thermal peak of NCA and NMC appears at the same temperature, but more profound for NCA.
- The second thermal peak of NCA appears late and smaller than that of NMC.



HIGH VOLTAGE ELECTROLYTE

- The electrolyte operated under high voltage in LIB is getting more attention since the cathode materials needs to be charged to higher voltage for high energy density requirement.
- Two electrolytes were obtained from Shenzhen Capchem Tech. and tested against internal standard Gen2 electrolyte (1.2M $LiPF_6$ EC/EMC 3/7 by weight).
- Graphite anode (A002B) and NMC532 cathode (C015A) materials fabricated by the CAMP Facility (BAT030) were used as active electrodes.

Electrode matching

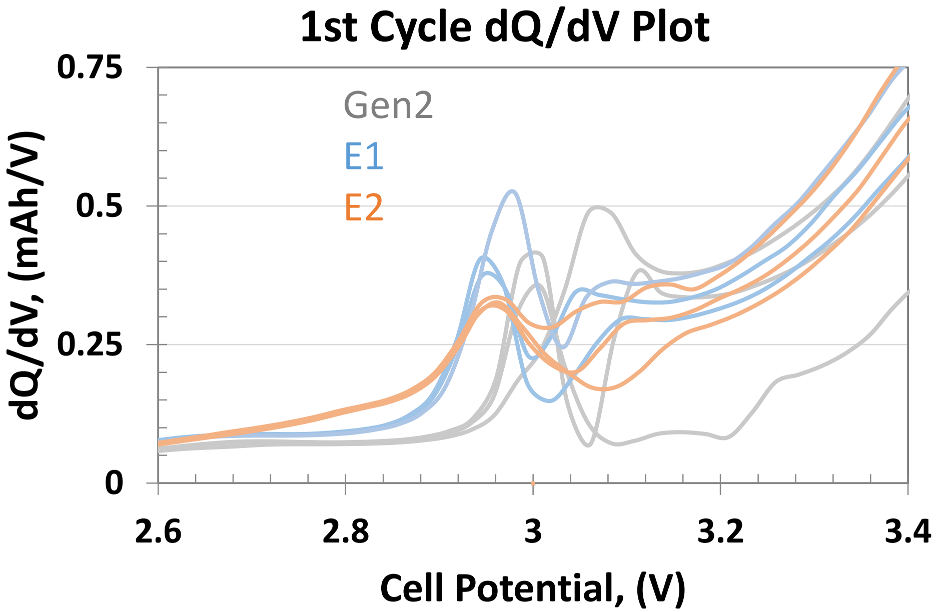


Cycling 3.0 → **4.5 V**, 30°C

5 formation cycles (C/10)

Cycling with C/3 rate

Gr/NMC532 FORMATION



3.0 – 4.5 V

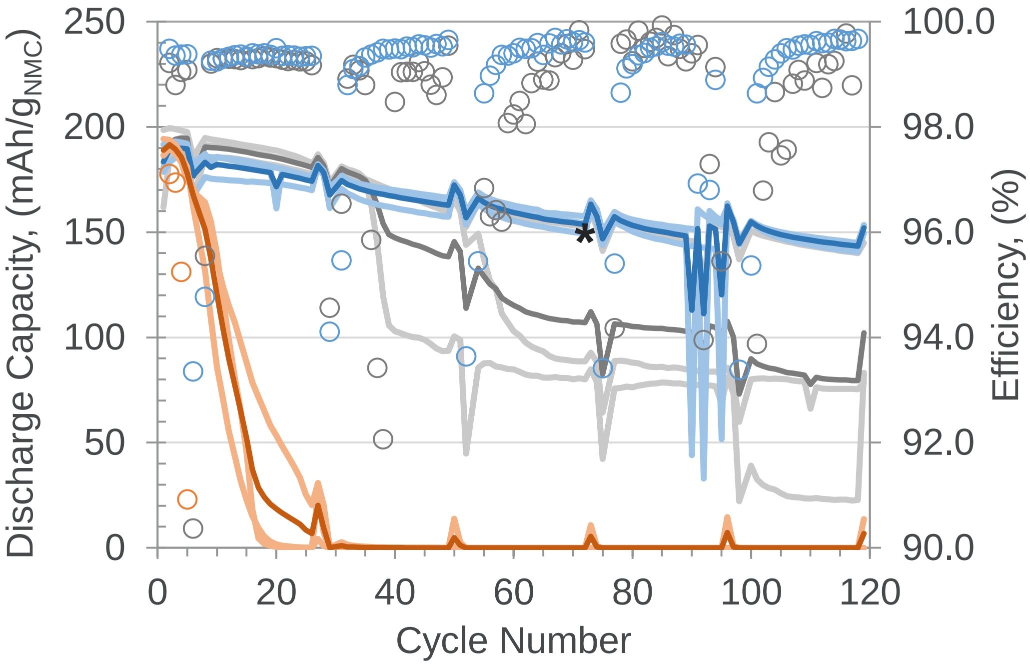
5th Cycle

	Ch. Cap (mAh/g)	Disch. Cap. (mAh/g)	CE (%)
Gen2	196 ± 3	195 ± 3	99.1
E1	191 ± 3	190 ± 2	99.4
E2	196 ± 3	178 ± 3	90.9

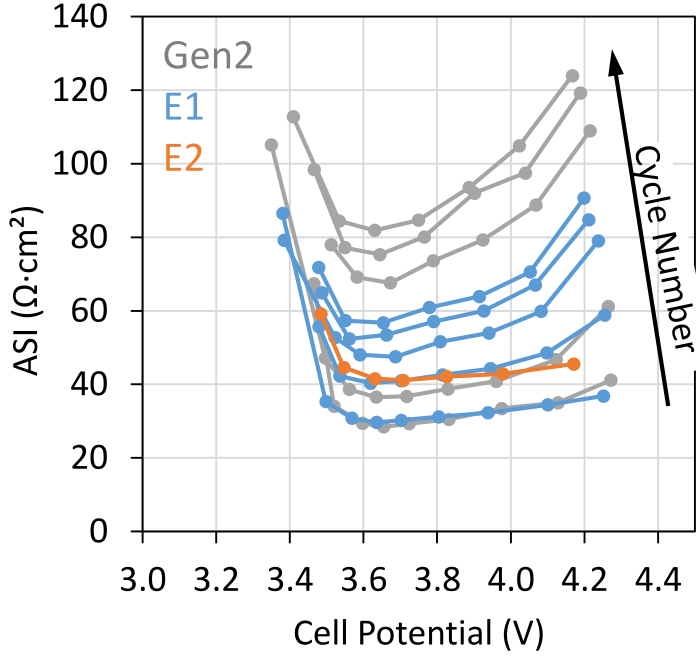
(error bars are ± 1σ, n = 3)
Capacity per gram NMC532

- Differential capacity plot during 1st formation cycle is a good indicator to check the stability of electrolyte and/or additives in LIB.
- The 1st cycle redox peaks around 3V vary from electrolyte to electrolyte, even with same electrode couples, which could affect the electrochemical performance.

Gr/NMC532 CYCLING



Voltage window: 3.0 to 4.5 V



- The Gr/NMC532 full cells with E2 electrolyte has worst cycle performance.
- However, the Gr/NMC532 full cells with E1 electrolyte showed enhanced capacity retention relative to Gen2.
- Correspondingly, ASI of Gr/NMC532 full cells with E1 electrolyte grows less during cycling compared to Gen2 electrolyte.

RESPONSE TO PREVIOUS YEAR REVIEWERS’ COMMENTS

No reviewers’ comments from FY2018 AMR

COLLABORATION

- The partners and collaborators include
  - National labs: Argonne, BNL, ORNL
  - Universities: IUPUI, University of Missouri, The George Washington University, Western Michigan University
  - Industries: BTR, Cabot, Osaka Titanium Corp., OSiAlC, Paraclete Energy, Shenzhen Capchem Tech., Silican, SiNode, Superior Graphite Co., Targray, Toda Kogyo
- The CAMP Facility is open to work with industries to advance the LIB technologies for EV application.

REMAINING CHALLENGES AND BARRIERS

- High energy active material identification and acquisition remain a challenge.
  - Existing commercial active materials can’t meet or exceed DOE/USABC the goals.
  - Getting access to advanced active materials is not always successful.
- As a benchmarking activity, the focus of this work is to simply validate the performance of cell materials (including electrochemical and thermal properties).
  - However, necessary understanding is inevitable.
  - A good balance between the validation and research needs to be fine-tuned.

FUTURE PLAN

- Finish prelithiation studies with LFO. Continue the prelithiation of anode electrode and/or powder.
- The focus will continue to acquire and characterize high energy anode/cathode materials,
  - New active materials, including new binders, electrolytes/additives, and advanced conductive additives to address the volume expansion and related capacity fading.
  - Thermal properties of high energy anode/cathode materials will be investigated.
- Continue to work closely with research institutions and industrial suppliers to enable the LIB technology for EV applications.

SUMMARY

- The capacity fading during both cycling life and calendar life tests were observed.
  - The capacity fade of the SiO/NCM532-LFO cells appear to be time-dependent, not cycle-number-dependent.
  - The detailed voltage profile and ASI change before and after rest suggest that the parasitic reaction on SiO electrode is root cause for capacity fading
- High nickel content (~90%) NMC and NCA were tested.
  - These two materials can deliver as high as 210 mAh/g capacity with 4.3 V vs. Li/Li^+ cut-off voltage, which is equivalent to >800 Wh/kg.
  - The capacity retention is above 93% in 50 cycles.
  - At same state of charge, different thermal behavior was observed.
- Two commercial high voltage electrolytes were tested using Gr/NMC532 full cells. One electrolyte outperformed internal standard Gen2 electrolyte.

CONTRIBUTORS AND ACKNOWLEDGMENTS

Argonne

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- Yang, Zhenzhen
- Zhang, Lu
- Zhang, Zhengcheng (John)

Facilities

- Advanced Photon Sources
- Battery Manufacturing Facility (ORNL)
- Center for Nanoscale Materials
- Material Engineering Research Facility (MERF)
- Post Test Facility (PTF)

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