MATERIALS BENCHMARKING ACTIVITIES FOR CAMP FACILITY

Project ID: BAT028

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VEHICLE TECHNOLOGIES OFFICE
ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING
WASHINGTON, D.C.
JUN 2ND, 2020

OVERVIEW

Timeline

- Start – Oct. 1st 2014
- Finish – Sep. 30th 2021
- 80% complete

Budget

- Total project funding in FY2019: $550K (as part of CAMP effort)
- 100% DOE

Barriers

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

Partners and Collaborators

- Coordinated effort with DOE-EERE-VTO BTMS, Next Generation Anodes, Next Generation Cathodes, ReCell, XCEL (INL, LBNL, NREL, ORNL, PNNL, SLAC, SNL)
- Argonne Facilities: MERF, EADL, CNM & PTF
- See Collaboration list at 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

- High energy density LIB using SiO with good cycle life was developed using CNT as an conductive additive.
- Completed method development for pre-lithiation of graphite powder & electrode via electrochemistry.
- Electrochemical characterization of 6K Inc NMC622 (DOE phase II) was completed.
- Performed molten lithium soldering onto LLZO disk with mixed results.
- Initiated solid-state-electrolyte and hybrid composite polymer scale-up design for roll to roll coating (**see BAT030**).

MILESTONES

Milestone	Planned End Date	Type	Status
Develop methods to fabricate pre-lithiated high-energy electrode couples on pilot-scale coater in dry room	9/30/2019	Quarterly Progress	Completed
Measure electrochemical performance of LLZO ceramic in symmetric lithium cells as a function of temperature	3/30/2020	Annual Progress	Delayed (Covid-19)

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.

USABC Requirements of Energy Storage Systems for EV

Characteristics at EOL	Unit	Cell level
Peak discharge Power Density (30 Sec)	W/L	1500
Peak Specific discharge Power (30 Sec)	W/kg	700
Peak Specific Regen Power (10 sec)	W/kg	300
Available Energy Density @ C/3 discharge rate	Wh/L	750

Test Protocol development

Electrochemical testing condition, such as C-rate and pulse current, was calculated for coin cells according to EV requirements.

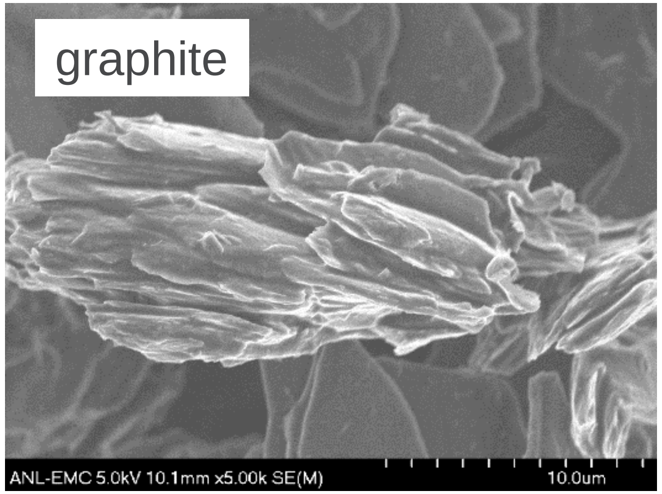
United States Advanced Battery Consortium Battery Test Manual For Electric Vehicles, U.S. Department of Energy Vehicle Technologies Program, Revision 3, INL, June 2015

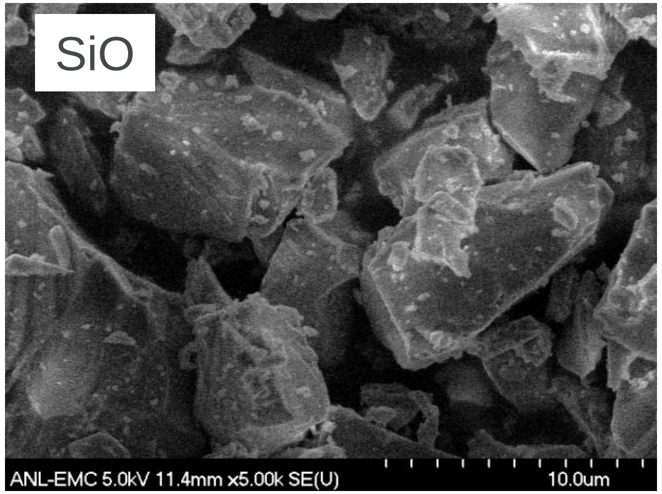
OBJECTIVES

- 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.

GRAPHITE-SiO COMPOSITE ANODE

- Silicon monoxide (SiO) can be considered having active Si nano-domain dispersed in inactive SiO_2 nano-domain, resulting in lower volume fluctuation with cycling than pure Si, which allows the use of larger particles without pulverization.
- We explore graphite-SiO (Gr-SiO) blend electrodes prepared by simple planetary slurry mixing. Comparable particle size of graphite and SiO were used in this work. We tune slurry formulations with the goal to optimize energy density and capacity retention.





GRAPHITE-SiO COMPOSITE ANODE

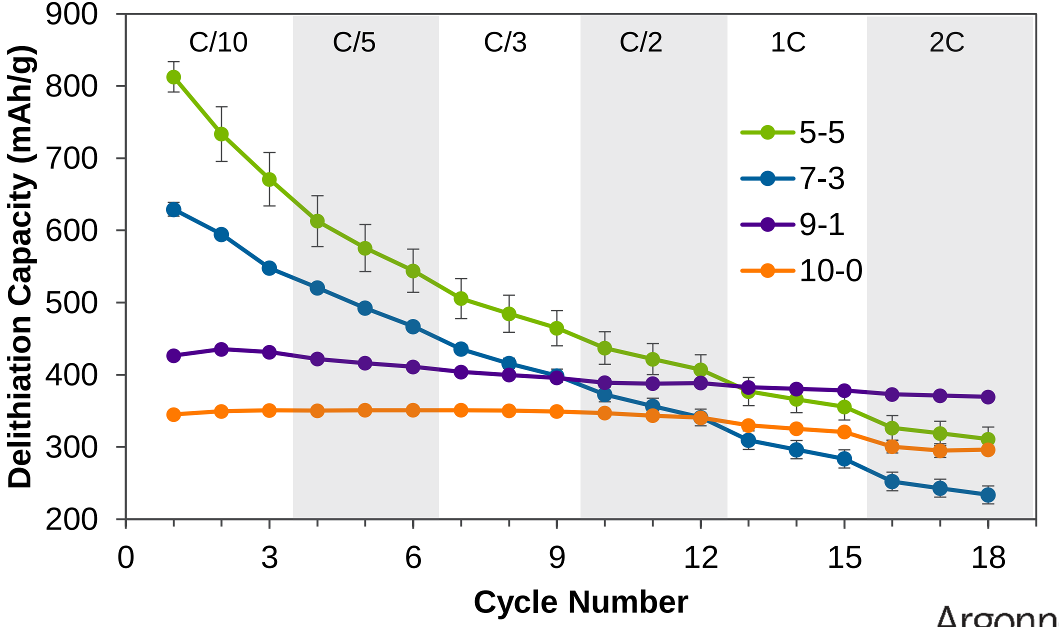
Carbon black (CB) conductive additive

- Graphite-SiO blend electrode was fabricated using commercial carbon black. The binder content in the composite electrode was adjusted with carbon black amount to ensure the optimized electrode integrity.
- Reasonably good performance is obtained when the Gr-SiO weight ratio is (9-1). Electrodes with (5-5) and (7-3) weight ratios display very fast capacity fade.

Electrode Composition

(Gr:SiO)-binder-CB	XL20	SiO	LiPAA	PVDF	C45	Theoretical capacity, mAh/g of Gr + SiO
(10-0)-6-2	92%	0%		6%	2%	372
(9-1)-10-2	79%	9%	10%		2%	506
(7-3)-14-3	58%	25%	14%		3%	773
(5-5)-18-4	39%	39%	18%		4%	1040
(0-1)-20-10	0%	70%	20%		10%	1710

Half Cell Testing: 10mV – 1.5V

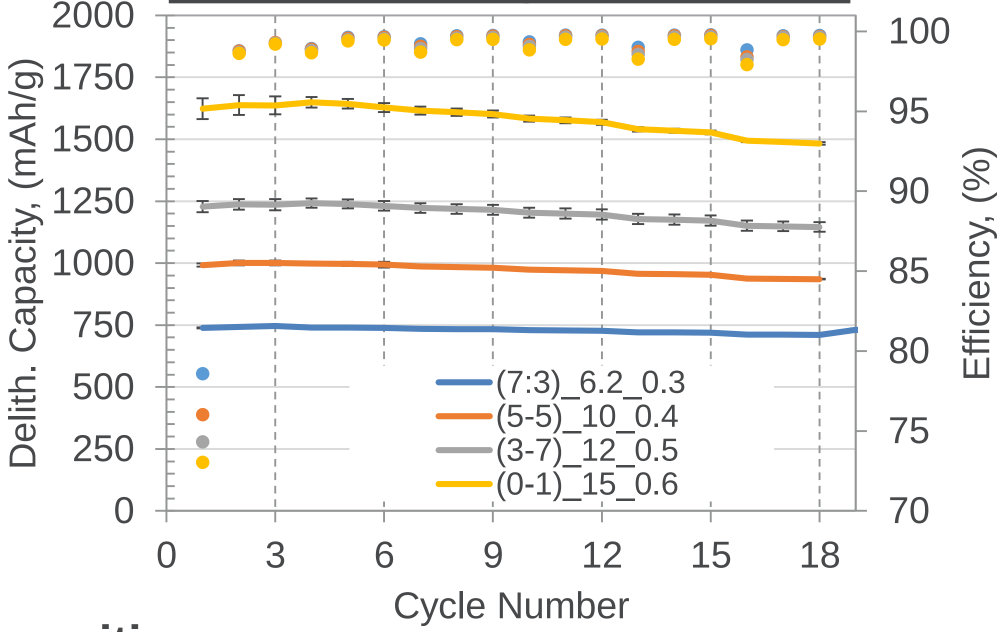


GRAPHITE-SiO COMPOSITE ANODE

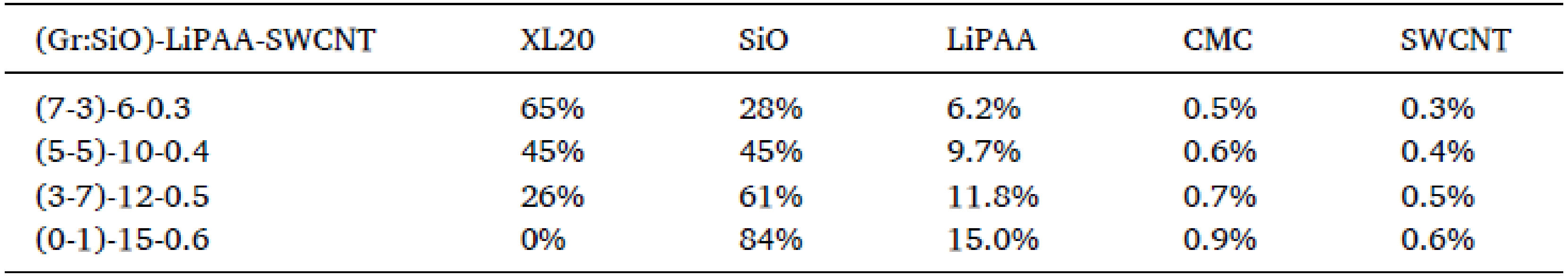
Single Wall Carbon Nano Tube (SWCNT) as conductive additive

- The capacity retention of the Gr-SiO blend electrodes with SWCNT conductive additive are significantly improved relative to the previous formulations with CB conductive additive.
- The good capacity is even obtained for SiO alone without graphite.

Half Cell Testing: 10mV – 1.5V



Electrode Composition

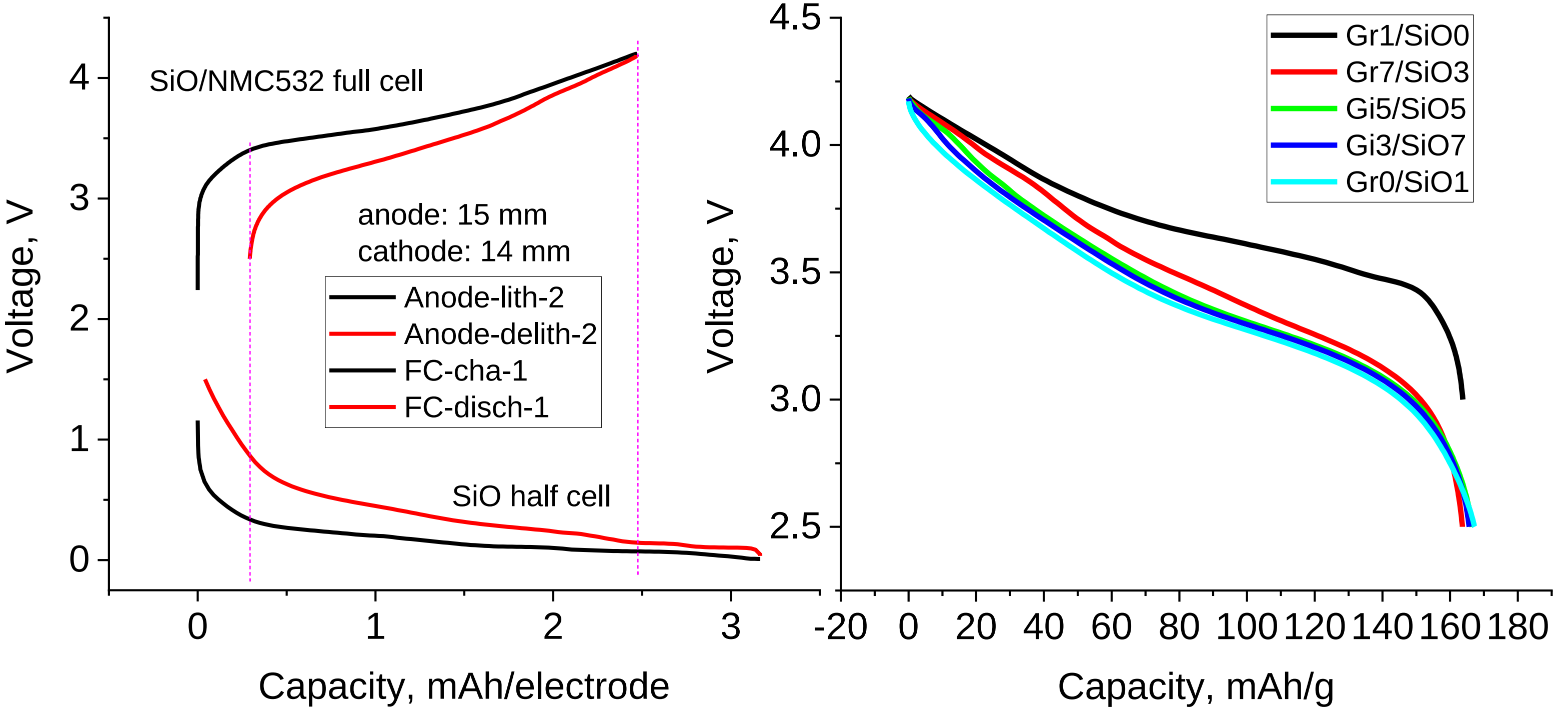


(Gr:SiO)-LiPAA-SWCNT	XL20	SiO	LiPAA	CMC	SWCNT
(7-3)-6-0.3	65%	28%	6.2%	0.5%	0.3%
(5-5)-10-0.4	45%	45%	9.7%	0.6%	0.4%
(3-7)-12-0.5	26%	61%	11.8%	0.7%	0.5%
(0-1)-15-0.6	0%	84%	15.0%	0.9%	0.6%

GRAPHITE-SiO COMPOSITE ANODE

Gr-SiO/NMC532 full cell with pre-lithiated Gr-SiO

- Pre-lithiation of Gr-SiO blend anodes were used to fabricate full-cells using CAMP NMC532 electrode.
- Only 30 wt.% SiO in gr-SiO blend anode significantly lowers the average voltage of full cell.
- Further increasing the SiO does not change full cell average voltage too much.

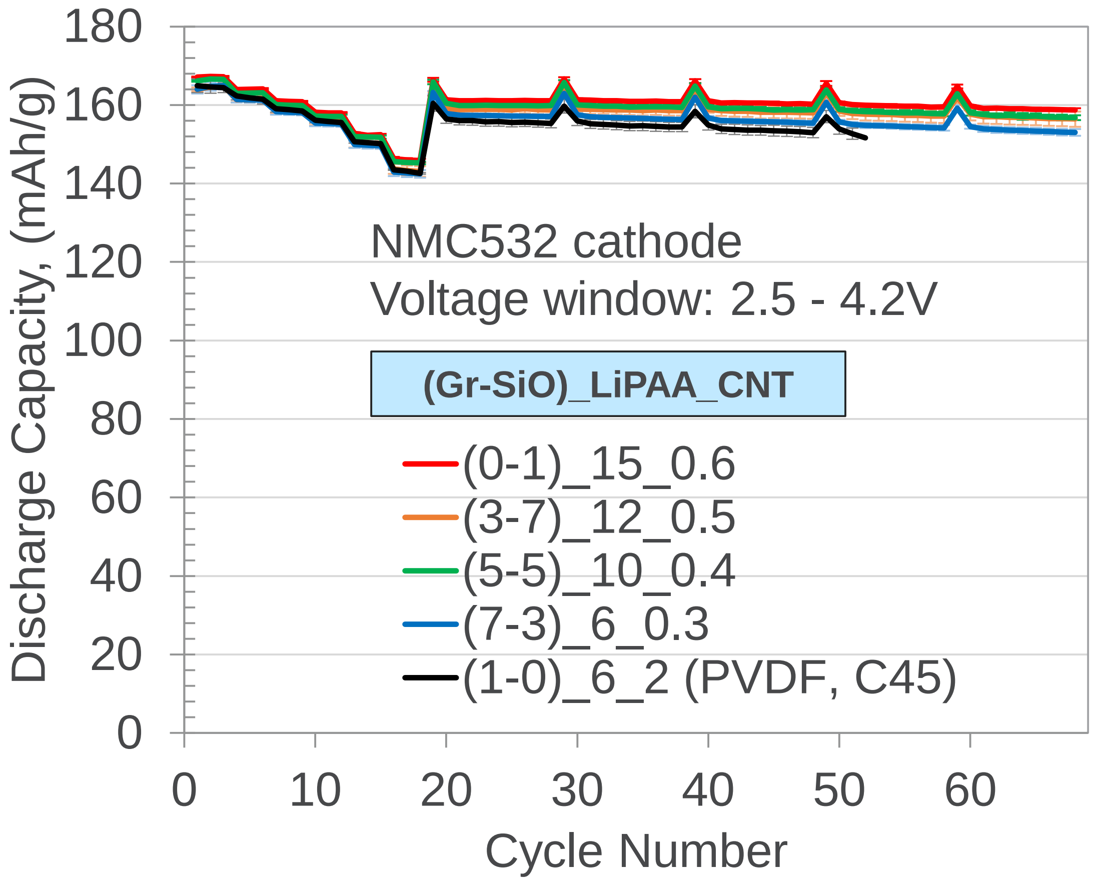


SiO w/ Pre-Lithiation

SiO Content Effect On Full Cell Voltage Profile

GRAPHITE-SiO COMPOSITE ANODE

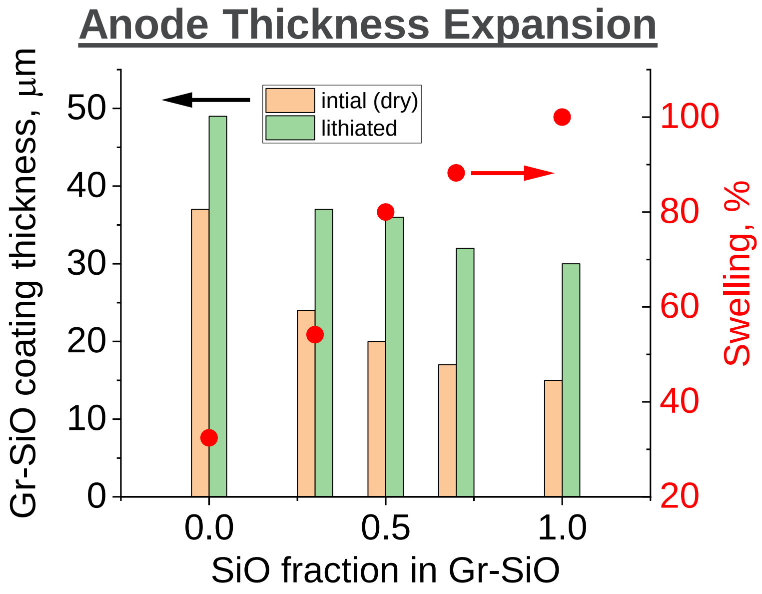
Gr-SiO/NMC532 full cell cycling performance

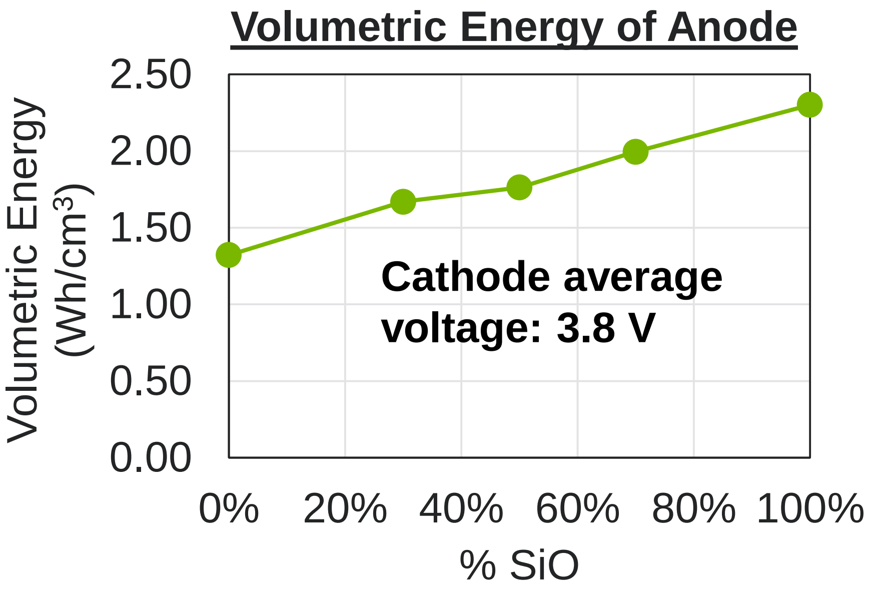


- All full-cells with Gr–SiO anode (pre-lithiated) using SWCNT exhibit comparable rate capability (first 18 cycles) to the standard graphite anode with CB conductive additive.
- Full-cell capacity retention is also comparable or even better for all cells containing the optimized Gr–SiO anodes relative to the control graphite anodes with CB additive.

GRAPHITE-SiO COMPOSITE ANODE

Gr-SiO electrode volume change and energy density calculation


Anode Thickness Expansion


Volumetric Energy of Anode

- Both the laminate swelling and increasing average voltage have the effect of decreasing volumetric energy of full cell when SiO is used as anode.

$$Volumetric\ energy\ density\ of\ anode = \frac{Anode\ capacity\ \times (V_{cathode} - V_{anode})}{Volume\ of\ anode}$$

- Significant improvements in anode energy density were achieved for all Gr–SiO blend formulations relative to the SiO-free graphite electrode, ranging from 26% improvement for the (7-3) formulation to 74% improvement for the graphite-free SiO formulation.

ELECTRODE PRE-LITHIATION

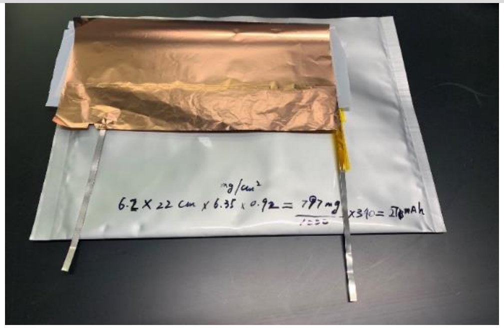
- The low 1st cycle coulombic efficiency of silicon electrodes results in a significant portion of lithium from the cathode to be used for irreversible reactions, leading to a significant lithium loss and low energy density of a full cell.
- Previously, we have successfully demonstrated the use of Li_5FeO_4 (LFO) to compensate the initial capacity loss of silicon monoxide (SiO). However, dead weight left by the pre-lithiation agent adversely affects the energy density of LIB.
- In this work, we explored the electrochemical pre-lithiation of anode materials as both electrode and powder forms.

GRAPHITE ELECTRODE PRE-LITHIATION

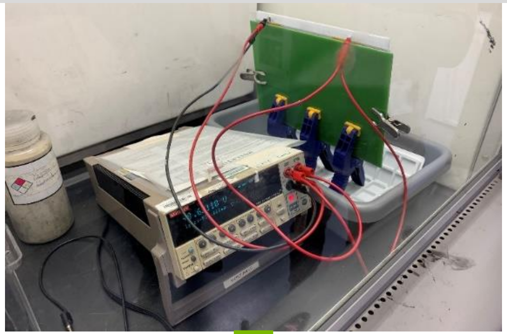
Experiment operated in dry room

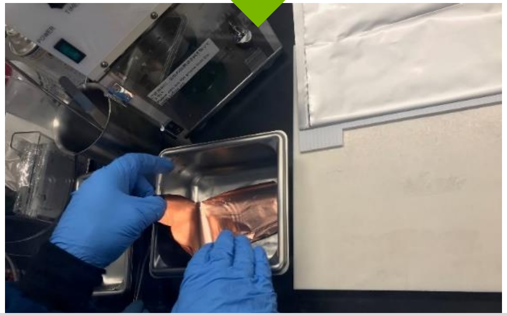
- Graphite electrode sheet was assembled against lithium foil and put into a large pouch cell.
- Constant current (C/10) was used for lithiation.
- The lithiated graphite electrode showed no sign of delamination and could be handled just like a pristine electrode.

Graphite electrode
6.2 cm x 12 cm
Coating 42 µm, 6.35 mg/cm²



Graphite half cell was put into an open pouch cell and charged using source meter at C/10 rate





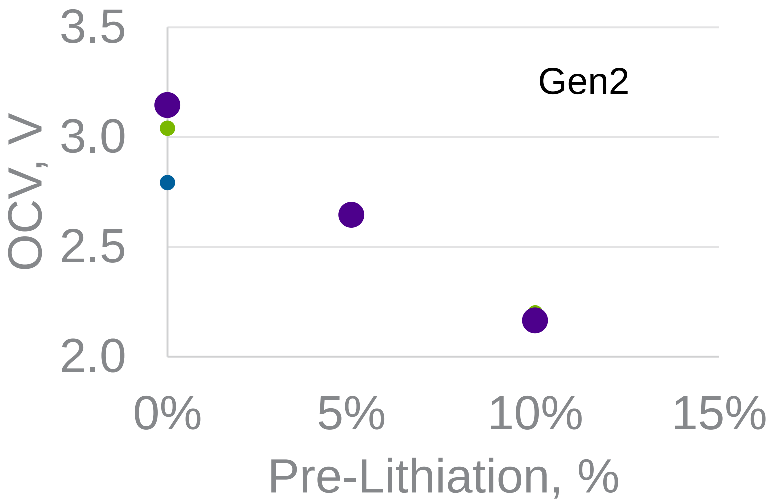
The charged electrode was rinsed using EMC solvent

The rinsed electrode was dried for testing.

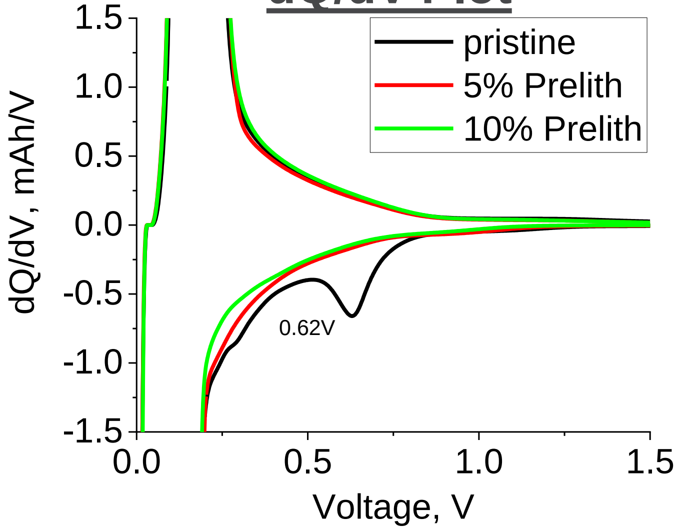
GRAPHITE ELECTRODE PRE-LITHIATION

Pre-Lithiated graphite characterization in half cell

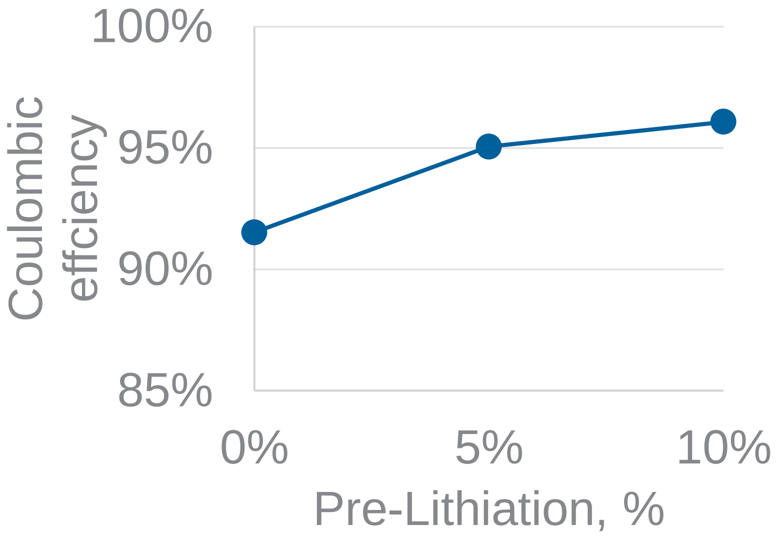
Open Circuit Voltage



dQ/dV Plot



Coulombic Efficiency

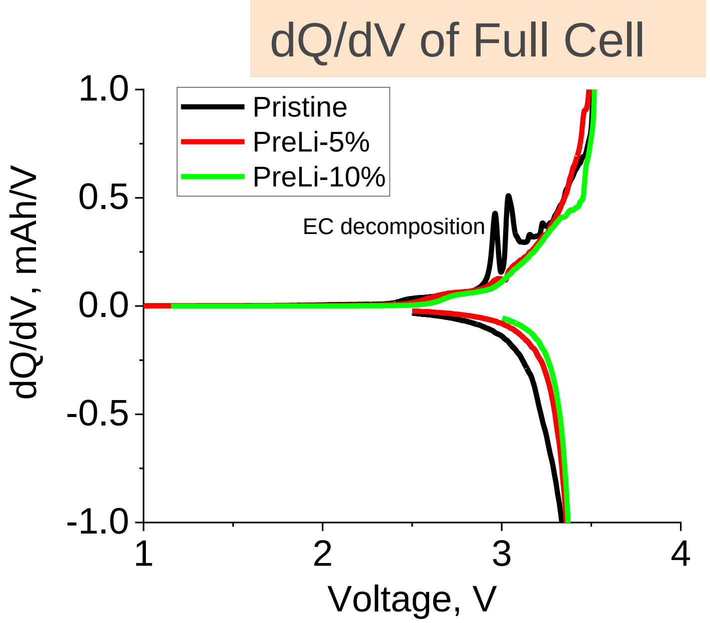


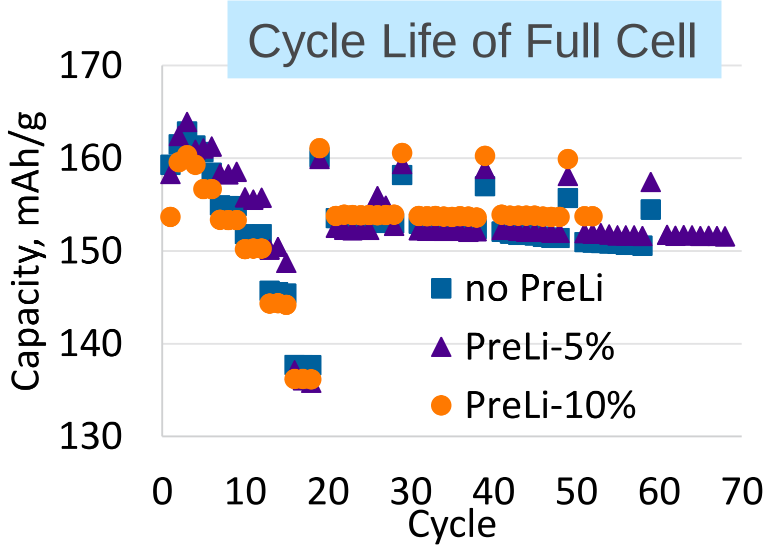
- The OCV of pre-lithiated graphite decreases with increasing pre-lithiation suggesting successful lithiation.
- With 5% and 10% pre-lithiation, the SEI formation peak at 0.62 V disappeared.
- 1st cycle Coulombic efficiency also increases with increasing pre-lithiation.

GRAPHITE ELECTRODE PRE-LITHIATION

Gr/NMC532 full cell testing

- The pre-lithiated graphite electrodes were tested in full cell against NMC532.
- Similar to half cell, the SEI formation peak on pre-lithiated graphite (5% and 10% pre-lithiation) electrode is also absent in full cell.
- There is almost no difference in terms of cycle performance between full cells with and without pre-lithiated graphite electrode.

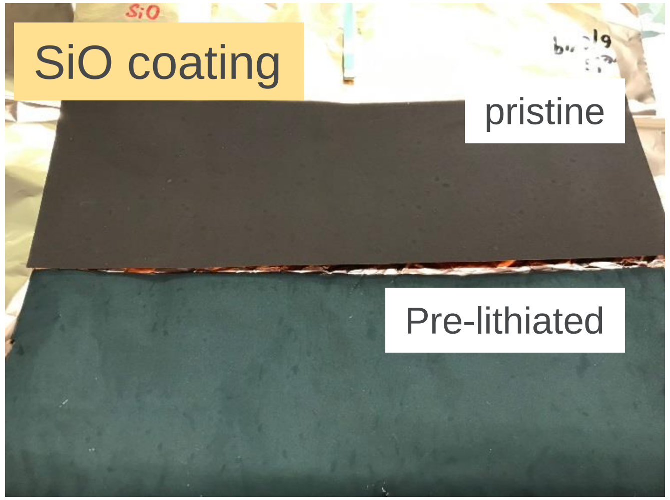




SiO ELECTRODE PRE-LITHIATION

SiO/CNT/LiPAA:
83%/0.6%/16%
Capacity: 480 mAh
C/10: 48 mA
30% pre-lithiation: 3 hr

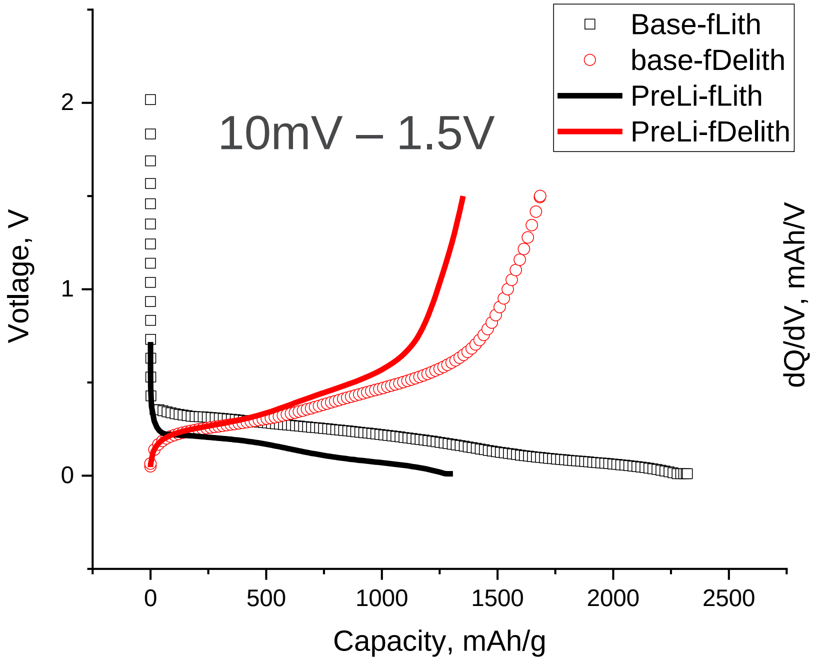
- SiO electrode was electrochemically pre-lithiated just like graphite electrode.
- 30% pre-lithiation on SiO electrode was applied at C/10 to compensate its capacity loss.
- The color of SiO electrode changed from brown to black after 30% pre-lithiation, indicating successful pre-lithiation.
- We observed the wrinkle on the back of Cu current collector, which may be due to the stress caused by the volume expansion of SiO electrode.



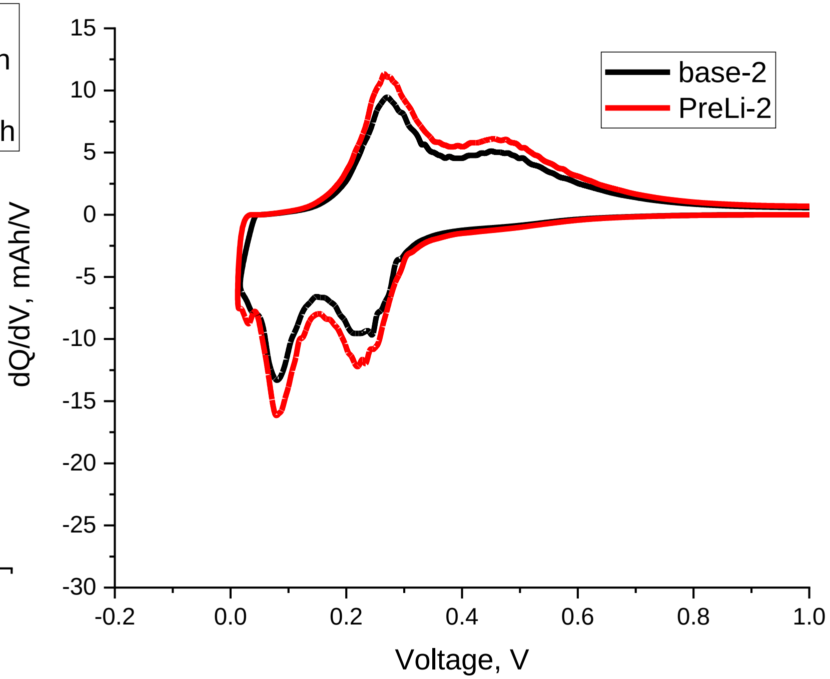
SiO ELECTRODE PRE-LITHIATION

Half cell formation

1st Formation Cycle of Pristine and Pre-Lithiated SiO Electrode



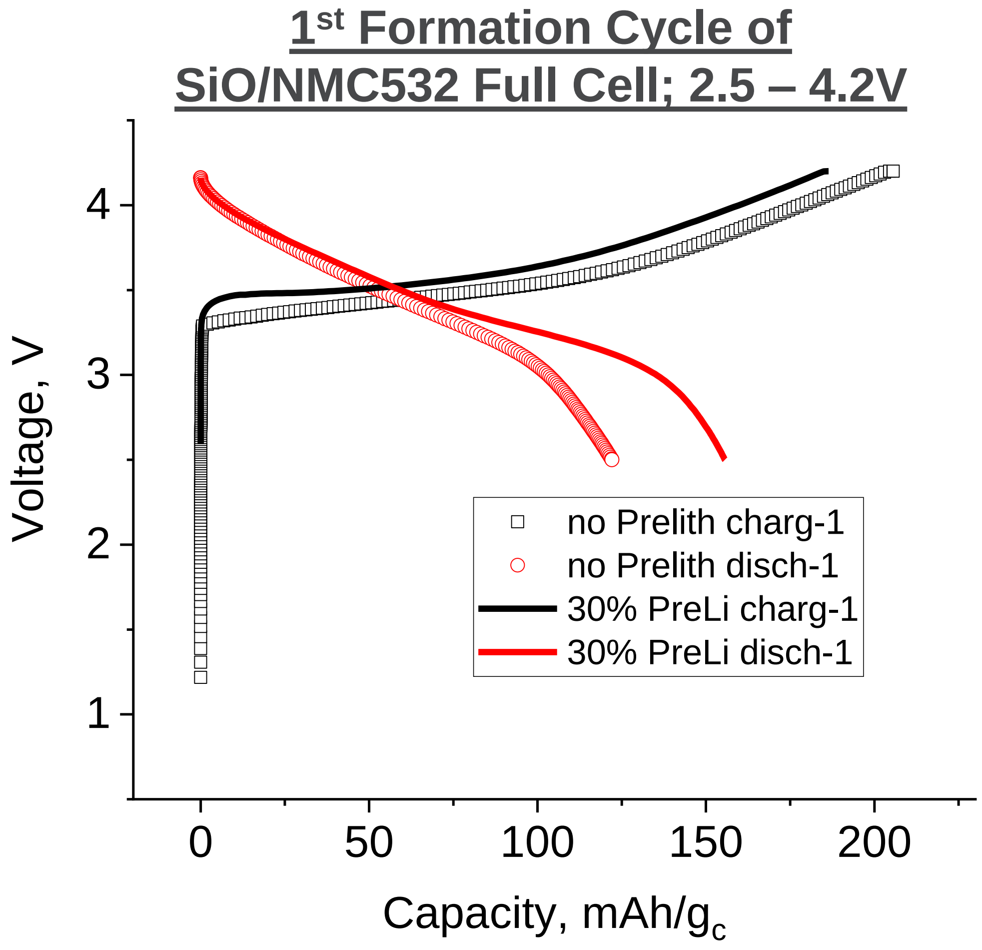
dQ/dV Plot of 2nd Formation Cycle of Pristine and Pre-Lithiated SiO Electrode

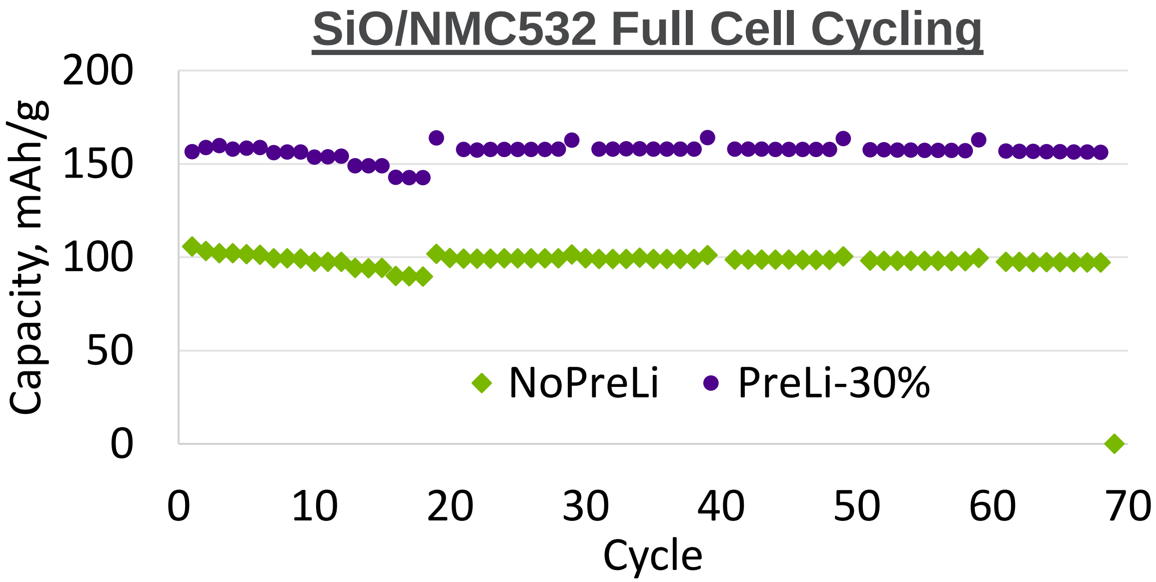


- The 1st cycle Coulombic efficiency of Li/SiO half cell increased from 70% to 100% after pre-lithiation.
- Almost identical differential capacity plots were obtained for both pristine and pre-lithiated SiO electrodes.

SiO ELECTRODE PRE-LITHIATION

Full cell testing



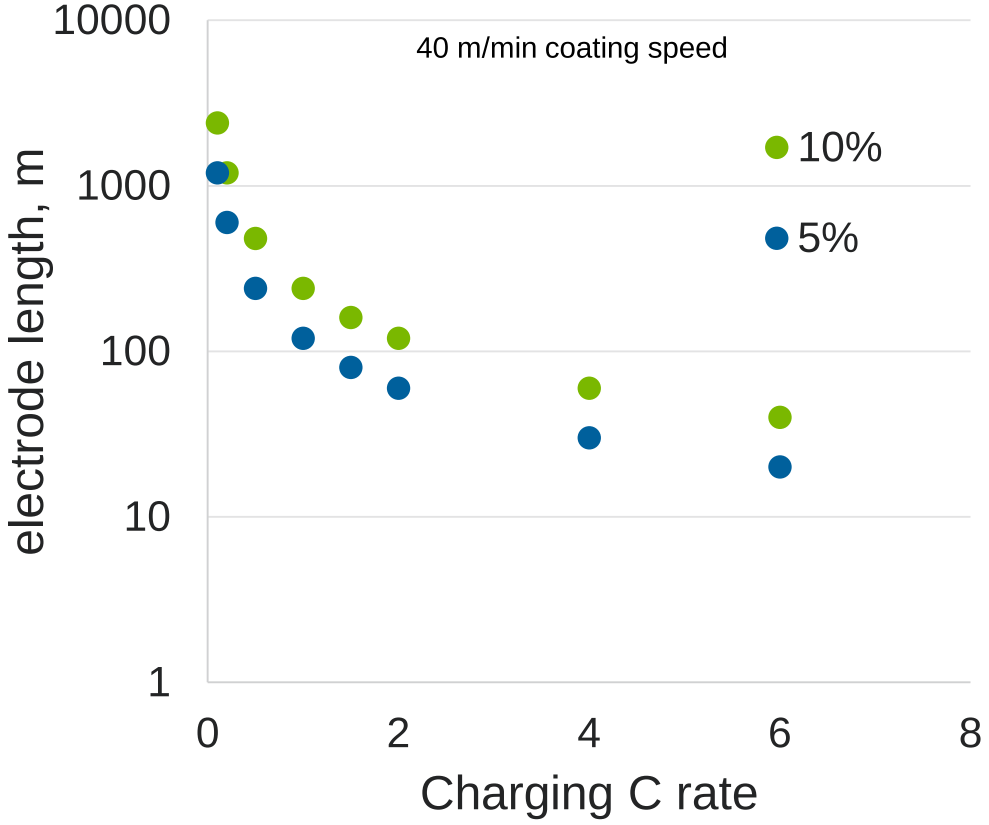


- The initial Coulombic efficiency of full cell increased from 60% to 83% for pre-lithiated SiO electrode.
- The cycle life of full cell containing SiO electrode w/ and w/o pre-lithiation are comparable and stable.

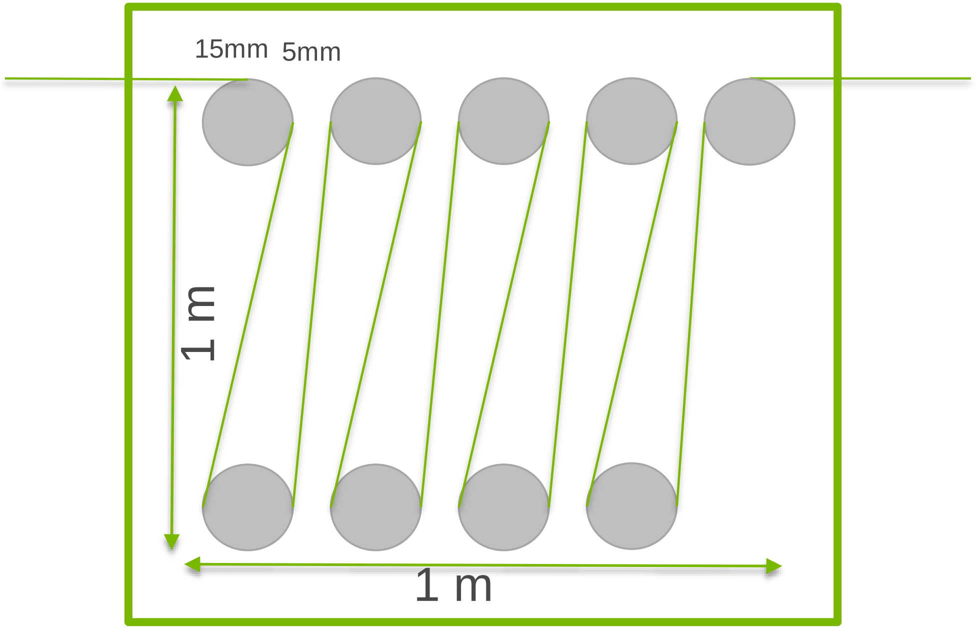
ELECTRODE PRE-LITHIATION

Lithiation speed challenging

Electrode Length vs. Charging Rate



Design to Reduce the Pre-Lithiation Space



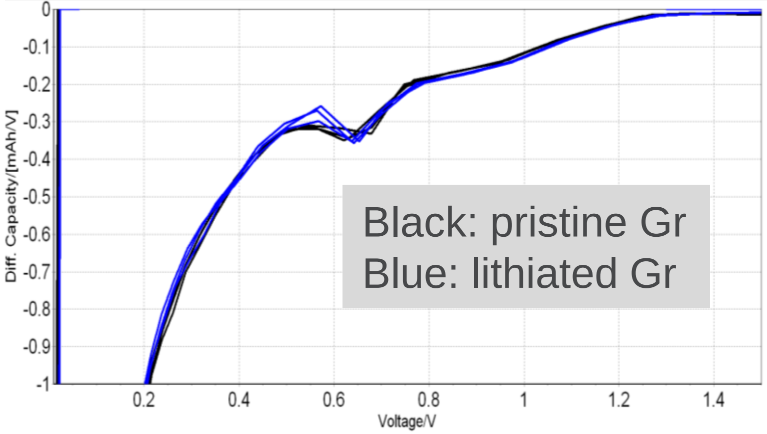
- In order to match the fast electrode coating speed (40 m/min), as long as 120 m electrode needs to be immersed in electrolyte for pre-lithiation, even with 2C charging rate for 10%, which will take a large footprint.

GRAPHITE POWDER PRE-LITHIATION

- Pre-lithiation setup:
  - Working electrode: graphite powder in copper beaker
  - Counter electrode: metal rod covered by lithium foil
  - Electrolyte: 1.2M $LiPF_6$ in EC/EMC
- Both constant current and constant voltage lithiation were attempted.
- Pre-lithiated graphite powder was rinsed and dried for electrochemical testing.
- The electrolyte reduction peak at 0.62 V appeared for both pristine and pre-lithiated graphite, suggesting that the pre-lithiation of powder was not successful.

Graphite Powder Lithiation Set-Up

dQ/dV of Prelithiated Graphite Powder



DOE SBIR PHASE II MATERIALS – 6K INC

6K Inc NMC 622 Material Evaluation

- 6K Inc produced NMC 622 powder using their patented UniMelt® system; a high frequency microwave based plasma process that allows for low cost, continuous flow, quick production of highly sustainable engineered advanced high performance material for Li-ion batteries.
- CAMP received 6K Inc NMC 622 powder **[d50=28µm; Li=0.99; Uncoated material]**, coated an electrode from the powder, and assembled half and full coin cells with it for electrochemical testing and performance validation.

CAMP made
6K Inc NMC 622 Electrode

89.9 wt% 6K Inc. NMC 622
5.05 wt% Timcal C-45
5.05 wt% Solvay 5130 PVDF

Estimated Areal Capacity
~1.66 mAh/cm^2

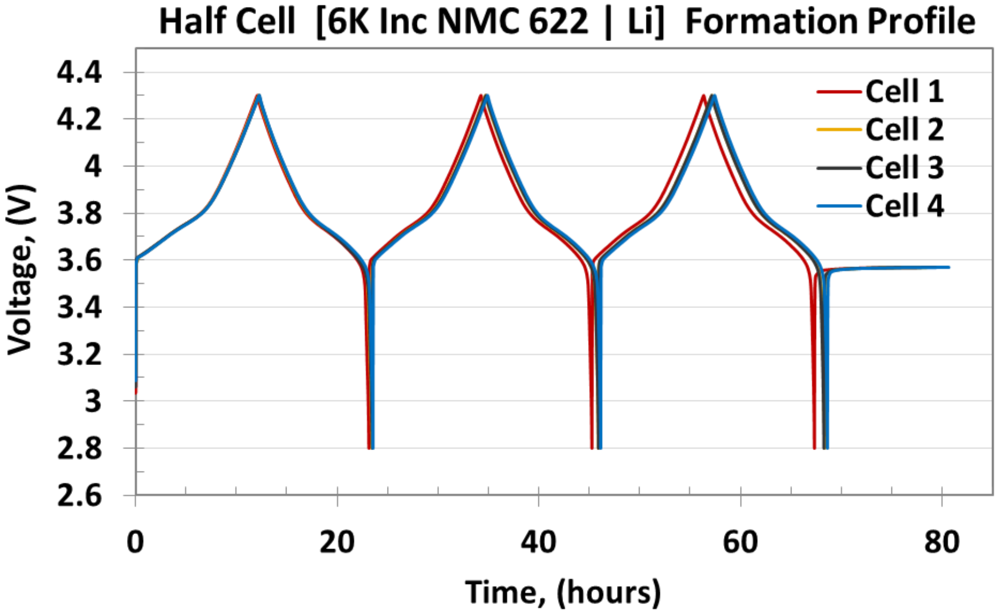
DOE SBIR PHASE II MATERIALS – 6K INC

Half Cell - Coin Cell Testing

Gen 2 Electrolyte = 1.2M $LiPF_6$ in EC:EMC (3:7 wt%)

Averaged Half Cell Data	Formation C/10 Cycles				Rate Study				
	1st Cycle Charge (mAh/g*)	1st Cycle Efficiency	3rd Cycle Discharge (mAh/g*)	Capacity Loss (mAh/g*)	Reversible Discharge Capacity (mAh/g*)				
					C/24	C/10	C/5	C/2	1C
6K Inc, 2.8-4.3V	194 (2.92 mAh)	92 %	177 (2.66 mAh)	17	179	173	168	161	155
Vendor A, 3.0-4.3V	197 (2.71 mAh)	89 %	179 (2.46 mAh)	18	182	178	173	166	160

* Grams of active cathode material



NMC 622 [14mm] | Li Metal [15.6mm],
PP:PE:PP Separator [16mm],
Gen 2 Electrolyte [1:4:4 drops (~100 µL Tot)],
cycled at 30°C

- 6K Inc half cell electrochemical data looked aligned with expected capacity.
- Matched an anode to the 6K Inc NMC 622 cathode and made full cells to test.

DOE SBIR PHASE II MATERIALS – 6K INC

Full Cell – Coin Cell Testing

- CAMP electrochemically cycled the full cells through a series of tests: Formation, Rate Study, HPPC, and Life Cycle.

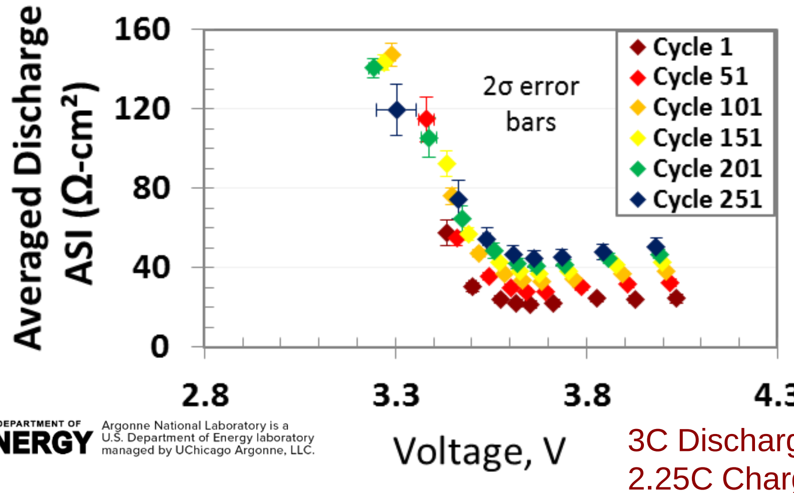
Formation and Rate Study Results

* Grams of active cathode material

Averaged Full Cell Data	Formation C/10 Cycles				Rate Study				
	1st Cycle Charge (mAh/g*)	1st Cycle Efficiency	3rd Cycle Discharge (mAh/g*)	Capacity Loss (mAh/g*)	Reversible Discharge Capacity (mAh/g*)				
					C/24	C/10	C/5	C/2	1C
6K Inc, 2.8-4.2V	**190** (2.86 mAh)	**87 %**	**171** (2.58 mAh)	**19**	**172**	**168**	**164**	**160**	**155**
Vendor A, 3.0-4.2V	**197** (2.73 mAh)	**83 %**	**165** (2.29 mAh)	**32**	**164**	**162**	**159**	**155**	**151**

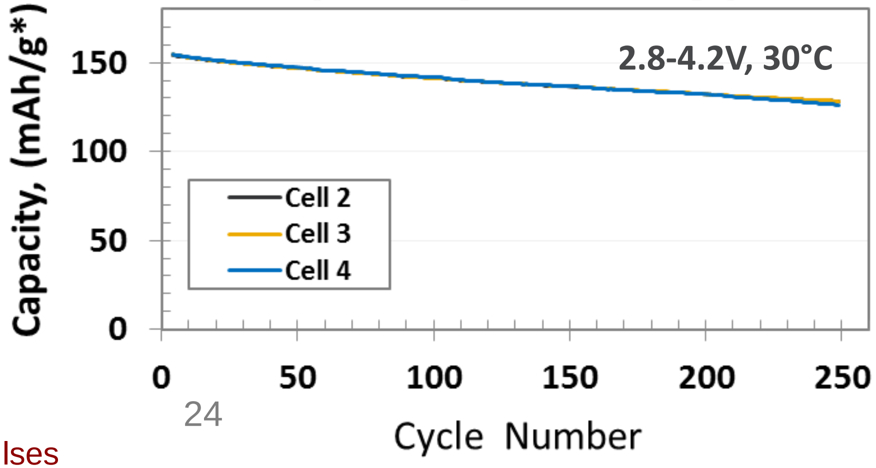
**NMC 622 [14mm]| Graphite [15 mm]
PP:PE:PP Separator [5/8"] ,
5:12:12 µL of Gen 2 Electrolyte,
cycled at 30°C**

Life Cycle with HPPC Results - 6K Inc Only



3C Discharge,
2.25C Charge Pulses

**Discharge Capacity from Life Cycling
[C/3 Charge, C/2 Discharge]**



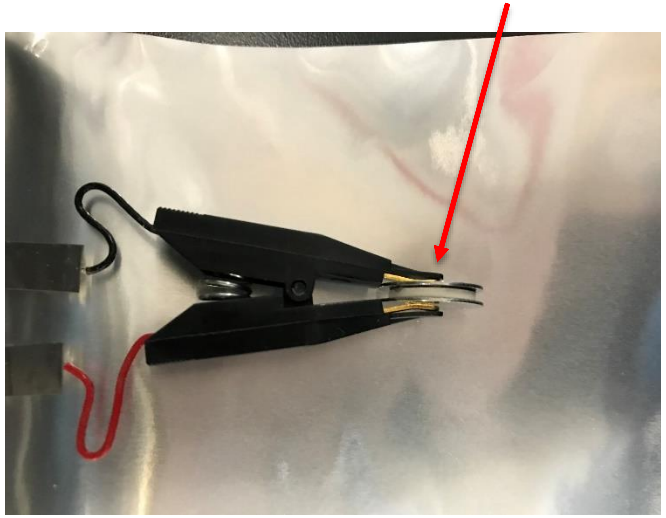
- **6K Inc material showed a discharge capacity retention of ~82.6% which is on par with Vendor A's performance of ~86.9% after ~250 cycles in a coin cell.**

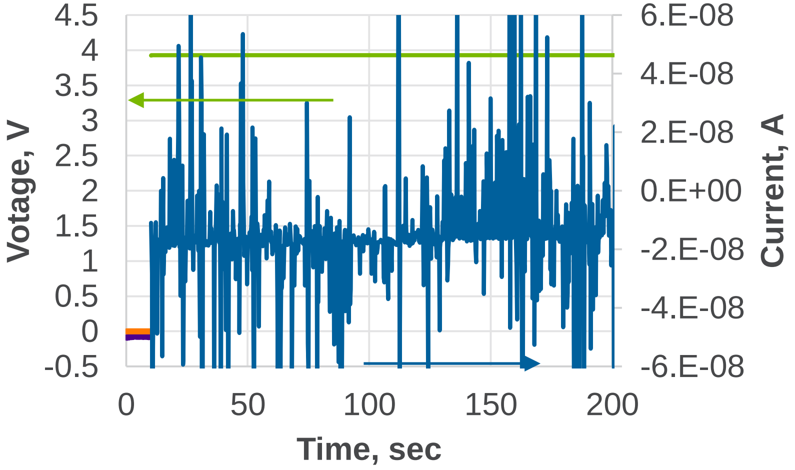
SOLID STATE ELECTROLYTE EFFORT

Sintered LLZO pellet at ANL

- The Li/LLZO/Li cell was assembled and sealed in pouch in dry room at the CAMP facility.
- The conductivity measurement of Li/LLZO/Li was tested at 75ºC.
  - Constant voltage was applied to the pouch cell and current response was recorded.
  - Noisy current with average of 2e^{-8} A (20 nA) was obtained.
- The measured low conductivity of LLZO is due to very thick pellet and poor connection between the pellet and Li foil. We are working to address these deficiencies.

Li/LLZO/Li Assembly





RESPONSE TO PREVIOUS YEAR REVIEWERS’ COMMENTS

Comments: Most reviewers agreed that this project is relevant to DOE objectives to support the early stage EV research and development and adopted a well-designed and feasible approach to address the barrier.
However, some reviewers are not clear how the test results for all materials will be summarized and communicated.

Response: For this project, we evaluate all kinds of available materials: cathode, anode, electrolyte and additive, separator, current collector, conductive additive, binder, etc., using internal developed protocol toward EV application. The annual report typically falls into following two categories.

1. Each year, we present our most relevant results related to the milestones. For instance, we showed prelthiation work and solid state electrolyte work in this report.
2. In addition to the work related to the milestones, we also highlight some interesting research results. In this report, we presented the high energy density anode development using commercially available SiO, graphite, and single wall carbon nano tube. We gain the understanding of the advanced materials and share it with community.

At last, we want to point out that not all the tested materials will be reported due to various reasons:

- The work is important to the material suppliers, but of less interested to general audience.
- The test results are not promising and not worthy of reporting.

FY19 – FY20 COLLABORATIONS

- The partners and collaborators include
  - National labs: Argonne, BNL, ORNL
  - Universities: IUPUI, University of Missouri, University of Arkansas, The George Washington University, Western Michigan University
  - Industries: 6K Inc, BTR, Osaka Titanium Corp., OSiAlC, Paraclete Energy, 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 validate the performance of cell materials (including electrochemical and thermal properties).
  - Research efforts between the validation and research needs to be balanced.

FUTURE PLAN

- We will continue solid state electrolyte (SSE) effort, focusing on its conductivity, stable voltage window, and fabrication scalability.
  - Prototype cells using two well studied oxide and sulfide SSE (LLZO, Li_6PS_5Cl) will be fabricated and tested.
- We will continue to acquire and characterize high energy anode/cathode materials.
  - New active materials, including new binders, electrolytes/additives, and advanced conductive additives.
  - 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

- We have shown that replacing carbon black conductive additive with a commercial SWCNT allows for graphite-SiO electrodes with highly stable cycling by simple planetary mixing procedures.
  - Increasing the mass ratio of SiO relative to graphite increases the volumetric energy density for all formulations, despite the higher de-lithiation potential and volume expansion of SiO compared to graphite.
- Electrochemical pre-lithiation was successfully carried out on a graphite electrode sheet and a SiO electrode sheet in dry room environment.
  - No damage and handling issues were encountered during subsequent cleaning, drying, cell fabrication, and testing.
  - According to calculation, the pre-lithiation roll-to-roll speed is challenging and needs to be addressed.
- 6K Inc material, NMC622, showed a discharge capacity retention of ~82.6% which is on par with Vendor A’s performance of ~86.9% after ~250 cycles in a coin cell.

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