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MATERIALS BENCHMARKING ACTIVITIES FOR The Cell Analysis, Modeling, and Prototyping (CAMP) FACILITY

Project ID: BAT028

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2024 U.S. DEPARTMENT OF ENERGY VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING, VIRTUAL CONFERENCE, JUNE 3RD – 6TH, 2024
VIRTUAL

OVERVIEW

Timeline

- Start – Oct. 1st, 2014
- Finish – On-going

Budget

- Total project funding (as part of CAMP effort)
  - FY2024: $400K
  - FY2025: $400K
- 100% DOE

Barriers

- Development of sustainable 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, Silicon Consortium Project (SCP), Earth-abundant Cathode Active Materials (EaCAM), ReCell, XCEL Phase II
- INL, LBNL, NREL, ORNL, PNNL, SLAC, SNL
- Argonne Facilities: APS, CNM, EADL, MERF, PTF
- See collaboration list in separate slide

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. Cell materials need to be validated internally to determine if they warrant further consideration.
- The benchmarking (validation) activities can also provide an objective opinion to material developers. Moreover, better understanding of active materials at the cell level will speed up material development efforts.

FY24 MILESTONES AND ACCOMPLISHMENTS

Milestone	Planned End Date	Type	Status
Validate novel battery materials for transportation use	12/22/2023	Quarterly Progress	Completed
Develop method to coat non-traditional composite electrolyte and/or electrodes	3/31/2024	Quarterly Progress	Completed
Provide supply of advanced prototype electrodes in Electrode Library	6/30/2024		In progress
Diagnostic studies on non-standard lithium-based battery cells	9/30/2024		In progress

Accomplishments

- New solid polymer electrolyte was developed and electrochemically tested.
- Micron-size silicon anode material development by Alkegen
- Multi-wall carbon nanotube materials (Chasm Advanced Materials) as conductive additives for lithium-ion batteries.
- Exploration of sodium-ion battery materials (cathode and anode)

APPROACH AND STRATEGY

- Collaborate with material developers and leverage Argonne's expertise in electrode design and cell testing.
- Cell materials that have an 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 protocols derived from USABC EV requirements.

United States Advanced Battery Consortium Battery Test Manual For Electric Vehicles, U.S. Department of Energy Vehicle Technologies Program, Revision 3.1, October 2020

USABC Requirements of Energy Storage Systems for EV		
Characteristics at EOL (30°C)	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

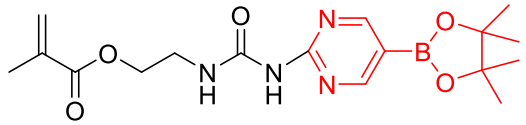
Electrochemical test protocols, such as formation, C-rate and cycle life, were established for half and full cells according to EV requirements.

OBJECTIVES

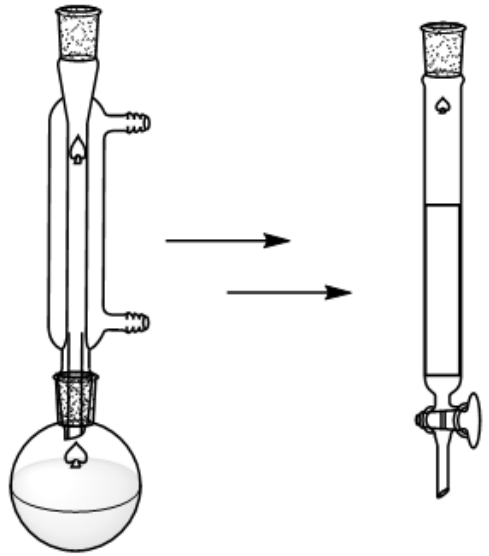
- To identify and evaluate sustainable low-cost cell chemistries that can simultaneously meet the following criteria for EV applications:
  - Electrochemical performance
  - Abuse tolerance
  - Cost
- To enhance the understanding of advanced cell components on the electrochemical performance and safety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

NEW STRUCTURES FOR SOLID POLYMER ELECTROLYTE

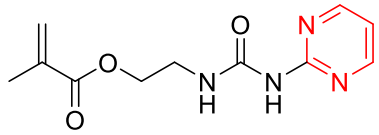
- Boric ester ureapyridine methacrylate (BU) was previously introduced as a co-cross-linking agent along with poly (ethylene glycol) diacrylate (PEGDA) to form a cross linking polymer matrix for polymer electrolyte.
  - Addition of **Bu improves ionic conductivity** of PEGA/LiTFSI polymer electrolyte**.**
- In this work, three new analogs of Bu were synthesized and characterized, with variation of moiety to adjust **solubility**, **H-bonding formation extent**, and **potential interfacial formation.**



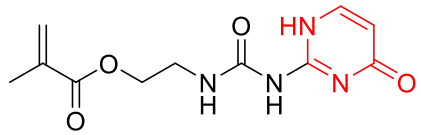
Bu



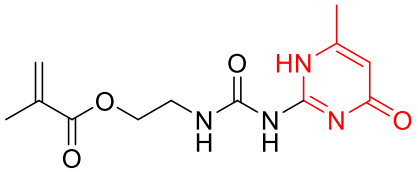
Analogs of Bu



Bu-H



Bu-C

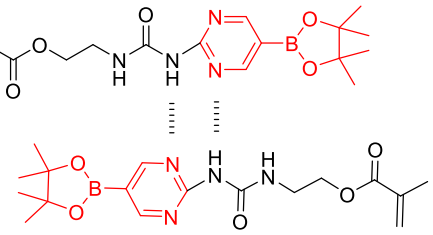


Bu-CMe

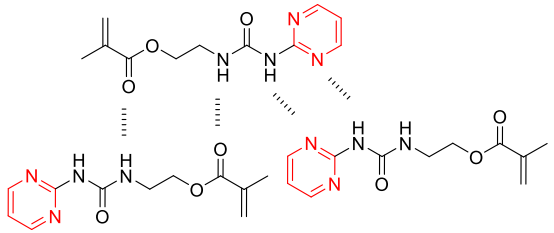
CHARACTERIZATION OF BU ANALOGS

H-bonding

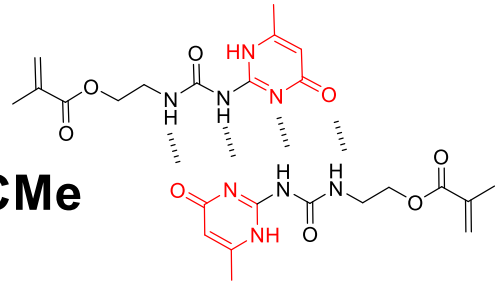
Bu



Bu-H



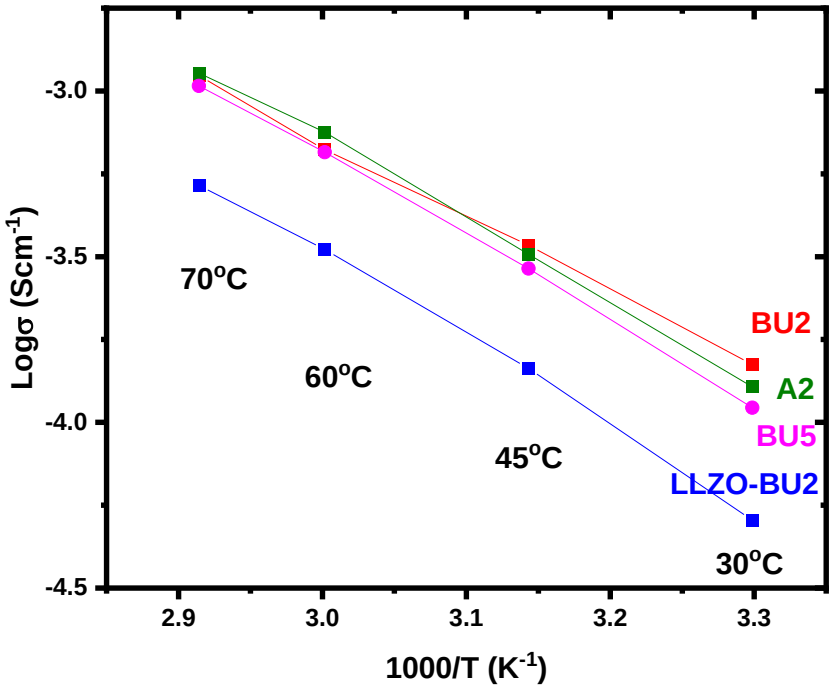
Bu-CMe



- Addition of **Bu-C** or **Bu-Cme** results in gel up of the polymer electrolyte which might be due to no solubility facilitating groups for **Bu-C** and **Bu-Cme.**
  - **Bu-CMe** shows 4 H-bonding with 2 units,
  - **Bu-H** show 4 with 3 units, and
  - **Bu** shows 2 with 2 units due to steric hindrance.
- Measured conductivities of Bu and Bu-H are all above $5*10^{-5}$ S/cm at 30°C for the PEs.
  - Slight improvement in ionic conductivity with incorporation of certain amount of Bu .

Weight%	LiTFSI	NMU	PC	PEGDA	Bu	LLZO
A2	33.3	16.6	16.9	33.2	0	0
BU2	33.3	16.6	16.5	32.9	0.7	0
BU5	32.7	19.9	13.4	32.7	0.7	0
BUH	33.1	16.6	16.4	32.9	Bu-H 0.7	0
LLZO-BU2	30.0	14.9	14.9	29.6	0.63	0.1

A2: baseline; LLZO: $Li_{6.25}La_3Zr_2Ga_{0.25}O_{12}$



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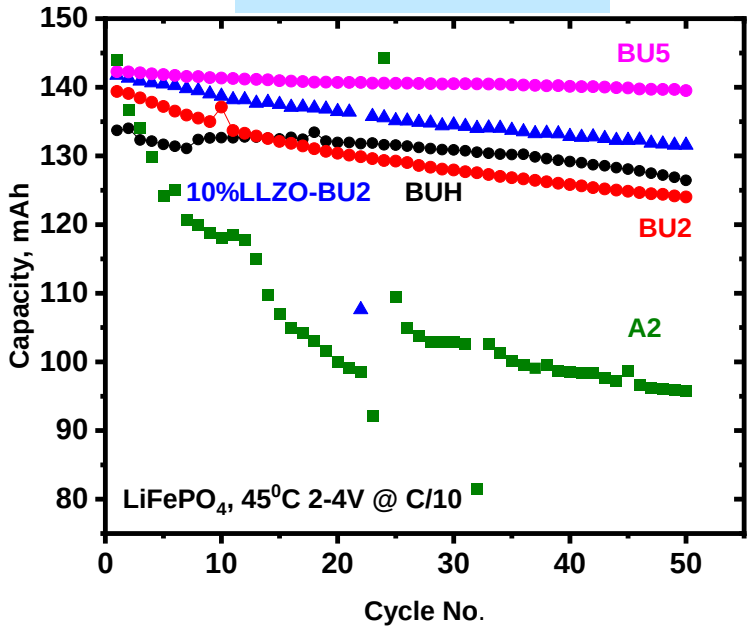
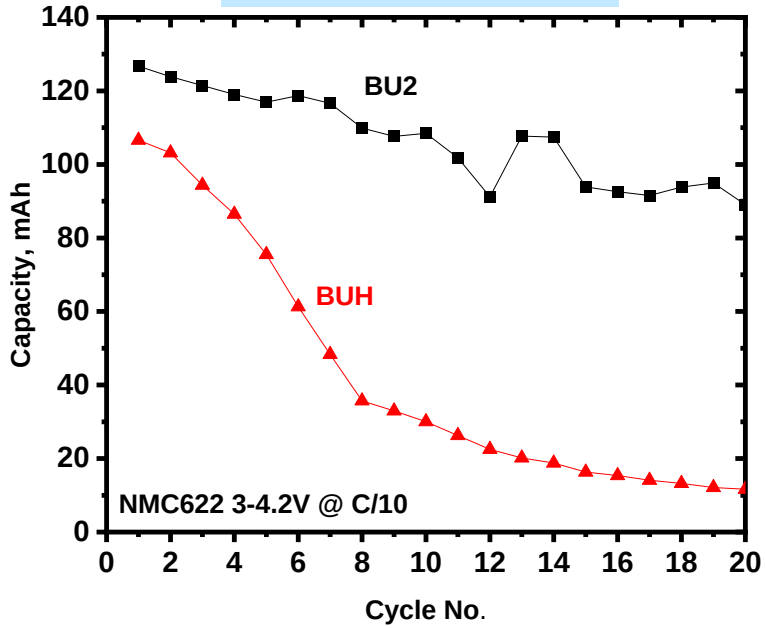
ELECTROCHEMICAL PERFORMANCE OF POLYMER ELECTROLYTE

Li/SPE/LFP cell



Li/SPE/NMC cell



Cell configuration	Anode	Electrolyte	Cathode
	Li	Free stand PE film	LFP or NMC622 electrode (d=16 mm)
Details	Li/SPE/LFP(NMC) coin cell, 2V-4V (3-4.2V) @30ºC and 45ºC, C-rate :**0.1C**		

$LiFePO_4$ 78%, C45 5%, PVDF 7%, BU2 10%

NMC622 80%, C45 5%, PVDF 5%, BU2 10%

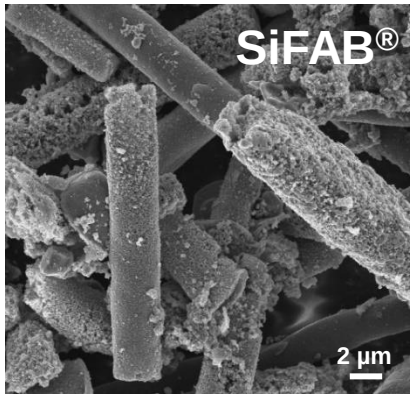
- With addition of Bu (different compositions) or Bu-H (BUH), Extra H-bonding improves the cycling performance.
- Addition of LLZO powder in the polymer electrolyte (LLZO-BU2) slightly improves the cyclability.
- $LiFePO_4$ has better performance than NMC622 when working with polymer electrolyte (PE).

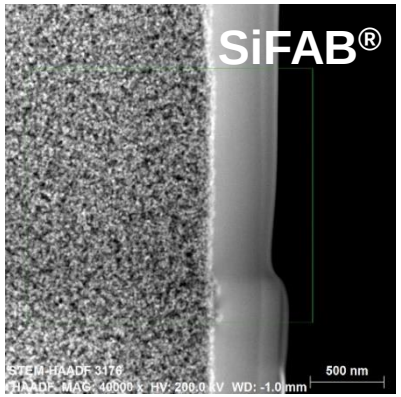
ALKEGEN

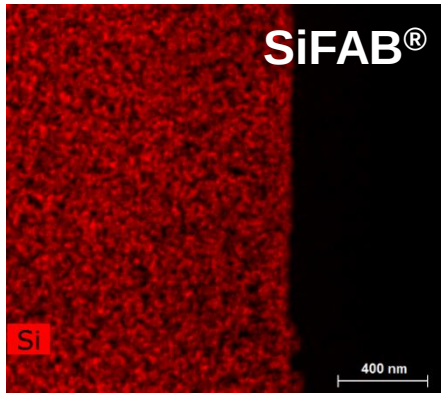
MICRON-SIZE FIBER-SHAPE SILICON ANODE

Structure and electrochemical properties

- Micron-size fiber-shape silicon particles (**SiFAB®**) were developed by Alkegen.
  - SEM and TEM images reveal their porous structure and uniform Si distribution.
- The micron-size particles are easy to process during electrode fabrication.
  - Over 2000 mAh/g reversible capacity was obtained in Li half-cells.

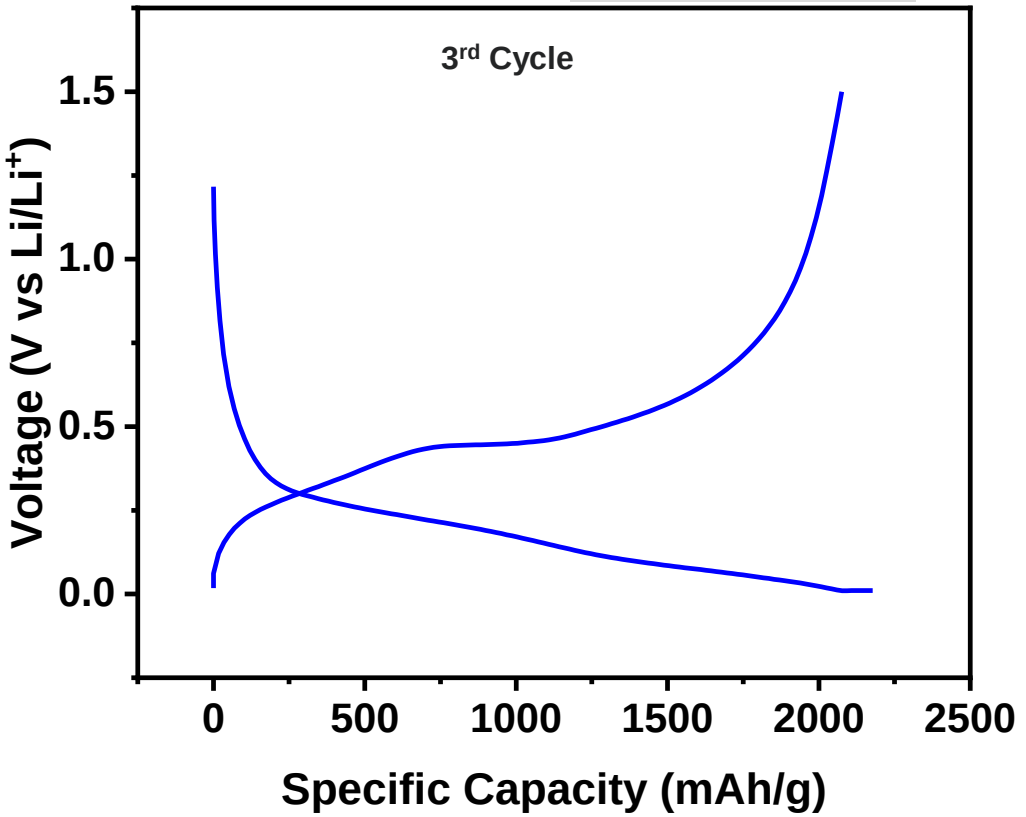






Si electrode
Si/CB/PI =

Li/Si half cell
10 mV – 1.5 V
C/10 at 30°C



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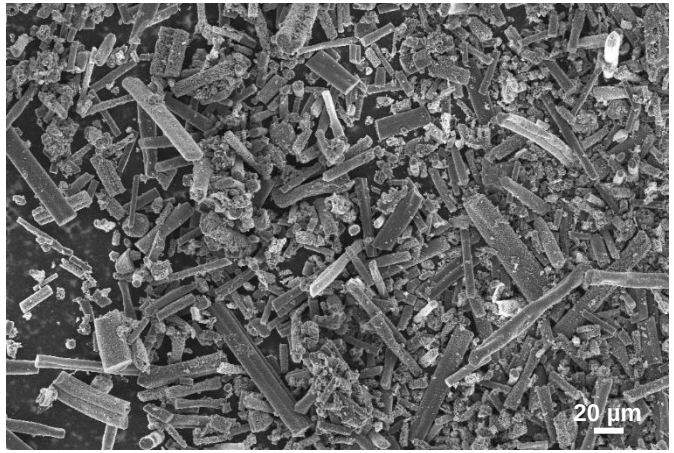
ALKEGEN

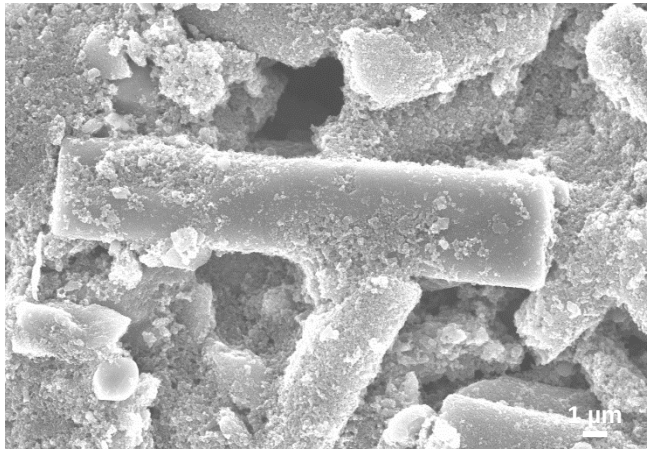
MICRON-SIZE FIBER-SHAPE SILICON ANODE

Volume change and particle integrity

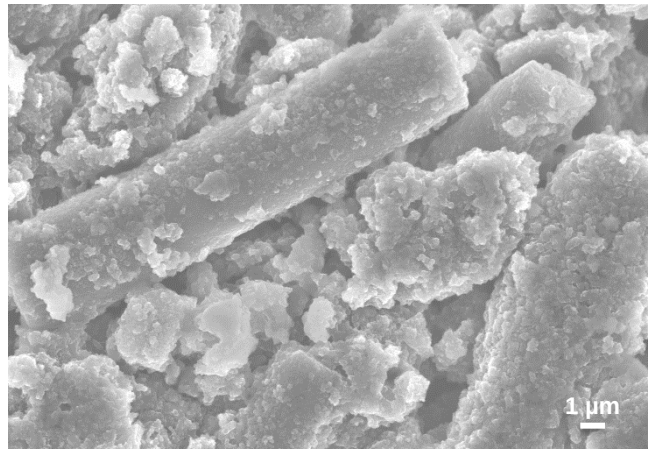
Si powder



Si pristine electrode before cycling



Si pristine electrode after cycling



- No shape or little size change was observed for micron-size silicon particles before and after electrochemical cycling.
  - The porous structure of micron-size fiber-shape silicon addressed the volume change.

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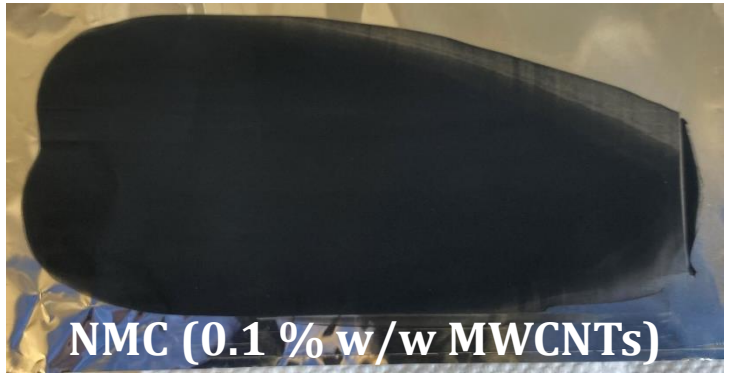
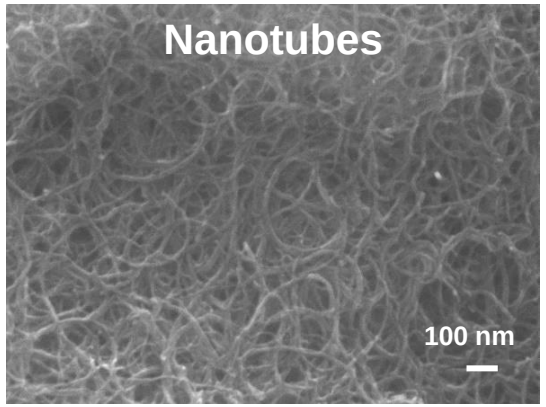
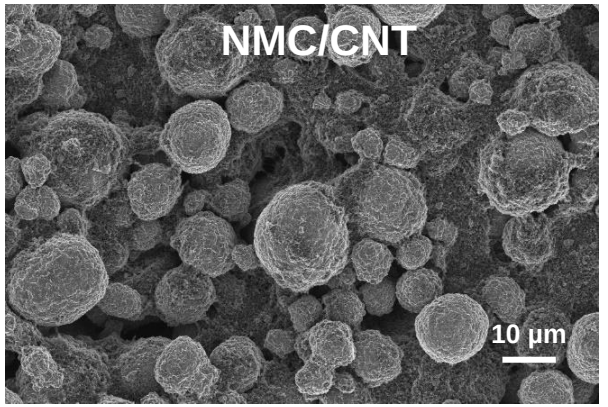
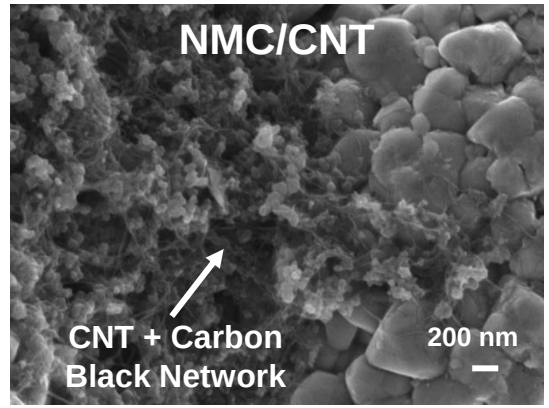
CARBON NANOTUBES FOR CATHODE



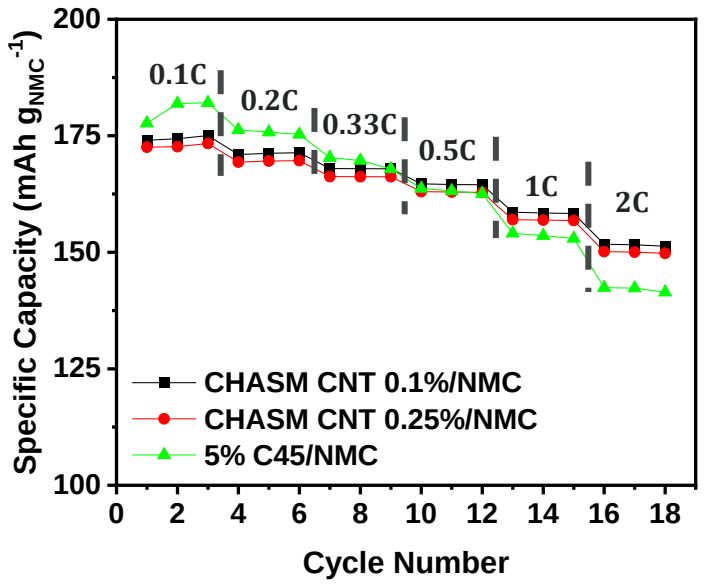


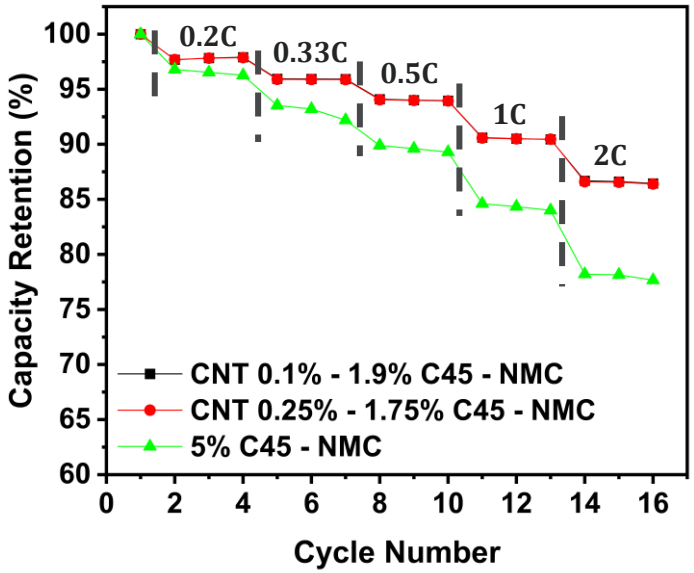




	NMC 811	Nanotubes	Carbon Black	Binder
Laminate-1	96%	0.1%	1.9%	2%
Laminate-2	96%	0.25%	1.75%	2%
Carbon Black	90%	0%	5%	5%

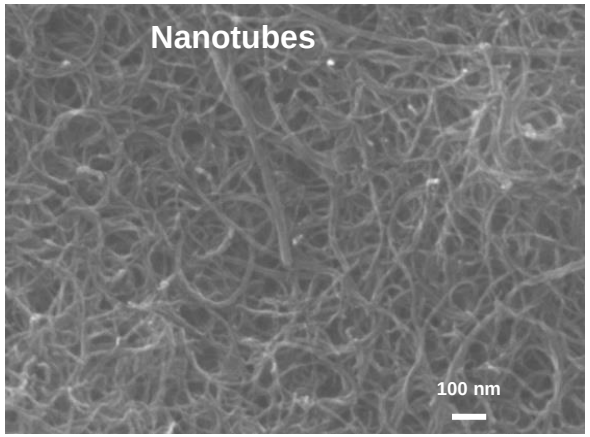
- Carbon black/CNTs blended network for cathode
- Uniform distribution of carbon network in the electrode - improves short range and long-range conductivity
- Capacity retention calculated with respect to the third lithiation cycle – better for electrodes containing CHASM carbon nanotubes

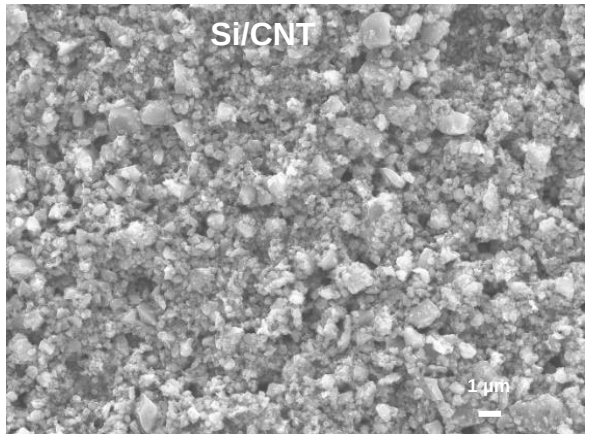


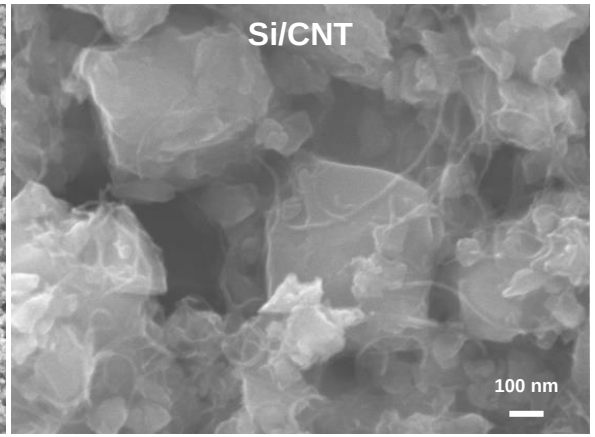


CARBON NANOTUBES FOR SILICON ANODE

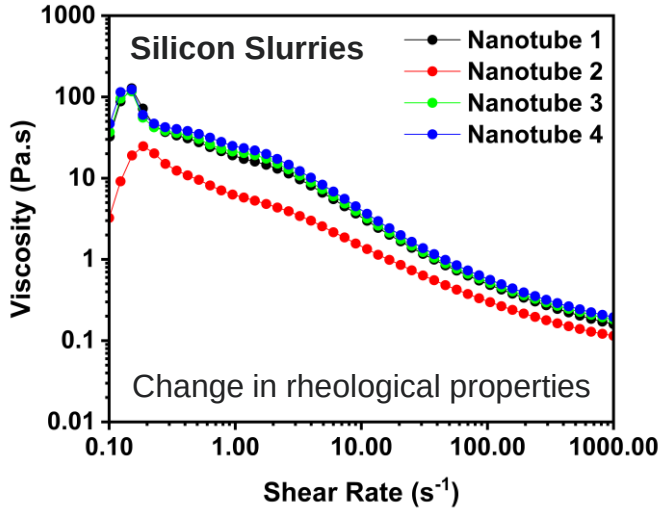
- Four different carbon nanotube dispersions were provided by Chasm Advanced Materials and used to develop silicon anodes
- High loading (~89%) silicon electrodes were assembled
  - The silicon slurry containing Nanotube -2 shows lower viscosity
  - Uniform nanotubes distribution in the silicon anode - nanotubes cover the silicon particle's surface
- Varying initial Coulombic efficiency (ICE) with the type of CNT dispersion is observed.
  - Si electrode made of Nanotube-2 has highest ICE

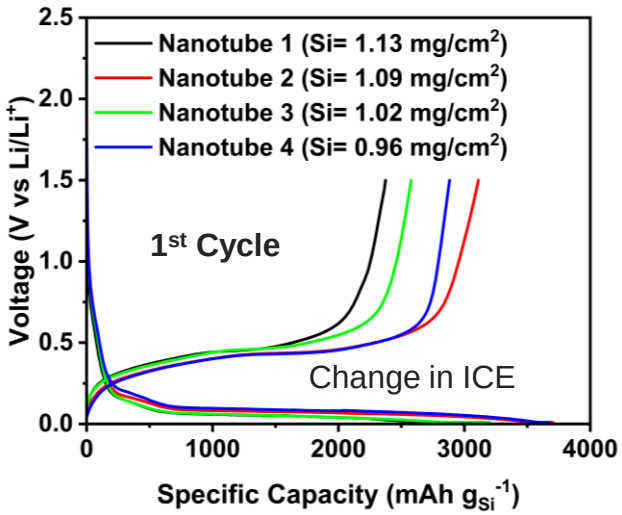






	Si	Nanotubes	Binder
Laminate-1	89%	1%	10%



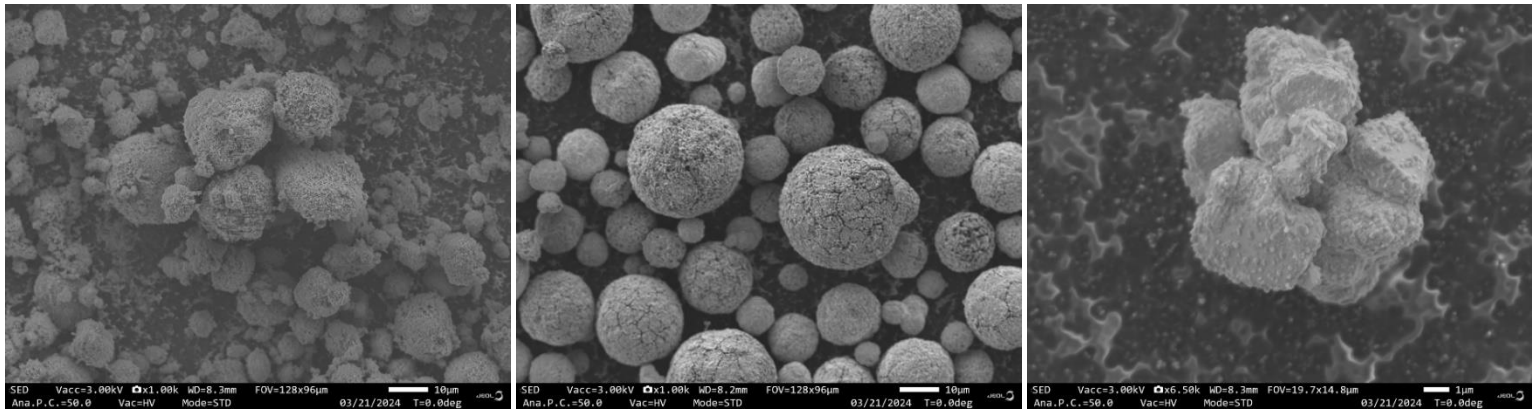


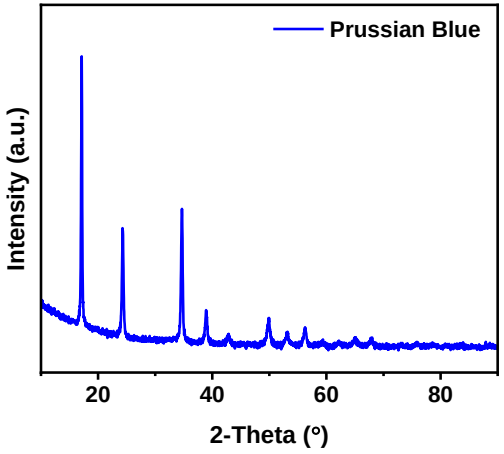
	ICE (%)
Nanotube 1	78
Nanotube 2	85.7
Nanotube 3	80.5
Nanotube 4	78.36

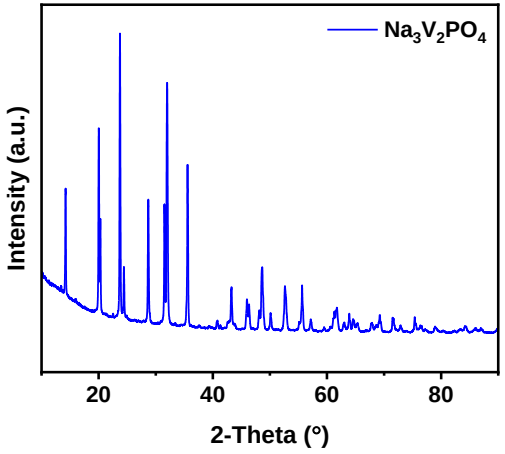
EXPLORATION OF SODIUM CATHODE MATERIALS

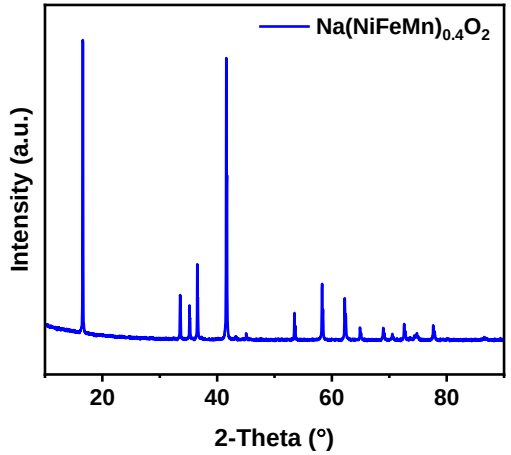
- Sodium is abundant, cost-effective, safer, and has environmentally benign production
- Three commercially available cathode materials for sodium ion batteries are being studied
  - Prussian Blue: $Na_2Fe_2(CN)_6$
  - NVP: $Na_3V_2(PO_4)_3$
  - $Na(NiFeMn)_{0.4}O_2$
- All powders show XRD patterns that match with the literature

Prussian Blue ($Na_2Fe_2(CN)_6$) | **NVP ($Na_3V_2(PO_4)_3$)** | **$Na(NiFeMn)_{0.4}O_2$**







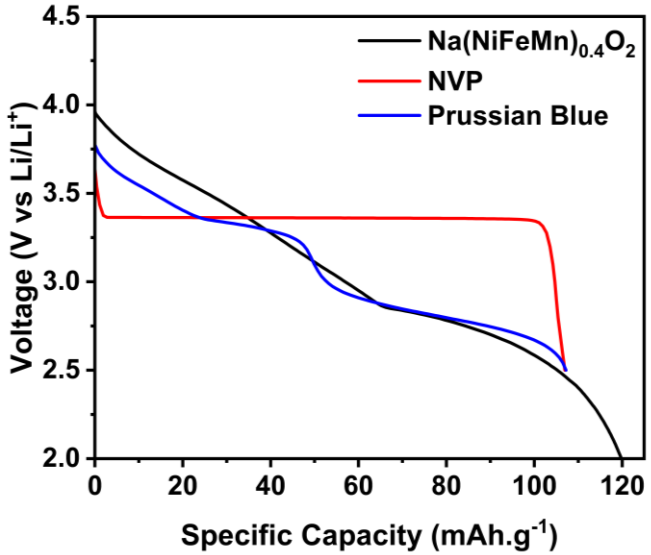


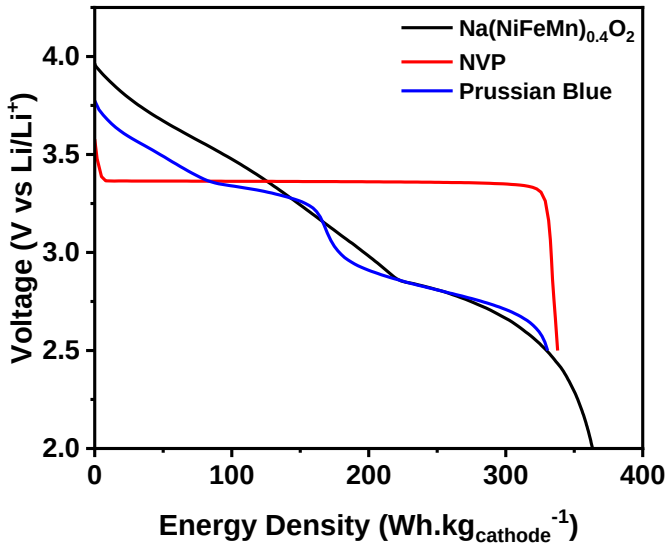
ELECTROCHEMICAL CHARACTERIZATION OF SODIUM CATHODE MATERIALS

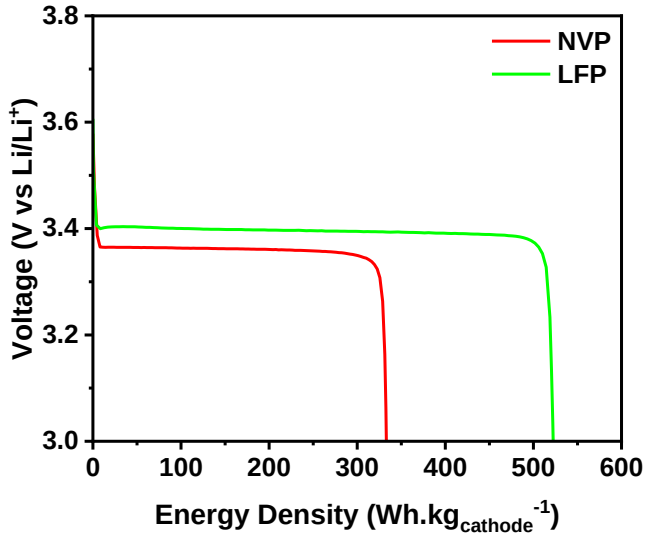
Na electrode composition:
Active Material: 90%
SWCNTs: 0.1%
Carbon Black: 4.9%
PVDF: 5%

Sodium Cathode Testing Procedure
- Half Cell using Na metal as counter electrode
- Electrolyte information: 1.0 M $NaPF_6$ in EC:EMC (30:70, by wt.)
- Formation: Three cycles at C/10 @ 30°C

	Theoretical Capacity (mAh/g)	No. of electrons
$Na(NiFeMn)_{0.4}O_2$	218.32	1
$Na_3V_2(PO_4)_3$	117.63	2
$Na_2Fe_2(CN)_6$	170.84	2







- All three cathode materials delivered similar amount of specific capacities and energy densities.
  - Incomplete de-sodiation of $Na(NiFeMn)_{0.4}O_2$ and Prussian blue, which leads to lower experimental capacities compared to theoretical values.
- NVP demonstrates performance very close to its theoretical capacity.
  - However, its energy density is much lower than its counter part, $LiFePO_4$.

RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

Not review comments from previous year.

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FY23 – FY24 COLLABORATIONS

- The partners and collaborators include
  - National labs: ANL, INL, LBNL, NREL, ORNL, PNNL, SLAC, SNL, SRNL
  - Universities: Bingham Young University, IUPUI, Northeastern University, University of Arkansas, University of Louisville, University of Missouri, University of North Carolina at Charlotte, Western Michigan University, University of Delaware
  - Industries: Alkegen, Applied Minerals, Ashland, Blue Ocean and Black Stone, Cabot, Chasm Advanced Materials, Conovate, Koura, Ntherma, Osaka Titanium Corp., OCSiAl,OXBOW, Paraclete Energy, Phillips 66, Superior Graphite Co., Targray, Toda Kogyo, Zeta Energy
- 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 may not meet or exceed DOE/USABC 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 RESEARCH

- Continue research on solid state electrolyte (SSE), including polymer electrolyte, focusing on its optimization, and fabrication scalability.
  - To fabricate and test composite electrolyte film using oxide and sulfide SSE (LLZO, Li_6PS_5Cl).
  - To optimize solid polymer electrolyte composition and fabrication process
- Continue to acquire and characterize high-energy anode/cathode materials from vendors.
  - New active materials, including new binders, electrolytes/additives, and advanced conductive additives, are of interest.
- Continue to explore sodium-ion battery materials and their potential application for EV.
- Continue to work closely with research institutions and industrial suppliers to enable the battery technology for EV applications.

SUMMARY

- New analogs of Bu were synthesized to adjust solubility, H-bonding formation extent, and potential interfacial formation of PEGDA-based solid polymer electrolyte. The new solid polymer electrolyte showed good electrochemical performance using Li/SPE/$LiFePO_4$ cell.
- Micron-size fiber-shape Si developed at Alkegen was tested in Li/Si half cell with over 2000 mAh/g. The porous structure greatly mitigates the volume change of Si electrode.
- Multi-wall carbon nanotube from Chasm Advanced Materials were tested in both NMC cathode and Si anode.
  - 0.1% MWCNT in NMC electrode can improve the rate performance.
  - With optimize MWCNT dispersion, better Coulombic efficiency was obtained for Si electrode.
- Three commercially available sodium cathode materials: Prussian blue, sodium vanadium phosphate, and sodium metal oxide were characterized and tested.
  - They all show similar energy density, which is less than $LiFePO_4$.

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- Silatronix

Facilities

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

Support from Haiyan Croft, Brian Cunningham, and Austin Brown of the U.S. Department of Energy's Office of Vehicle Technologies Program is gratefully acknowledged.