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

Project ID: BAT028

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U.S. DEPARTMENT OF ENERGY
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OVERVIEW

Timeline

- Start – Oct. 1st, 2014
- Finish – Sep. 30th, 2022

Budget

- Total project funding in FY2021: $400K (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, Silicon Consortium Project (SCP), Realizing Next Generation Cathodes (RNGC), ReCell, XCEL (BNL, INL, LBNL, NREL, ORNL, PNNL, SLAC, SNL)
- Argonne Facilities: APS, CNM, EADL, MERF, 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. 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, the better understanding of the active materials at cell level will speed up material development efforts.

FY21 MILESTONES AND ACCOMPLISHMENTS

Milestone	Planned End Date	Type	Status
Develop methods to coat hybrid ceramic polymer composites with reverse comma coater in dry room conditions. **(also see BAT030)** – Produce 5 meter of coating without major pinholes.	3/31/2021	Quarterly Progress	Completed
Develop methods to coat electrode-ceramic structures using reverse comma coating methods. **(also see BAT030)** – Produce 10 meter of electrode-ceramic on foil with at least 3 mAh/cm² loading.	7/30/2021	Quarterly Progress	On Schedule

Accomplishments

- Flexible solid electrolyte thin films were fabricated using multi approaches
  - Stand-alone PEGDA solid polymer electrolyte fabrication
  - Direct-casting PEDGA solid polymer and composite electrolyte on LTO electrode (also see BAT030)
  - Stand-alone LLZO composite electrolyte was fabricated and electrochemically tested in Li/SSE/LFP cell.
- Si derived from Halloysite were electrochemically tested with good coulombic efficiency and high specific capacity.
- Binder- solution-free NMC cathode were investigated using holey graphene as conductive.

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 test protocol, such as formation, C-rate and cycle life, were established for half and full 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.

SOLID ELECTROLYTE FILM DEVELOPMENT

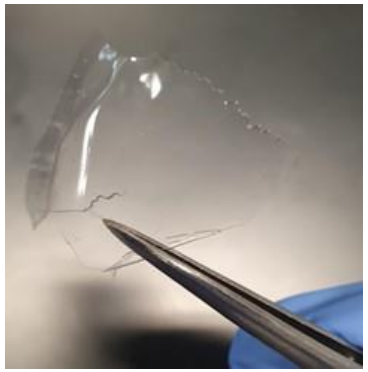
Stand-alone Solid Polymer Electrolyte

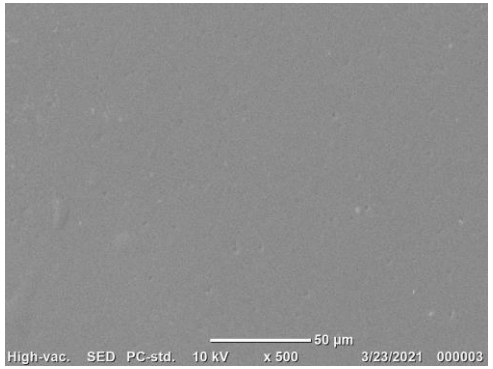
Poly (ethylene glycol) diacrylate (PEGDA) has been used as a cross-linking agent to copolymerize with other monomers in the application of solid polymer electrolytes (SPE).

Instead of UV curing, PEGDA based SPE were prepared through an in-situ **thermal polymerization method** of a blended precursor solution in liquid electrolyte.

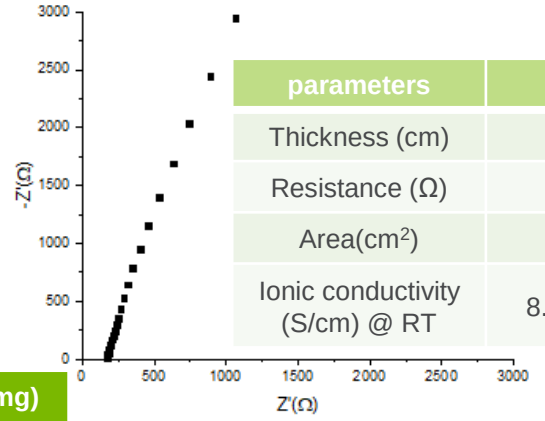
Two approaches were attempted to process SPE thin film, **direct-casting** SPE on electrode and **stand-alone** thin film fabrication.

SEM of SPE





ac impedance



parameters	value
Thickness (cm)	0.038
Resistance (Ω)	225
Area(cm^2)	2.01
Ionic conductivity (S/cm) @ RT	8.4×10^{-5}

Total weight (g)	PEGDA (wt%)	LiTFSI (wt%)	GN (wt%)	AIBN (mg)
2g	40	30	30	8

AIBN: 2,2′-Azobis(2-methylpropionitrile, GN: Glutaronitrile

1. PEGDA monomer was mixed with AIBN (heat initiator), GN (plasticizer), and LiTFSI (salt).
2. The solution was casted on to poly propylene film and cured at 90°C for 2 hours.

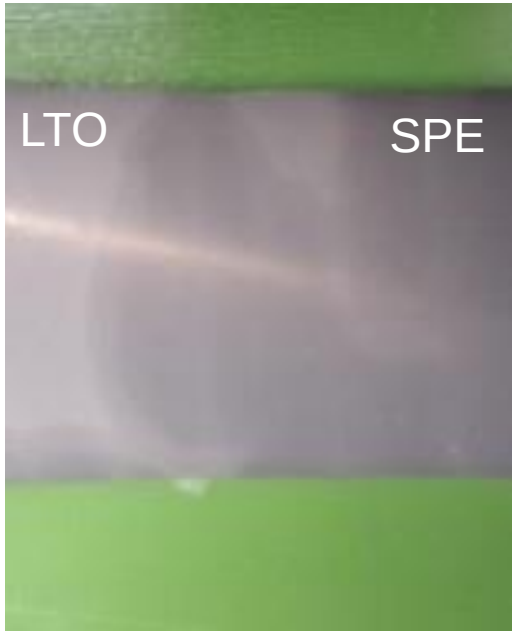
- Transparent free-standing SPE was obtained. SEM/EDS results suggest uniform component distribution.
- Lithium ionic conductivity from ac impedance was determined to be around 0.1 mS/cm.

SOLID ELECTROLYTE FILM DEVELOPMENT

Direct-casting Solid Polymer Electrolyte

SPE direct-casting

Using same composition and procedure, SPE was directly coated and cured on LTO electrode. The direct-casting will wet the electrode and improve the electrode conductivity.



Composite SPE direct-casting

Al_2O_3 (wt%)	PEGDA (wt%)	LiTFSI (wt%)	GN (wt%)	AIBN (mg)
10	36	27	27	8
20	32	24	24	8
30	28	21	21	8
40	24	18	18	8
50	20	15	15	8

Various amounts of ceramic particles (Al_2O_3) was introduced into the polymer electrolyte solution. The composite Al-SPE was directly coated and cured on LTO electrode.



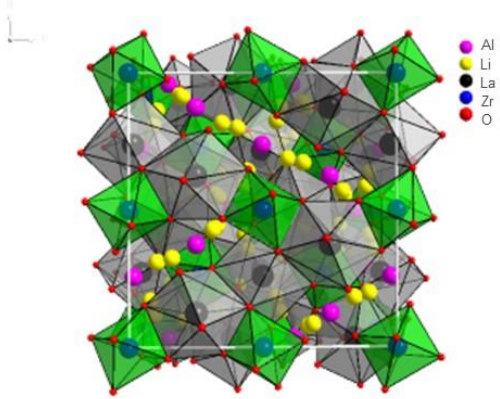
- Both SPE and composite SPE consisting of Al_2O_3 particles were successfully directly coated on LTO electrode.
- Large scale thin polymer electrolyte coating was achieved by the CAMP facility (See BAT030).

SOLID ELECTROLYTE FILM DEVELOPMENT

LLZO/LiTFSI/PVDF Composite Film

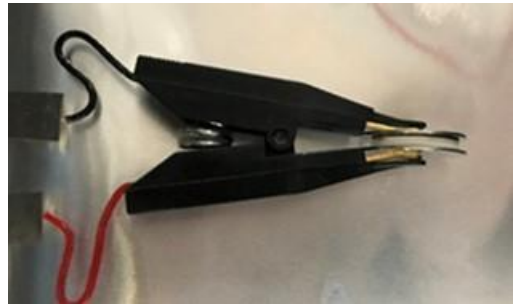
- SPE is easy to synthesis, and compatible with large-scale manufacturing processes. However, polymer chains locked in a crystal lattice hinder the motion of cations, makes it low ionic conductivity electrolyte.
- Solid inorganic electrolytes (SIE), such as LLZO, have high ionic conductivity, which have issues of manufacturing difficulties, poor interfacial charge transport, and the risk of metal dendrite growth.
- By combining the best merits of SIE and SPE, we attempted to develop LLZO/LiTFSI/PVDF composite solid-state electrolyte.

$Li_{6.25}La_3Zr_2Al_{0.25}O_{12}$

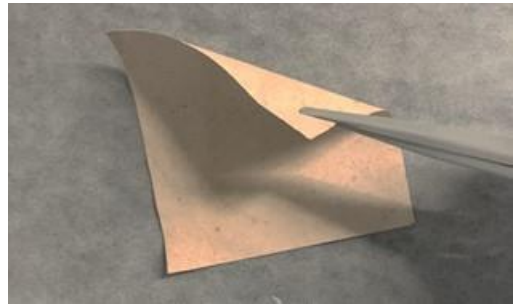


Simple mixing LLZO, LiTFSI, and PVDF/NMP solution with PTFE, thin and flexible stand-alone composite film (80 μm) was fabricated in the lab.

LLZO pellet



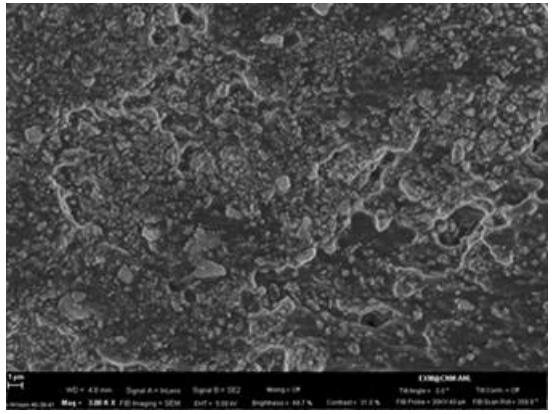
LLZO/LiTFSI/PVDF



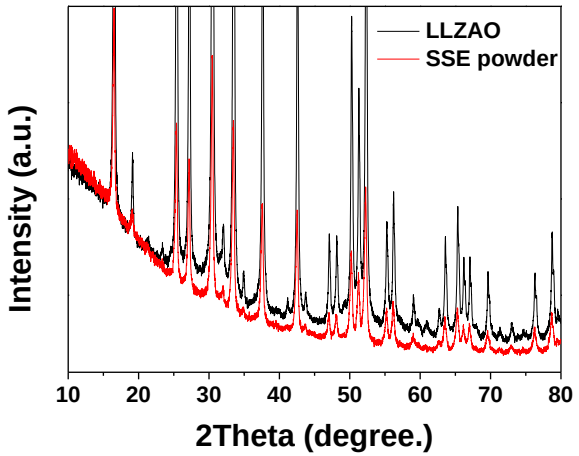
SOLID ELECTROLYTE FILM DEVELOPMENT

SSE Characterization

SEM image

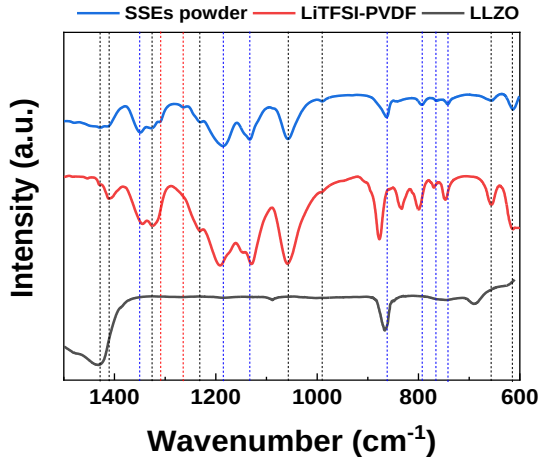


XRD

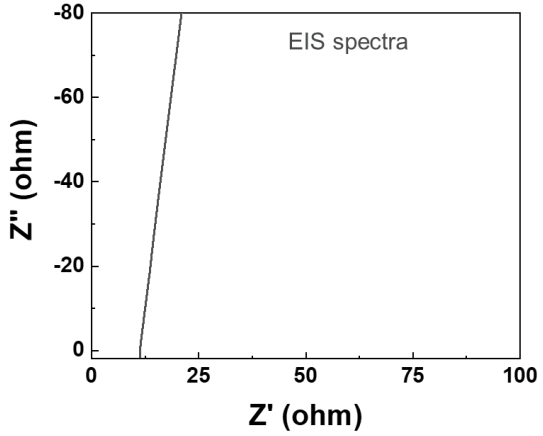


- XRD results indicates that LLZO structure was kept intact after SSE preparation.
- FTIR suggests that there is interaction between LLZO and polymer.

FTIR

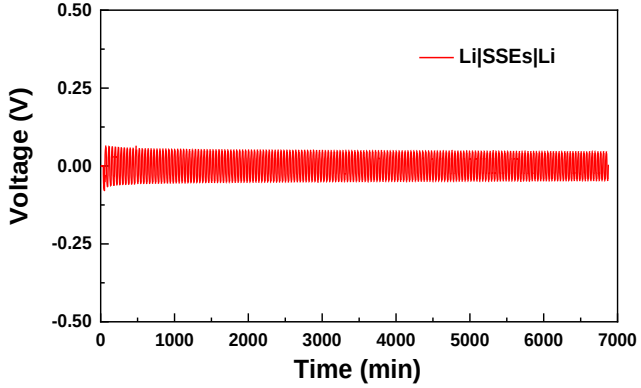


ac impedance



- The LLZO composite film has high conductivity (>1 mS/cm and good cycling performance in symmetric cell.

Cycler life of Li/SSE/Li cell

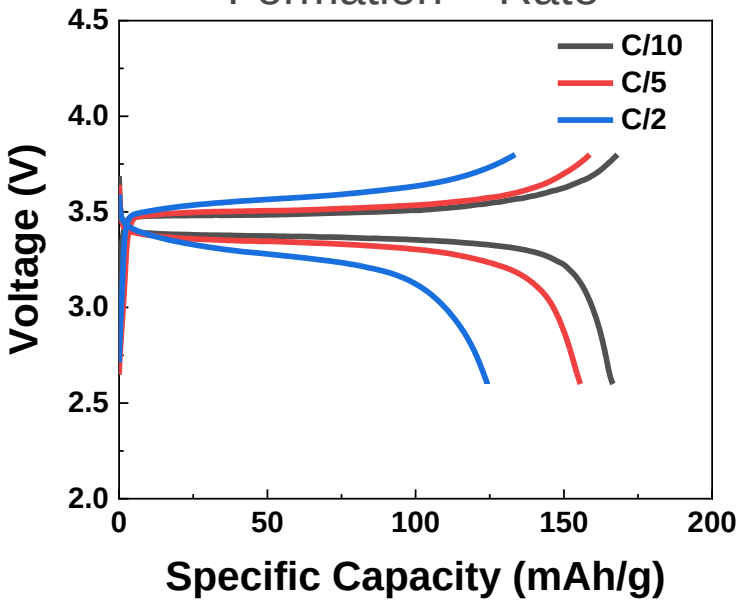


SOLID ELECTROLYTE FILM DEVELOPMENT

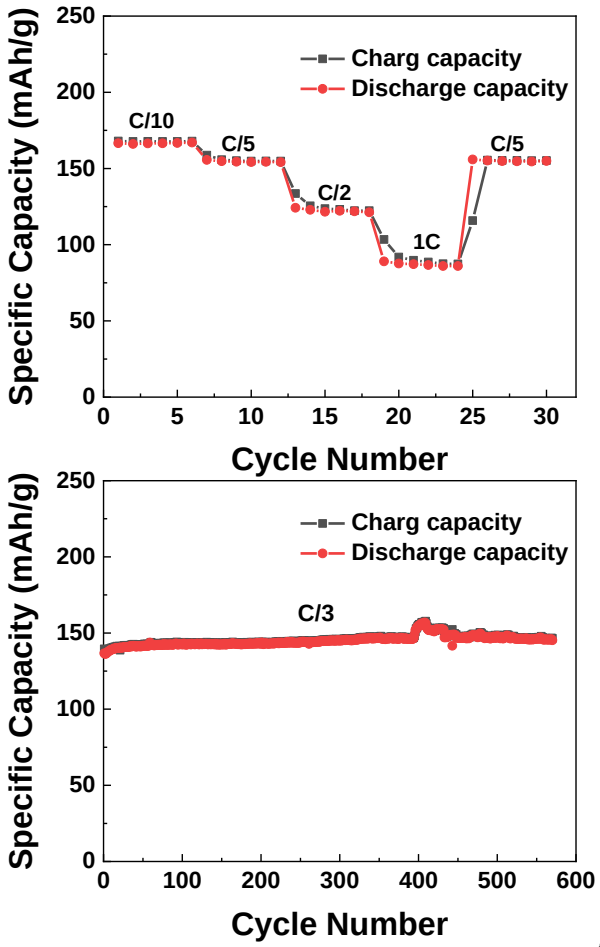
Electrochemical Performance of Li/SSE/LFP Cell

Li/SSE/LFP 2032 coin cell
2.6V - 3.8V, 30°C
Electrochemical test:
Formation: C/10
Rate: C/5, C/2, 1C (charge = discharge)
Cycling: C/3 (charge = discharge)

Formation + Rate



Rate



- With C/10 rate, the LFP electrode exhibited a specific capacity of ~170 mAh/g, closing to that of theoretical value.
- Excellent cycle life was achieved with C/3 rate.

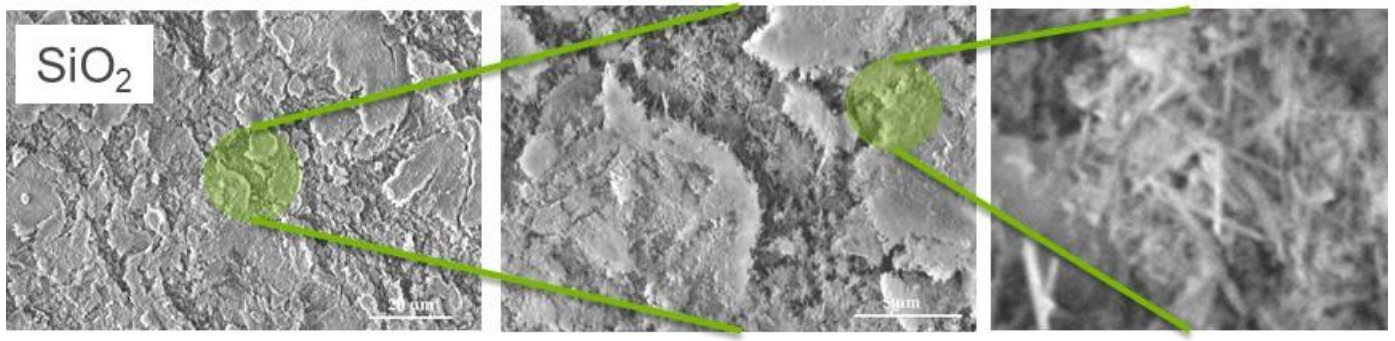
Special thanks to Prof. Dean Wheeler and Brian Mazzeo (BYU) and Dr. Sharad Mathur (Applied Minerals) for their support on Si work.

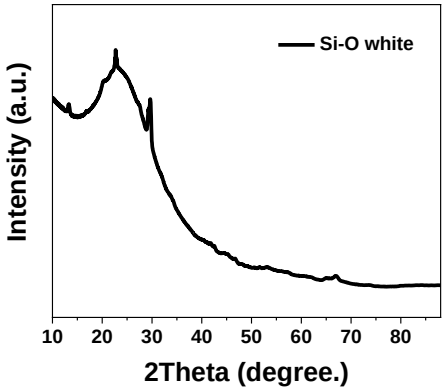
SILICON FROM HALLOYSITE

Yang Ren @ APS
Yuzi Liu @ CNM

- Halloysite, with a stoichiometric composition of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$, is a kind of naturally abundant in USA.
- Owing to its existing nano-cylindrical shape, the silicon that is made from halloysite may preserve the nano structure and make it the promising anode material for lithium-ion batteries.
- Halloysite turns to SiO_2 after acid washing. Si will be obtained after SiO_2 reduction.

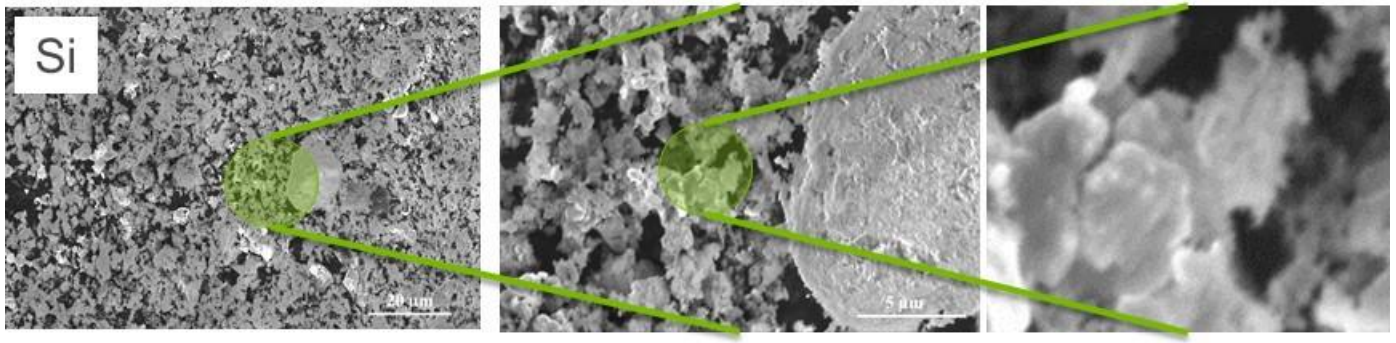
Intermediate product SiO_2

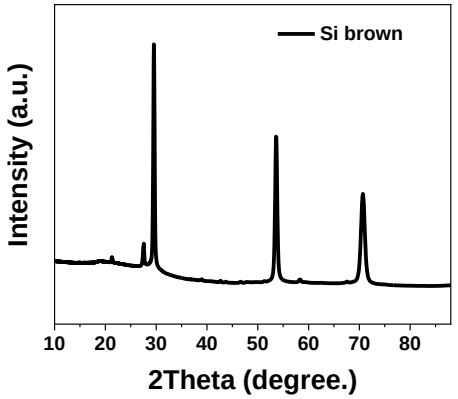




The intermediate product SiO_2 derived from halloysite keeps the tubular shape. XRD suggests that the product is mostly amorphous SiO_2.

Final product Si





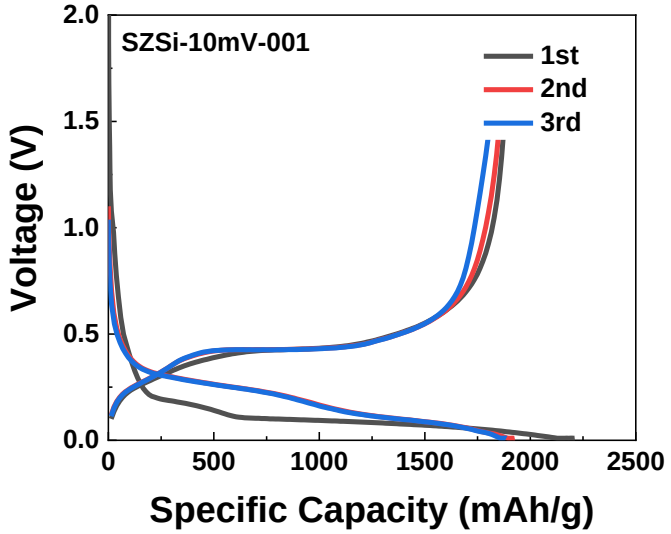
The final product is mainly crystalline Si.

SILICON FROM HALLOYSITE

Electrochemical Performance

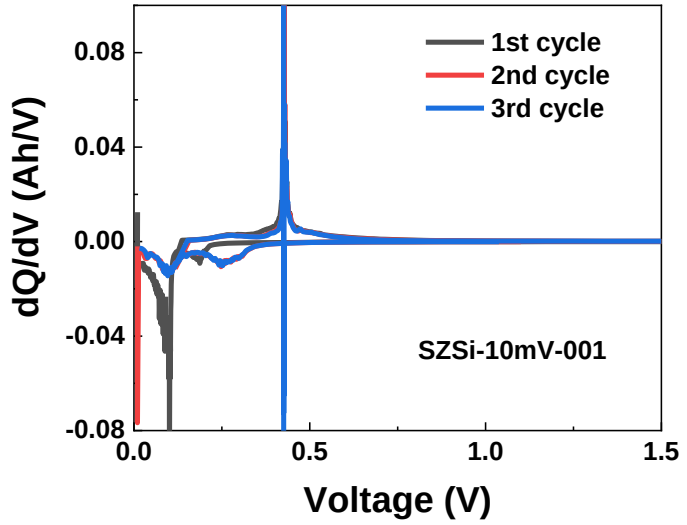
Slurry-casting	**Materials**	Si	Binders (LiPAA)	Timical C45	DI water
	Ratio (wt%)	70	20	10	-
Calender	**Si electrode**	Electrode diameter: 14mm; coating thickness: 20 μm; loading: 1mg/cm2; porosity: 50~55%			

Li| Gen2+10%FEC|Si (~2 mAh/cm^2, 1 mg/cm^2)
Test condition: 10mV-1.5V
3 Formation cycle + rate test from C/5 to 2C

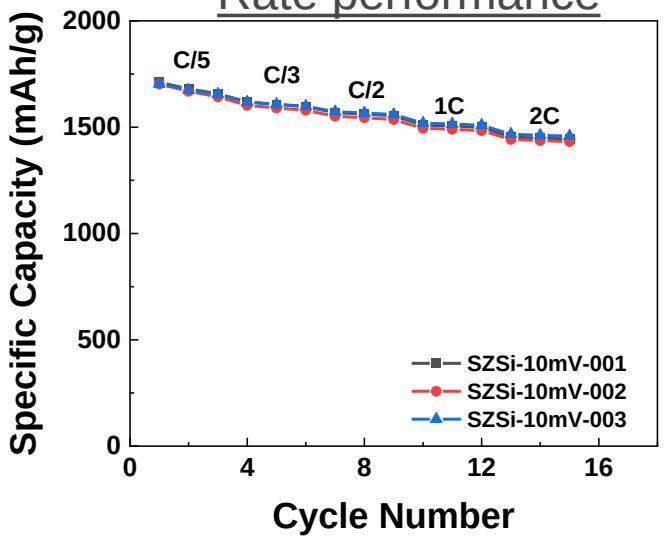


- The Si has over 1800 mAh/g reversible specific capacity and about 85% 1st cycle coulombic efficiency.
- At 2C discharge rate, the Si electrode still delivers 1450 mAh/g.

dQ/dV plot of Si electrode



Rate performance



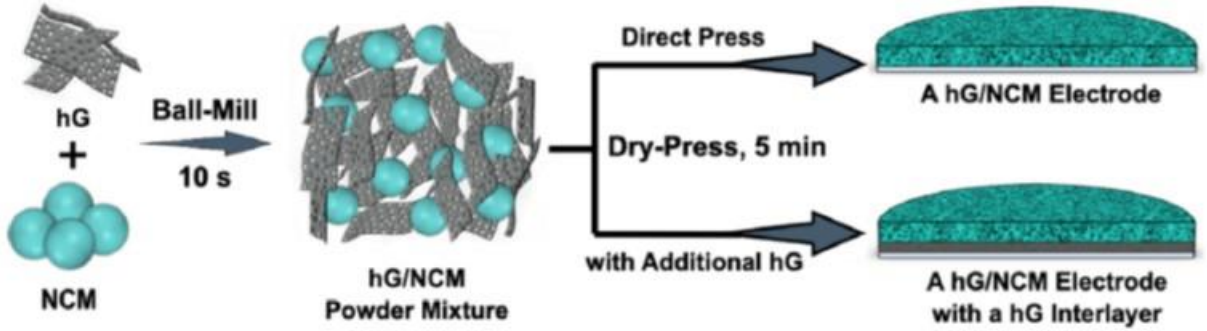
Special thanks to Dr. Yi Lin (NASA) for his support on holy-graphene work.

HOLEY-GRAPHENE CONDUCTIVE SCAFFOLD

hG-NCM Cathode Fabrication

- Holey graphene (hG), a structural derivative of graphene that exhibits arrays of nanometer-sized holes distributed across the lateral nanosheet surface was developed at National Institute of Aerospace (NASA).
- The hG is capable to be used to make binder and solvent free electrode. This new electrode structure may lead to low cost and high energy density of lithium-ion batteries.

Binder/solvent free hG-NCM electrode fabrication



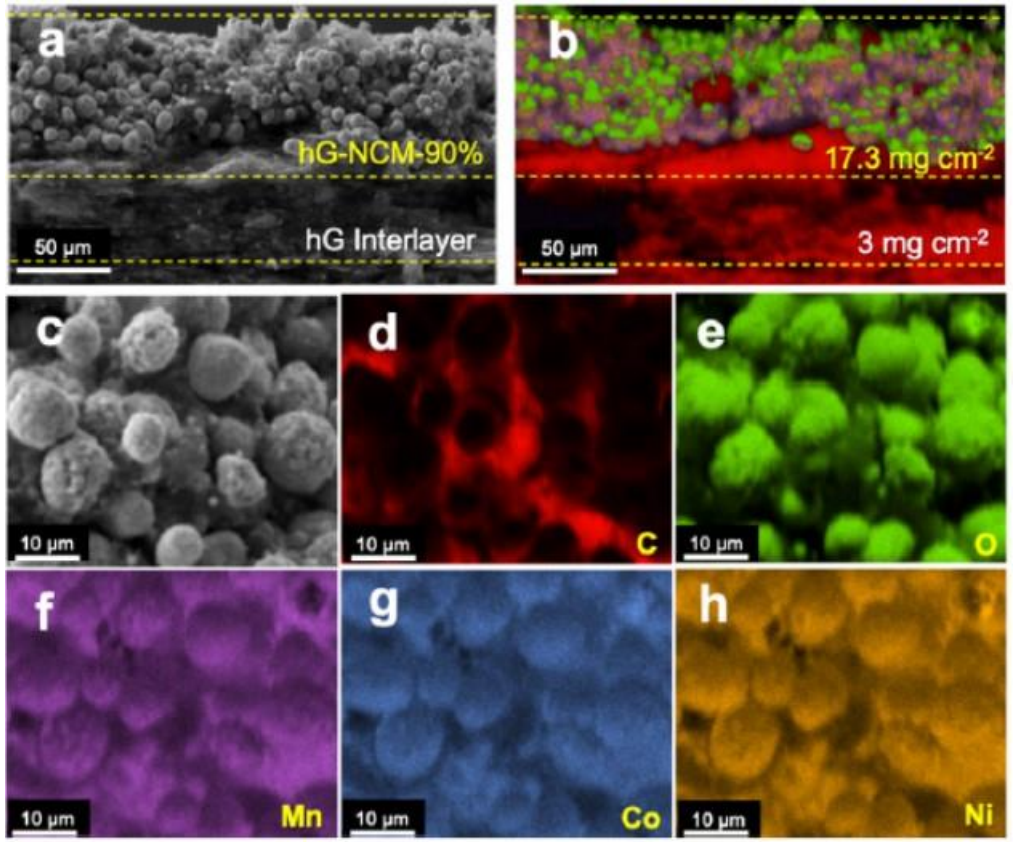
- Dry mix NCM523 and hG (1/9 weight ratio) using ball mill method.
- As-prepared hG/NCM powder mixture was loaded into a die (d=1.485 cm) and pressed into hG-NCM523 electrode disc using a hydraulic press (~20 Mpa)

Brandon A Walker; Christian O Plaza-Rivera, Sam-Shajing Sun, Wenquan Lu, John W Connell, Yi Lin, Electrochimica Acta, Vol 362 (2020), 137129.

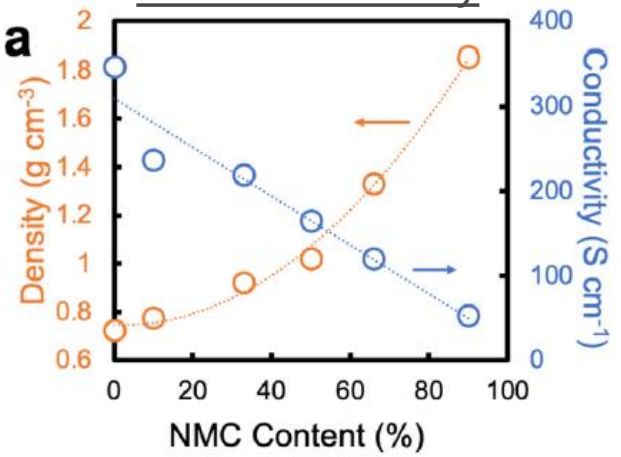
HOLEY-GRAPHENE CONDUCTIVE SCAFFOLD

hG-NCM Electrode Characterization

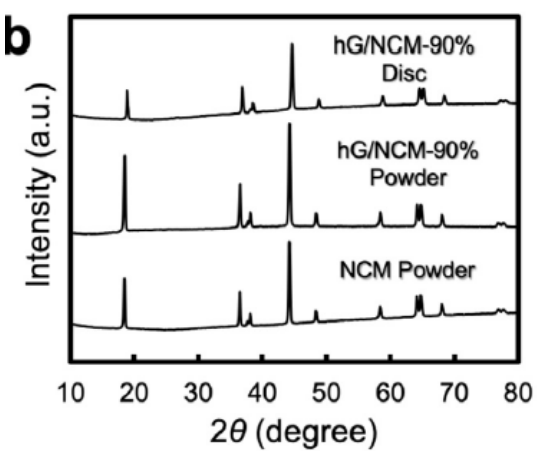
Cross section of hG-NCM SEM and EDS



Electrode density and conductivity



XRD of hG-NCM



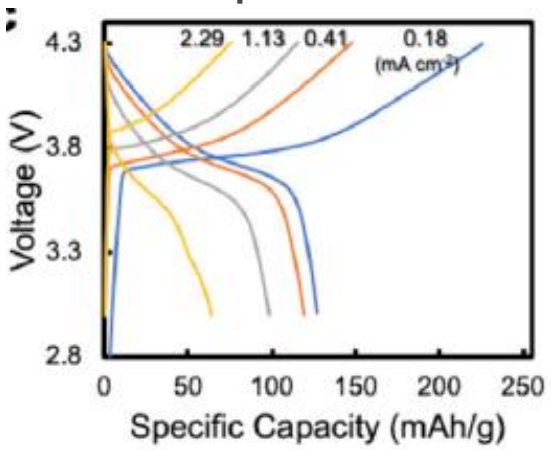
- According to SEM and EDS, high loading, uniform distribution, thick electrode was obtained.
- Surface conductivity as high as 53 S/cm for a hG/NCM-90% disc was observed.
- The mixing and cold compression processes did not induce any structural changes to NCM as evidenced by the results from XRD analyses

HOLEY-GRAPHENE CONDUCTIVE SCAFFOLD

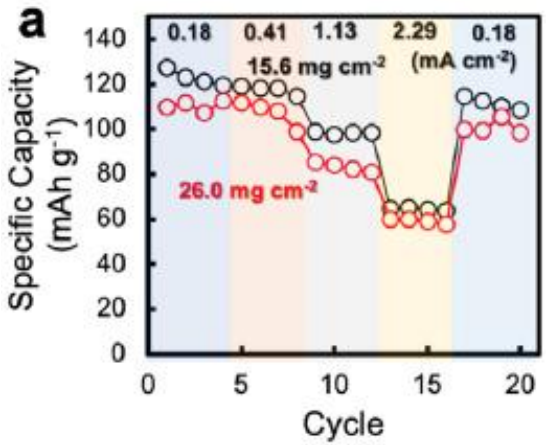
Electrochemical Performance of hG-NCM Electrode

Li/NCM523 half cell
CR2032 coin cell
NCM523 loading:
15.6 mg/cm^2, and
26.0 mg/cm^2
Celgard 2325 separator
1M LiPF6 in EC/DMC (3/7)
3.0V – 4.3V

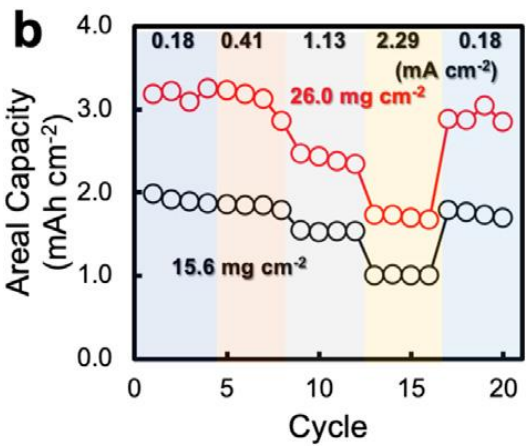
Rate performance



Specific Capacity

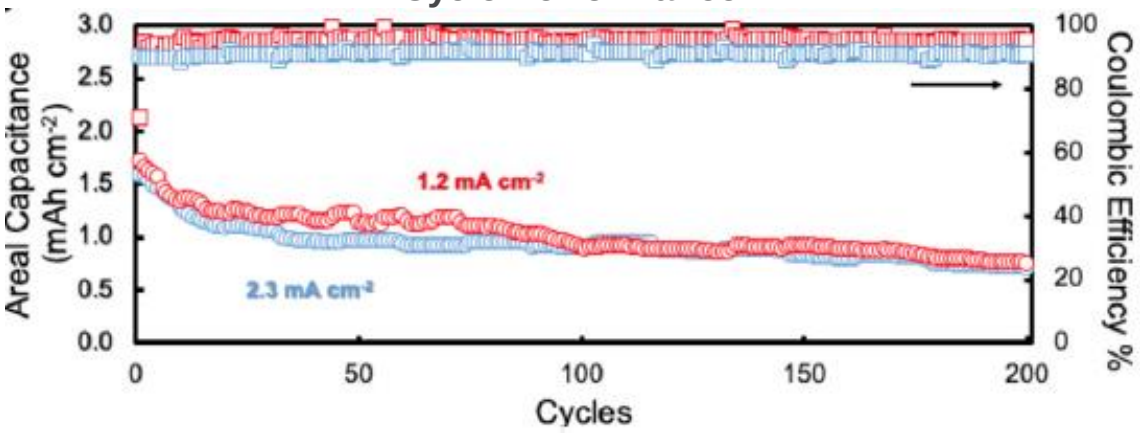


Areal Capacity



- High NCM523 loading did not adversely affect the rate performance of hG-NCM electrode.
- Comparable cycle performance was obtained for both high and low loading hG-NCM electrodes.

Cycle Performance



RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

No reviewer comments from 2020 merit review

FY20 – FY21 COLLABORATIONS

- The partners and collaborators include
  - National labs: Argonne, BNL, ORNL, PNNL, NASA
  - Universities: IUPUI, University of Missouri, University of Arkansas, The George Washington University, Western Michigan University, Bingham Young University, University of Louisville
  - Industries: Applied Minerals, Jolt Energy Storage Technologies, Koura, Lubrizol, NEI, Osaka Titanium Corp., OSiAlC, Paraclete Energy, Phillips 66, 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 RESEARCH

- 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 from domestic vendors.
  - 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

- Both stand-alone and direct-casting solid state electrolytes thin films were explored this year.
  - For stand-alone electrolytes, we successfully fabricated PEGDA SPE and LLZO composite electrolyte. The latter was electrochemically tested using LFP cathode.
  - For direct-casting electrolyte, we developed the formulation and optimized the curing condition for PEGDA SPE.
- Owing to its existing nano-cylindrical shape, the silicon that is made from halloysite preserves its nano structure and makes it a good anode material. Electrochemical test results show that it has high specific capacity >1800 mAh/g and good coulombic efficiency ~85%.
- Binder and solvent free NMC electrode were fabricated using holey graphene. Good electrochemical performance of NCM electrode with very high loading 26 mg/cm^2 suggests this approach can lead to high energy density and low cost of lithium-ion batteries.

CONTRIBUTORS AND ACKNOWLEDGMENTS

Argonne

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- Christian Plaza-Rivra (NASA)
- Sam-Shajing Sun (Norfolk State University)
- John Connell (NASA)
- Yi Lin (NASA)
- Fei Sun (BYU)
- Nathan Clarke (BYU)
- Brian Mazzeo (BYU)
- Dean Wheeler (BYU)
- Gabriel Veith (ORNL)
- Jianlin Li (PNNL)
- Chongmin Wang (PNNL)
- Zoey Huey (NREL)
- Sharad Mathur (Applied Minerals

Facilities

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

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