CATHODE MATERIALS FOR NEXT GENERATION LITHIUM-ION BATTERIES: ESTABLISHING MATERIALS AND COMPONENT TESTING PROTOCOLS

Project ID: BAT476

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Argonne National Laboratory
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2021 DOE Vehicle Technologies Office
Annual Merit Review

Overview

Timeline

- Start: October 1, 2018
- End: September 30, 2021
- Percent complete: 85%

Budget

- Total project funding:
  FY20 $4.0M
- ANL, NREL, ORNL, LBNL, PNNL

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost
  - Performance
  - Safety
  - Cobalt content

Partners

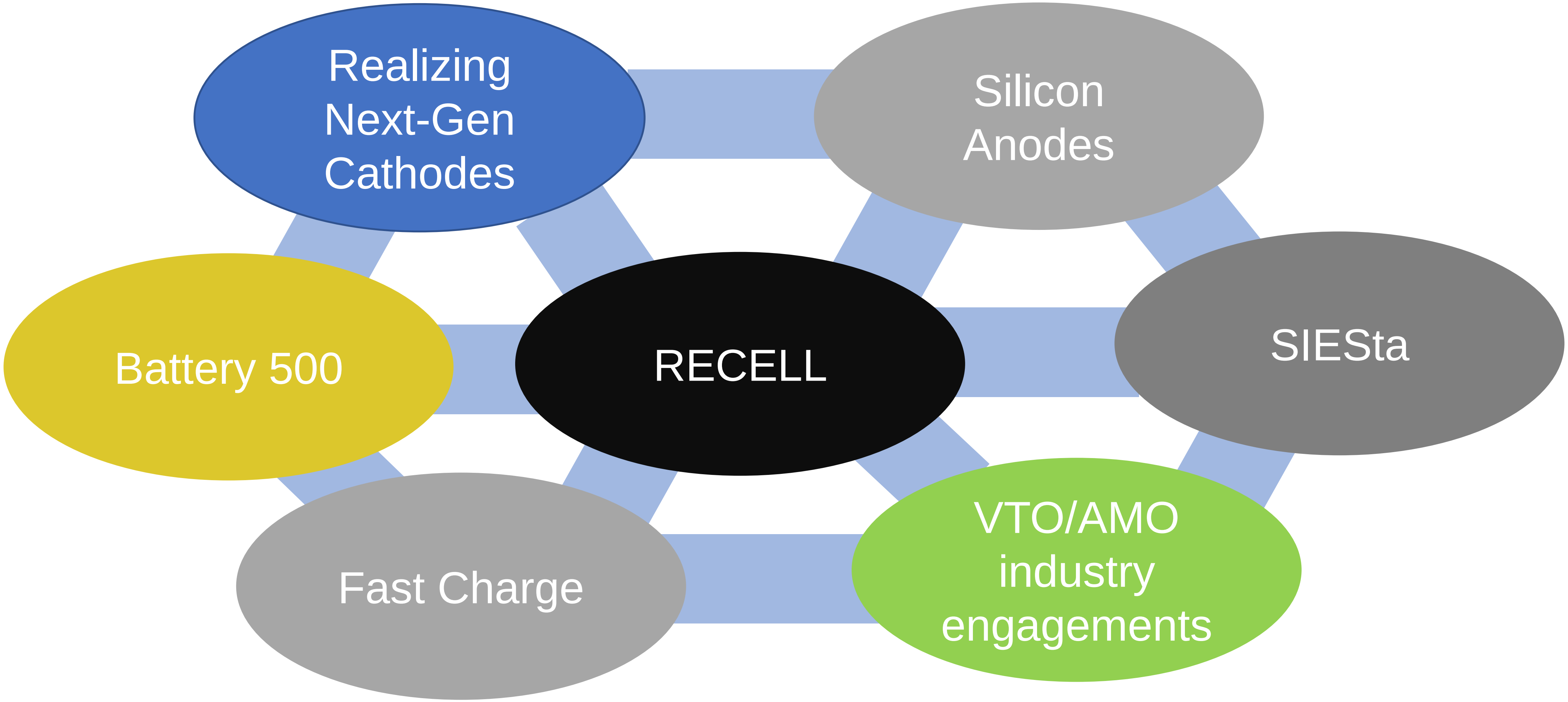
- ANL, NREL, ORNL, LBNL, PNNL

Students supported from:

- University of Illinois at Chicago
- University of Rochester
- Oregon State University

Relevance

Multi-lab/institution efforts



Standardized testing for direct comparisons is crucial

Milestones

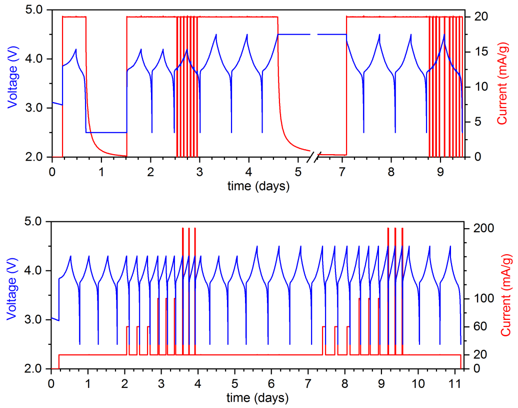
See also BAT251, 252, 253, 167

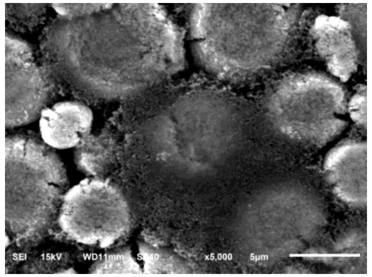
This project thrust is tasked with the development of standards and protocols that arise as needed for the multi-institutional Deep Dive effort in systematically understanding the properties and performance of lithium-ion materials and electrochemical cells

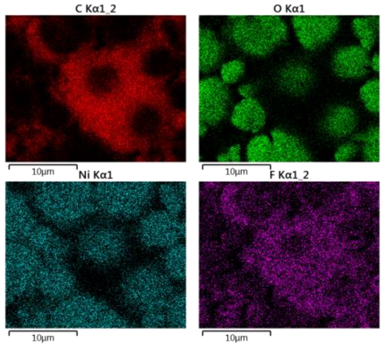
Approach

See also BAT251, 252, 253, 167

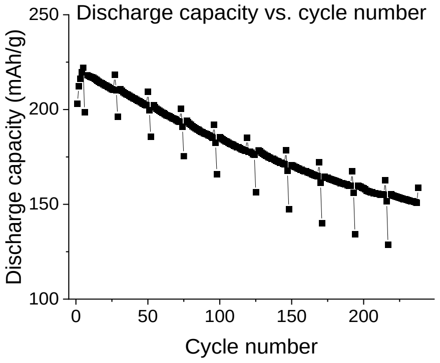
Screening/characterization

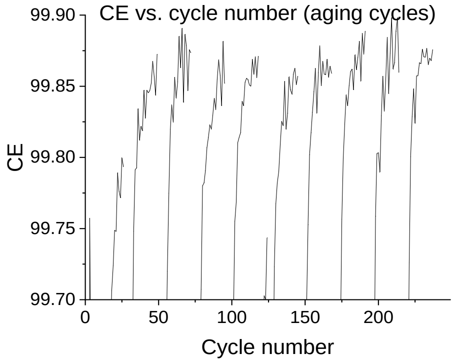


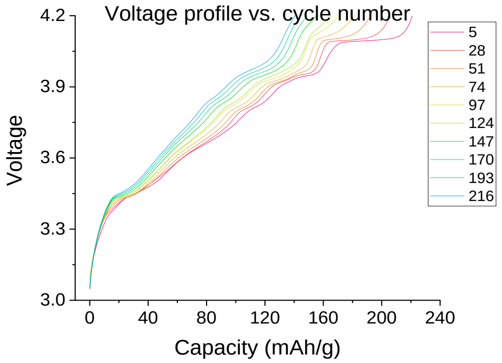


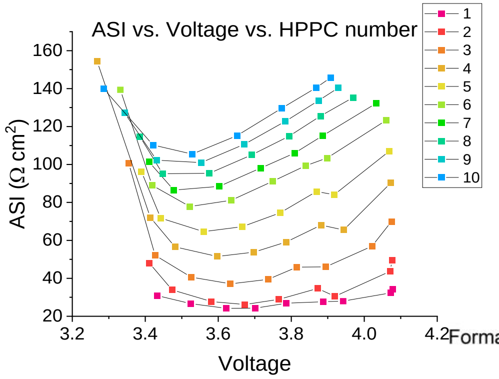


Performance evaluation

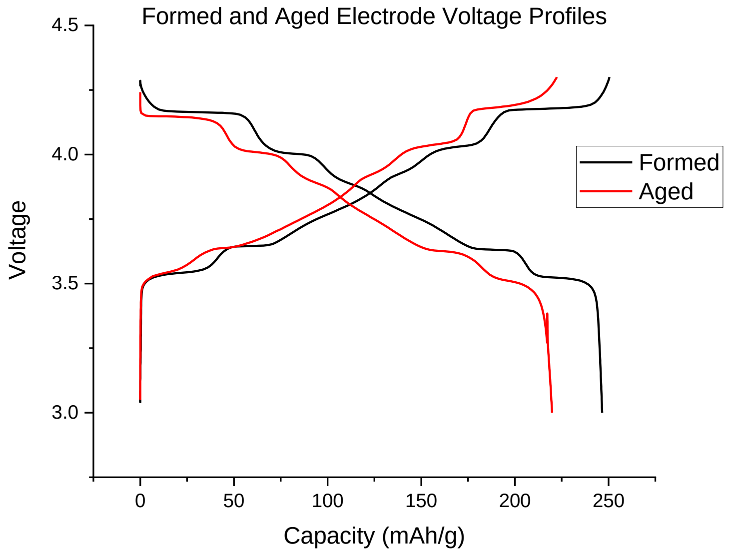


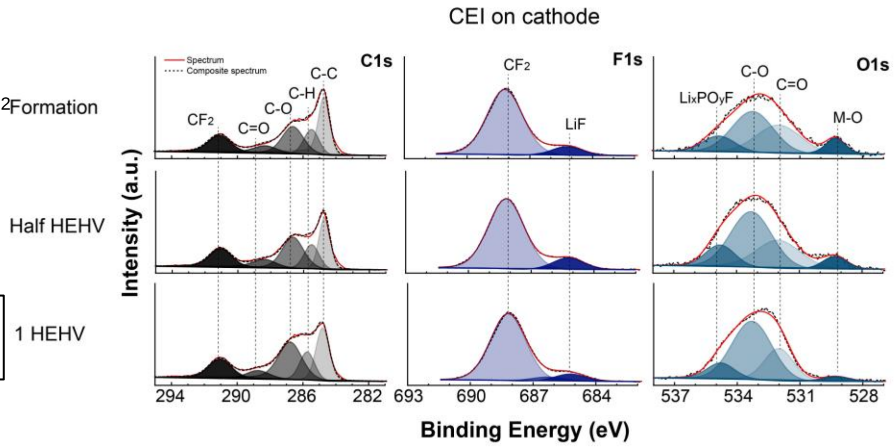






Post-test characterization

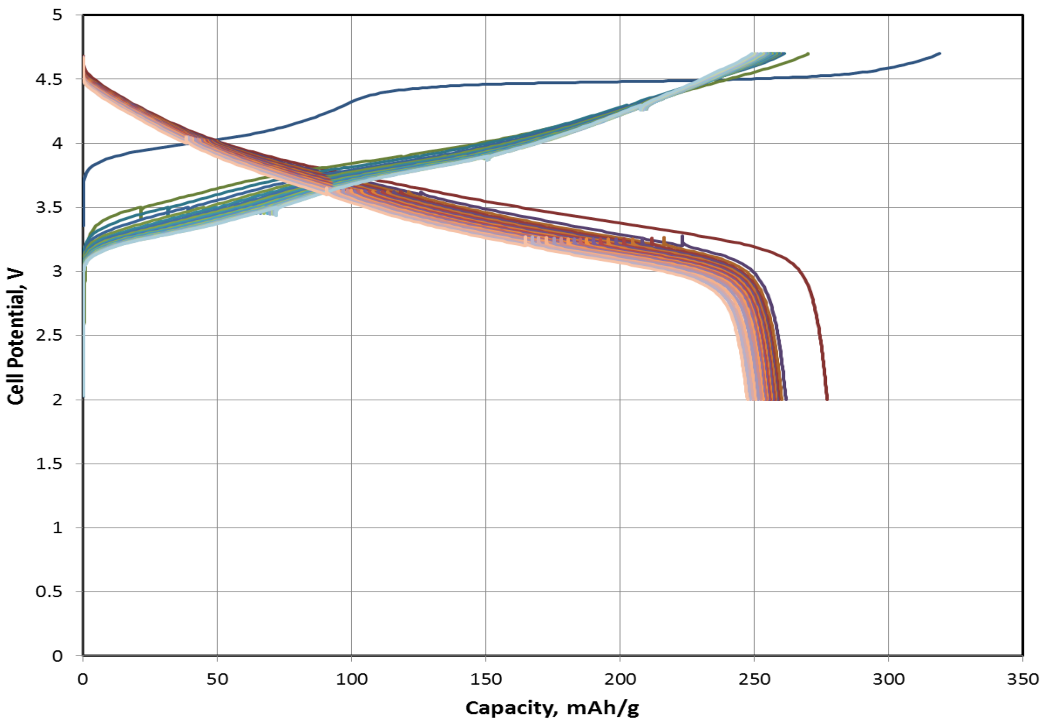


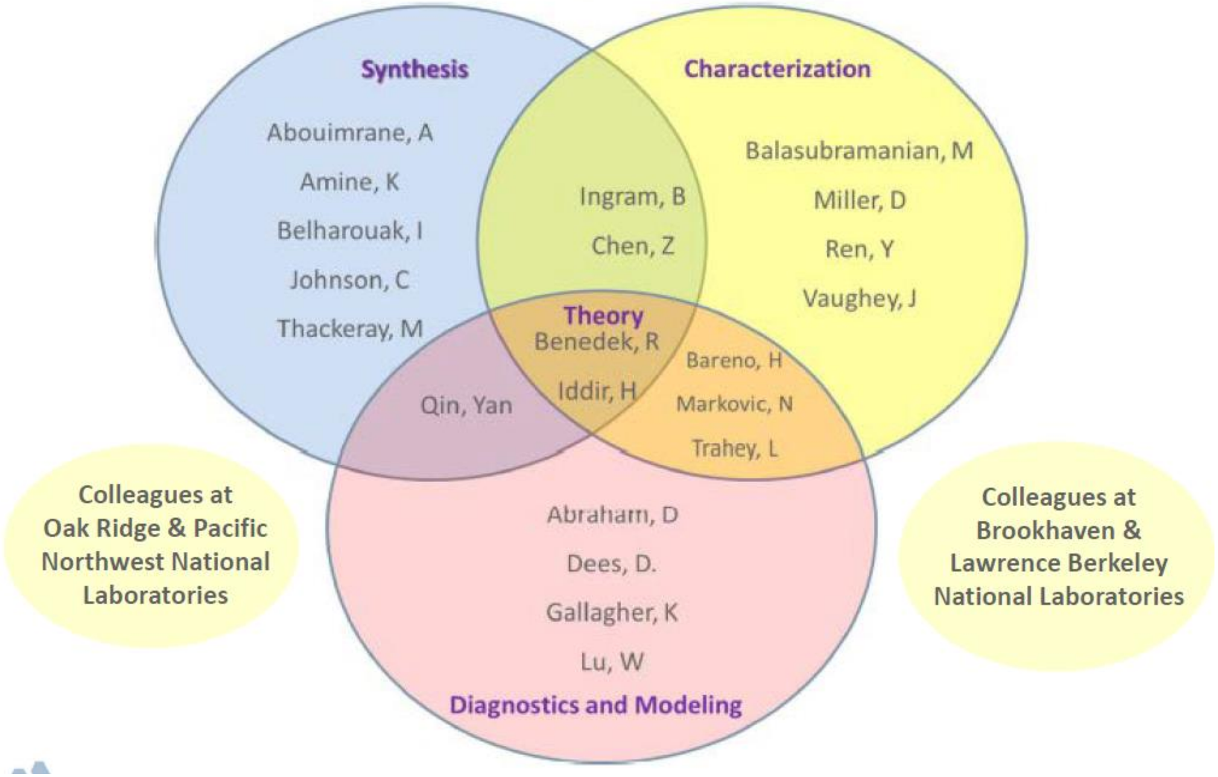


Significant amount of data generated

“Voltage Fade” spanned multiple DOE laboratories

Coordination between researchers requires a standardized testing protocol





Advantages of our methodology

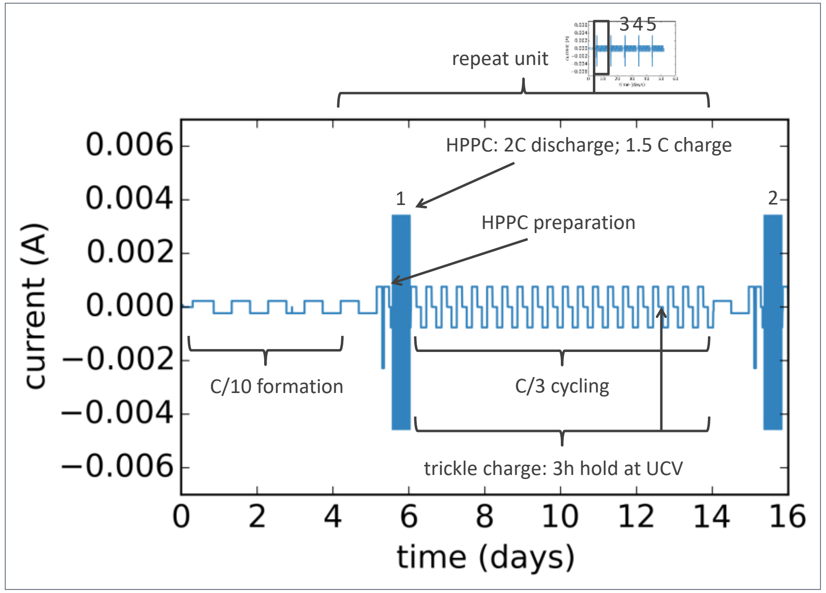
- Eases comparison between similar materials under similar testing conditions
- Good & reasonably fast tracking of an “average quasi-OCV” during cycling
- Tracking of other materials-related properties: capacities, and energy densities
- Measurement of the average cell resistance

Daniel Abraham, “Electrochemical Characterization of Voltage Fade in LMR-NMC cells”, U.S. Department of Energy Vehicle Technologies Office 2013 Annual Merit Review and Peer Evaluation Meeting, May 13 - 17, 2013, Washington, D.C., Vehicle Technologies Office.

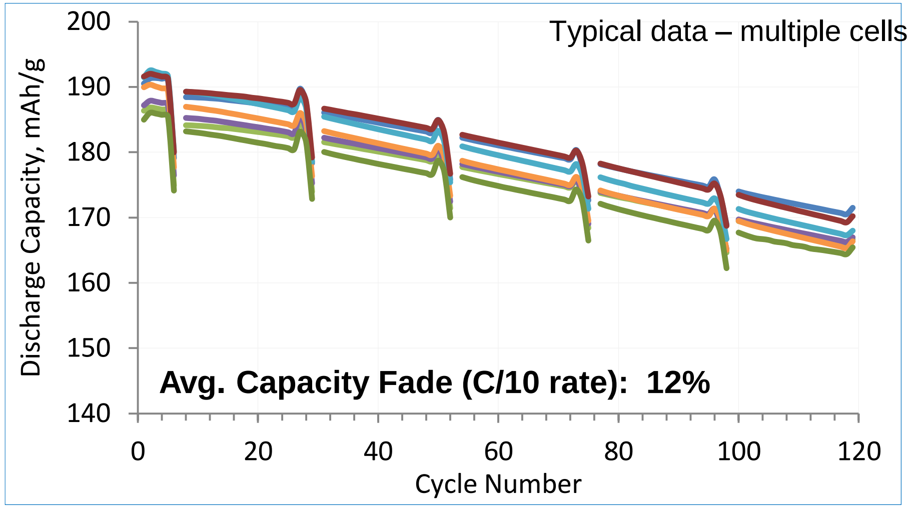
See also BAT252

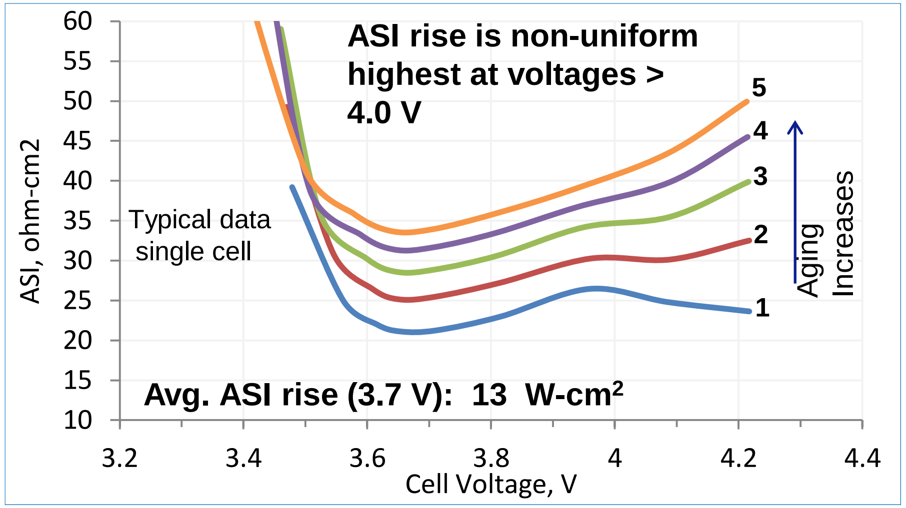
"High-Energy High-Voltage" required protocol standardization

Protocol needed to show meaningful differences between mitigation strategies



Standard protocol developed to track performance changes





Balanced

Testing had to show data in a reasonable amount of time, yet comprehensive enough to provide quality information

Robust

Different researchers assembling cells in different locations had to compare data: reproducibility is key

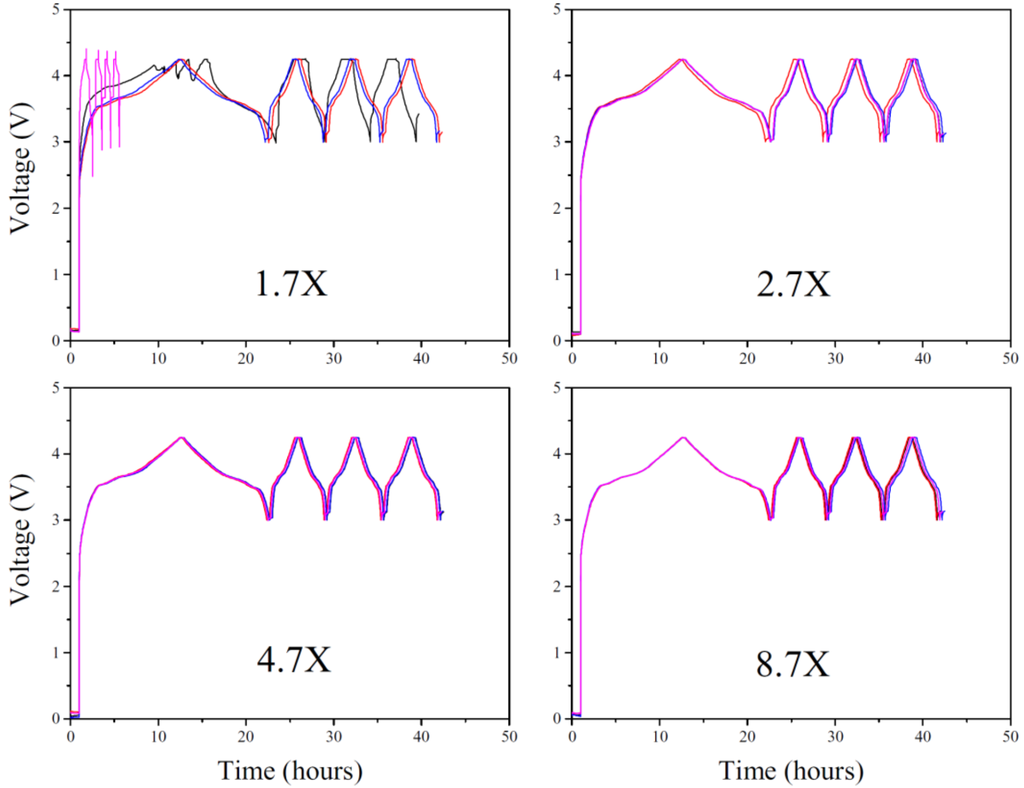
Aggressive

Protocol had to show degradation intrinsic to the aggressive environments (high voltage)

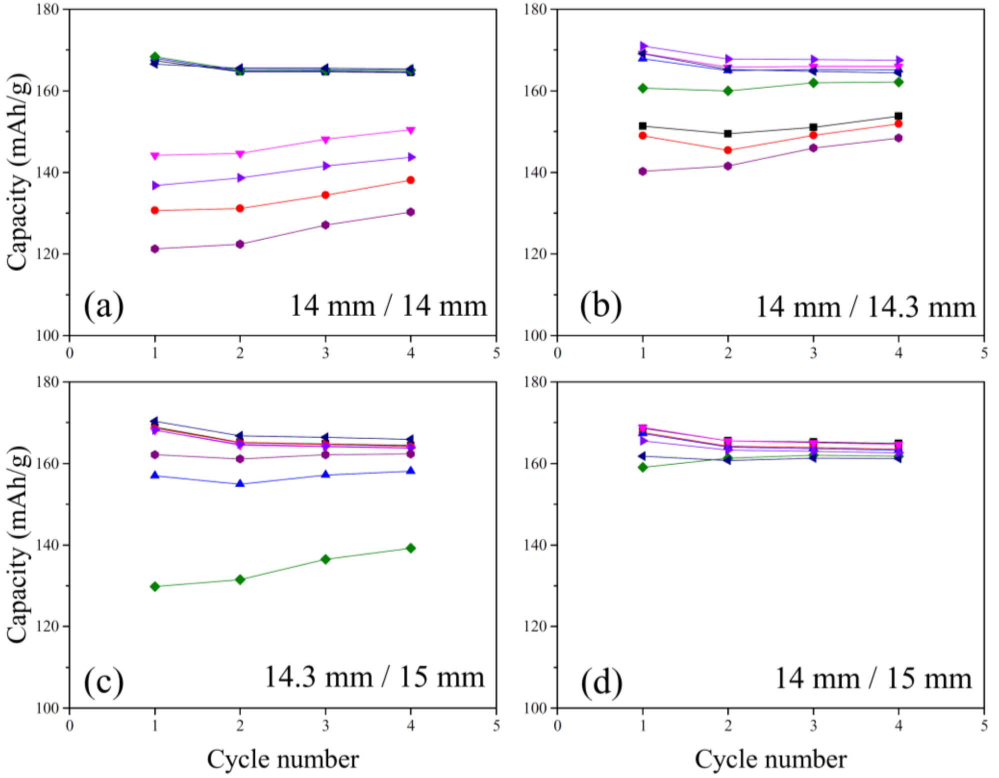
Influence of parameters for test reproducibility

Assembly parameters were chosen to increase reproducibility across coin cells

Electrolyte volume as a function of cell stack pore volume shows minimum necessary electrolyte for cell-to-cell reproducibility



Cathode diameter (mm) / anode diameter (mm) shows best degree of overhang for cell-to-cell reproducibility



Extensive work showed cell assembly parameters needed for reproducibility

Long et al., J. Electrochem Soc., 163, 2016

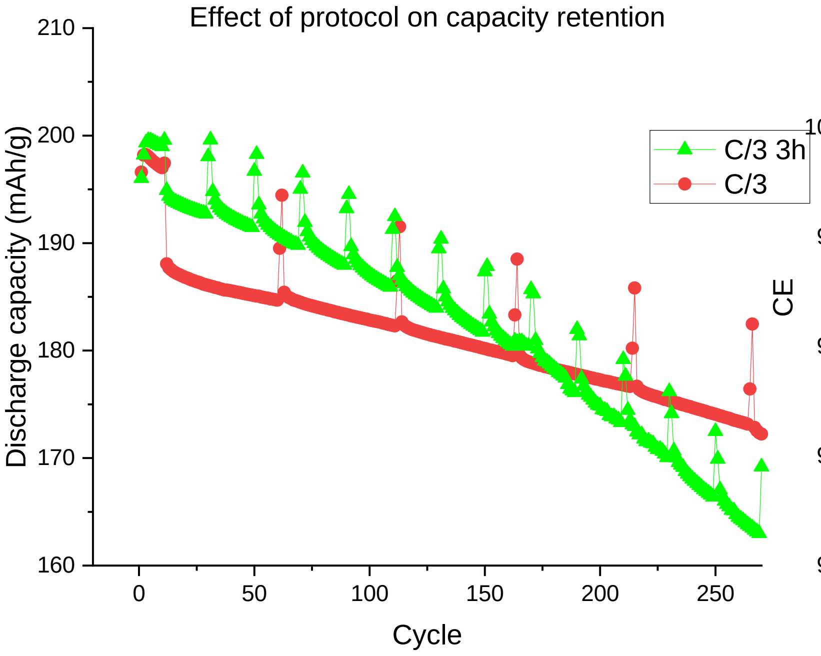
Influence of protocol parameters on cycling results

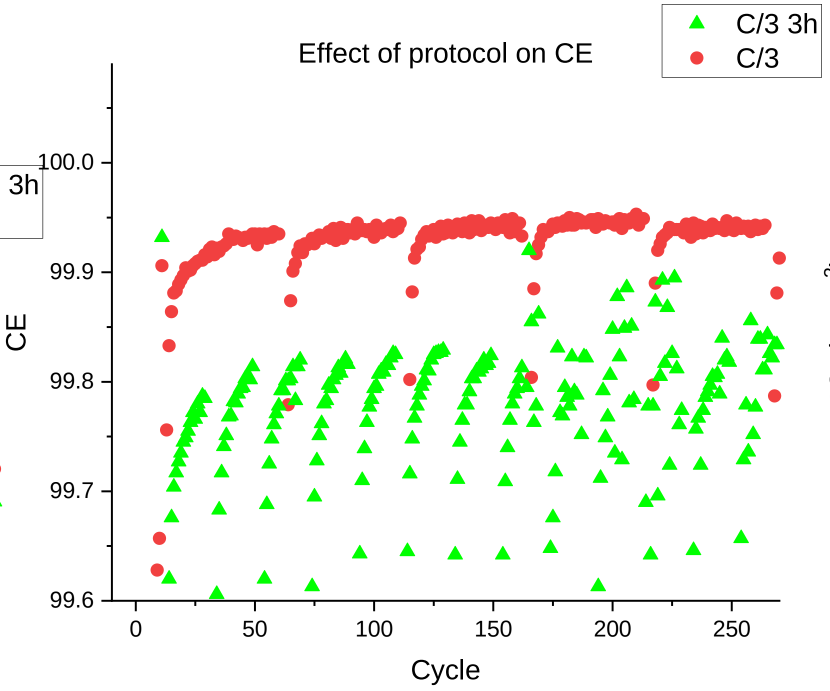
The developed protocol is aggressive, with 300 h at top of charge over a 119 cycle protocol

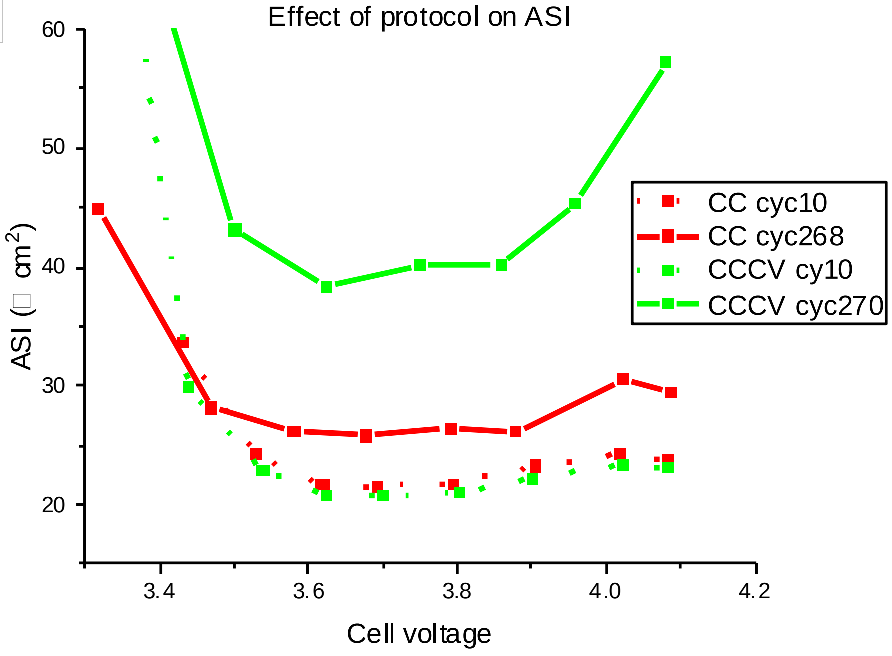
3 h hold at top of charge leads to slightly higher capacity, but worse capacity retention

3 h hold at top of charge leads to lower CE

3 h hold at top of charge leads to larger ASI increase at same cycle number







This aggressive protocol highlights known issues of the material; simpler protocols show higher retention and CE

How do we evaluate new materials?

Standardized procedures enable reproducible results

Laminate coating

- Amount of active material, carbon, binder
- Mixing and defoaming RPM and timing
- Coating/calendering thickness

Electrochemical testing protocols

- Same electrochemical tests
- Li and graphite anodes
- Fixed-temperature cycling

Coin cell assembly

- Electrodes from one source
- Anode, cathode, and separator diameter
- Electrolyte amount

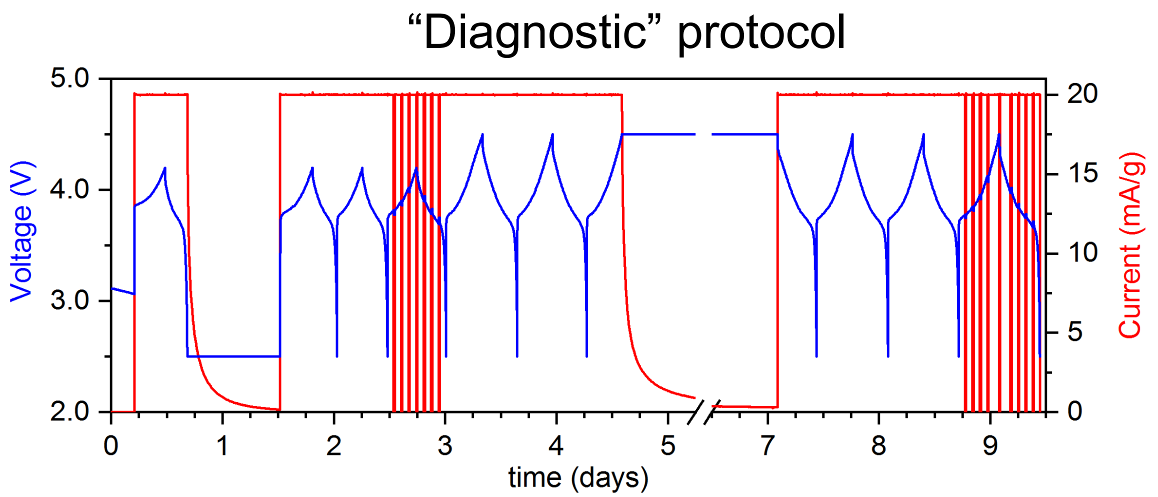
Other characterization

- Gassing, DSC, in-situ XRD
- ICP, XPS, NMR, SEM, STEM

See also BAT251, 252, 167

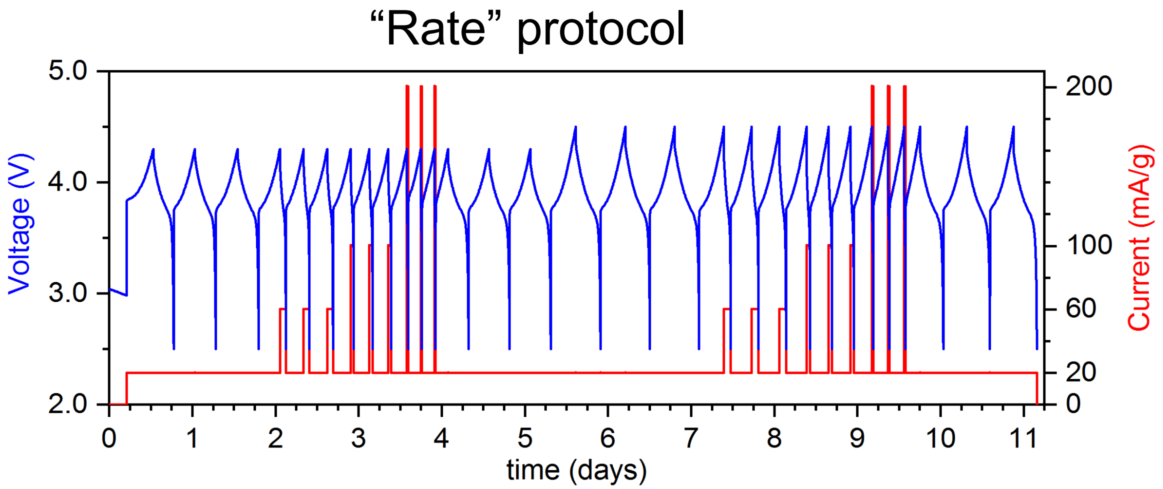
Standardized half-cell protocols

~2 week protocols to quickly evaluate hand-coated laminates for material properties.



"Diagnostic" protocol

- Uses 4.2 V and 4.5 V UCV
- Uses potentiostatic holds at LCV and UCV to evaluate stability and kinetics, sources of ICL
- Uses current interrupts to evaluate overpotentials during charge and discharge at both UCVs



"Rate" protocol

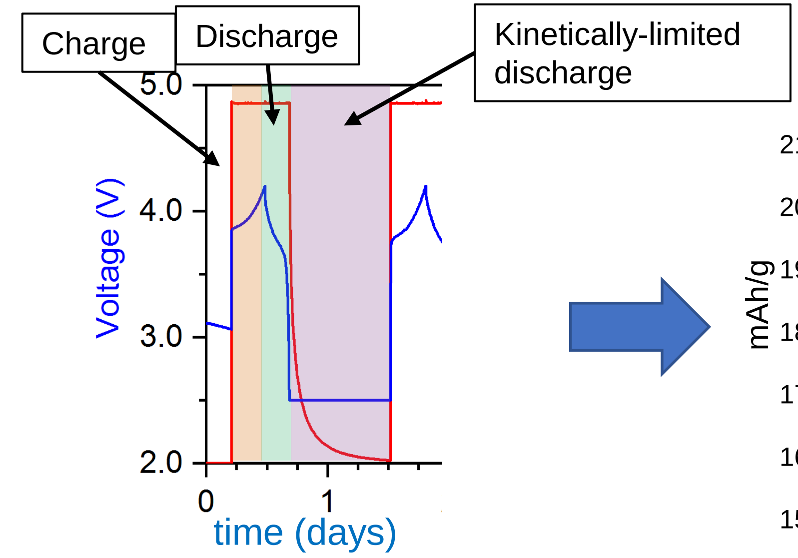
- Uses 4.3 V and 4.5 V UCV
- Incorporates constant charging current and variable discharge currents
- Repeats slow cycles at the beginning and end of each UCV to evaluate rate- and cycle-induced damage

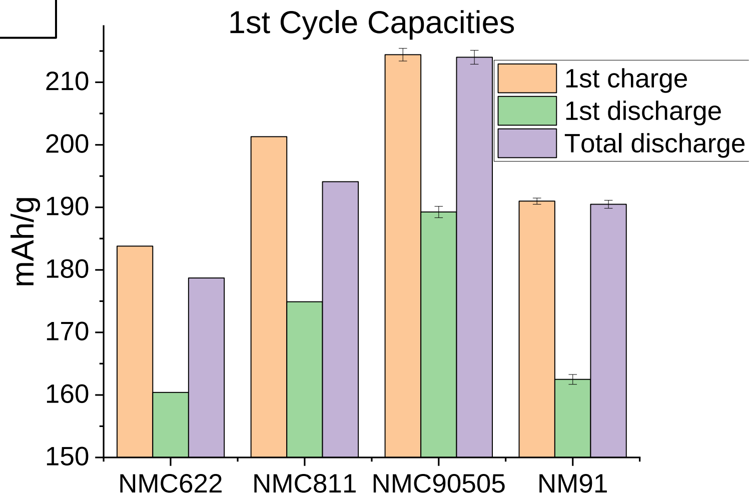
Strong performers are scaled up for full-cell evaluation

See also BAT251, 252, 167

Standardized half-cell protocols for material evaluation

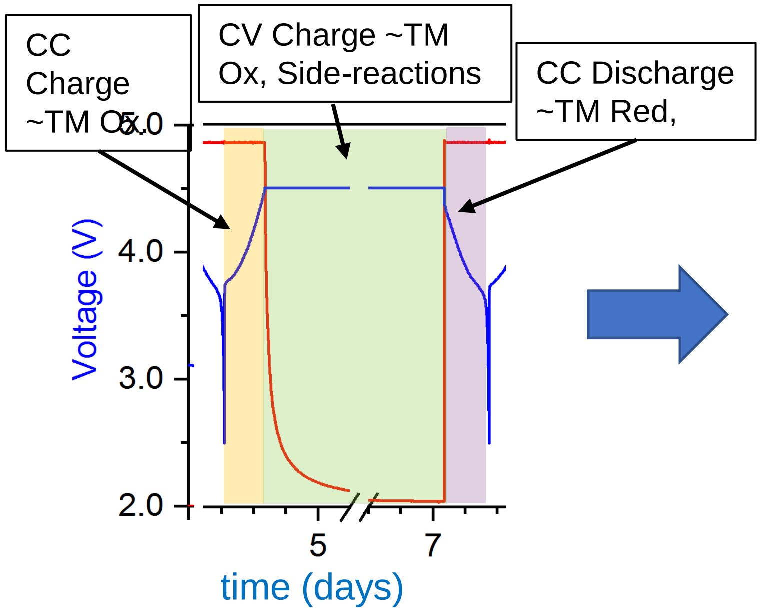
Diagnostic electrochemical protocols can indicate important material properties

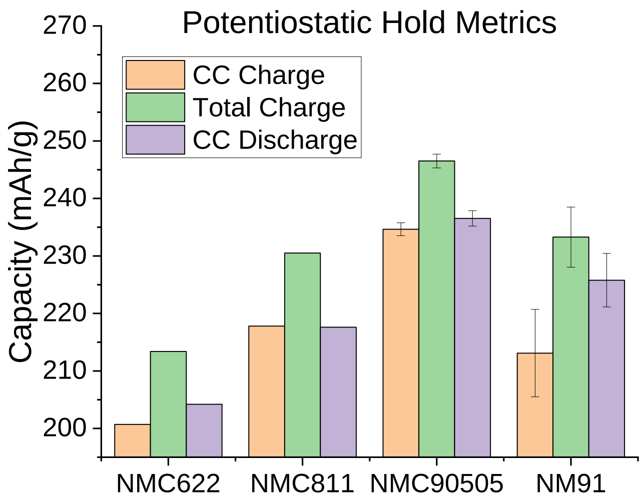




First cycle reactions

- First cycle indicates important properties of capacities and kinetics
- The low voltage hold separates true ICL from kinetic ICL
- Even LNO-based materials have excellent reversibility





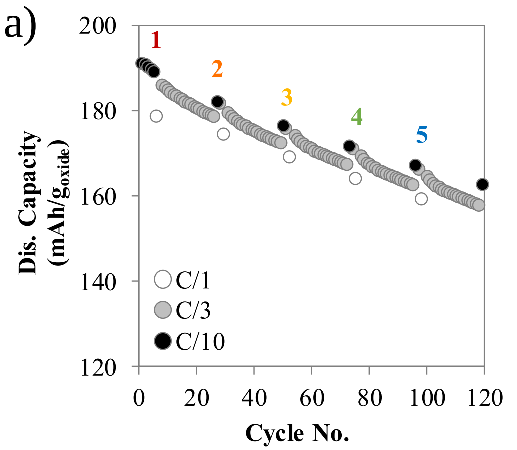
Potentiostatic hold metrics

- Potentiostatic hold at high voltage shows stability and polarization
- Discharge after potentiostatic hold shows polarization influence at high voltage
- Even LNO-based materials have limited reactivity at high-voltage

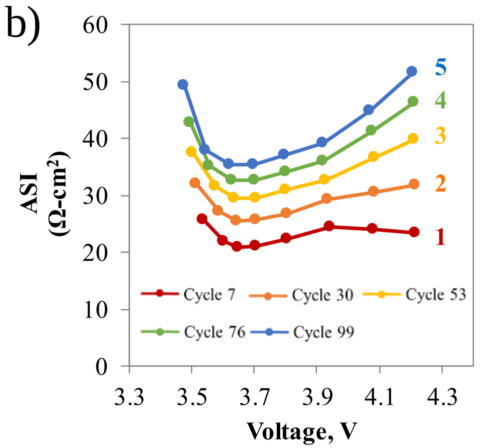
See also BAT251, 252, 253, 167

Standardized HEHV protocol is used for full-cell evaluation

~6 week, aggressive (300 h at 100% SOC) protocol evaluates capacity and power retention

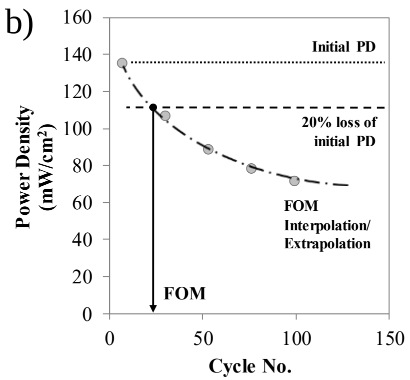


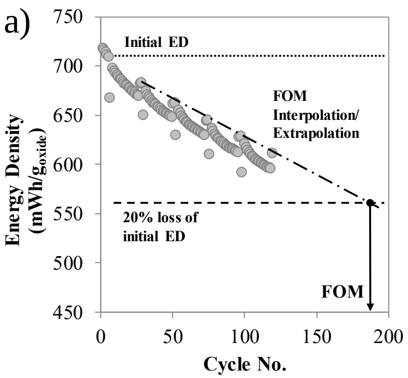
Discharge capacity dropped ~15% over the protocol



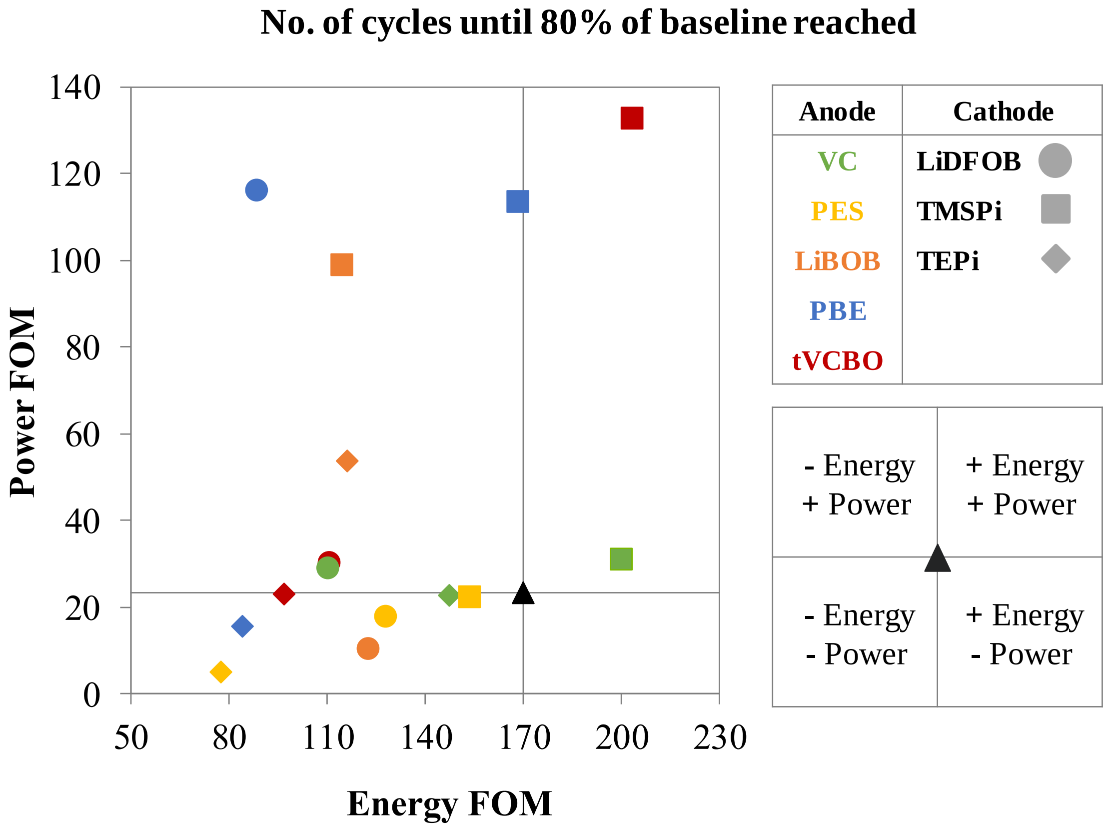
ASI increased ~80% over the protocol

FOM determined by cycle number at 80% of initial baseline value





Different electrolyte combinations can be independently evaluated



Assembly, testing, and evaluation standards allow for comparison between changes in the system

Tornheim et al., J. Power Sources., 365, 2017

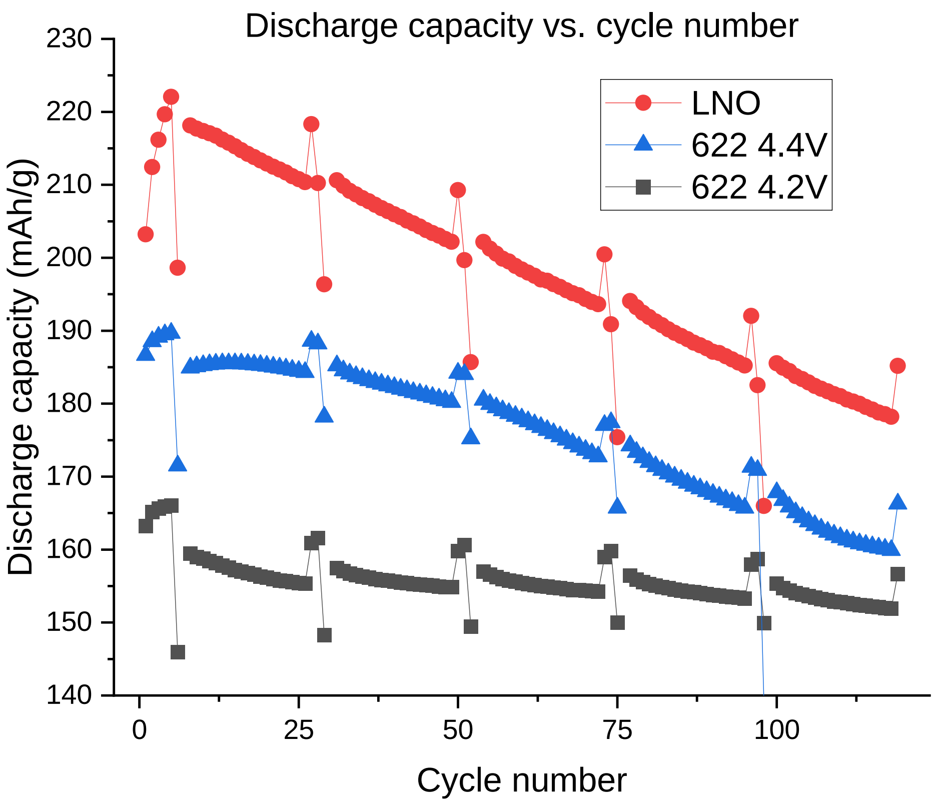
See also BAT251, 252, 253, 167

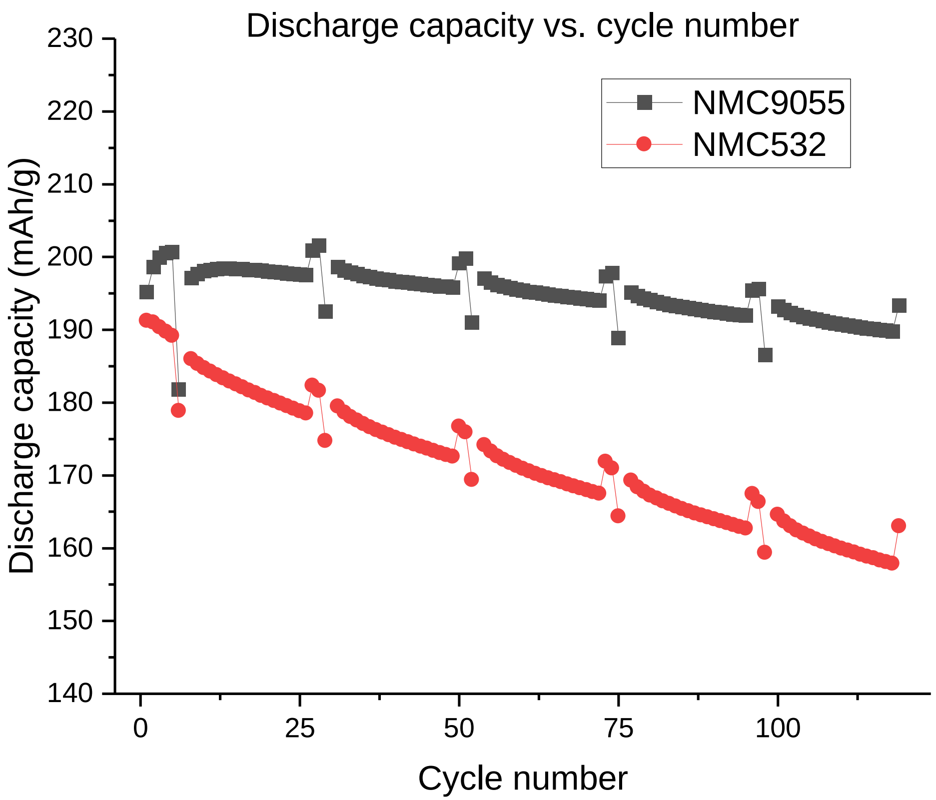
Standardized protocol allows for direct comparisons

Flexible parameters allow for direct comparisons between materials, and across projects

LNO and NMC622 (both synthesized and coated under RNGC) are compared at multiple UCVs

NMC9055 (baseline RNGC compositions, synthesized and coated under RNGC) and NMC532 (HEHV project baseline) are compared





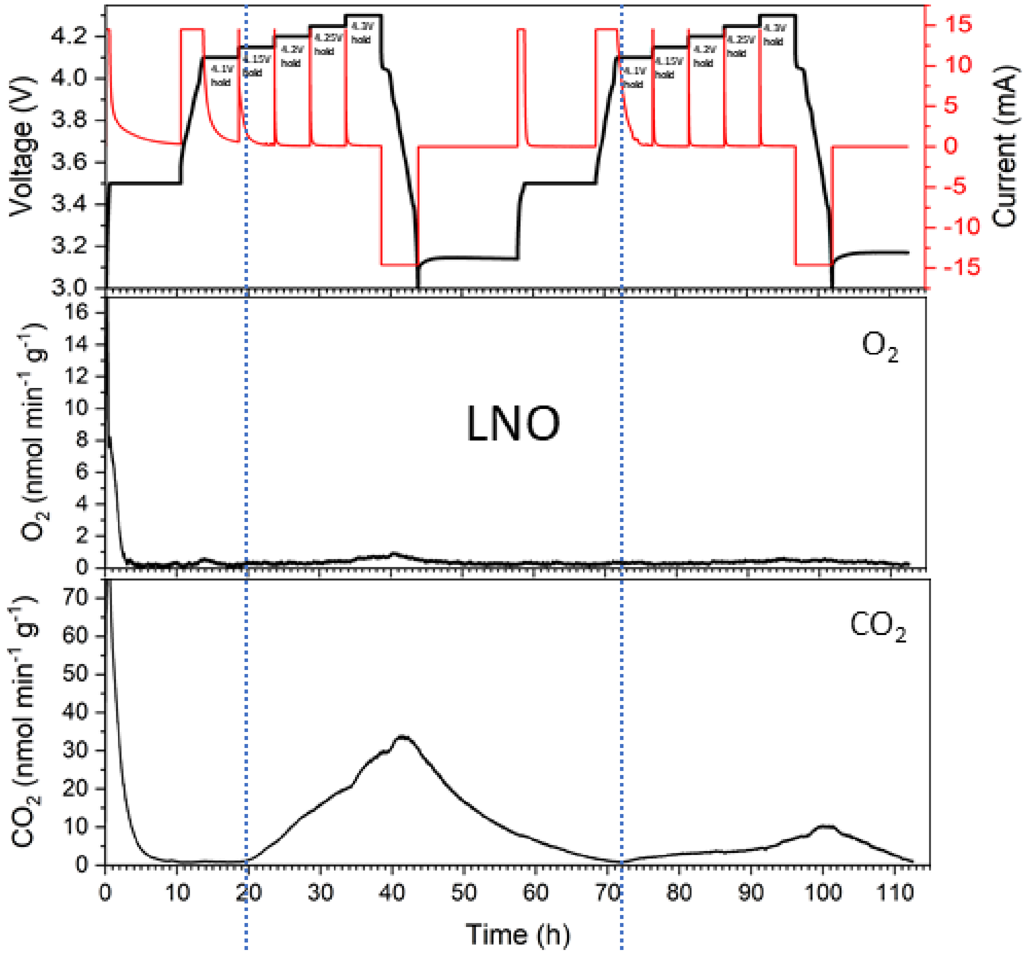
Continuity of standardized protocols can compare different materials from different projects

See also BAT251, 252, 253, 167

Gassing protocol development

Determination of onset voltage and gas released for electrodes produced under RNGC

- Oxygen evolution and thermal stability are key factors that limit the use of LNO-based materials
- Understanding the onset voltage and gas species released at the interface would help identify how new strategies could stabilize the materials
- A standardized protocol, including voltage range, potentiostatic hold times, and charging currents, was developed to characterize all the cathodes coated by the CAMP facility for this project



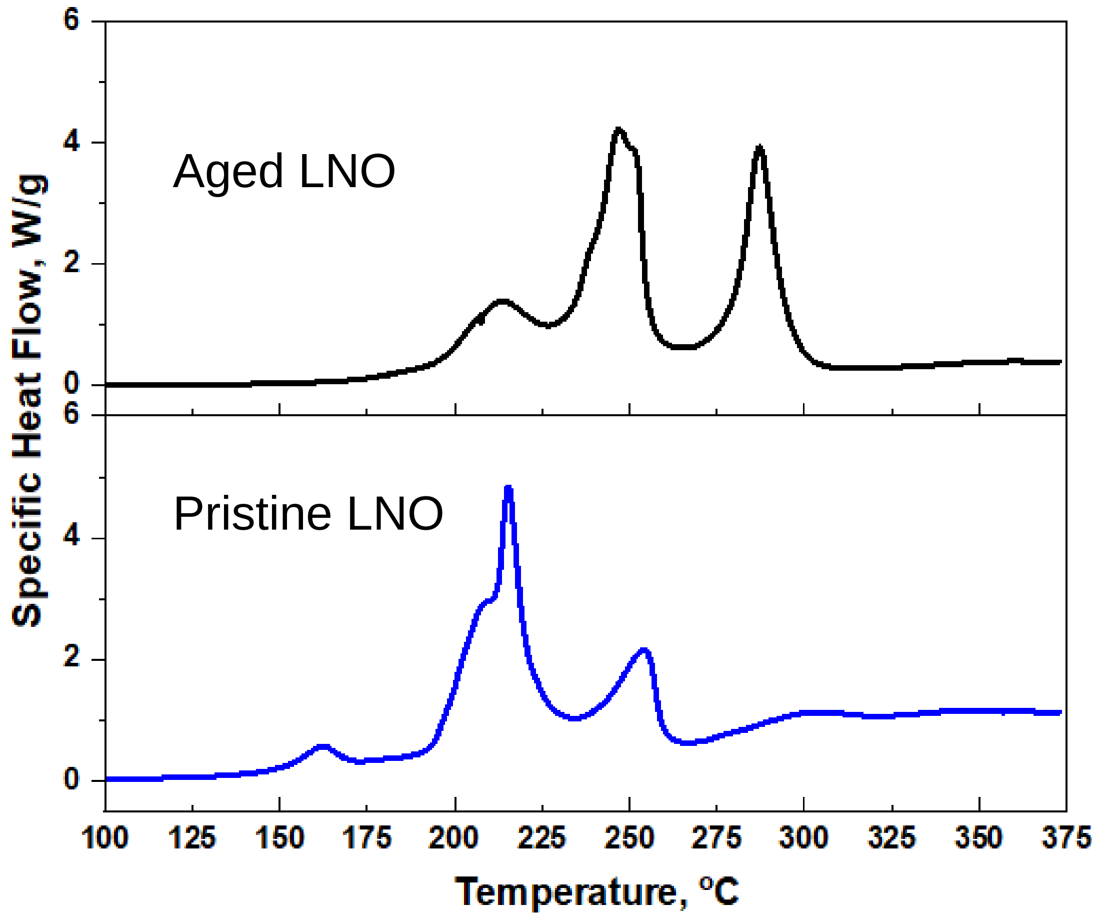
See also BAT251, 252, 253, 167

DSC protocol development

Sample preparation and test protocol consistent across samples

Standardized processes include

- Electrochemical preparation – consistent end state across samples
- Rinsing procedure – amount of solvent
- Drying conditions, temperature and time
- Sample amount, as well as added electrolyte/sample
- Thermal equilibration time, temperature ramp speed, final temperature
- Number of repeats



Standardized DSC protocol allows for comparisons of onset temperature, 1st peak temperature, and total heat released between compositions/formulations

See also BAT251, 252, 253, 167

Cathodes generated in this project undergo standardized tests

	Cathode	Precursor Synthesis	Final Product (scale-up)	XRD	SEM	ICP	NMR	Li Cell echem	CAMP electrodes	HEHV echem	Gassing	DSC	(in situ) Spectro.	XPS
Control samples	60-20-20	x	x	x	X			x	x	x	x		X	
	LNO	x	x	x	X	x	x	x	x	x	x		X	X
Effect of Co	95-0-5	x	x	x	x	x		x	x	x	x	x	X	X
	90-0-10	x	x	x		x		X	X	x				
Effect of Mn	95-5-0	x	x	x		x		X	x	x				
	90-10-0	x	x	x	x	x	x	x	X	x	x	x	X	X
Effect of Mn & Co	95-2.5-2.5	x	x					x	x					
	90-5-5	x	x	x	x	x	x	x	x	x	x	x	x	X
w/wo surface/bulk Al	94-0-6	x	x	x	x	x	x	x	x	x	x	x	X	X
	92-0-6-2	x	X	x	x	x	x	x	X		x			X

Standardized tests are underway for all scaled-up materials in this project

See also BAT251, 252, 167

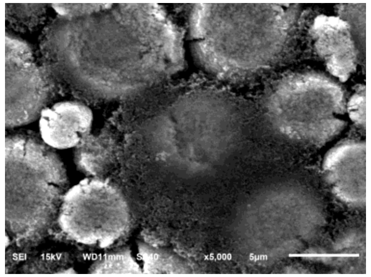
Sample of generated data (LNO)

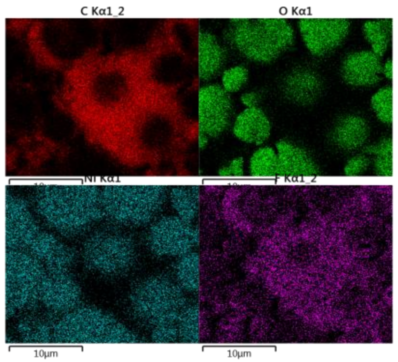
Pristine, cycling, and post-test data all collected for LNO generated in this project.

Screening/characterization

Performance evaluation

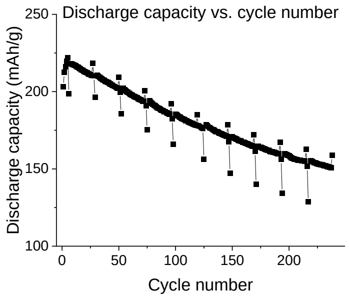
Post-test characterization

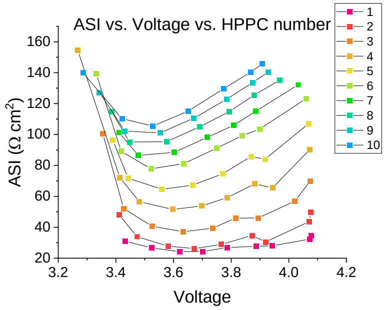


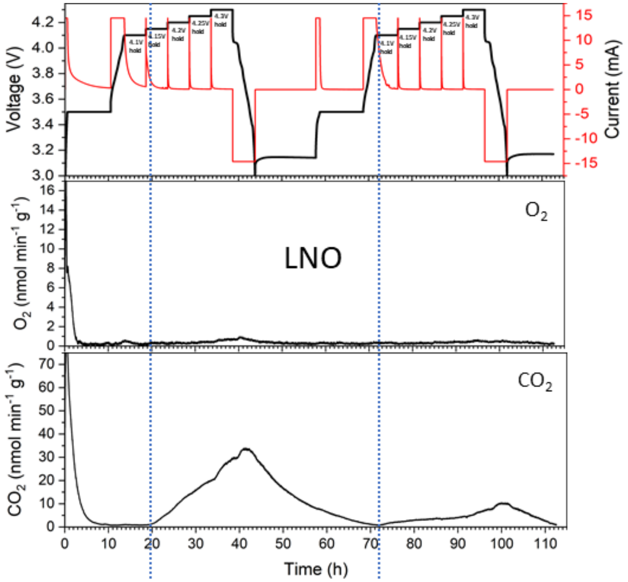


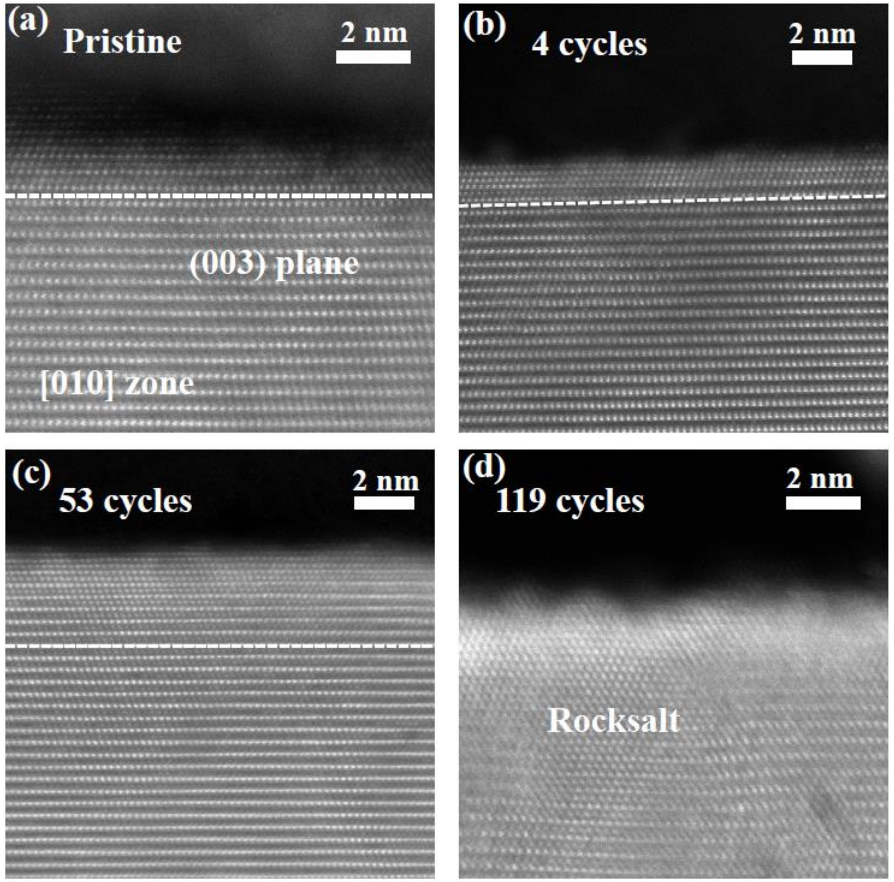
Map Sum

Spectrum Element	W.t. %	s
C	42.6	0.2
Ni	32.1	0.2
O	20.2	0.1
F	5.0	0.1
S	0.1	0.0









Results across multiple tests can be easily tracked and compared

Next-Gen Cathode Project Contributors

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Major Research Facilities

- Materials Engineering Research Facility
- Post-Test Facility
- Cell Analysis, Modeling, and Prototyping
- Spallation Neutron Source
- Environmental Molecular Sciences Laboratory
- Advanced Light Source
- Battery Manufacturing Facility
- Advanced Photon Source (APS)
- Laboratory Computing Resource Center (ANL)
- NMR Spectroscopy Lab (ANL)
- National Energy Research Scientific Computing Center (LBNL)
- Stanford Synchrotron Radiation Light Source

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Summary

See also BAT251, 252, 253, 167

- Standardizing testing procedures is crucial for identifying improvements to the system under test
- Multiple iterations of VTO-funded, multi-institutional projects require coordination between lab members
- The protocols developed under these projects highlight the known issues with the materials
- Significant work has been performed to create robust testing procedures to enable reproducibility across multiple researchers and National Labs
- Characterization procedures have been standardized to allow for direct comparisons between compositions/formulations
- These kinds of protocols are broadly applicable and can be adjusted to suit the properties and limitations of the material under test
- Standardizing protocols across the community is imperative to make direct comparisons and enable future improvements