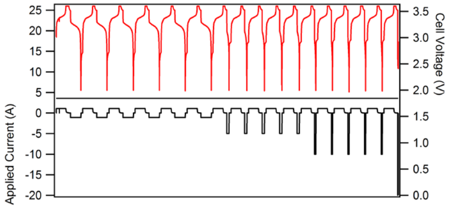
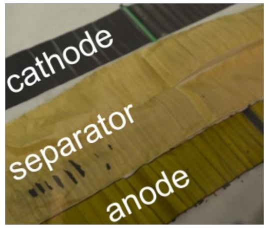
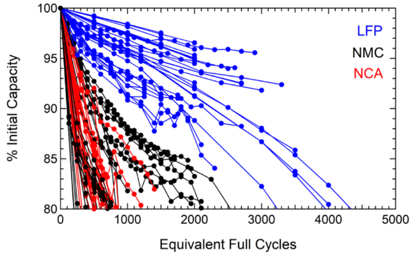
SAND2021-4787C

Sandia National Laboratories

Degradation of Commercial Li-ion Cells Beyond 80% Capacity







PRESENTED BY

Yuliya Preger

Energy Storage Systems Safety & Reliability Forum

April 20, 2021

U.S. DEPARTMENT OF ENERGY NNSA

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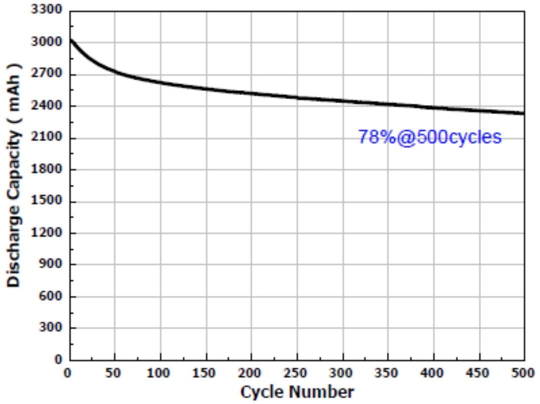
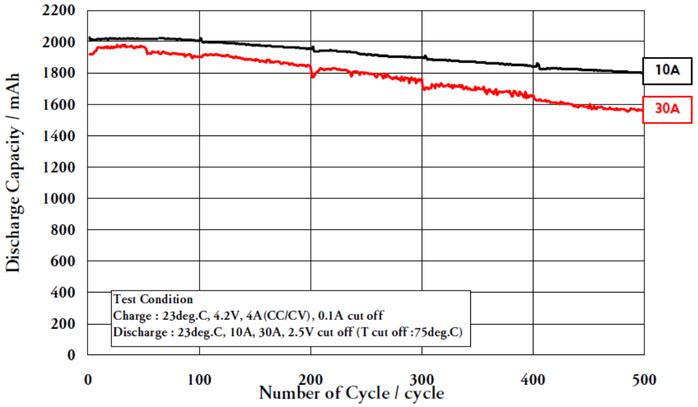
Moving Beyond 80% Capacity for Grid Applications

- 80% capacity is a common reference point in manufacturer spec sheets

Examples:





- 80% capacity is a holdover from the EV world
  - USABC 1996: "*EV batteries should be removed from automotive use when* ***current battery capacity is 80% of initial battery capacity*** *and current battery power capability is 80% of initial battery power capability*"
  - At this time, EVs were primarily powered by Ni-based batteries

- Unrealistic criteria for Li-ion batteries with higher energy density and power capability

Overview

1) Recent experimental work on battery degradation beyond 80% capacity

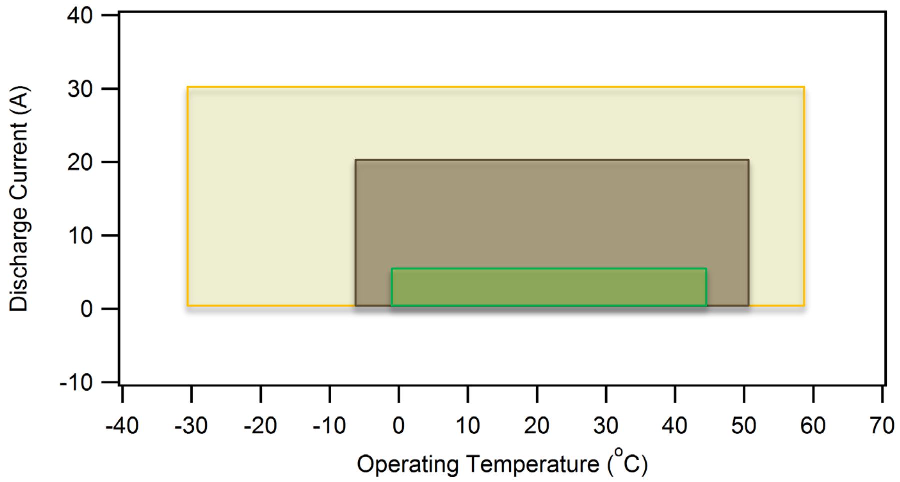
2) Review of battery degradation tipping points

3) Visualization tools for battery lifecycle analysis

Scope of Current Study at SNL: Cells and Manufacturer Specifications

Positive Electrode Chemistry	AKA	Vendor	Specific Capacity (Ah)	Max Discharge Current	Acceptable Temperature (°C)
$LiFePO_4$	LFP	A123	1.1	30	-30 to 60
$LiNi_{0.81}Co_{0.14}Al_{0.05}O_2$	NCA	Panasonic	3.2	6	0 to 45
$LiNi_{0.84}Mn_{0.06}Co_{0.1}O_2$	NMC	LG Chem	3.0	20	-5 to 50

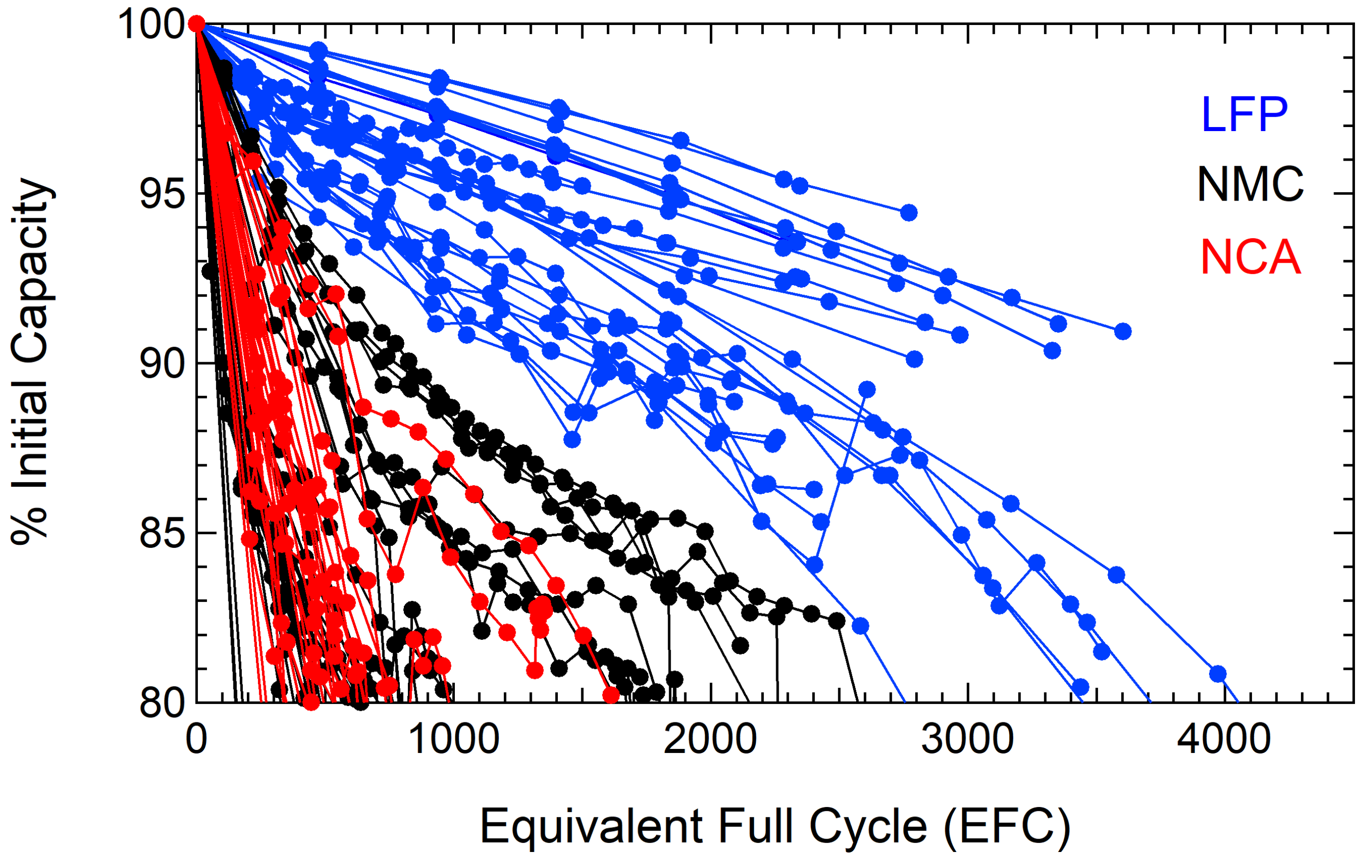
LFP NCA NMC



Variables:

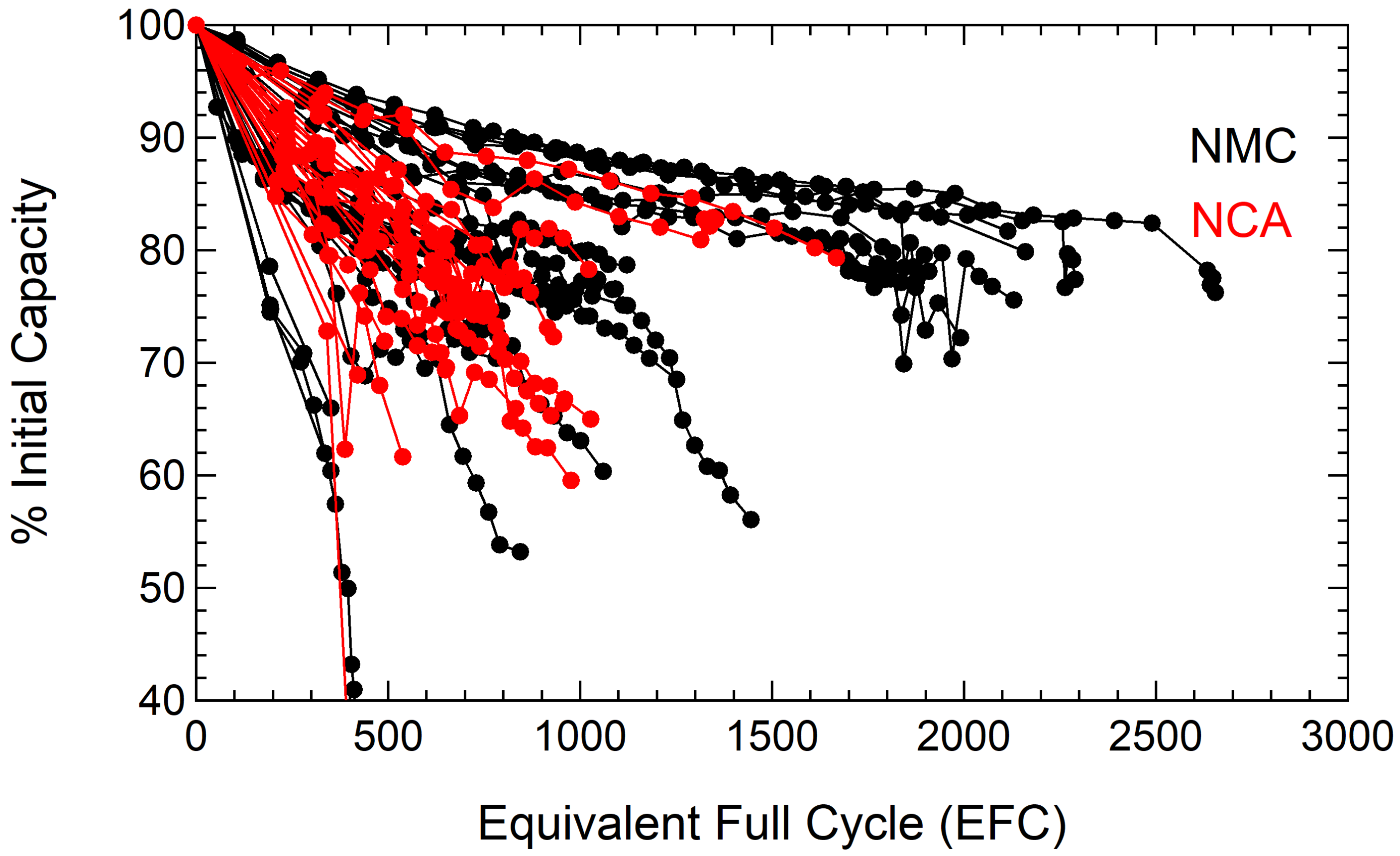
- Charge Rate: 0.5C
- Discharge Rate: 0.5C, 1C, 2C, 3C
- SOC Range: 40-60%, 20-80%, 0-100%
- Temperature: 15°C, 25°C, 35°C

Cycling to 80%



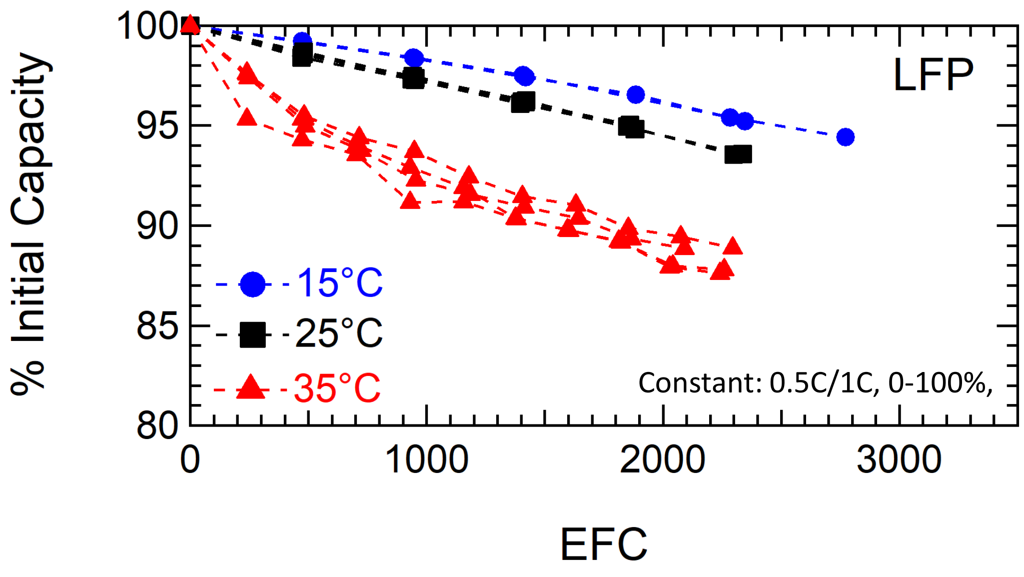
Data based on range of cycling conditions (within manufacturer's spec)

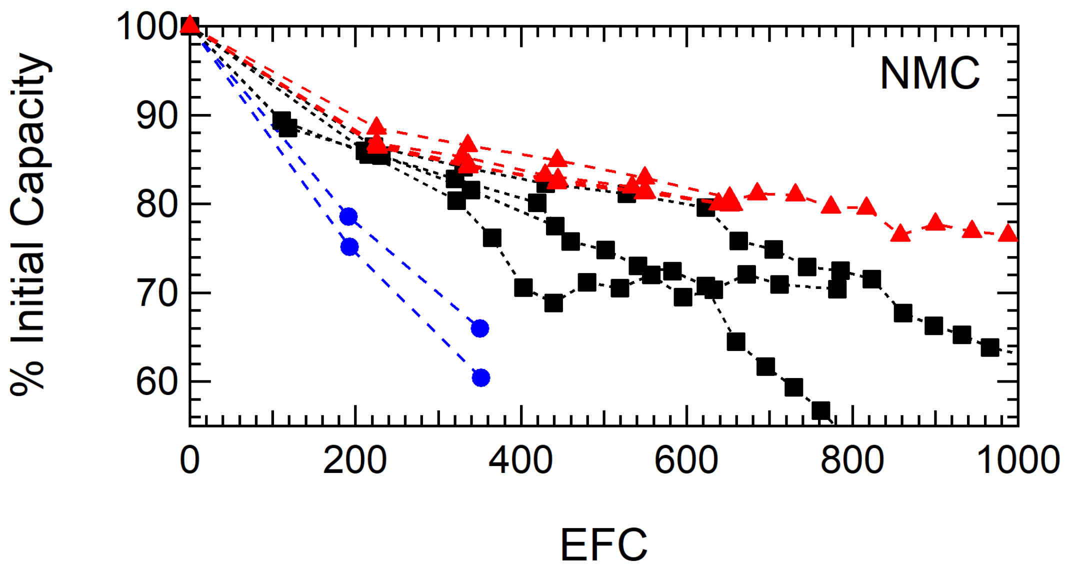
Cycling Past 80%: Preliminary Insights

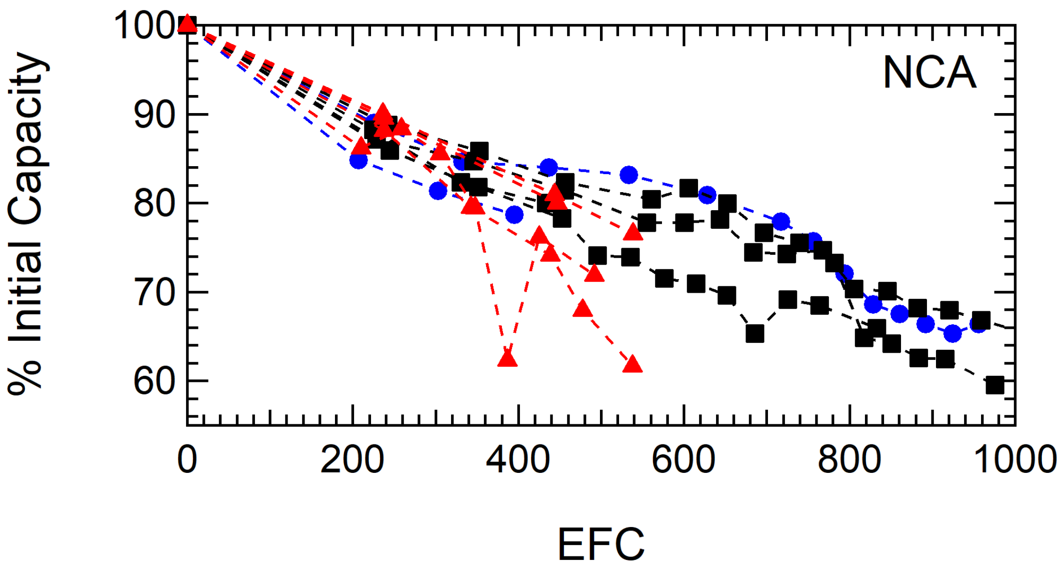


Work led by Reed Wittman, Armando Fresquez

Long-Term Cycling: Temperature Dependence

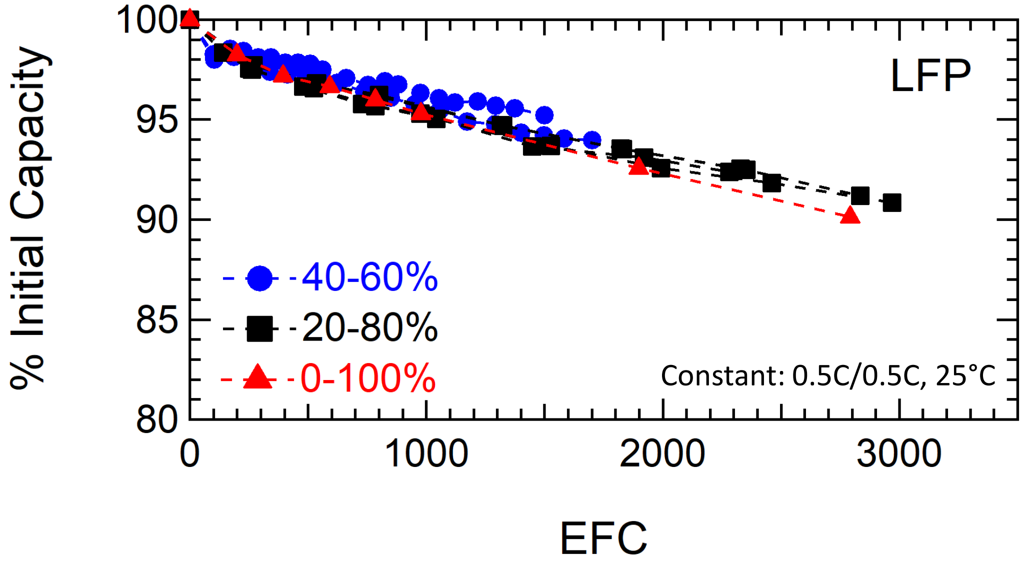


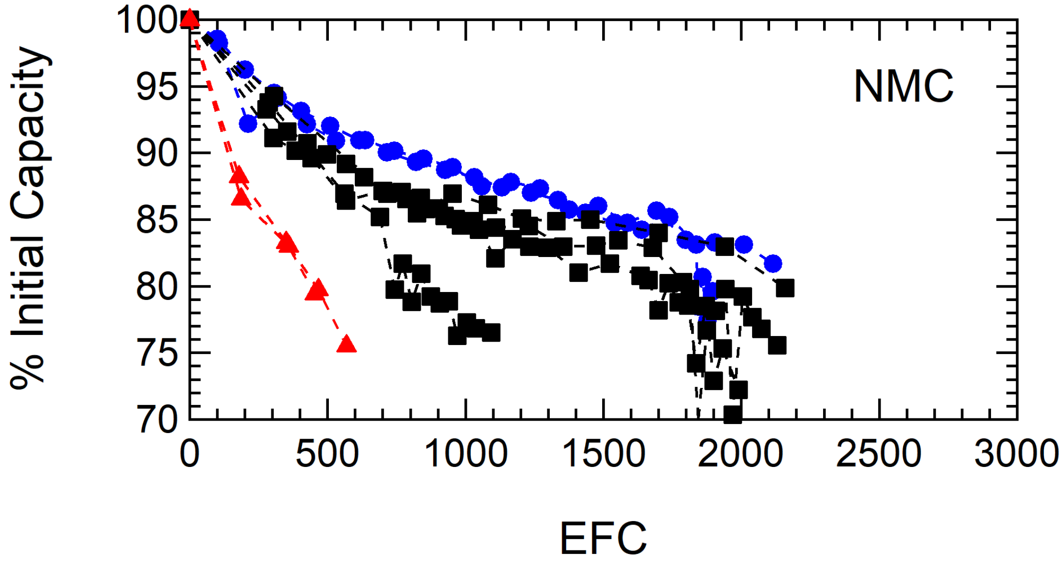


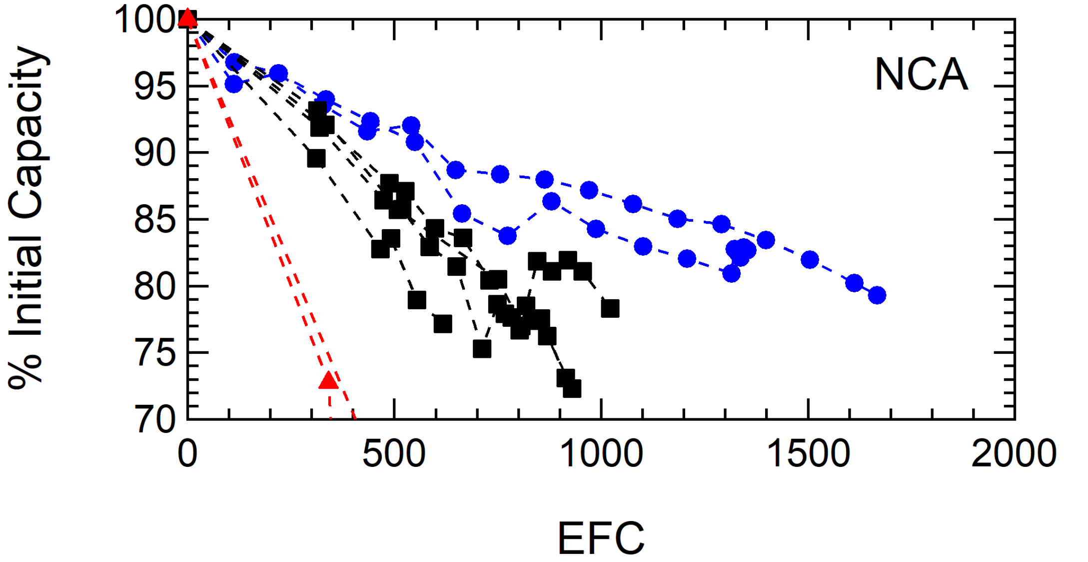


LFP and NMC exhibit inverse dependence on temperature

Long-Term Cycling: SOC Dependence

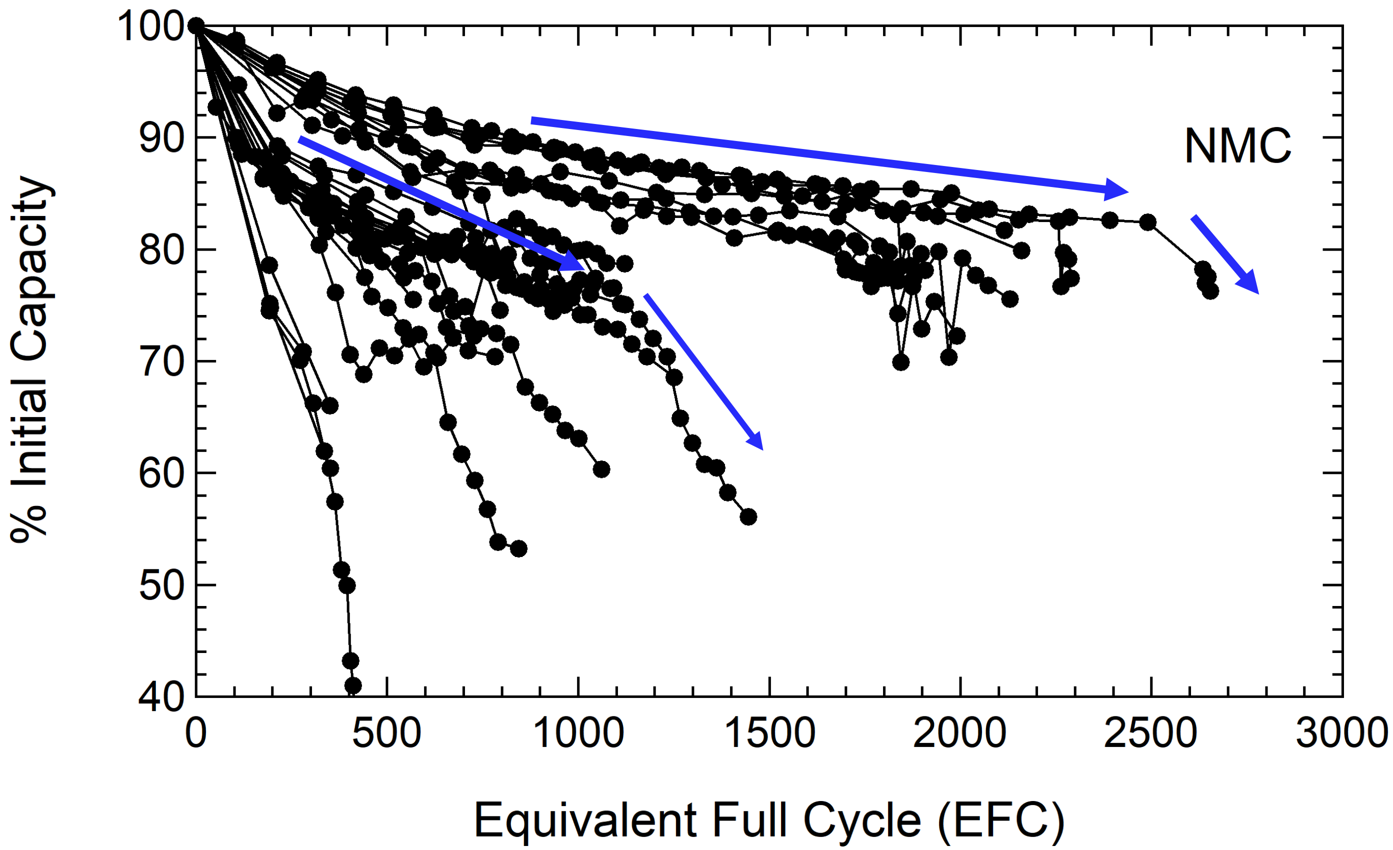






NCA and NMC more sensitive to full discharge

Knees Beginning to Emerge



Overview

1) Recent experimental work on battery degradation beyond 80% capacity

2) Review of battery degradation tipping points

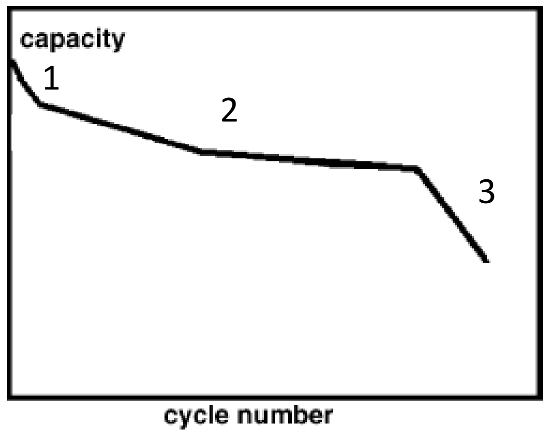
3) Visualization tools for battery lifecycle analysis

How Far Beyond 80% Should We Go?

One possible criteria: until a battery undergoes rapid degradation

- Typical model of LiB degradation assumes a transition from linear behavior
  - Phase 1: SEI formation
  - Phase 2: linear degradation
  - Phase 3: rapid capacity fade

- Transition to rapid capacity fade has many names
  - Transition point, tipping point, knee, rollover



Spotnitz et al. *J. Power Sources* **2003**, *113*, 72.

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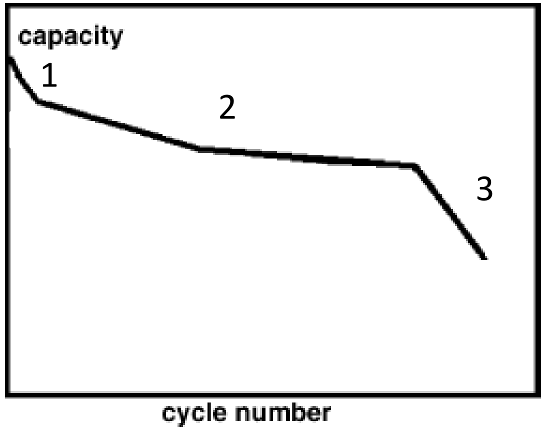

Spotnitz et al. *J. Power Sources* **2003**, *113*, 72.

What causes the knee point?

Multi-Institution Team Reviewing Empirical Causes and Mechanisms of Knee Points

A*STAR (Edwin Khoo, Ouyang Liu)
NREL (Paul Gasper)
Carnegie Mellon University (Shashank Sripad, Alec Bills)
University of Michigan (Anna Stefanopoulou, Valentin Sulzer)

RWTH Aachen University (Philipp Dechent)
University of Warwick (Ferran Brosa Planella)
University of Oxford (David Howey, Sam Greenbank)
Peter Attia, Abhishek Soni

“Perturbation” of Any Variable Can Induce Knees – I. Cell Design

"Perturbation" of Any Variable Can Induce Knees – I. Cell Design

Variable	Cell Description	Range of Variable	Knee Acceleration
Electrode loading	Lab-made pouch NMC/Gr	14.4-21.2 mg/cm^2	Higher positive electrode loading

“Perturbation” of Any Variable Can Induce Knees – I. Cell Design

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Positive electrode coating	Lab-made pouch NMC/Gr	Ti-based coating	Uncoated positive electrode

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Graphite type	Lab-made pouch NMC/Gr	artificial, natural	Natural graphite

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Graphite type	Lab-made pouch NMC/Gr	artificial, natural	Natural graphite
Additive package and concentration	Lab-made pouch LCO/Gr-Si	NA	FEC consumed
	Lab-made coin LFP/Gr-Si	0-20 wt.% FEC	FEC consumed
	Lab-made pouch NMC/Gr	0-20% methyl acetate additive	Higher methyl acetate concentration

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	Lab-made coin LFP/Gr-Si	0-20 wt.% FEC	FEC consumed
	Lab-made pouch NMC/Gr	0-20% methyl acetate additive	Higher methyl acetate concentration
Salt concentration	Lab-made pouch NMC/Gr	0.2-1.2M $LiPF_6$	Higher salt concentration
	Lab-made pouch NMC/Gr	1.2-1.5M $LiPF_6$	Lower salt concentration
	Lab-made pouch LCO/Gr	0.5-2M $LiPF_6$	Higher salt concentration

"Perturbation" of Any Variable Can Induce Knees – II. Testing Conditions

"Perturbation" of Any Variable Can Induce Knees – II. Testing Conditions

Variable	Cell Description	Range of Variable	Knee Acceleration
Charging rate	OMT OMLIFE-8AH-HP LFP/Gr	1-8C	Higher charging rate
	Commercial 26650 LFP/Gr	0.5-1C	Higher charging rate
	Panasonic 18650 NCA/Gr	0.1-1C	Higher charging rate
	Cylindrical NCA/Gr	0.25-1C, single vs. multi-step CC, optional CV	Higher charging rate, CV
	E-One Moli Energy IHR18650A NMC/Gr	0.2-1C	Higher charging rate
	A123 APR18650M1A LFP/Gr	3.6-8C	Higher charging rate
	Samsung ICR18560-26F NMC/Gr	0.25-2C with AC pulse, current derating, current interrupt	Higher charging rate, no AC pulse or current interrupt
	Cylindrical NMC/Gr	0.7-1C	Higher charging rate

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	A123 APR18650M1A LFP/Gr	3.6-8C	Higher charging rate
	Samsung ICR18560-26F NMC/Gr	0.25-2C with AC pulse, current derating, current interrupt	Higher charging rate, no AC pulse or current interrupt
	Cylindrical NMC/Gr	0.7-1C	Higher charging rate
Discharging rate	a) Sanyo UR18650SA LMO+NMC/Gr b) Sony US18650VT1 LMO+LCO/Gr c) A123 APR18650M1A LFP/Gr	a) 2.4-4C b) 2.7-4.5C c) 2.7-4.5C	a) Higher discharging rate b) No difference c) Higher discharging rate
	Cylindrical NMC/Gr	1-2C	Lower discharging rate
	Commercial 18650 NCA/Gr	1-4C	Lower discharging rate
	Commercial cylindrical LFP/Gr	1-15C	Higher discharging rate
	Pouch LCO/Gr	0.7-2C	No difference at 10-45°C

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	Cylindrical NMC/Gr	1-2C	Lower discharging rate
	Commercial 18650 NCA/Gr	1-4C	Lower discharging rate
	Commercial cylindrical LFP/Gr	1-15C	Higher discharging rate
	Pouch LCO/Gr	0.7-2C	No difference at 10-45°C
Voltage limits	Saft VLE NCA/Gr	50%-100% storage SOC	Higher SOC
	Lab-made pouch NMC/Gr	4.3-4.4V charge cutoff voltage	Higher voltage
	Sanyo UR18650E NMC/Gr	1) 0.5%-100% DOD, 50% SOC midpoint 2) 10% DOD and midpoint SOC of 10%-95%	1) Higher DOD 2) Extreme midpoints
	Commercial 26650 LFP/Gr	30-50% vs. 5-95% SOC	Higher DOD
	E-One Moli Energy IHR18650A NMC/Gr	0.56-1.2V DOD, 3.6V midpoint	Higher DOD
	Commercial prismatic NMC+LMO/Gr	0-20%, 20-60%, 60-100%, 0-100% SOC	1) Higher DOD 2) Higher midpoint SOC
	Commercial 26650 LFP/Gr	0-80% vs. 0-100% SOC	Higher DOD
	Samsung INR 18650 25R NMC+NCA/Gr	20-60% DOD, 15-85% SOC midpoint	Lower SOC

"Perturbation" of Any Variable Can Induce Knees – II. Testing Conditions

Variable	Cell Description	Range of Variable	Knee Acceleration
Rests	Cylindrical NMC/Gr	10-900s at TOC and BOD	Longer rest time
	Lab-made pouch NMC/Gr	0-30min at TOC and BOD	Longer rest time
	Commercial prismatic NMC/Gr	0-every 100 cycles	Shorter rest time

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	Lab-made pouch NMC/Gr	0-30min at TOC and BOD	Longer rest time
	Commercial prismatic NMC/Gr	0-every 100 cycles	Shorter rest time
Temperature	NMC/Gr	25-45°C	Temperature above and below 25°C
	Saft VLE NCA/Gr	20-60°C	Higher temperature
	E-One Moli Energy IHR18650A NMC/Gr	25-50°C	Temperature above and below 35°C
	Commercial 26650 LFP/Gr	25-45°C	Higher temperature
	Commercial 18650 NMC+LMO/Gr	-20-70°C	Temperature above and below 25°C
	Commercial 18650 NMC+LMO/Gr Commercial 18650 NMC/Gr	0-25°C	Lower temperature
	Cylindrical NCA/Gr	0-60°C	Temperature below 25°C

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Temperature	NMC/Gr	25-45°C	Temperature above and below 25°C
	Saft VLE NCA/Gr	20-60°C	Higher temperature
	E-One Moli Energy IHR18650A NMC/Gr	25-50°C	Temperature above and below 35°C
	Commercial 26650 LFP/Gr	25-45°C	Higher temperature
	Commercial 18650 NMC+LMO/Gr	-20-70°C	Temperature above and below 25°C
	Commercial 18650 NMC+LMO/Gr Commercial 18650 NMC/Gr	0-25°C	Lower temperature
	Cylindrical NCA/Gr	0-60°C	Temperature below 25°C
Pressure	Commercial pouch NMC/Gr	4 bracing approaches	More rigid bracing or zero bracing
	Pouch LCO/Gr	0-5 MPa	Higher stack pressure or zero pressure
	E-One Moli Energy IHR18650A NMC/Gr		Heterogeneous compression

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	E-One Moli Energy IHR18650A NMC/Gr	25-50°C	Temperature above and below 35°C
	Commercial 26650 LFP/Gr	25-45°C	Higher temperature
	Commercial 18650 NMC+LMO/Gr	-20-70°C	Temperature above and below 25°C
	Commercial 18650 NMC+LMO/Gr Commercial 18650 NMC/Gr	0-25°C	Lower temperature
	Cylindrical NCA/Gr	0-60°C	Temperature below 25°C
Pressure	Commercial pouch NMC/Gr	4 bracing approaches	More rigid bracing or zero bracing
	Pouch LCO/Gr	0-5 MPa	Higher stack pressure or zero pressure
	E-One Moli Energy IHR18650A NMC/Gr		Heterogeneous compression

In summary: knee points are complex and occur under many conditions

Next step: link all experimental observations to broad mechanisms of failure (e.g. Li plating, loss of active material, resistance growth)

Overview

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2) Review of battery degradation tipping points

3) Visualization tools for battery lifecycle analysis

What is the Battery Data Challenge?

Little raw data are publicly available
(difficult to extract info from figures)

Variables - Cell1.cyc0000.C1ch

Cell1 | Cell1.cyc0000 | Cell1.cyc0000.C1ch | Cell1.cyc0000.C1ch.t

Cell1.cyc0000.C1ch

Field	Value
t	3510x1 double
v	3510x1 double
q	3510x1 double
T	3510x1 double

```
File  Edit  Format  View  Help
Time       Status  code     Status  category  Status  color    Pgm  code
0.000000      8      3      3      0      1      2      2
0.940317      8      3      3      0      1      2      2
1.954083      8      3      3      0      1      2      2
2.950567      8      3      3      0      1      2      2
3.945600      8      3      3      0      1      2      2
4.940633      8      3      3      0      1      2      2
5.937117      8      3      3      0      1      2      2
6.952317      8      3      3      0      1      2      2
7.948800      8      3      3      0      1      2      2
8.942400      8      3      3      0      1      2      2
9.938883      8      3      3      0      1      2      2
10.952633     8      3      3      0      1      2      2
11.944800     8      3      3      0      1      2      2
12.952800     8      3      3      0      1      2      2
13.940633     8      3      3      0      1      2      2
```

Even when raw data are available,
they're not standardized

Cycle_Ind	Start_Tim	End_Time	Test_Time	Min_Curre	Max_Curr	Min_Volta
1	02:10.0	22:45.3	15645.31	-0.55	0.55	1.998
2	22:45.3	40:11.8	31091.75	-0.55	0.55	1.995
3	40:11.8	57:06.2	46506.17	-0.55	0.55	1.997
4	57:06.2	26:31.6	69871.59	-1.1	0.55	1.995
5	28:31.6	34:59.9	81179.92	-1.1	0.55	1.993
6	37:00.0	43:14.7	92474.68	-1.1	0.55	1.995
7	45:14.7	51:21.0	103761	-1.1	0.55	1.998
8	53:21.1	59:21.1	115041.1	-1.1	0.55	1.995
9	01:21.2	07:15.5	126315.5	-1.1	0.55	1.995
10	09:15.6	15:06.6	137586.6	-1.1	0.55	1.996
11	17:06.6	22:52.5	148852.5	-1.1	0.55	1.998
12	24:52.5	30:37.9	160117.9	-1.1	0.55	1.994

This makes it difficult to compare results from different groups and do larger-scale analyses.

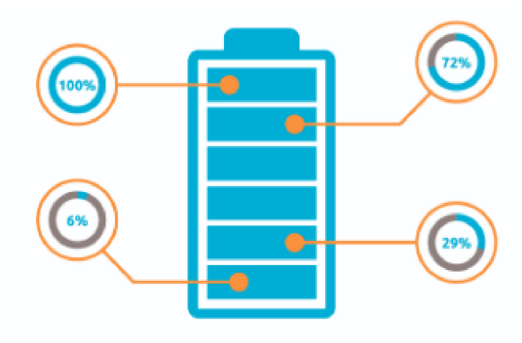
First Public Battery Cycling Database

Core site development: Valerio De Angelis
Front end: Sam Roberts-Baca

BatteryArchive.org

A repository for easy visualization, analysis, and comparison of battery data across institutions

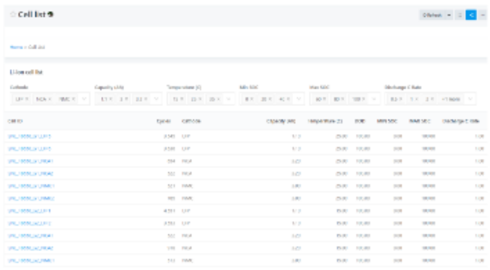
View Data



Features

1

Filter battery data



Query and filter for specific experimental conditions.

2

Visualize and compare data

Display battery data, including voltage curves and capacity fade.

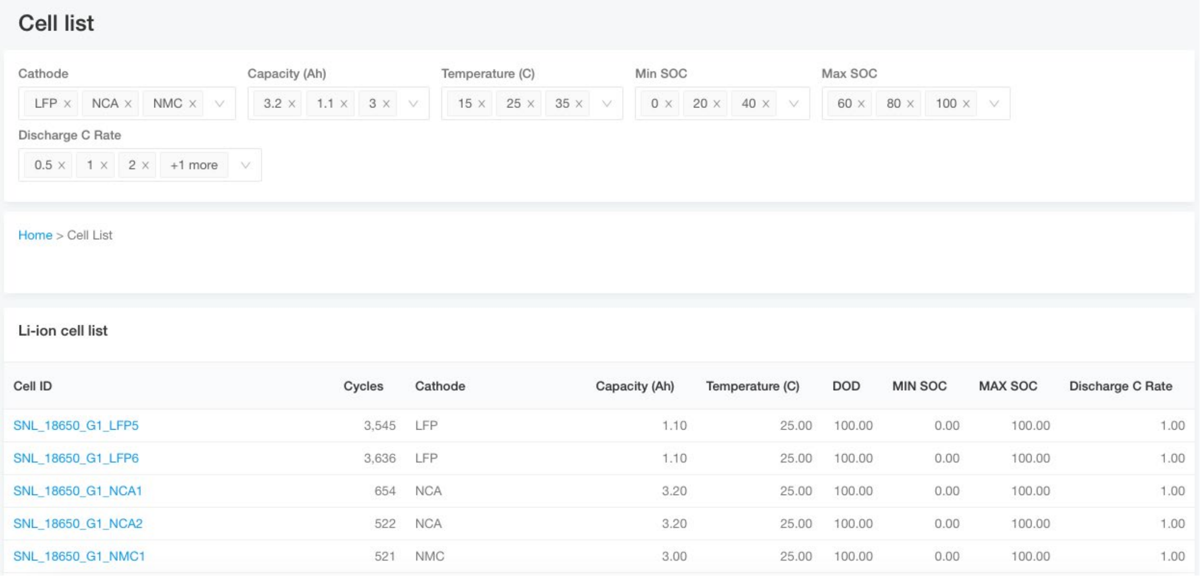
3

Compare data with models

Apply performance and degradation models to battery data.

First Public Battery Cycling Database

Search by metadata related to cell + cycling conditions



Cell list

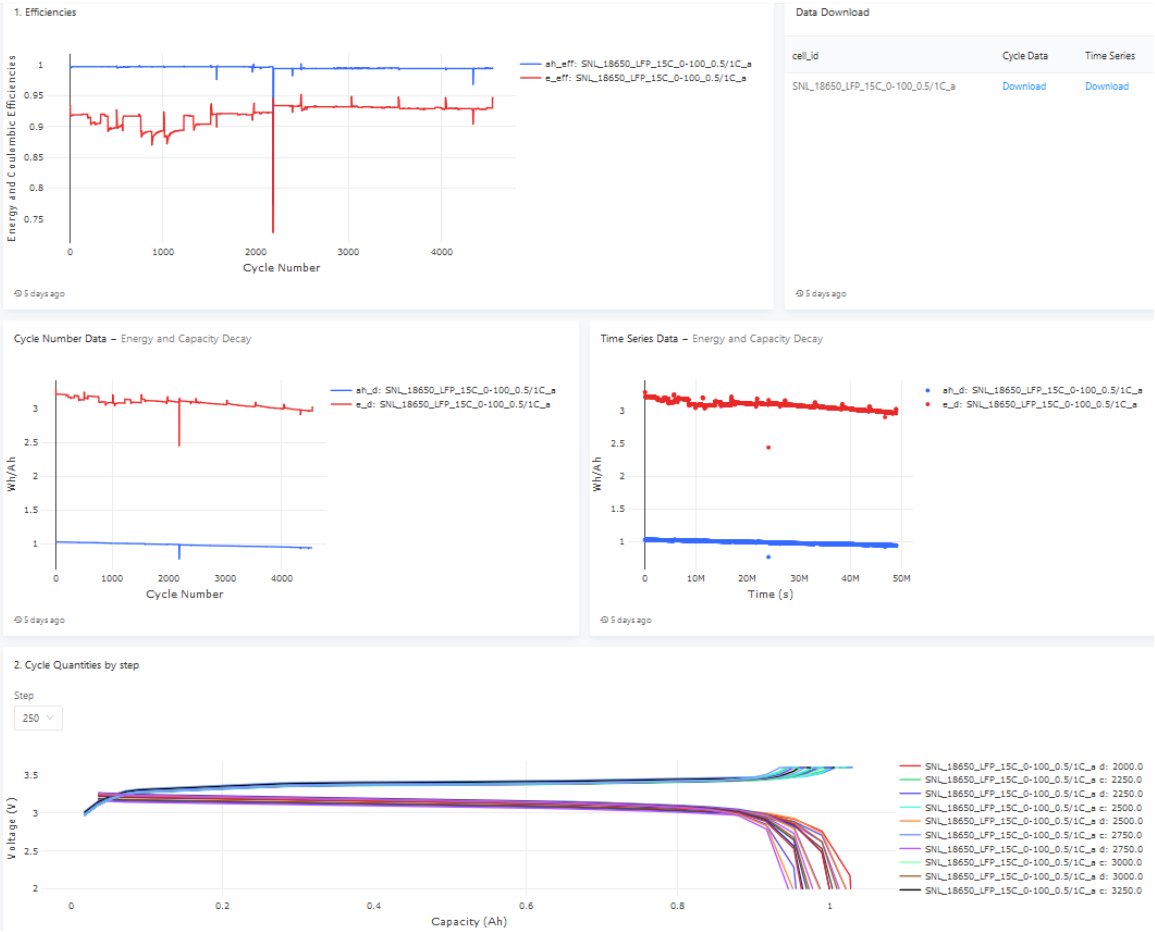
Cathode: LFP × NCA × NMC ×
Capacity (Ah): 3.2 × 1.1 × 3 ×
Temperature (C): 15 × 25 × 35 ×
Min SOC: 0 × 20 × 40 ×
Max SOC: 60 × 80 × 100 ×
Discharge C Rate: 0.5 × 1 × 2 × +1 more

Home > Cell List

Li-ion cell list

Cell ID	Cycles	Cathode	Capacity (Ah)	Temperature (C)	DOD	MIN SOC	MAX SOC	Discharge C Rate
SNL_18650_G1_LFP5	3,545	LFP	1.10	25.00	100.00	0.00	100.00	1.00
SNL_18650_G1_LFP6	3,636	LFP	1.10	25.00	100.00	0.00	100.00	1.00
SNL_18650_G1_NCA1	654	NCA	3.20	25.00	100.00	0.00	100.00	1.00
SNL_18650_G1_NCA2	522	NCA	3.20	25.00	100.00	0.00	100.00	1.00
SNL_18650_G1_NMC1	521	NMC	3.00	25.00	100.00	0.00	100.00	1.00

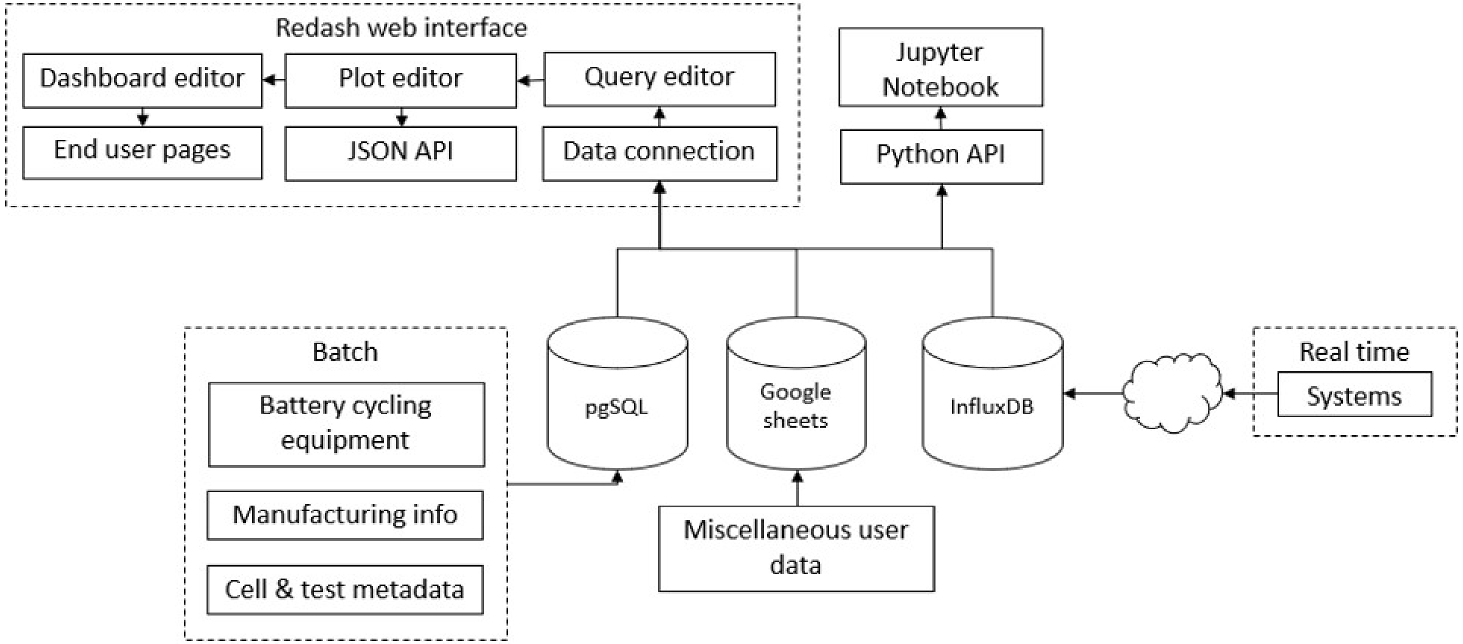
Efficiencies, capacity and energy decay, and voltage curves automatically plotted for selected cells



Open-Source Platform Underpinning Battery Archive Released to Community

- Public site is based on the Battery Lifecycle Framework (BLC) - an open-source platform that provides tools to visualize, analyze, and share battery data through the technology development cycle

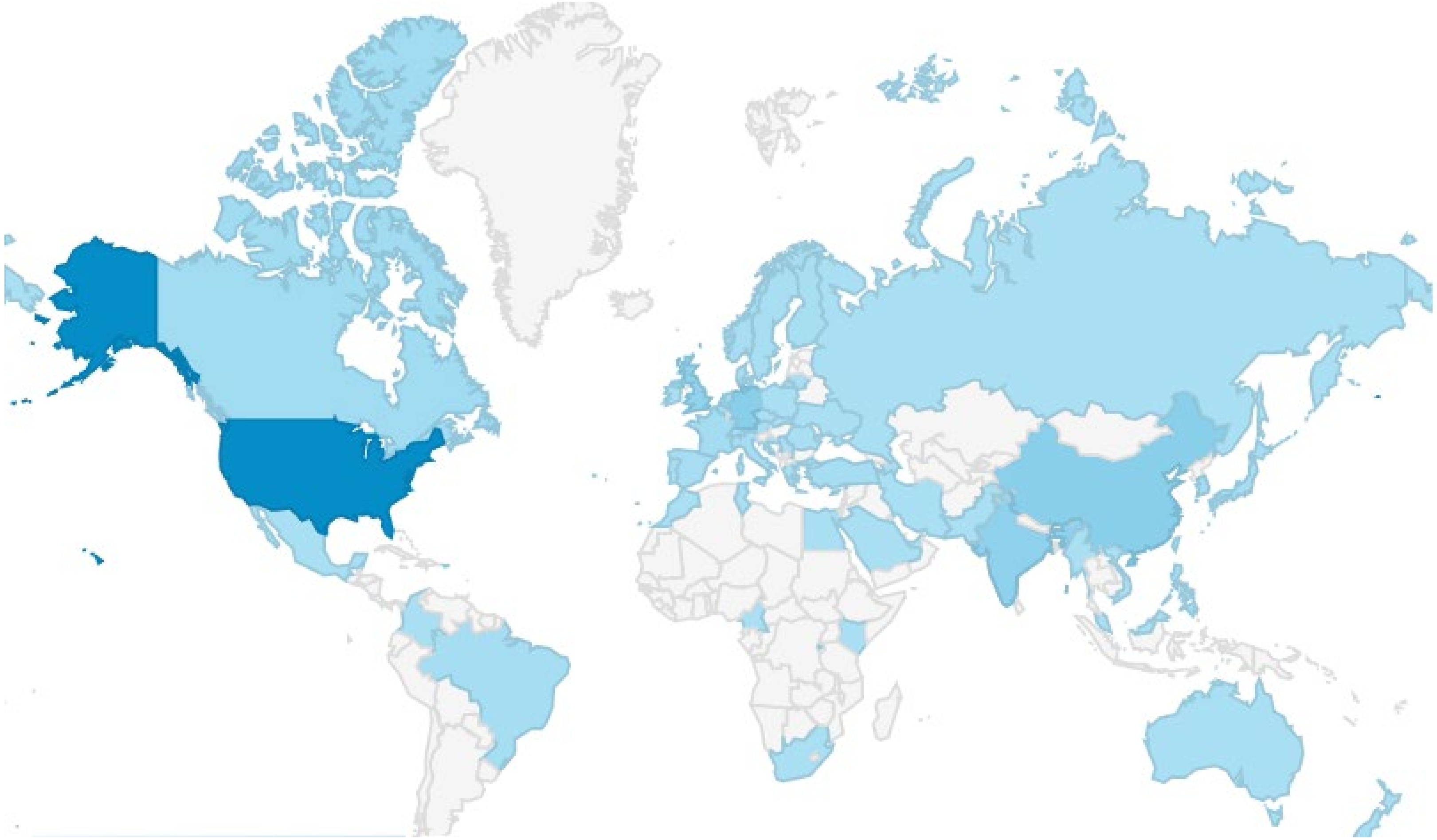
- BLC has four components: (1) data importers, (2) one or more databases, (3) a front-end for querying the data and creating visualizations, (4) an application programming interface to process the data



Preprint: https://ecsarxiv.org/h7c24

Current Impact

Nearly 2000 site users, many return visits, from over 40 countries, academia and industry



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Sources of datasets & collaborators

- Datasets online
- Datasets in pipeline
- Software interoperability
- Battery database network

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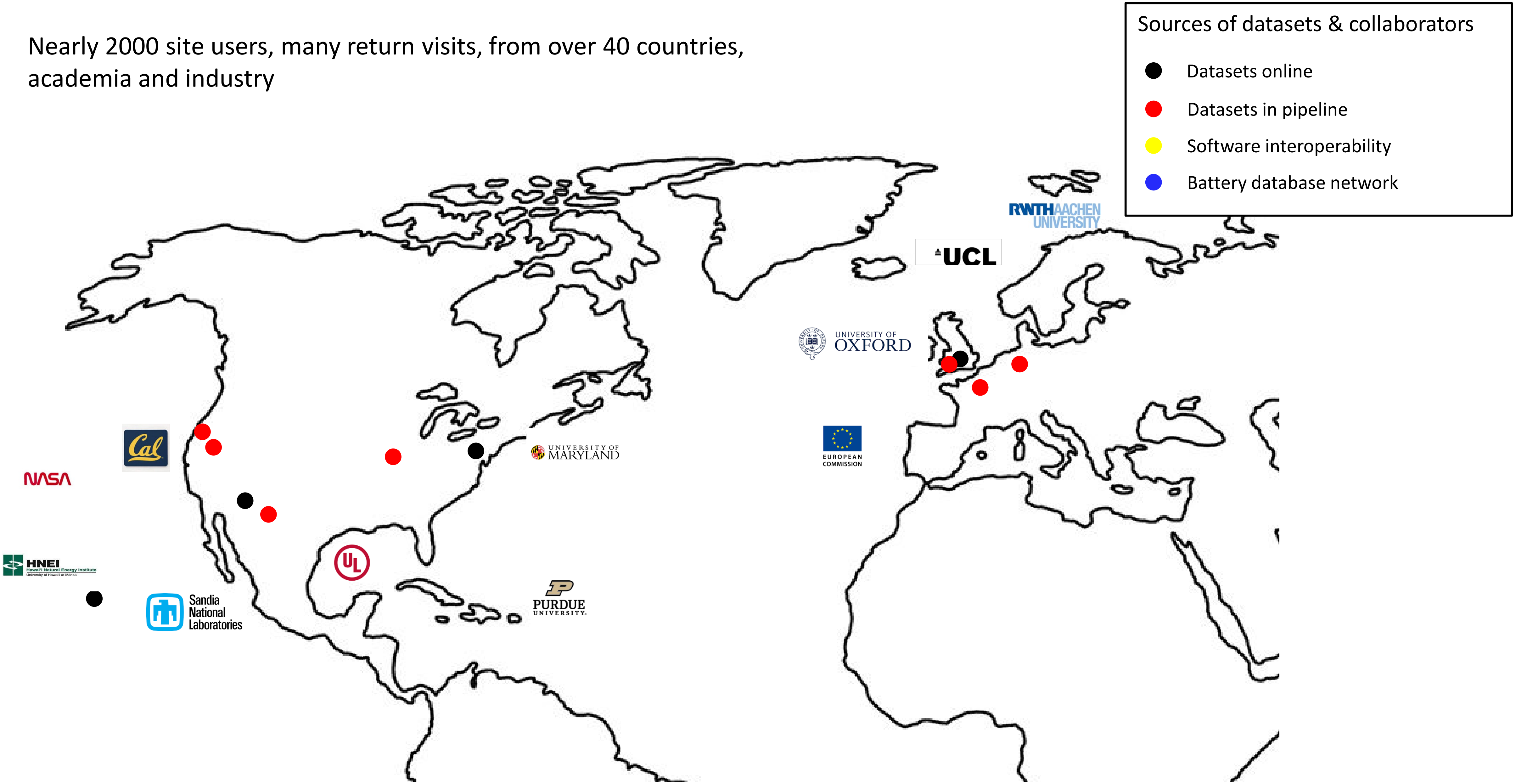

Current Impact

Nearly 2000 site users, many return visits, from over 40 countries, academia and industry

Sources of datasets & collaborators

- Datasets online (black)
- Datasets in pipeline (red)
- Software interoperability (yellow)
- Battery database network (blue)

Current Impact

Nearly 2000 site users, many return visits, from over 40 countries, academia and industry

Sources of datasets & collaborators

- Datasets online
- Datasets in pipeline
- Software interoperability
- Battery database network

Summary

1) Recent experimental work on battery degradation beyond 80% capacity

- Some cells cycled to 40%
- Beginning to see knee points

2) Review of battery degradation tipping points

- Can be induced by perturbation of any variable (cell design, testing conditions)

3) Visualization tools for battery lifecycle analysis

- BatteryArchive.org public site developed to aid standardized battery data viewing
- Underlying framework released as open-source software

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