Enabling High-Energy/Voltage Lithium-Ion Cells for Transportation Applications:
Part 1 Baseline Protocols and Analysis

Project ID: ES252

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Argonne National Laboratory

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DOE Vehicle Technologies Program
Arlington, VA
8-12 June, 2015

Overview

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2017
- Percent complete: 15%

Budget

- Total project funding
- FY15 - $3000K

Barriers

- Calendar/cycle life of lithium-ion cells being developed for PHEV and EV batteries that meet or exceed DOE/USABC goals

Partners

- Lead PI: Anthony K. Burrell
- Collaborators: ORNL, NREL
- Burrell, Anthony K.; Abraham, Daniel; Balasubramanian, Mahalingam; Bareno Garcia-Ontiveros, Javier; Bloom, Ira D.; Long, Brandon R.; Croy, Jason R.; Dees, Dennis W.; Dogan, Fulya; Gallagher, Kevin G.; Iddir, Hakim; Ingram, Brian J.; Johnson, Christopher; Lu, Wenquan; Ren, Yang; Vaughey, John T.; Wu, Huiming; Wu, Rinaldo, Steven G.; Jansen, Andy; Polzin, Bryant; Trask, Steven; Krumdick, Gregory; Shin, YoungHo; Zhang, Zhengcheng; Liao, Chen; Tenent, Robert, Ban, Chunmei; Wood, David; Daniel, Claus; Nanda, Jagjit

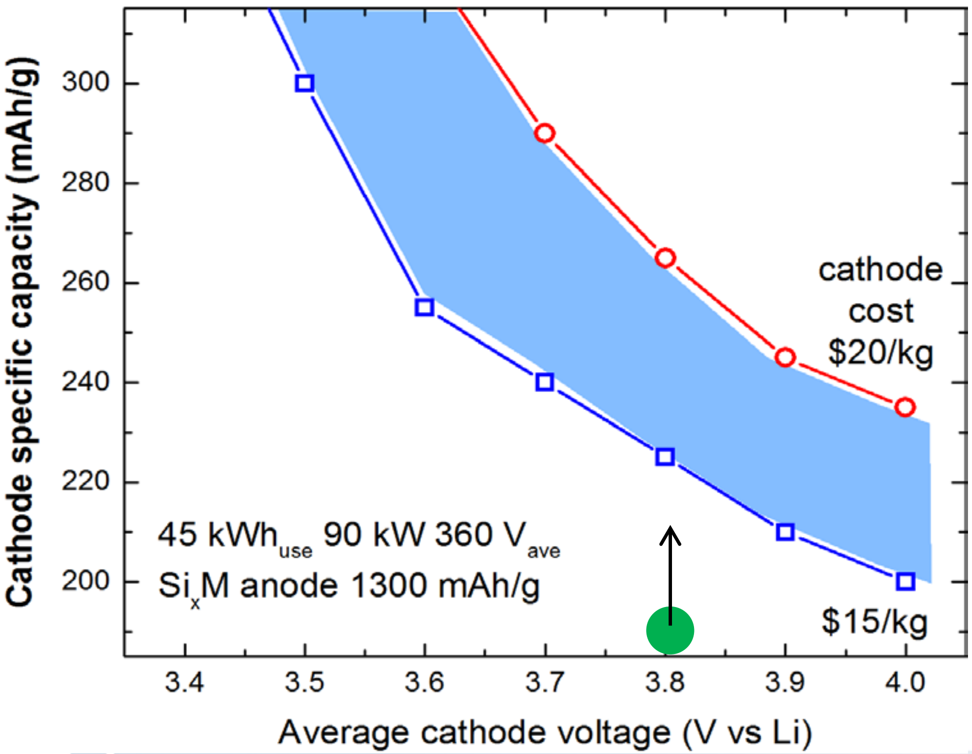
Relevance

Commercial cathode performance

Material	Voltage (Ave. vs Li/Li⁺)	Capacity (mAh/g)	Sp. En. (Wh/Kg)
$LiCoO_2$	3.8	150	570
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC)	3.7	170	629
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	3.7	185	685
$LiMn_2O_4$	4.0	110	440
$LiFePO_4$	3.4	160	544

Commercial Li-ion cathodes give moderate energy densities w.r.t. xEV applications

High voltage instabilities significantly limit practical capacities (theo. ~280 mAh/g)



Currently: ~150-180 mAh/g at ~3.5-3.8 V (Li) giving <700 Wh/kg_{oxide}

Target: anything in the shaded region meets USABC EV targets

Charging to higher voltages can increase energy: HV >~4.3 V vs. graphite

Approach Materials and Baselines

Baseline electrochemical protocols and analysis procedures will be established as benchmarks using commercial materials

- NMC-532 and NCA cathodes
- A12 graphite anodes
- $LiPF_6$-based electrolytes
- Celgard separators

- Baseline testing format will be 2032-type coin-cells as well as single- and multi-layer pouch cells; ~400 mAh cells from ANL and up to ~5Ah cells from ORNL

- Argonne's CAMP facility will provide commercial-grade electrode laminates of baseline materials to all partners/collaborators

- Argonne's MERF facility will be utilized to engineer high quality materials, in large quantities, of any newly developed materials for further testing

Approach Procedures and Metrics

Quantify performance parameters of baseline materials with confidence

- Test large number of cells under various protocols → coin-cell format
- Gain information on process → improve reproducibility
- Analyze cycling data and evaluate protocols
- Refine and repeat to obtain baseline data and process control

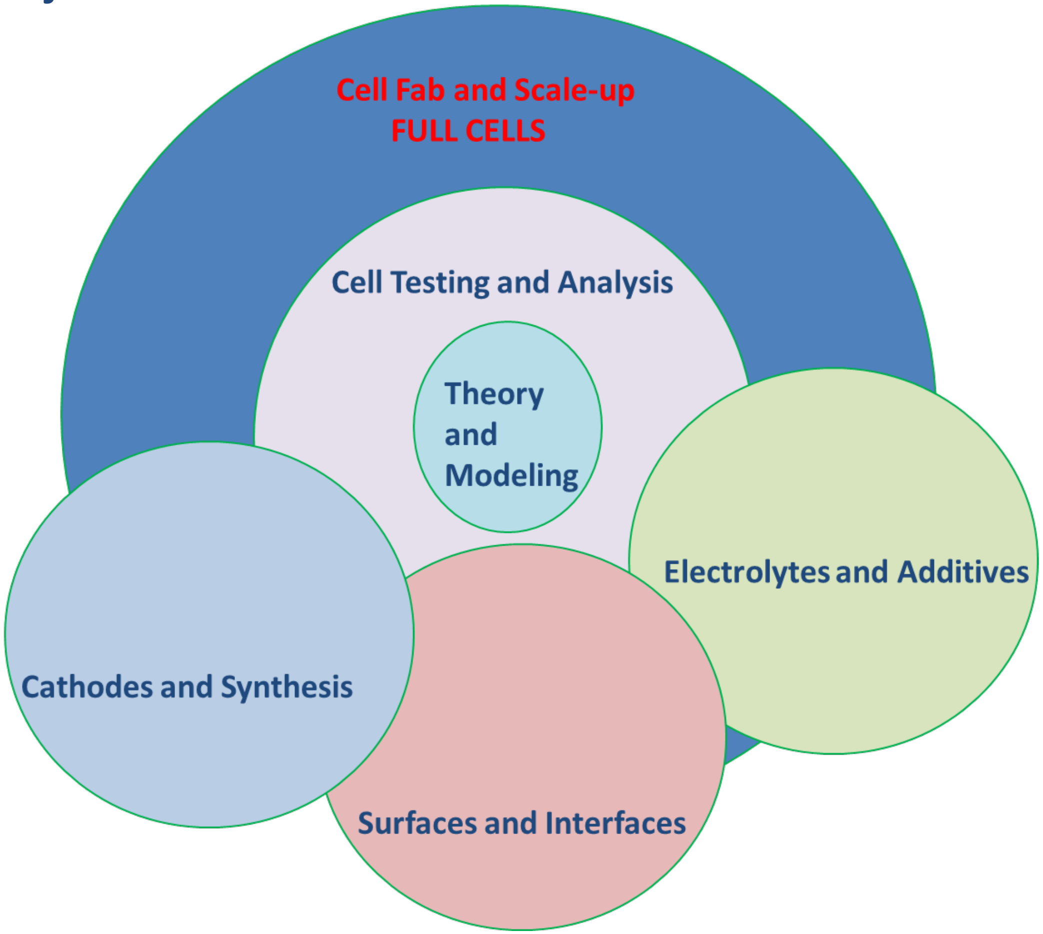
Quantify when an improvement is statistically relevant to overall goals

- Statistically describe baseline cell behavior without bias
- Define confidence levels for process
- Define, statistically, what constitutes real improvements between data sets

Establish the relationship between coin-cell and pouch-cell formats

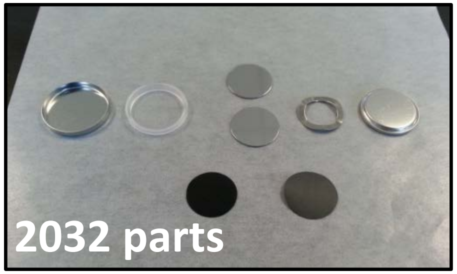
- Show how the coin-cell format can be used to reasonably predict large format, pouch-cell behavior

Approach Project Thrusts

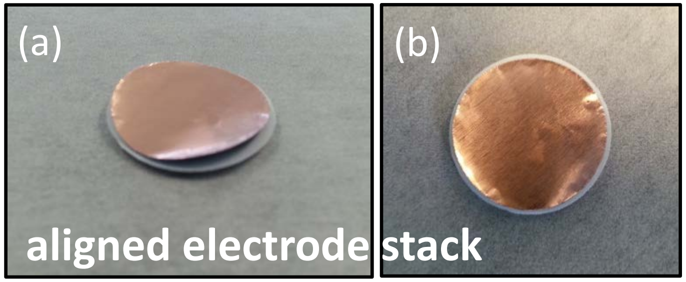


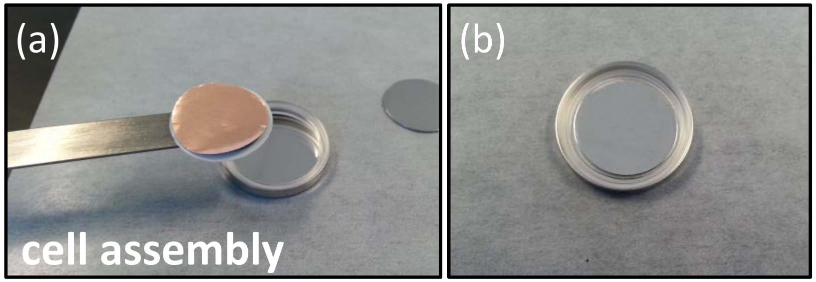
- Subgroups within the overall project have been formed to define and focus on specific challenges of high voltage operation
- Subgroup tasks are highly correlated and experimental plans, collaborations, and lines of communication have been established

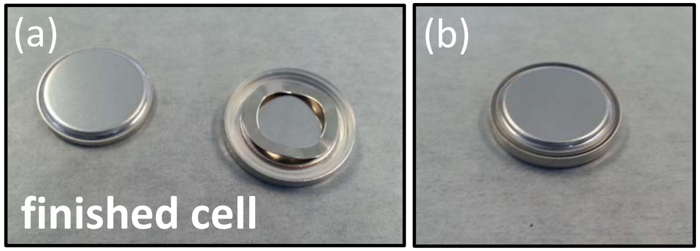
Progress Assembly of 2032-type, Full Cells



Step-by-step manual for building cells has been written and distributed to the team for better process control and reproducibility

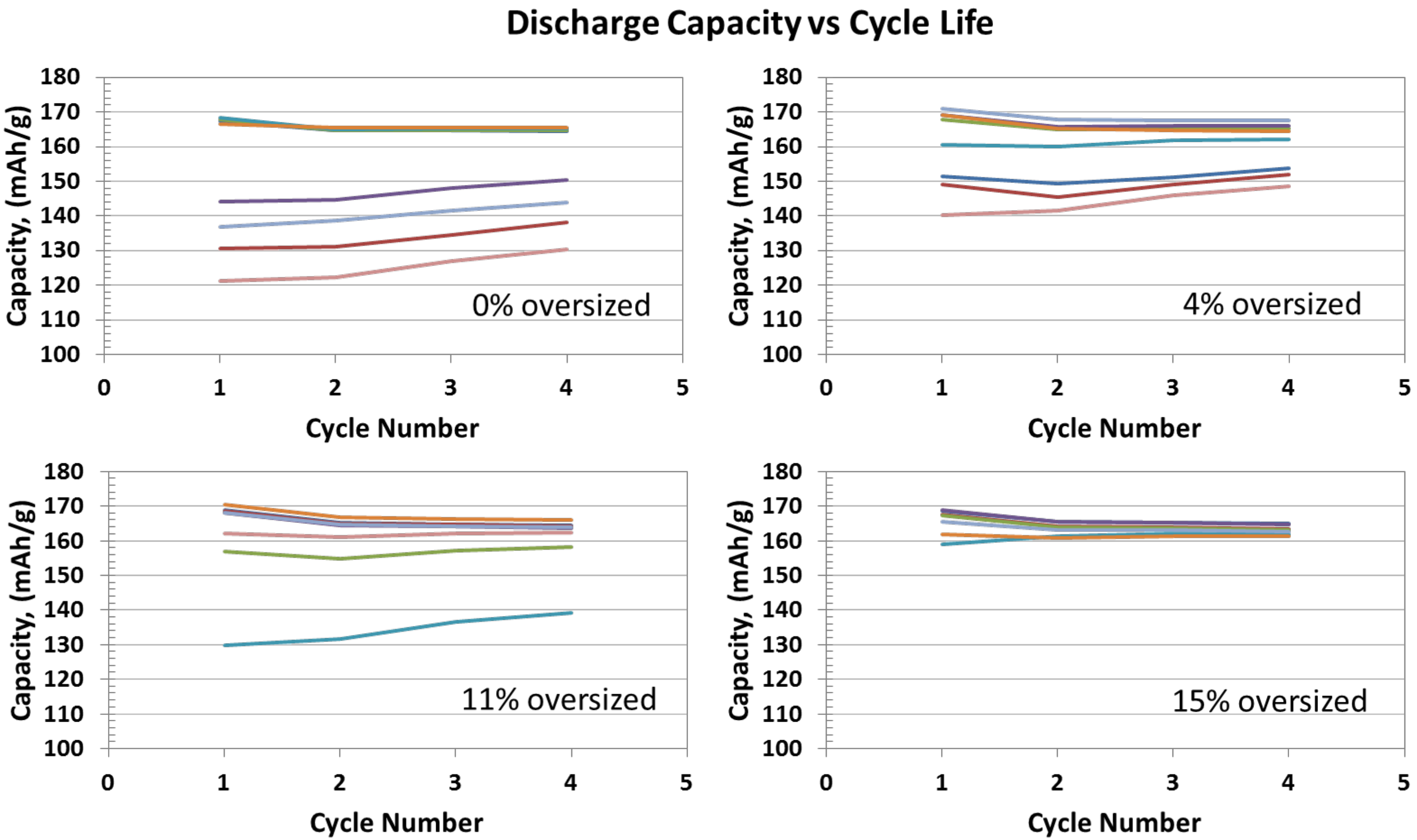






Progress Cathode to Anode Area & Process Control

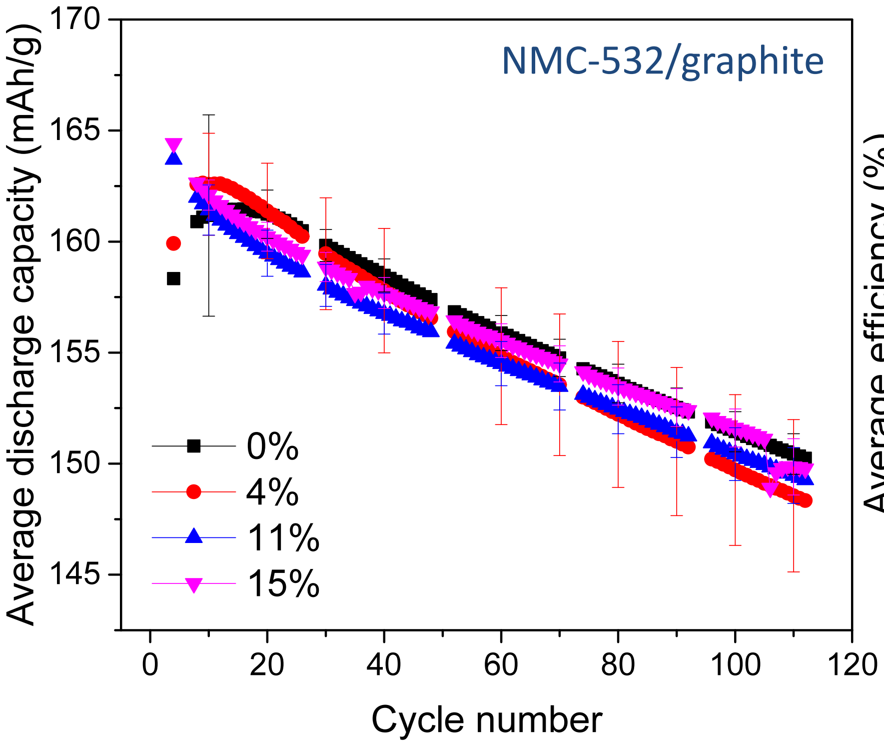
NMC-532/graphite

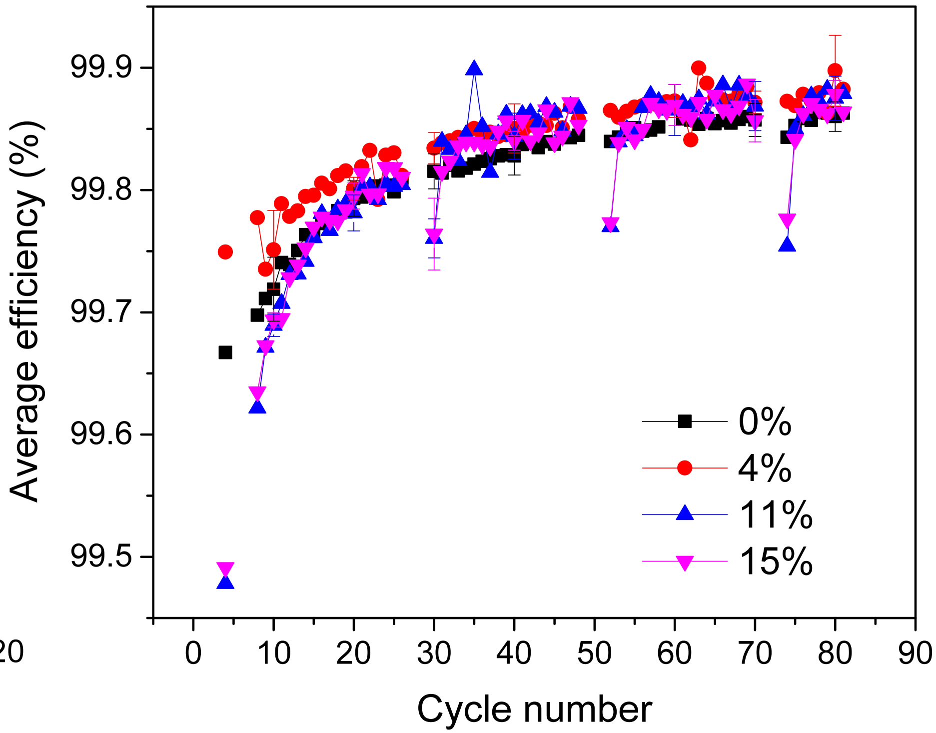


- Physical assembly of full cell, coin-cells is challenging due to electrode alignment → oversizing anode (% w.r.t cathode) improves reproducibility as shown above

Increasing anode to cathode size leads to more reproducible construction of cells

Progress Cathode to Anode Area and Cell Performance

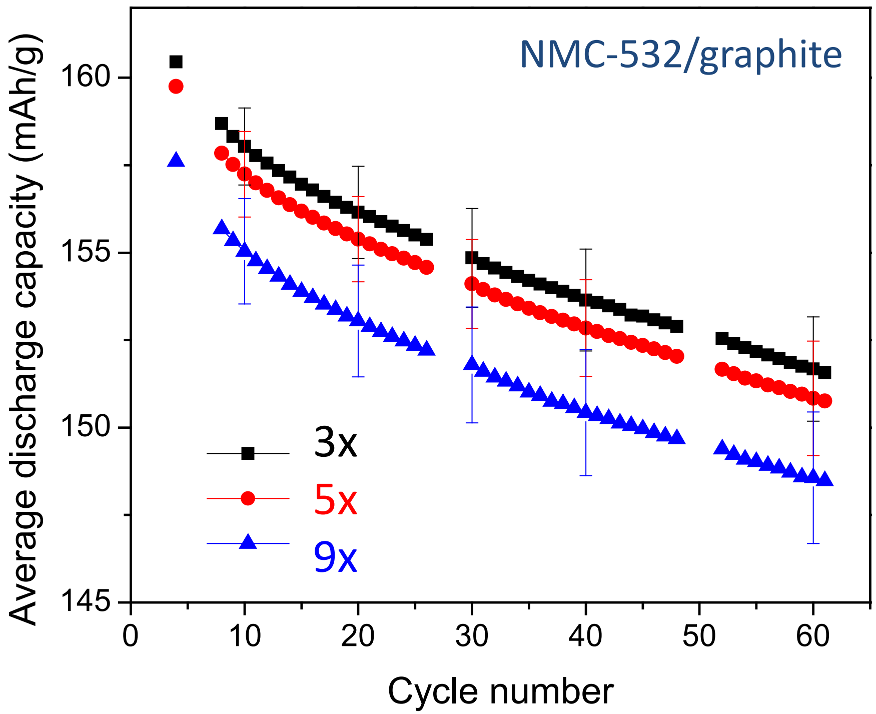


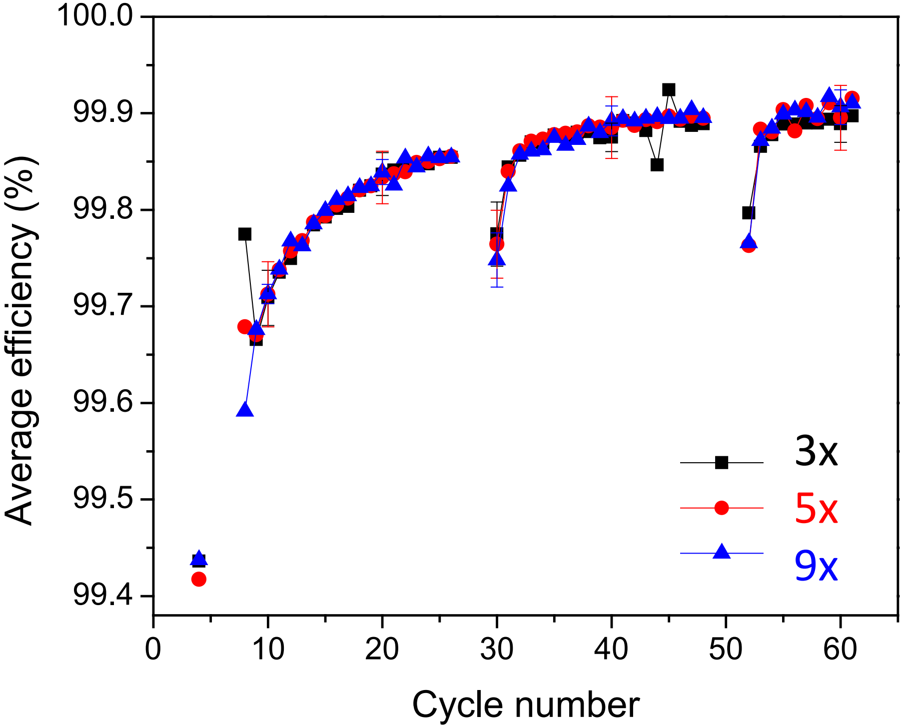


- Graphite anodes with increasing % areas (w.r.t. cathode) were tested against NMC-532 cathodes under the same cycling protocols

No evidence that the 1.15 ratio adversely effects performance→ due to increased reproducibility, this configuration will be chosen as the baseline

Progress Electrolyte Volume





- The minimum amount of electrolyte is preferred in real cells
- Control volume must be established – important for future studies (e.g., additives)
- Volumes of less than ~2x total pore volume gave poor performance (not shown)

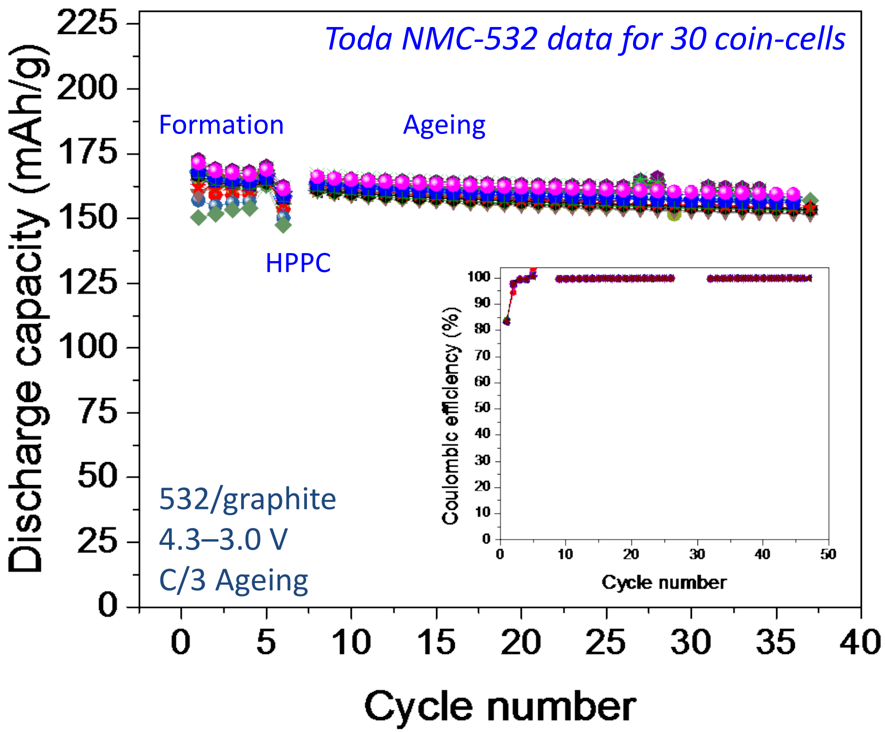
Electrolyte volumes of ~3x the total pore volume (cathode, anode, separator) do not adversely effect performance → starting baseline for coin-cell format

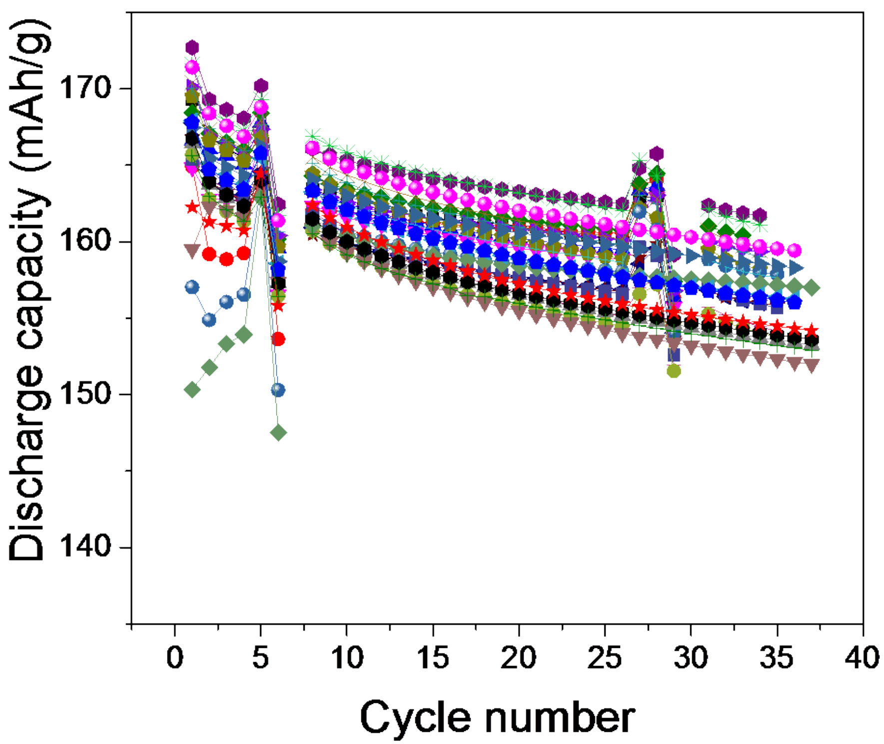
Summary of Coin-Cell Standardization

- Procedures for assembly of coin-cells have been formalized and distributed
- Physical cell parameters have been determined by a series of tests
- Oversized anodes (1.15 N:P area) are important for reproducible assembly and perform similar to lower ratio configurations
- Electrolytes volumes as low as ~3 times the total pore volume give equivalent or better cycling performance than higher volumes

Part	Size/Volume	Type
Cathode 1	14.0 mm	NMC, NCA
Anode 2	15.0 mm	A12
Electrolyte	3x pore volume	1.2 M $LiPF_6$ in EC:EMC (3:7)
Separator	16.0 mm	Celgard-2325
Spacers	15.8 mm	Stainless
Seal	16.0 mm (i.d.)	Plastic
Spring	---	Stainless

Progress Data Analysis

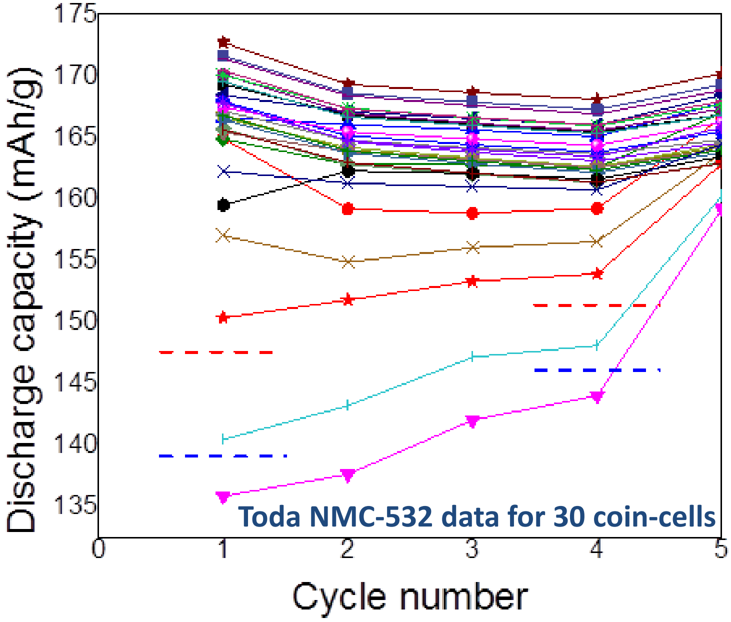




- Bad choice of scale can mask important information *(Left)*
- Proper scale reveals the real variability from cell to cell *(Right)*

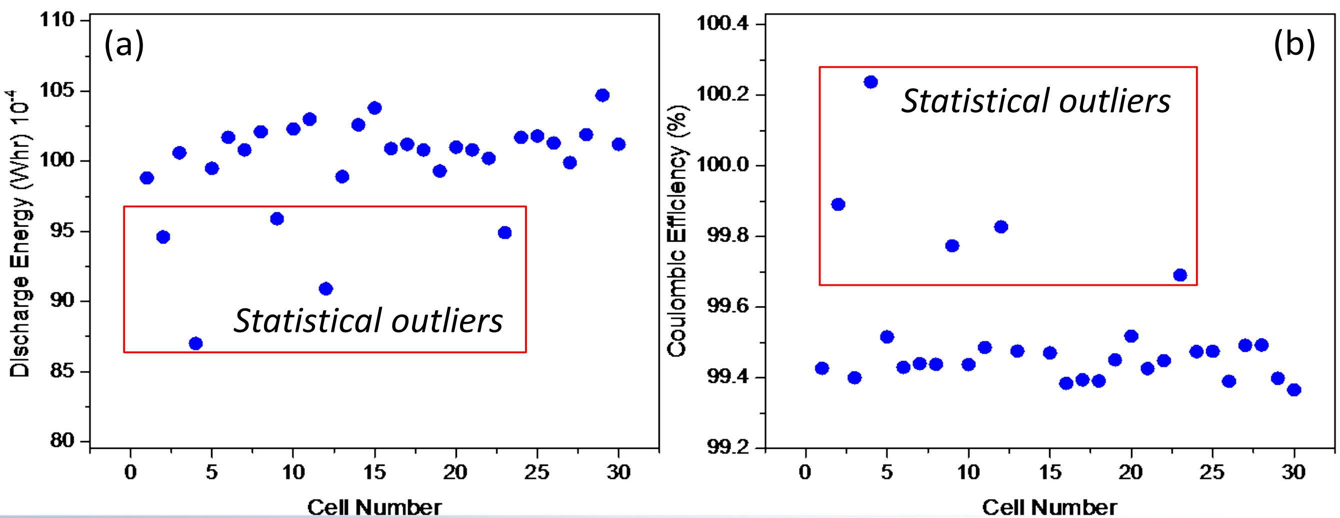
Need to determine/treat outliers to improve process control and increase confidence in data

Progress Addressing Variability



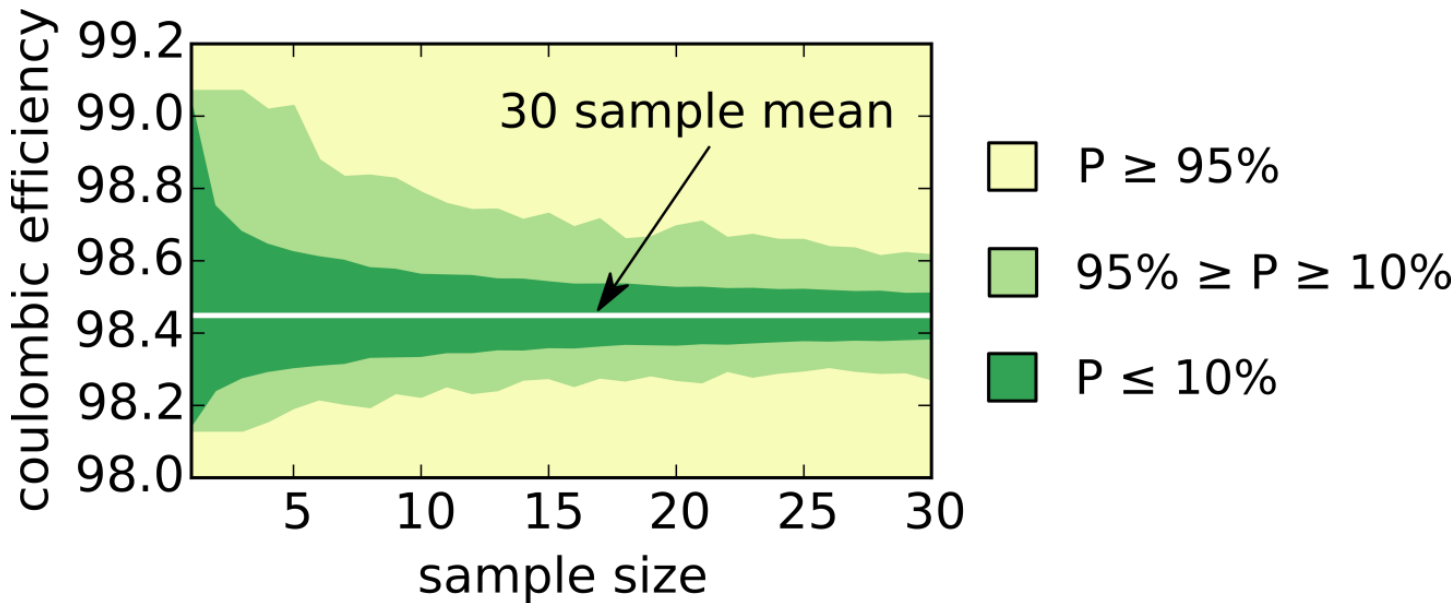
- Formation cycles for ***30 cells***
- Dashed lines represent 2 and 3 standard deviations – ***controlled to a large extent by process***
- Systematic approach to identify outliers and improve process

Modified Grubb's test applied to 30 cell data set



How Do We Use This Going Forward?

- Not “throwing out” outliers, but rather using them to improve process
- Improved process → minimize outliers
- Outlier tests typically require >10 samples
- Suggest using a gate to test smaller sample sizes (N≥~5):



For critical data, and to connect with pouch cells, larger data sets should be used

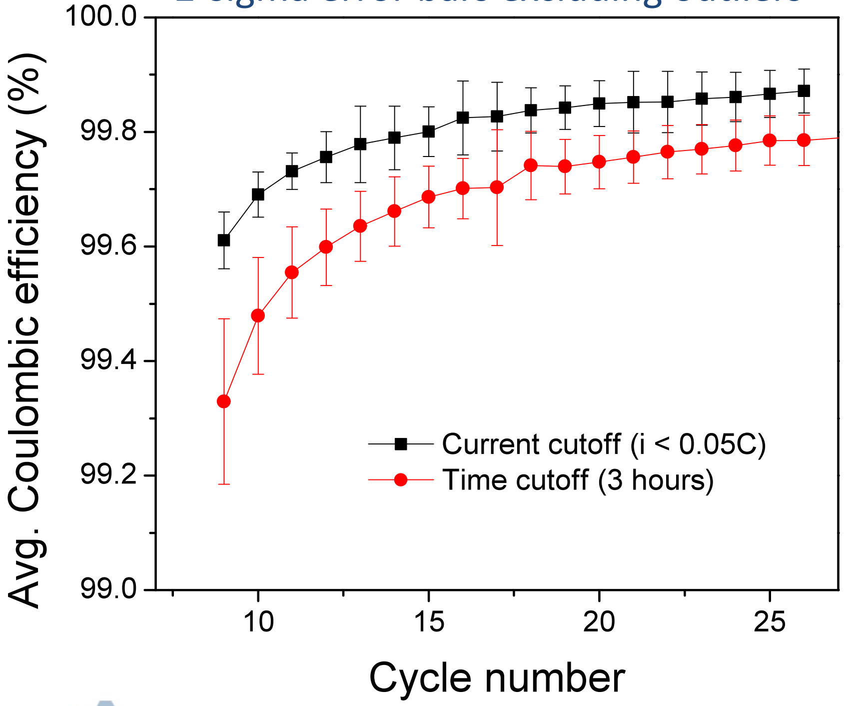
- A user friendly program is being developed for standardized analysis

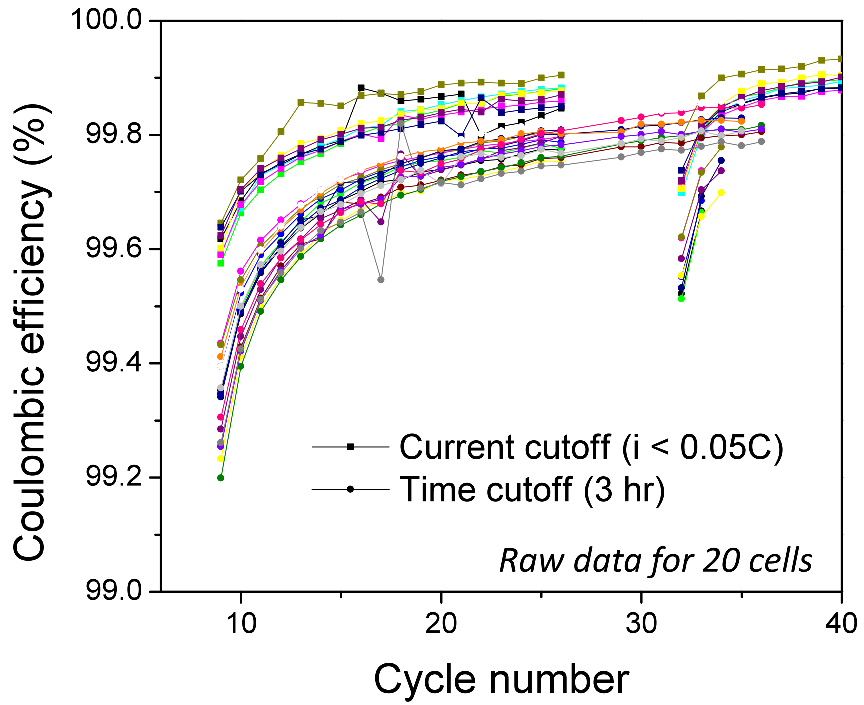
Progress Example of Protocol-Based Comparisons

Coulombic efficiency for NMC-532/graphite cells using two test protocols:

- Current cutoff at TOC
- Time/Voltage hold at TOC

2-sigma error bars excluding outliers





Analysis shows that in the first ~15 cycles there is a real and measureable difference of <0.3% in Coulombic efficiencies.

Small changes in important parameters can be objectively identified

Future work planned

- Finalize version 1.0 of electrochemical protocols and analysis software
- Collect and analyze cycling data on baseline cells using the established protocols
- Socialize and distribute results to partners and the ABR community, including publication in peer-reviewed journals
- Begin understanding state-of-the-art electrodes/electrolytes through experimental plans already in place
- Use understanding to identify **real, meaningful** advances
- Engage partners in productive collaborations

Summary

Producing relevant, baseline, electrochemical benchmarks requires:

- ***Training to produce the "same cell"***

  Protocols and procedures have been established and distributed

- ***Reproducible Full cells with limited electrolyte volume***

  Studies have been done to optimize all cell components including electrolyte volumes based on total cell porosity (cathode, anode, separator)

- ***Statistical analysis and connection to large format cells***

  Outlier tests and analysis procedures are in place and have proven capable of highlighting small changes in important parameters

- ***Accurate Communication and Comparison of Data Sets***

  Electrochemical cycling protocols are being established and distributed, a user friendly analysis program is being developed for standardized analysis

Acknowledgments

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