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Lifecycle Evaluation of Li-ion Battery Chemistries under Grid Duty Cycles

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Objectives

- How does use of Li-ion batteries for grid services affect their life?
- Comparison between different Li-ion battery chemistries (high energy vs. high power)
- Understanding degradation mechanism and factors that affect the battery performance.
- It will put a dollar cost on battery usage for various grid services.
- Accomplishments :
  - Frequency regulation service testing procedures developed per the DOE-OE Energy Storage Performance Protocol have been used for initial 90 cycle results.
  - Initial results show variations in performance of different Li-ion battery chemistries including cell reliability, round trip efficiency, charge/discharge energy and internal resistance with cycling.

Approach

- Cylindrical cells are selected from commercial vendors
  - **$LiNi_{0.85}Co_{0.1}Al_{0.05}$ (NCA) - high energy**
    - **18650, 3.2 Ah, 2.5 - 4.2V, C/2 charge, 4C max. discharge**
  - **$LiFePO_4$ (LFP) - high power**
    - **26650, 2.6 Ah, 2.0 - 3.6V, 1C charge, 20C max. discharge**
- Subjected to the Frequency Regulation (FR) duty cycle per the DOE-OE Energy Storage Performance Protocol (led by PNNL and Sandia) using PJM duty cycle.
- Compared degradation versus baseline cells that are discharged to the same depth of discharge (DOD) and rested for the same duration.
- Determine internal resistance by applying pulse charge and discharge currents (1C for NCA cells, 2C for LFP cells).

Approach

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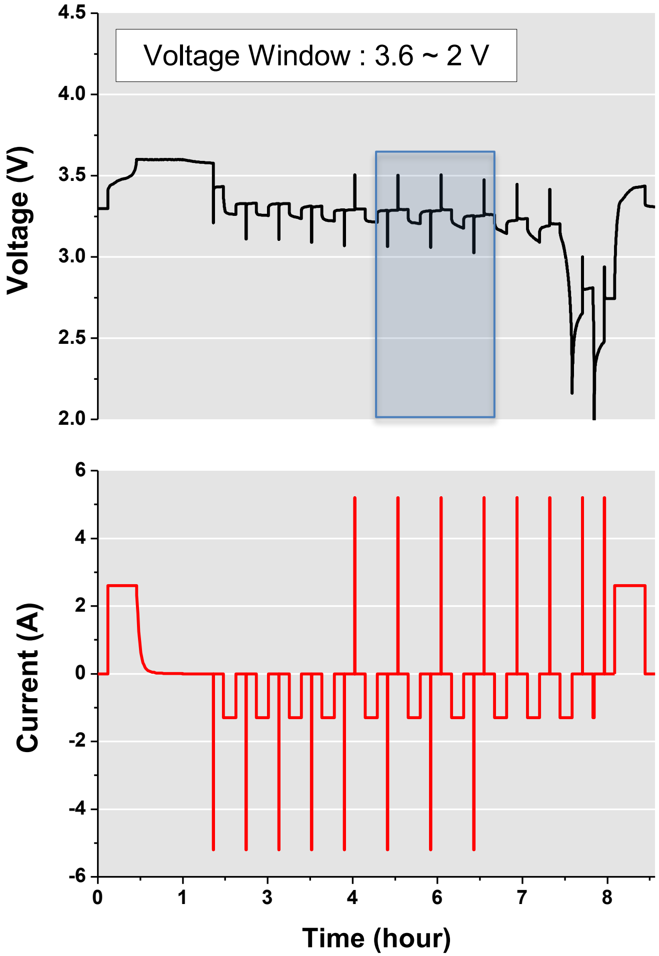
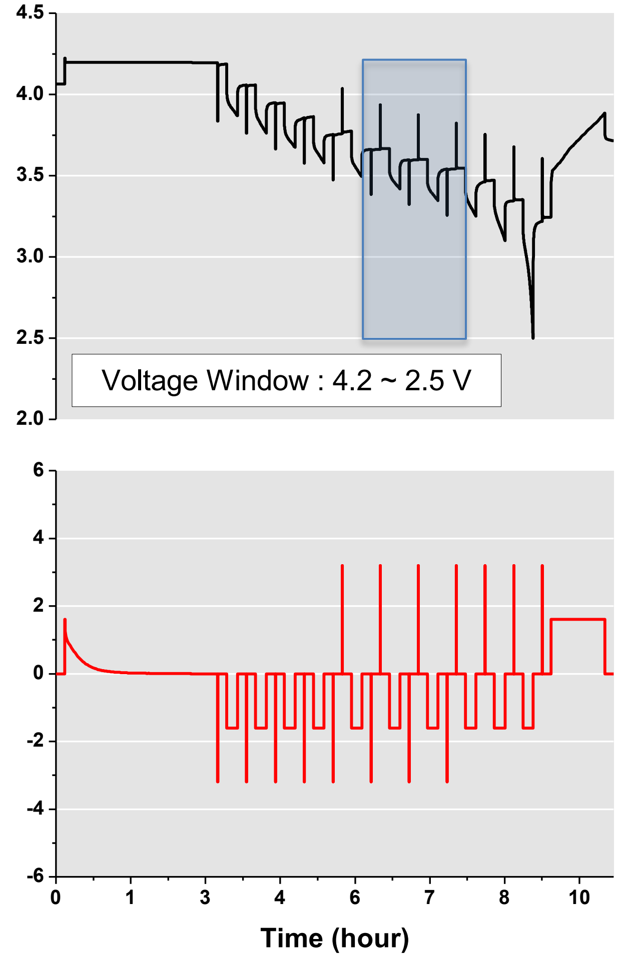
- Apply tight voltage limits (2% above upper and below lower limit for each chemistry) and capacity limits within 0.2 Ah of cell capacity.
- All tests are started at the same time with temperature monitoring.
- Degradation metrics during frequency regulation (FR):
  - Round trip efficiency (RTE)
  - Charge and discharge cumulative energy during frequency regulation
  - Internal resistance measured during frequency regulation
  - Cell variation and reliability
  - Aging effect
  - C/2 rate capacity (after every 40 cycles)
  - Internal resistance at various SOC (after every 40 cycles)

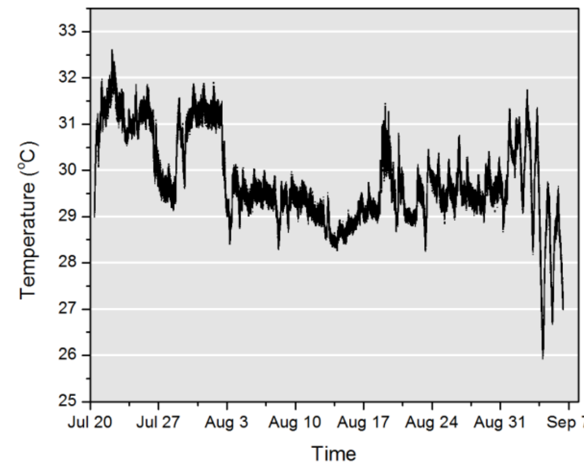
Li-ion Battery Chemistries



LFP 26650 Cell

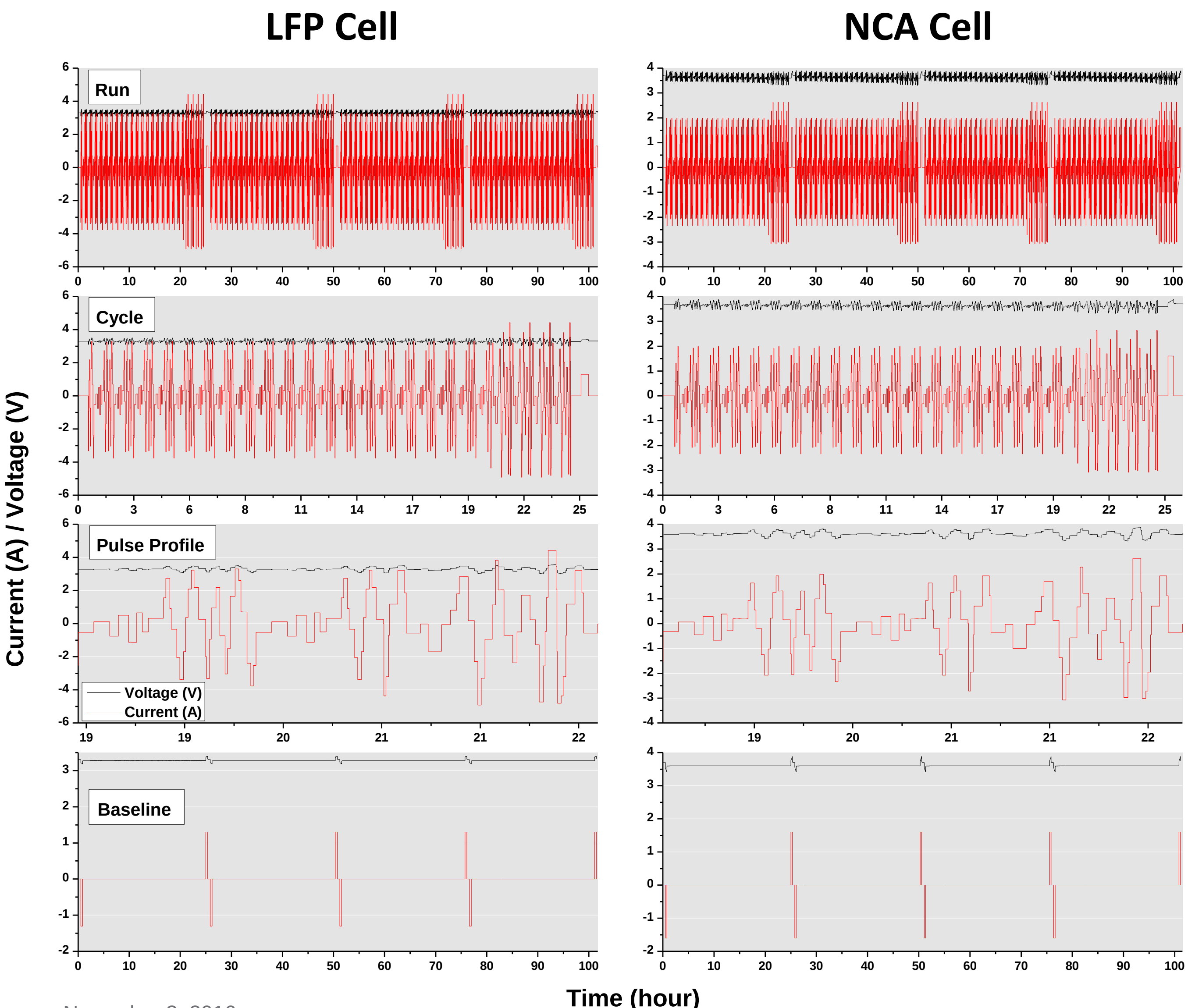


NCA 18650 Cell



- To find right testing condition without compromising safety, pulse tests were conducted every 10% SOC levels.
- Safety limits are set according to the product specifications.
- Tests were done within safe voltage window (blue area).
- Temperature is monitored every 10 seconds.
  - Average temp: 29.8 ± 0.6°C

Frequency Regulation Testing



- 1 FR cycle consists of 20 shallow and 4 aggressive pulse-profiles.
- Aggressive pulse contains 50% higher current than each battery specifications.
- After every 40 cycles, all cells are subjected to capacity and pulse tests.
- RTE is calculated by dividing the sum of all discharge energy by the sum of all charge energy.
- Tests start at 50% SOC.
- SOC test range :

  LFP FR: 22~58%

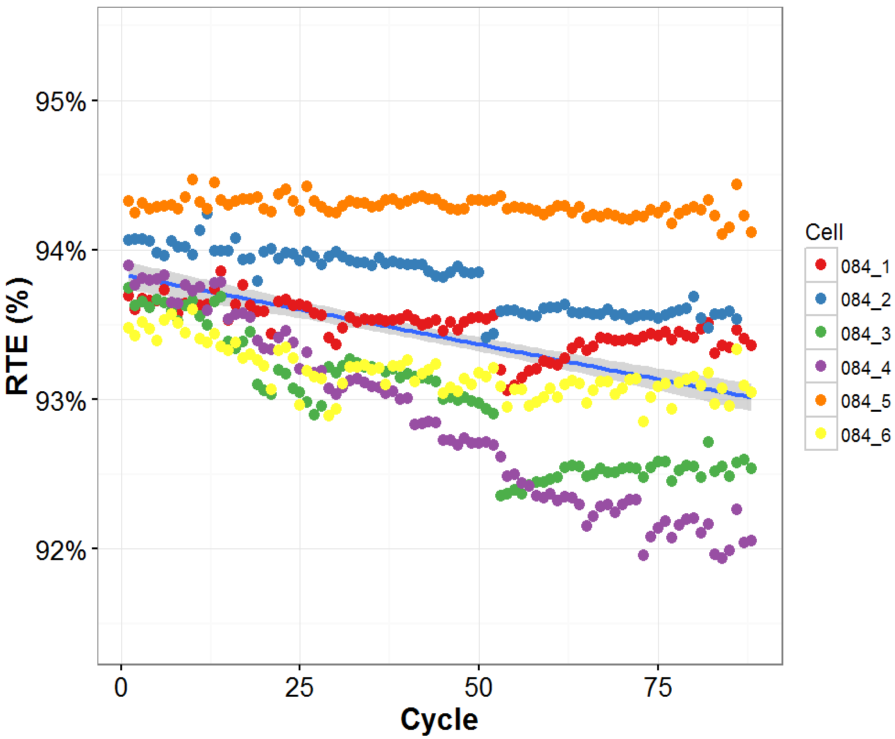
  Baseline: 32%

  NCA FR: 27~55%

  Baseline: 36%

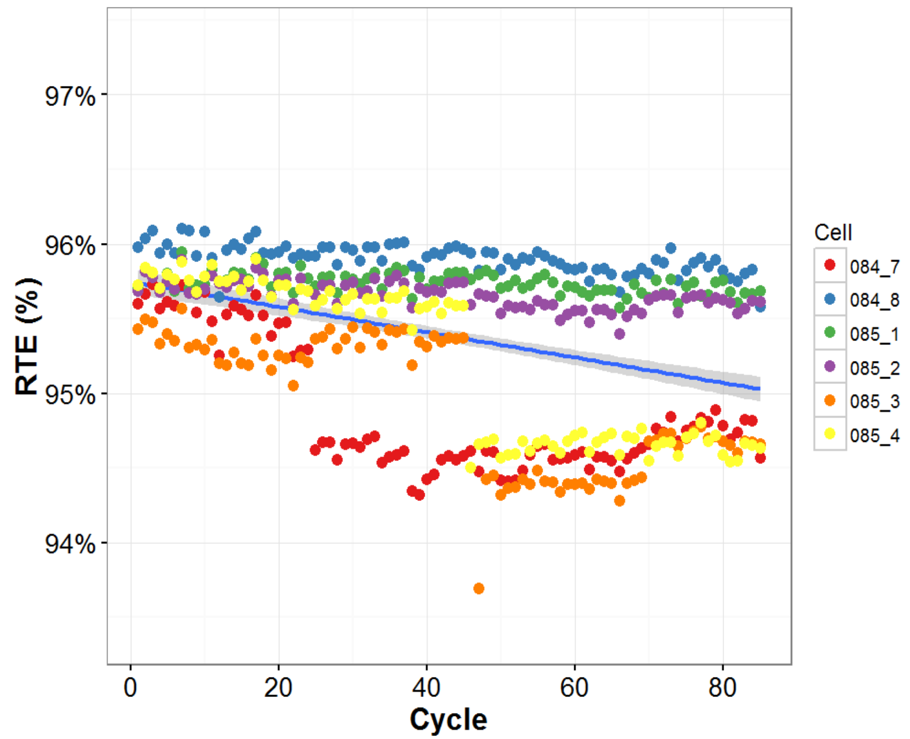
LFP Round Trip Efficiency

Frequency Regulation



Trend: -9.4% ± 1.0% / 1000 Cycles

Baseline



Trend: -8.5% ± 0.9% / 1000 Cycles

NCA Round Trip Efficiency

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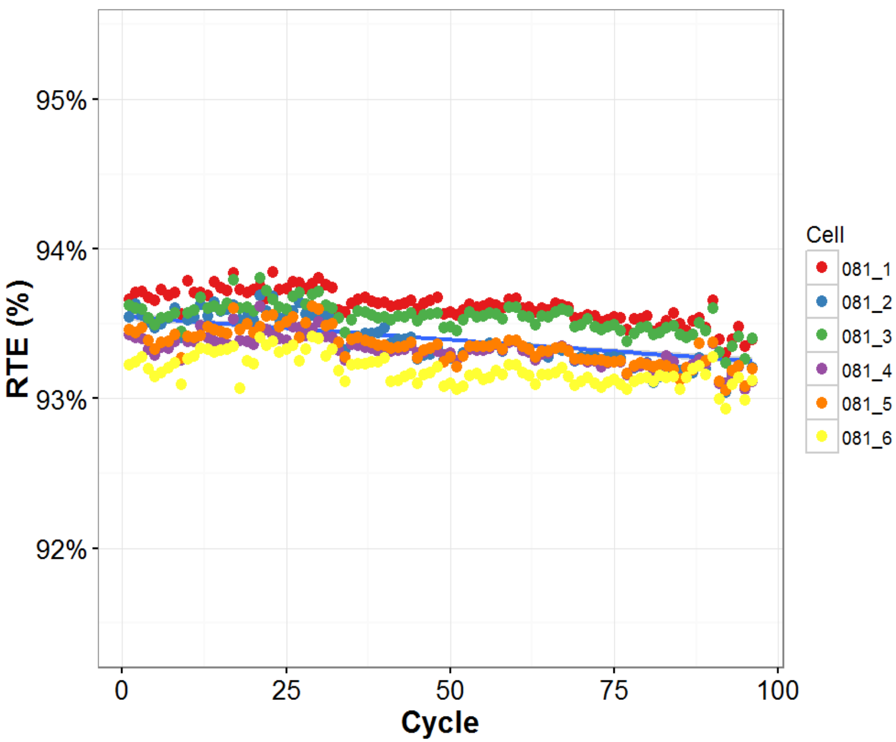
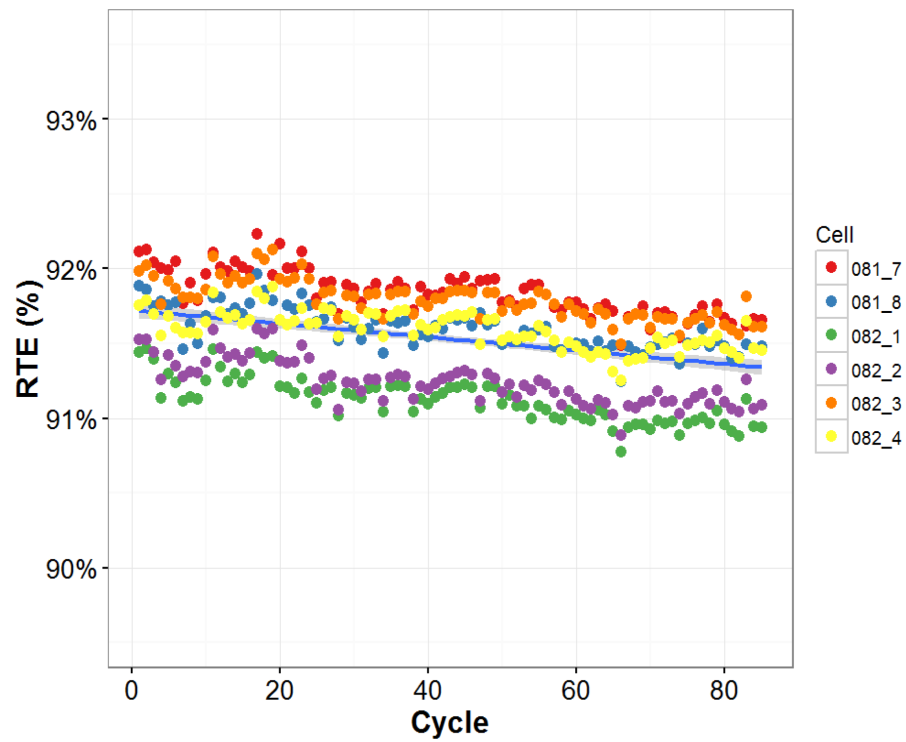
Frequency Regulation



Trend: -3.1% ± 0.2% / 1000 Cycles

Baseline

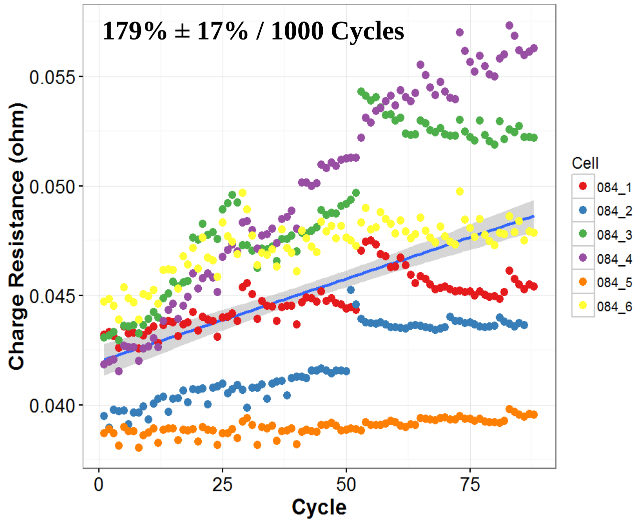


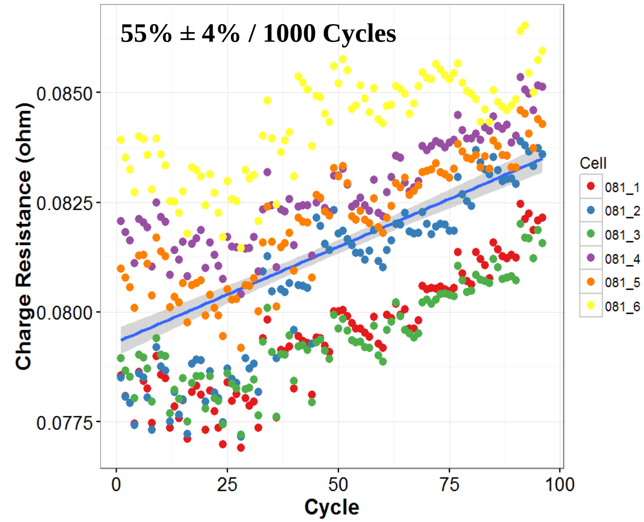
Trend: -4.5% ± 0.5% / 1000 Cycles

LFP & NCA Resistance

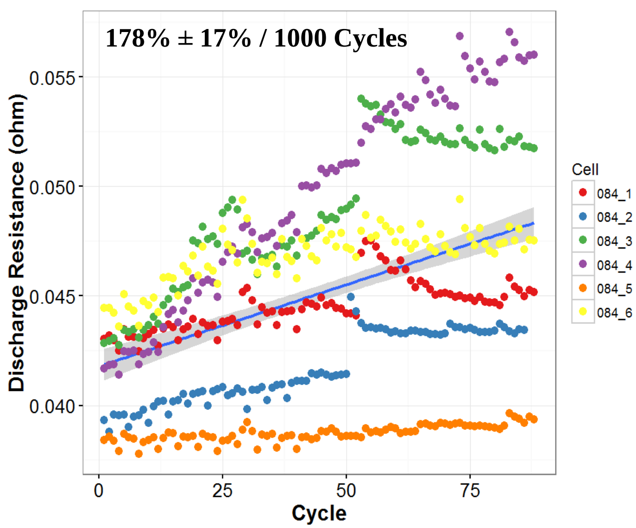
LFP | NCA

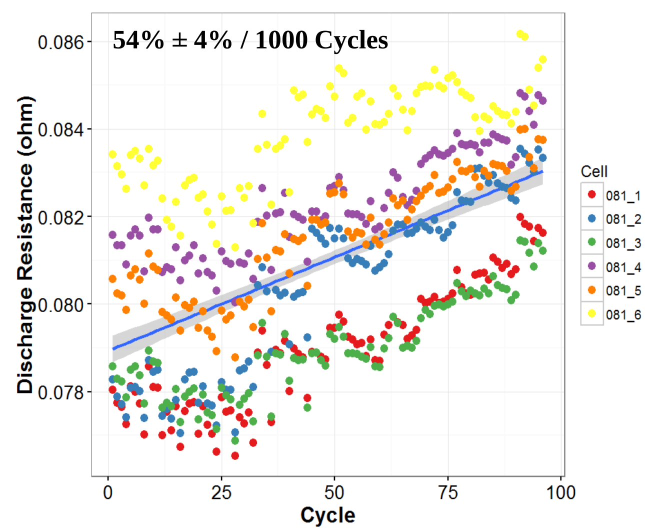
Charge





Discharge



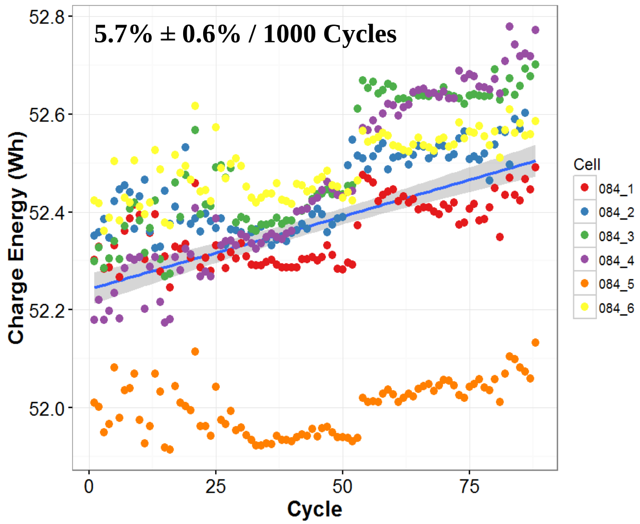


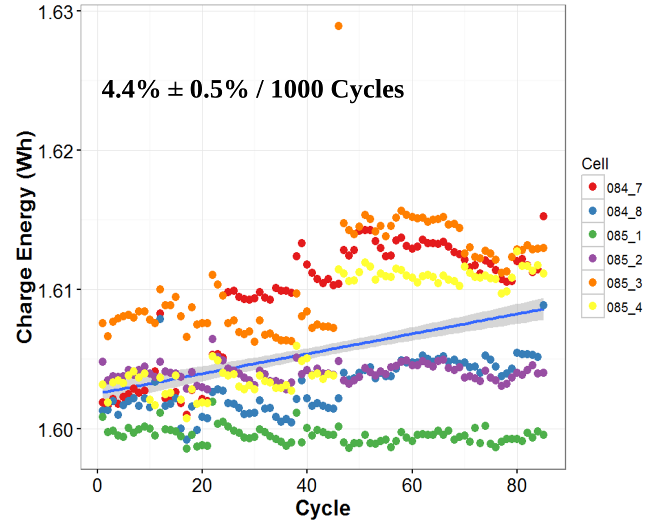
LFP Energy

Frequency Regulation

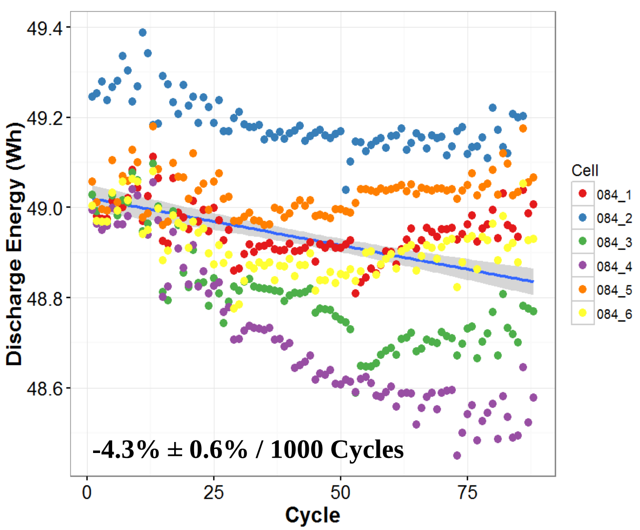
Baseline

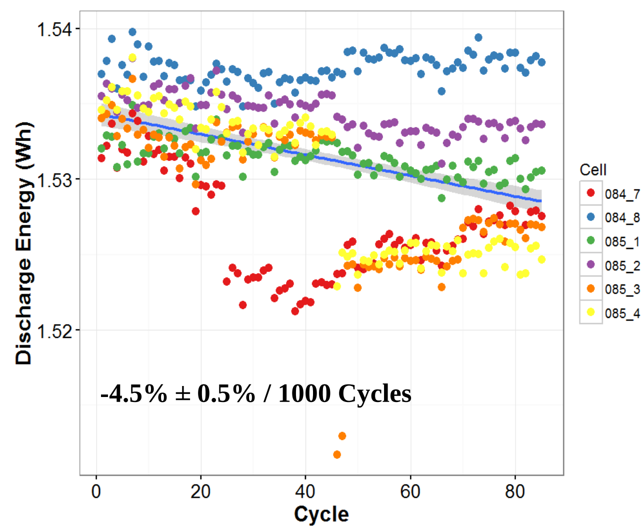
Charge





Discharge





NCA Energy

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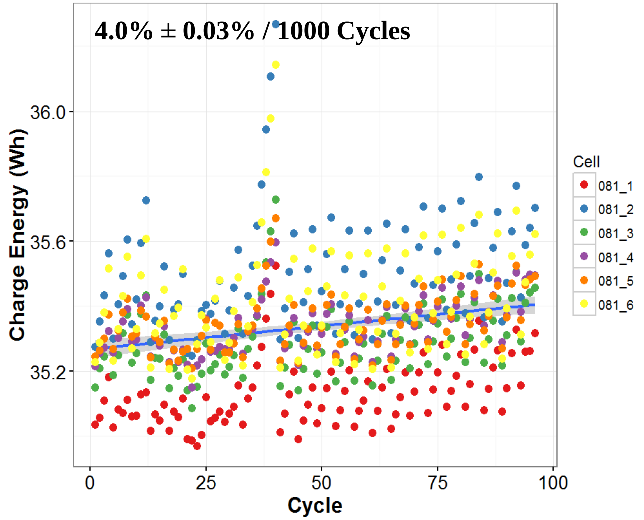
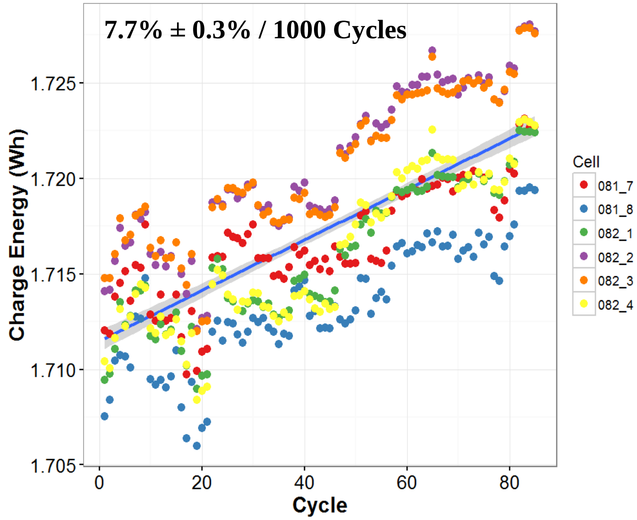
Frequency Regulation

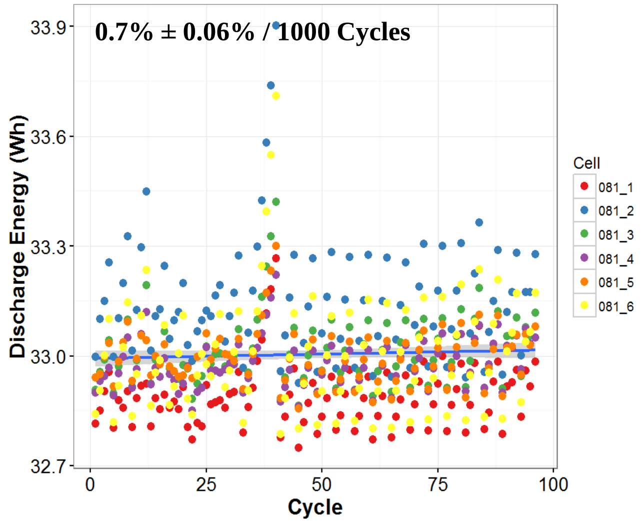
Baseline

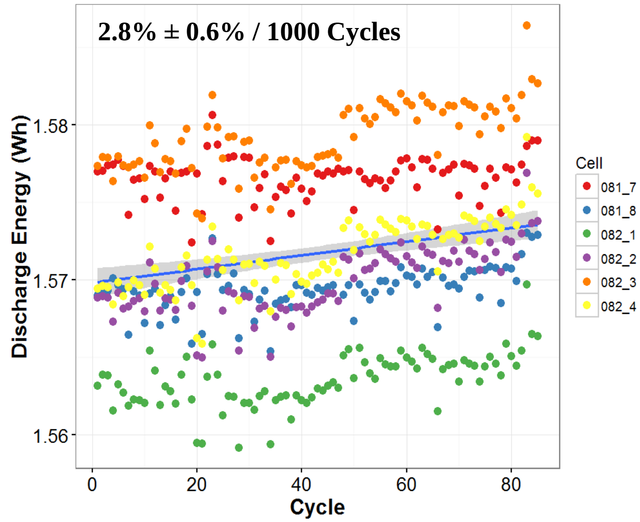
Charge





Discharge





Reliability Test Results

- Overview of the trends - each entry is the change per thousand cycles for RTE, charge/discharge energy as % of initial energy, and internal resistance during FR.
- Far right two columns are metrics for how well behaved the data is - the RMS difference in RTE between cells performing the same tests, and the RMS deviation from a linear trend.

Type	RTE	Energy		Resistance		RMS Deviation (% in RTE)	
		Charge	Discharge	Charge	Discharge		
	(%/1000 cycles)	(% in Wh/1000 cycles)		(% in Ohm/1000 cycles)		between cells	from trend
LFP FR	-9.4	5.7	-4.3	179	177	0.6	0.1
LFP FR BS	-8.5	4.4	-4.5	-	-	0.5	0.2
NCA FR	-3.1	4.0	0.7	55	54	0.2	0.1
NCA FR BS	-4.5	7.7	2.8	-	-	0.3	0.1

Conclusions

- From tests performed within battery specifications and limited SOC ranges, baseline cell do not show significantly better stability than batteries under frequency regulation service.
- On average, LFP based cell showed higher RTE degradation than NCA based cell but some LFP cells show better stability than NCA cells.
- Cell performance deviation was larger for high power LFP based Li-ion battery.
- LFP cells show increase in charge but decrease in discharge energy while NCA cells show increase in charge/discharge energy with cycling.
- Due to high power capability, LFP cells utilized 1.6 times more energy than NCA cells during our test.
- So far, cells show linear degradation trend.

Future Work

- Extended cycling needed
  - More accurate RTE
  - Linear or nonlinear trend ?
  - Cell performance variation
  - Internal resistance change at various SOC levels
  - Capacity degradation
- Different SOC ranges and battery formats need to be evaluated.
- Testing under temperature controlled conditions (Thanks to James Ortega of Sandia National Laboratory for providing information).
- Analyses of cell internals at various stages of degradation would be useful.

Acknowledgements

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