Daikin Advanced Lithium Ion Battery Technology – High Voltage Electrolyte

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DOE Annual Merit Review
June 20, 2018

Project ID: ES312

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Overview

Timeline

- Start Date: 10/1/16
- End Date: 9/30/19
- 50% Complete

Target and Barriers

- Performance – 300-1000 cycles at 4.6 V
- Failure mechanisms at high voltage

Budget

- Total - $1,826,895
  - DOE - $1,250,000
  - Daikin America - $576,895
- Expenditure of Gov't Funding
  - FY2017 524 K
  - FY2018 ~ 291 K (estimate)

Partners

- Interactions/Collaborations
  - None (2017)

Relevance/Objectives

Project Objective: to develop a stable (300 – 1000 cycles), high-voltage (up to 5 volts), and safe (self-extinguishing) formulated electrolyte.

- Performance Objective
  - Understand mechanisms for cell failure via electrolyte
  - Propose electrolyte solvent systems through DOE methods for high voltage battery systems. This includes optimization of additives
  - Optimize additive packages for increased cycle life

- Impact to DOE VT mission
  - Electrolytes which facilitate stable high voltage cycling of lithium ion batteries present a pathway to higher energy batteries.
  - Higher energy batteries enabled by simple material substitution not only positively impact gravimetric and volumetric energy density targets but also are beneficial towards DOE cost targets (wH/$)

Milestones - 2017

Task Number (Q)	Task or Subtask Title	Milestone Type (Milestone or Go/No Go Decision Point)	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Status
1.1	Establish baseline and review current state of art	Milestone	Establish current physical and performance baselines for fluorinated electrolyte	Report profile performance of current best electrolyte in baseline cells	Complete
1.2	Gas composition	Milestone	Gas composition as function of voltage and cathode surface	Understand changes in gas composition with changing chemistry and conditions	Complete
1.3	Gassing kinetics of FEC	Milestone	Gassing dynamics of FEC	Study pathway and kinetics of FEC decomposition	Complete
1.4	Gas kinetics based on cathode surface composition	Go/No Go	Gassing as function of metal ratio in cathode	Determine if gassing can be minimized through electrolyte composition	Complete

Milestones - 2018

Task Number (Q)	Task or Subtask Title	Milestone Type (Milestone or Go/No Go Decision Point)	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)	Status (completion date)
2.1	Film Thickness vs time/voltage	Milestone	Film thickness at different voltages and time	Determine film growth parameters via surface techniques	In progress (12/31/18)
2.2	Film composition vs time/voltage	Milestone	Rough elemental chemistry of film over time	Determine elemental composition via surface techniques	In progress (12/31/18)
2.3	Film composition vs time/voltage	Milestone	Detailed chemistry of film over time	Understand how film is formed by TOF-SIMS	In progress (12/31/18)
2.4	Battery thickness (non-gas) vs. time/voltage	Milestone	Make real time thickness measurements and relate back to individual electrodes	Determine if film growth can be controlled through chemistry	In progress (12/31/18)
2.5	Submit current optimized cells to DOE for evaluation	Go/No Go	Fabricate interim cells for evaluation by DOE	Testing at DOE laboratory to determine if target is met	

Milestones - 2019

Task Number (Q)	Task or Subtask Title	Milestone Type (Milestone or Go/No Go Decision Point)	Milestone Description (Go/No-Go Decision Criteria)	Milestone Verification Process (What, How, Who, Where)
3.1	Metal dissolution vs. time/voltage	Milestone	Finish chemical analysis of electrodes	Relate chemistry of electrode to performance
3.2	Cathode surface structure vs. time/voltage	Milestone	Determine cathode surface structure on cycling	Assess role of fluoro chemicals in protection of cathode surface
3.3	Compilation of phenomena/performance data and selection of new electrolyte composition	Milestone	Compile and combine data to determine solitary and combined interactions of phenomena with performance	Rank the effect of hypothesized failure modes with respect to electrochemical performance
3.4	Submit final cells and report to DOE	Go/No Go	Fabricate cells containing improved electrolyte based on study of failure mechanisms	Submit final report and cells for testing

Technical approach

Target

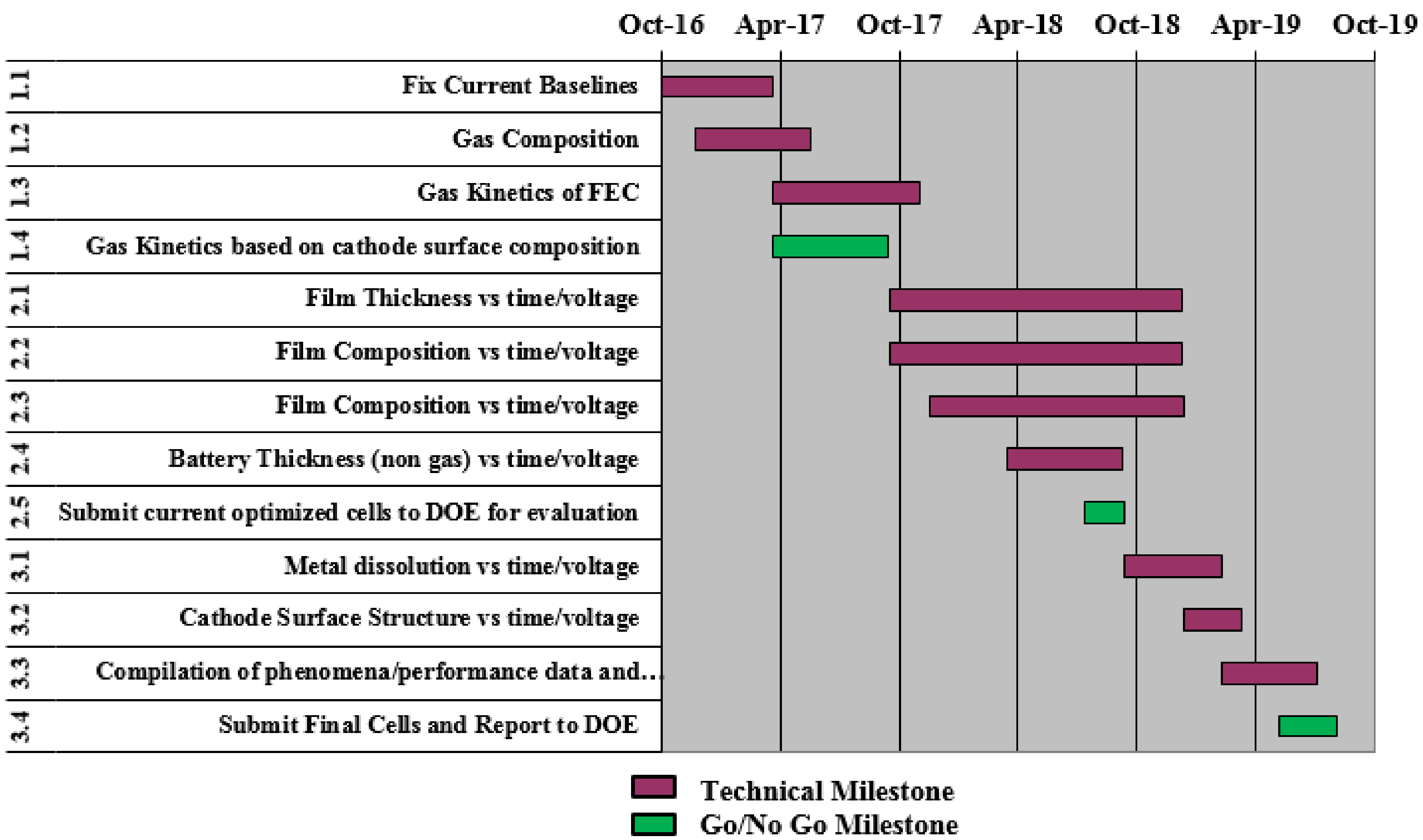
Development of a stable (300 – 1000 cycles), high-voltage (4.6 V), and safe (self-extinguishing) formulated electrolyte through understanding of current electrolyte failure mechanisms

Approach

- Year 1 - Understand causes and nature of gas generation in high voltage cells and it's impact on electrochemical performance.
- Year 2 - Observe and quantify SEI films formed on electrodes as they relate to reduced gas generation
- Year 3 – Explore other failure points in the high voltage batteries which are not related (dissolution, xtal structure changes…etc). Propose solutions to achieve above target

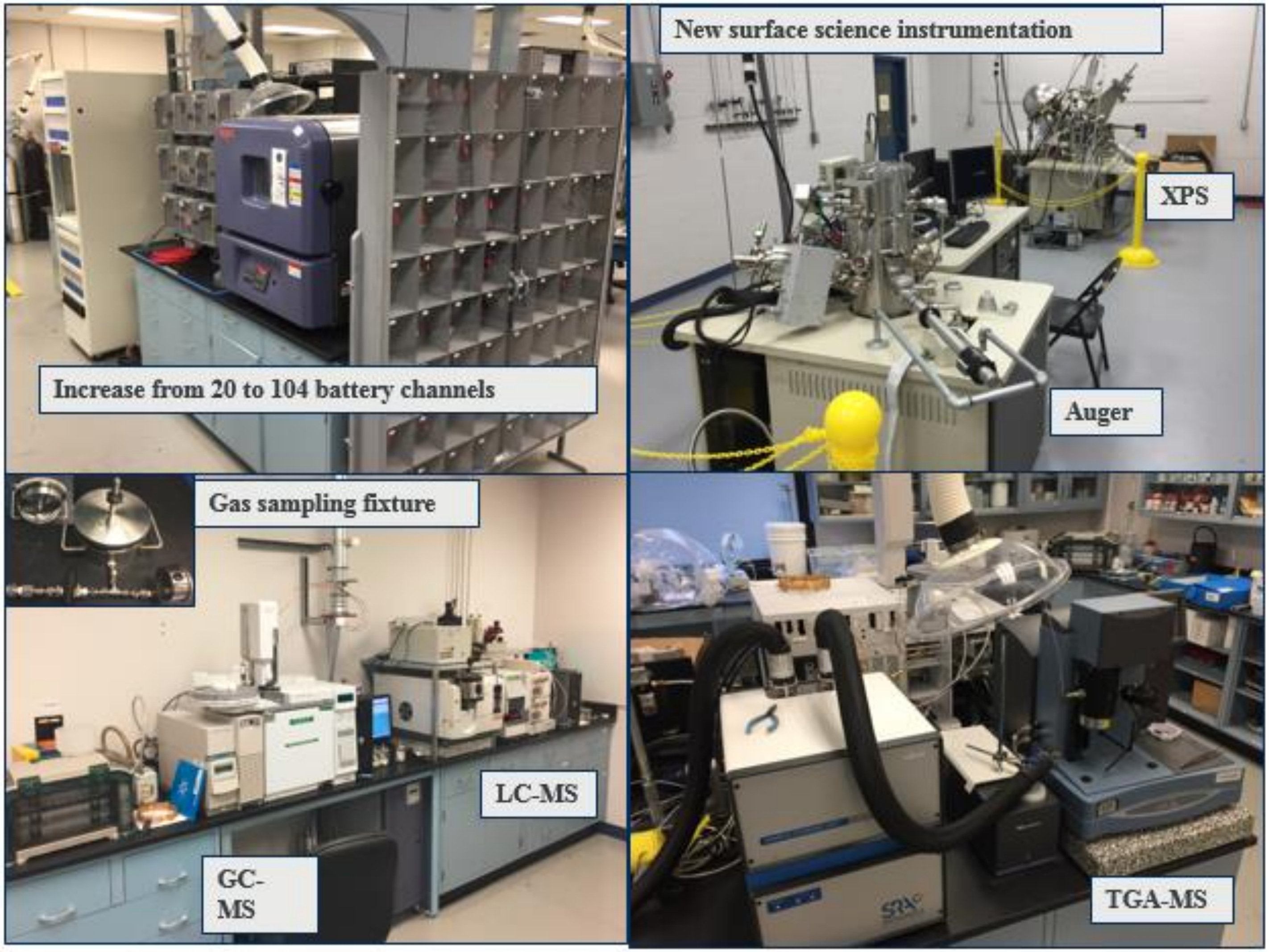
Technical Approach - Schedule

Schedule has been modified due to complexity of surface measurements



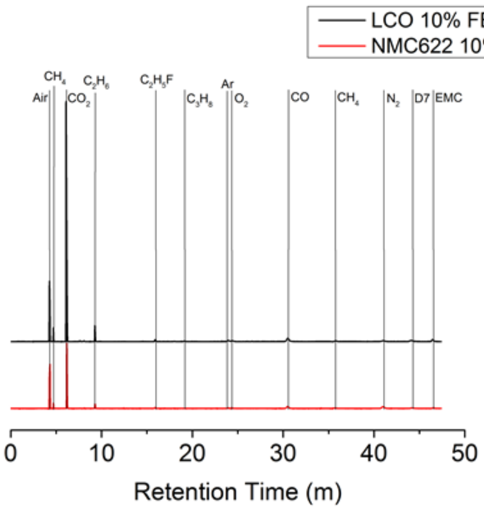
FY17 Technical Accomplishments – Resource Increase

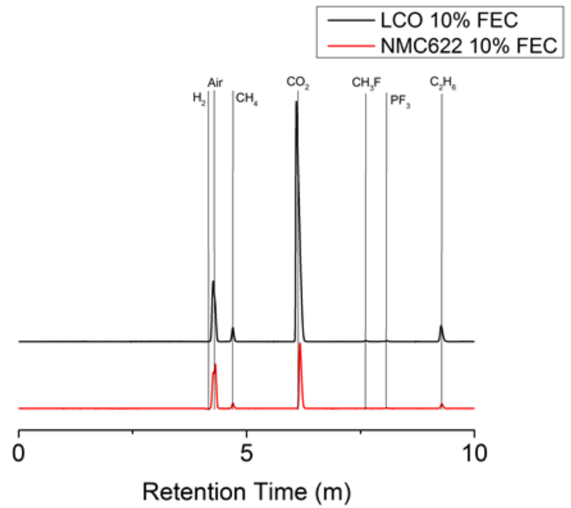
- Hiring and training of additional project staff (postdoc, 2 co-op students)
- Lab equipment build out



Gas Composition as a Function of [FEC], Nickel, and Voltage
Milestone 1.2

TCD Spectra of Select 200 mAh Cells





- Initial gas analysis and method development was performed on calendar aged LCO and NMC622 cells at 4.6V

- Hydrocarbon (CH_4, C_2H_6, C_2H_4), Fluoro-hydrocarbon (CH_3F and C_2H_5F), and Permanent gases (O_2, H_2, CO_2, and CO) are present

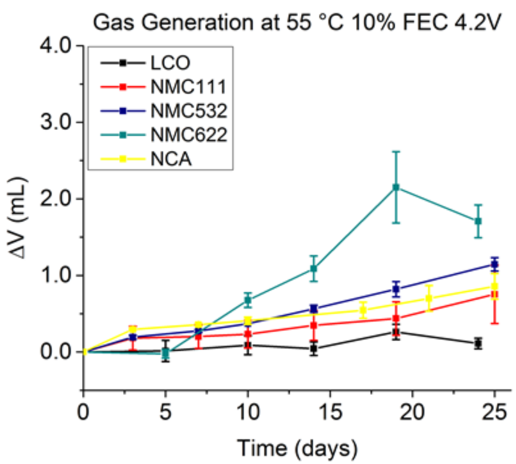
Gas Composition as a Function of [FEC], Nickel, and Voltage – Milestones 1.3 and 1.4

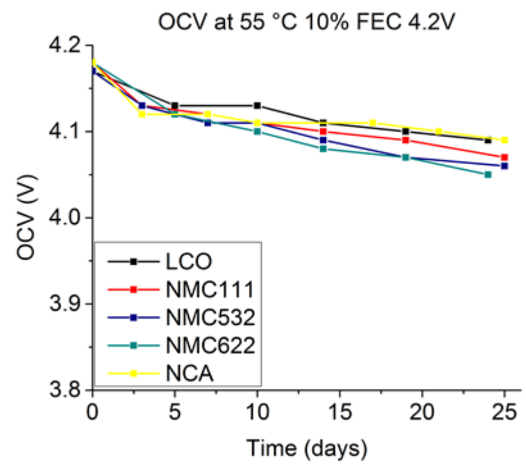
Qualitative Gas Composition Table at 4.6 V

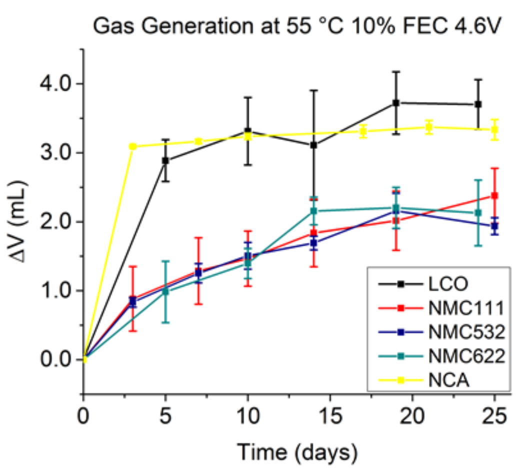
[FEC]	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_4H_{10}	CH_3F	C_2H_5F	CO	CO_2	O_2	H_2	PF_3
LCO 10%	X		X	X	X	X	X	X	X	X	X		X
LCO 20%	X	X		X		X	X	X	X	X	X		
NMC111 10%	X		X	X			X	X	X	X	X	X	
NMC111 20%	X		X	X			X	X	X	X	X	X	
NMC532 10%	X		X	X			X	X	X	X	X	X	
NMC532 20%	X		X	X			X	X	X	X	X	X	
NMC622 10%	X		X	X			X	X	X	X	X	X	
NMC622 20%	X	X		X			X	X	X	X	X	X	

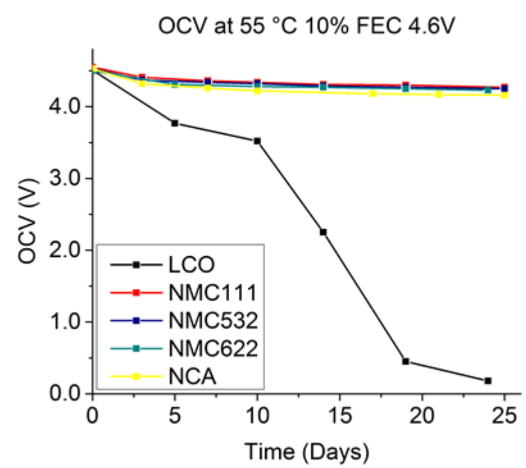
- **Higher hydrocarbons (C_3H_6 and C_4H_{10}) are limited to LCO cells**
- **Fluoro-hydrocarbons are present at higher voltage > 4.5 indicating breakdown of fluorinated components in electrolyte**
- **Quantification of gases is currently in progress (CH_4, C_2H_6, C_2H_4, CO, CO_2, H_2, and O_2)**

Gassing Kinetics as a Function of [FEC], Nickel, and Voltage – Milestone 1.3 and 1.4



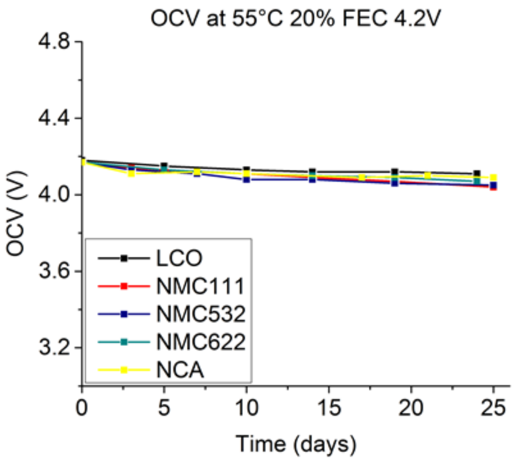


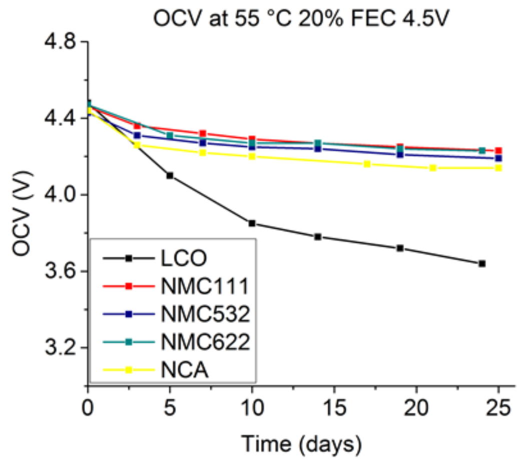


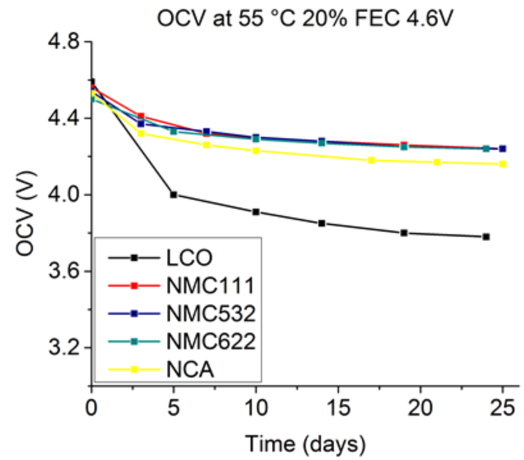


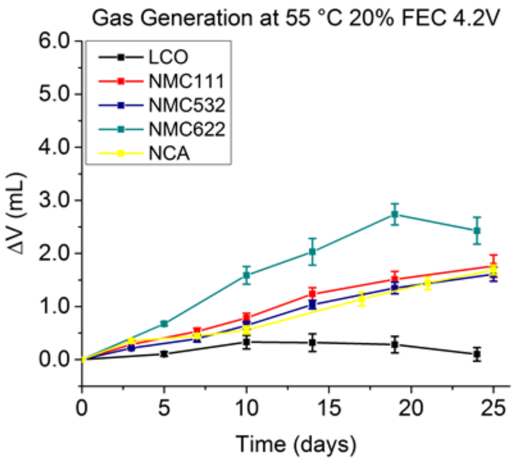
- **The majority of gas produced was observed within the first 5 days of a calendar life test at 55 °C**
- **Gas generation can be correlated to the observed OCV drop indicating cathode reduction**
- **LCO and NCA generated more gas than cells with NMC cathodes (622, 532, and 111)**

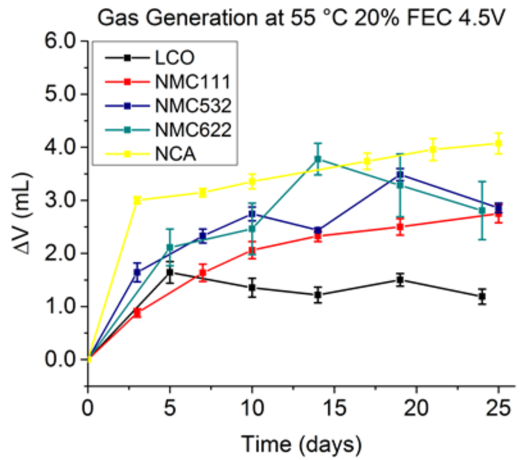
Gassing Kinetics at 4.2, 4.5 and 4.6 V – Milestone 1.3 and 1.4

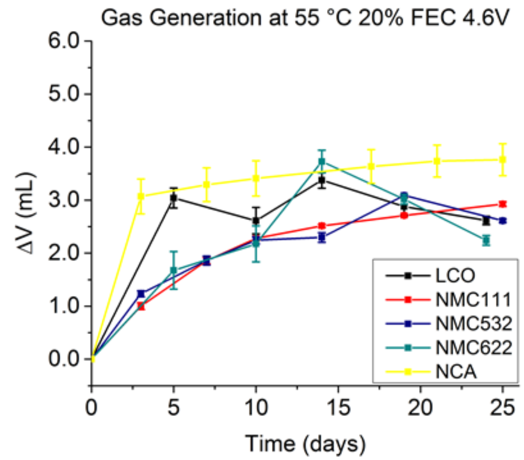












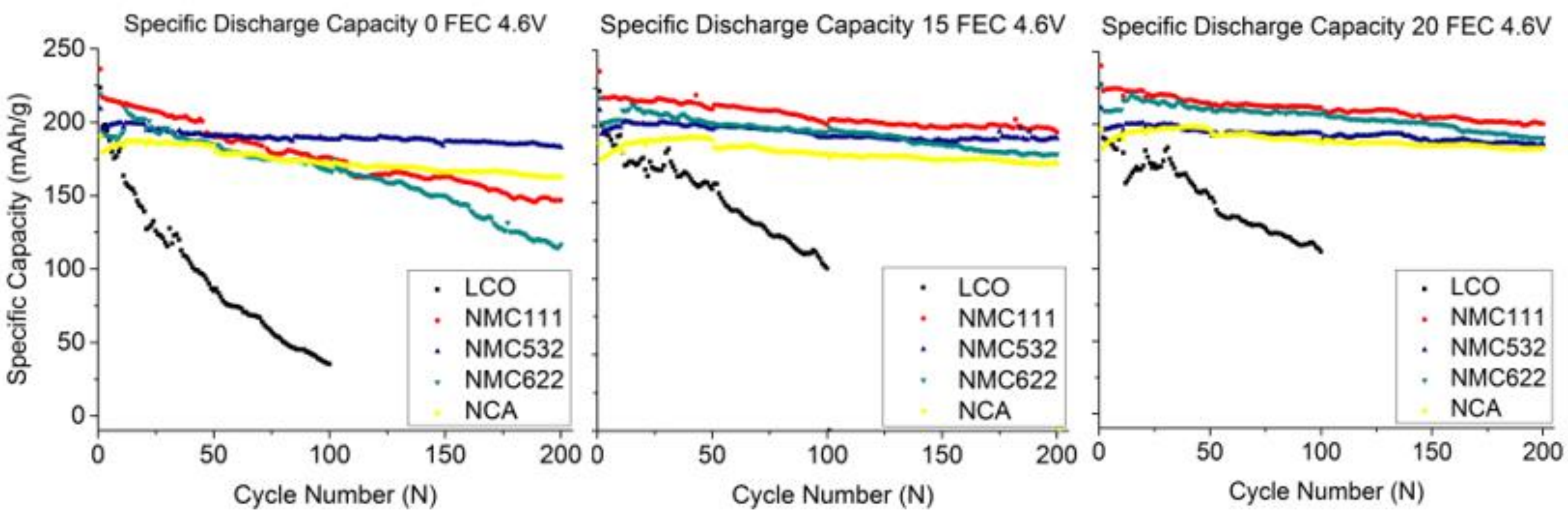
Gassing Kinetics as a Function of [FEC], Nickel, and Voltage – Milestone 1.3 and 1.4

- **Increasing the amount of FEC in the electrolyte leads to better performance at 4.5 and 4.6V. However, it also increases the amount of gassing.**
- **NMC111, 532, and 622 have similar performance in terms of gassing and OCV loss at 4.5 and 4.6V.**
- **LCO and NCA exhibit significant gassing at high voltage. Sources of this accelerated gassing are being determined**

20% FEC (v/v) at 55 °C

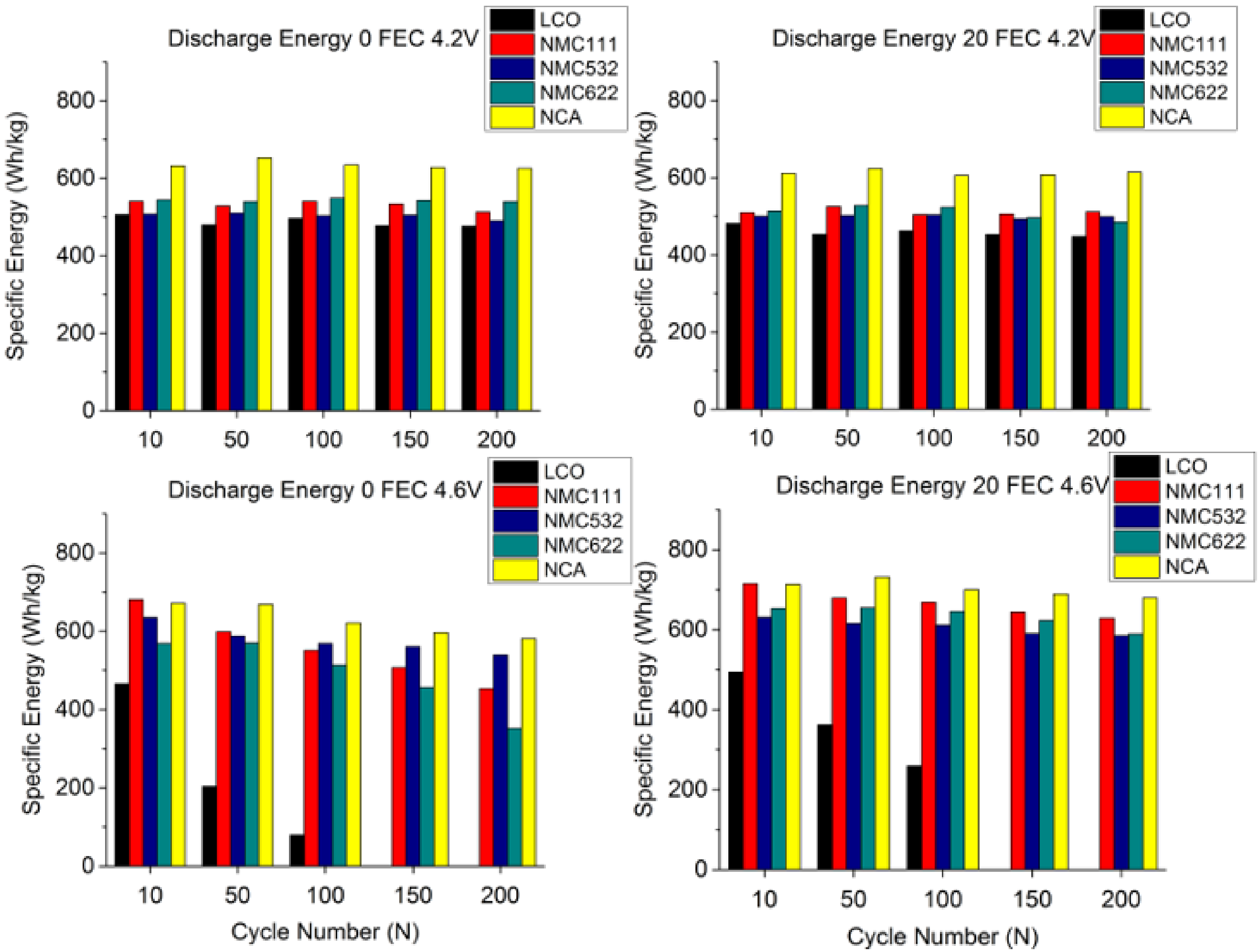
Cathode	OCV Retention at 4.2V (%)	OCV Retention at 4.5V (%)	OCV Retention at 4.6V (%)
LCO	98.0	81.2	82.4
NMC111	96.9	94.6	93.0
NMC532	97.1	94.7	93.3
NMC622	97.6	94.4	94.0
NCA	97.8	93.2	91.8

Cycle performance to 4.6 V as a Function of [FEC] and cathode nickel content– Milestone 1.3 and 1.4



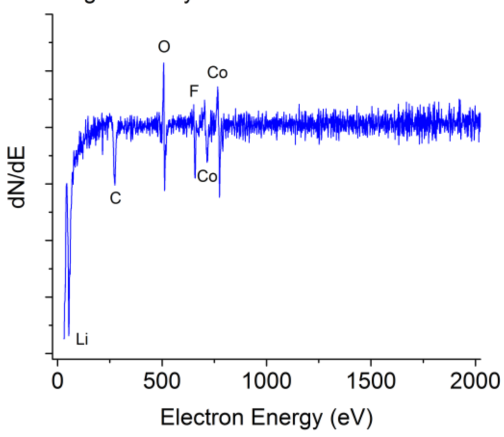
- **Cycling experiments performed at r.t. at 0.7C with CC charge/CC discharge**
- **FEC is necessary at 4.6V, 15% (v/v) minimum**

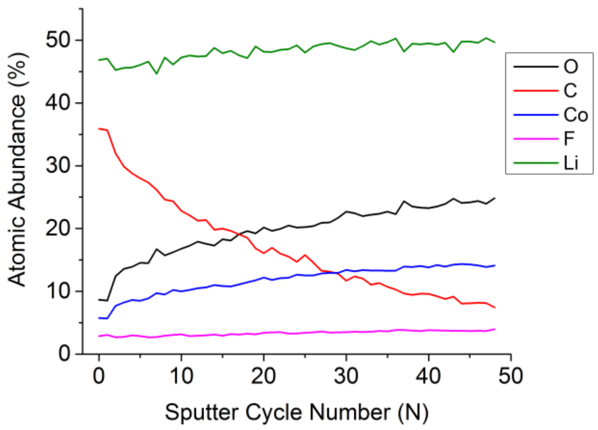
Cell Energy as a Function of [FEC], Nickel, and Voltage – Milestone 1.3 and 1.4

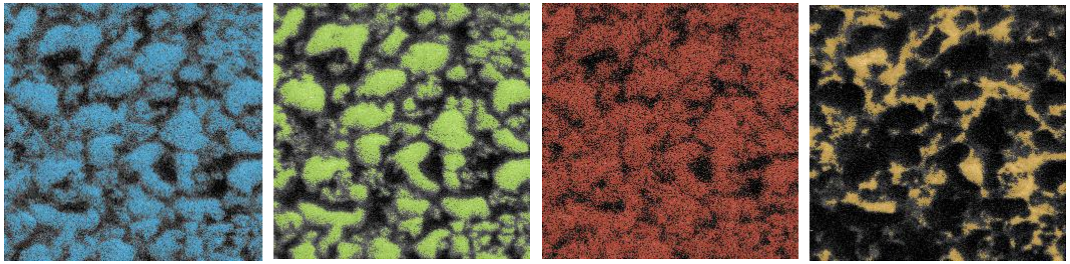


- **The addition of FEC at cells cycled at 4.2V did not result in increased performance**
- **FEC offers a significant performance boost at 4.6V, with NMC111 (38.8%) and NMC622 (67.8%) yielding the greatest increase in specific energy**

Film Composition (Elemental) as a Function of [FEC], Nickel, and Voltage – Milestone 2.2



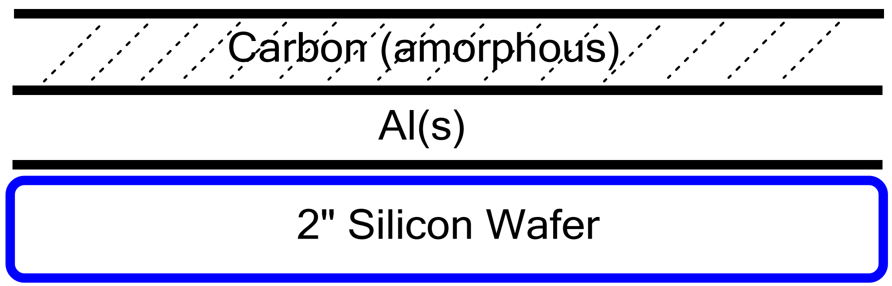




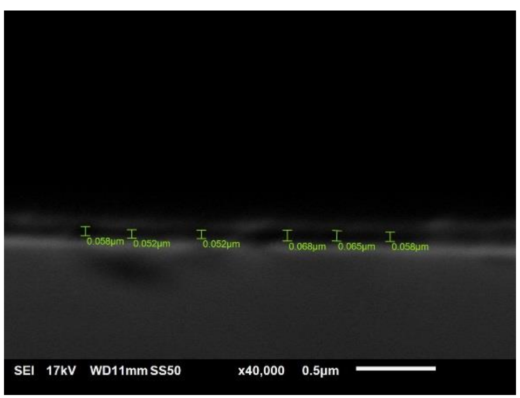
Post-Sputter Elemental Maps of Co (blue), O (lime), F (red, and C (yellow) of a 4.5V LCO Cell Cycled at .7C

- **Auger Electron Spectroscopy (AES) will be one avenue utilized to measure the SEI layer composition and thickness**
- **Carbon is a significant contributor to the SEI layer's elemental composition**
- **Fluorine is present from multiple sources in both the SEI layer and cathode material**

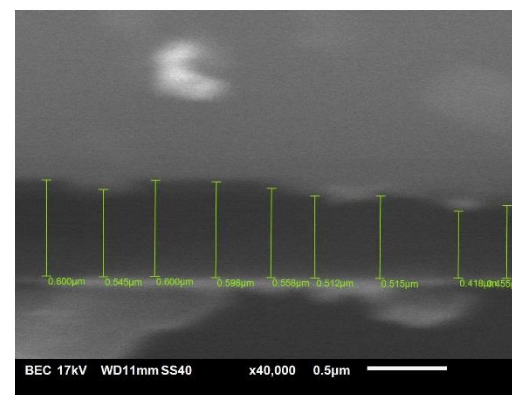
SEI Layer Analysis: Thickness and Composition – Milestone 2.1 and 2.2



- Various thicknesses of amorphous carbon samples will be used to calibrate the sputter gun (AES), which will allow us to accurately measure the SEI thickness and elemental composition



SEM images of 500 Å (left) and 5000 Å (right) thick amorphous carbon films



Proposed Future Work – remainder of FY18

Estimated completion date 12/31/18

- Complete surface analysis to quantify thickness/composition of electrode films
  - In house EDS measurements with external sample preparation
  - In house thickness measurement by XPS/Auger using custom carbon film standards
  - Outside collaboration with UT-Dallas for TOF SIMS
  - Possible collaboration with Stanford for cryo-TEM
- Real time thickness measurements as a function of charge discharge regime
  - Determine what is cause for increase in anode thickness
- Summarize all current knowledge on failure mechanisms to propose chemical additive solutions for interim cell build
- Build and submit interim cells to DOE for end of second budget period

Any proposed future work is subject to change based on funding levels

Response to previous year reviewer comments

- Reviewer suggested putting more weight on 5 V stability
  - Daikin Industries has committed significant resources to develop 5 V electrolyte with national lab partners. Daikin is now focusing on chemistries which are closer to commercialization and the subject of this project
- Reviewer suggests lack of quantified milestones and that technical risks/mitigation strategies need to be discussed more
  - This project has 12 distinct milestones which are centered around analytical experiments. It is difficult to place quantified milestones in a project where the main focus is to identify failure mechanisms. The collected and collated data are the deliverables for each milestone.
- Reviewer advised greater attention should be paid to the compatibility of these solutions with practical (e.g. graphite) anodes
  - All cells used in this study are commercial grade cells (production overruns) which contain graphite anodes.
- Reviewer suggested that project team needs to demonstrate understanding of the electrolyte/high voltage cathode stability issues and provide rationale to suggest how fluorochemical additives can enable stability above 4.6 V
  - Work in the past year has shown the relationship between the oxidized cathode and the electrolyte in several voltage windows. These results allow Daikin to judiciously choose additives based on failure mechanism (ie. Direct oxidation of electrolyte, electrode surface decomposition…)

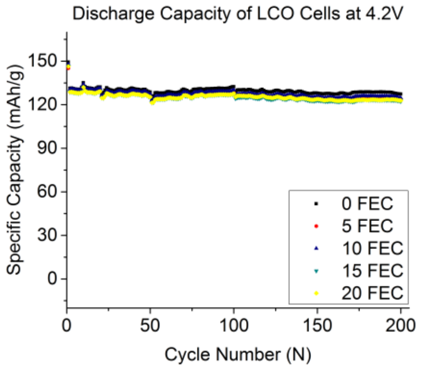
Response to previous year reviewer comments

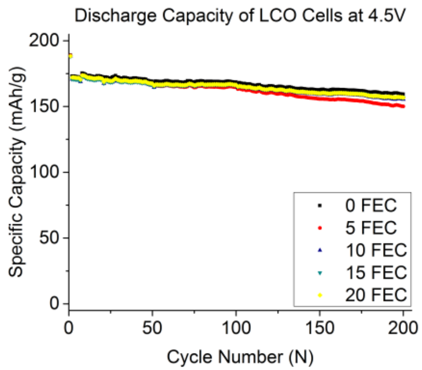
- Multiple reviewers cited Daikin lack of collaboration. In addition, one reviewer stated that it was unclear where surface characterization would be accomplished.
  - In the current year, Daikin will accomplish all the surface characterization milestones. Outside collaboration will be sought for samples preparation and characterization which will include techniques such as TOF SIMS. Daikin will perform some surface experiments (XPS, Auger) in house.
- Review asserted that the stability of the anode/electrolyte interface must be improved for these electrolytes to have practical applications
  - Daikin recognizes that anode/electrolyte stability will need to be achieved to enable long term cycle performance. The efforts of this project have been focused on the cathode/electrolyte interface due to its direct link to high voltage failure. When this problem has been suitably addressed, the focus will move to other components of the cell.
- Reviewer suggested the project team to understand whether fluorocarbon performance between 4.5 and 4.6 V is due to cathode or electrolyte
  - The work in this last project year was focused on this topic. It has been found that this performance decrease is due to both the cathode as well as at least one component of the fluorinated electrolyte (FEC).
- Reviewer Daikin needs to establish connection of this study to the overall objective of developing stable high voltage electrolyte
  - Researchers at Daikin believe the quickest route to developing high voltage electrolyte is to understand the failure modes of current state of the art electrolyte which is the objective of this project.

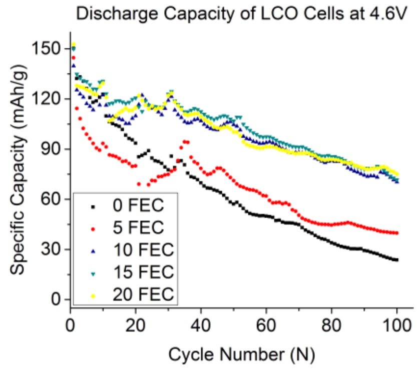
Technical Backup Slides

Battery Performance as a Function of [FEC], Nickel, and Voltage

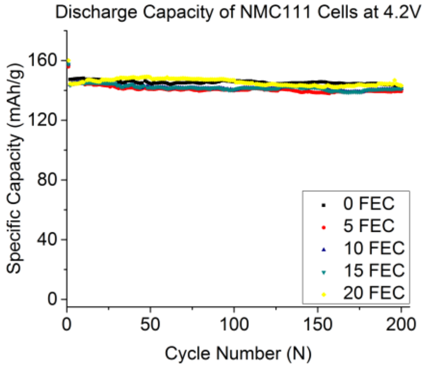
LCO 200 mAh Cells

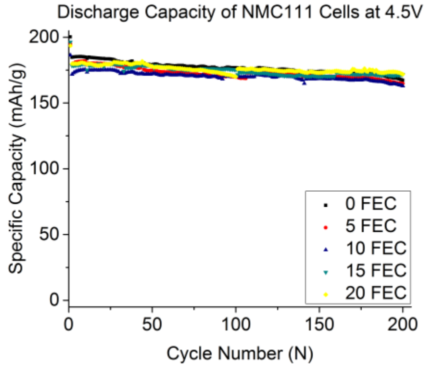


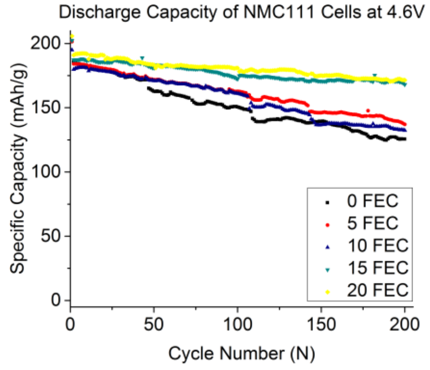




NMC111 200 mAh Cells

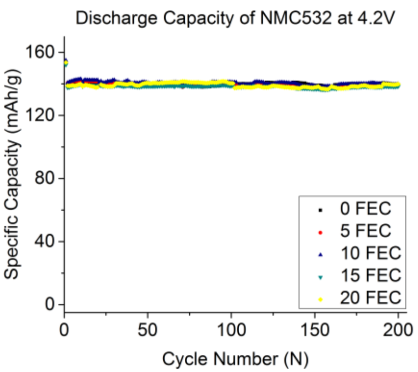


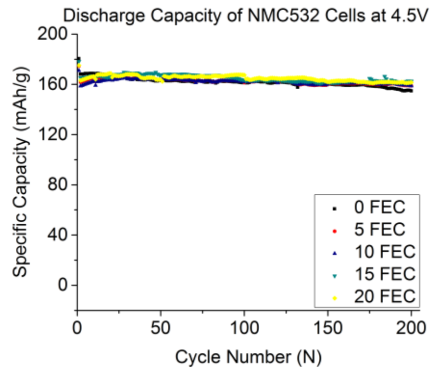


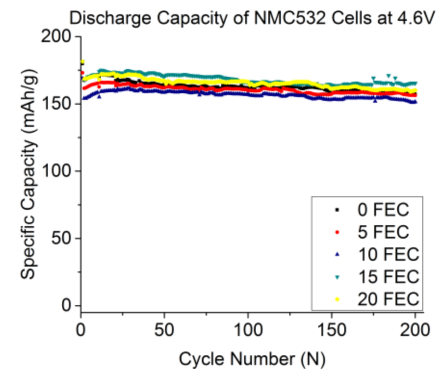


Battery Performance as a Function of [FEC], Nickel, and Voltage

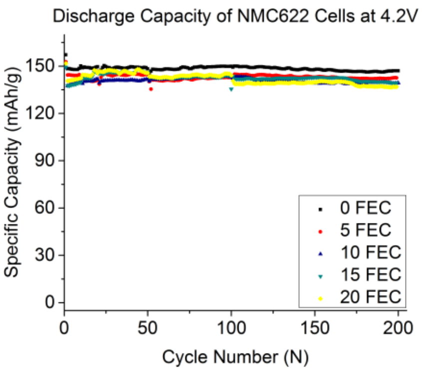
NMC532 200 mAh Cells

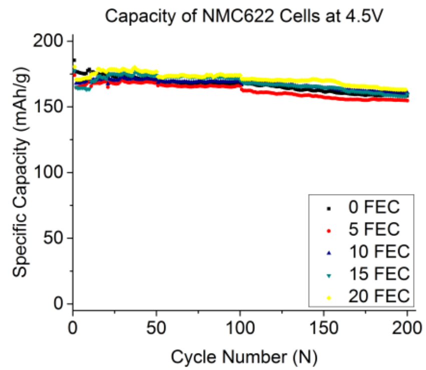


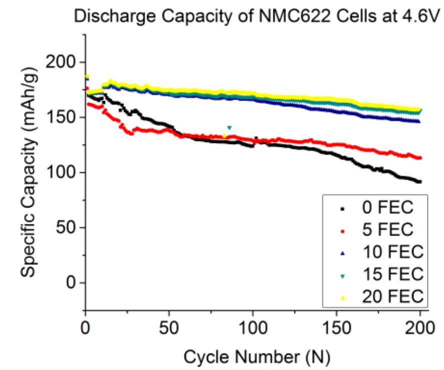




NMC622 200 mAh Cells

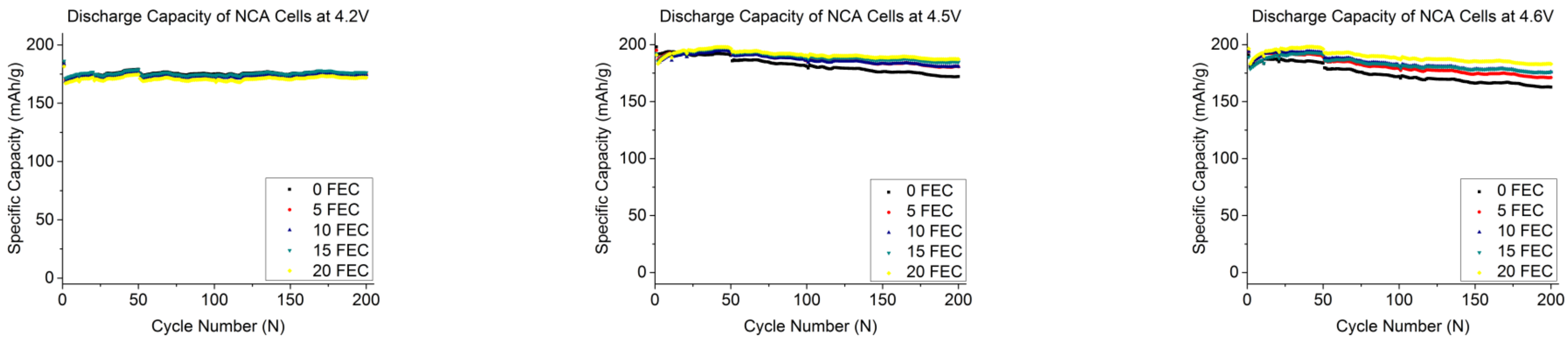






Battery Performance as a Function of [FEC], Nickel, and Voltage

NCA 200 mAh Cells



- Cathodes with the largest amount of Nickel (NMC622 and NCA) have decreased capacity compared to NMC111 and NMC532 under our initial cycling experiments at .7C and CC charge/CC discharge

- FEC significantly increases performance at high voltage, with 10-15% being optimal based on our results

Battery Performance as a Function of [FEC], Nickel, and Voltage

4.2V Capacity Retention After Cycling at .7C

Cathode	Cycles	Capacity % (0 FEC)	Capacity % (20 FEC)
LCO	200	94.4	93.5
NMC111	200	94.4	96.9
NMC532	200	98.2	98.8
NMC622	200	98.1	92.3
NCA	200	98.3	98.5

4.6V Capacity Retention After Cycling at .7C

Cathode	Cycles	Capacity % (0 FEC)	Capacity % (20 FEC)
LCO	100	17.8	58.0
NMC111	200	67.8	89.1
NMC532	200	91.5	92.8
NMC622	200	55.9	86.3
NCA	200	85.3	92.3

- > 80% capacity retention after 200 cycles with 20% FEC at 4.6V in all cells containing Nickel in the cathode (NMC111, 532, 622, and NCA)