DAIKIN AMERICA, INC.

Daikin Advanced Lithium Ion Battery Technology – High Voltage Electrolyte

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DOE Annual Merit Review
June 8, 2017
Project ID: ES312

This presentation does not include proprietary, confidential or otherwise restricted information

Timeline

- Start Date: 10/1/16
- End Date: 9/30/19
- 17% Complete

Target and Barriers

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

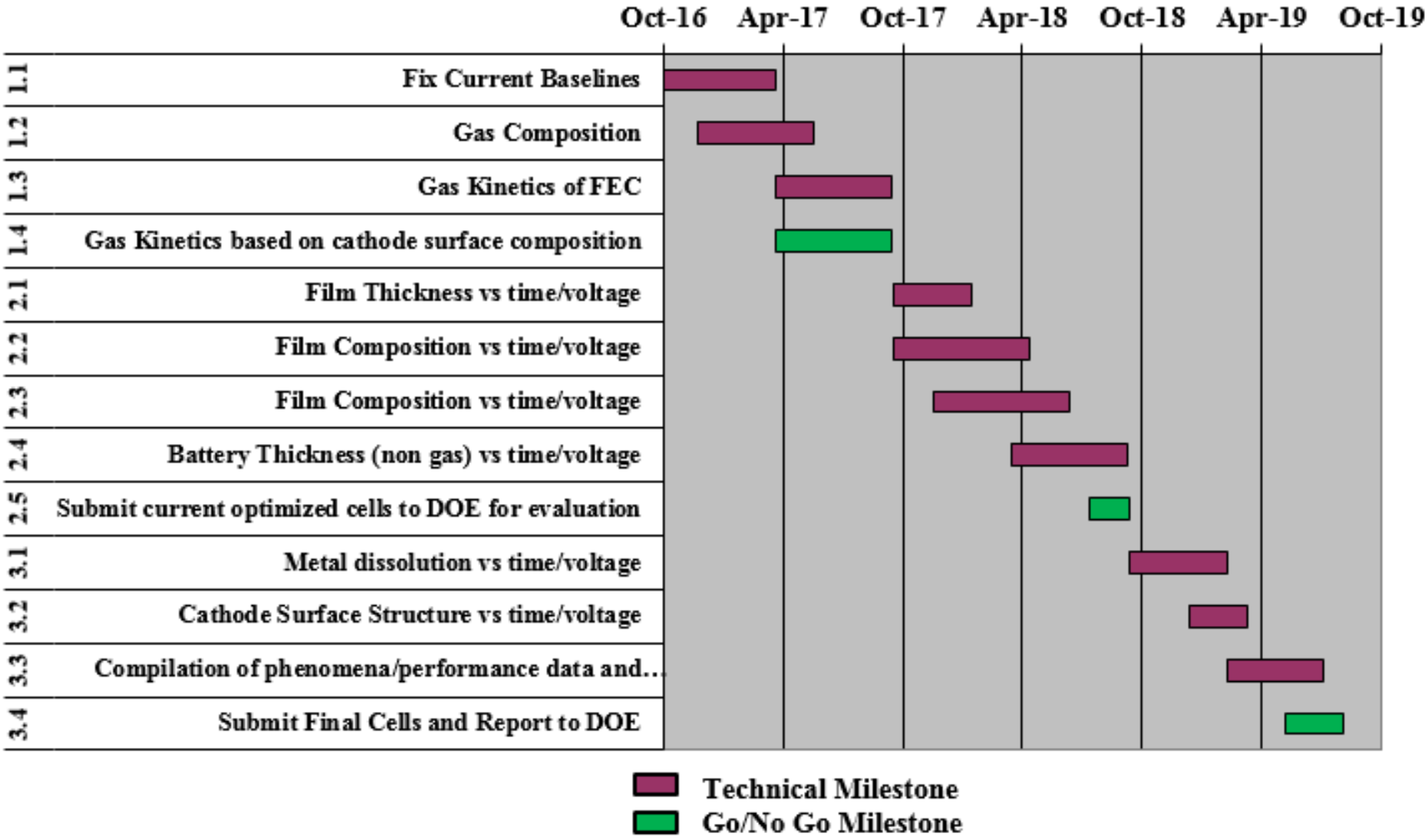
Budget

- Total - $1,826,895
  - DOE - $1,250,000
  - Daikin America - $576,895
- Expenditure of Gov't Funding
  - FY2017 ~ 152K (estimate)

Partners

- Interactions/Collaborations
  - None (2017)

Effect of fluorochemicals additives on the electrolyte/electrode interaction



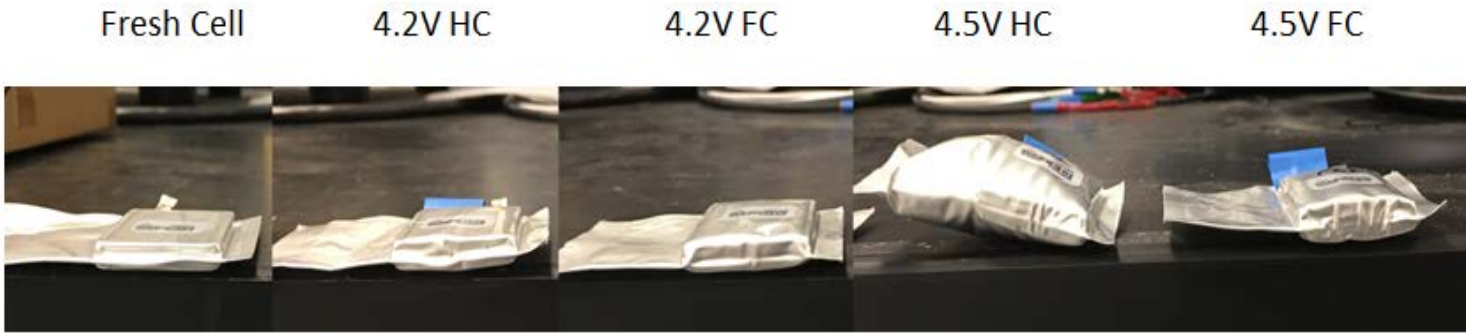
Milestones 2017

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)
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
1.2	Gas composition	Milestone	Gas composition as function of voltage and cathode surface	Understand changes in gas composition with changing chemistry and conditions
1.3	Gassing kinetics of FEC	Milestone	Gassing dynamics of FEC	Study pathway and kinetics of FEC decomposition
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

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

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

- Safety Objective
  - Integrate safe solvent combinations into optimized electrolyte formulation
  - Develop safety testing methods for evaluation of candidate electrolytes.



Gas + **Liquid** + **Solid**

Gas Chromatography
Mass Spectrometry
GC/MS

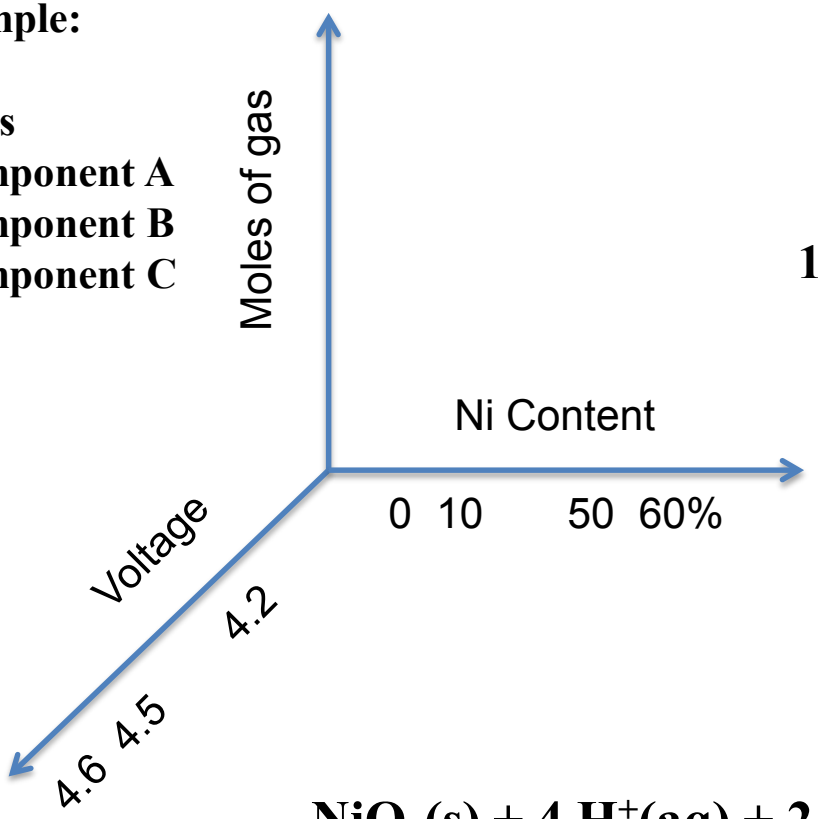
Liquid Chromatography
Mass Spectrometry
LC/MS

Thermogravimetric Analysis
Mass Spectrometry
TGA/MS for embedded species
+
Time of Flight
Secondary Ion Mass Spectrometry
TOF-SIMS +
Xray Photoelectron Spectroscopy
XPS
Surface species

Dissolved Species Analysis
Metal dissolution of cathode
Graphite furnace atomic absorption
X-ray diffraction

For example:

Total Gas
Gas Component A
Gas Component B
Gas Component C
Etc.



Composition baselines

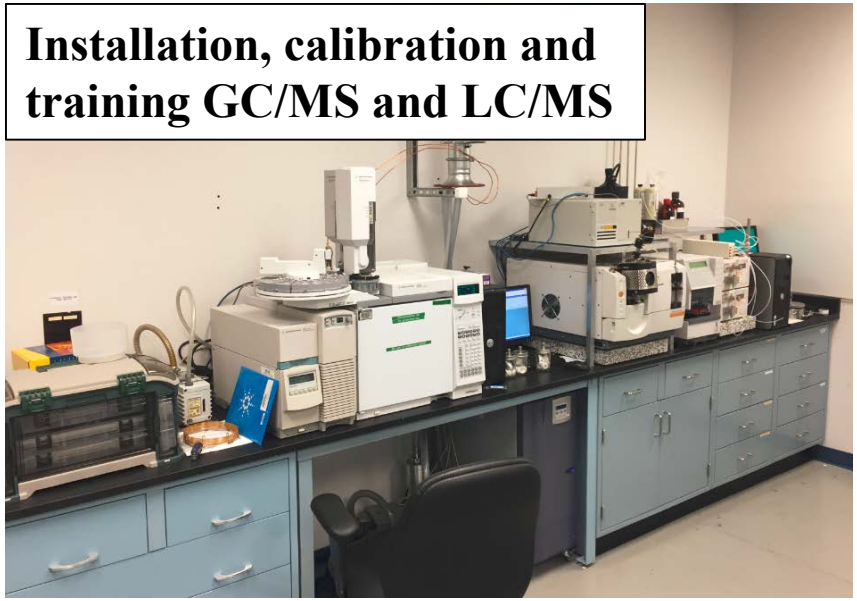
1.2M $LiPF_6$ EC/EMC (2/8) + 1% PS
1.2M $LiPF_6$ EC/EMC/FE (2/6/2) + 1% PS
1.2M $LiPF_6$ FEC/EMC/FE (2/6/2) + 1% PS

$NiO_2(s) + 4\ H^+(aq) + 2\ e^- \rightarrow Ni^{2+}(aq) + 2\ H_2O$ +1.7 V
$CoO_2(s) + 4\ H^+(aq) + 2\ e^- \rightarrow Co^{3+}(aq) + 2\ H_2O$ +1.42 V
$MnO_2(s) + 4\ H^+(aq) + 2\ e^- \rightarrow Mn^{2+}(aq) + 2\ H_2O$ +1.23 V

Purpose: To find key failure elements to propose solutions
e.g. diluents, surface protection…..

Increase in capability

Installation, calibration and training GC/MS and LC/MS



Sampling fixture GC/MS

Additional glove box for cell fabrication

Current bottleneck – sample preparation
Expansion from 20 ➞102 channels

Verification of reproducible results

1 A-hr pouch cell

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111) cathode

Graphite anode

Cells are anode limited and balanced for 4.2 V

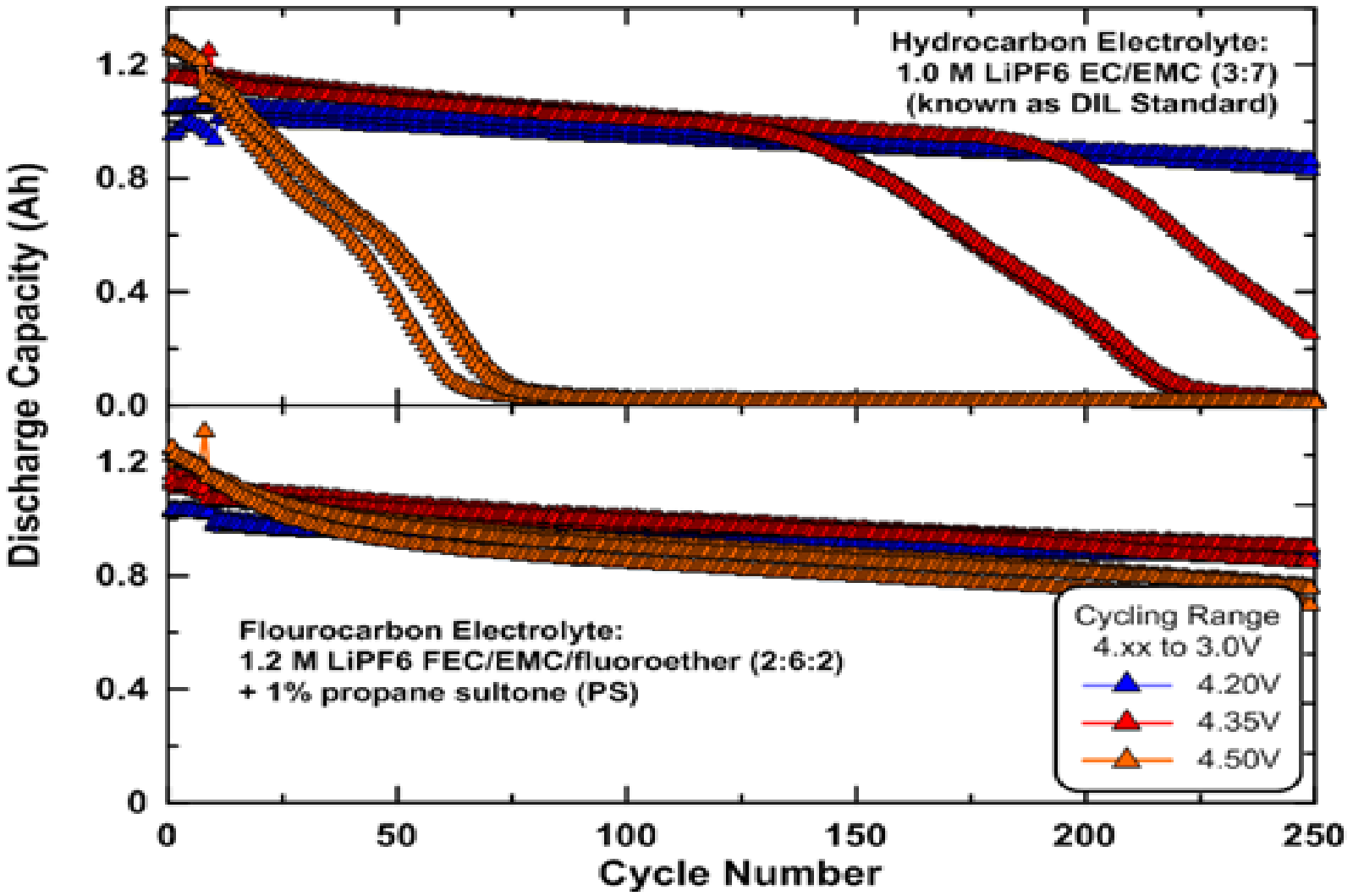
200 mA-hr pouch cell

$LiCoO_2$ (LCO) cathode
$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) cathode
$LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) cathode
$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) cathode
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode

Graphite anode

Cells are anode limited and balanced for 4.4 V

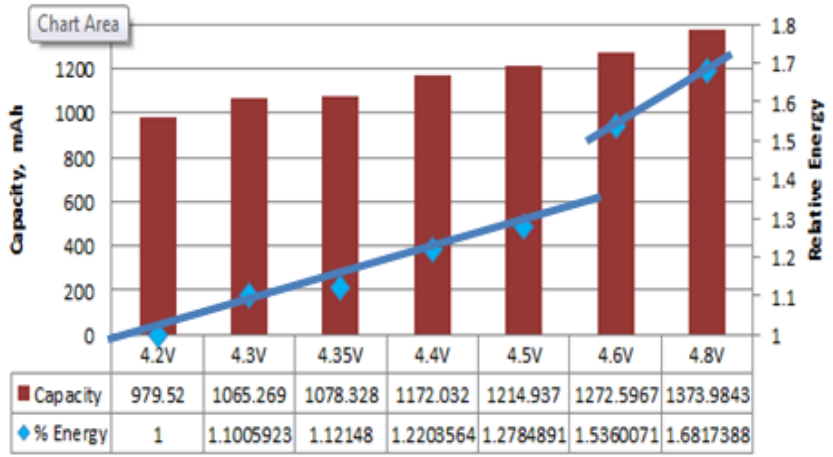
Establish baselines - voltage



Establish baselines - voltage

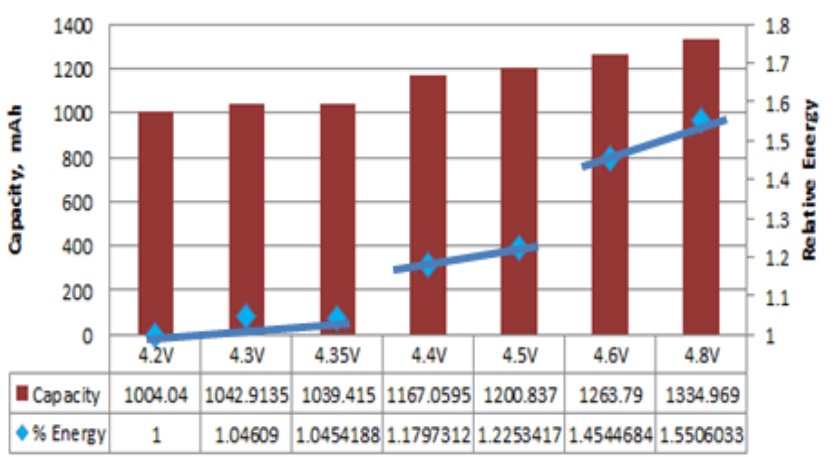
Discontinuities in the energy vs voltage plots at 4.4 V (gassing) and 4.6 V (?)

Fluorocarbon Electrolyte Performance(0.2C)



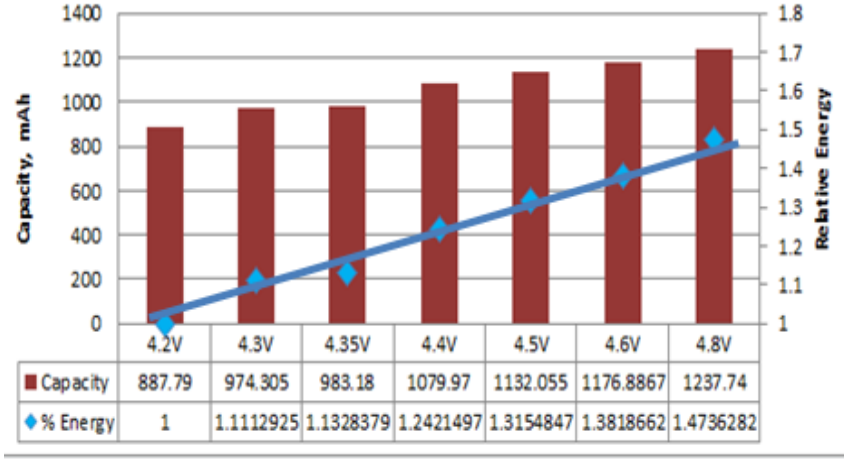
	4.2V	4.3V	4.35V	4.4V	4.5V	4.6V	4.8V
Capacity	979.52	1065.269	1078.328	1172.032	1214.937	1272.5967	1373.9843
% Energy	1	1.1005923	1.12148	1.2203564	1.2784891	1.5360071	1.6817388

Hydrocarbon Electrolyte Performance(0.2C)



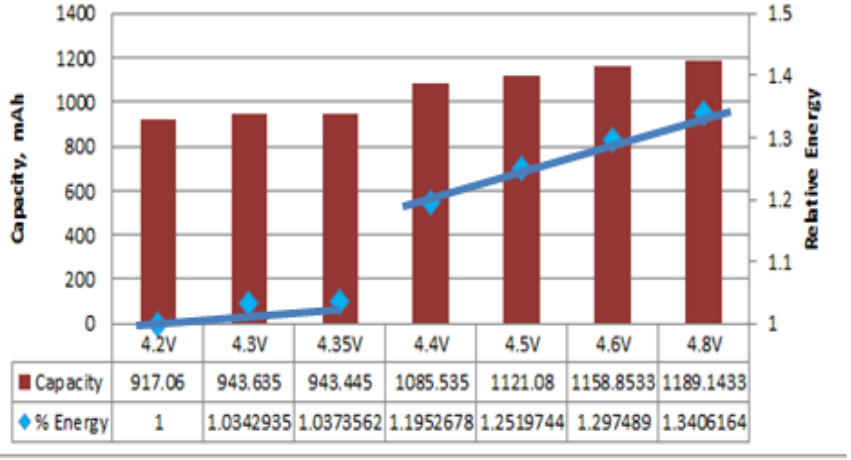
	4.2V	4.3V	4.35V	4.4V	4.5V	4.6V	4.8V
Capacity	1004.04	1042.9135	1039.415	1167.0595	1200.837	1263.79	1334.969
% Energy	1	1.04609	1.0454188	1.1797312	1.2253417	1.4544684	1.5506033

Fluorocarbon Electrolyte Performance(1.0C)



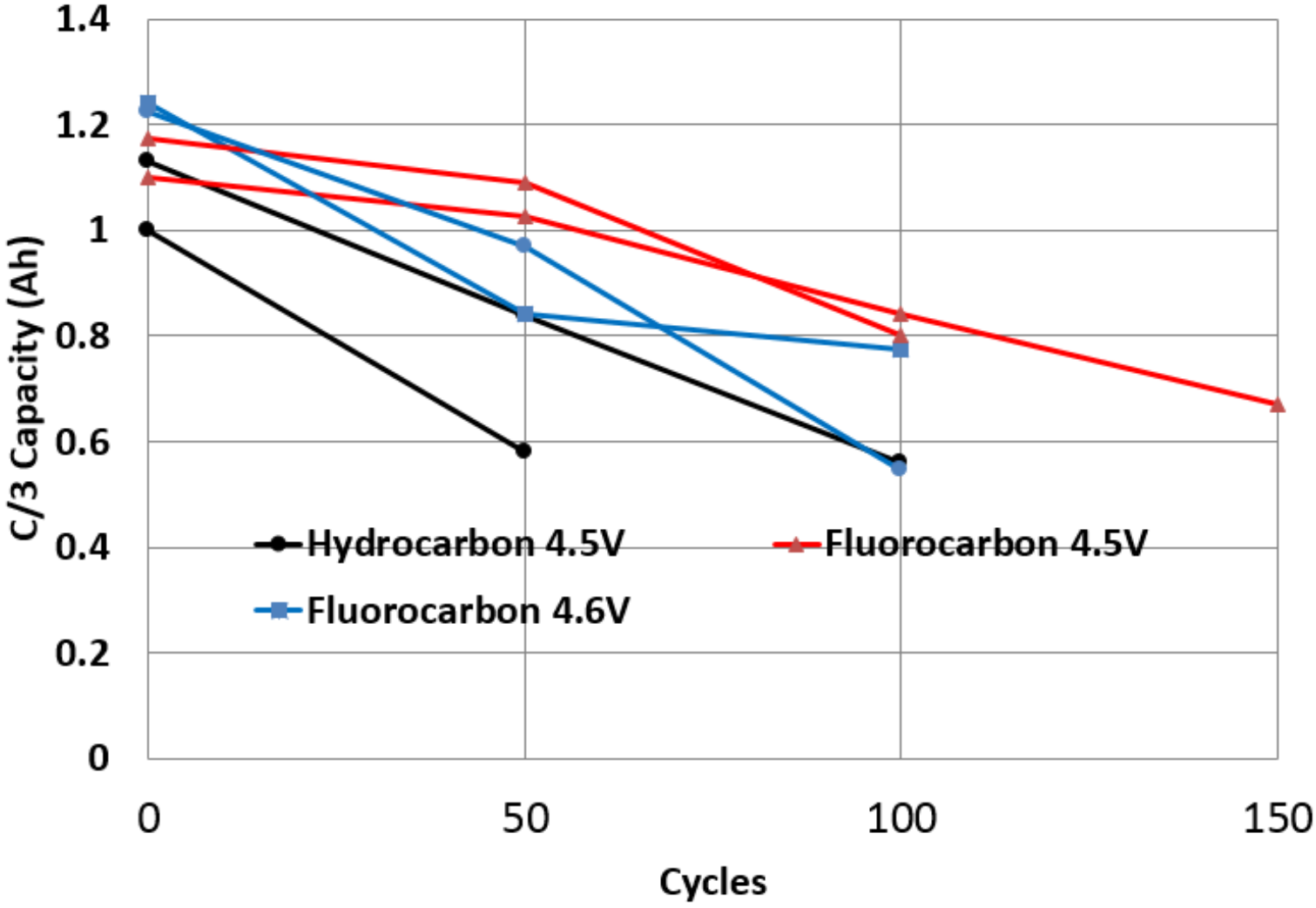
	4.2V	4.3V	4.35V	4.4V	4.5V	4.6V	4.8V
Capacity	887.79	974.305	983.18	1079.97	1132.055	1176.8867	1237.74
% Energy	1	1.1112925	1.1328379	1.2421497	1.3154847	1.3818662	1.4736282

Hydrocarbon Electrolyte Performance(1.0C)

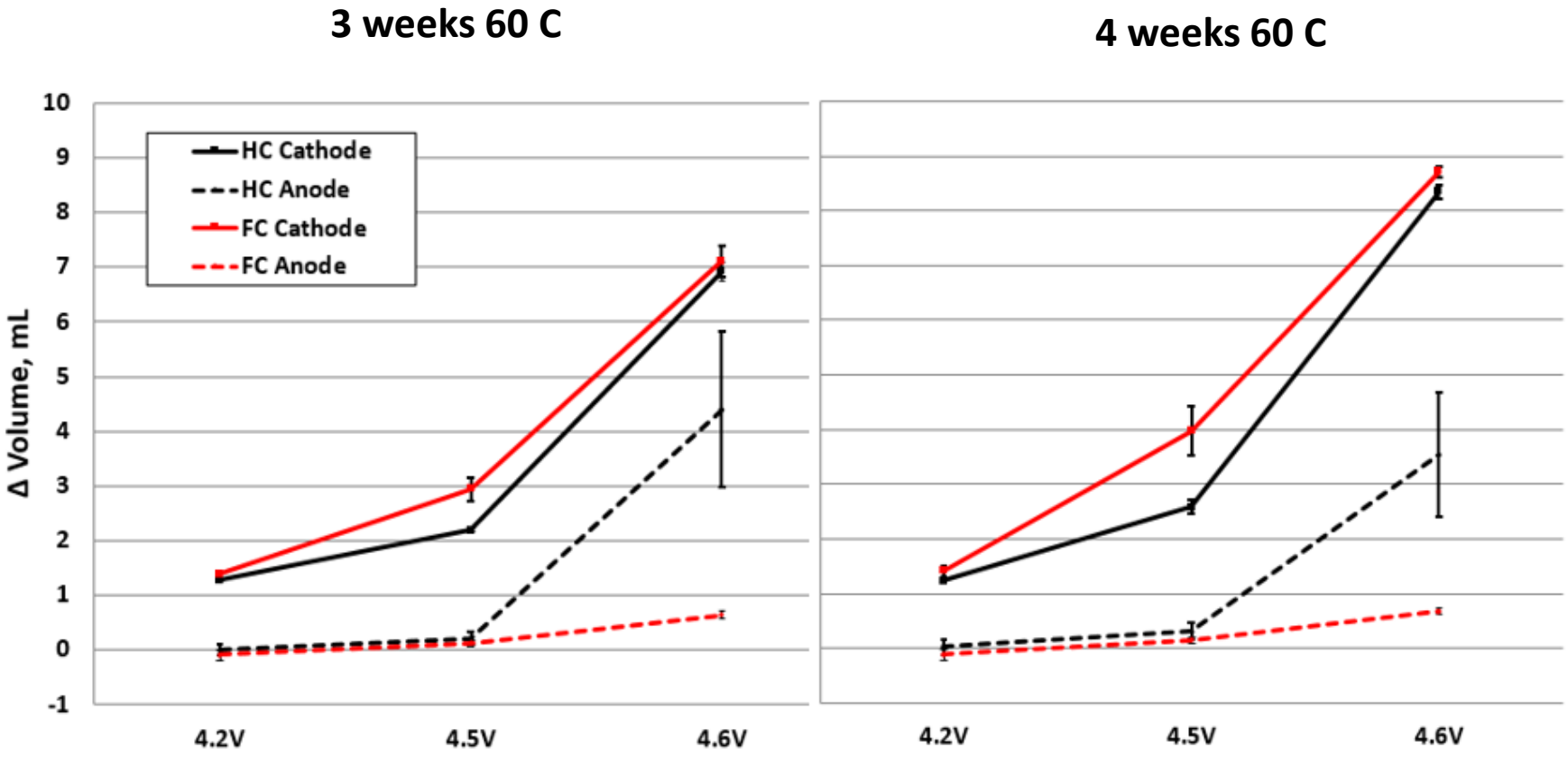


	4.2V	4.3V	4.35V	4.4V	4.5V	4.6V	4.8V
Capacity	917.06	943.635	943.445	1085.535	1121.08	1158.8533	1189.1433
% Energy	1	1.0342935	1.0373562	1.1952678	1.2519744	1.297489	1.3406164

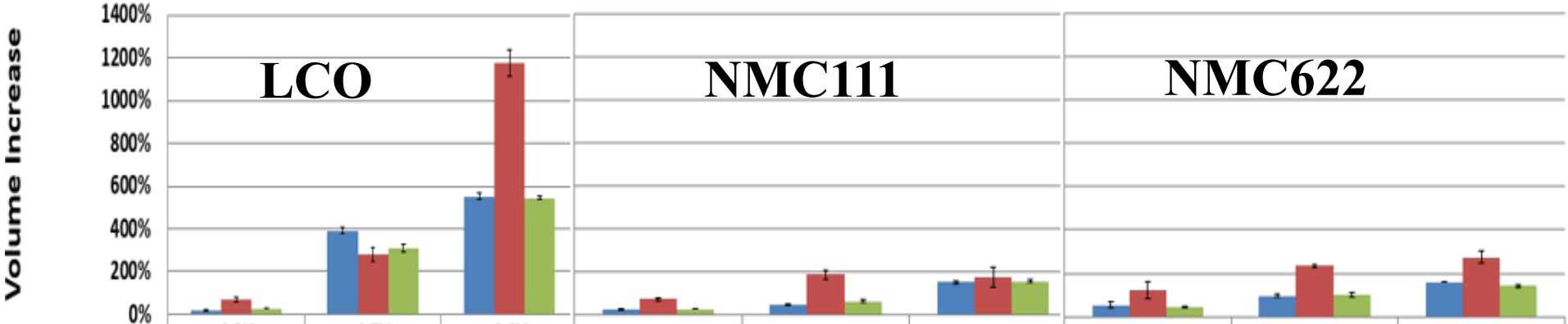
Cycle data from Argonne confirms fluorocarbon performance decrease between 4.5 and 4.6 V



Using cut and weighed pieces of electrode removed from charged cells – chemical interaction



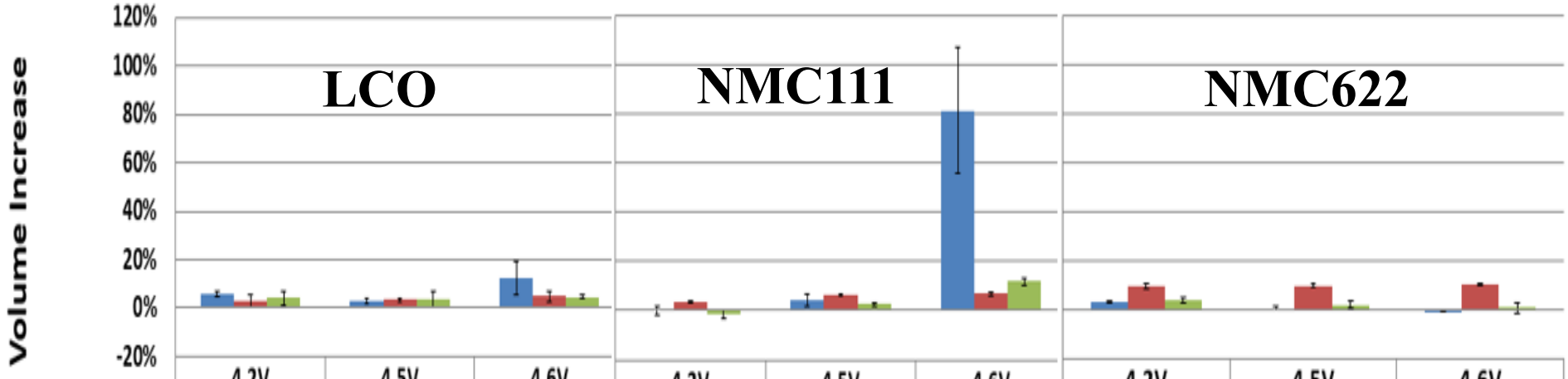
Majority of gas generation is at cathode. Higher gassing for LCO is consistent with the hypothesis.



	LCO			NMC111			NMC622		
	4.2V	4.5V	4.6V	4.2V	4.5V	4.6V	4.2V	4.5V	4.6V
EC/EMC(2:8)	17.5%	390.1%	549.6%	26.9%	48.3%	152.6%	52.2%	95.2%	158.8%
FEC/EMC/FE(2:6:2)	69.4%	281.9%	1175.3%	73.7%	189.1%	175.9%	121.5%	232.5%	272.9%
EC/EMC/FE(2:6:2)	28.5%	308.0%	542.1%	30.3%	65.6%	158.7%	41.7%	101.3%	140.0%

Note: Scale 0-1400%

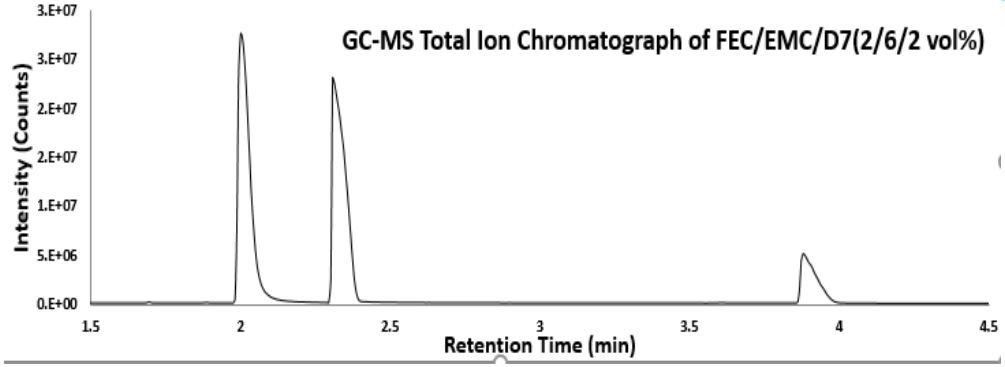
Gas generation is minimal at most anodes. NMC111 cell anodes are from different cell manufacturer (different graphite anode)

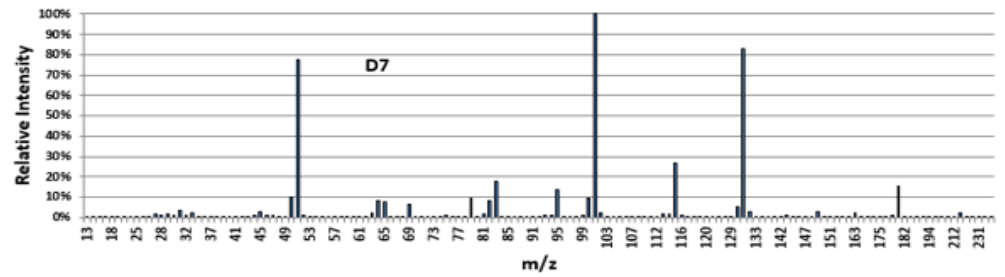


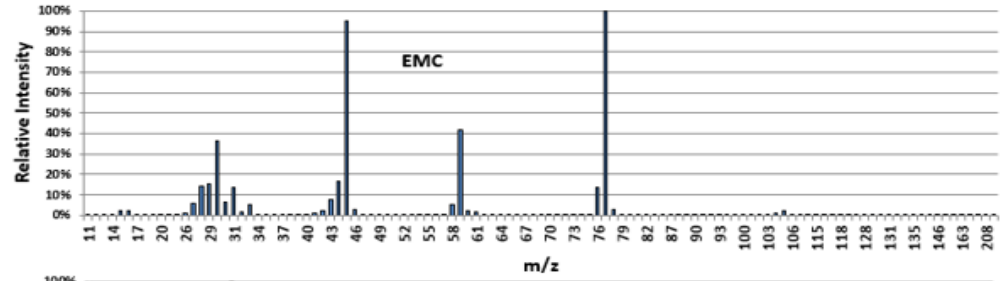
	LCO			NMC111			NMC622		
	4.2V	4.5V	4.6V	4.2V	4.5V	4.6V	4.2V	4.5V	4.6V
EC/EMC(2:8)	6.1%	2.8%	12.6%	0.1%	4.1%	81.3%	3.3%	0.8%	-0.3%
FEC/EMC/FE(2:6:2)	2.6%	3.3%	4.9%	3.8%	6.2%	7.0%	9.9%	10.1%	10.4%
EC/EMC/FE(2:6:2)	4.1%	3.4%	4.6%	-1.4%	2.6%	11.8%	4.2%	2.3%	1.0%

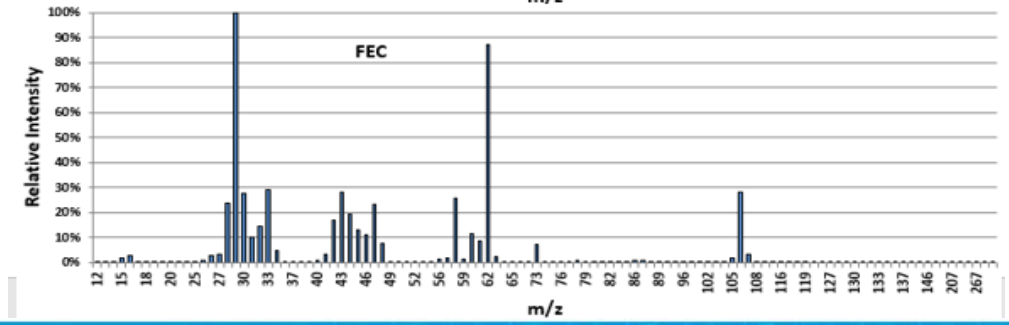
Note: Scale 0-120%

Baseline GC/MS analyses









Fluoroether

Ethyl Methyl Carbonate (EMC)

Fluoroethylene Carbonate (FEC)

Technical Summary

- Expansion of lab facilities expected to be complete by June 2017

- Baselines have been established for:
  - Electrolyte composition
  - Nickel content of cathode
  - Operating voltages
  - Cycle time
  - Cycle current
  - Temperature

- Static measurements have been made on several cathodes with varying nickel content. Charged LCO cathode shows the largest degree of electrolyte decomposition

- Charged anode for NMC111 cell shows gassing anomaly. The measurement needs to be reproduced

- GC/MS measurements have been made on candidate electroytes.

- Determination of gas composition and kinetics as function of voltage and nickel content will be completed through the end of FY 2017
  - A study of gassing kinetics as a function of FEC content in the electrolyte to be completed

- Beginning in 2018, detailed study of electrode films will be undertaken from samples made for gassing study.

Critical Assumptions

- Lab capability needs to proceed on schedule for sample production

New Project