DAIKIN AMERICA, INC.

Daikin Advanced Lithium Ion Battery Technology – High Voltage Electrolyte

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Daikin Technical Center, Decatur, Alabama

DOE Annual Merit Review
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Project ID: ES217

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

Timeline

- Start Date: 10/1/13
- End Date: 9/30/15
- 75% Complete

Target and Barriers

- Performance – 300-1000 cycles at 4.6 V
- Safety – Safe, reduced flammability formulation

Budget

- Total - $1,291,029
  - DOE - $912,021
  - Daikin America - $379,008
- Expenditure of Gov't Funding
  - FY2014 ~ 316K (estimate)
  - FY2015 ~ 210K (est., YTD March)

Partners

- Interactions/Collaborations
  - Coulometrics, LLC: Cell Fabrication and Testing.

Technical Approach

Oct 2013	Jan 2014	Apr 2014	July 2014	Oct 2014	Jan 2015	Apr 2015	July 2015

Background – Literature Search, Material Evaluation, Internal data

Choice of electrolyte components – solvents and additives

Solvent maps – optimization

Additive maps - optimization

Best candidate electrolytes (3-4)

Cycle testing commercial cells

Internal Testing of candidate cells- delivery of preliminary cells to DOE

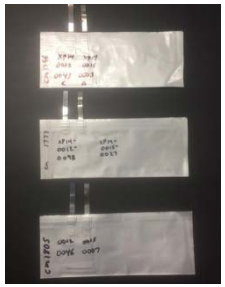
Fabrication, Testing, and Delivery of finished cells and reports to DOE

Finalization of cell chemistry

Procurement of cell components

Partner with cell fabrication company

Fabrication of dry test cells



Milestones

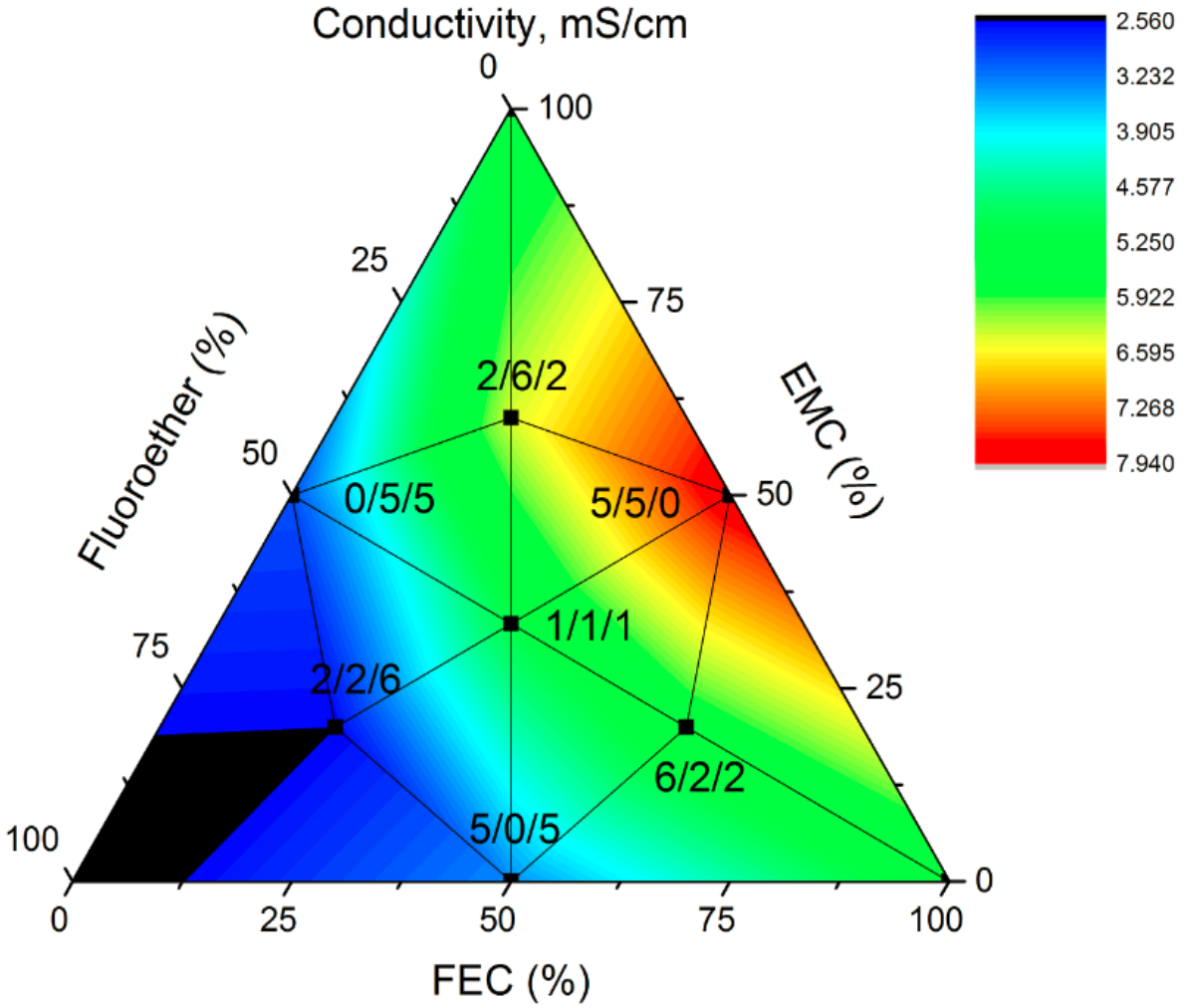
Milestone	Type	Description	Completion Date/Status
Complete Identification of Promising Electrolyte Formulations	Technical	Experimental design completed with consistent data sufficient to build models. Promising electrolyte formulations are identified which are suitable for high-voltage battery testing.	October 2014/ complete
Fabrication and Delivery of Interim Cells	Technical	Successful fabrication of 10 interim cells and delivery of cells to DOE laboratory to be specified.	January 2015 / complete
Demonstrate Stable Performance at 4.6 volts	Go/No Go	Electrochemical and battery cycle tests are completed and promising results are obtained which demonstrate stable performance at 4.6 volts	June 2015/ in progress
Confirm Final Electrolyte Formulations	Technical	Confirm correlations of battery tests, surface analysis compositional analysis, and electrochemical results and use the complete data set to identify best performing electrolyte compositions.	September 2015
Fabrication and Delivery of Final Cells	Technical	Successful fabrication of 10 improved cells and delivery of cells to DOE laboratory to be specified. Cell test plans, cell design, and cell performance and abuse test documentation is completed.	October 2015

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
  - 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.

(FEC, EC) / (EMC, DMC, DEC) /Fluoroether



Make mixture "phase" diagrams based on phenomena

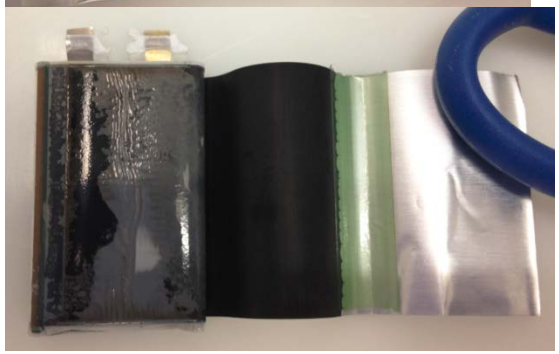
Solvents (vary 0-100%)

- Conductivity
- Voltage Stability
- Gas Generation
- Cell Impedance
- Viscosity
- Initial Capacity

Additives (vary 0-2%)

- Gassing
- Capacity % at 50 cycles
- Capacity % at 100 cycles
- High Performance Coulometry

Daikin baseline cells



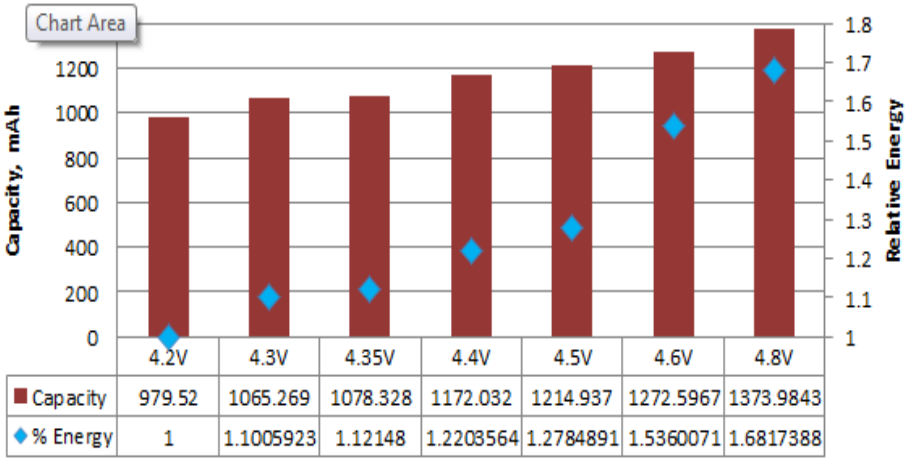
1 A-hr pouch cell

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode
Graphite anode
Cells are anode limited and balanced for 4.2 V

Wound electrode
Purchased dry from China
Electrolyte fill at A5 Daikin

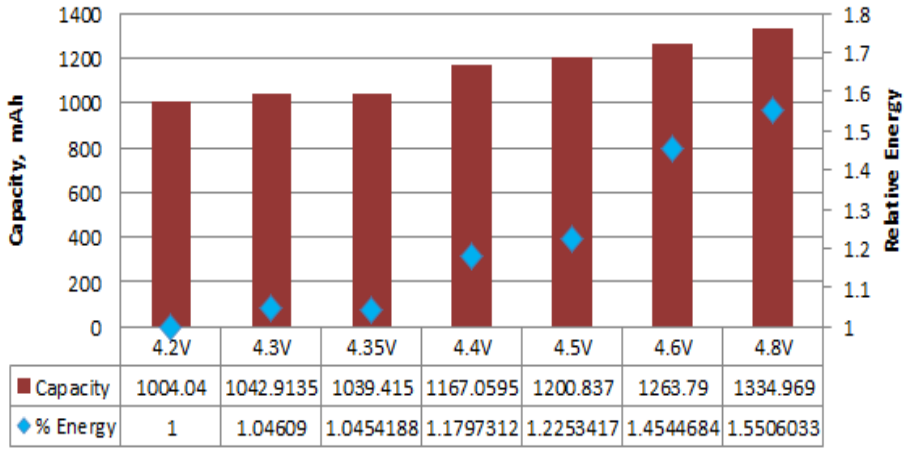
High Voltage Performance – Daikin Cells

Fluorocarbon Electrolyte Performance(0.2C)



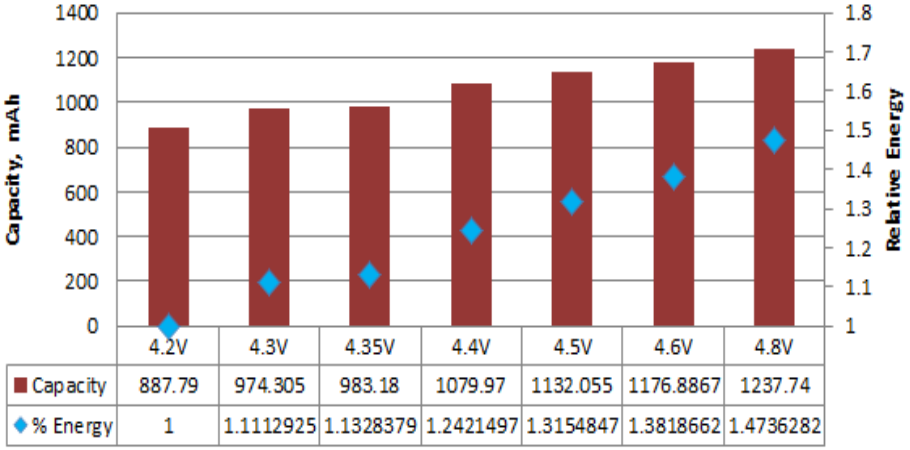
	4.2V	4.3V	4.35V	4.4V	4.5V	4.6V	4.8V
Capacity	979.52	1065.269	1078.328	1172.032	1214.937	1272.5967	1373.9843
% Energy	1	1.1005923	1.12148	1.2203564	1.2784891	1.5360071	1.6817388

Hydrocarbon Electrolyte Performance(0.2C)



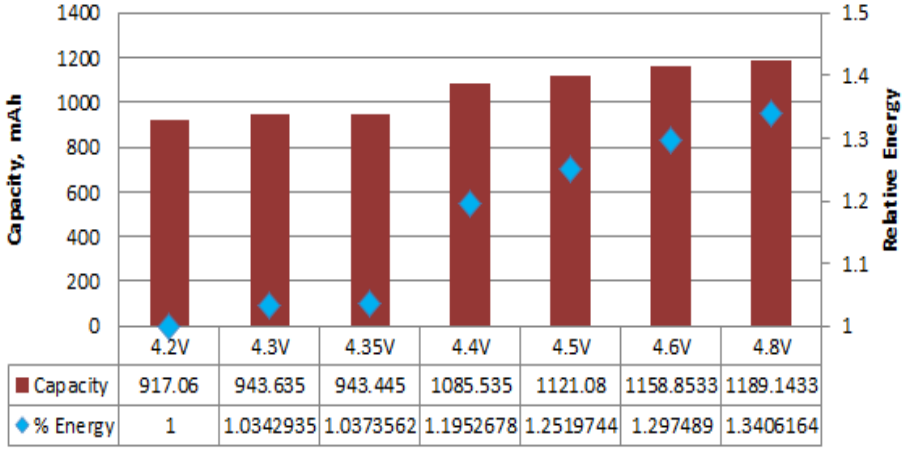
	4.2V	4.3V	4.35V	4.4V	4.5V	4.6V	4.8V
Capacity	1004.04	1042.9135	1039.415	1167.0595	1200.837	1263.79	1334.969
% Energy	1	1.04609	1.0454188	1.1797312	1.2253417	1.4544684	1.5506033

Fluorocarbon Electrolyte Performance(1.0C)



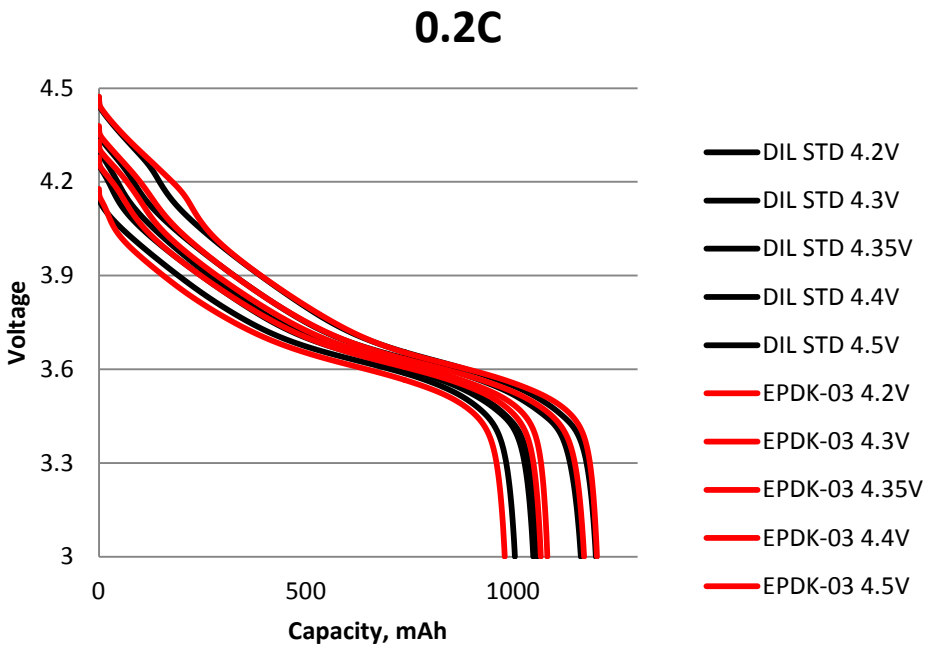
	4.2V	4.3V	4.35V	4.4V	4.5V	4.6V	4.8V
Capacity	887.79	974.305	983.18	1079.97	1132.055	1176.8867	1237.74
% Energy	1	1.1112925	1.1328379	1.2421497	1.3154847	1.3818662	1.4736282

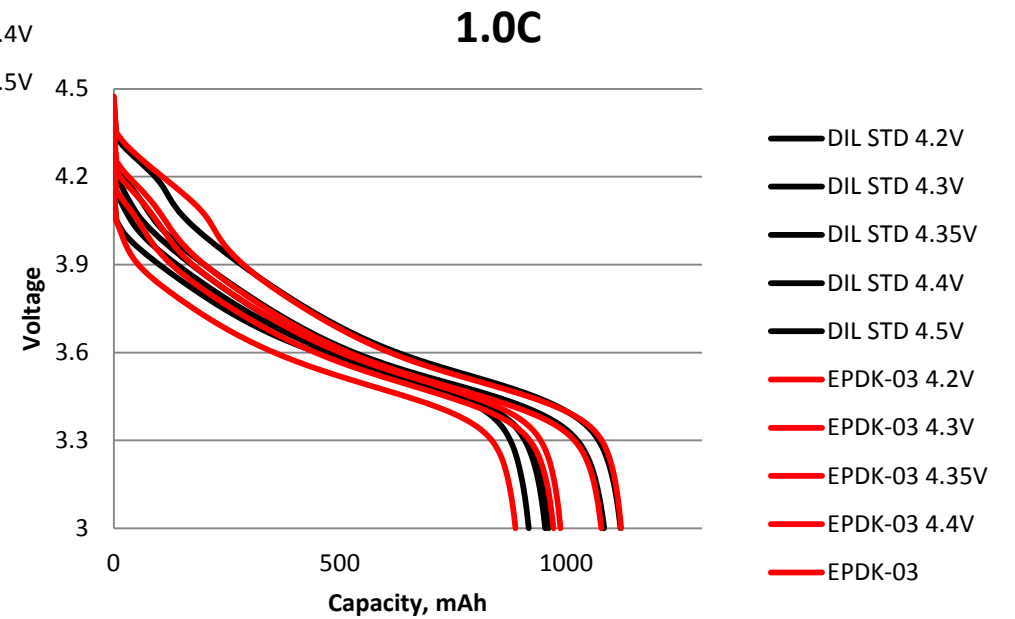
Hydrocarbon Electrolyte Performance(1.0C)



	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

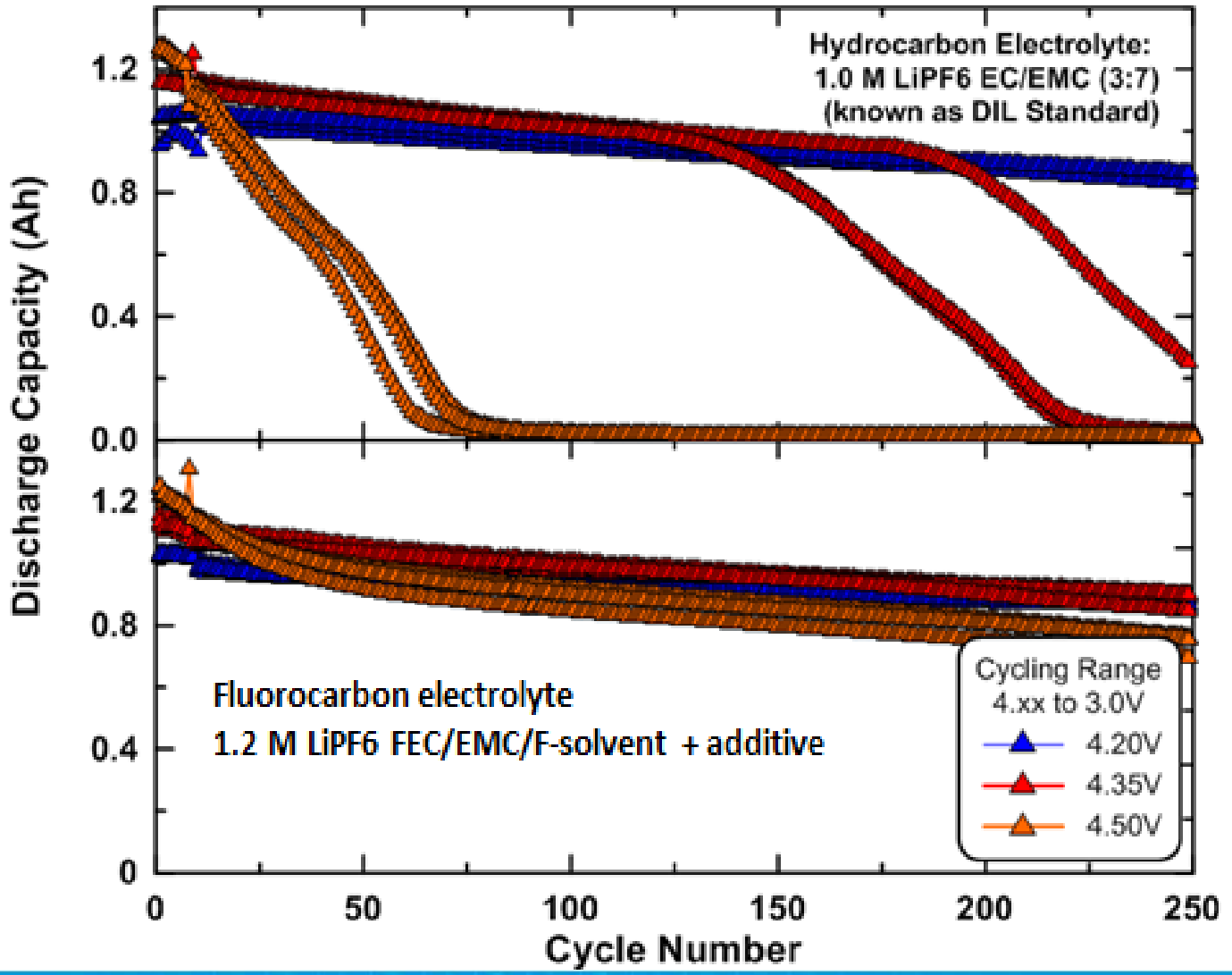
Discharge Curves NMC(111)/graphite





High voltage cycling 60 °C

Cells filled with conventional hydrocarbon electrolyte are failing at app. 200 cycles when cycled to 4.35 V



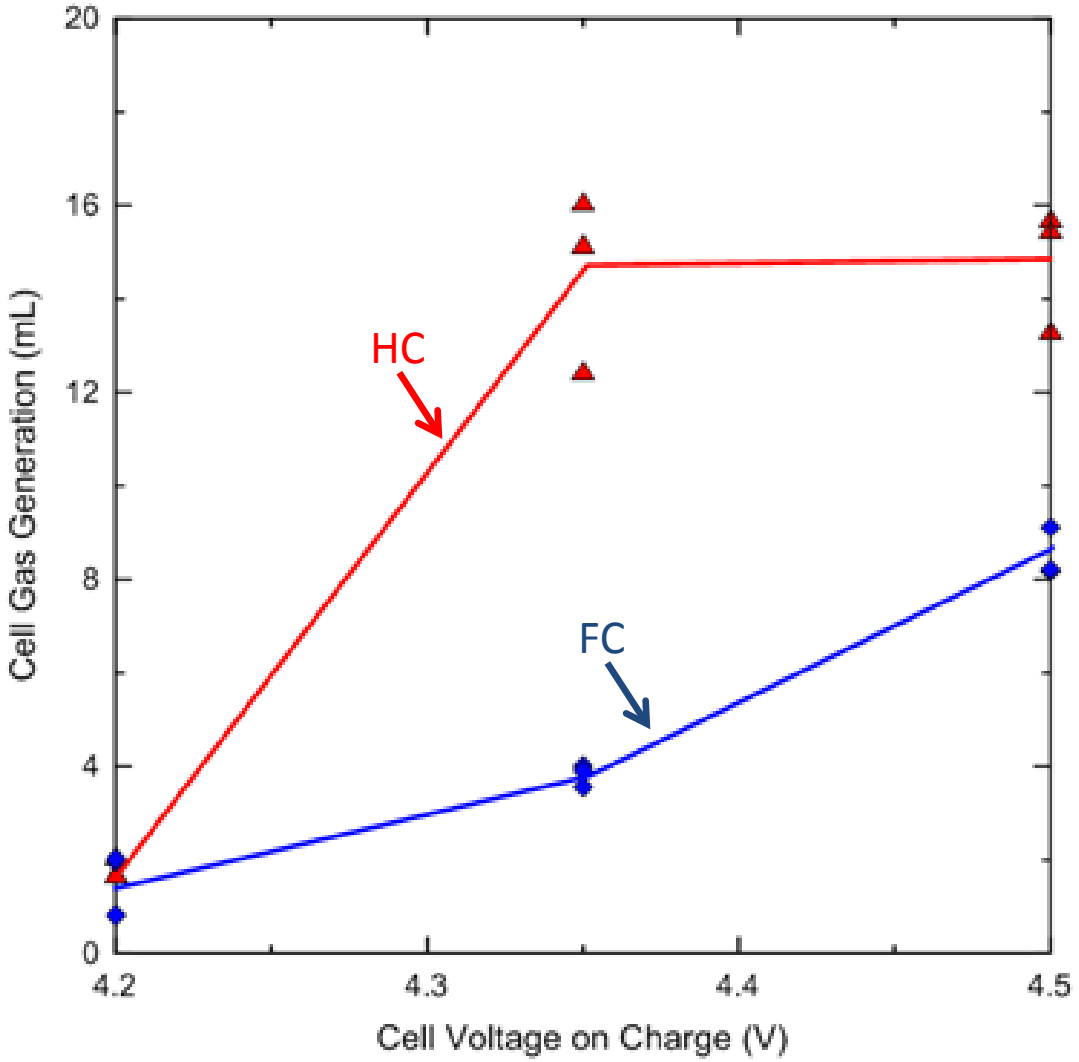
Daikin cells – post 60 °C cycling

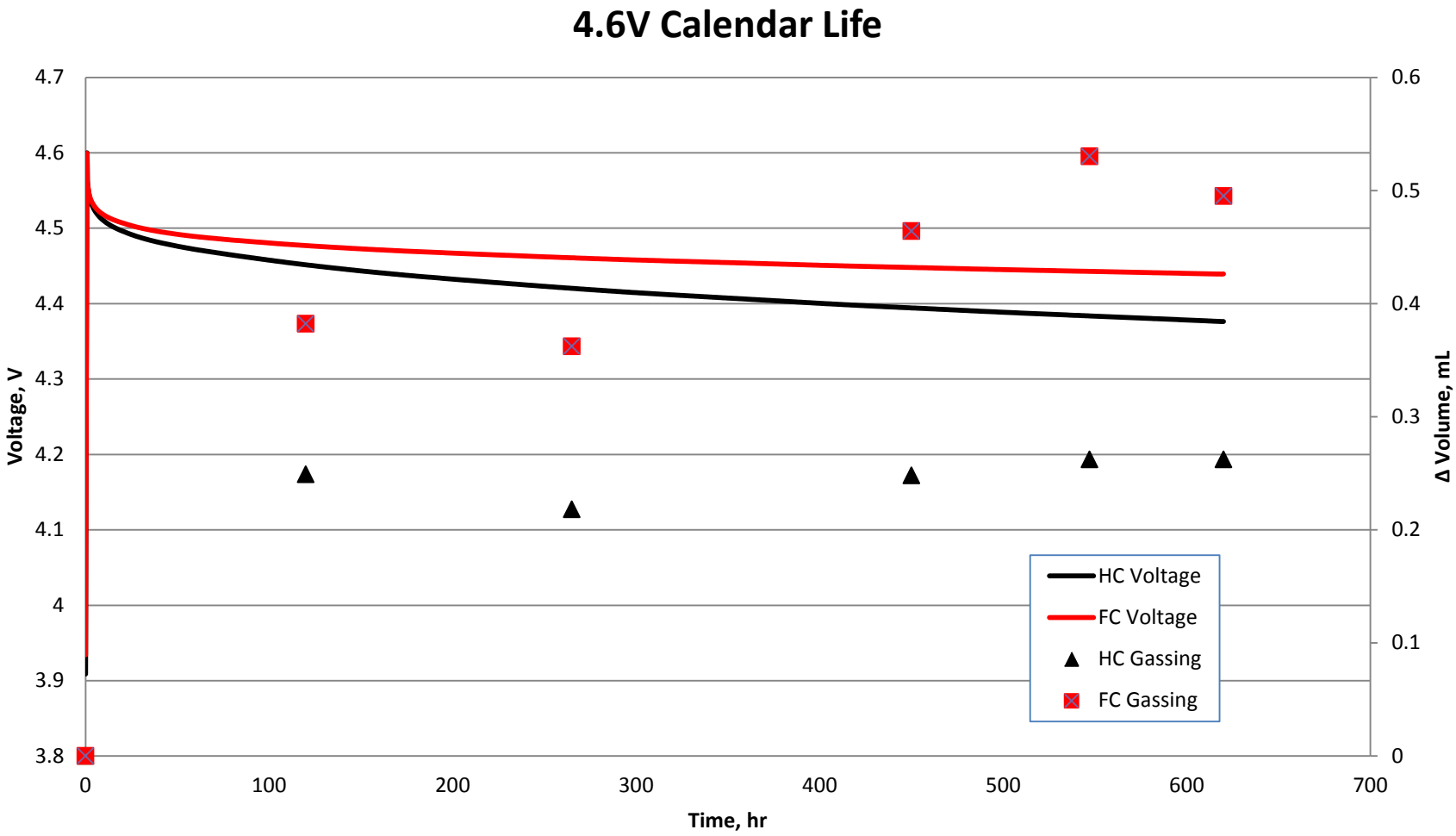
Conventional hydrocarbon electrolyte

Daikin fluorocarbon electrolyte

Daikin cells – quantitative gassing

- Gas measured after 250 cycles or until cell failure
  - Volume difference from initial cell volume
  - Archimedes method with water
  - No cell voltage change
- HC electrolyte – cells cycled to 4.35 and 4.5 have failed
  - Gas volume also terminates
  - Can be used to indicate cell capacity
- FC electrolyte cells performing much better



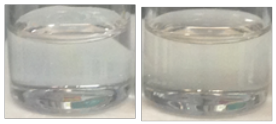

4.6V Calendar Life
Voltage, V
Δ Volume, mL
Time, hr
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4
3.9
3.8
0.6
0.5
0.4
0.3
0.2
0.1
0
0
100
200
300
400
500
600
700
HC Voltage
FC Voltage
HC Gassing
FC Gassing

Thermal Properties - Electrolytes

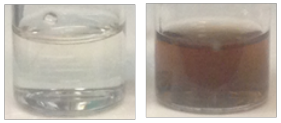
Thermal aging of electrolyte shows salt decomposition in FEC based electrolytes

60 C 85 C

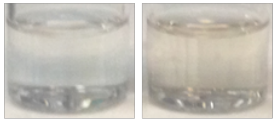
DIL STD - EMC/EC (7:3)

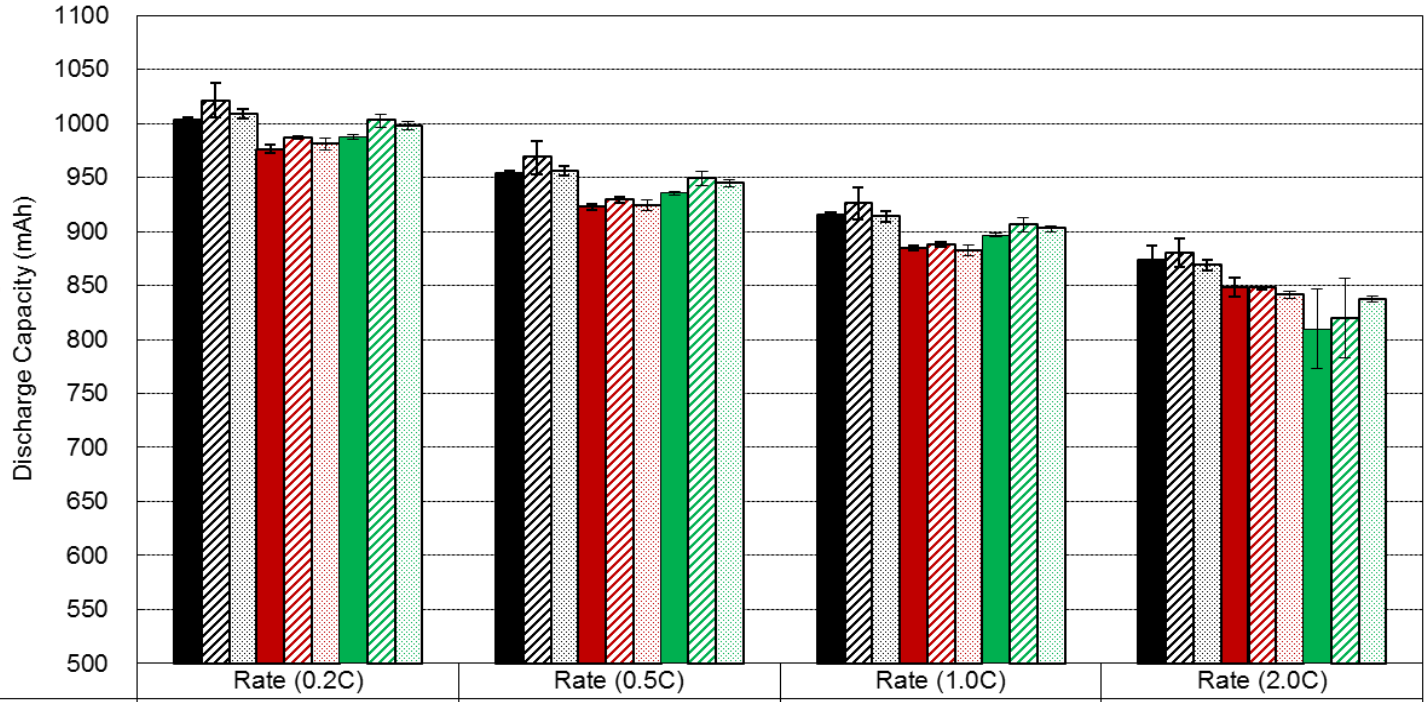


DAI-03 - FEC/EMC/FE (2:6:2)



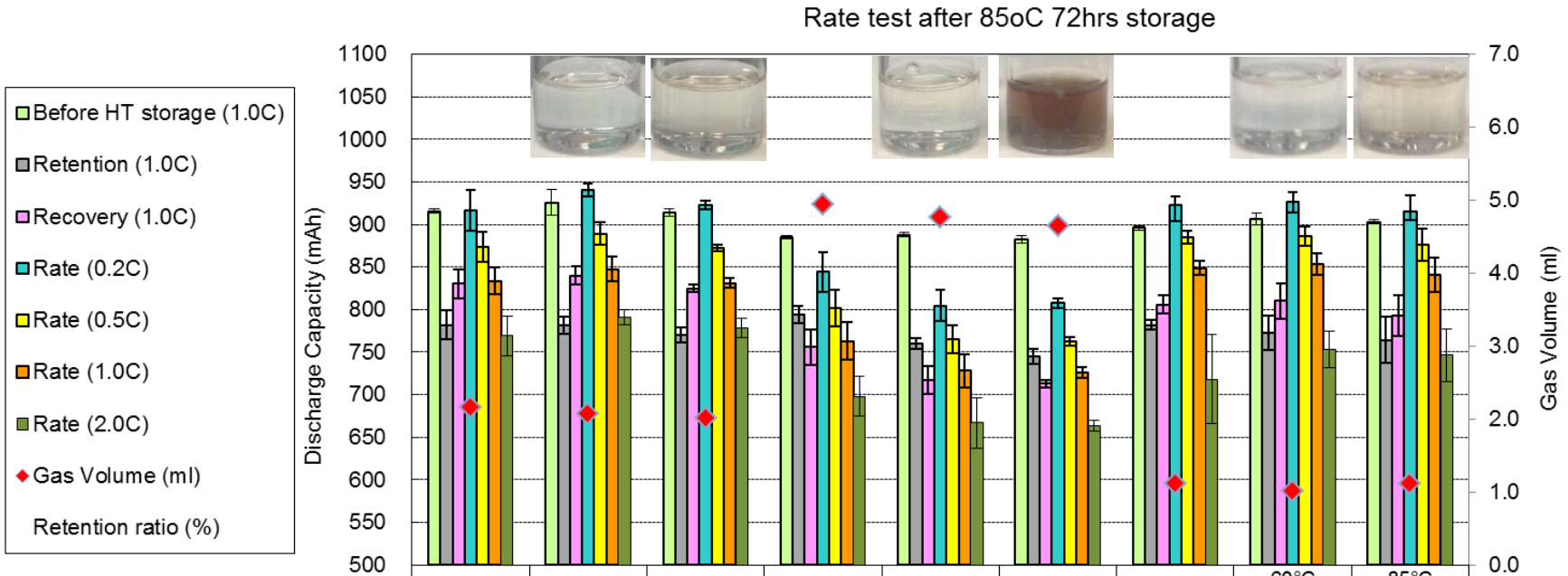
EC/EMC/FE (2:6:2)





	Rate (0.2C)	Rate (0.5C)	Rate (1.0C)	Rate (2.0C)
Charged (DIL STD)	1003.3	953.8	915.8	873.9
60°C Electrolyte Storage (DIL STD)	1021.2	968.7	925.9	880.0
85°C Electrolyte Storage (DIL STD)	1008.8	956.2	914.1	869.2
Charged (DAI-03)	976.5	922.8	885.2	848.5
60°C Electrolyte Storage (DAI-03)	986.7	929.4	887.7	847.8
85°C Electrolyte Storage (DAI-03)	980.8	924.1	882.5	841.0
Charged (EC/EMC/FE)	987.7	935.5	896.7	809.9
60°C Electrolyte Storage (EC/EMC/FE)	1002.7	948.8	906.0	819.9
85°C Electrolyte Storage (EC/EMC/FE)	998.0	944.5	902.6	837.0

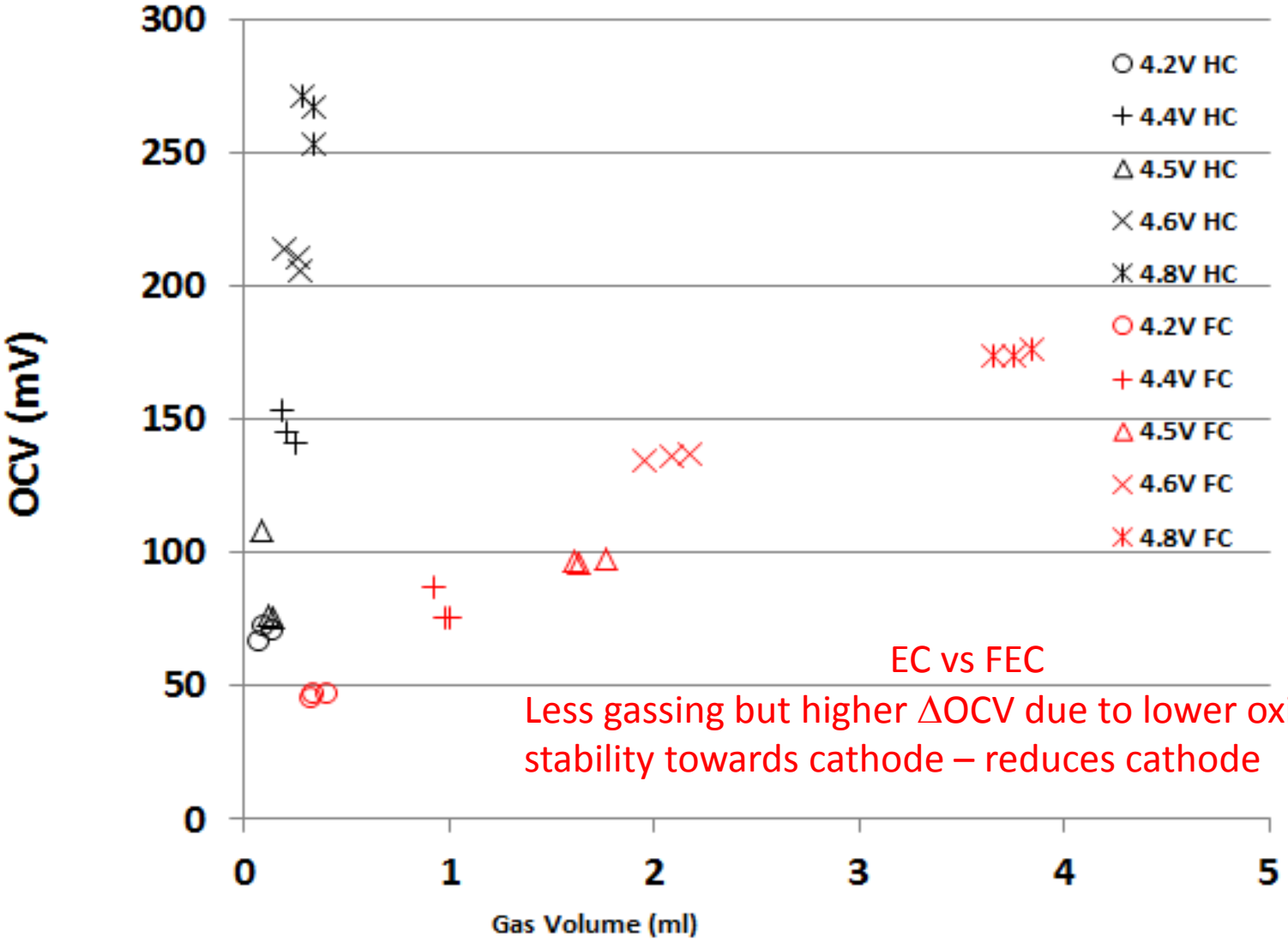
Thermal Properties - Electrolytes



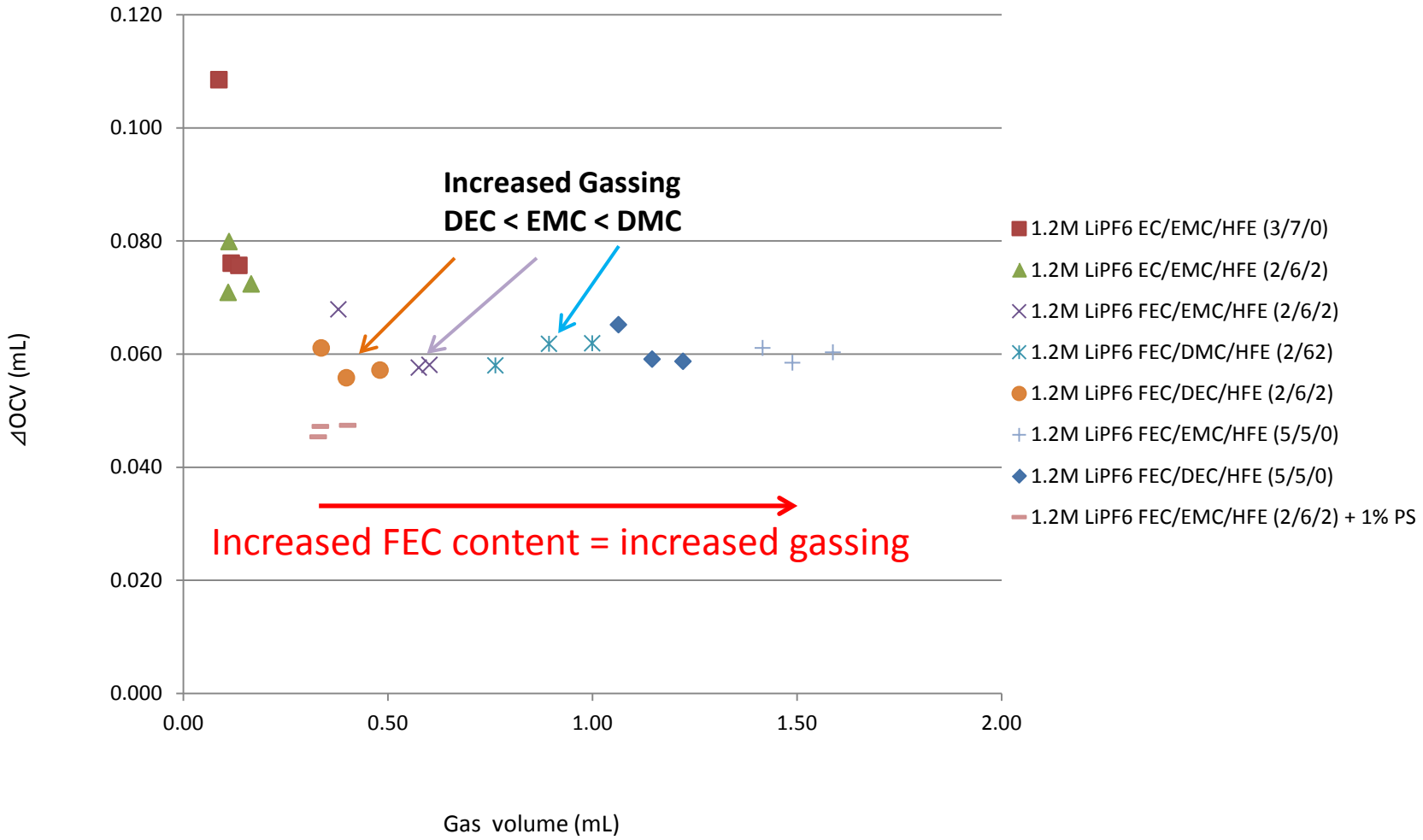
	Charged (DIL STD)	60°C Electrolyte Storage (DIL STD)	85°C Electrolyte Storage (DIL STD)	Charged (DAI-03)	60°C Electrolyte Storage (DAI-03)	85°C Electrolyte Storage (DAI-03)	Charged (EC/EMC/FE)	60°C Electrolyte Storage (EC/EMC/FE)	85°C Electrolyte Storage (EC/EMC/FE)
Before HT storage (1.0C)	915.8	925.9	914.1	885.2	887.7	882.5	896.7	906.0	902.6
Retention (1.0C)	782.1	781.8	770.1	793.9	759.9	745.4	781.9	772.2	763.9
Recovery (1.0C)	830.2	839.8	824.6	755.8	716.8	712.8	805.8	810.1	793.2
Rate (0.2C)	916.3	940.8	922.7	844.3	804.8	807.7	922.9	926.0	915.2
Rate (0.5C)	873.7	889.1	872.4	801.9	764.9	762.4	884.7	886.2	876.0
Rate (1.0C)	833.8	847.4	831.2	762.7	728.1	726.1	848.8	853.1	841.3
Rate (2.0C)	768.8	791.1	778.3	697.6	666.7	663.1	718.3	753.1	746.3
Gas Volume (ml)	2.15	2.07	2.01	4.94	4.77	4.65	1.11	1.00	1.12
Retention ratio (%)	85.4	84.4	84.2	89.7	85.6	84.5	87.2	85.2	84.6

Gassing vs ΔOCV storage 60 C– Daikin Cells

Gas evolution and OCV drop is linear with voltage for same composition

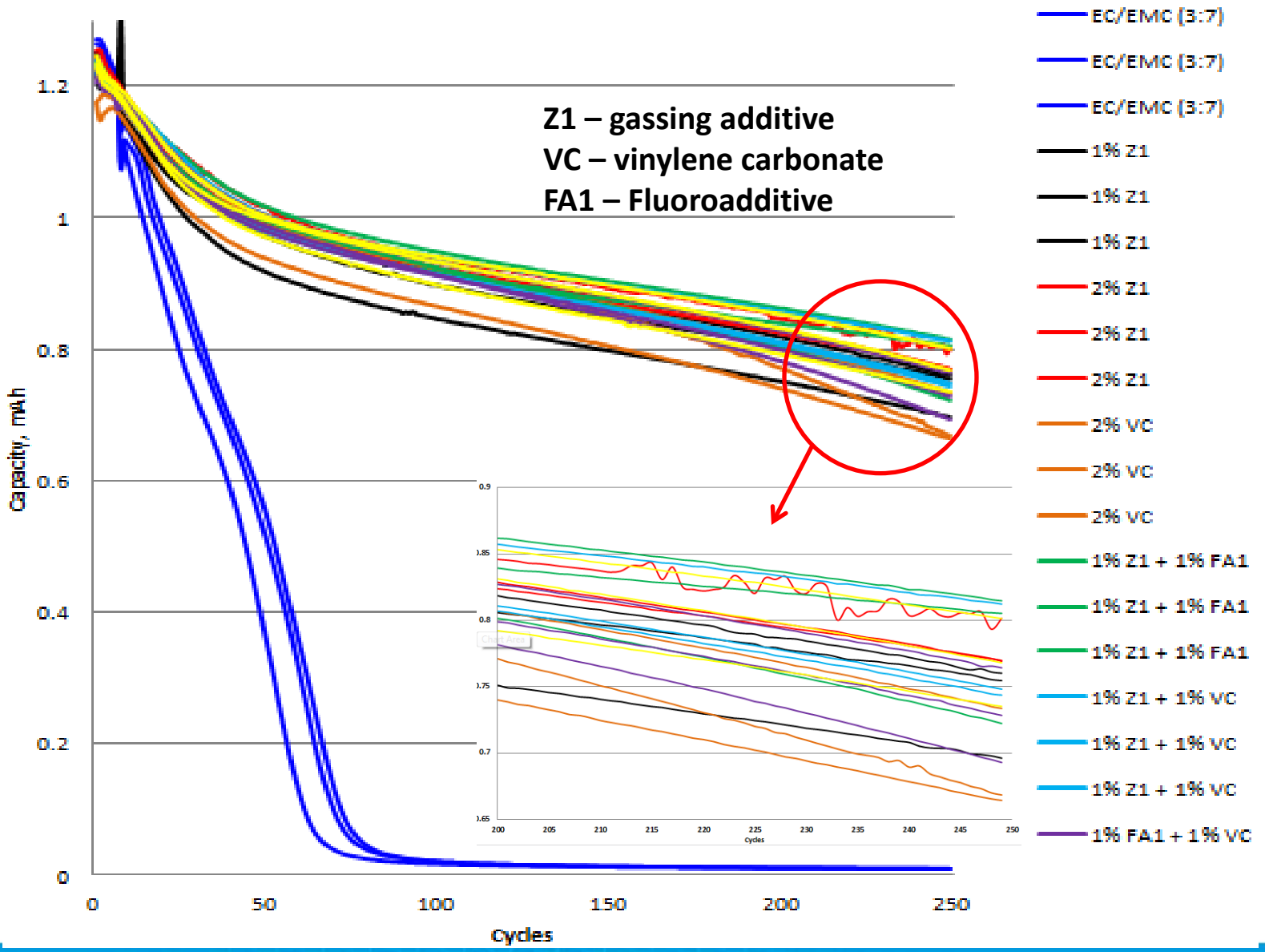


Gassing vs ΔOCV storage 60 C– Daikin Cells



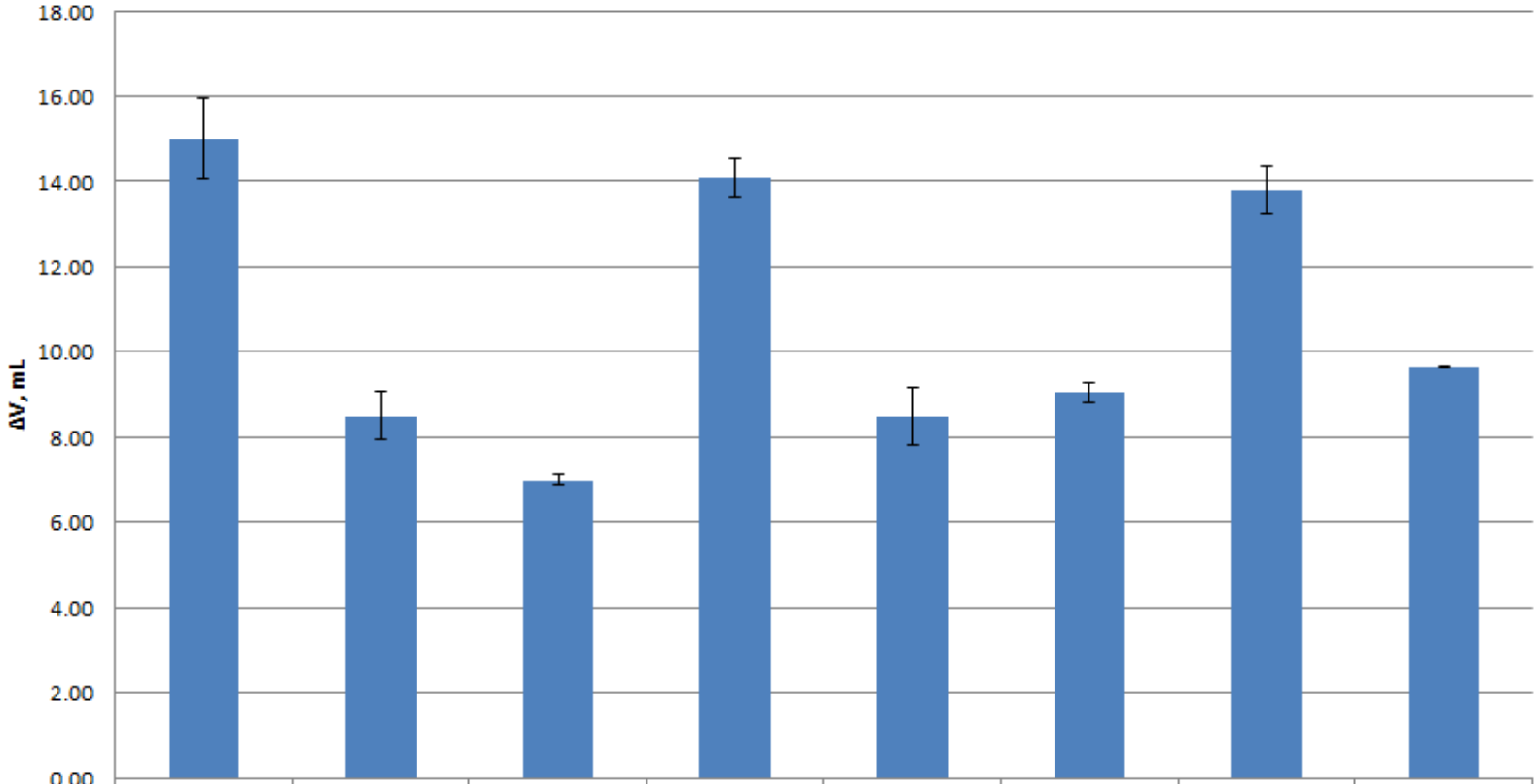
Work is now aligned at altering FEC with other highly polar molecules

Additive package optimization



Additive package optimization

Gassing is generally a problem using VC at high voltage and temperature.

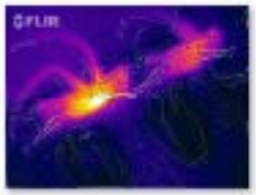


	EC/EMC (3:7)	+1% Z1	+2% Z1	+2% VC	+1% Z1 + 1% A9	+1% Z1 + 1% VC	+1% A9 + 1% VC	+0.67% Z1 + 0.67% A9 + 0.67% VC
Gas Generation	15.00	8.50	6.99	14.09	8.49	9.04	13.80	9.65

FEC/EMC/HFE (2:6:2)

Overcharge 18 V/2 A constrained

IR images of overcharge testing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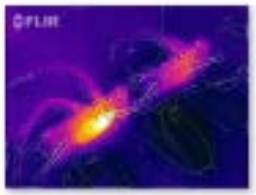
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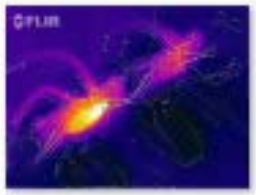
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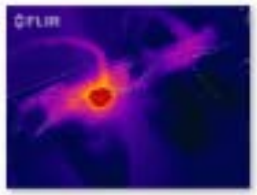
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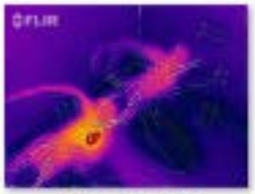
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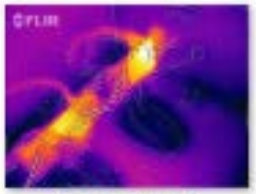
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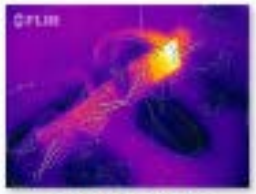
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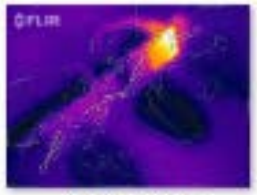
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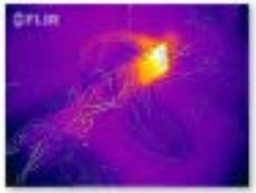
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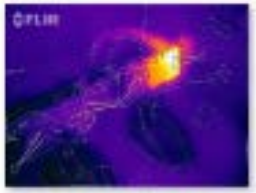
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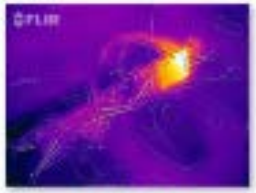
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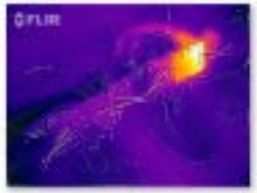
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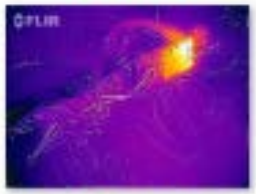
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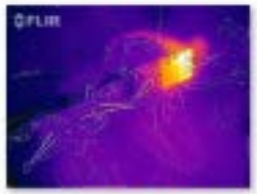
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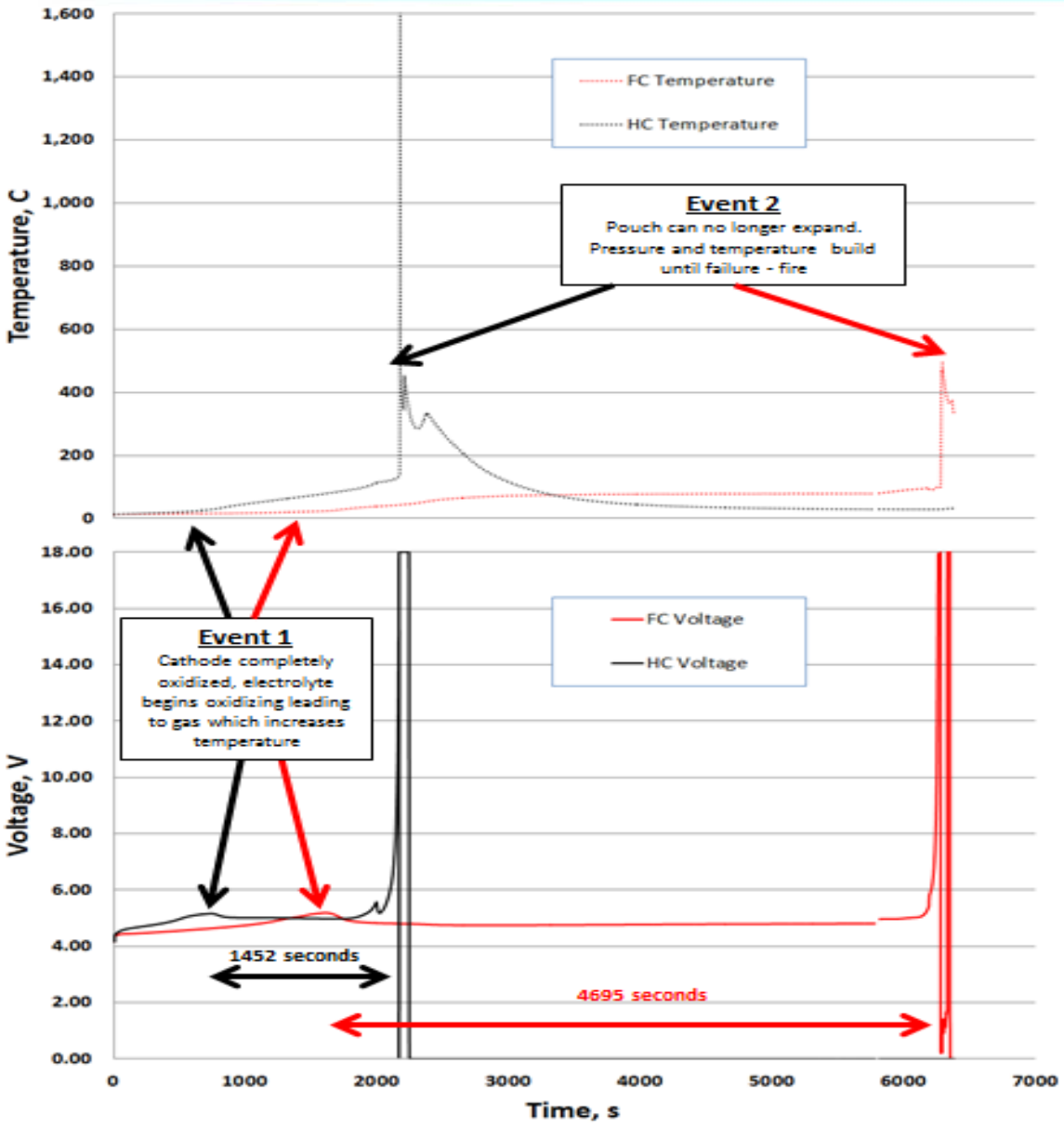
Voltage/Temperature Data – Overcharge



Technical Summary

- Using a property mapping technique, solvent and additive compositions were optimized in a first pass.
- Measurements show a 30% energy gain in a NMC (111)/graphite cell run at 4.5 V. The cells measured were not balanced and included no SEI additives.
- Electrolytes containing fluorinated compounds have superior cycling characteristics in NMC/graphite cells at elevated temperature (60 C) and voltage (4.5 V)
- Calendar life is impacted by FEC content in electrolyte. Mitigation strategies are in place.
- Fluorinated electrolytes help to mediate overcharge hazard and show reduce flammability

Future Work

- Strategies for optimization are now aimed at reducing FEC content in final electrolyte
- Experiments are being completed to determine source of gas generation in cell (eg. Electrode surface reaction, electrolyte reaction)
- Surface analysis of the SEI films made by fluoro-additives is being completed which includes composition, physical characteristics and energetics of film formation.
- Final cells and reports to DOE with recommendation in October.

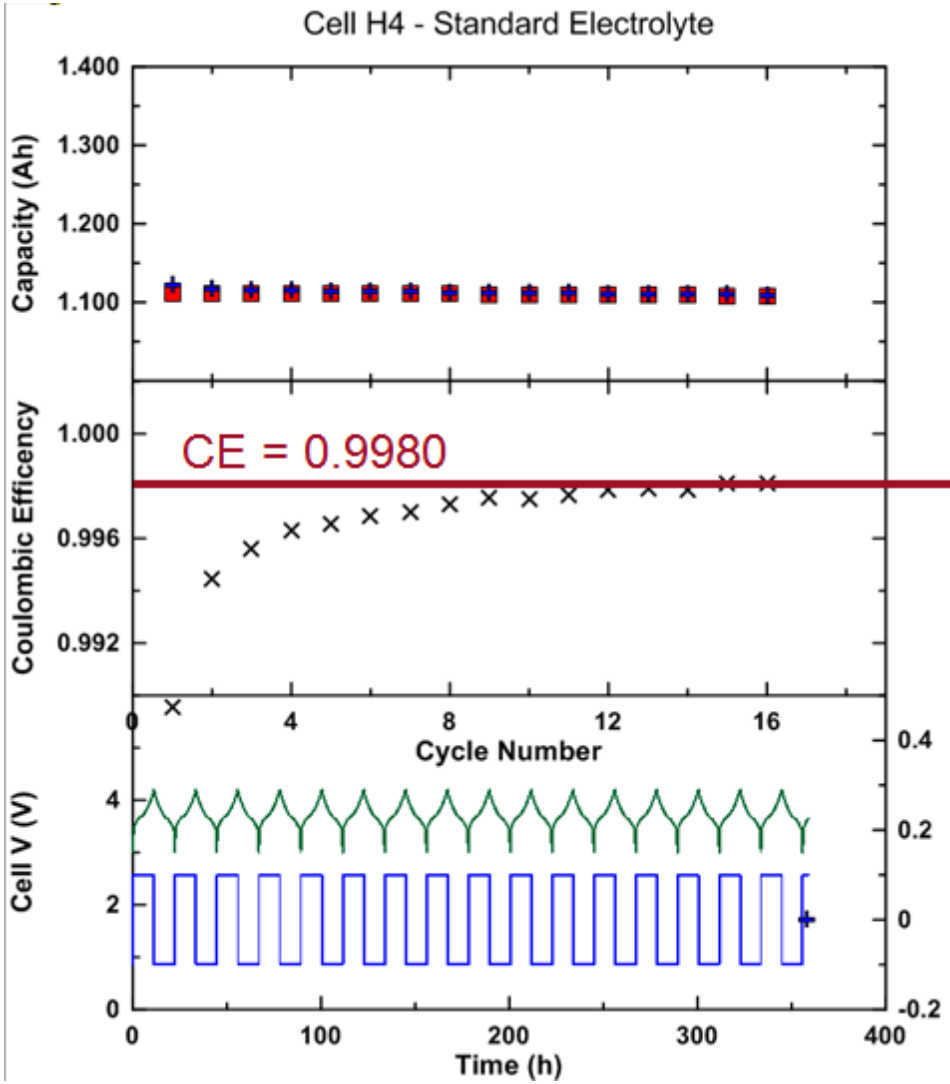
Response to reviewer's comments

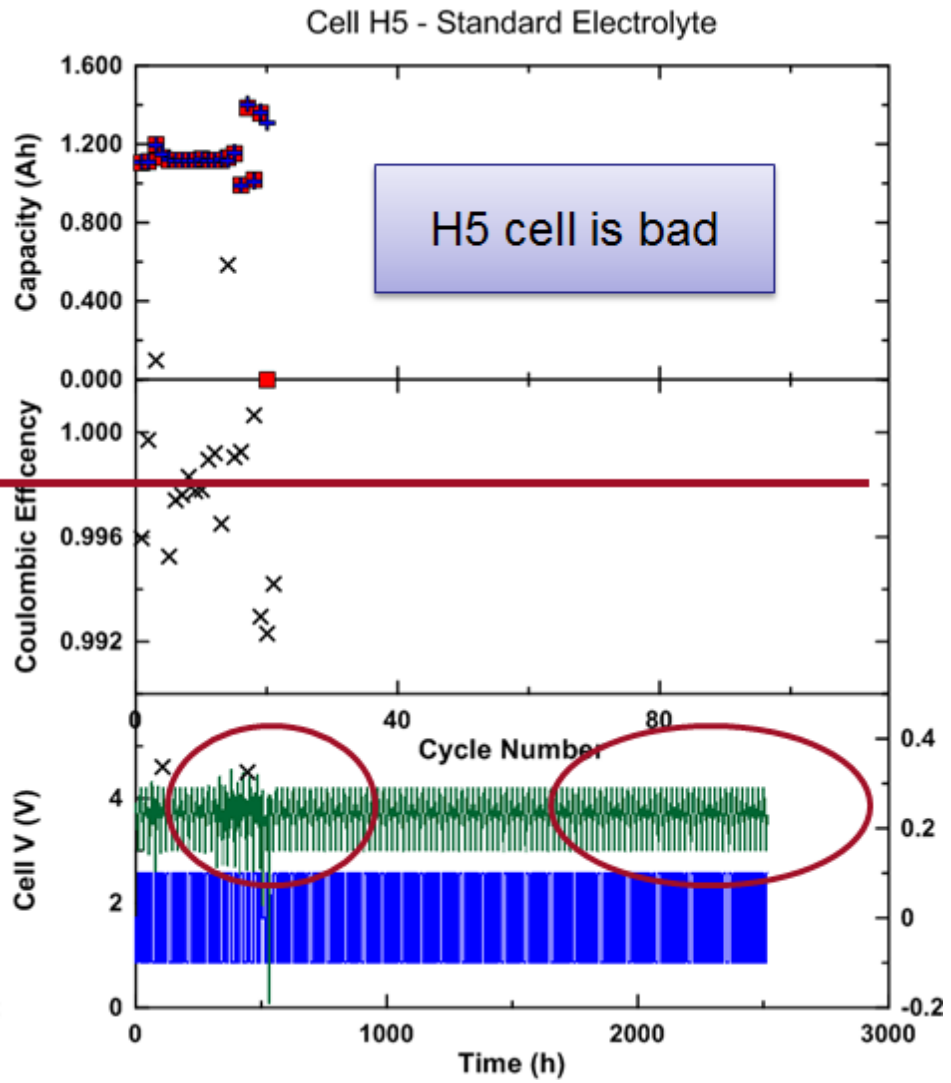
- Reviewer recommends for electrochemical window evaluation that glassy carbon should be considered along with platinum
  - Daikin is pursuing measurements on glassy carbon on a limited basis for comparison with platinum electrode data
- Reviewer requests cost estimates for baseline vs. improved formulations
  - The cost of improved electrolytes will be greater containing fluoro-chemicals, but without final formulation in place and volume estimates it is very difficult to get a realistic number. A significant part of Daikin R&D is revolved around lower cost manufacturing of fluoro-chemicals.
- Reviewer reiterates that the objective of the project is to develop an electrolyte up to 5 volts which is safe.
  - Daikin has elected to look at extending the electrolyte at least up to 4.6 V. Above that, we believe other factors in the battery impact the performance to an extent that the electrolyte measurements may be confounded.
- Multiple reviewers suggest that Daikin pursue more collaboration
  - The primary investigation involves electrolytes containing fluoro-chemicals which is specialized with respect to tasks. Daikin has pursued collaborations with Coulometrics for battery fabrication. In addition, the last part of the project involves surface characterization which Daikin will have to pursue wholly outside the company.

Additional Slides

High precision coulometry HC 4.2 V

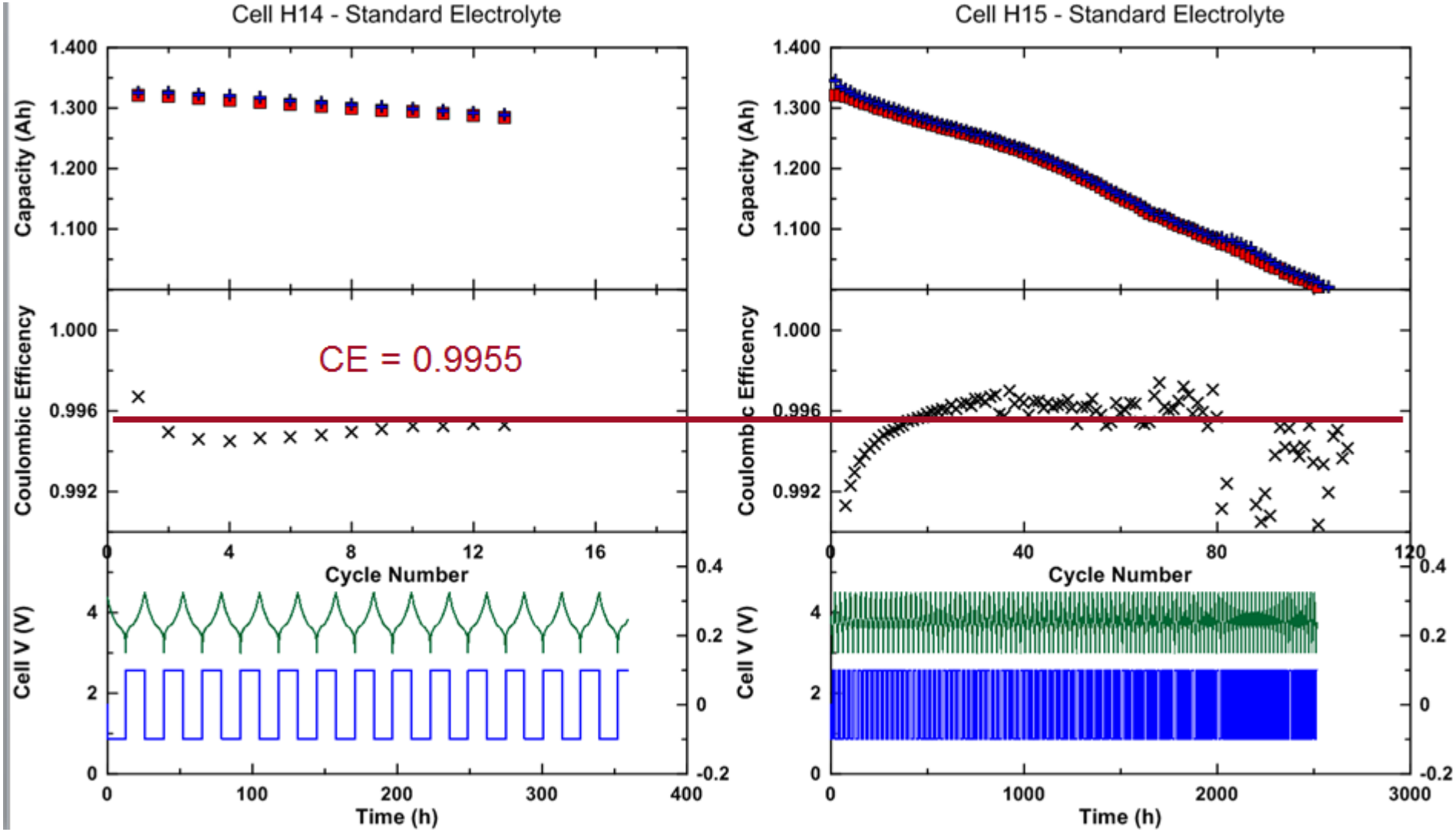
HC 4.2 V, 40 C





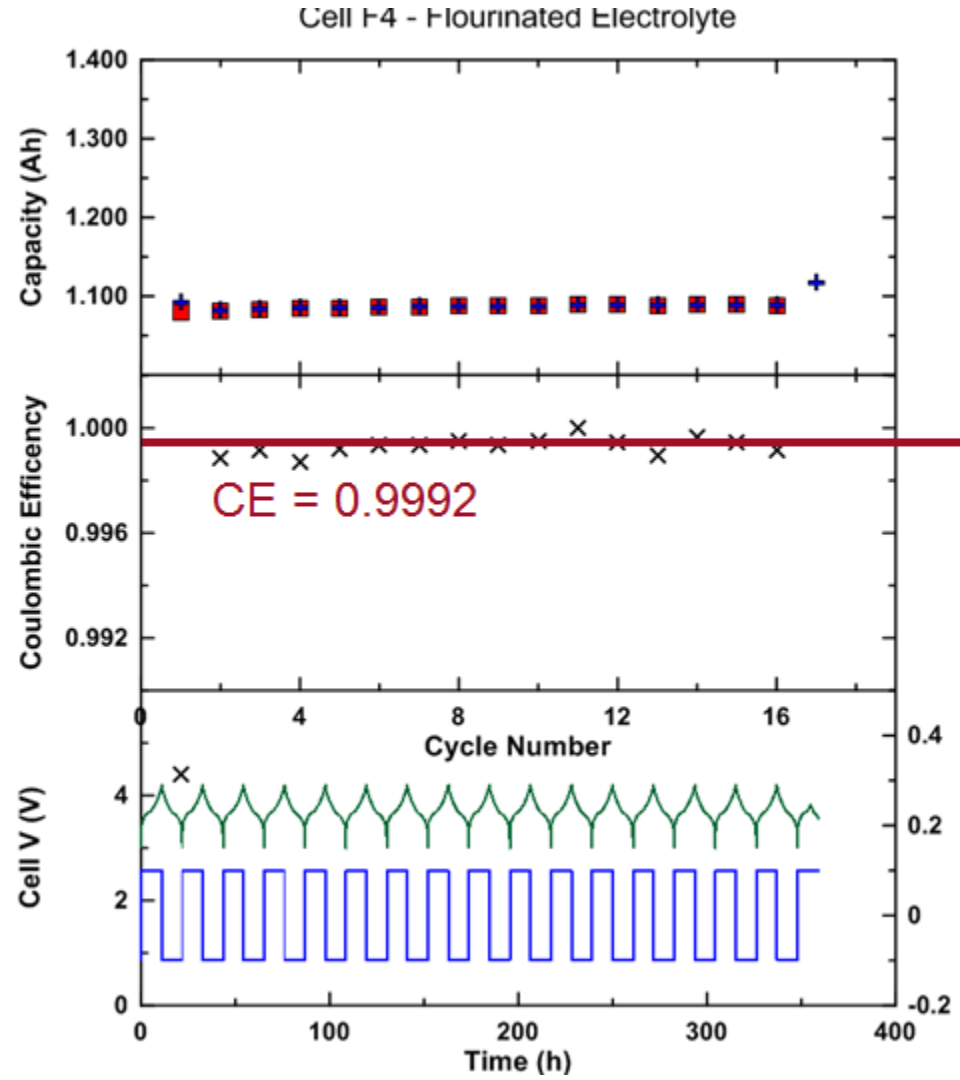
High precision coulometry HC 4.5 V

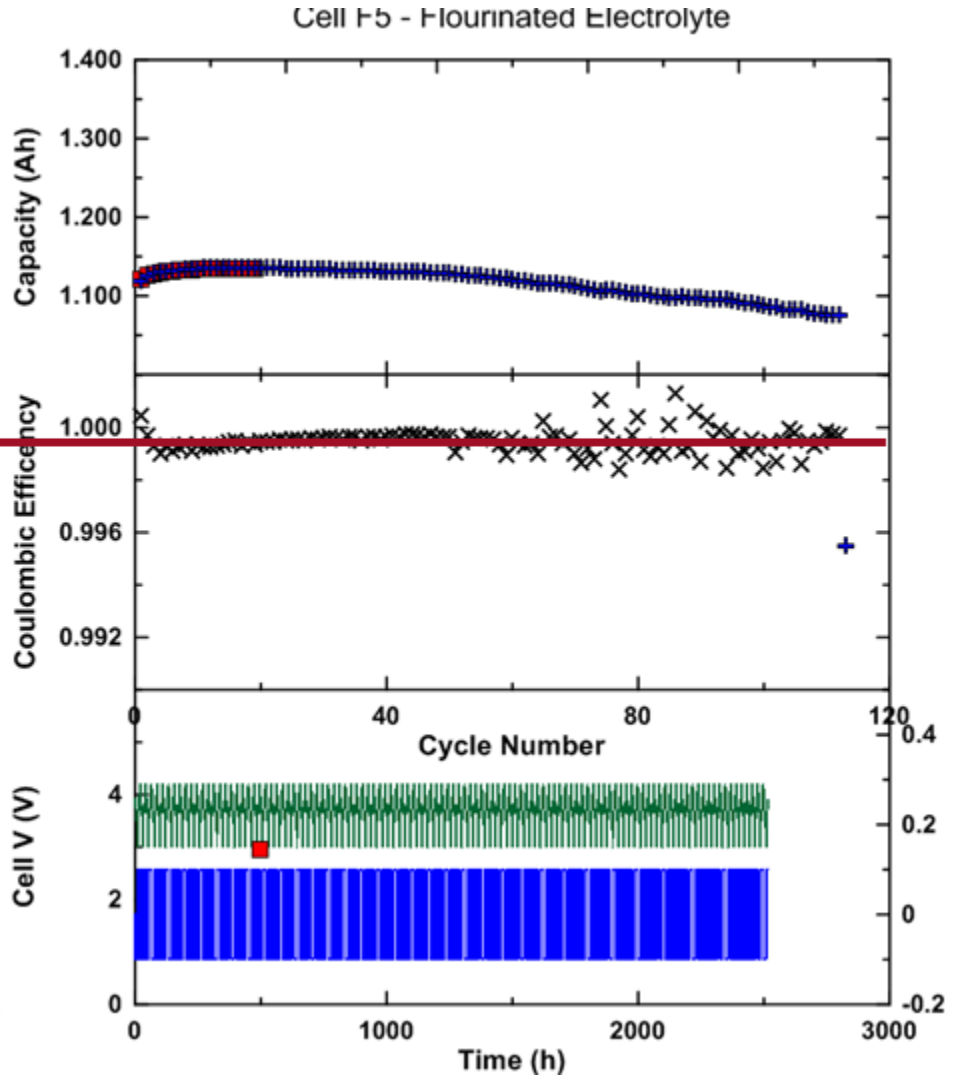
HC 4.5 V, 40 C



High precision coulometry FC 4.2 V

FC 4.2 V, 40 C





High precision coulometry FC 4.5 V

FC 4.5 V, 40 C