Daikin Advanced Lithium Ion Battery Technology – High Voltage Electrolyte

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Project ID: ES217

Overview

Timeline

- Start Date 10/1/13
- End Date 9/30/15
- 25% Complete

Target and Barriers

- Start Date 10/1/13
- End Date 9/30/15
- 25% Complete

Budget

- Total - $1,291,029
  - DOE - $912,021
  - Daikin America - $379,008
- Expenditure of Gov't Funding
  - FY2014 – YTD TBD

Partners

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

Relevance/Objectives

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

Objectives through March 2014

- Identify high voltage battery materials suppliers – get quotes - Complete
- Determine location and get quotes for electrode fabrication – Complete
- Collect and summarize all existing internal data regarding fluoroethers - Complete
- Collect and review literature to summarize current state of knowledge for electrolyte additives/solvents - Complete
- Determine base formulations and prepare DOE – In progress
- Basic property measurements – conductivity, viscosity, solublity and voltammetry – In progress

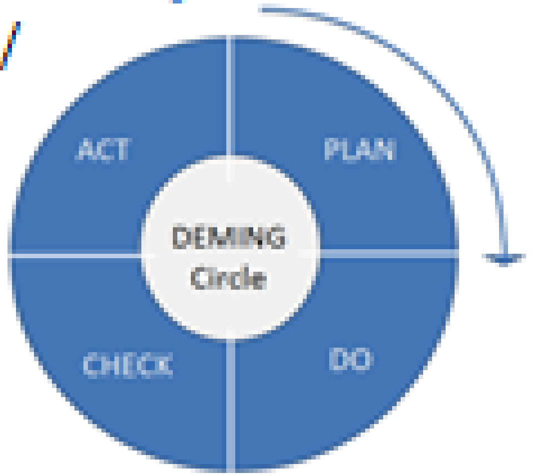
Milestones

Milestone	Type	Description
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. In Progress
Fabrication and Delivery of Interim Cells	Technical	Successful fabrication of 10 interim cells and delivery of cells to DOE laboratory to be specified.
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

Approach

Technical Approach: Exploratory Development

Using a stable, established cell chemistry (4.6 V LMNO/graphite), we will conduct 4 PDCA cycles to develop a high-voltage electrolyte.

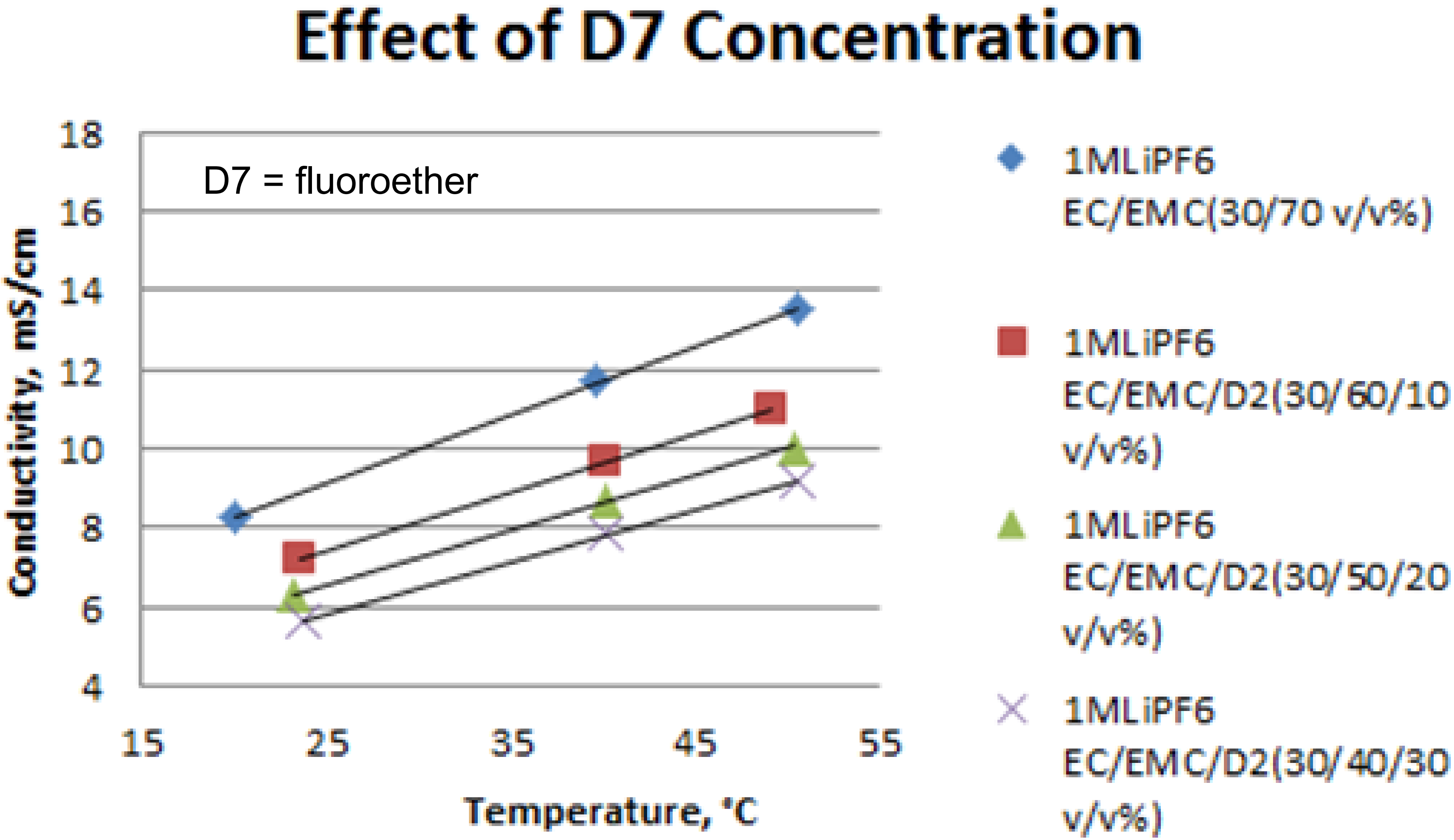


- 2 PDCA cycles to identify optimum base solvent and salt formulation utilizing basic property measurements
- 1 PDCA cycle to identify best available fluorinated anode/cathode additives which form stable SEI layers at high cell voltage
- 1 PDCA cycle to identify and optimize out gassing/acid scavenger additives
- Each PDCA cycle includes basic property measurements (conductivity, viscosity, electrochemical measurements and brief cycle testing in full cell test batteries

Status: First PDCA cycle underway

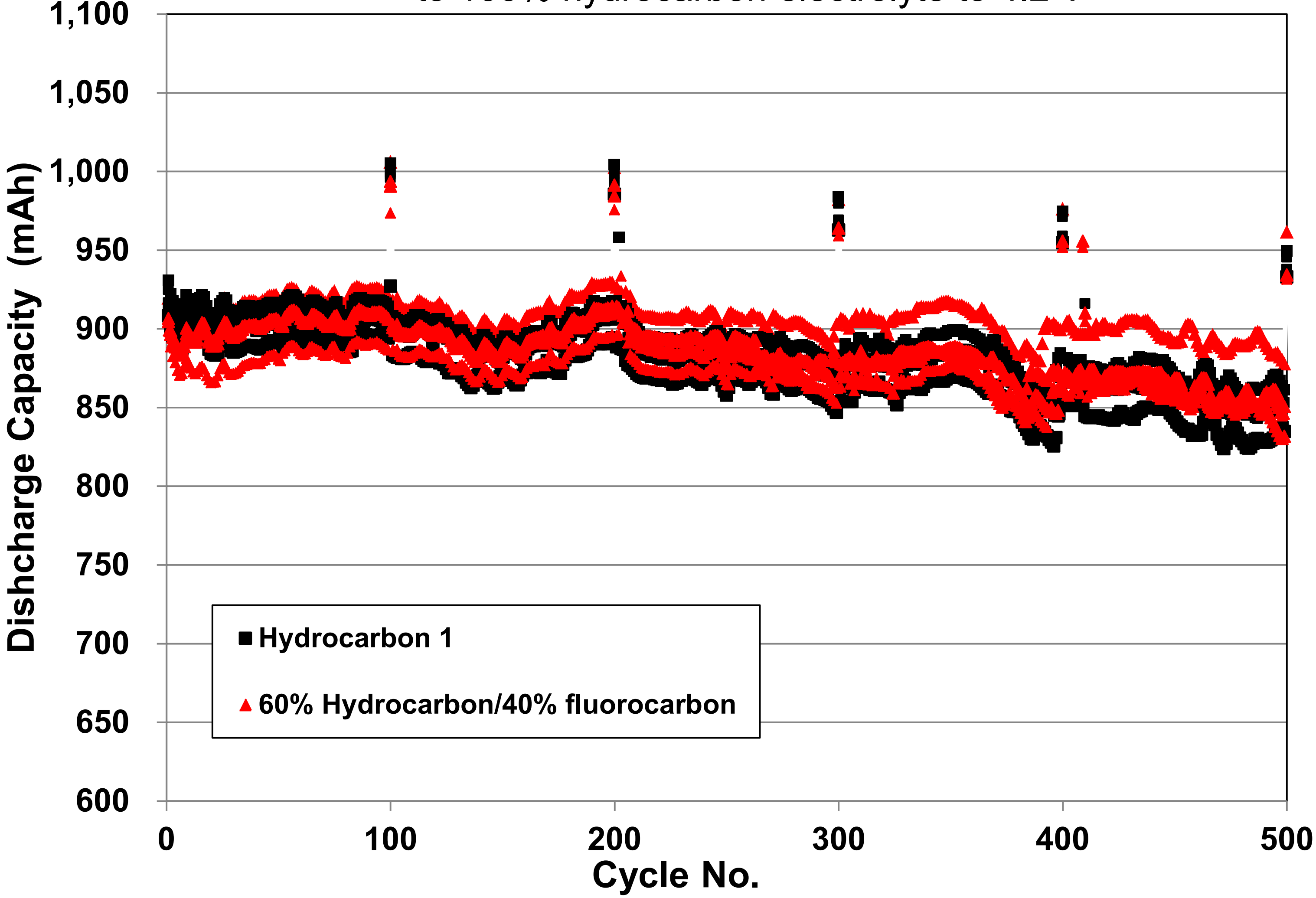
Conductivity of Baselines

Hydrocarbon vs. Flourocarbon

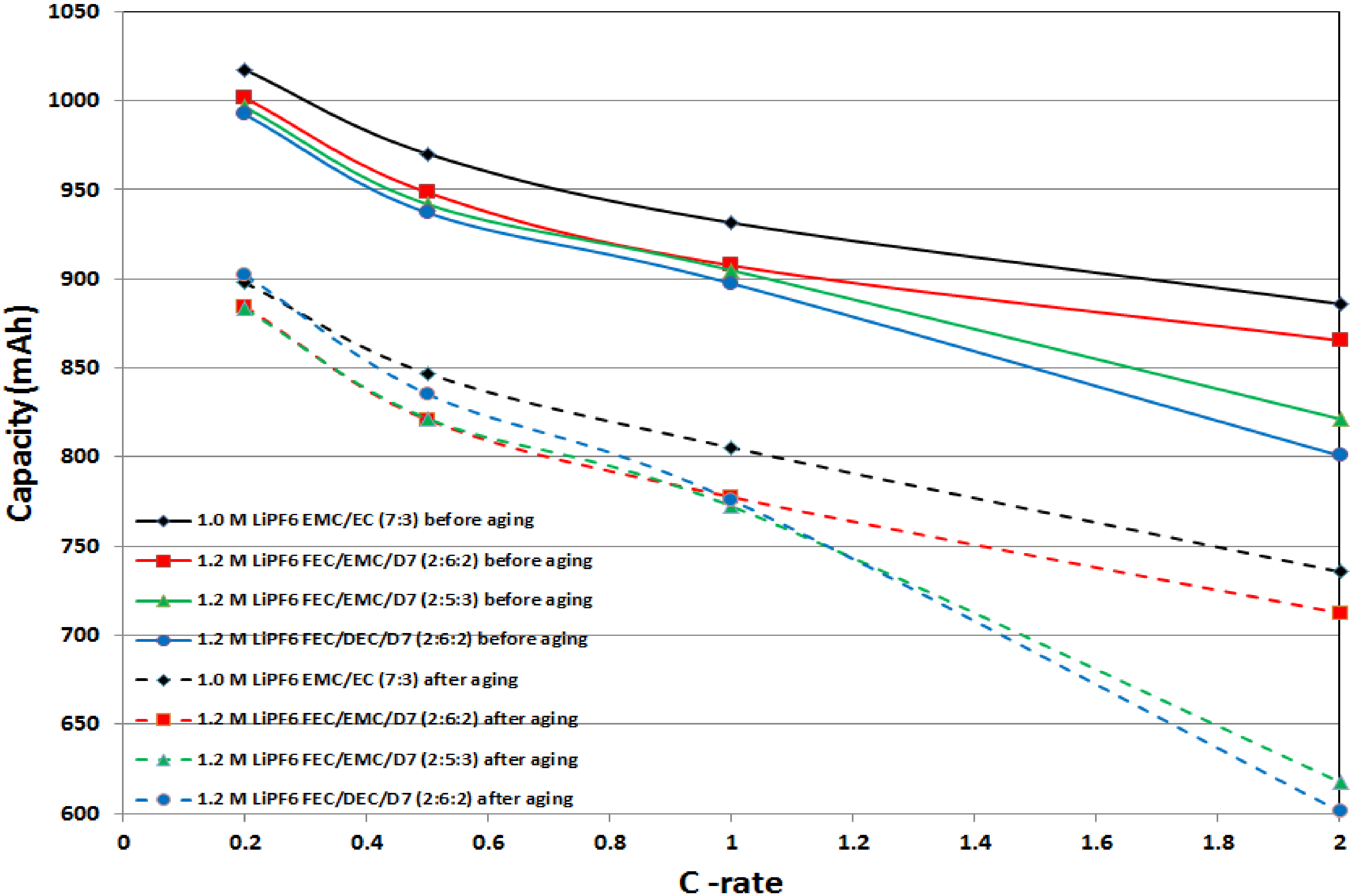


Baseline Cycling Behavior 3.0-4.2 V RT

Cycling performance of a 6:4 Hydrocarbon/Fluorocarbon is comparable to 100% hydrocarbon electrolyte to 4.2 V



Capacity as function of C-rate shows marked decrease at 2C not consistent with conductivity change



Temperature Stability

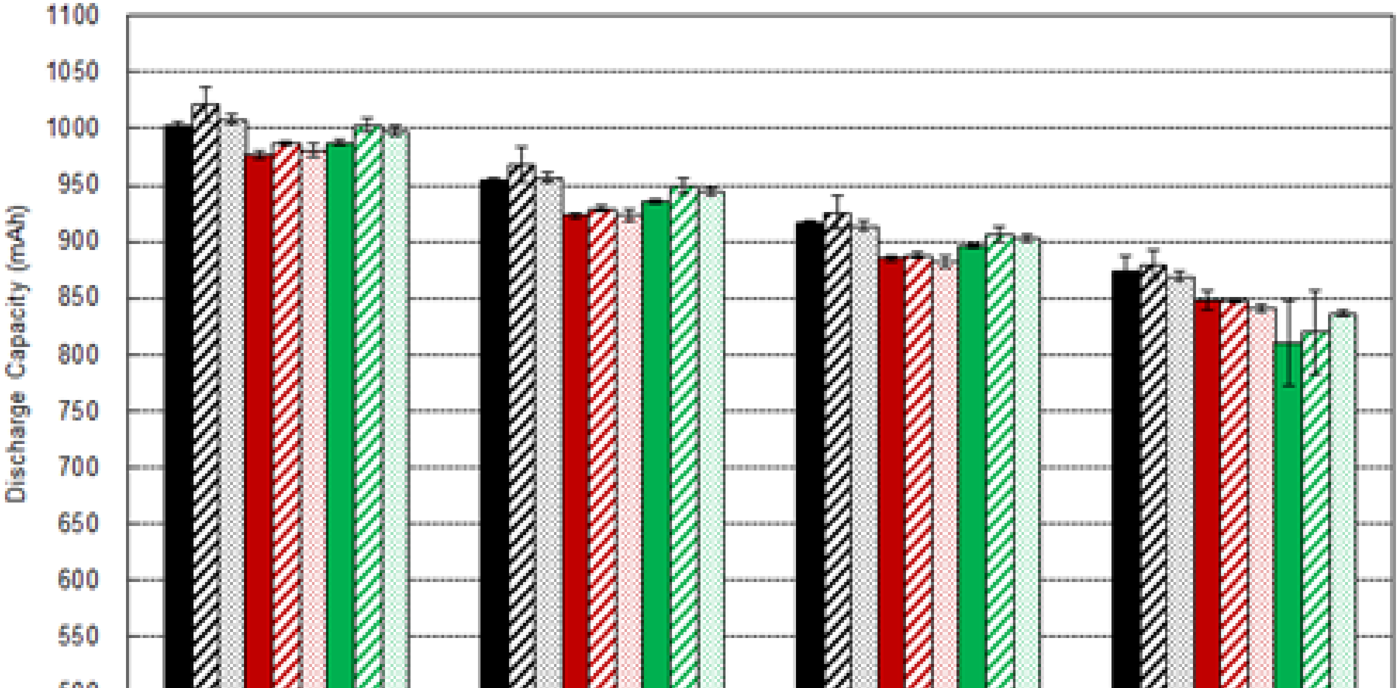
Electrolytes containing FEC not stabile over 60 C

60 C 85 C

DIL STD - EMC/EC (7:3)

DAI-03 - FEC/EMC/D7 (2:6:2)

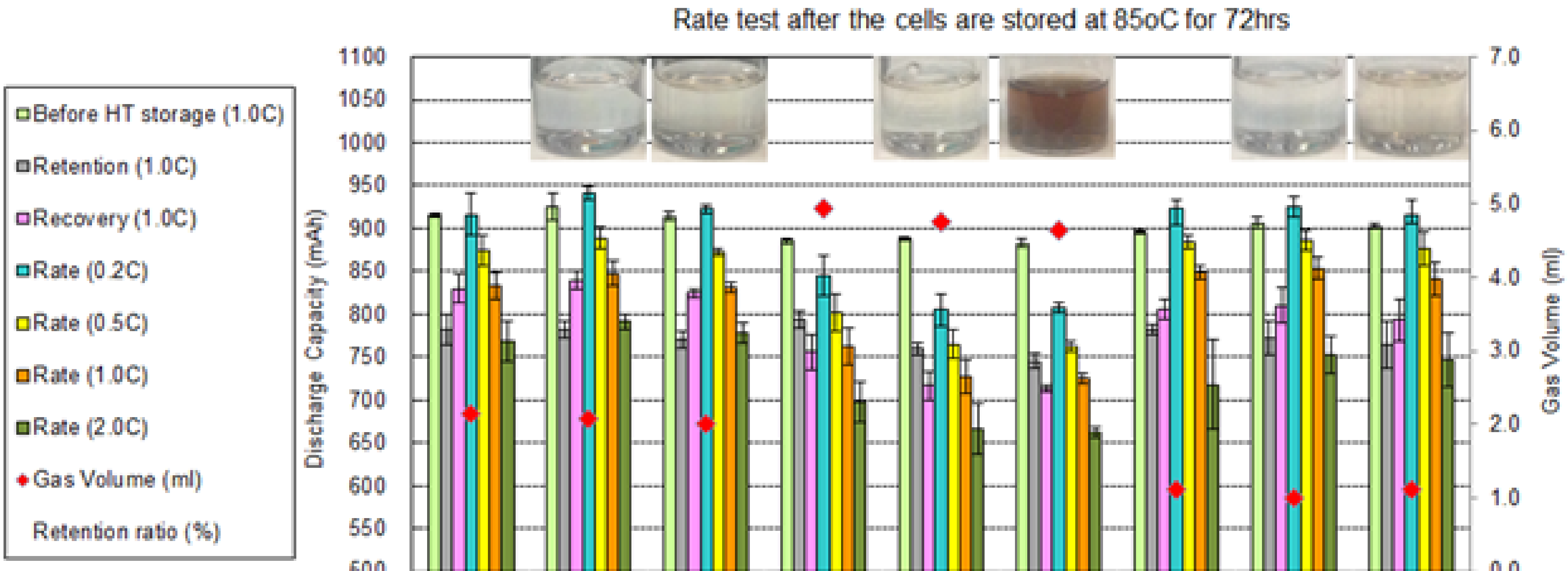
EC/EMC/D7 (2:6:2)



	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/D7)	987.7	935.5	896.7	809.9
60°C Electrolyte Storage (EC/EMC/D7)	1002.7	948.8	906.0	819.9
85°C Electrolyte Storage (EC/EMC/D7)	998.0	944.5	902.6	837.0

Temperature Stability

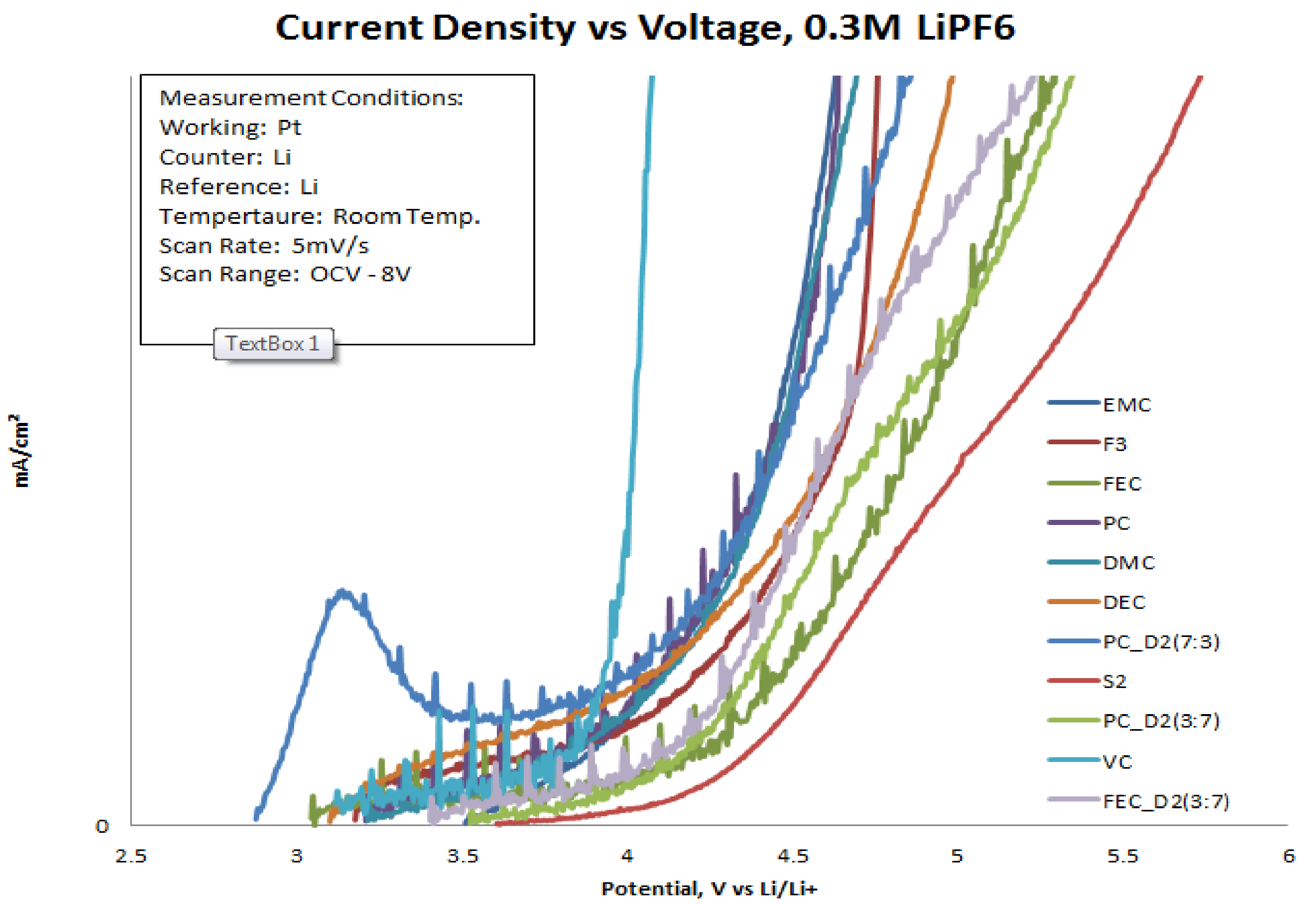
Electrolytes containing FEC show increased gassing on storage



	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/D 7)	60°C Electrolyte Storage (EC/EMC/D 7)	85°C Electrolyte Storage (EC/EMC/D 7)
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

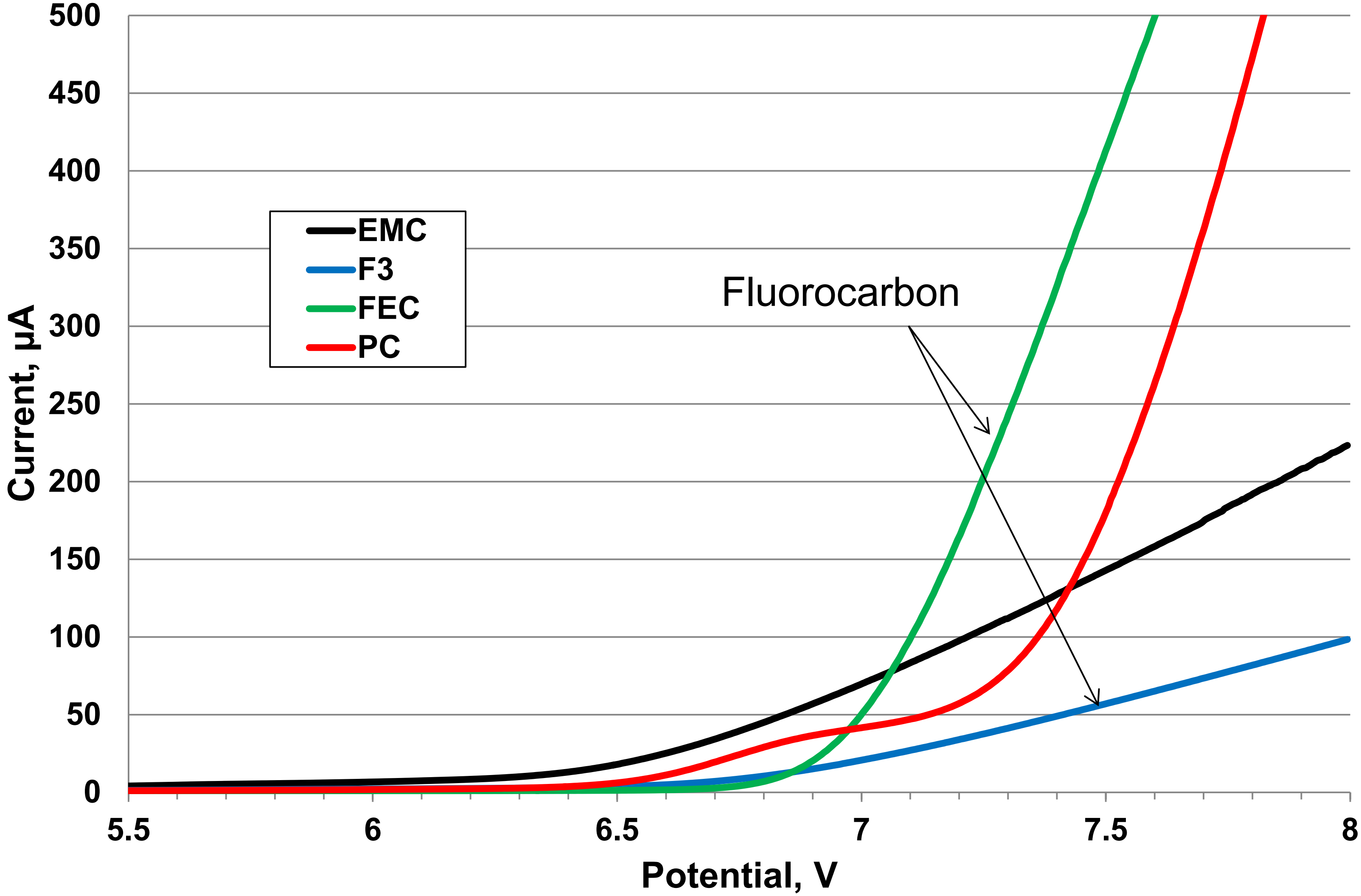
Linear Scanning Voltammetry

Fluorocarbons generally show higher voltage stability

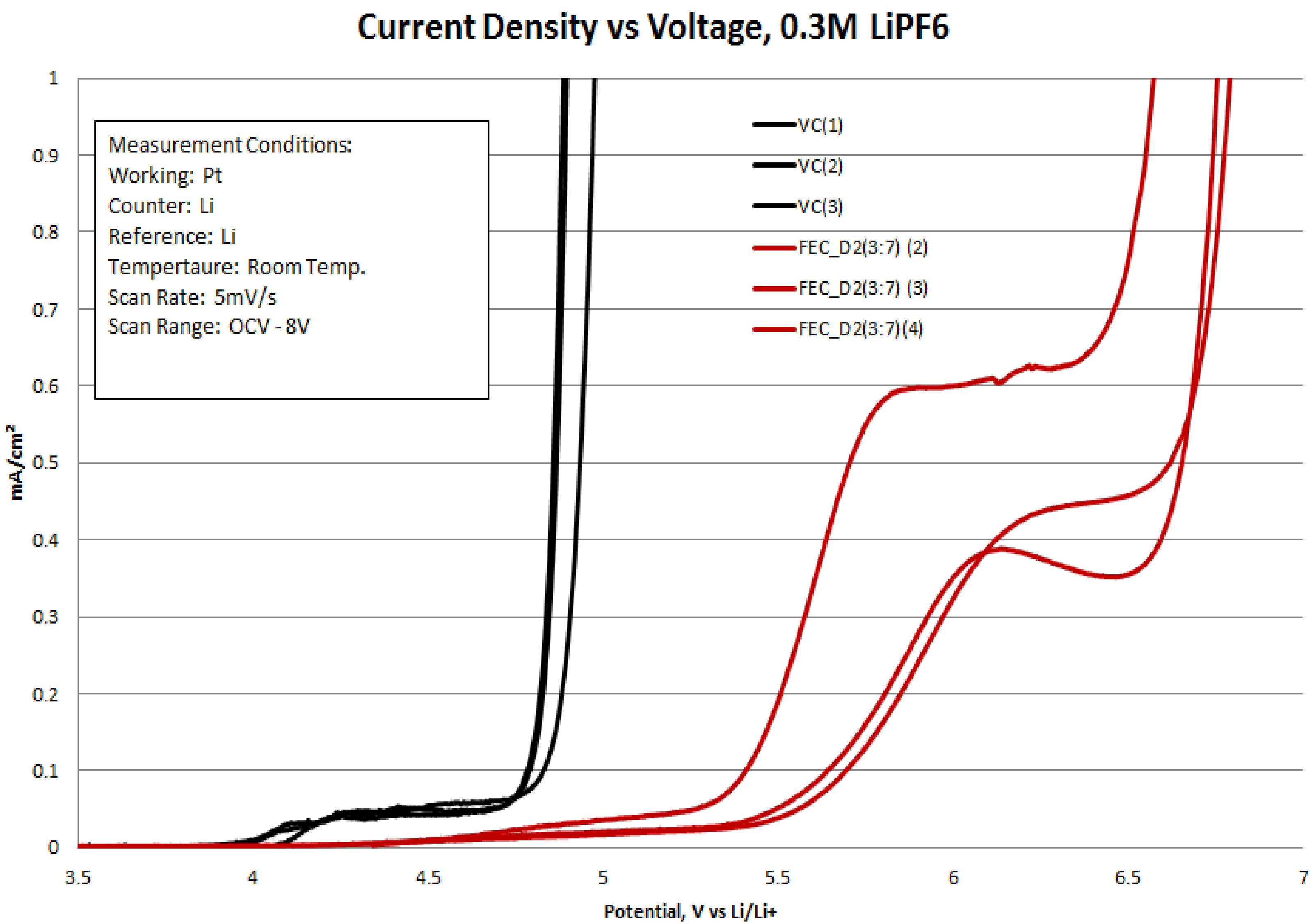


Linear Scanning Voltammetry

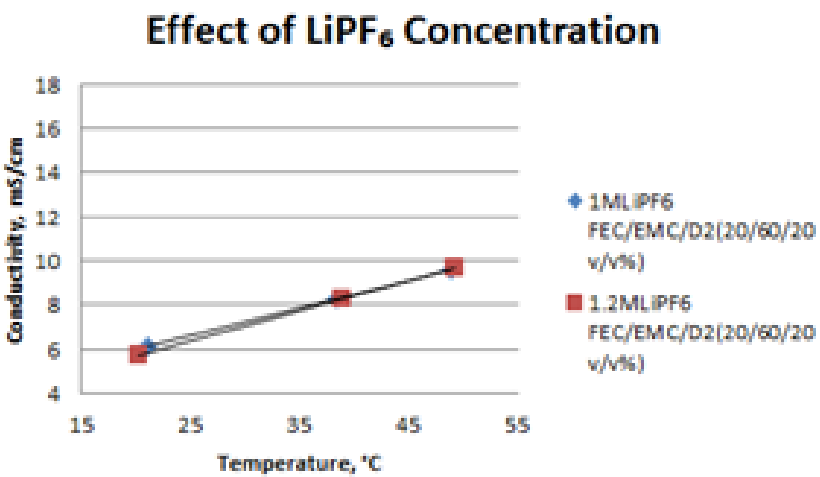
Fluorocarbons generally show higher voltage stability

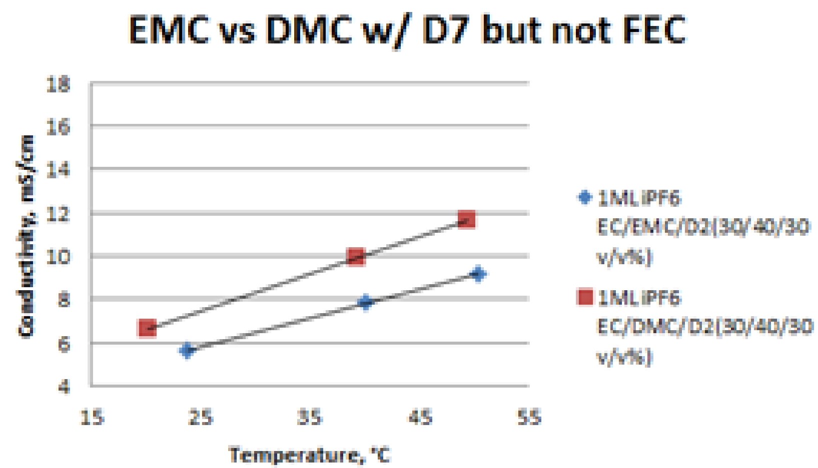


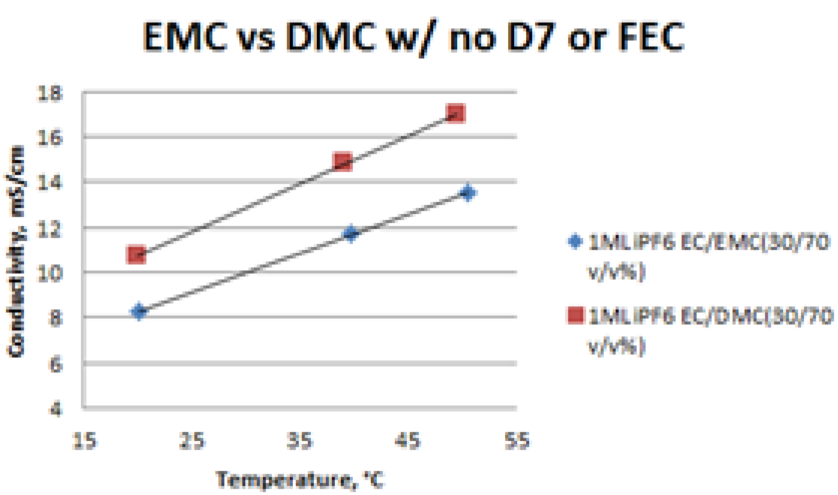
Linear Scanning Voltammetry of fluorinated SEI additive vs VC



Conductivity

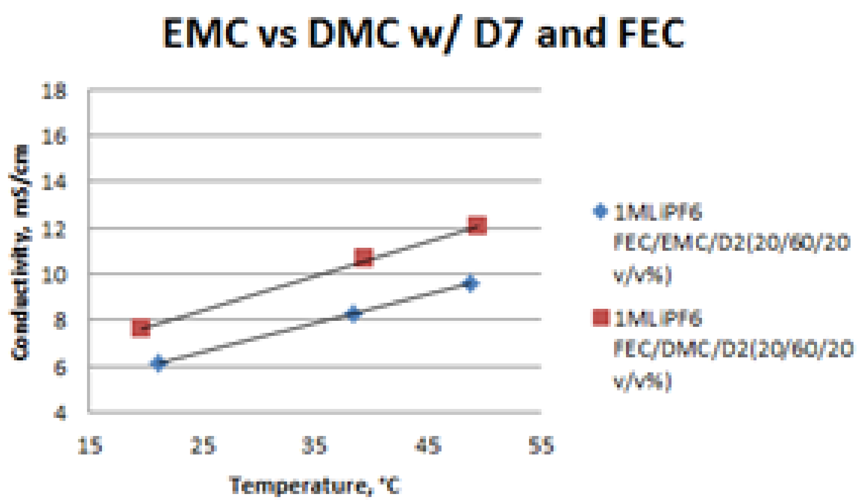


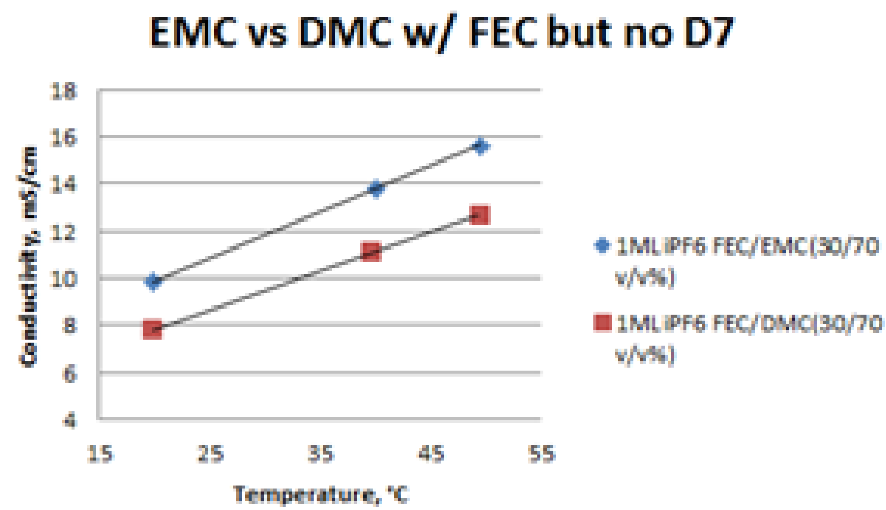


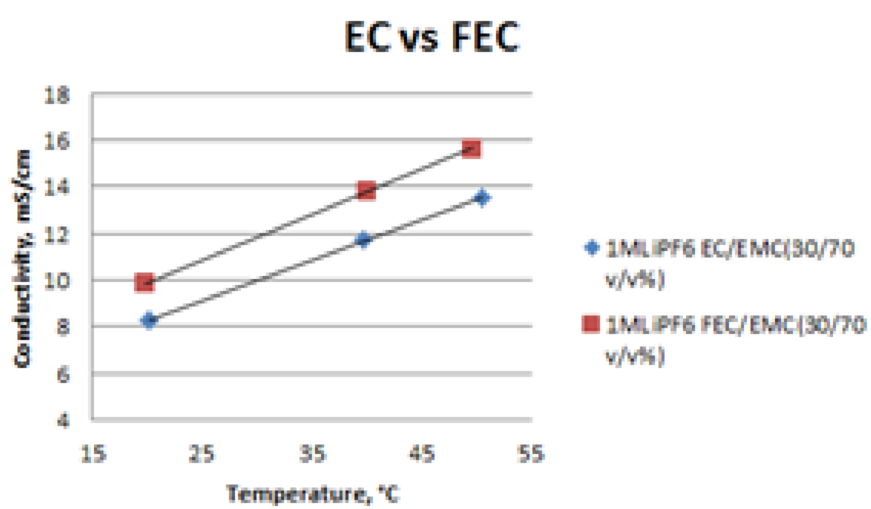


- No benefit of increased salt concentration
- DMC electrolytes have generally higher conductivities both in the presence of absence of fluoroether D7.

Conductivity







- FEC generally higher conductivity than EC
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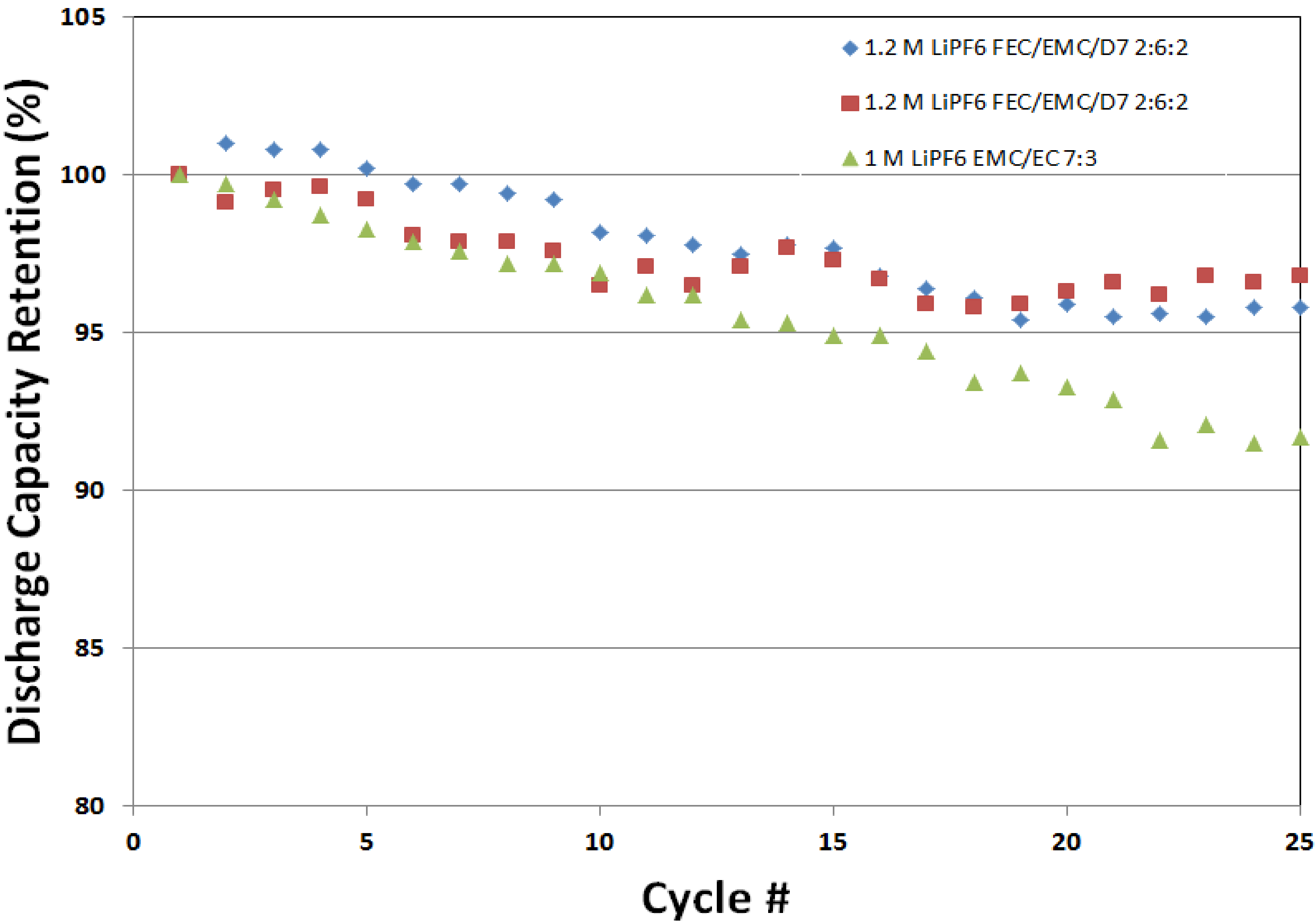
High Voltage Cycling 3.0 to 4.6 V

Preliminary data shows increase capactity retention at 4.6 V for fluorocarbon based electrolyte

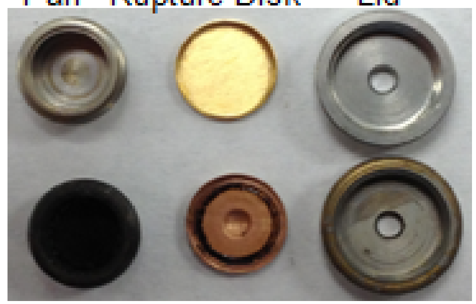


Differential Scanning Calorimetry Safety Testing

•<u>**CAREFULLY**</u> disassemble charged battery

New

Pan Rupture Disk Lid



Pan Rupture Disk Lid

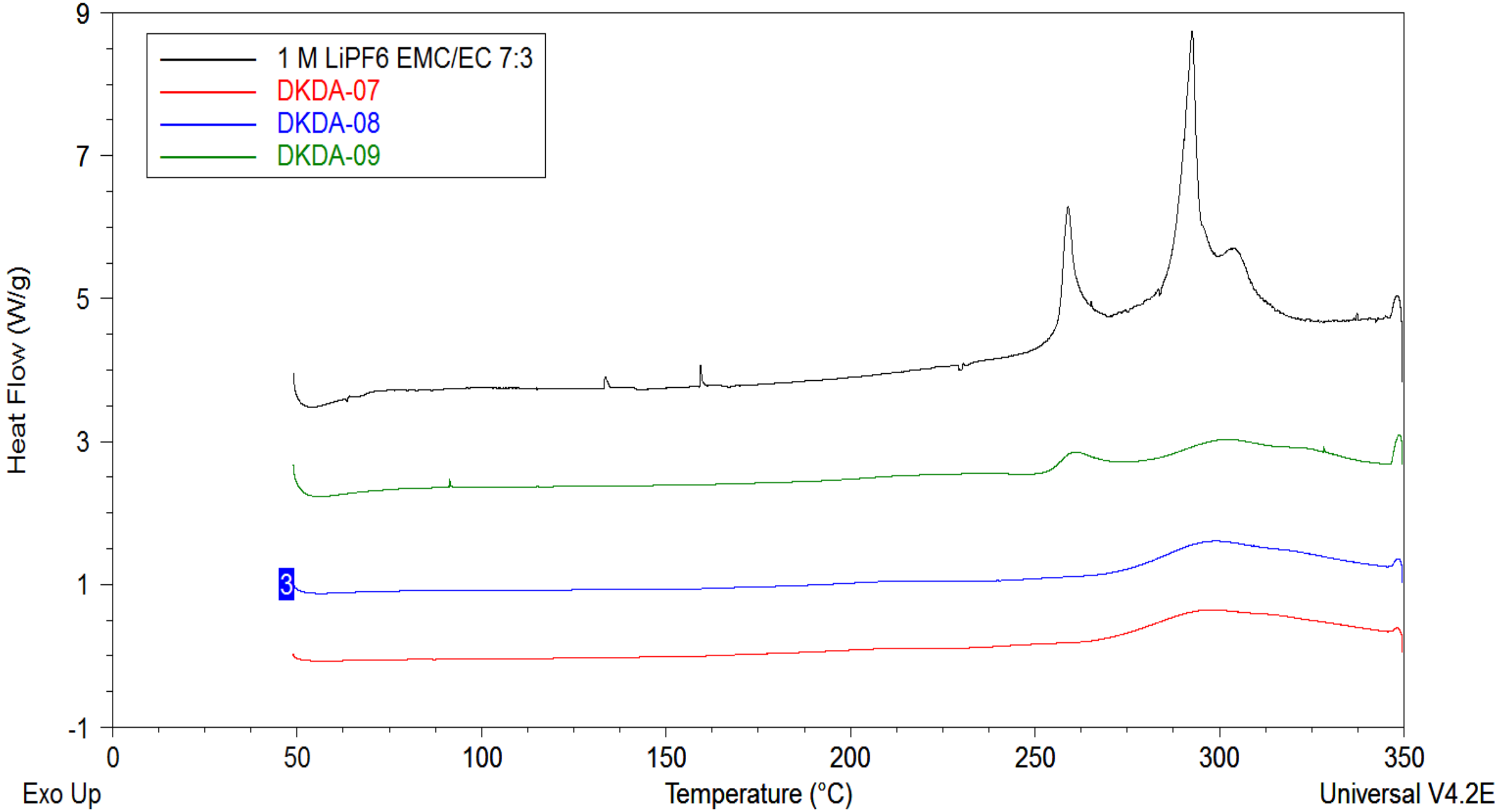
Used

•Hermetically sealed pan rated for 6.9 Mpa (1000 psi)

•DSC run under nitrogen gas, equilibrate at 50 C, ramp 10 C/min to 350 C, and isothermal at 350 C for 15 minutes

Purpose – to provide safety data about electrolyte behavior in actual battery

DKDA samples show increased stability with charged cathode (DKDA-07 FEC/EMC/DKD7 2:6:2, DKDA-08 FEC/EMC/DKD7 2:5:3, DKDA-09 FEC/DEC/D2 2:6:2 all one molar)



Future Work

- Completion of DOE which includes variations of two baseline electrolytes optimized for rate and cycle performance
- Begin PDCA cycle 2 which is a continuation of solvent package optimization
- Begin screening film forming characteristics of SEI additives both electrochemically and through physical surface analysis
- High voltage cathode electrode fabrication needs to be completed.
- Construct and evaluate high voltage NMC/graphite and LMN/graphite cells for future testing.
- Begin initial constant temperature high voltage (4.6 V) cycle testing

Technical Summary

- A comprehensive review of internal data and external literature was completed initially. Based on this review two electrolyte compositions were chosen for baselines. They are:
  - 1.0 M $LiPF_6$ EC/EMC 3:7 (hydrocarbon standard)
  - 1.2 M $LiPF_6$ FEC/EMC/D7 fluoroether 2:6:2 (fluorocarbon standard)
- The rate performance and 4.2 cycling data were collected and compared for the baselines.
  - 4.2 V cycling at 1 C shows parity performance for both baselines
  - Discharge capacities of fluorinated baseline are not significantly different until higher rate discharge (2 C). This is not consistent with only the conductivity change of the baselines.
  - 4.6 V cycling at 1 C shows improved performance for the fluorinated baseline
  - Calorimetric safety performance shows marked decrease in exothermic events between charged electrodes and fluorinated electrolytes
- Voltage stabilities were assessed using linear scanning voltammetry for all the native hydrocarbons and fluorocarbons as well as mixtures.
- Conductivities have been measured for a series of electrolytes containing hydrocarbons/fluorocarbons.