High Energy Density Ultracapacitors

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Project ID: ES038

This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Project start date: 2008
- Project end date: 2012
- 50% Complete

Budget

- Funding received in FY09: $250K
- Funding for FY10: $350K
- Project cost shared by Navy (equipment utilization)

Barriers

- Energy Density
- Cycle Life
- Affordability
- Voltage Decay
- Abuse Tolerance
- Low Temperature Performance

Collaborators

- Michael Wartelsky (SAIC);
  Steven Dallek and Glenn Zoski (Spectrum Technology Group)
  - Thermal stability of electrode materials
  - Electrolyte assessment
- Deyang Qu (University of Massachusetts, Boston)
  - Assessment of carbon materials
- Steve G. Greenbaum (Hunter College of CUNY)
  - Stability of SEI layer
- Linda Zhong (Maxwell Technologies)
  - Ultracapacitors
- Jae Sik Chung (PCTest)
  - ARC Testing

Why Ultracapacitors? Relevance of Project

Strengths

- High specific power → Good for power assist
- Fast charge acceptance → Good for regenerative energy capture
- Excellent cycle life → Fewer replacements required
- Excellent low temperature performance → Good for engine start

Weaknesses

- Low specific energy → Limited operational time
- High self discharge → Requires frequent charge

Advantages of Hybridizing Battery and Ultracapacitor

- Reduced battery operating current. Lower I^2R heating.
- Reduced power pack weight.
- Extended battery life. Reduce replacement cost.
- Better low-temperature performance for cold engine starts.

Energy Density: 3 Wh/kg
Power Density: 650 W/kg
Operating Range: -30 to +52°C
Survival Range: -46 to +66°C
Cycle Life: 750,000 cycles

USABC
UNITED STATES ADVANCED BATTERY CONSORTIUM

FreedomCAR

FreedomCar UC EOL Requirements

System Attributes	12V Start-Stop (TSS)		42V Start-Stop (FSS)		42V Transient Power Assist (TPA)	
Discharge Pulse	4.2 kW	2s	6 kW	2s	13 kW	2s
Regenerative Pulse	N/A		N/A		8 kW	2s
Cold Cranking Pulse @ -30°C	4.2 kW	7 V Min.	8 kW	21 V Min.	8 kW	21 V Min.
Available Energy (CP @1kW)	15 Wh		30 Wh		60 Wh	
Recharge Rate (kW)	0.4 kW		2.4 kW		2.6 kW	
Cycle Life / Equiv. Road Miles	750k / 150,000 miles		750k / 150,000 miles		750k / 150,000 miles	
Cycle Life and Efficiency Load Profile	UC10		UC10		UC10	
Calendar Life (Yrs)	15		15		15	
Energy Efficiency on UC10 Load Profile (%)	95		95%		95%	
Self Discharge (72hr from Max. V)	<4%		<4%		<4%	
Maximum Operating Voltage (Vdc)	17		48		48	
Minimum Operating Voltage (Vdc)	9		27		27	
Operating Temperature Range (°C)	-30 to +52		-30 to +52		-30 to +52	
Survival Temperature Range (°C)	-46 to +66		-46 to +66		-46 to +66	
Maximum System Weight (kg)	5		10		20	
Maximum System Volume (Liters)	4		8		16	
Selling Price ($/system @ 100k/yr)	40		80		130	

USABC Protected Battery Information
DAIMLERCHRYSLER - Ford - General Motors
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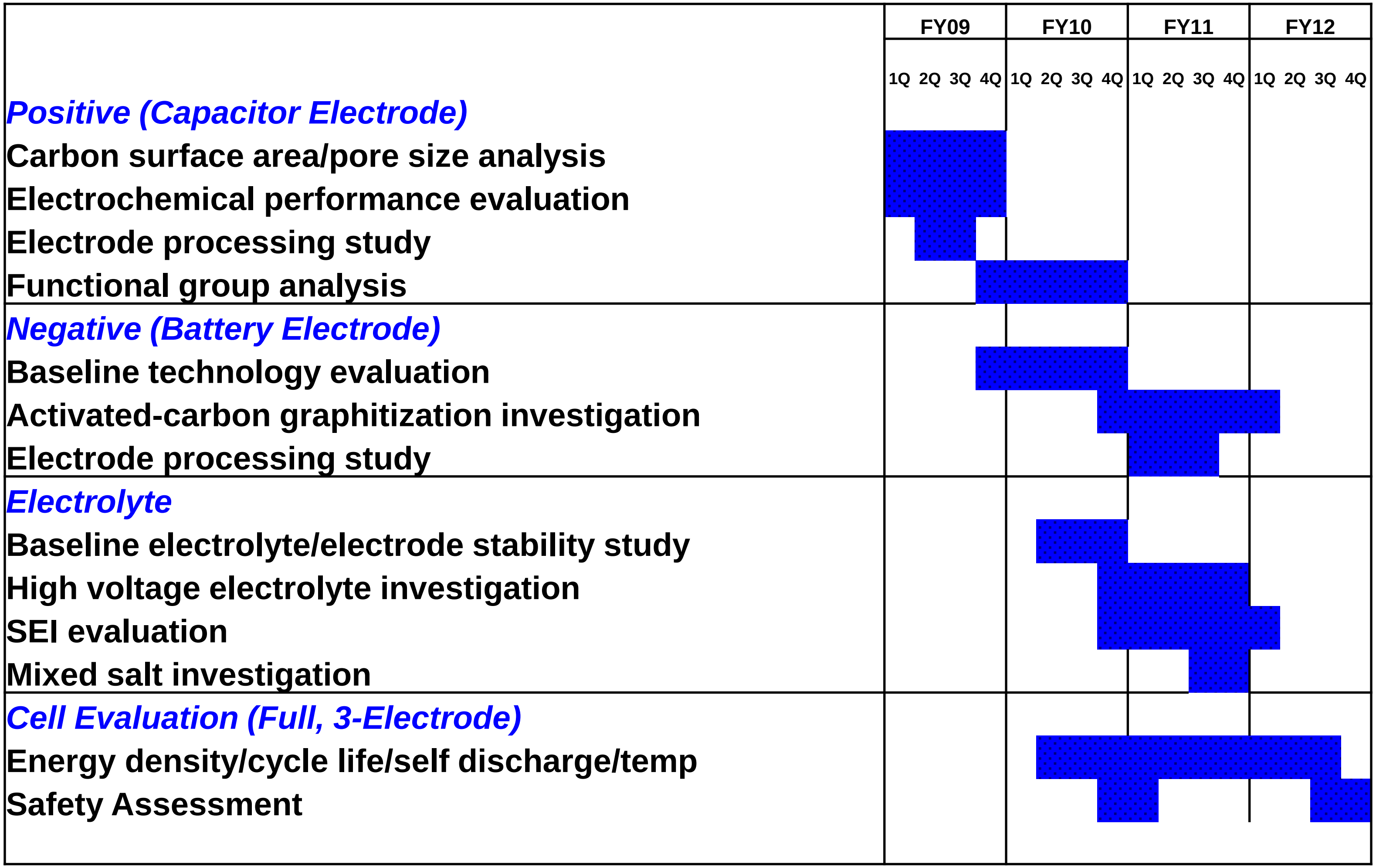
Objectives

- Develop electrode/electrolyte materials that will enable an ultracapacitor to meet power assist and regenerative braking goals.
  - 15-20 Wh/kg, 650 W/kg at cell level
  - 750,000 - 1,000,000 cycles
  - -30 to 52^{o}C operational temp.
  - -46 to 66^{o}C survivability temp.

Approach

- Advance the lithium ion capacitor technology in order to meet the challenging vehicle energy density requirements.
- Identify high capacity/capacitance electrode materials to increase the energy density. Understand the physico-chemical properties responsible for high capacity/capacitance
- Explore new electrolyte solvent systems that have a wide electrochemical potential window and will allow the capacitor to meet cycle life and operating temperature goals
- Evaluate reactivity of electrode materials with electrolyte

Milestones



FY09
FY10
FY11
FY12
1Q 2Q 3Q 4Q 1Q 2Q 3Q 4Q 1Q 2Q 3Q 4Q 1Q 2Q 3Q 4Q
Positive (Capacitor Electrode)
Carbon surface area/pore size analysis
Electrochemical performance evaluation
Electrode processing study
Functional group analysis
Negative (Battery Electrode)
Baseline technology evaluation
Activated-carbon graphitization investigation
Electrode processing study
Electrolyte
Baseline electrolyte/electrode stability study
High voltage electrolyte investigation
SEI evaluation
Mixed salt investigation
Cell Evaluation (Full, 3-Electrode)
Energy density/cycle life/self discharge/temp
Safety Assessment

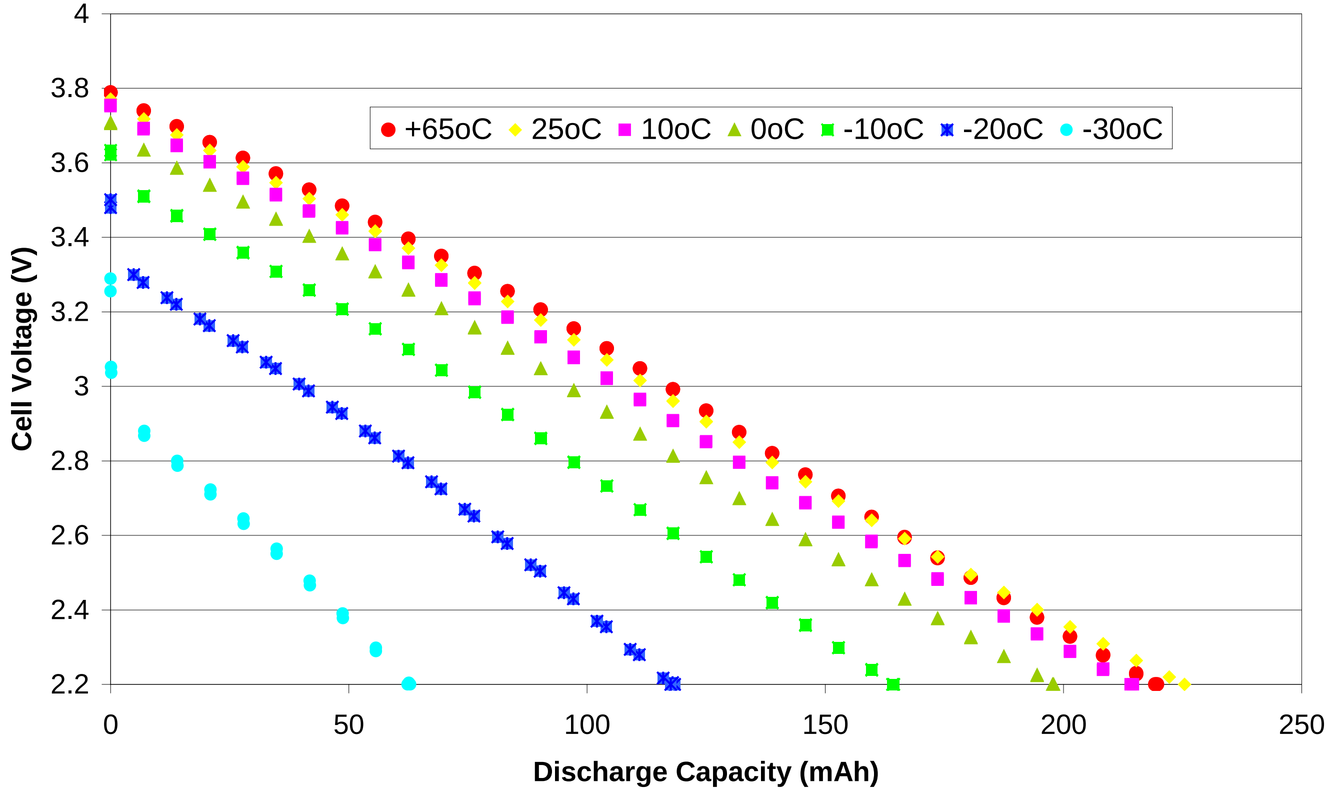
Previous Technical Accomplishments

- The electrochemical performance of carbon materials derived from various precursor materials and activated by either steam, KOH or H_3PO_4 was investigated. Excellent performance (~160 F/g) was observed with carbons (~2,000 m^2/g) activated by KOH.
- Electrode processing techniques were assessed to ensure that the benefit of high capacitance carbons was not diminished with pore-blocking binders (PVDF, UHMWPE, PTFE). Positive electrode carbons were distributed to various electrode manufacturers. Electrodes utilizing PTFE binder yielded highest capacitances.
- Carbon's functional group analysis was determined by Boehm Titrations. Thermogravimetric analysis (TGA) results show a correlation between weight loss and electrochemical performance.
- Three-electrode cell and full cell investigations of lithium ion capacitors utilizing either graphite or lithium titanate negative electrodes were conducted. Although the titanate promised greater cycle life, it did not yield the energy density of the graphite system (10-12 Wh/kg vs. 12-15 Wh/kg).
- The self discharge of three-electrode lithium ion capacitor and lithium titanate capacitor cells at 25^{o}C was found to be lower (1-7%) than that of conventional ultracapacitors (17-19%).

Understanding Performance Limitations of 1st Generation Lithium Ion Capacitor (C vs. C)

Effect of Temperature on Discharge Performance

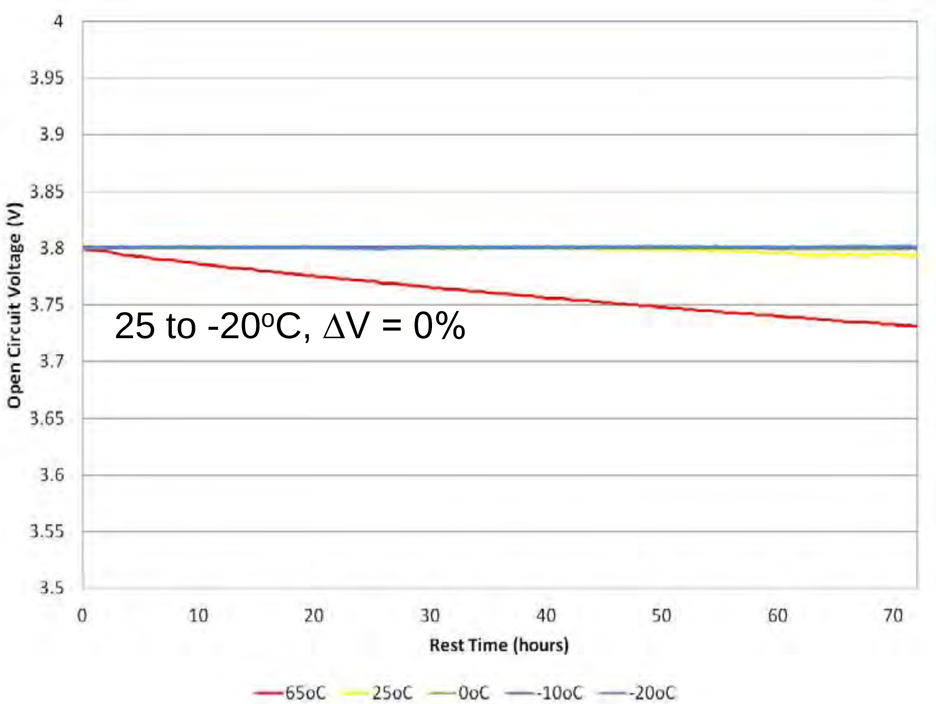
500 F Cells, Cycled at 2.5A, 1st Generation Electrolyte: $LiPF_6$ in EC:PC:DEC



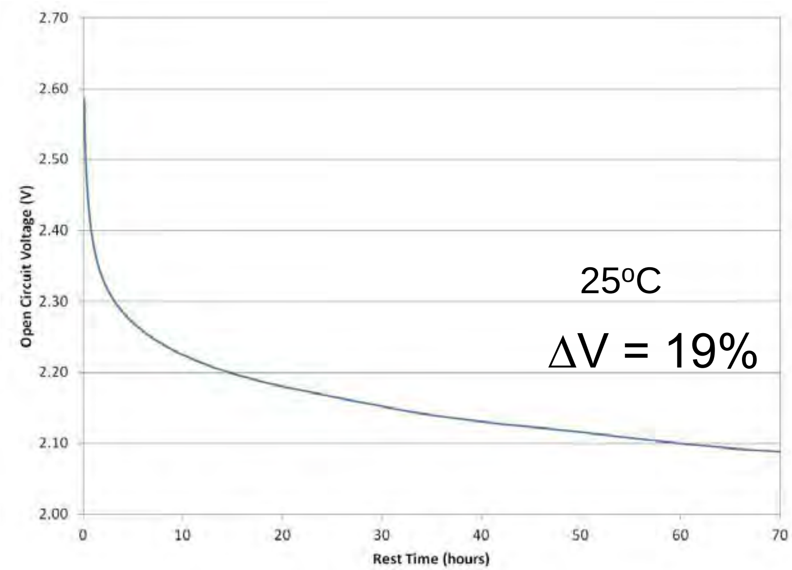
Cells cycled at 25^{o}C and 65^{o}C exhibited excellent performance delivering 225 mAh (15 Wh/kg, 26 Wh/L). When the temperature was lowered, capacity was significantly reduced (~27 % at -10^{o}C, ~48% at -20^{o}C, and ~73% at -30^{o}C) compared to their performance at 25^{o}C.

Effect of Temperature on the Voltage Decay

1st Generation 500F Ultracapacitor



3,000F Ultracapacitor*

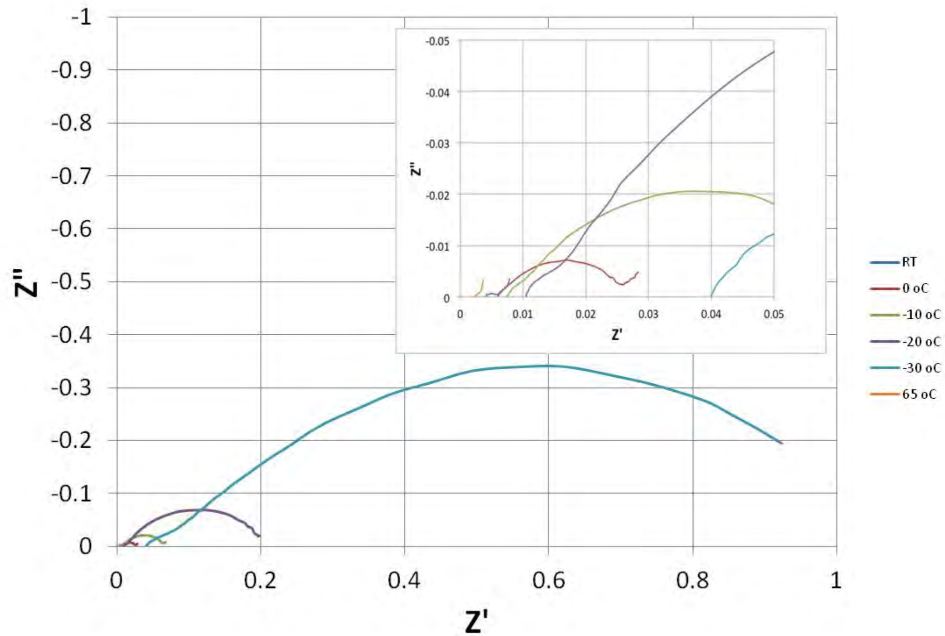


* Data courtesy of Maxwell Technologies

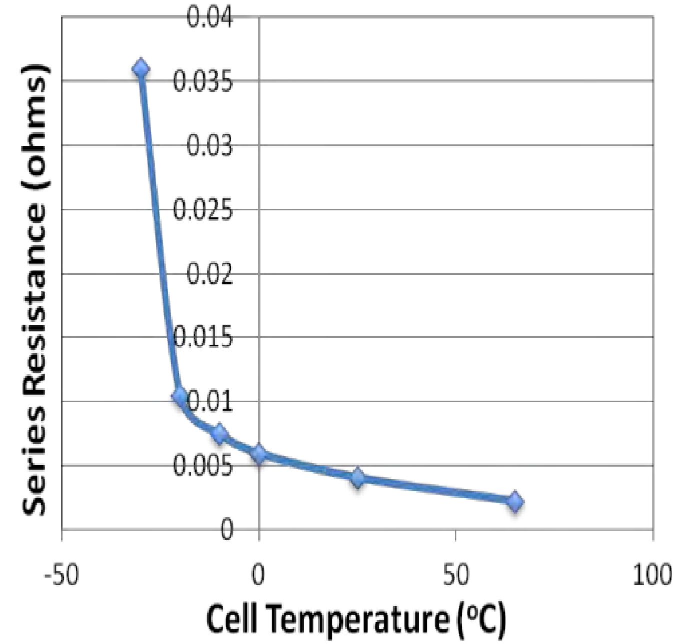
Ultracapacitors are known to have a much higher self-discharge rate than that of batteries. This can be a major limitation especially if they are used for standby purposes. The data revealed that the lithium ion capacitor has a significantly lower self-discharge rate than ultracapacitors.

Increased ESR Observed As Temperature is Lowered in 1st Generation Cells

Nyquist Plots of 500F LIC Cells at Various Temperatures



Plot of ESR vs. Cell Temperature

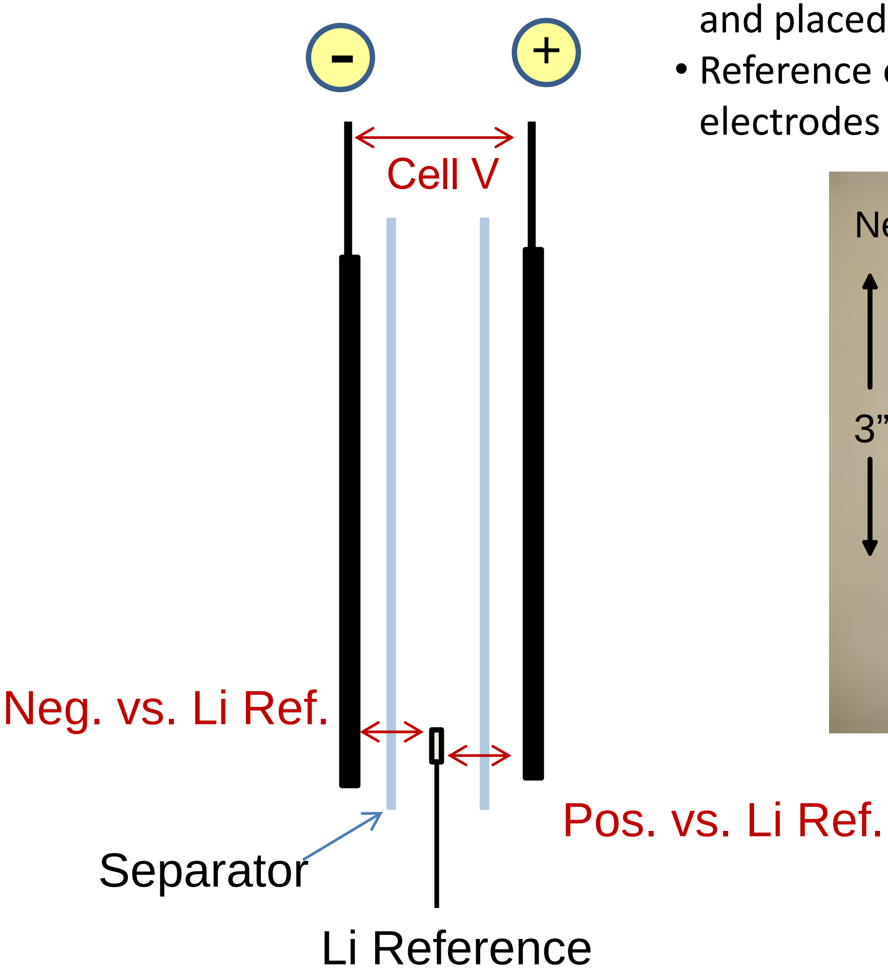


First Generation Electrolyte Solvents

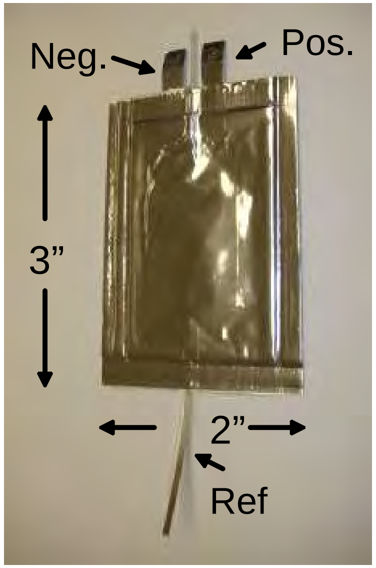
Solvent	Freezing Point
Ethylene carbonate (EC)	39.4°C
Propylene carbonate (PC)	-49°C
Diethyl carbonate (DEC)	-43°C

Reduced cell capacity at -20°C and -30°C is attributed to an increase in cell resistance caused by EC's high freezing point.

Understanding Performance Limitations of 1st Generation Lithium Ion Capacitor



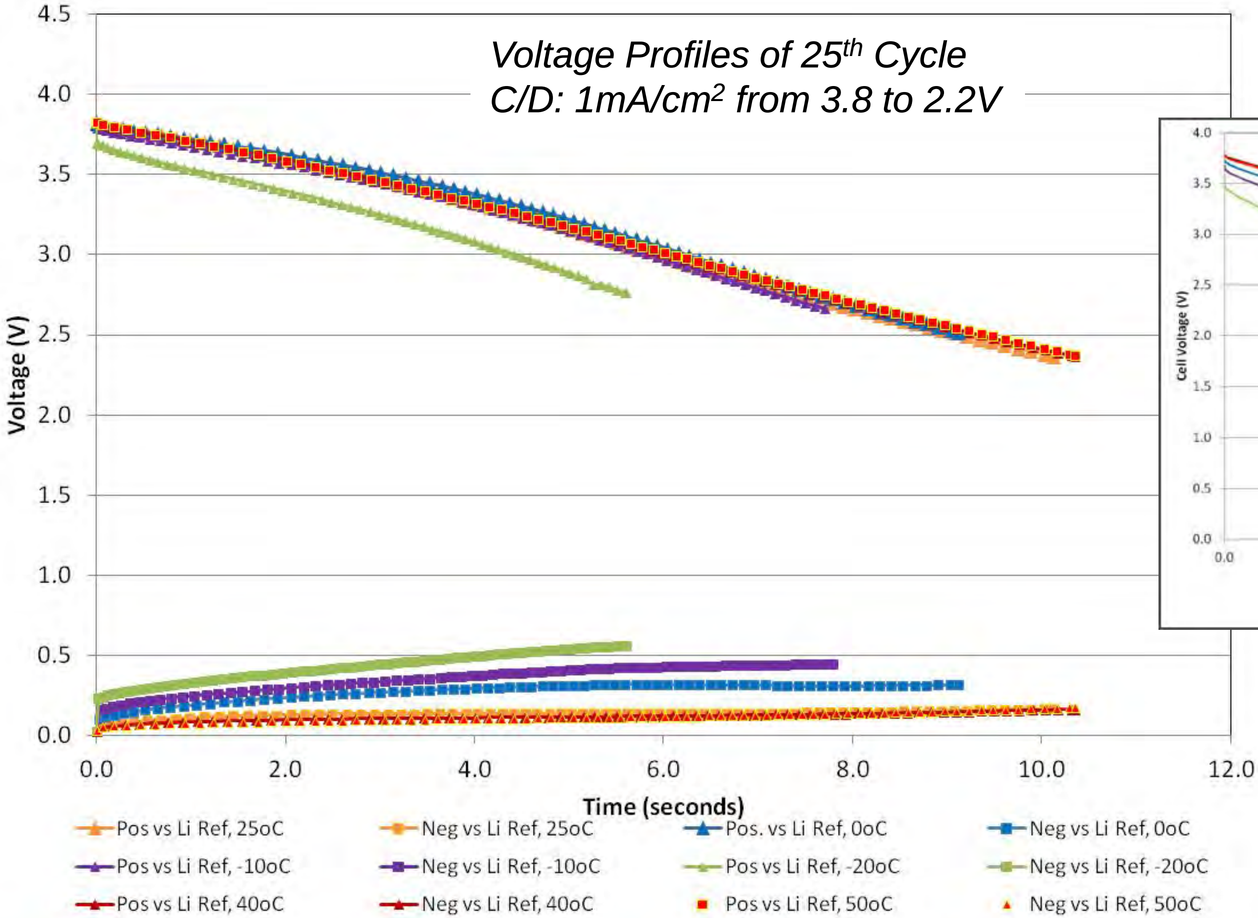
- Positive and negative electrodes were harvested from 500F cells and placed in pouch cells.
- Reference electrodes allowed the monitoring of individual electrodes and identification of cell failure mechanisms.

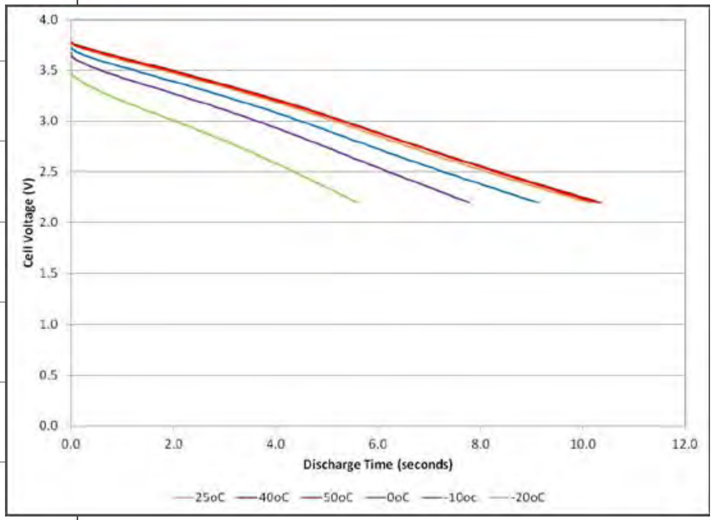


1 Kg weight placed on top of the pouch cell to maintain electrode stack pressure

Cell Voltage = (Positive Electrode vs. Li Ref.) – (Negative Electrode vs. Li Ref.)

3-Electrode Pouch Cell Evaluation of 1st Generation Lithium Ion Capacitor Electrodes and Electrolyte

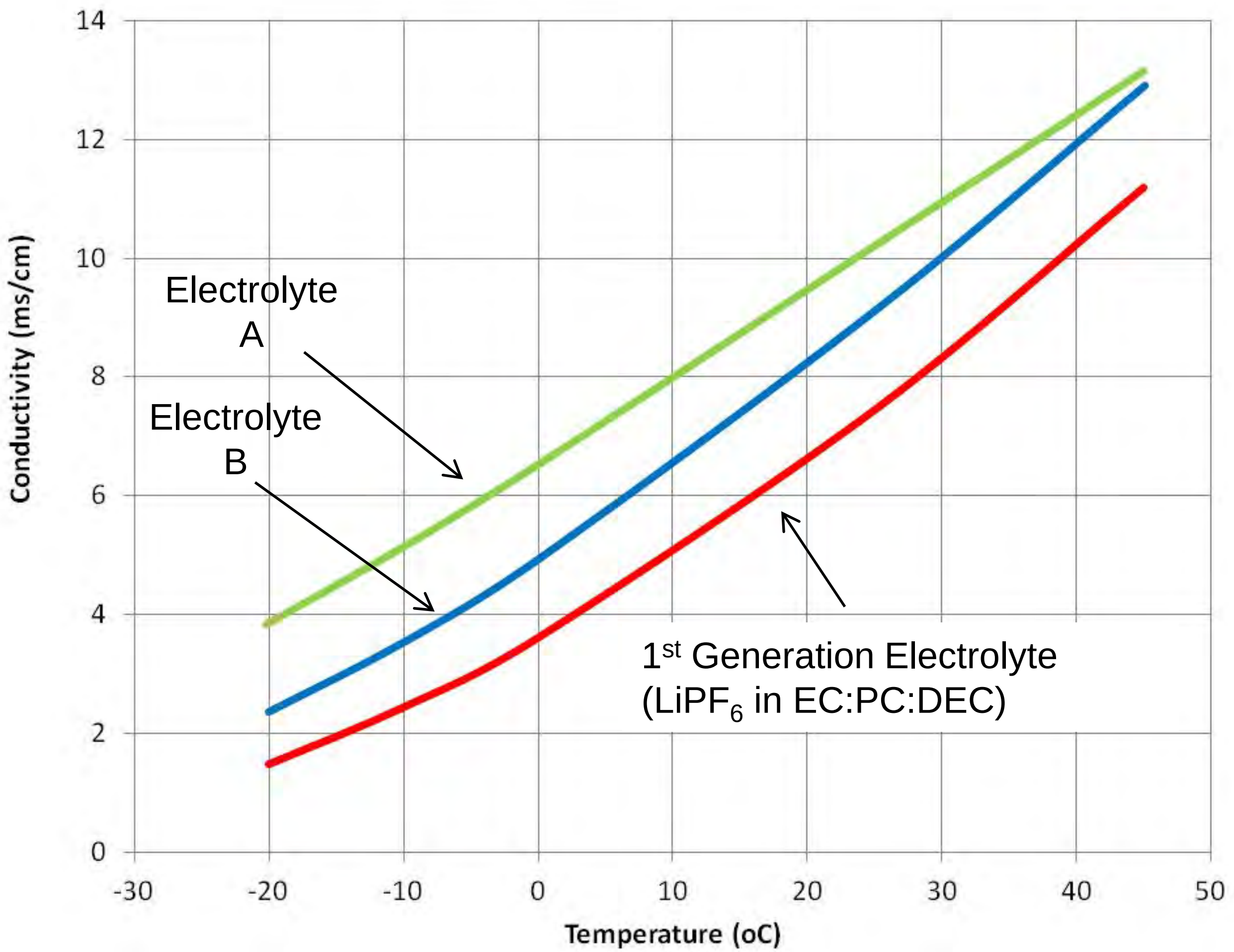




Pouch cells contained a Li reference. The + and - electrodes were harvested from 500F cells.

The performance of 1st Generation 500F cells was shown to be limited by the positive electrode. The positive voltage drop ranged between 1.45V (25°C) and 1.18V (-10°C) while the negative electrode voltage drop ranged between 0.14V (25°C) and 0.42V (-10°C). As the temperature was lowered, the negative electrode began to polarize at a faster rate than the positive electrode.

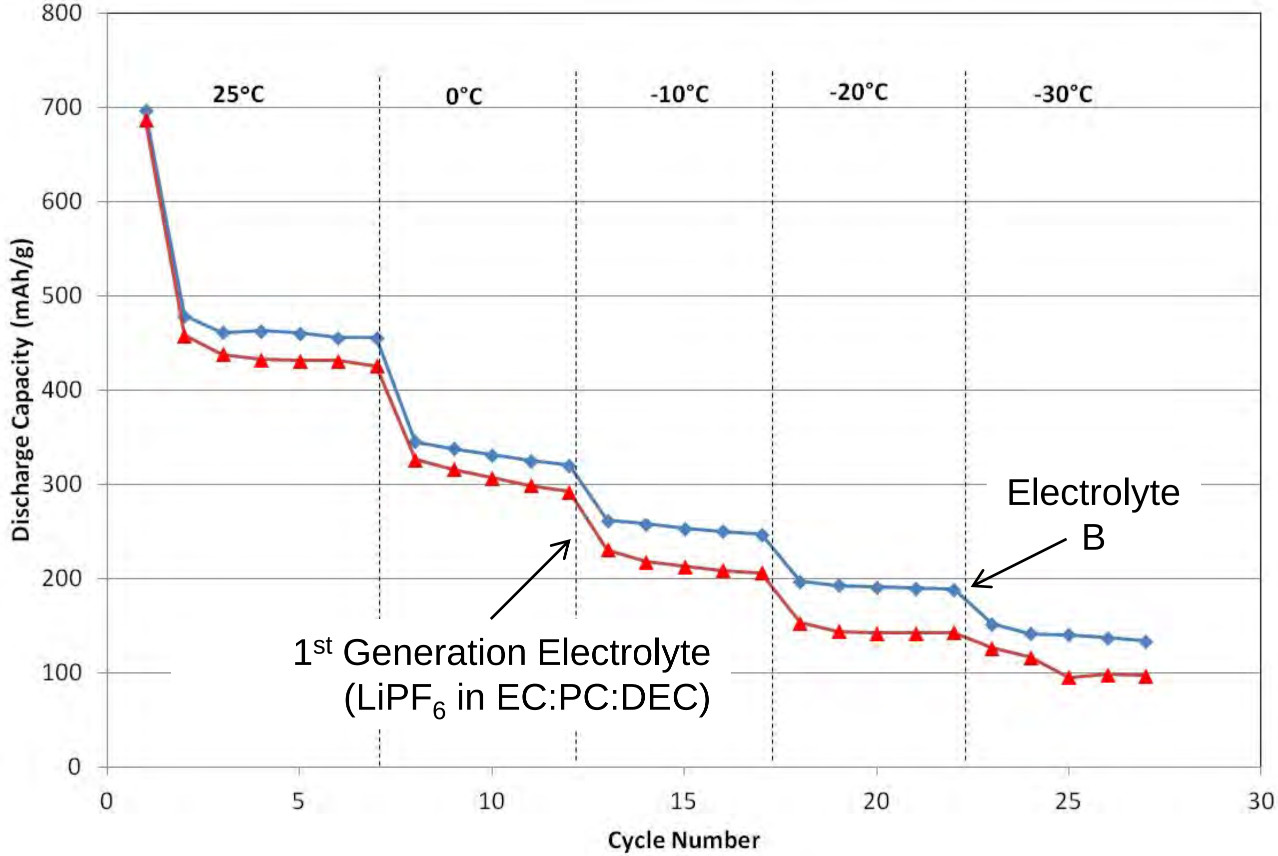
Alternative Electrolytes for Improved Lithium Ion Capacitor Performance



Two carbonate electrolytes were evaluated. The selected two electrolytes A and B revealed ~ 150% and ~53% higher conductivity, respectively compared to that of the 1st generation lithium ion capacitor electrolyte at -20°C.

Effect of Electrolyte on Negative Electrode Performance, ½ Cell Evaluation (C vs. Li)

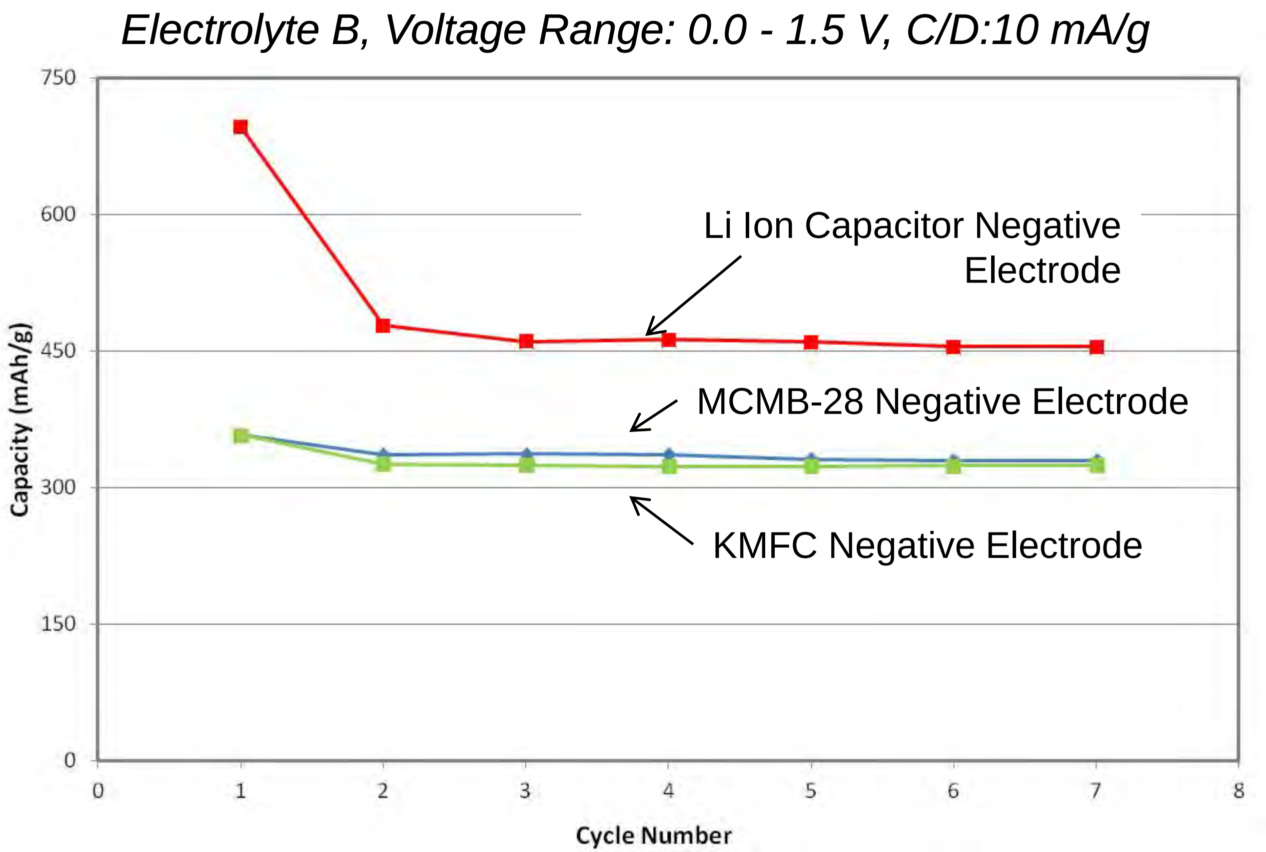
Voltage Range: 0.0 - 1.5 V, Charge/Discharge: 10 mA/g



The irreversible capacity loss of the 1st generation electrolyte was approximately equal to electrolyte ”B” (34% and 31% respectively). Anode capacity was approximately 35% higher for cells using electrolyte “B” than cells containing the 1st generation electrolyte at -20°C. Experiments are presently being conducted for electrolyte “A”.

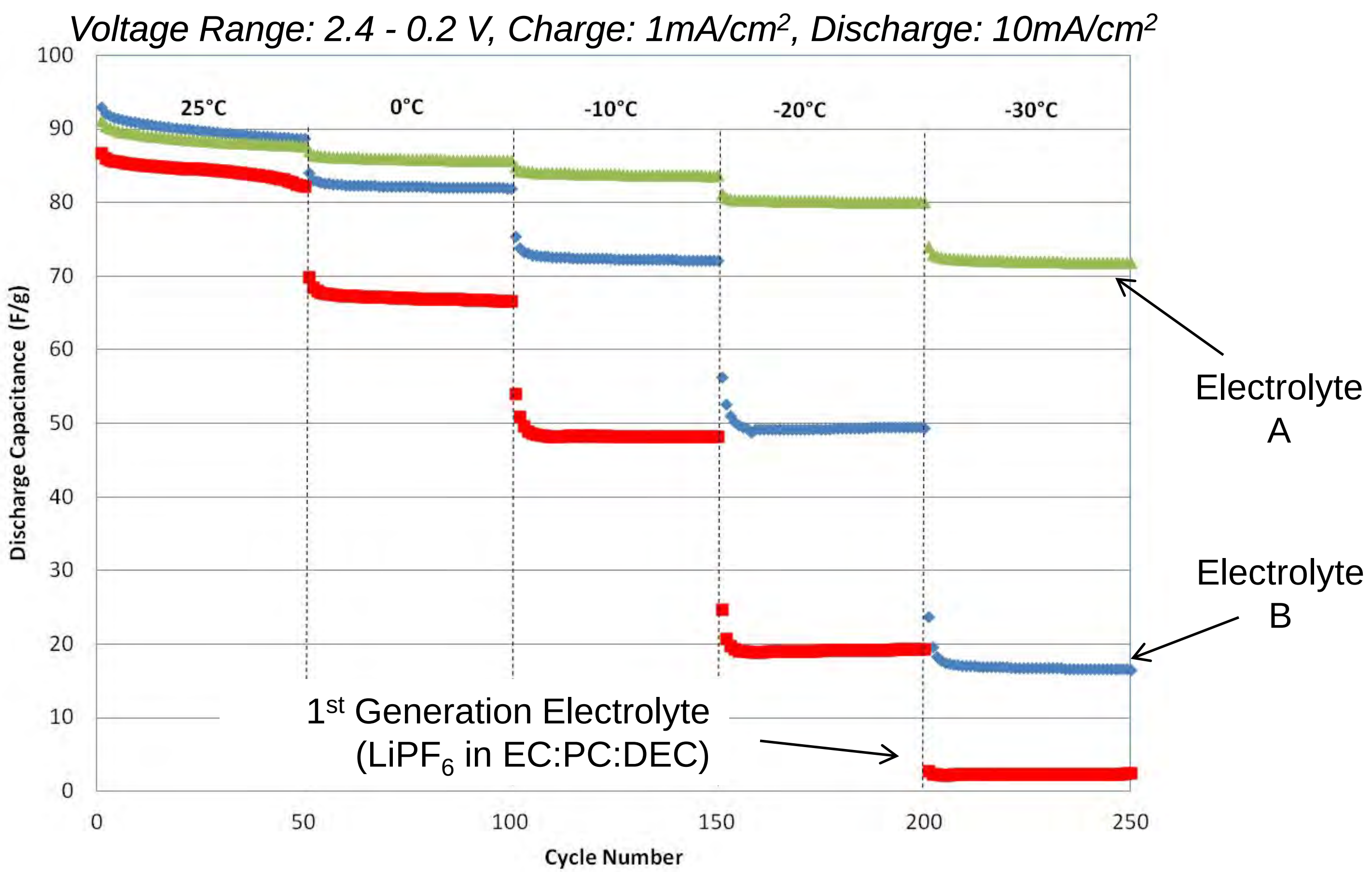
Lithium Ion Capacitor

Evaluation of Negative Electrode Carbon Materials at 25^{o}C



A lithium ion capacitor carbon electrode was compared to two commercially available carbon materials (MCMB-28, KMFC) in ½ cells containing Electrolyte B. The capacitor carbon's irreversible capacity loss was found to be significantly greater (31% vs. 9%) than MCMB-28 and KMFC. The reversible capacity after 7 cycles was ~ 450 mAh/g. Efforts are on-going to investigate its long-term stability.

Effect of Electrolyte on Positive Electrode Performance, Symmetric Cell Evaluation (C vs. C)

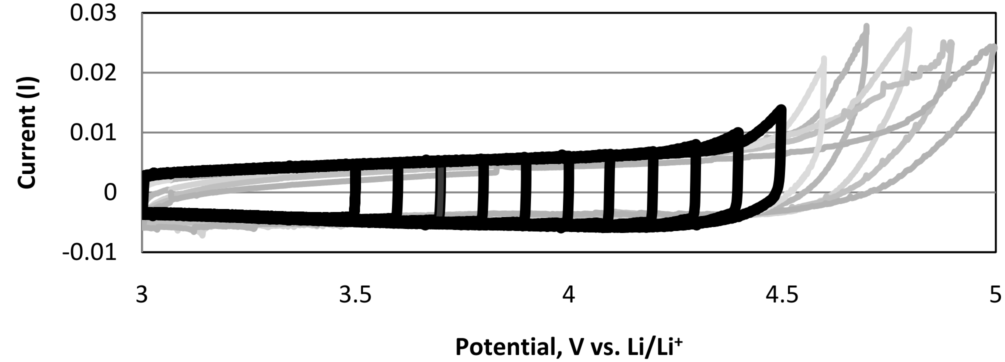


The positive electrode study showed a dramatic improvement in capacitance with electrolyte "A" at low temperatures. The following trend was observed in capacitance: Electrolyte "A", 80 F/g (3.84 mS/cm @-20^{o}C) > Electrolyte "B", 49 F/g (2.36 mS/cm @-20^{o}C) > 1st Generation Electrolyte, 20 F/g (1.55 mS/cm @-20^{o}C).

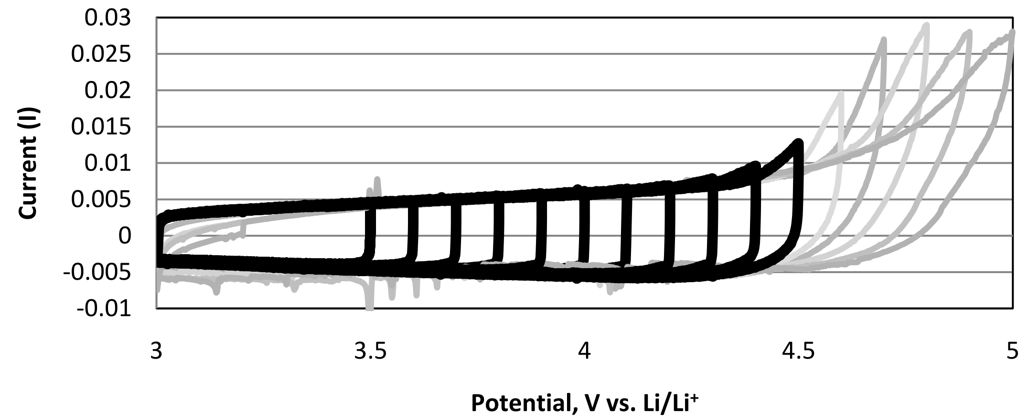
Electrochemical Potential Window of New Electrolytes

Working electrode: Carbon positive electrode material
Sweep rate: 0.5 mV/s

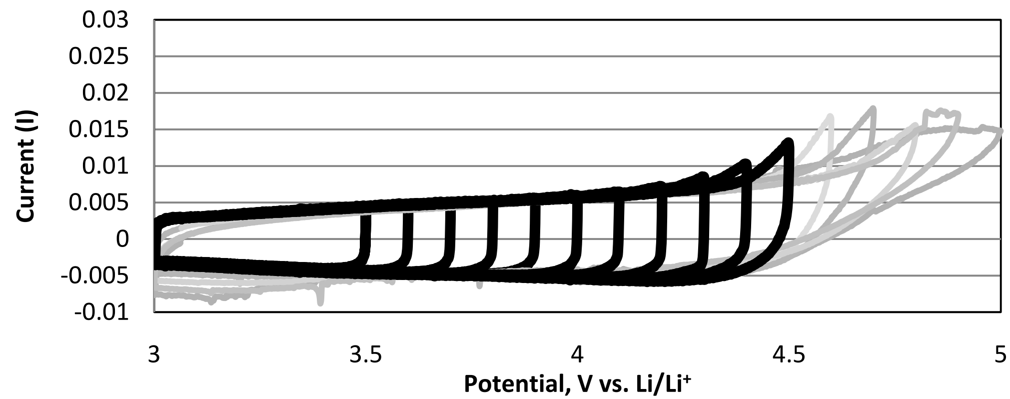
1st Generation Electrolyte (LiPF$_6$ in EC:PC:DEC)



Electrolyte A

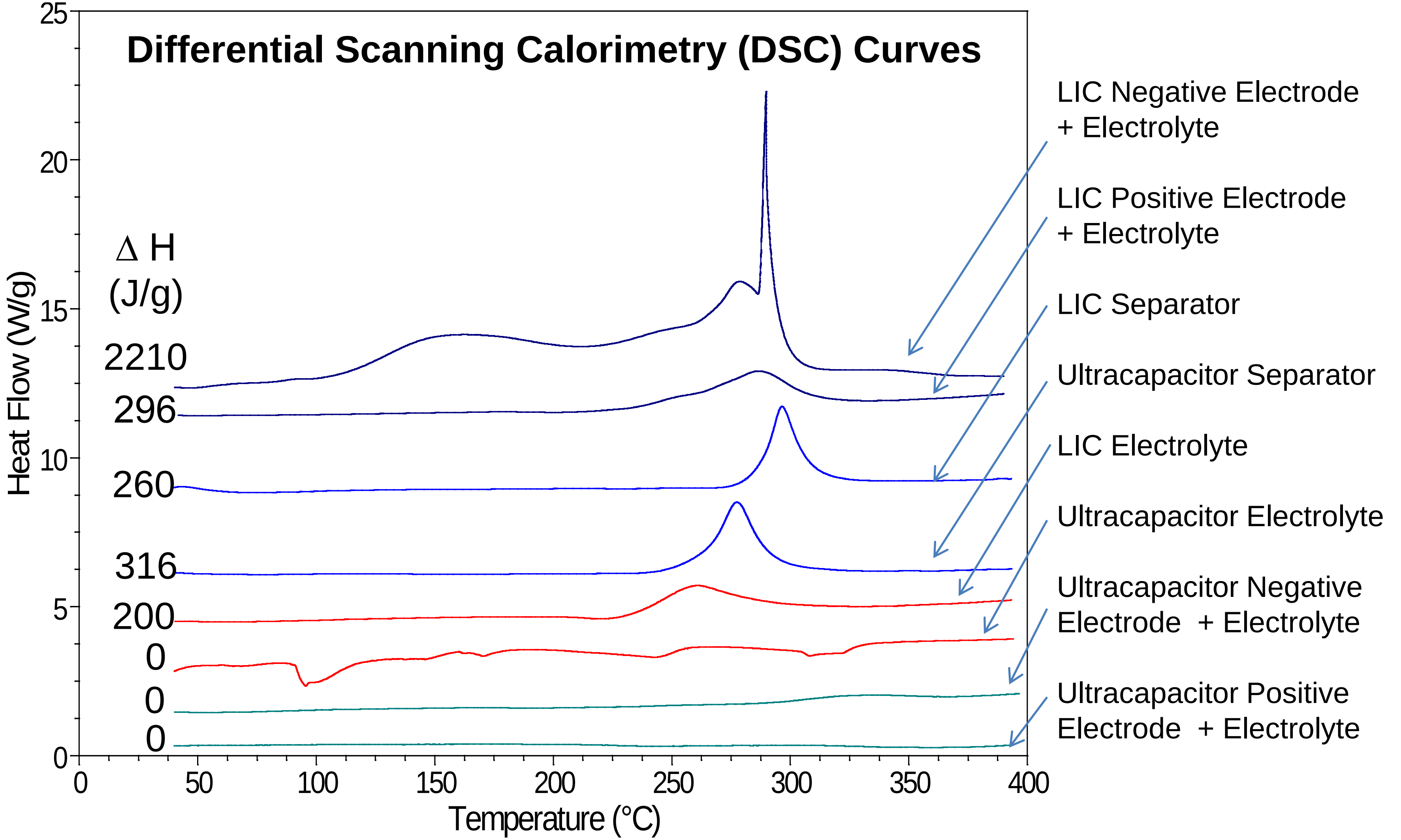


Electrolyte B



All three electrolytes are stable to ~ 4.5 V vs. a lithium reference.

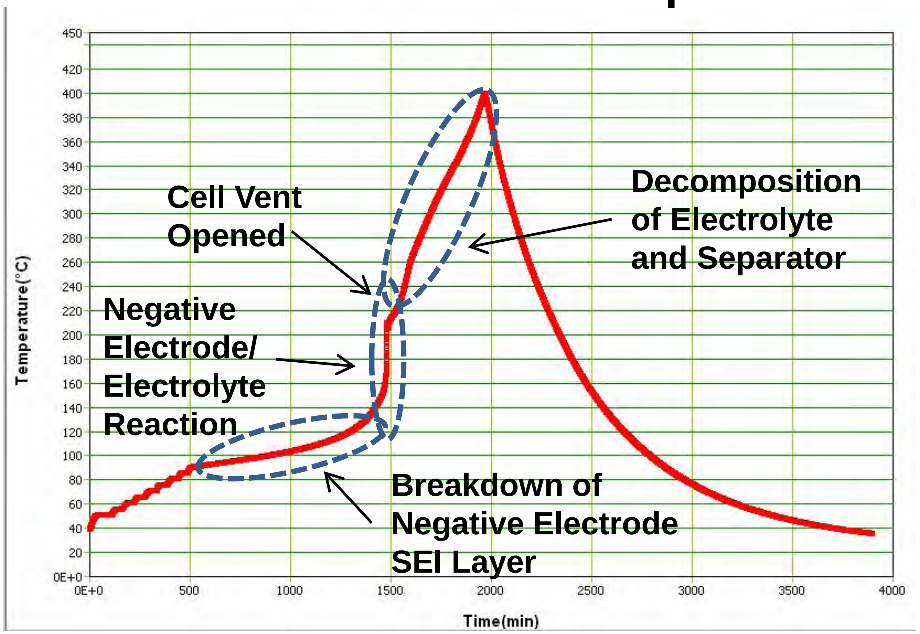
Thermal Stability of Ultracapacitor Materials



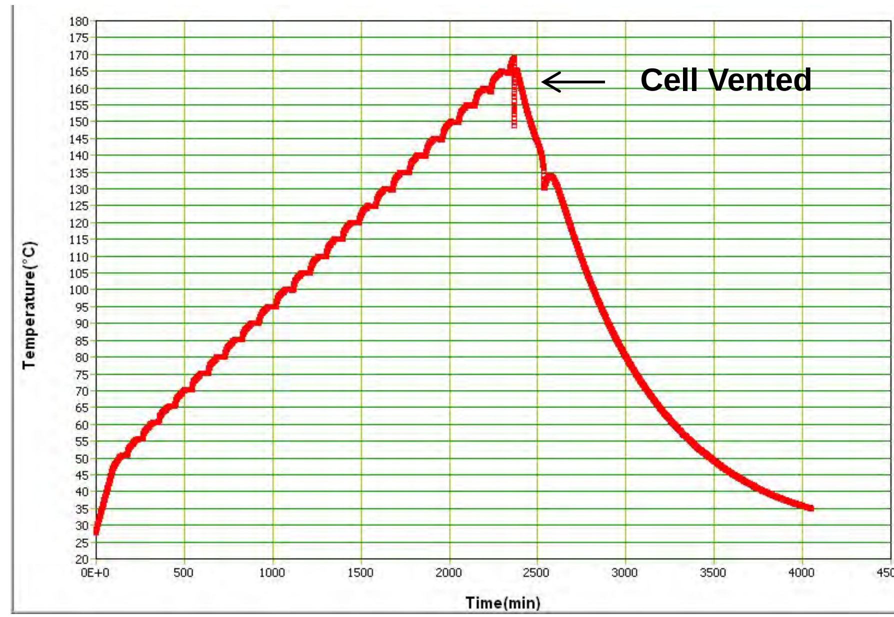
Fully-charged, 1st generation lithium ion capacitor anodes are much less thermally stable than a fully-charged ultracapacitor anode. Other components of the capacitors (fully-charged cathode, separator) displayed similar thermal behavior.

Accelerating Rate Calorimetry (ARC) Study of 2,000F Capacitors

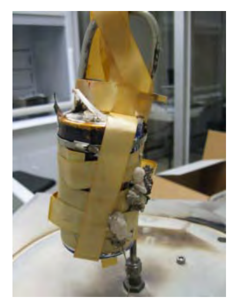
1st Gen. Lithium Ion Capacitor



Conventional Ultracapacitor



Cell Design: Pouch
Electrolyte: $LiPF_6$ in a mixture of ethylene carbonate, propylene carbonate, and diethyl carbonate



Cell Design: Cylindrical
Electrolyte: Et_4NBF_4 in acetonitrile

Self heating occurred in the lithium ion capacitor at ~ 90°C and the cell's vent opened at 210°C. The temperatures reached as high as 400°C during the test. In comparison, the ultracapacitor demonstrated no measureable self heating and vented at 170°C.

Summary

- Three-electrode pouch cells were fabricated using electrodes harvested from the 1st generation 500F cells and containing 1st generation (baseline) electrolyte.
  - The limiting electrode was found to be the positive between at 50^{o} and -20^{o}C.
- A lithium ion capacitor negative electrode was compared to MCMB-28 and KMFC electrodes.
  - The capacitor carbon's irreversible capacity loss with Electrolyte B was found to be significantly higher (31% vs. 9%) than MCMB-28 and KMFC. The reversible capacity after 7 cycles was ~ 450 mAh/g.
- Two carbonate electrolytes were investigated and compared to the 1st generation electrolyte.
  - The new electrolytes A and B displayed ~ 150% and ~ 53% higher conductivity, respectively compared to that of the 1st generation electrolyte at -20^{o}C. This paralleled the capacity/capacitance improvement achieved for both negative and positive cell studies.
- The safety assessment study was initiated
  - DSC data analysis revealed that a fully-charged, 1st generation lithium ion capacitor anode has a lower thermal stability than a fully-charged ultracapacitor anode.
  - ARC data analysis revealed that 1st generation, 2,000F lithium ion capacitor self heating occurred at approximately 90^{o}C.

Future Work FY11-12

- Continue electrolyte solvent systems investigation to identify a system with a wide electrochemical voltage window and good low temperature conductivity.
- Assess safety and performance of new electrolyte system at both cell and material level. Compare to conventional ultracapacitor and lithium ion batteries. Utilize:
  - Solid-state ^{7}Li NMR measurements to determine quantitatively the fraction of Li in the irreversible solid electrolyte interphase (SEI) layer as compared to Li in the active electrode. (Collaborative effort with Hunter College of CUNY)
  - DSC to determine the exothermicity of electrode/ electrolyte reactions (ΔH).
  - ARC to determine thermal behavior of cells.
- Evaluate the stability of the 1st generation negative material. Identify higher energy, high-power density negative electrode materials for next generation lithium ion capacitor. (Collaboration with U of Mass.- Boston, Cabot, Ener2)
- Assess performance (energy/power) limitations of 2nd generation technology. Identify cell limitations.

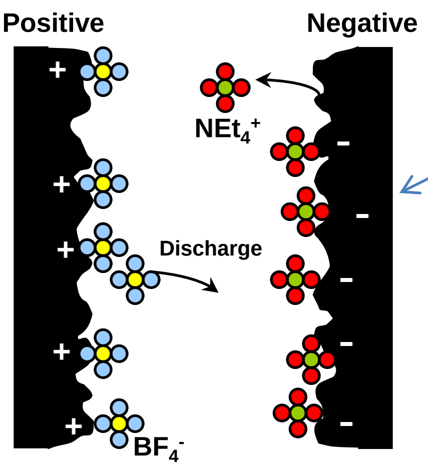
Acknowledgements

The support of this work from DOE-EERE, Office of Vehicle Technologies (Mr. David Howell and Mr. Tien Duong) is gratefully acknowledged.

TECHNICAL BACK-UP SLIDES

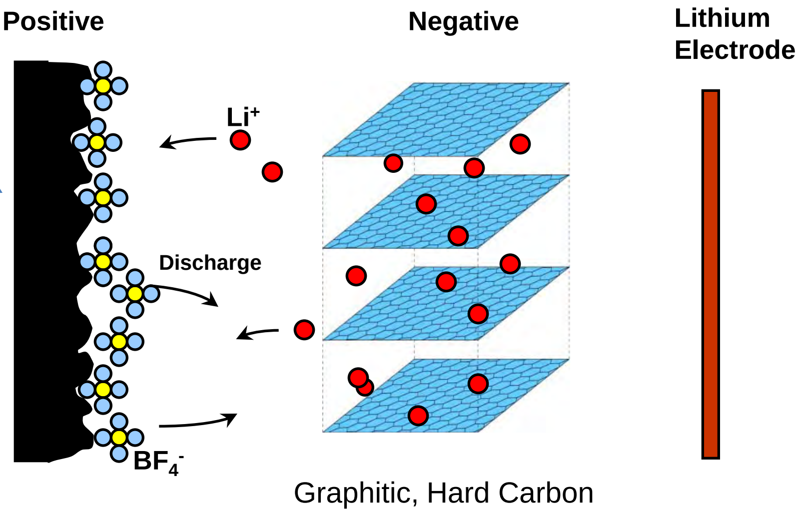
Comparison of Conventional Ultracapacitor and Lithium Ion Capacitor

Conventional Ultracapacitor



High Surface Area
Activated Carbon

Lithium Ion Capacitor (LIC)

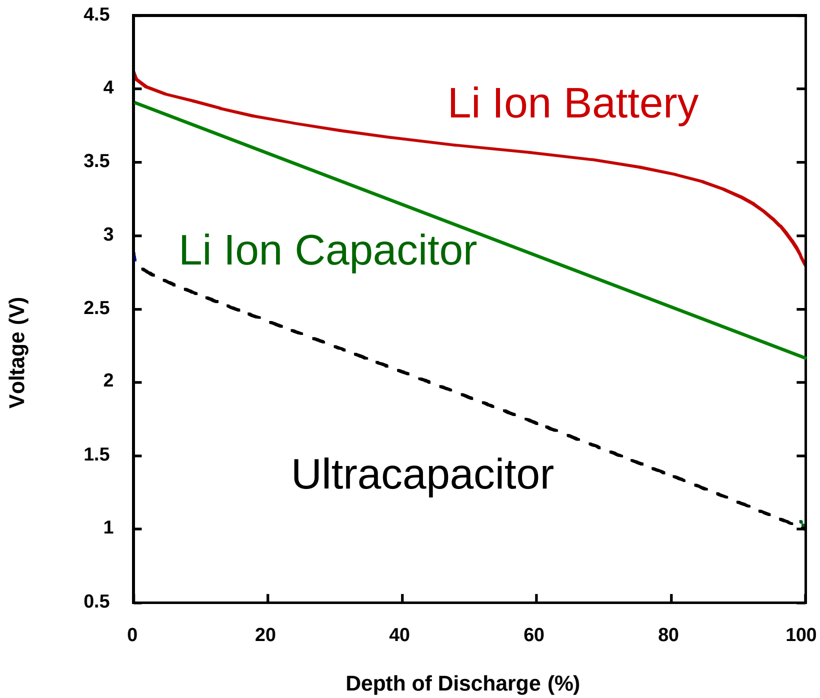


- 2 Non-Faradaic electrodes
- Energy stored electrostatically at the interface of electrolyte and electrodes
- High cycle life and long service life
- High power density
- Low energy density

- Combines Faradaic and non-Faradaic electrodes
- Higher energy density than conventional ultracapacitors due to increased capacitance and operating voltage, $E= 1/2CV^2$
- Requires sacrificial lithium electrode to pre-charge negative

Voltage Comparisons

Cell Discharge Profiles of Various Electrochemical Devices



Voltage Swing of Individual Capacitor Electrodes