High Energy Density Ultracapacitors

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NAVSEA NAVAL SEA SYSTEMS COMMAND

This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Project start date: 2008
- Project end date: 2012
- 35% Complete

Budget

- Funding received in FY09: $250K
- Funding for FY10: $250K
- Project cost shared by Navy

Barriers

- Energy Density
- Cycle Life
- Affordability
- Shelf Life
- Abuse Tolerance

Collaborators

Within DOE Program

- Deyang Qu
  - University of Massachusetts, Boston
  - Assessment of carbon materials

Outside of DOE Program

- Steven Dallek
  - G.J. Associates
  - Thermal stability of electrode materials
- Stephen Lipka
  - University of Kentucky
  - Inexpensive carbon materials
- Curtis Martin, Rebecca Smith
  - NSWC-CD
  - X-ray diffraction, Prototype safety tests
- Robert Waterhouse
  - ENTEK Membranes
  - Electrode Materials
- Linda Zhong
  - Maxwell Technologies
  - Prototype LIC cells

Why Ultracapacitors?

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

- Reduces battery operating current. Lower I^2R heating.
- Reduces power pack weight.
- Extends 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
1

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 50^{o}C operational temp.
  - -46 to 65^{o}C survivability temp.

Approach

- Identify high capacity/capacitance electrode materials to increase the energy density of ultracapacitors. Understand the physico-chemical properties responsible for high capacity/capacitance.

- Develop electrolyte solvent systems that have a wide electrochemical voltage window and will allow the cell to meet cycle life and operating temperature goals.

- Evaluate reactivity of electrode materials with electrolyte.

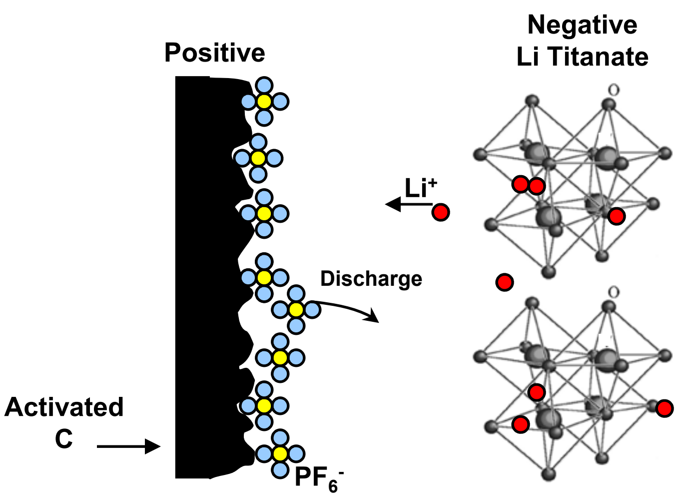
- Fabricate and evaluate prototype capacitors in order to assess energy density, cycle life, self-discharge and safety.

Candidate Systems: Li Ion Capacitors

Combines Lithium Ion Battery-Type Anode (-) with Capacitor Carbon Cathode (+)

Lithium Titanate Anode

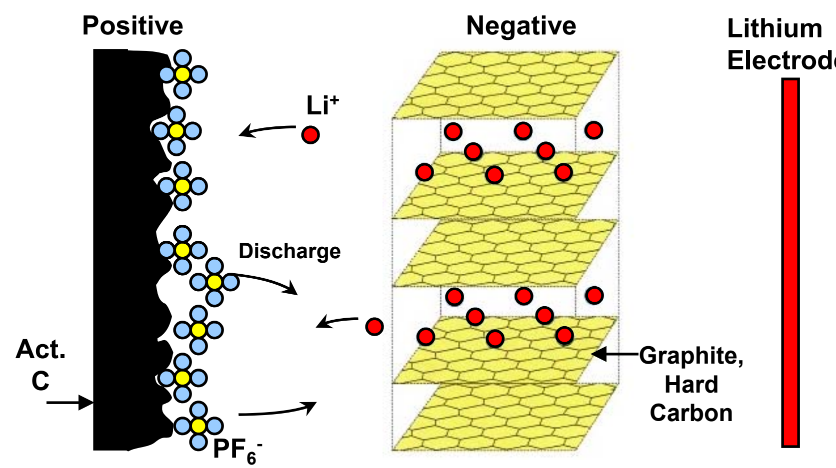
- Outstanding cycle life (1M cycles) due to the $Li_4Ti_5O_{12}$ spinel structure. Exhibits < 1% volume change during intercalation/de-intercalation.
- Nanomaterial exhibits high rate capability.



G. Amatucci, J. Electrochem. Soc., 148(8), A930, 2001.

Hard or Graphitic Carbon Anode

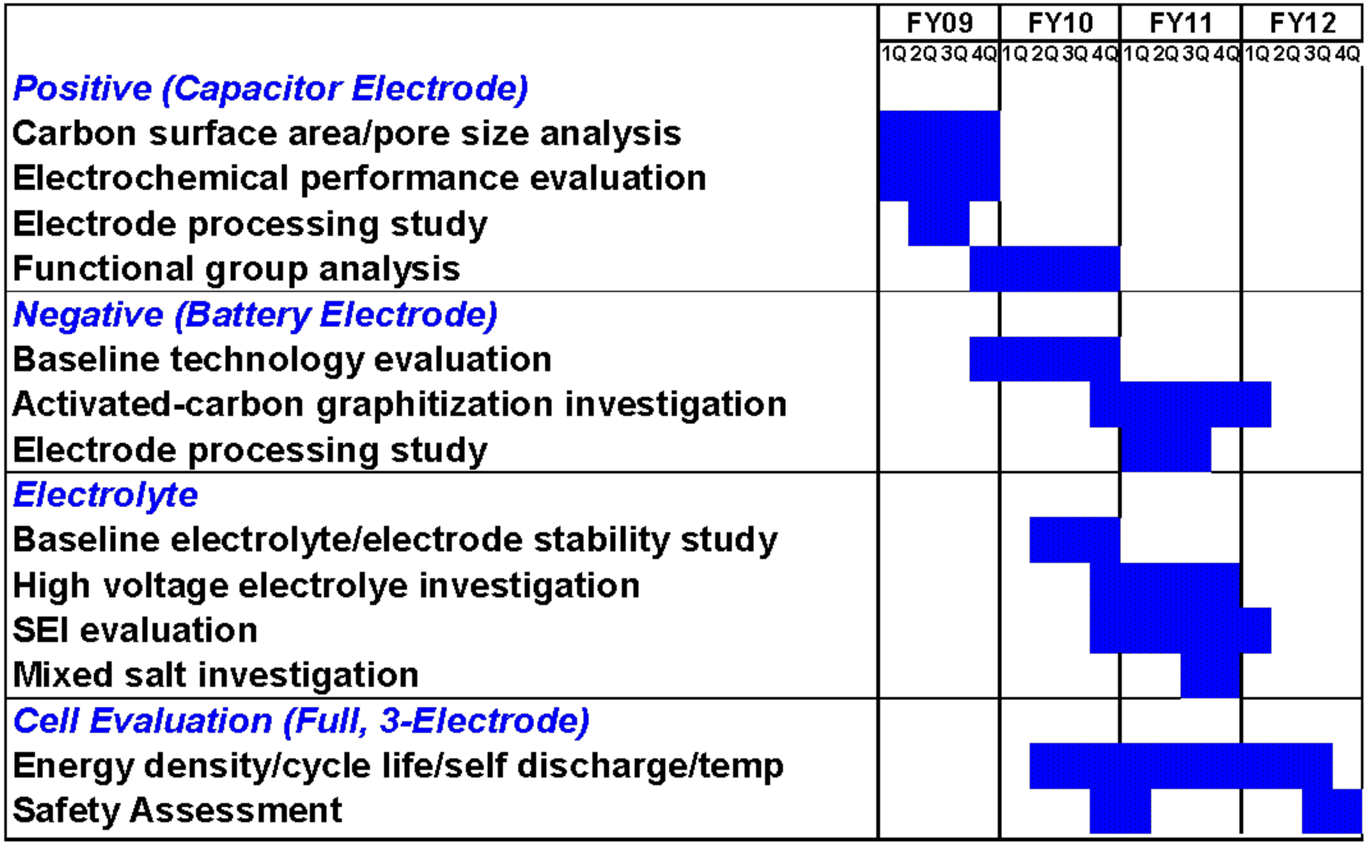
- Requires sacrificial Li electrode to pre-charge negative.
- Demonstrates high operating voltage due to low negative potential of Li_xC_6.
- In theory, greater energy density than titanate. At expense of cycle life and safety?



A. Yoshino, J. Electrochem. Soc., 151(12), A218, 2004.

Both systems would benefit from higher-capacitance activated carbons (+ electrode).

Milestones



FY09 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). Carbon was distributed to various electrode manufacturers. Electrodes utilizing PTFE binder yielded highest capacitances.

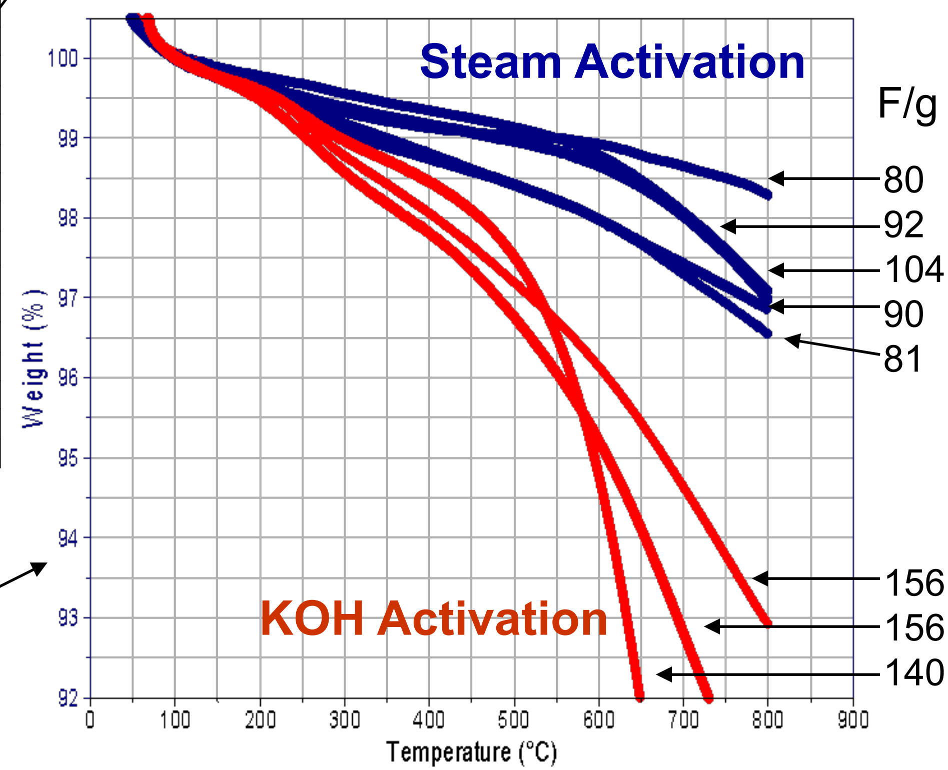
Evaluation of Activated Carbons For Positive Electrode

Capacitance of Various Activated Carbon Electrodes (+)

2" X 3" Symmetric Cells, Cells Charged at $1 mA/cm^2$ and Discharged at $10 mA/cm^2$. Capacitance of 50th discharge

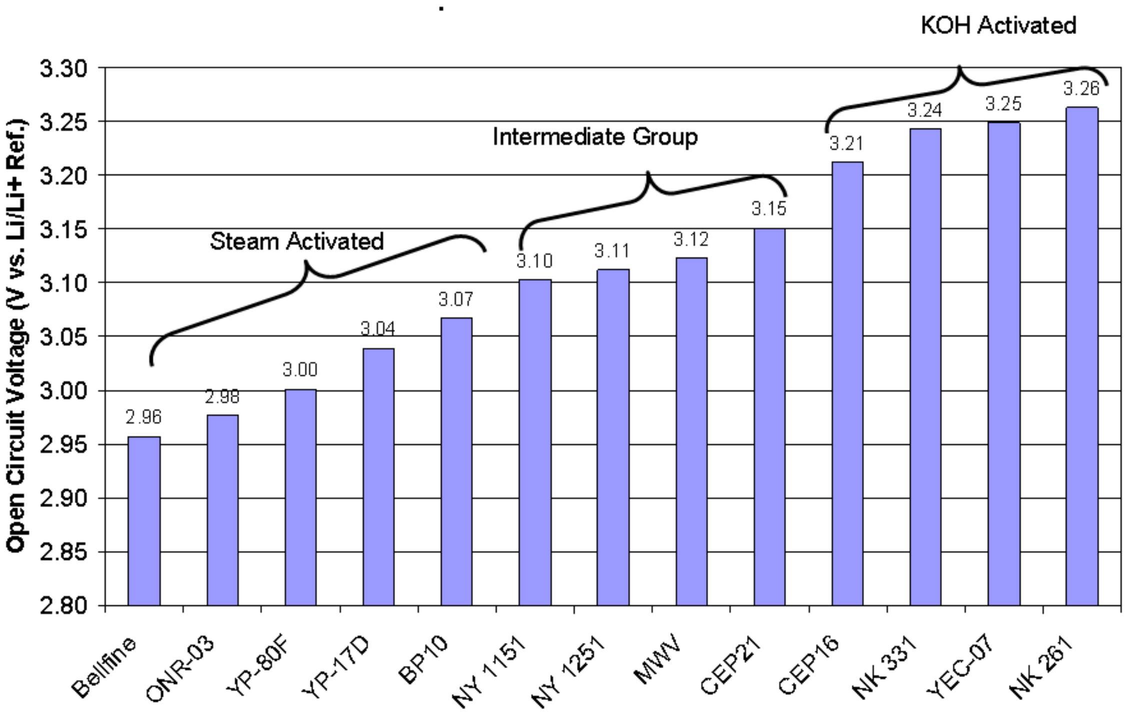
Carbon (% active material)	Carbon Supplier	Binder	1M $LiPF_6$ 50%EC:50%EMC (F/g)	2M $LiBF_4$ AN (F/g)
Grade 1 (100)	MarkeTech International	none	22	28
RP-15 (92)	Kuraray	UHMWPE	83	90
YP-18X (84)	Kuraray	UHMWPE	87	92
YP-17D (82)	Kuraray	UHMWPE	83	88
NK-260 (80)	Kuraray	UHMWPE	85	154
NK-261 (82)	Kuraray	UHMWPE	100	156
NK-331 (80)	Kuraray	UHMWPE	TBD	140
Nuchar RGC (80)	MeadWestvaco	UHMWPE	86	82
Supra 50 (80)	Norit	UHMWPE	76	81
SX-Ultra (80)	Norit	UHMWPE	52	55
BP-10 (80)	Pica	UHMWPE	77	80
TDA-1 (81)	TDA	PVDF	100	86
TDA-2 (81)	TDA	PVDF	113	101
TDA-3 (81)	TDA	PVDF	104	91
TDA-AMS 62C (81)	TDA	PVDF	99	100
Generation 1 (80)	U of Kentucky	PVDF	TBD	86
Generation 2 (82)	U of Kentucky	UHMWPE	TBD	98
YEC-07 (82)	Fuzhou Yihuan	UHMWPE	TBD	156
LIC Present Tech.	Proprietary	Proprietary		120

Last Year:
High capacitance (>150F/g) achieved with carbons activated by KOH



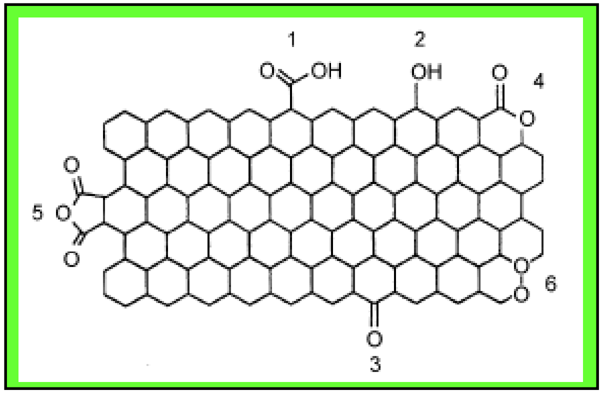
This year:
Thermogravimetric analysis (TGA) results show a correlation between weight loss and electrochemical performance.

Correlation of Open Circuit Voltages and Functional Groups



In collaboration with R. Waterhouse, Entek

Functional Groups

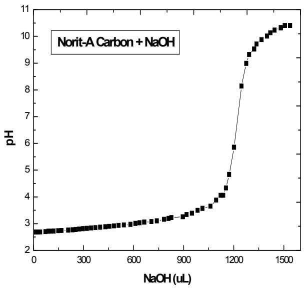


1. carboxyl, 2. phenolic, 3. quinone, 4. lactone, 5. carboxyl anhydride, 6. peroxide

Functional Groups Affect:

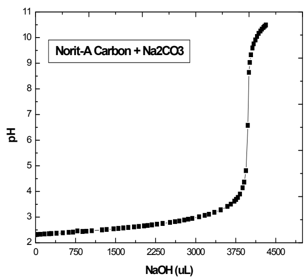
- Capacitance (Redox Reactions)
- Wet-ability
- Open Circuit Voltage
- Voltage Decay
- Cyclability (Electrolyte Decomposition)

Characterization of Carbon Surface Functional Groups by Boehm Titrations



0.05 M NaOH (Sodium Hydroxide)

Neutralizes carboxylic, lactonic and phenolic groups



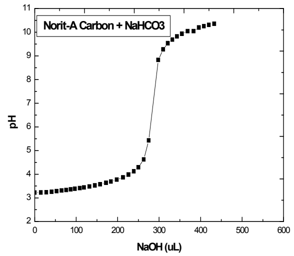
0.05 M Na_2CO_3 (Sodium Carbonate)

Neutralizes carboxylic and lactonic groups

Results of Boehm Titration (meq./100g)

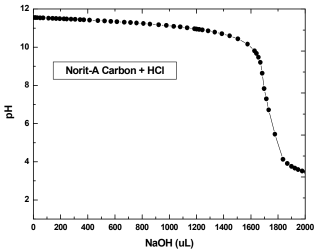
Sample	Carboxylic	Lactonic	Phenolic	Basic	Acidic	All Groups
M-20	11.7	13.5	7.8	45.5	33.0	78.5
Nor-A	7.4	9.5	0.2	58.2	17.1	75.3
Calgon-PWA	10.4	9.1	0.0	43.5	16.4	59.9
M-30	21.5	8.0	4.2	33.7	77.2	110.9
Kuraray-(YP-17D)	2.9	-	28.0	48.7	28.7	77.6
Norit SX Ultra	-	2.39	1.53	42.5	3.74	46.24

In collaboration with Deyang Qu, U of Mass.



0.05 M $NaHCO_3$ (Sodium Bicarbonate)

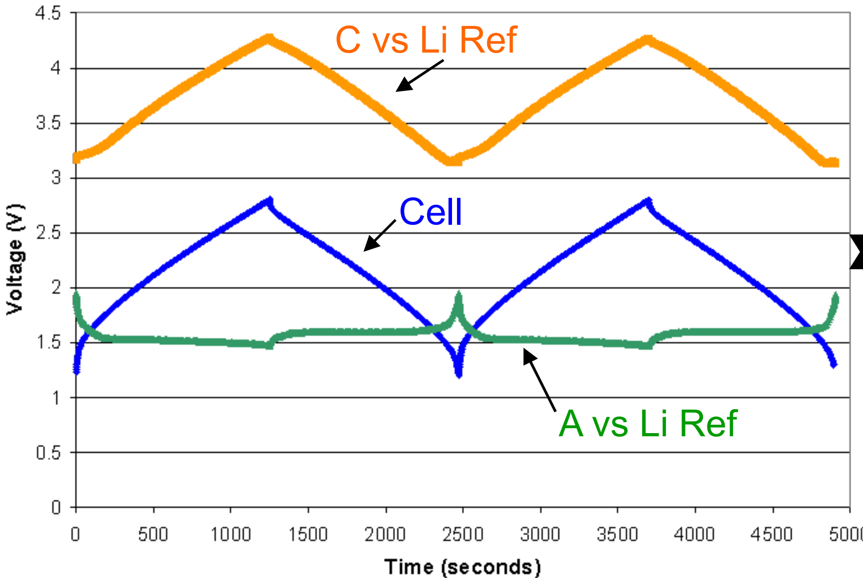
Neutralizes only carboxylic groups



0.05 M HCl (Hydrochloric Acid)

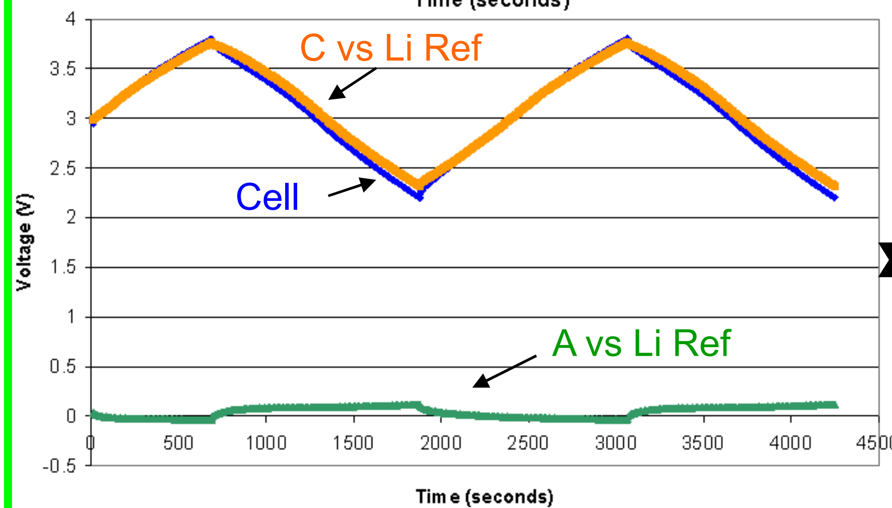
Neutralizes all basic groups

Comparison of Li Ion Capacitors



Lithium Titanate Anode
Activated Carbon Cathode

- Energy Density: **<u>10</u>**-15 Wh/kg
- Power Density: 1000-2000 W/kg
- Cycle Life: >100,000 cycles (1,000,000 cycles demonstrated in laboratory cells- G. Amatucci)

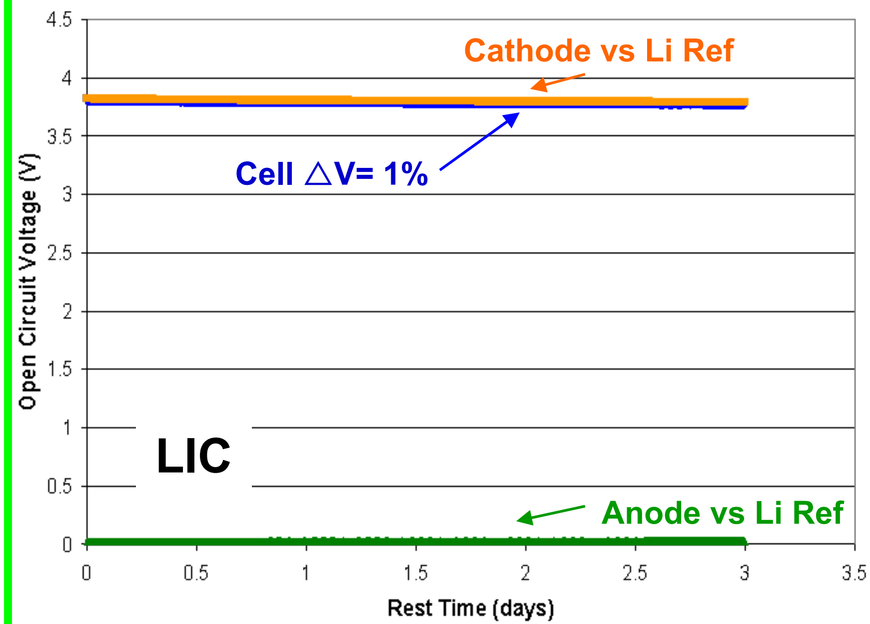


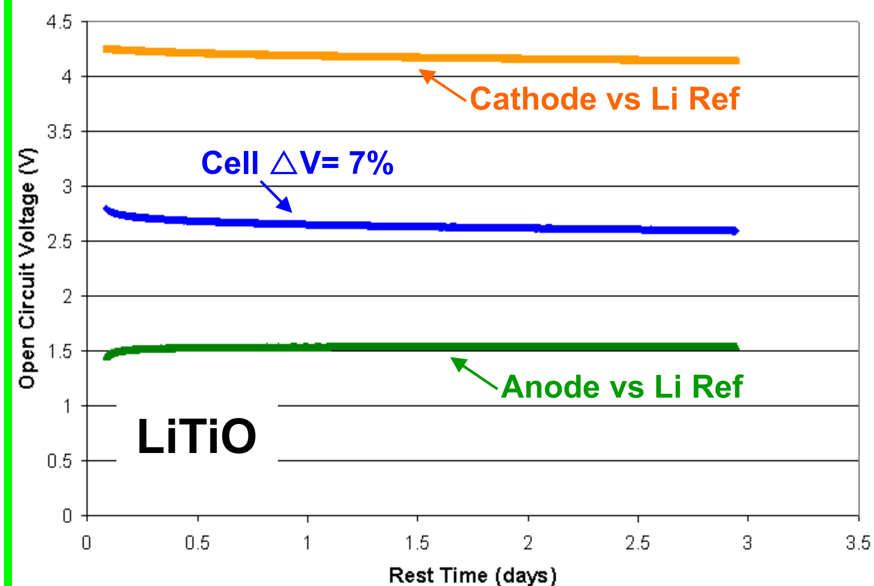
Graphitic or Hard Carbon Anode
Activated Carbon Cathode
(LIC)

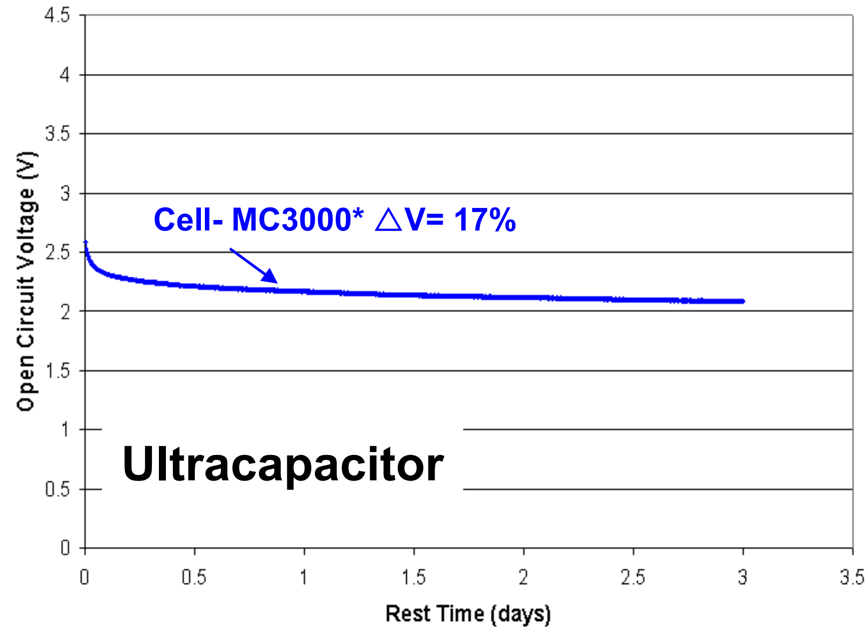
- Energy Density: 10-**<u>15</u>** Wh/kg
- Power Density: 1000-3000 W/kg
- Cycle Life: 100,000 cycles

Lithium ion capacitors display high energy density, high power density and long cycle life.
Conventional ultracapacitors: 3-5 Wh/kg, 1000 –6000 W/kg, 500,000 - 1M cycles

Capacitor Voltage Decay at 25°C



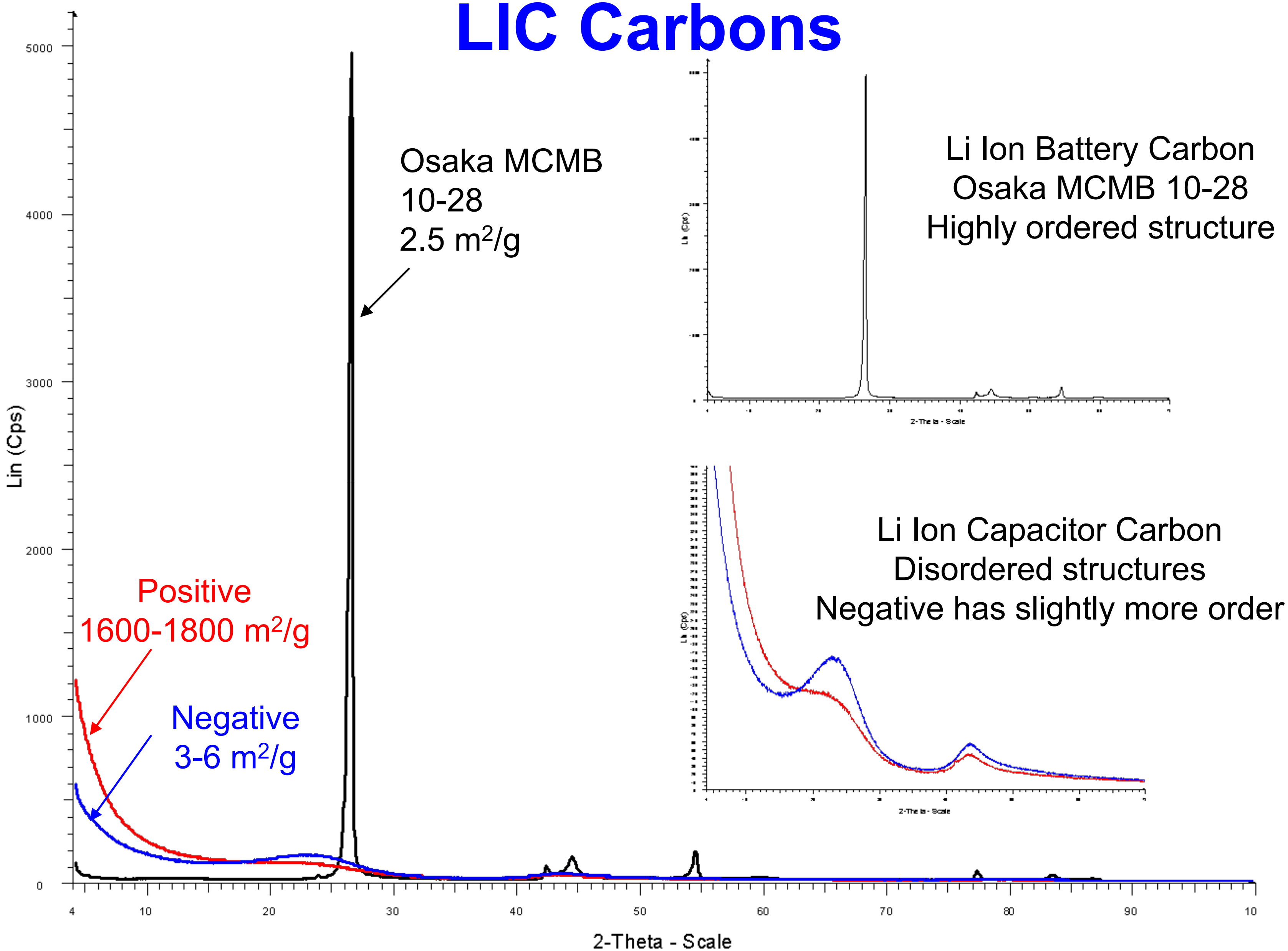




Self discharge of lithium ion capacitors found to be lower than conventional ultracapacitors.

*Ultracapacitor data courtesy of Linda Zhong, Maxwell Technologies

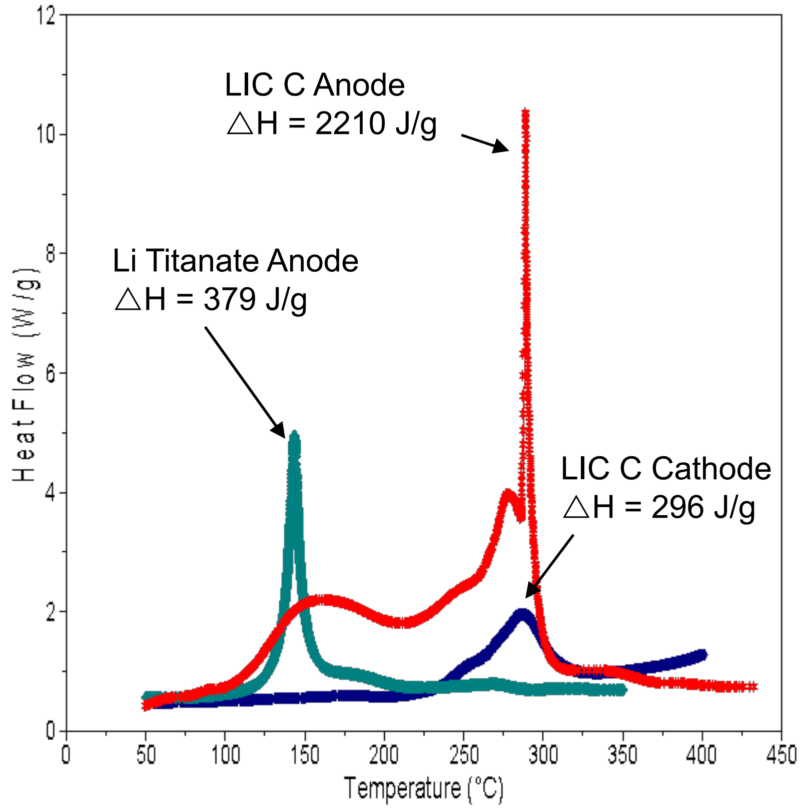
X-Ray Diffraction Pattern Of Baseline LIC Carbons



Thermal Stability of Ultracapacitor Materials

Exothermicity of Electrode/Electrolyte Reactions

Differential Scanning Calorimetry (DSC) of Fully Charged Electrodes



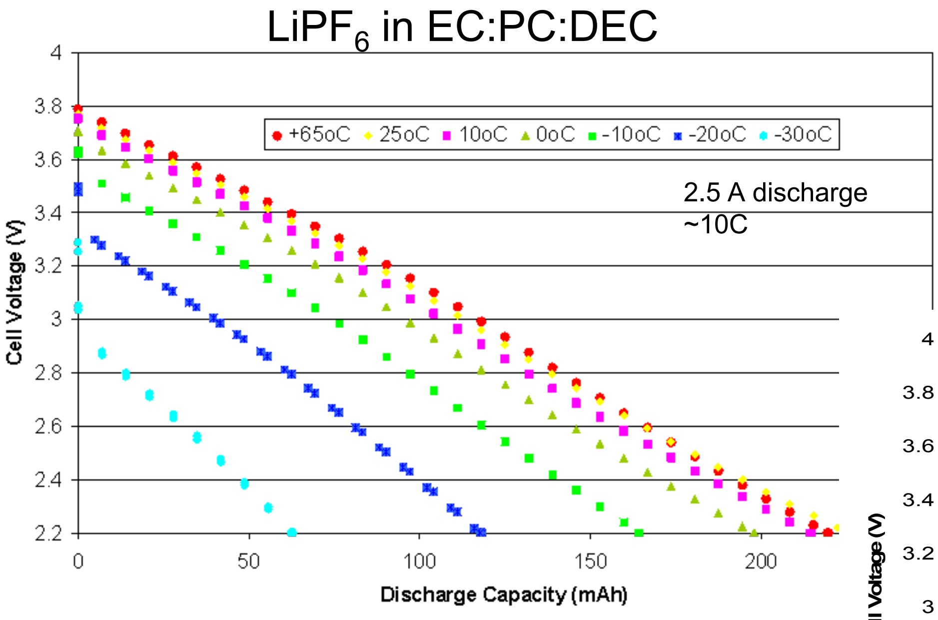
Literature Values

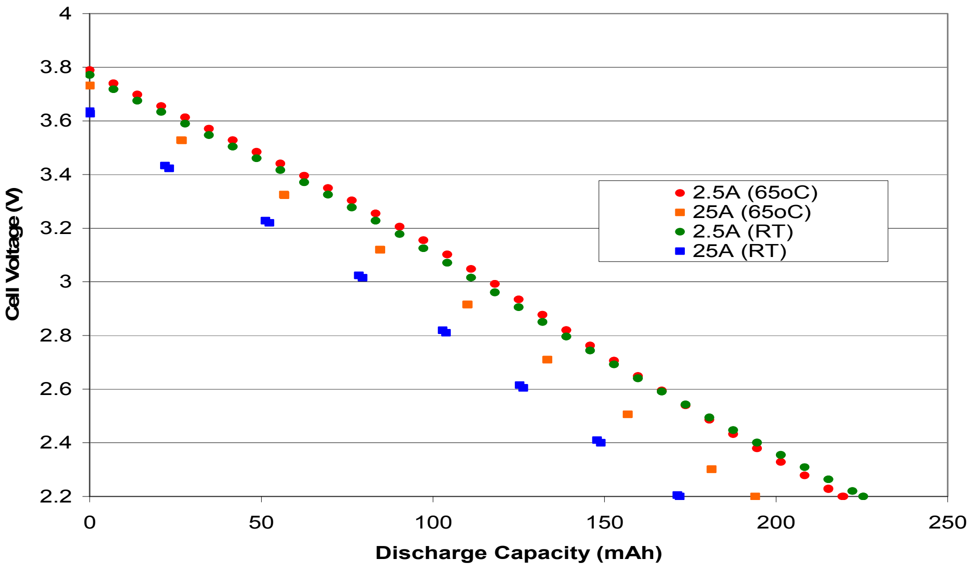
Electrode	△H (J/g)
Lithium Titanate Anode	383*
Graphitic Carbon Anode	2750*
$Li_{0.55}(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$	790**

* I. Belharouak, Y.-K. Sun, W. Lu, K. Amine, J. Electrochem. Soc. 154 (2007) A1083.
**I. Belharouak, Wenquan Lu, Jun Liu, D. Vissers, K. Amine, J. Power Sources, 174, 905 (2007).

- Exothermicity: Amorphous LIC anode < graphitic, lithium ion battery anode
- NSWC and Argonne National Lab △H values for lithium titanate virtually identical
- Capacitor carbon cathode △H value < typical battery cathode material

Effect of Temperature and Discharge Rate on LIC Capacity





- Excellent high temperature performance. Observed 30,000 cycles at 200C rate, 65^{o}C.
- Poor low temperature performance points to a need for improved electrolytes
- Use “lessons learned” from lithium-ion battery development efforts

Summary

- Investigations are underway to develop lithium ion asymmetric electrochemical capacitors. Promises significantly higher energy densities (>20 Wh/kg) than conventional symmetric C/C capacitors (3-5 Wh/kg).
- Higher energy densities achieved with lithium Ion capacitor prototypes utilizing carbon negative electrodes than with lithium titanate electrodes.
- Reactivity of fully-lithiated, amorphous LIC anode and electrolyte is less than a fully-lithiated, graphitic Li ion battery anode and electrolyte ($\triangle H$ = 2210 J/g and 2750 J/g, respectively). LIC anode >> LiTO.
- Shelf discharge of lithium ion capacitors (1-7%) found to be lower than that of conventional ultracapacitors (17%).
- Lithium ion capacitors display poor low temperature performance in comparison to conventional ultracapacitors (activated carbon/activated carbon).

Future Work (FY10-11)

- Continue carbon functional group analysis. Identify groups using TGA/MS. Determine if there is a correlation between nature of functional groups and electrochemical performance (capacity, voltage decay)

- Complete assessment of lithium ion capacitor (LIC and LiTO) baseline electrochemistry. Cells will undergo a series of electrochemical experiments (galvanostatic cycling, cyclic voltammetry, AC impedance) to evaluate the benefits and limitations of the two systems.

- Extend voltage decay investigation to -30^{o}C and 65^{o}C. Identify source of low-temperature performance using 3-electrode cells.

- Explore the effect of activated carbon graphitization on cell performance (capacity, rechargeablility). Understand the properties of the SEI layer that forms.

- Initiate electrolyte solvent system investigation to identify a system with a wide electrochemical voltage window

- Assess safety (at both cell and material level). Compare to conventional ultracapacitors and lithium ion batteries.

Acknowledgement

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