Performance of Advanced Ultracapacitors and Prospects for Higher Energy Density

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45th Power Sources Conference
Las Vegas, Nevada
June 11-14, 2012

Outline of the Presentation

- Introduction
- Recent test data for carbon/carbon devices
- Projections using advanced activated carbons
- Recent test data for hybrid ultracapacitors
- Conclusions

Recent test data for new devices with higher performance

These devices have significantly higher energy density and/or higher power capability than presently available devices.

- lower resistance coatings
- higher F/g activated carbon
- graphitic carbons
- lithiated graphite
- electrolytes allowing increased voltage
- carbon/metal oxide material mixes

Summary of ultracapacitor device characteristics

Device	V rate	C (F)	R (mOhm) (3)	RC sec	Wh/kg (1)	W/kg (95%) (2)	W/kg Match. Imped.	Wgt. (kg)	Vol. lit.
Maxwell	2.7	2885	.375	1.1	4.2	994	8836	.55	.414
Maxwell	2.7	605	.90	.55	2.35	1139	9597	.20	.211
Vinatech	2.7	336	3.5	1.2	4.5	1085	9656	.054	.057
Vinatech	3.0	342	6.6	2.25	5.6	710	6321	.054	.057
Ioxus	2.7	3000	.45	1.4	4.0	828	7364	.55	.49
Ioxus	2.7	2000	.54	1.1	4.0	923	8210	.37	.346
Skeleton Technol.	2.85	350	1.2	.42	4.0	2714	24200	.07	.037
Skeleton Technol.	3.4	840	.58	.49	6.7	3846	34364	.145	.097
Yunasko*	2.7	510	.9	.46	5.0	2919	25962	.078	.055
Yunasko*	2.75	480	.25	.12	4.45	10241	91115	.060	.044
Yunasko*	2.75	1275	.11	.13	4.55	8791	78125	.22	.15
Yunasko*	2.7	7200	1.4	10	26	1230	10947	.119	.065
Yunasko*	2.7	5200	1.5	7.8	30	3395	30200	.068	.038
Ness	2.7	1800	.55	1.0	3.6	975	8674	.38	.277
Ness	2.7	3640	.30	1.1	4.2	928	8010	.65	.514
Ness (cyl.)	2.7	3160	.4	1.3	4.4	982	8728	.522	.379
LS Cable	2.8	3200	.25	.80	3.7	1400	12400	.63	.47
BatScap	2.7	2680	.20	.54	4.2	2050	18225	.50	.572
JM Energy	3.8	1100 2300	1.15 .77	1.21 1.6	10 7.6	2450 1366	21880 12200	..144 .387	.077 .214

(1) Energy density at 400 W/kg constant power, Vrated - 1/2 Vrated

(2) Power based on P=9/16*(1-EF)*V2/R, EF=efficiency of discharge

(3) Steady-state resistance including pore resistance

* All devices except those with * are packaged in metal/plastic containers: those with * are laminated pouched packaged

Skeleton Technologies 900F

Skeleton 900F Device characteristics

Carbon/carbon, acetronitrile 3.4V

Packaged Weight 145 gm, volume 97 cm3

Constant current discharge

Current A	Time sec	Capacitance F	Resistance mOhm Steady-state R	RC sec
20	70.9	844	----	---
40	35.2	838	----	---
80	17.2	839	----	---
120	11.3	837	.54	.45
200	6.6	838	.58	.49
300	4.2	840	.60	.50
350	3.5	842	---	---

Discharge 3.4V to 0V , resistance calculated from extrapolation of the voltage to t=0

Constant power discharge

Power W	W/kg	Time sec	Wh	Wh/kg	Wh/L
45	309	76	.95	6.52	9.9
82	563	43.2	.983	6.74	10.2
123	845	28.5	.974	6.69	10.2
185	1271	18.8	.966	6.63	10.1
244	1675	13.9	.942	6.48	9.8
302	2074	10.9	.914	6.27	9.5
351	2410	9.2	.897	6.16	9.3
400	2747	8.0	.889	6.11	9.3

Discharge 3.4V to 1.7V

95% efficiency pulse

$P = 9/16 \times (1 - eff)\, V_0^{\,2}/R = 9/16 \times (.05)\,(3.4)^2/.00058 = 560W$

(W/kg) = 560/.145 = 3846

UCDAVIS ITS

SPC carbon from Lipka at the University of Kentucky

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Our research group has prepared carbon spheres ranging from 50 nm to about 10 μm using a variety of commercial sugars and industrial biomass products. The HTS has very good conversion yields (C in/out ~ 90%). Finally, functional groups have been added to the sphere surface which greatly improves hydrophilicity and chemical reactivity.

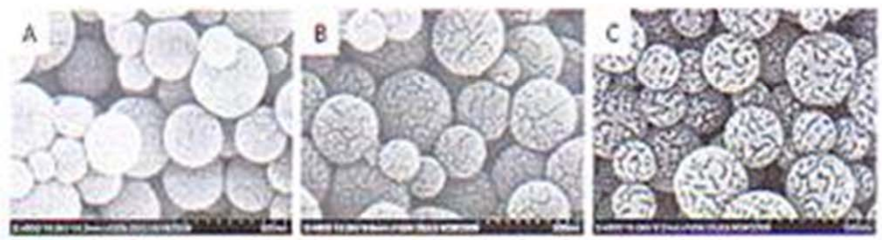

Figure 1. Representative electron micrographs showing (A) pristine carbon nanospheres prepared by HTS, (B) carbon spheres after carbonization, (C) carbon spheres after graphitization

Coin cell using 1.5M TEMABF4 in PC; Activated carbon from Steve Lipka, University of Kentucky, USA

Active material: 17 mg. Testing: constant current from 1-8 mA, charge to 2.7V, discharge to 1.35V, 10 cycle per current. Constant current at 30 mA

Current	Current	Discharging Time	Capacitance
mA	mA/g	sec.	F/g (AM)
1	59	1003	175
2	118	497	173
3	177	326	170
4	235	242	169
5	295	192	167
6	354	159	166
7	413	136	166
8	471	119	166
For stability			
15	882	63	165
30	1765	29	157

Testing at 30 mA still ongoing. No reduction after 10000 cycles.

F/g	Wh/kg*
75	4.2
100	5.6
125	7.0
150	8.4
175	9.8
200	11.2
225	12.6

*** unpackaged, incl. electrolyte and current collector $V_0 = 2.7V$**

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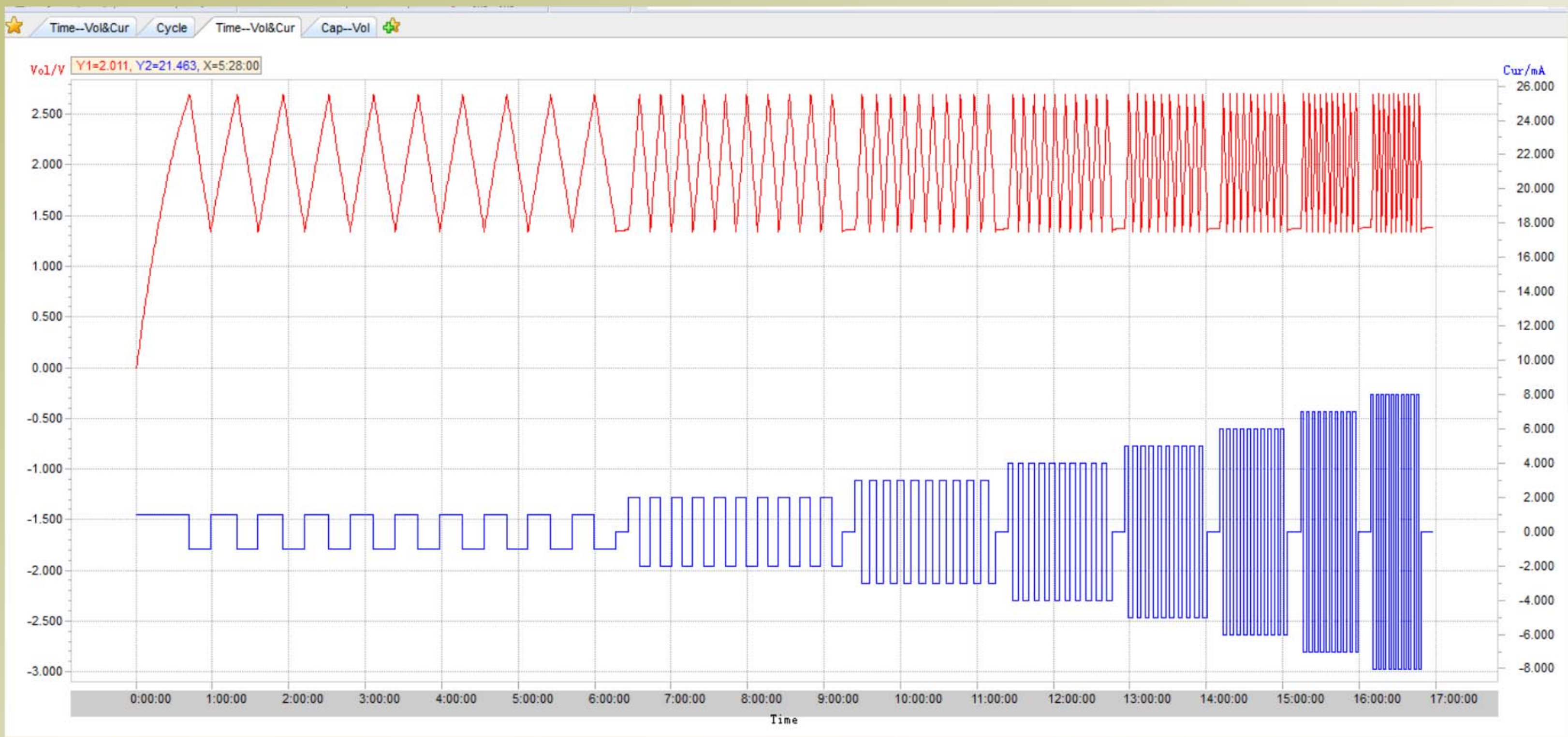
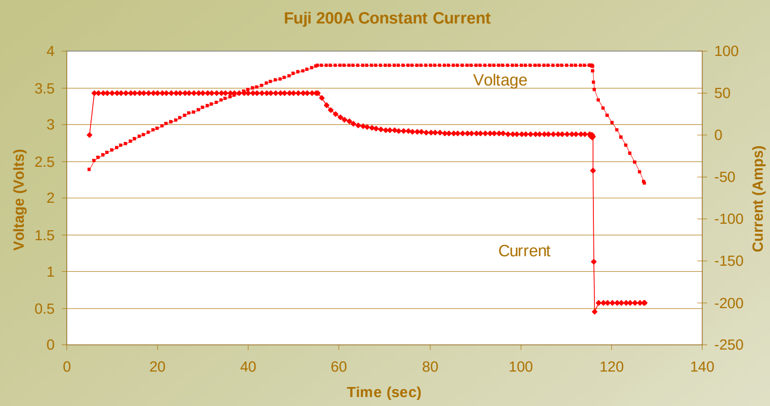
Voltage traces at various constant currents using the UnivKty carbon

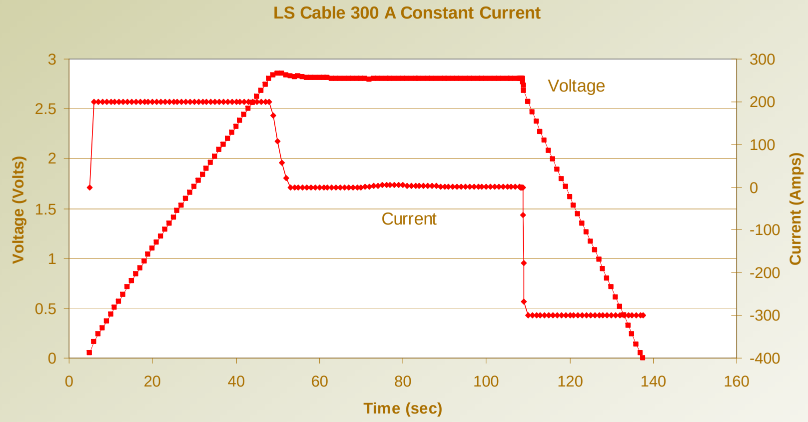


Hybrid ultracapacitor devices

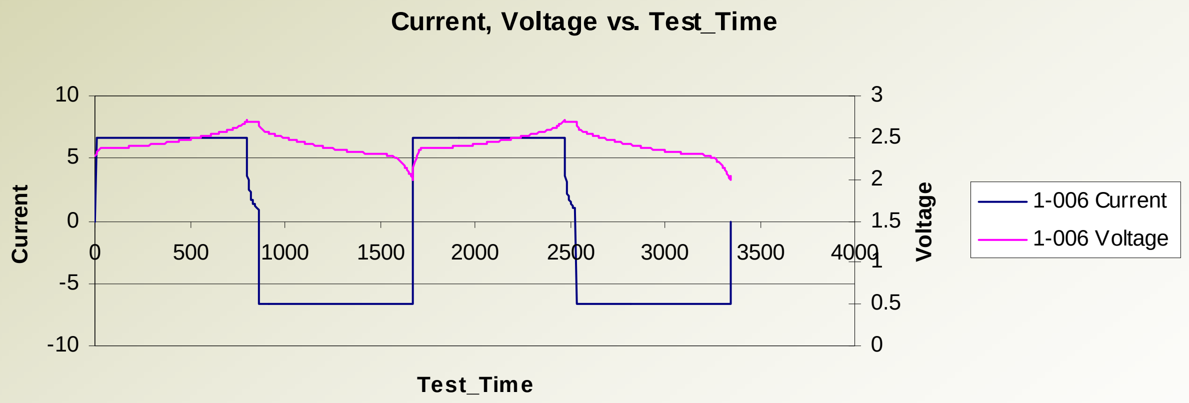
AC Carbon/graphitic carbon



AC carbon/AC carbon



Yunasko hybrid ultracapacitor
(AC carbon mixed with metal oxide in both electrodes)



Photographs of the JM Energy 1100F and 2300F devices

Positive- activated carbon, negative- lithiated graphitic carbon

Characteristics of the JM Energy 1100F ultracap cell

Constant Current discharge 3.8V – 2.2V

Current (A)	Time (sec)	C(F)	Resistance (mOhm) **
20	86.4	1096	
40	41.9	1078	
60	27.2	1067	
75	21.4	1063	1.2
100	15.7	1057	1.15
150	10.1	1056	1.1

** Resistance is steady-state value from linear V vs. time discharge curve

Constant Power discharges 3.8V – 2.2V

Power (W)	W/kg	Time(sec)	Wh	Wh/kg *	Wh/L *
50	347	106.7	1.47	10.2	19.1
83	576	61.9	1.43	9.9	18.6
122	847	40.1	1.36	9.4	17.7
180	1250	26.2	1.31	9.1	17.0
240	1667	19.1	1.27	8.8	16.5

* based on the measured weight and volume of the cell as tested
Laminated pouch cell weight 144 gm, 77 cm3, 1.87 g/cm^3

Peak pulse power at 95% efficiency R=1.15 mOhm

P= 9/16*.05* $(3.8)^2$/.00115 = 353 W, 2452 W/kg

Photograph of the 5000F Yunasko hybrid ultracapacitor

Both electrodes activated carbon and metal oxide

Characteristics of the 2012 Yunasko hybrid ultracap/battery

Constant current

	2.7-2.0V					2.7-1.35	
Current A	Time sec	Ah	Resistance short time mOhm		Time sec	Ah	Capacit. F
50	83.7	1.16			88.9	1.25	3556
100	36.1	1.0	1.53		44.9	1.25	3870
150	25.1	1.05	1.59		29.5	1.23	4060
200	7.1	.39			21.1	1.17	3801
250	4.1	.28			15.2	1.06	4130

Constant power

		2.7-2.0V				2.7-1.35		
Power W	W/kg	Time sec	Wh	Wh/kg		Time sec	Wh	Wh/kg
55	743	164	2.5	33.8		172	2.63	35.5
155	2094	58.1	2.5	33.8		62.8	2.7	36.5
252	3405	23.8	1.66	22.4		35.4	2.42	32.7
303	4095	16.6	1.4	18.9		28.3	2.38	32.2
350	4730	11.9	1.16	15.7		22.4	2.18	29.5
400	5405	8.3	.92	12.4		17.3	1.92	25.9
500	6756	4.3	.60	8.1		10.8	1.5	20.3

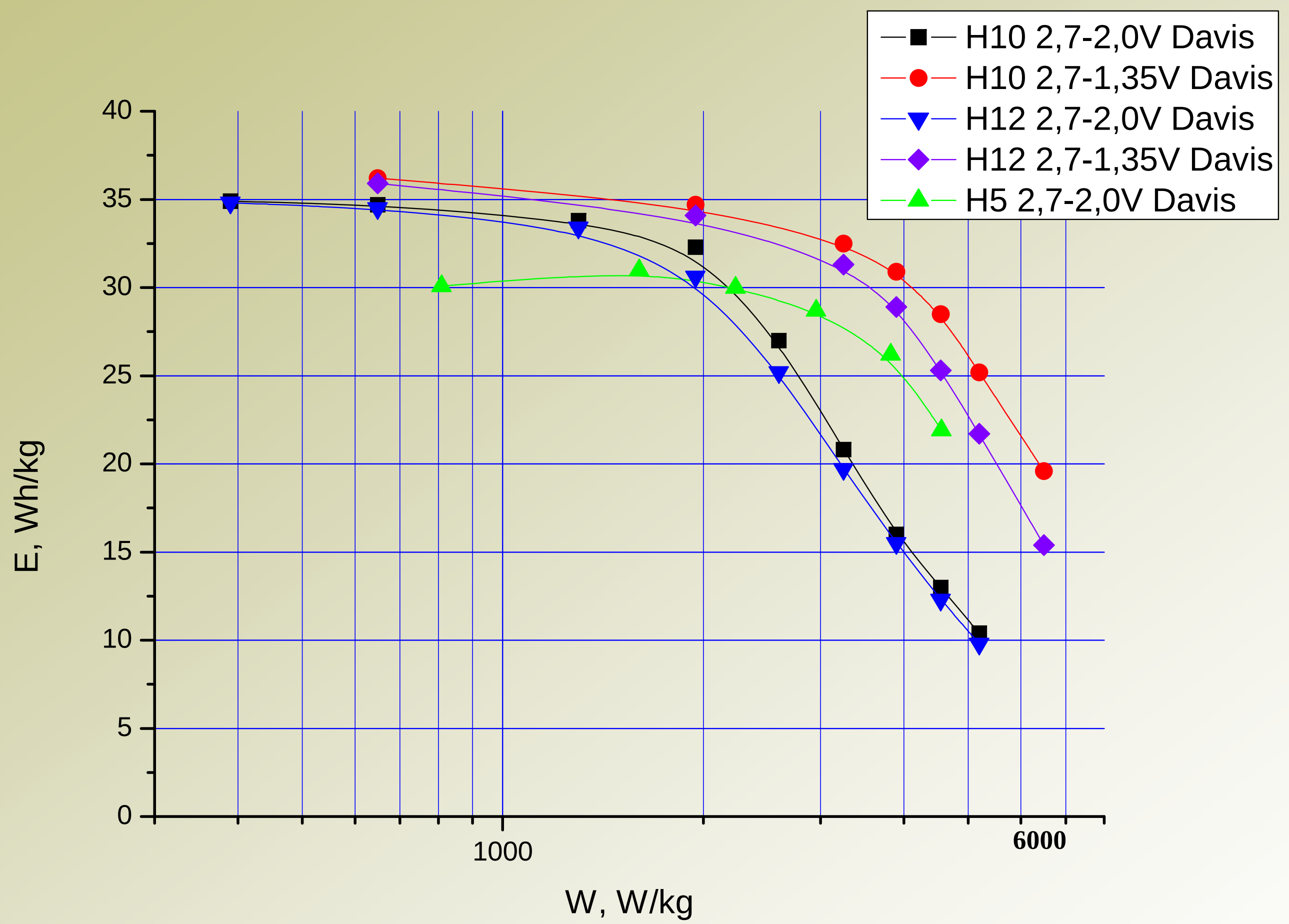
Weight 74 g, volume 38 cm3 pouch packaged

Pulse efficiency 95%

$P = .95x.05\ V^2/R = .95x.05x\ (2.7)^2/.0015 = 231$

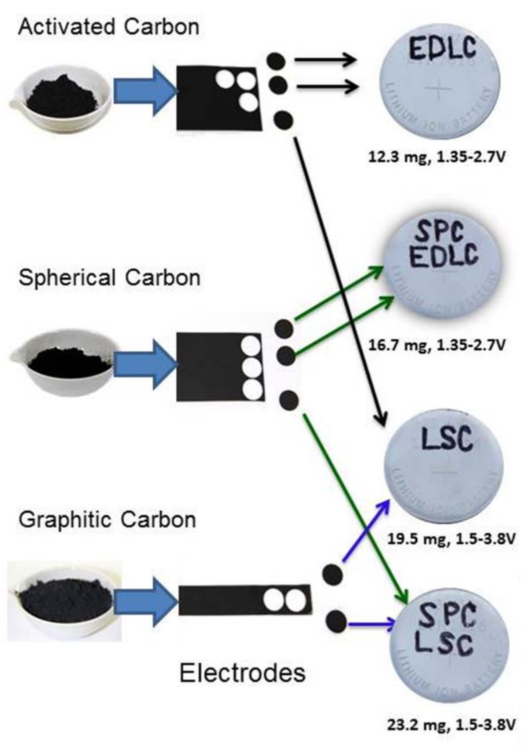
$(W/kg)_{95\%} = 3120$, $(W/L)_{95\%} = 6078$

Ragonne Curves for the Yunasko Hybrid devices



Projected characteristics of high energy density ultracapacitors based on tests of coin cells

Test data for coin cells of various chemistries



Current			Disch. Time	Capacity	Energy
mA	mA/cm²	mA/g	Sec.	mAh/g	Wh/kg
2	1	163	225	10	20
4	2	325	106	10	19
8	5	488	52	9	18

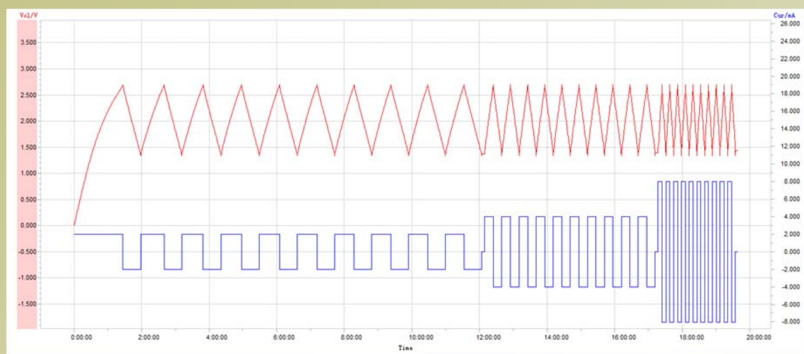
Current			Disch. Time	Capacity	Energy
mA	mA/cm²	mA/g	Sec.	mAh/g	Wh/kg
2	1	120	514	18	36
4	2	240	257	17	35
8	5	479	129	17	34

Current			Disch. Time	Capacity	Energy
mA	mA/cm²	mA/g	Sec.	mAh/g	Wh/kg
2	1	102	1194	34	88
4	2	205	572	33	64
8	5	409	265	30	76

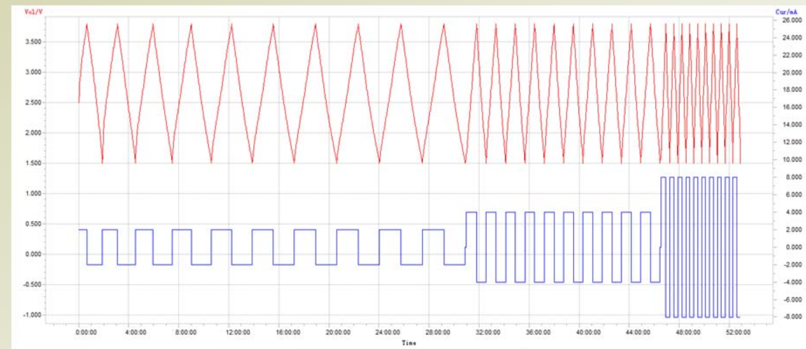
Current			Disch. Time	Capacity	Energy
mA	mA/cm²	mA/g	Sec.	mAh/g	Wh/kg
2	1	86	2712	68	174
4	2	173	1262	63	161
8	5	346	559	56	140

LSC Coin Cell Prototyping

EDLC



LSC



LSC Using Common AC and Graphitic Carbon

Metric	EDLC	LSC
Positive	AC	AC
Negative	AC	G. C
Electrolyte	1M LPF	1M LPF
Voltage (V)	2.7-1.35	3.8-1.9
Capacitance (F/g)cell	22	46
Energy (Wh/kg)	16	70

LSC Using AC of High F/g & Graphitic Carbon

Metric	EDLC	LSC
Positive	AChf	AChf
Negative	AChf	G.C.
Electrolyte	1M LPF	1M LPF
Voltage (V)	2.7-1.35	3.8-1.9
Capacitance (F/g)cell	28	53
Energy (Wh/kg)	22	80

LSC Prototyping

Coin cells, flat pouch cells, and jellyroll pouch cells

All cells charged and discharged under constant current ≥ 4.5 mA/cm^2

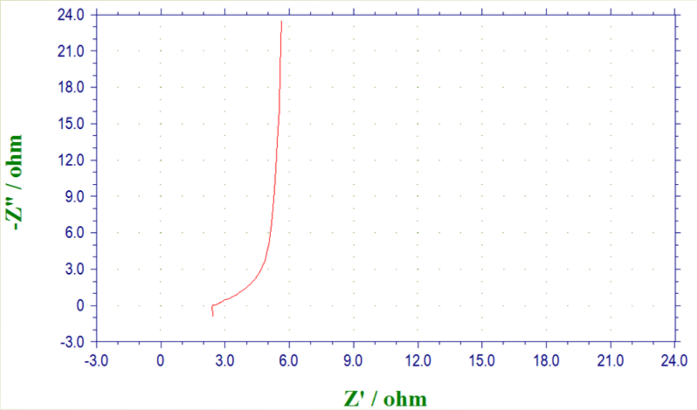
Supercap Using Spherical Carbon

Metric	EDLC	LSC
Positive	SPC	SPC
Negative	SPC	G.C.
Electrolyte	1M LPF	1M LPF
Voltage (V)	2.7-1.35	3.8-1.9
Capacitance (F/g)cell	45	90
Energy (Wh/kg)	34	135

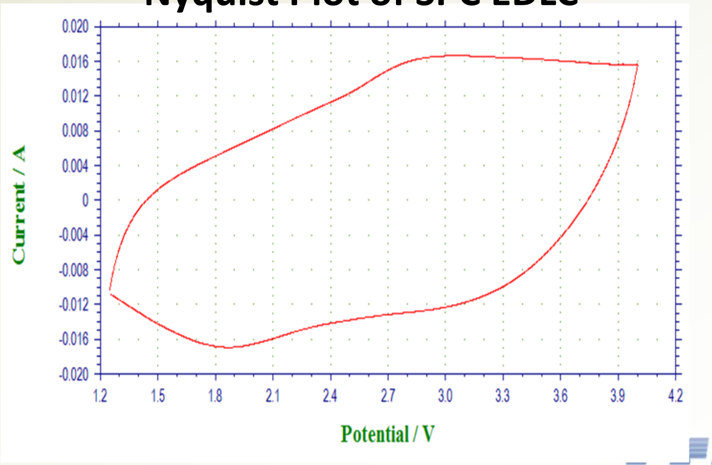
SPC: Low cost spherical carbon made from biomass via hydrothermal method

G.C.: Low cost graphitic carbon

Electrolyte & Separator: commonly used in Li-ion Batteries



Nyquist Plot of SPC EDLC



Cyclic voltammetry of LSC: 1.25-4.0V, Scan rate @ 10mV/s

Projected characteristics of hybrid devices using Lipka (SPC) carbon

Device	ELDC	ELDC	HSC	LIC
Negative material	Standard activated carbon	SPC	SPC	Lithiated graphite
Positive material	Standard activated carbon	SPC	graphite	SPC
voltage	2.7-1.35V	2.7-1.35V	3.4 -1.7V	3.8-1.5
Wh/kg *	4.3	12.8	22	51.4
Wh/L *	4.6	16.0	25	69.8

* package in a pouch

Cost $/Wh = $/kg/ Wh/kg

Examples: $/Wh = 40/4 = 10 EDLC

$/Wh = 30/40 = .75 LSC

Achievable goals for high energy density supercapacitors

- **30 Wh/kg, 50 Wh/L (useable energy)**
- **> 2 kW/kg 95% efficient pulse**
- **> 100K deep discharge cycles**
- **> 10 year calendar life**
- **< 1 $/Wh cost**

Key uncertainties concerning hybrid ultracapacitors

- **calendar and cycle life**
- **cost relative to carbon/carbon devices**
- **trade-offs between energy and power densities**

Summary and conclusions

- Proto-type carbon/carbon cells have energy density of 6-10 Wh/L and 95% eff. Power of 6-12 kW/L –considerably better than commercially available cells

- Progress is being made on the development of hybrid capacitors with energy densities up to 30 Wh/kg and power densities up to 3.5 kW/kg. Cycle life of the hybrid devices is likely to be less than 100k.

- Further relatively large improvements in the energy density are projected using advanced activated carbons, better use of metal oxides, and additives to electrolytes to increase cell voltage.

- Energy densities up to 40-50 Wh/kg, 50-60 Wh/L appear to be possible using existing materials for hybrid ultracapacitors using carbon in one electrode