Testing of Supercapacitors: Capacitance, Resistance, and Energy Energy and Power Capacity

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Outline of the Presentation

- Introduction and objectives
- Approaches
    - USABC
    - IEC
    - UCDavis
- IEC Committee on testing EDLCs
    - Proposed procedures
    - Application of procedures and test data
- UC Davis test procedures and data
- Determination of resistance
    - Theoretical basis
    - Methods
- Summary and modification to test procedures

Introduction and objectives

- There is a need to standardize the test procedures for determining the capacitance, resistance, and energy density of supercapacitors
- Statements concerning the power capability of supercapacitors are particularly confusing and unreliable
- There are a number of approaches to determining the performance of supercapacitors and relating the device characteristics to requirements for various applications

Ultracapacitor testing approaches

- cyclic voltametry (small currents)
- AC impedance tests at various frequencies (small currents)
- DC with variable large currents *******

Performance of Electrochemical Capacitor Devices

- **Energy density (Wh/kg vs. W/kg)**
- **Cell voltage (V) and capacitance (F)**
- **Series and parallel resistance (Ohm and Ohm-cm^2)**
- **Power density (W/kg) for a charge/discharge at 95% efficiency**
- **Temperature dependence of resistance and capacitance especially at low temperatures (20 deg C)**
- **Cycle life for full discharge**
- **Self discharge at various voltages and temperatures**
- **Calendar life (hours) at fixed voltage and high temperature (40-60 deg C)**

Test procedures

- Constant current charge/discharge

  Capacitance and resistance for discharge times of 60 sec to 5 sec.
- Pulse tests to determine resistance
- Constant power charge/discharge

  Determine the Ragone Curve for power densities between 100 and at least 1000 W/kg for the voltage between V_{rated} and ½ V_{rated}. Test at increasing W/kg until discharge time is less than 5 sec. The charging is often done at constant current with a charge time of at least 30 sec.
- Sequential charge/discharge step cycling

  Testing done using the PSFUDS test cycle with the max. power step being 500 W/kg. From the data, the roundtrip efficiency for charge/discharge is determined.
- Tests modules with at least 15-20 cells in series

Summary of the characteristics of various ultracapacitors being developed all over the world

Device	V rated	C (F)	R (mOhm)	RC (sec)	Wh/kg (1)	W/kg (95%) (2)	W/kg Match. Imped.	Wgt. (kg)	Vol. lit.
Maxwell*	2.7	2885	.375	1.08	4.2	994	8836	.55	.414
Maxwell	2.7	605	.90	.55	2.35	1139	9597	.20	.211
ApowerCap**	2.7	55	4	.22	5.5	5695	50625	.009	---
Apowercap**	2.7	450	1.3	.58	5.89	2766	24595	.057	.045
Ness	2.7	1800	.55	1.00	3.6	975	8674	.38	.277
Ness	2.7	3640	.30	1.10	4.2	928	8010	.65	.514
Ness (cyl.)	2.7	3160	.4	1.26	4.4	982	8728	.522	.379
Asahi Glass (propylene carbonate)	2.7	1375	2.5	3.4	4.9	390	3471	.210 (estimated)	.151
Panasonic (propylene carbonate)	2.5	1200	1.0	1.2	2.3	514	4596	.34	.245
EPCOS	2.7	3400	.45	1.5	4.3	760	6750	.60	.48
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
Power Sys. (activated carbon, propylene carbonate) **	2.7	1350	1.5	2.0	4.9	650	5785	.21	.151
Power Sys. (graphitic carbon, propylene carbonate) **	3.3 3.3	1800 1500	3.0 1.7	5.4 2.5	8.0 6.0	486 776	4320 6903	.21 .23	.15 .15
JSR Micro (AC/graphitic carbon)	3.8	1000 2000	4 1.9	4 3.8	11.2 12.1	900 1038	7987 9223	.113 .206	.073 .132

(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

* Except where noted, all the devices use acetonitrile as the electrolyte

** all device except those with ** are packaged in metal containers

All these ultracapacitors have been tested at UC Davis

Approach <u>USABC</u>

- United States vehicle manufacturers
- FreedomCAR Ultracapacitor Test Manual
- Characterization tests based on a Imax value set by manufacturer (somewhat arbitrary)
- Procedures are not well tailored to testing ultracapacitors – often are closely related to testing batteries
- Pulse power characterization tests are vehicle application oriented and not easily applied to proto-type devices
- Procedures not well suited for device evaluation in general

Calculation of the pulse power characteristics of ultracapacitors using the USABC and energy efficiency methods

USABC method

$P_{ABC} = V_{min}(V_{nom.OC} – V_{min})/R = 1/8\ V_{rated}/R$ discharge

$P_{ABC} = V_{max}(V_{max} - V_{nom.OC})/R = 1/4\ V_{rated}/R$ charge

V_{nomOC} is the open-circuit voltage at a mid-range voltage (3/4 V_{rated})

V_{min} is the minimum discharge voltage for the cap (1/2 V_{rated})

V_{max} is the maximum regen voltage for the cap (V_{rated})

R is the effective pulse resistance of the ultracapacitor

Pulse efficiency method

$P_{EF} = 9/16(1\text{-}EF)\ V^{2}_{rated}\ /\ R$ both charge and discharge pulses at ¾ V_{rated}

Differences in the maximum peak power predicted by the USABC and the EF methods for supercapacitors

discharge

$P_{EF} / P_{ABC} = 9/2\ (1\text{-}EF)$

charge

$P_{EF} / P_{ABC} = 9/4\ (1\text{-}EF)$

Example: Ultracapacitor

$V_{rated} = 2.7$, $V_{min} = 1.35$, $V_{max} = 2.7$, $V_{nom} = 2.025$

Efficiency EF	**Discharge P_{EF}/ P_{ABC}**	**charge P_{EF}/ P_{ABC}**
.95	.225	.11
.90	.45	.23
.85	.675	.34
.80	.9	.45
.75	1	.56
.70	1	.68

Calculation the pulse power characteristics of batteries using the USABC and energy efficiency methods

USABC method

$P_{ABC} = V_{min} (V_{nom.OC} – V_{min})/R$ discharge

$P_{ABC} = V_{max} (V_{max} - V_{nom.OC})/R$ charge

V_{nomOC} is the open-circuit voltage at a mid-range SOC

V_{min} is the minimum voltage at which the battery is to be operated in discharge

V_{max} is the maximum voltage at which the battery is to be operated in charge (regen)

R is the effective pulse resistance of the battery

Pulse efficiency method

$P_{EF} = EF(1-EF) V^2_{nomOC} / R$ both charge and discharge pulses

Differences in the maximum peak power predicted by the USABC and the EF methods

discharge

$P_{EF} / P_{ABC} = EF(1\text{-}EF) / [(V_{mim}/V_{nomOC})(1\text{-}V_{min}/V_{nomOC})]$

charge

$P_{EF} / P_{ABC} = [(V_{nomOC}/ V_{max,ch})^2 / (1\text{-} V_{nomOC}/ V_{max,ch})]\ EF(1\text{-}EF)$

Example: Iron Phosphate

$V_{nomOC} = 3.2,\ V_{min} = 2,\ V_{max} = 4.0$

Efficiency	EF(1-EF)	Discharge P_{EF}/ P_{ABC}	charge P_{EF}/ P_{ABC}
.95	.0475	.20	.15
.90	.09	.38	.29
.85	.1275	.54	.41
.80	.16	.68	.51
.75	.1875	.80	.60
.70	.21	.90	.67

Example: Nickel Cobalt

$V_{nomOC} = 3.7,\ V_{min} = 2.5,\ V_{max} = 4.3$

Efficiency	EF(1-EF)	Discharge P_{EF}/ P_{ABC}	charge P_{EF}/ P_{ABC}
.95	.0475	.22	.25
.90	.09	.41	.48
.85	.1275	.58	.68
.80	.16	.73	.85
.75	.1875	.86	1.0
.70	.21	.96	.1.0

Power Systems Nano-Storage Carbon Ultracapacitor

56 V, 90 F

Pulse cycle tests of the Power Systems 14 cell module

USABC UC10 test
4 sec discharge at 54A (100C)
4 sec rest
4 sec charge at 54A
Repeat 5 times
Repeat 10 times

Roundtrip efficiency 95.8%

USABC Pulse Characterization
5 sec at 100 A (211C)
55 sec rest I=0
5 sec at 75 A

PSFUDS test

500 W peak power pulse 12 seconds

three cycles 91%, 91.9%, 92%

1000W peak power pulse 6 seconds

three cycles 84.9%, 85.2%, 86%

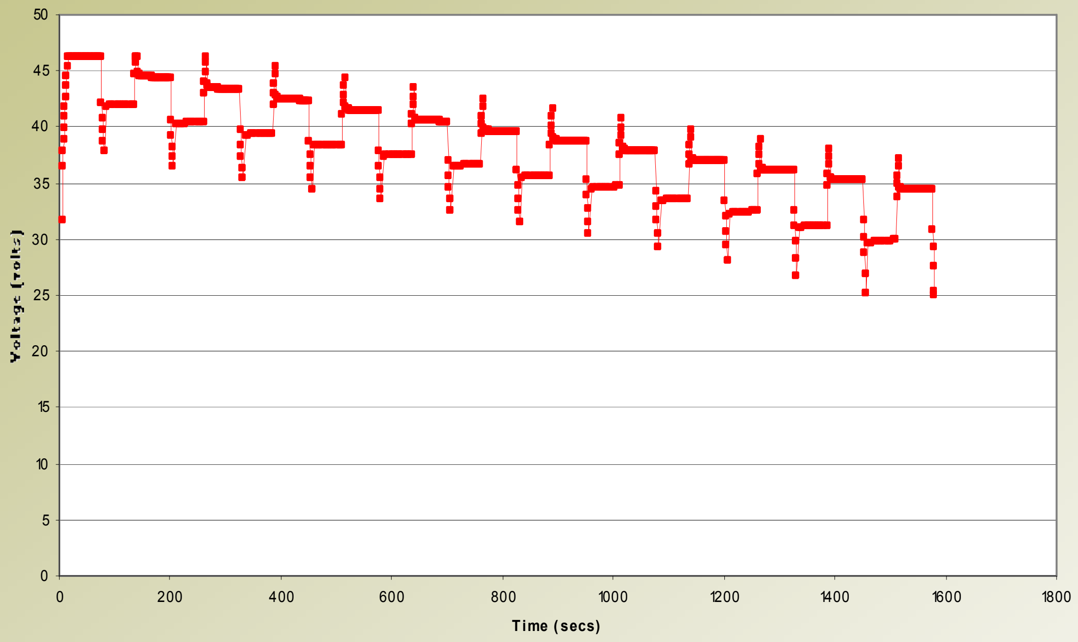
USABC Pulse Efficiency test

125 Wh unit - 15 kg cells

Time step sec	Full power kW	Cell test power W	W/kg	Net energy W-sec
9	10 disch	117	557	1053
27	rest	0	0	1053
2	16 charge	188	895	677
4	11 charge	129	614	161
4	6 charge	71	338	-121
26	rest	0	0	-121

Roundtrip efficiency 93.5%

USABC Pulse Characterization Test of the PS14 cell module



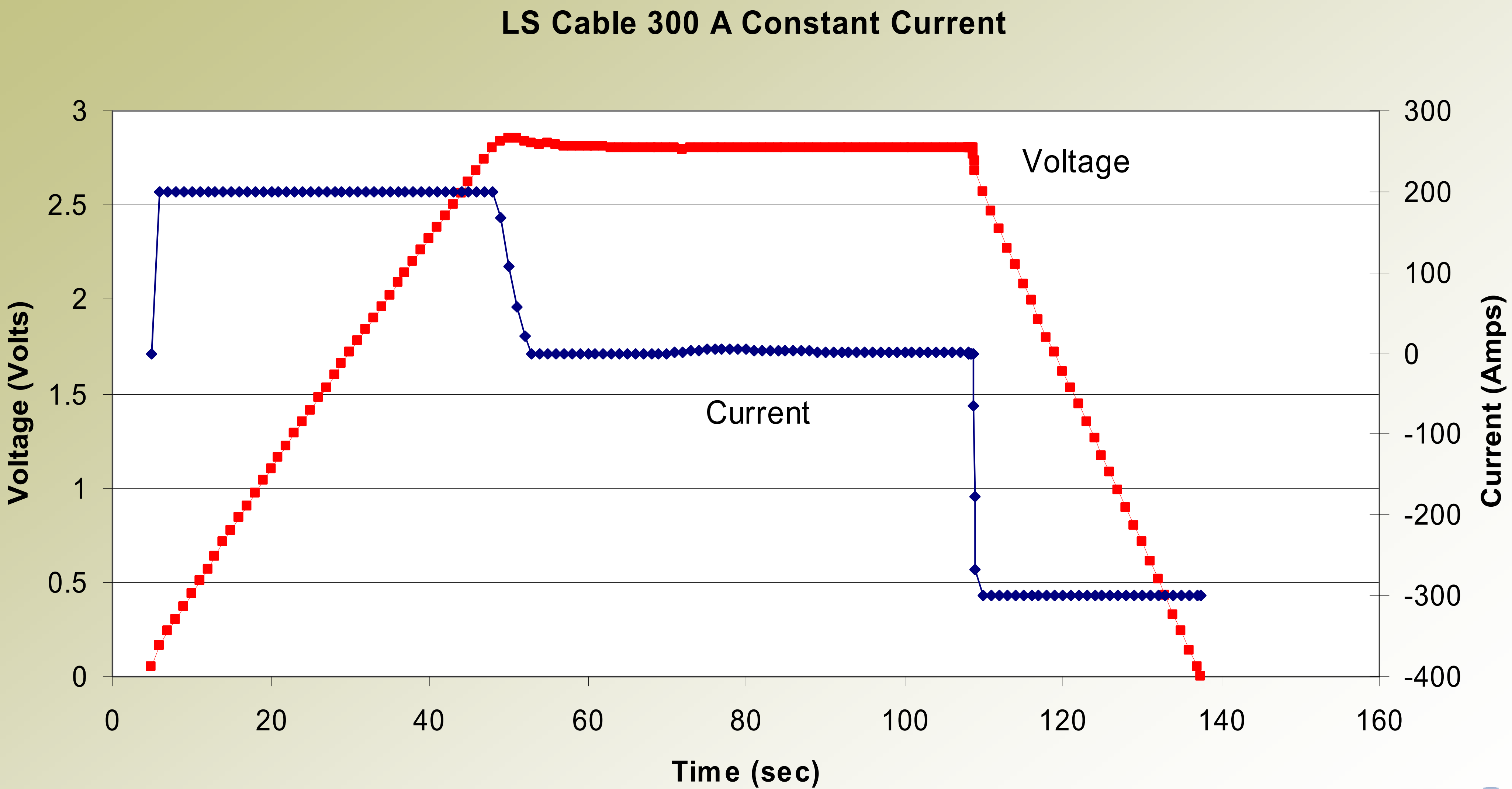
Discharge	89.9	0.0247	95.7
Charge	67.9	-0.0216	
Discharge	84.3	0.0239	94.8
Charge	62.5	-0.0221	-87.5
Discharge	79.0	0.0234	94.1
Charge	57.4	-0.0224	-89.8
Discharge	73.8	0.0232	93.2
Charge	52.3	-0.0228	-92.0
Discharge	68.6	0.0228	91.5
Charge	47.3	-0.0240	-94.0
Discharge	63.6	0.0223	88.7
Charge	42.1	-0.0251	-95.5
Discharge	58.8	0.0217	84.6
Charge	36.7	-0.0267	-96.2
Discharge	54.0	0.0216	80.5
Charge	30.9	-0.0289	-96.2
Discharge	49.1	0.0210	75.2
Charge	24.6	-0.0312	-94.0
Discharge	44.3	0.0208	69.2
Charge	17.9	-0.0340	-91.7
Discharge	39.6	0.0205	61.6
Charge	10.4	-0.0372	-88.2

SOC= V-Vmin/Vmax-Vmin
Vmax=3.3, Vmin=2.0

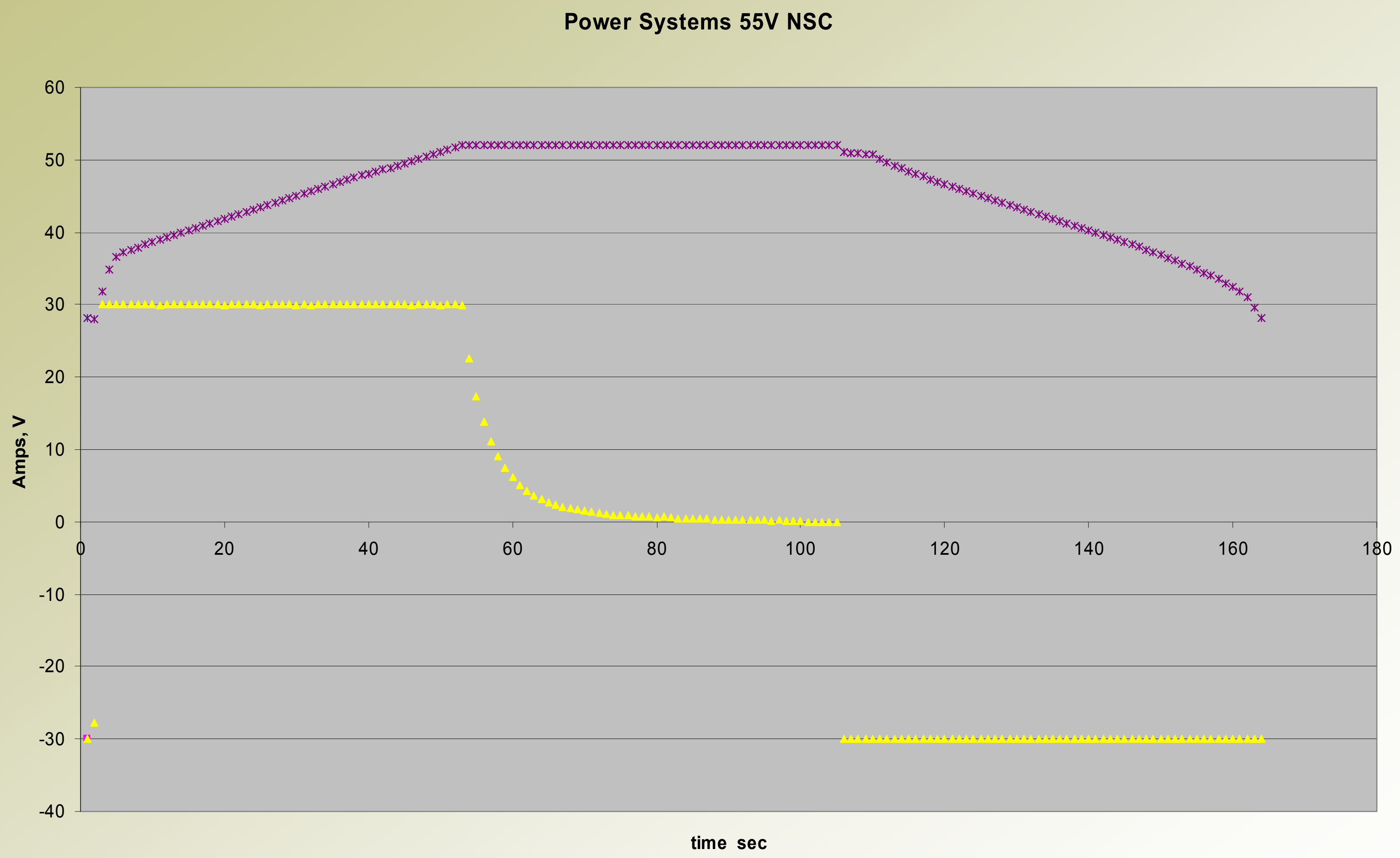
Approach <u>IEC</u> (International Electrotechnical Commission)

- New test procedure recently voted on and approved
- Device oriented- application neutral
- Assumes ideal EDLC to derive test conditions
- 95% efficient charge and discharge; constant current test
- Ich = Vr/38R, Idisch = Vr/40R
- Determination of capacitance from discharge between .9Vr and .7Vr
- Determination of resistance from initial IR drop at initiation of the discharge
- Maximum power is given as P= Vr2/4R (matched impedance) – determining useful power is still a key issue
- No consideration of energy density or effect of discharge rate on capacitance or energy stored included

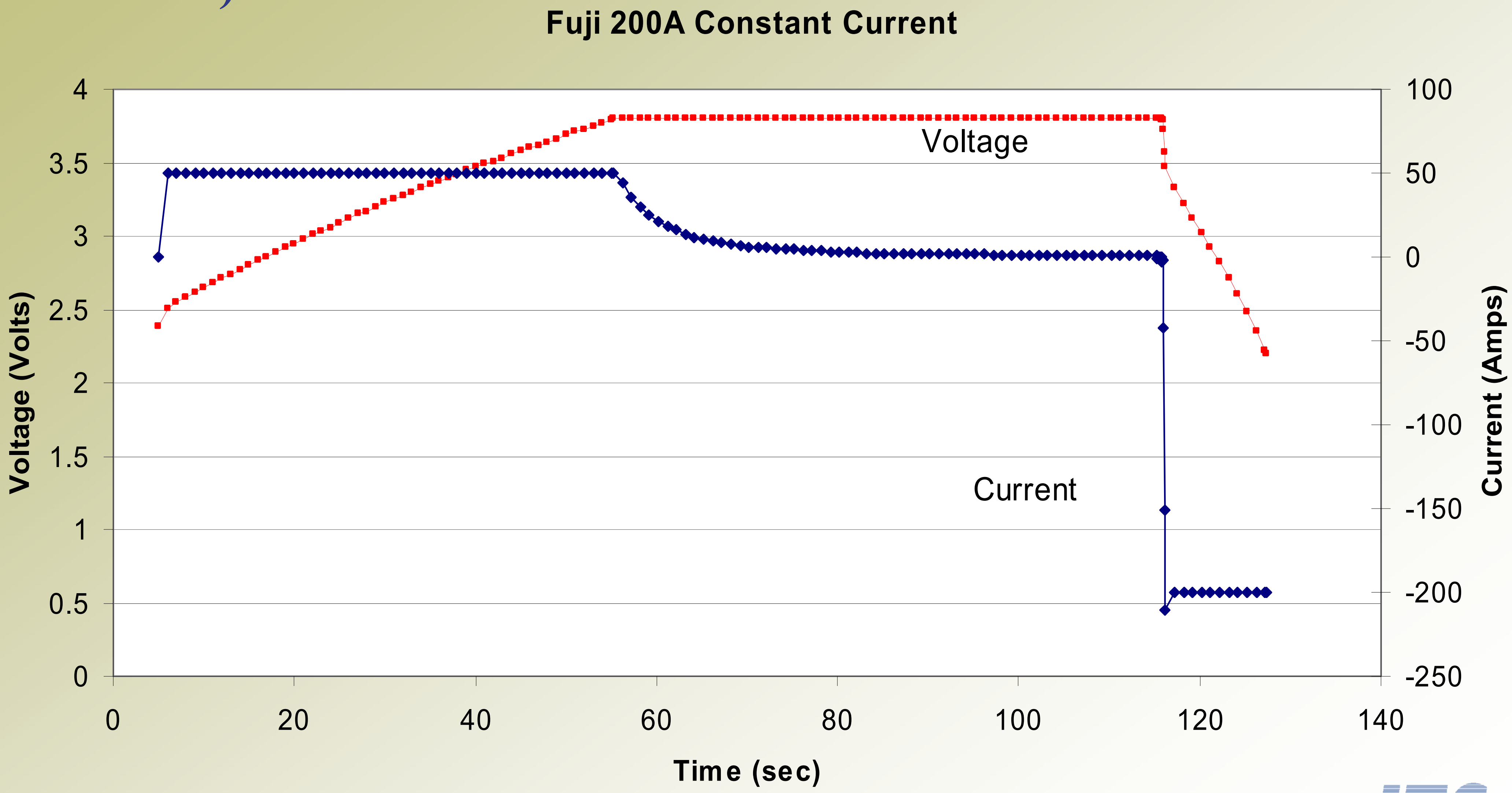
Voltage vs. time for a carbon/carbon capacitor



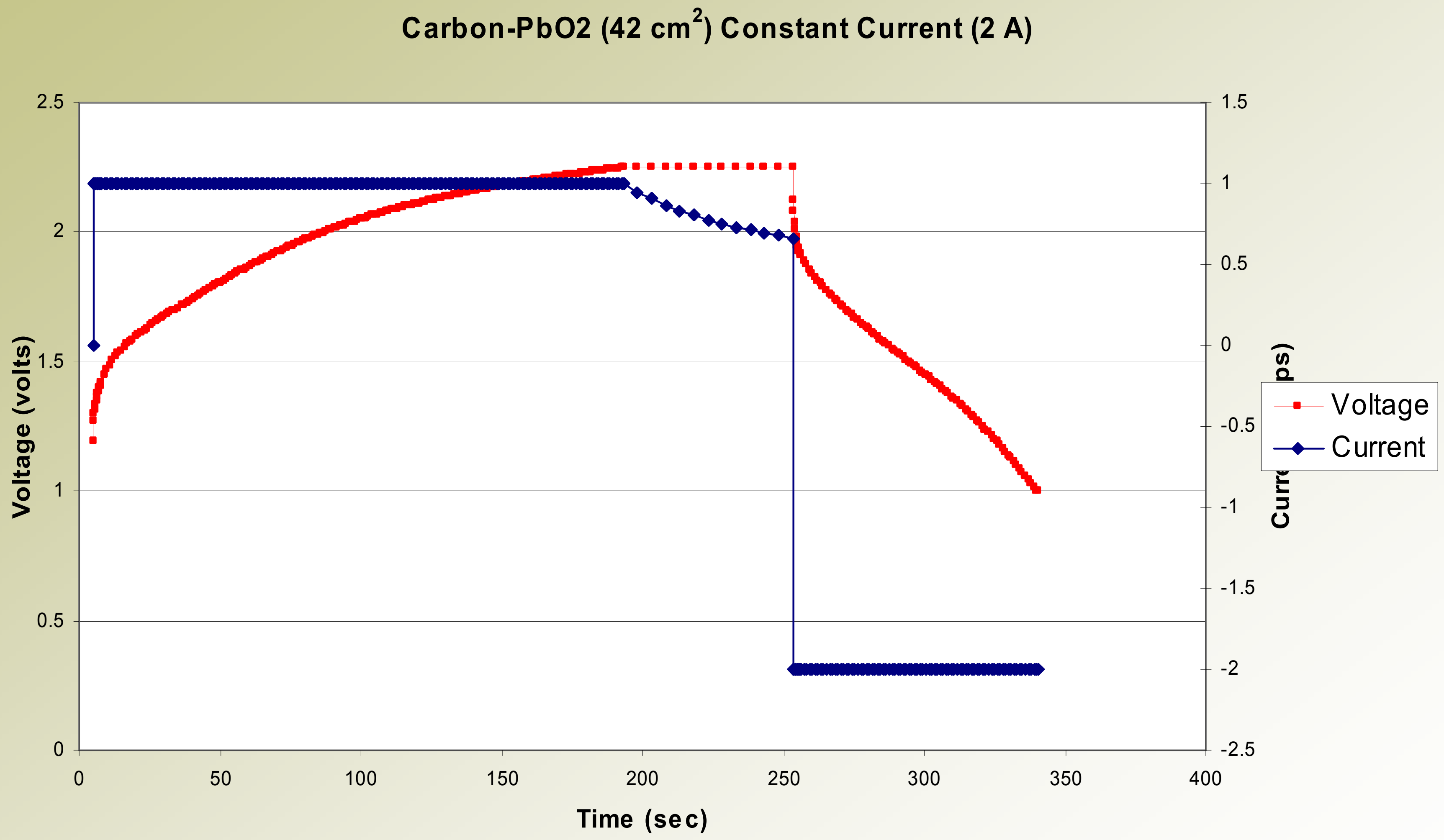
Voltage vs time at constant current (30A)



Voltage vs. time for a hybrid capacitor (carbon/ met. Oxide)

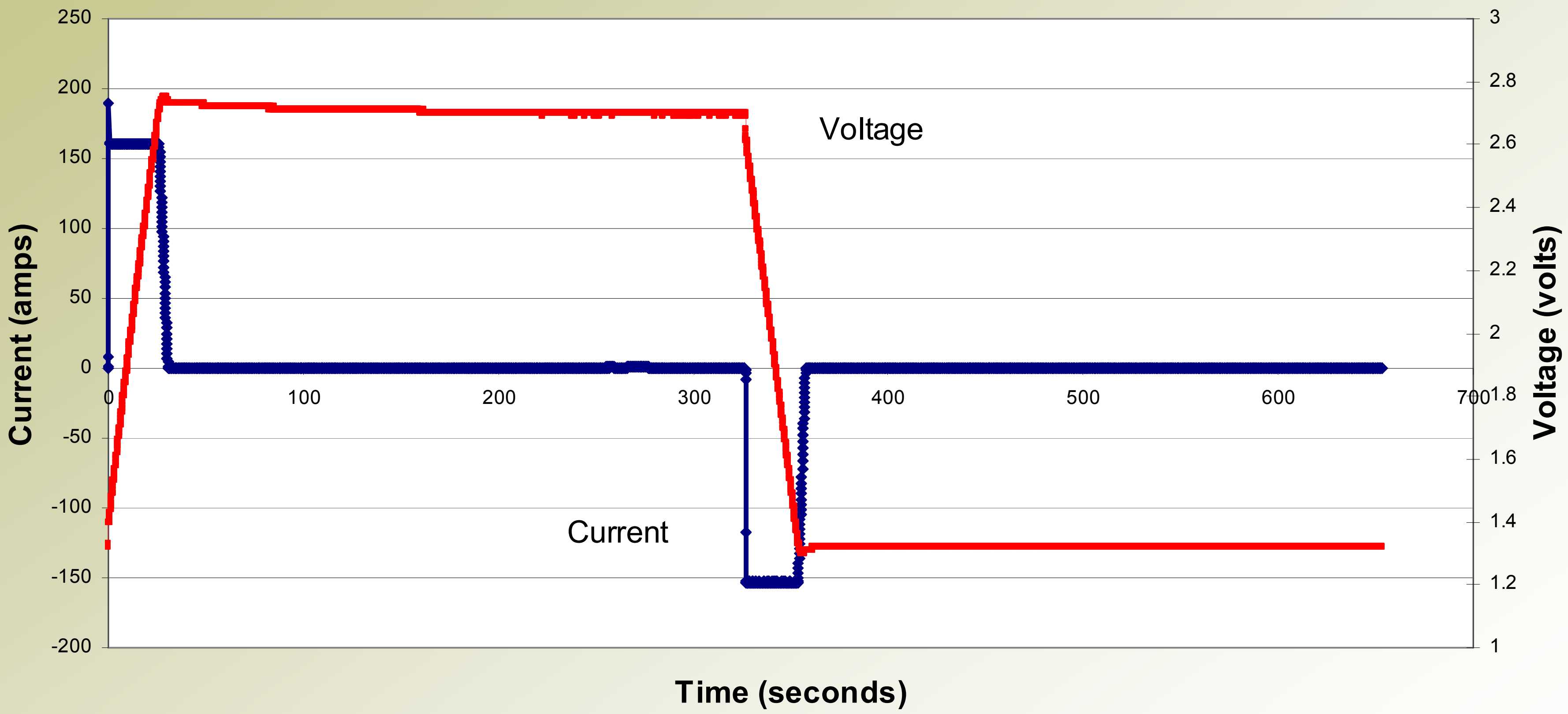


Voltage, current traces for the C/PbO2 device



Test data for application of the IEC test procedures

IEC Test Cycle
Maxwell Capacitor



Sample IEC test data for several supercapacitors

		Cap (F)						
		IEC	Full V	Eff (1)	Eff (2)	R mOhm	R mOhm meas	Av.cur.A
LS Cable	round-trip eff.	3045	3071	83.5	85	0.37	0.44	194
	ch/disch eff			0.91	0.92			
Maxwell	round-trip eff.	3202	3168	88.4	89.2	0.44	0.45	157
	ch/disch eff			0.94	0.94			
Ness	round-trip eff.	3254	3285	86.9	88.6	0.47	0.45	147
	ch/disch eff			0.93	0.94			
Ness-term conn	round-trip eff.	3253	3266	85	87	0.28	0.275	245
	ch/disch eff			0.92	0.93			
JSR	round-trip eff.	2070	1900	89.1	89.5	2.6	2.7	37
	ch/disch eff			0.94	0.95			

charge or discharge efficiency = sqroot (roundtrip efficiency)

Capacitance from 0.9 Vmax to 0.7 Vmax (2.43 - 1.89)

For JSR from 3.48 to 2.84

Full V means the discharge from Vrated to 1.35 V

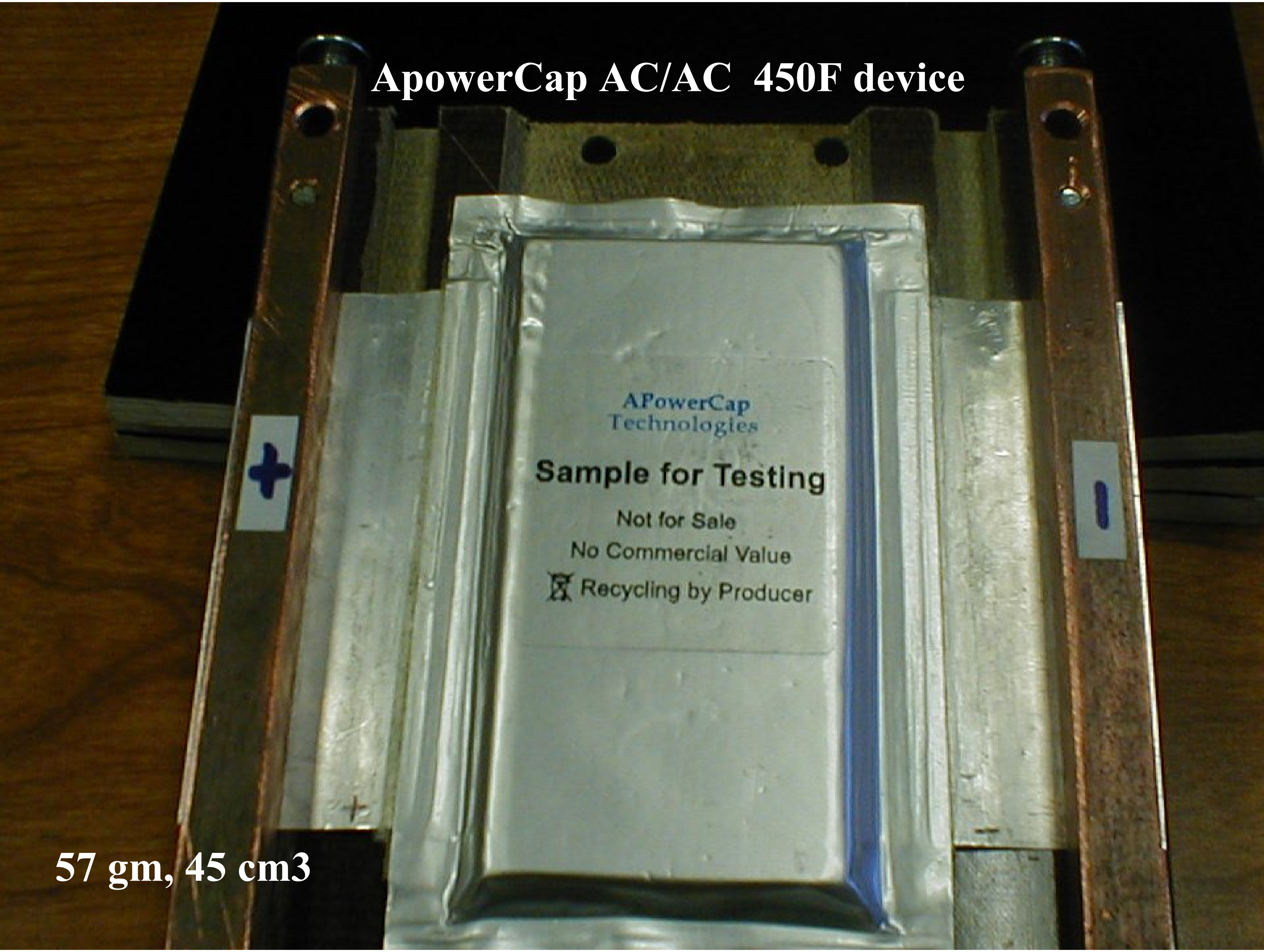
Approach UCDavis (Burke)

- Based on constant current, constant power, and pulse tests of devices
- Capacitance determined from constant current tests using the simple relation $C = Q/(V1-V2)$
- Resistance determined from the constant current tests using the data at the initiation of the discharge by extrapolating the linear voltage curve back to t=0.
- Pulse tests done to check resistance determined from the constant current tests
- Energy density determined from the constant power tests over voltage range Vr and Vr/2 or that set by device manufacturer in the case of hybrid supercapacitors.
- Peak pulse power calculated from the relationship

$$P = 9/16\,(1-\mathrm{Eff})\,V_r^{\,2}/R$$

(pulse at $V = \frac{3}{4} V_r$)

ApowerCap AC/AC 450F device



57 gm, 45 cm3

Test data for the Pouch packaged APowerCap device

Constant current discharge data 2.7V - 0

Current A	Time sec	Capacitance F	Resistance mOhm
10	120.5	450	Not calculate
20	60.3	453	Not calculate
40	30	453	Not calculate
80	14.7	452	1.4
120	9.6	455	1.4
160	7.1	456	1.3

Constant power discharges data 2.7 – 1.35V

Power W	W/kg *	Time sec	Wh	Wh/kg	C_{eff}
12.5	219	95.5	.332	5.82	437
22	385	54.9	.336	5.89	442
41.5	728	28.8	.332	5.82	437
80.5	1412	14.6	.326	5.72	429
120	2105	9.1	.303	5.31	399

* weight of device - 57 gm as tested

$C_{eff} = 2(\text{W-sec})/.75\ (2.7)^2$

Maxwell 3000F and 650F devices

Test data for the 3000F Maxwell device

Constant current discharge data 2.7V - 0

Current A	Time sec	Capacitance F	Resistance mOhm
50	153.4	2869	Not calculate
100	76.7	2883	Not calculate
200	38	2900	.375
300	25	2885	.333
400	18.4	2886	.40

Constant power discharges data 2.7 – 1.35V

Power W	W/kg *	Time sec	Wh	Wh/kg	C_{eff}
63	115	135.3	2.349	4.27	3093
102	186	82.7	2.332	4.24	3071
201	365	40.8	2.278	4.14	3000
301	547	26.5	2.216	4.03	2918
400	727	19.4	2.156	3.92	2839
500	909	15.1	2.097	3.81	2761

* weight of device - .55 kg

$C_{eff} = 2(\text{W-sec})/.75(2.7)^2$

Nesscap 2.7V, 3000F Supercapacitor

Test data for the 3000F Nesscap cylindrical device

Constant current discharge data 2.7V to 0

Current A	Time sec	Capacitance	Resistance mOhm
50	171	3190	---
100	84.3	3181	.44 (1)
200	41.3	3157	.42
300	27	3140	.37
400	20	3150	.40

Constant power discharge data 2.7-1.35 V

Power W	W/kg *	Time sec	Wh	Wh/kg	C_{eff}
100	192	84.8	2.36	4.52	3107
200	383	41.8	2.32	4.44	3055
300	575	27.1	2.26	4.33	2976
400	766	19.7	2.19	4.20	2884
500	958	15.4	2.14	4.1	2818
700	1341	10.9	2.12	4.06	2792

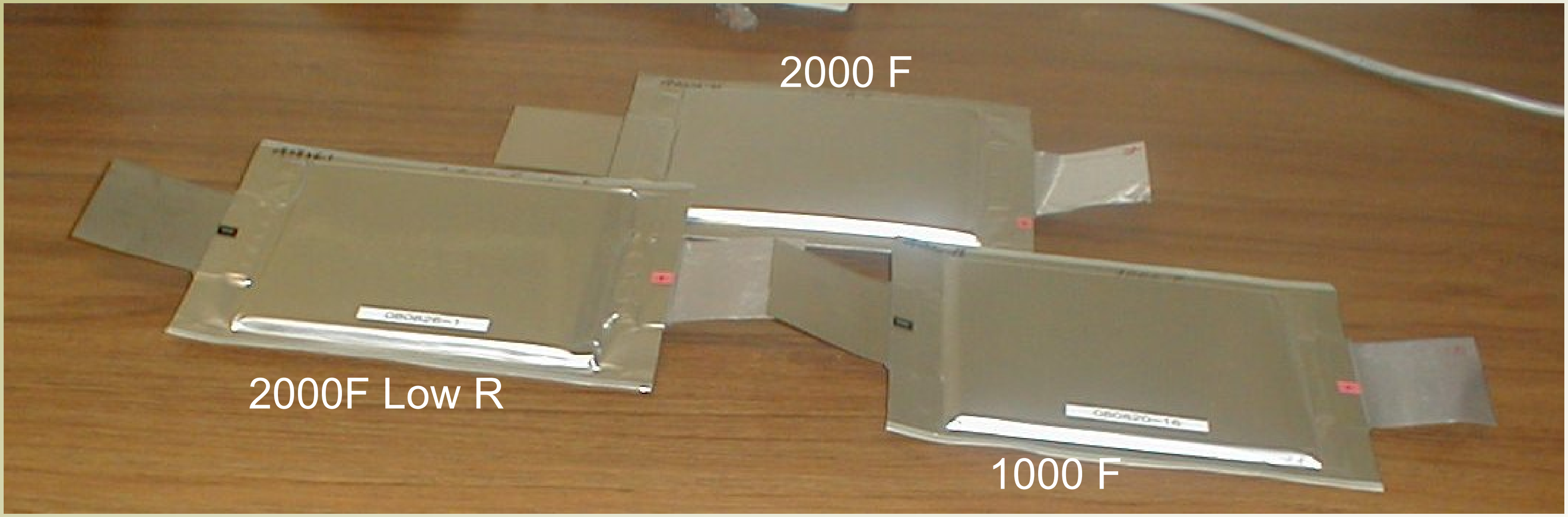
* Weight of device .522 kg ,

$C_{eff} = 2(\text{W-sec})/.75(2.7)^2$

Dimensions of the device 6 cm D, 13.4 cm length

(1) voltage probes connected to the bus bar

JSR - Mixed carbon lithium capacitors



High energy density – 12 Wh/kg

Characteristics of the JSR Micro 2000F ultracap cell

Constant Current discharge 3.8V – 0V

Current (A)	Time (sec)	C(F)	Resistance (mOhm) **
30	102.2	2004	---
50	58.1	1950	---
80	34.1	1908	---
130	19.1	1835	2.0
200	11.1	1850	1.9
250	8.2	1694	1.84

** 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 *	C_{eff}	Wh/L *
102	495	88.3	2.5	12.1	1698	18.9
151	733	56	2.35	11.4	1596	17.8
200	971	40	2.22	10.8	1508	16.9
300	1456	24.6	2.05	10.0	1392	15.7
400	1942	17	1.89	9.2	1283	14.4
500	2427	12.5	1.74	8.5	1181	13.3

* based on the weight and volume of the active cell materials

Cell weight 206 gm, 132 cm3

$C_{eff} = 2(\text{W-sec})/(3.8^2 - 2.2^2)$

Pulse resistance tests results

	Resistance (mOhm)	
Current (A)	Pulse test (5sec)	RC (sec)
100	2	3.8
200	1.9	3.5

Peak pulse power at 95% efficiency R=1.9 mOhm

$P = 9/16 * .05 * (3.8)^2 / .0019 = 214$ W, 1038 W/kg

Determination of the capacitance

- No problem if capacitance is constant with voltage, but it is not the case even for carbon/carbon devices
- Calculation of the capacitance from the data is dependent on voltage range considered

Effect of voltage range on the determination of the capacitance of devices from test data

	V_{max} to 0V		V_{max} to 1.35V	
Device/developer				
3000F/Maxwell	100A 2880F	200A 2893F	100A 3160F	200A 3223F
3000F/Nesscap	50A 3190F	200A 3149F	50A 3214F	200A 3238F
450F/ApowerCap	20A 450F	40A 453F	20A 466F	40A 469F
	3.8 to 2.2V		3.8 to 2.6V	
2000F/JSR Micro	80A 1897F	200A 1817F	80A 1941F	200A 1938F

Seems appropriate to use the same voltage range for calculating C as used in the energy density tests – that is V_{max} to $V_{rated}/2$.

Effective capacitance from the discharge energy W-sec and from charge (A-sec) are not in good agreement for the hybrid carbon capacitor

Sample IEC test data for several supercapacitors

		Cap (F)					
		IEC	Full V	Eff (1)	Eff (2)	R mOhm	R mOhm meas
LS Cable	round-trip eff.	3045	3071	83.5	85	0.37	0.44
	ch/disch eff			0.91	0.92		
Maxwell	round-trip eff.	3202	3168	88.4	89.2	0.44	0.45
	ch/disch eff			0.94	0.94		
Ness	round-trip eff.	3254	3285	86.9	88.6	0.47	0.45
	ch/disch eff			0.93	0.94		
JSR	round-trip eff.	2070	1900	89.1	89.5	2.6	2.7
	ch/disch eff			0.94	0.95		

Capacitance from 0.9 Vmax to 0.7 Vmax (2.43 - 1.89)
For JSR from 3.48 to 2.84

Full V is from roughly when current reaches full value to 1.35 V
For JSR from roughly when current reaches full value to 2.2 V

Methods of determining the resistance

- IR drop at the initiation of a constant current discharge
- Constant current pulse (< 5sec) at a specified voltage
- Bounce back of voltage at end of constant current discharge
- AC Hz impedance (often at 1000 Hz)

Mathematical solution for constant current charge/discharge

Transient constant current solution

Solution of the partial differential equations for the electron current in the solid carbon and the ion current in the electrolyte through the porous electrode. Derive the voltage and currents as a function of x (position in electrode) and time. The solution for V is the following:

$$V=V_0 - I*t/C_{cell} - I*R_{ss}\{1 - (4/\pi^2 (2/3+Lsep/\ L_{electrode}))\ *A(t')\} \qquad *$$

$$\text{where}\quad A(t') = \sum_{n=0}^{\infty} 1/n^2\ e^{-n2\,t'} \quad ,\ A(t' = \infty) = 0$$

$$t' = t/\tau\ ,\ \ \tau = 3/\pi^2\ R_{ss}\, C_{cell}$$

* Assumes capacitance per unit volume and conductivities are constant.

$R_{ss} = 2/3 * L_{electrode}$ * effective resistivity of electrolyte + contact resistance

$R(t=0)$ = contact resistance + $2L_{electrode} / A_x (\sigma_{carbon} + \sigma_{electrolyte}) + L_{sep}/A_x\, \sigma_{electrolyte}$),
$R_0 = 2L/A_X\, \sigma_{carbon}$

Transient Power Losses in Electrochemical Capacitors during Galvanostatic Cycling by C.J. Farahmandi, published ?

Mathematical Modeling of electrochemical Capacitors by Srinivasan, V. and Weidner, J.W., published in Journal of Electrochemical Society, 1998

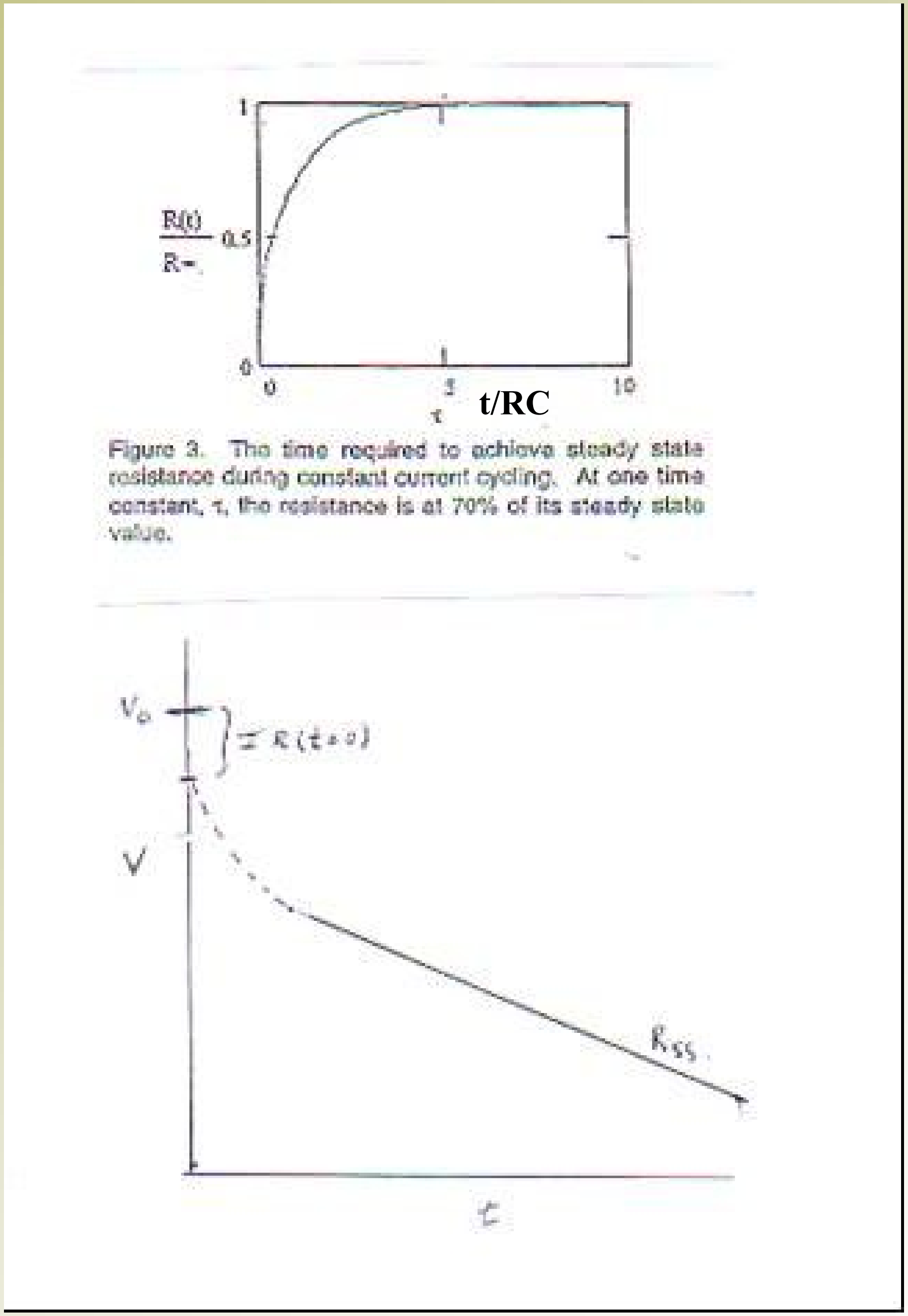
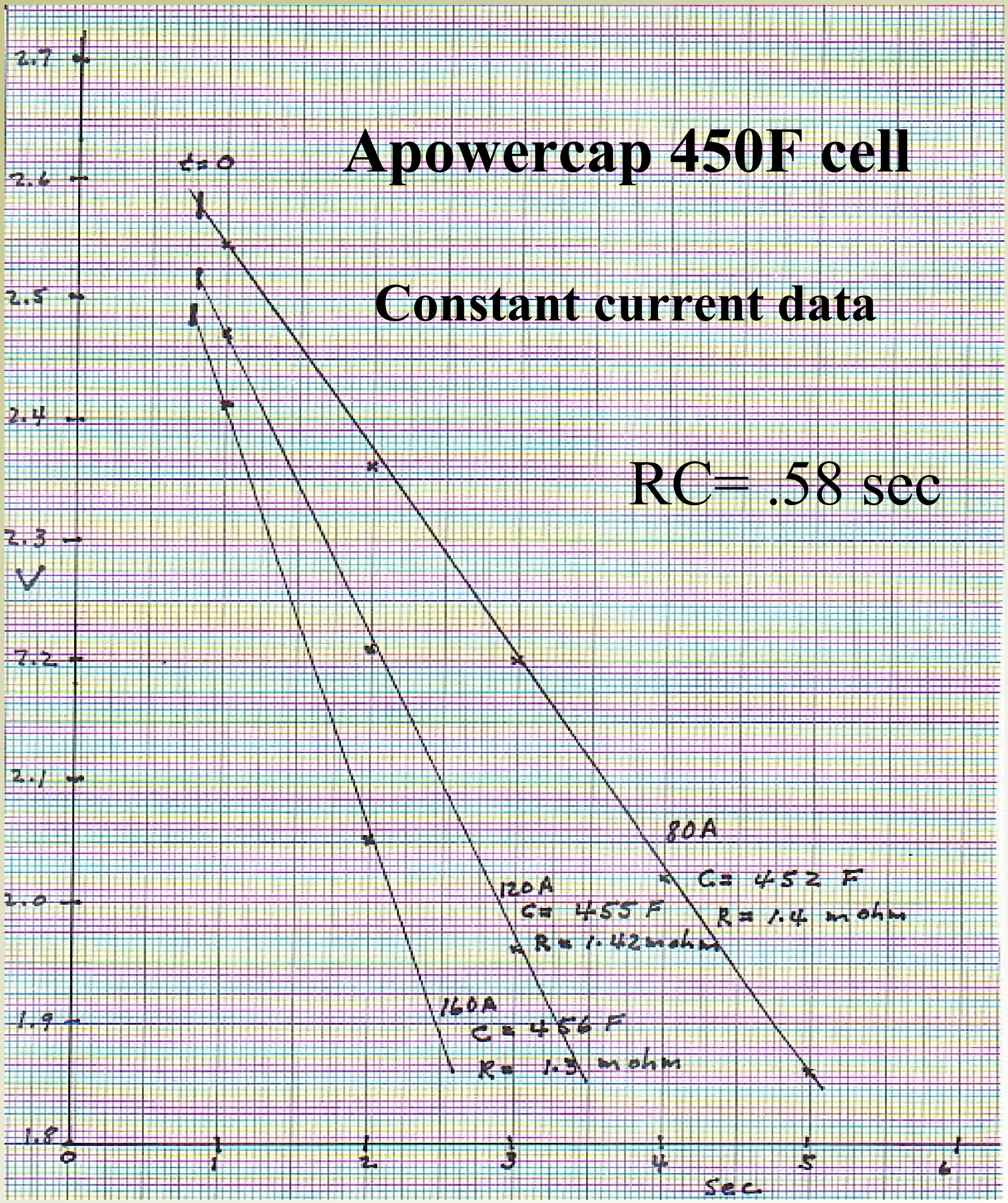


Figure 3. The time required to achieve steady state resistance during constant current cycling. At one time constant, τ, the resistance is at 70% of its steady state value.

Method of determining the resistance of devices from V vs. time



Apowercap 450F cell

Constant current data

RC= .58 sec

Time Sec	current A	voltage
0.1	0	2.06
0.2	0	2.06
0.3	0	2.06
0.4	0	2.06
0.5	0	2.06
0.6	-0.3	2.06
0.7	-0.3	2.06
0.8	-71.6	2.04
0.9	-192.3	1.99
1	-270	1.95
1.1	-313.6	1.93
1.2	-299.9	1.92
1.3	-299.9	1.9
1.4	-300	1.89
1.5	-300	1.88
1.6	-300	1.88
1.7	-300	1.86
1.8	-300	1.85
1.9	-300	1.84
2	-300	1.83
2.1	-300	1.82
2.2	-300	1.81
2.3	-300	1.8
2.4	-300	1.79
2.5	-300	1.78
2.6	-300	1.77
2.7	-300	1.76
2.8	-300	1.75
2.9	-300	1.74
3	-300	1.73

Resistance from pulse test data

Nesscap 3000F device

R = (2.06 – 1.95 - delta Q/C)/300
Delta Q/C= 53.4 A-sec/3100 = .017 V

R = (2.06-1.95-.017)/300 = .31 mOhm

Question? What value of resistance should be used to assess the performance of a supercapacitor unit?

By performance is meant - losses/efficiency and heat dissipation/thermal management

My experience indicates that Rss is the proper measured resistance to use and it is a well-defined value for all devices

This is consistent with the IEC procedure and the 95% efficiency of the charge/discharge cycle test

Summary and recommendations

- There is a need to standardize test procedures to determine the capacitance, resistance, and energy density of supercapacitors

- The uncertainty is largest for the resistance of devices; the steady- state resistance determined from the initiation of discharge is well-defined and relatively easily determined from constant current discharge data

- The effective capacitance of microporous carbon/carbon devices is well-defined from constant current data, but varies with the voltage range used to determine it ; it is recommended that the voltage range of Vr and Vr/2 be used.

- Further work is needed to determine the effective capacitance and resistance of hybrid supercapacitors.

- The energy density should be measured in constant power discharges and not calculated from $E=1/2CV^2$; this is especially the case for hybrid supercapacitors