Power Source 1994

RP-94-11

ELECTROCHEMICAL CAPACITORS FOR ELECTRIC VEHICLES - A TECHNOLOGY UPDATE AND RECENT TEST RESULTS FROM THE IDAHO NATIONAL ENGINEERING LABORATORY

A.F.Burke
Idaho National Energy Laboratory
EG&G Idaho, Inc.
Idaho Falls, ID 83415-3830

Abstract

The DOE Electrochemical Capacitor (ultracapacitor) Development Program is reviewed and the technologies being pursued to meet the near-term and advanced energy density goals of 5 Wh/kg and 15 Wh/kg, respectively, are identified and their status assessed. Capacitor testing at the Idaho National Engineering Laboratory (INEL) is summarized with special attention being given to tests of the Panasonic 3 V, 1500 F device at temperatures between -25°C and +65°C and tests of a 168 V pack of Panasonic 3 V, 500 F devices at powers up to 25 kW.

Introduction

The first paper on the use of electrochemical (double-layer) capacitors for electric vehicle applications was given at the 34th Power Sources Symposium in June 1990 (Reference 1). Specifications for devices to be used in vehicles were presented at that time and the United States Department of Energy (DOE) initiated a program to develop devices that would meet those specifications in 1992. At the present time (1994), it is now widely recognized that high energy density capacitors (often referred as ultracapacitors) can be used to load level the batteries in electric vehicles thereby reducing the peak power requirement for the battery. This permits the battery to be designed for maximum energy density and cycle life and minimum cost with much less attention being given to peak power. There are now programs underway in the United States, Europe, and Japan to develop capacitors for electric and hybrid vehicle applications. The goals of the DOE Ultracapacitor Program are given in Table 1, but the goals of the programs outside the United States are thought to be essentially the same.

The conclusion reached in 1990 that capacitors could be developed with an energy density of at least 5 Wh/kg and suitably low resistance (about 0.1 ohm-cm^2) was based in large part on the work on mixed metal oxide capacitors that was underway at Pinnacle Research Institute (References 2 and 3). Since 1990, work on a number of other material technologies for ultracapacitors has been started and there appear to be several technologies that show good promising of meeting the DOE advanced ultracapacitor goal of 15 Wh/kg. A summary of the current DOE Ultracapacitor Program is given in Reference 4 and that paper also contains a bibliography of recent publications pertinent to the DOE Program. In this paper, an update of ultracapacitor technology, as of 1993, is given along with recent test data taken at the Idaho National Engineering Laboratory (INEL) as part of the ongoing DOE Ultracapacitor Program.

The Status of Ultracapacitor Technology (1993)

There are a number of ultracapacitor development projects in progress in the United States and abroad. The distinguishing characteristic of each of these programs is the material being used in the electrodes, which include the following:

- Carbon/metal fiber composites
- Foamed (aerogel) carbon
- Activated, synthetic, monolithic carbon
- Doped conducting polymer films on carbon cloth
- Mixed metal oxides

A summary of the status of each of these technologies as of the end of 1993 is given in Table 2. When available data permitted, the performance values given in Table 2 for the various technologies are based on testing done at the INEL. The status of several of the technologies is discussed briefly in the following paragraphs.

The only high energy density power capacitors commercially available are those from Panasonic, which utilize particulate carbon with a binder on an aluminum foil and an organic electrolyte in a spiral wound, 3 V single cell configuration. Panasonic now markets 70 F, 500 F, and 1500 F devices. All these devices, which have been extensively tested at the INEL, have energy densities of 2.3 Wh/kg and 2.9 Wh/L for charging to 3 V. The resistance of the 500 F device is 3 to 4 milli-ohms permitting discharge at a power density of 500 W/kg with a relatively small IR voltage drop. The Panasonic capacitors are suitable for performing laboratory testing of battery and capacitor systems, but their energy densities are not high enough for packaging in electric vehicles.

Laboratory tests of single cells and bipolar stacks of devices fabricated as part of the DOE Ultracapacitor Development Program have shown energy densities of 1 to 2 Wh/kg for devices using aqueous electrolytes (sulfuric acid and KOH) and 6 to 8 Wh/kg using organic electrolytes. The resistances of the 1 V cells using aqueous electrolytes are in the range of 0.2 to 0.5 ohm-cm^2 and for the 3 V cells using organic electrolytes, the range is 1 to 2 ohm-cm^2. PSFUDS testing of cells using aqueous electrolytes has shown round-trip efficiencies of 90 to 92% and those using organic electrolytes efficiencies of 85 to 88%. Tests of bipolar stacks have indicated that stacking capacitors should not prove difficult as only minimum difficulty with cell imbalance has been encountered with both the carbon-based and mixed metal oxide technologies. The test results obtained in 1993 indicate that it will be difficult to reach the DOE near-term goal of 5 Wh/kg in carbon-based devices using an aqueous electrolyte unless the carbon loading can be increased to at least 1 gm C/cm^3. However, test results indicate that the near-term goal can be reached or exceeded in carbon-based devices using an organic electrolyte, but with a significant increase in cell resistance. Work on packaging cells and bipolar stacks in a completely sealed manner is progressing well with indications that within a year packaged bipolar devices will be available with energy densities of 2 to 3 Wh/kg using aqueous electrolytes and 6 to 10 Wh/kg using organic electrolytes.

Work supported by the U.S. Department of Energy Assistant Secretary for Energy Efficiency and Renewable Energy (EE), under DOE Idaho Operations Office, Contract DE-AC07-76ID01570

Future Projections of Ultracapacitor Performance and Cost

The major questions regarding ultracapacitor technology are concerned with energy density and cost. As indicated in Table 1, the DOE energy density goal is 5 Wh/kg for the near-term and 15 Wh/kg for the long-term. The cost goal is to achieve $ 0.5 to 1.0/Wh. There appear to be at least three technical approaches that have a reasonable chance of meeting the long-term energy density goal. They are:

1. Highly loaded (>1 gmC/cm^3), carbon-based substrates using an organic electrolyte
2. Mixed metal oxides with 10 to 20 micron thick substrates with an aqueous or organic electrolyte
3. Doped polymer substrates with an organic electrolyte

For the electric and hybrid vehicle applications, it is necessary to meet the energy density goal and at the same time have a low enough resistance that the capacitor can be discharged at a power density of at least 1.5 kW/kg. In addition, cycle life and cost goals must also be met. Results of a simple analysis of the carbon-based technologies are shown in Tables 3 and 4 for the case of a carbon loading of 1 gm/cm^3 in the substrates of the cell. The results indicate that meeting the long-term goal of 15 Wh/kg requires a cell voltage of at least 2 to 3 V (in other words, the use of non-aqueous electrolytes) and that meeting the cost goal of $0.5 to 1/Wh requires a carbon cost of $2 to 5/lb even for devices having energy densities of 10 Wh/kg or greater.

Recent Capacitor Testing at the INEL

Testing of high energy density capacitors for electric vehicle applications has been underway at the INEL since 1991. Summaries of the test procedures used and results obtained are given in References 5 through 8. The test equipment now available at the INEL for capacitor testing is listed in Table 5. This equipment, which was designed to be used for testing batteries, has been adapted for testing capacitors with little difficulty. The standard types of tests performed on capacitors are listed in Table 6.

In addition to testing capacitors delivered to the INEL from industrial contractors and the National Laboratories as part of the DOE Ultracapacitor Development Program (Reference 4), testing has been performed in recent months to determine the characteristics of the Panasonic 3 V, 1500 F devices and modules and packs consisting of up to one-hundred sixty eight (168) of the Panasonic 3 V, 500 F devices, which will used at INEL to test capacitor/battery systems with and without interface electronics between the capacitor and battery packs. Photographs of the Panasonic devices, modules, and packs are shown in Figures 1 through 3. Test data for the Panasonic 1500 F device are given in Table 7 for constant current and constant power discharges. The constant power discharge data are compared in Figure 4 with similar data for the 500 F devices. The characteristics of the larger 1500 F device scale as expected from those of the smaller 500 F device in that the energy density of the two devices are essentially the same and the resistance of the larger device is approximately one-third that of the smaller device.

A four-cell string of the Panasonic 1500 F devices was tested at temperatures between -20°C and +65°C in an environmental chamber. The data for 100 A and 300 A discharges of the cells are shown in Figure 5 and Table 8. The test results indicate that the capacitance is essentially independent of temperature, but the resistance increases monotonically with decreasing temperature due primarily to the decreasing conductivity of the electrolyte. The resistance of the capacitor at -20°C is about 20% higher and at +65°C, it is about 20% lower than at a standard ambient temperature of 25°C.

Prior to assembling the one-hundred sixty eight (168) 3 V, 500 F devices into fourteen (14) 12 V modules, each of the devices was characterized using a standard test in which they were successively charged and discharged at 25, 50, and 100 A. The average capacitance of each device was calculated based on the measured charge/discharge times for each current. The average capacitance and standard deviation for the 170 devices are given in Table 9. Fifty-six sets of three devices for the fourteen 12 V modules were formed by taking successively one device from each end (low and high) and one from the middle of the distribution. The capacitance of the three device sets was 1470 F with a very small standard deviation of 0.93 F indicating the distribution of the capacitances of the devices themselves was very symmetric about the mean of 489 F. The capacitor pack of the fourteen (14) 12 V modules was then discharged at constant powers up to 25.5 kW (500 W/kg) and on the PSFUDS cycle for several hours. The capacitor pack functioned satisfactorily in all the tests and is ready for further testing with a battery pack and interface electronics.

References

(1) Burke, A.F., Hardin, J.E., and Dowgiallo, E.J., "*Applications of Ultracapacitors in Electric Vehicle Propulsion Systems*," Proceedings of the 34th Power Sources Symposium, Cherry Hill, NJ, June 25-28, 1990.

(2) Tong, R.R., Mason, G.E., Lee, H.L., and Bullard, G.L., "*Power Characteristics of the Ultracapacitor*," Proceedings of the 33rd International Power Sources Symposium, Cherry Hill, NJ, June 13-16, 1988.

(3) Bullard, G.L., Alcazar, H.B.S., Lee, H.L., and Morris, J.L., "*Operating Principles of the Ultracapacitor*," IEEE, 4th Symposium on Electromagnetic Launch Technology, Austin, TX, April 1988.

(4) Burke, A.F., Electrochemical Capacitors for Electric and Hybrid Vehicles - The DOE Program and the Status of the Technology-1993, The Annual Automotive Technology Development Contractor's Coordination Meeting - 1993, October 1993.

(5) Burke, A.F., "*Laboratory Testing of High Energy Density Capacitors for Electric Vehicles*," EG&G Idaho, Inc. Report No. EGG-EP-9885, October 1991.

(6) Burke, A.F., "*The Development of Ultracapacitors for Electric and Hybrid Vehicles - The DOE Program and the Status of the Technology*," The Annual Automotive Technology Development Contractors' Coordination Meeting, 1992, SAE P-265, pp 377-389, October 1992.

(7) Burke, A.F., and Dowgiallo, E.J., "*Ultracapacitors for Electric and Hybrid Vehicles - A Technology Update*," Proceedings for the 11th International Electric Vehicle Symposium, Florence, Italy, September 1992.

(8) Burke, A.F., "*Testing of Ultracapacitors and Batteries for Electric Vehicle Applications*," Proceedings of the Third International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL December 1993.

Table 1. Near-term and advanced goals for the DOE Ultracapacitor Development Programs.

Battery w/o Capacitor	Near-Term	Advanced
Weight (kg)	500 to 600	200 to 300
Power Density (W/kg) Average Gradeability Peak (accel)	 10 30 to 50 80	 20 110 to 160 375 to 550
Ultracapacitor Unit		
Energy stored (Wh)	500	750
Maximum Power (kW)	50	80
Weight (kg)	<100	<50
Volume (L)	<40	<20
Energy density (Wh/kg)	>5	>15
Maximum useable power density (W/kg)	>500	>1600
Round trip efficiency (%)	>90	>90
Vehicle Acceleration		
0 to 88 km/h (sec)	<20	<8

Table 3. Simple calculations of energy density (carbon-based ultracapacitors).

V_{cell}	(F/gmC)[1]	Wh/kg[2]
1	250	5.75
2	175	16.1
3	125	25.9
4	90	33.1

(1) Capacitance for a single electrode

(2) Cell is 66% carbon by weight

$$\frac{Wh}{kg} = \frac{1}{8}\,\frac{(F/gmC)}{1.5}\,\frac{V^2}{3.6}$$

Table 2. Summary of ultracapacitor technology (Status 1993, Future Projections).

	Construction			Performance						Status			
Name	Config.	Electrode Mat'l	Electrolyte	Wh/kg	Wh/L	Resistance ohm-cm^2	(W/kg) pk[1]	Effic[2] (%)	Cost	Size (cm^3)	Voltage	Cap. (F)	Basis for Projection
NEC Supercap													
FY	prismatic	carbon	sulfuric acid	0.33	0.55	45	'	'	low	4	5	2.2	Mfg Spec Sheet
FE	prismatic	carbon	sulfuric acid	0.01	0.18	1.9	'	'	low	4	5	1.5	Mfg Spec Sheet
Panasonic	spiral wound, single cell	carbon	organic	2.2	2.9	7	400	80-90	low	single cell	3 V	500-1500	Lab Tests
Evans	prismatic	carbon	sulfuric acid	0.2	0.5	1	'	'	low	6	11	0.5	Mfg Spec Sheet
Seiko Instruments	button cell	polyacene polymer	organic	1.9	4.9	12	'	'	'	3	5	2.5	Mfg Spec Sheet
Pinnacle Research Institute	bipolar	mixed oxides (Ru, Ta) Adv. Design	sulfuric acid	5	14	$<10^{-2}$	>10,000	>95	high	2	100 V	0.01	Mfg Testing
				13	40	$<10^{-2}$	'	>95	med	200	'	'	Projections
Maxwell/ Auburn	bipolar	carbon/metal composite	KOH	1.2	2	0.2	800	90	med	20	1 V	55	Lab Tests
			organic	7	9	1.5	2000	'	med	20	3 V	13	Lab Tests
Livermore Nat'l Lab	bipolar	aerogel carbon particulate	KOH	1	1.5	'	'	90	med	58	1 V	35	Lab Tests
Sandia Nat'l Lab	bipolar	synthetic, activated carbon	aqueous	1.4	1.7	0.35	1000	'	med	2	1 V	3.5	Lab Tests
Los Alamos Nat'l Lab	bipolar	conducting polymer on carbon	organic	10-20	'	'	'	'	low	'	'	'	Projections

(1) Maximum power at which the energy recoverable from capacitor is at least 80% of that recoverable at 100 W/kg.

(2) Efficiency on the PSFUDS cycle for the peak power step at (W/kg)pk = 300.

Table 4. Simple calculations of cost (carbon-based ultracapacitors).

	$/Wh			
$/lbC	5 Wh/kg	10 Wh/kg	20 Wh/kg	30 Wh/kg
2	0.59	0.30	0.15	0.10
5	1.47	0.74	0.37	0.25
10	2.9	1.45	0.73	0.49

$$\$/Wh = \frac{(\$/kgC)}{1.5\,(Wh/kg)_{dev}}$$

Table 5. Test equipment at the INEL for capacitor testing.

Bitrode Tester (2)

- Up to 20 V
- 500 A discharge, 150 A charge
- Sequential charge/discharge cycles with programmable current or power and voltage limits for both charge and discharge

Maccor Tester

- 5 channels 20 V, 12.5 A
- 2 channels 100 V, 12.5 A
- 1 channel 100 V, 50 A
- All channels program for power and current and voltage limits
- Can do sequential charge/discharge cycles
- Used to test 1 V cells

Energy Systems Tester (1)

- 500 V, 500 A limits
- Can do sequential charge/discharge cycles with programmable voltage limits
- Used to test a capacitor unit. It tracked power in discharge of less than one second

Table 6. Standard ultracapacitor tests.

1. Constant current charge/discharge
2. Constant current charge/constant power discharge
3. PSFUDS cycle (200 sec) $(W/kg)_{max}$ = 300 or 500
4. Self-discharge test from rated voltage (48 hours)
5. Leak current test at rated voltage (3 hours)
6. Repeat test 1 through 5 at temperatures above and below ambient (-20° to 55°C)

Table 8. Calculation of the effect of temperature on cell resistance and capacitance.

Temp °C	V_1[1]	V_2[2]	R/cell mohm	V_3	V_4	C/cell farads
100 A DISCHARGE						
65	10.25	9.62	1.58	9.0	6.85	1860
40	10.3	9.7	1.50	9.1	7.03	1932
25	10.2	9.45	1.88	8.84	6.65	1826
5	10.2	9.45	1.88	8.84	6.6	1786
-10	10.1	9.28	2.05	8.63	6.26	1688
-20	9.98	9.08	2.25	8.35	6.03	1724
300 A DISCHARGE						
65	10.25	8.2	1.7	7.58[5]	5.55[6]	1773
40	10.3	8.45	1.54	7.86	5.8	1747
25	10.2	8.2	1.67	7.58	5.55	1773
5	10.2	8.2	1.67	7.58	5.45	1690
-10	10.1	7.65	2.04	7.05	5.03	1782
-20	10.0	7.23	2.31	6.6	4.74	1777

(1) Voltage at t = 0 before discharge

(2) Voltage at t = 0 after discharge is initiated

(3) Voltage at t = 3 sec

(4) Voltage at t = 13 sec

(5) Voltage at t = 1 sec

(6) Voltage at t = 4 sec

$$R = (V_1 - V_2/I$$

$$C = \frac{(\Delta c)(I)}{V_3 - V_4}$$

Table 7. Summary of test data for a Panasonic 3 V, 1500 F. capacitor.

Test Condition	Test No.	Charge Time (sec)[1]	Dischg Time (sec)[2]	Amp-Sec[4]	Watt-Sec	Resist. mOhms[3]
CONSTANT CURRENT						
100 A	1	53.5	42.4	-4238.5	-7074.7	1.247
100 A	2	53.5	42.6	-4259.8	-7139.6	1.232
100 A	3	52.5	42.2	-4219.4	-7047.0	1.301
50 A	4	52.5	70.5	-3525.1	-6702.8	1.467
50 A	5	52.5	70.5	-3525.1	-6747.9	1.400
50 A	6	52.5	71.0	-3550.1	-6786.0	1.467
150 A	7	53.5	22.5	-3359.6	-6251.2	1.299
150 A	8	52.5	22.0	-3314.6	-6153.6	1.299
150 A	9	52.5	22.2	-3314.5	-6160.5	1.199
300 A	10	53.0	9.7	-2856.1	-4973.8	1.399
300 A	11	53.0	9.9	-2916.4	-5101.9	1.299
300 A	12	53.0	10.0	-2946.1	-5151.4	1.299
CONSTANT POWER						
90 W	13	50.5	71.0	-3302.2	-6431.9	1.365
90 W	14	50.5	71.5	-3314.6	-6476.0	1.365
90 W	15	50.5	71.5	-3307.7	-6476.1	1.290
180 W	16	50.5	33.8	-3131.6	-6105.6	1.245
180 W	17	50.5	33.6	-3122.2	-6069.1	1.241
180 W	18	50.5	33.6	-3126.2	-6070.7	1.241
360 W	19	50.5	14.6	-2713.3	-5227.9	1.199
360 W	20	50.5	14.8	-2736.3	-5302.1	1.299
360 W	21	50.5	14.6	-2704.7	-5229.7	1.199
450 W	22	50.5	10.7	-2481.4	-4759.7	1.299
450 W	23	50.5	10.9	-2537.9	-4851.0	1.299
450 W	24	50.5	10.9	-2537.9	-4851.0	1.299
720 W	25	50.5	6.1	-2336.6	-4098.5	1.299
720 W	26	51.5	6.1	-2336.9	-4098.1	1.199
720 W	27	50.5	6.0	-2324.6	-4007.4	1.299
900 W	28	51.5	5.1	-2316.5	-3836.7	1.299
900 W	29	51.5	5.3	-2405.3	-3975.6	1.299
900 W	30	51.5	5.2	-2353.8	-3930.0	1.299

Device Characteristics:

Weight: 887 gm	Diameter: 7.7 cm
Length 14.9 cm	Single Cell
Spiral wound	Carbon-based
Organic electrolyte	

(1) All charge done at 100 A between 0 to 3 V

(2) Discharge to 0.5 V

(3) Resistance calculated from voltage change from end-of-charge to beginning of discharge

(4) Maximum test current is 500 A during constant power discharges

Table 9. Statistical characteristics of Panasonic 3 V, 500 F power capacitors.

Weight (grams)	
Average	307.4
Standard deviation	3.47

Capacitance (Farads)	
Average	489.4
Standard deviation	15.7
99% confidence	489 ±40

Statistics based on tests of 170 devices.

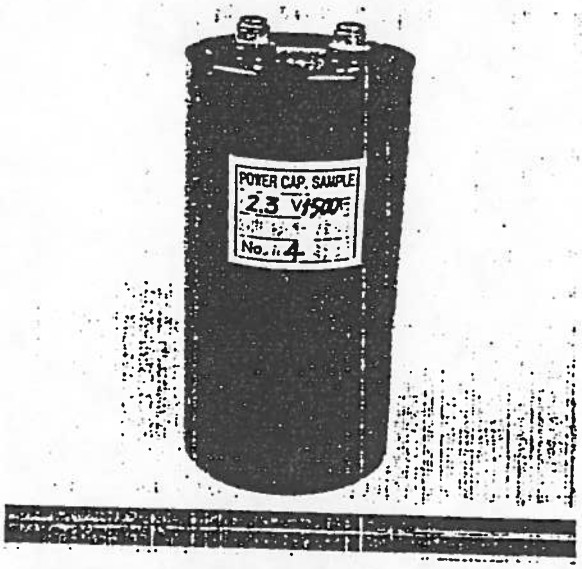

Figure 1. The Panasonic 3 V, 150 F power capacitor.

Figure 2. A 12 V module of 3 V, 500 F Panasonic power capacitors.

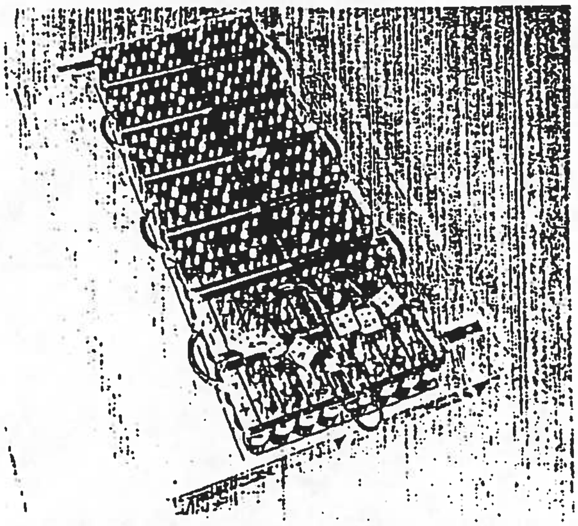

Figure 3. The 168 V pack of 3 V, 500 F Panasonic power capacitors.

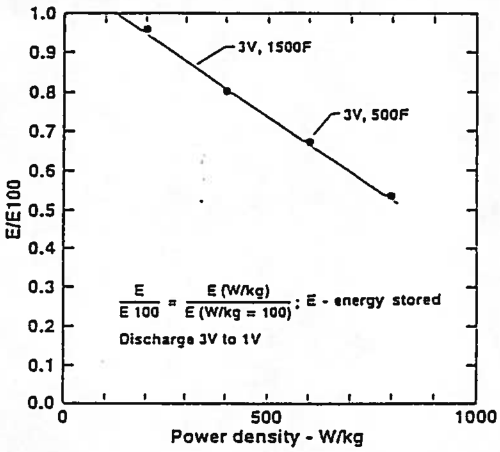

Figure 4. Comparison of discharge data for the Panasonic 3 V, 500 F and 1500 F capacitors.

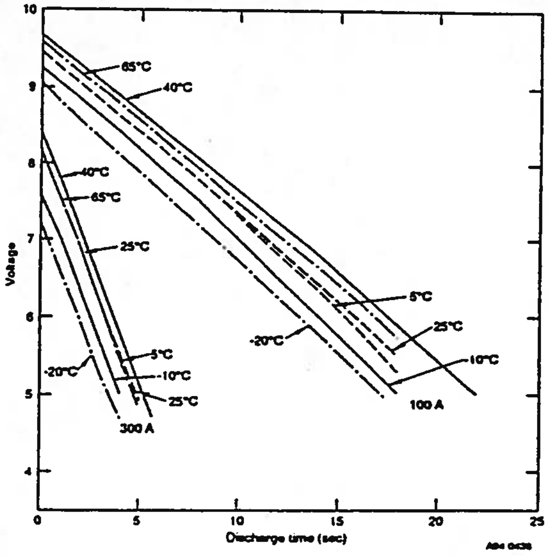

Figure 5. Discharge characteristics of the Panasonic 3 V, 1500 F capacitor at temperatures between -20° and 65°C.