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ELECTROCHEMICAL CAPACITORS FOR ELECTRIC AND HYBRID VEHICLES - THE DOE PROGRAM AND THE STATUS OF THE TECHNOLOGY-1993

A. F. Burke
Idaho National Engineering 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 described. These technologies, denoted by the materials used in the substrates of the capacitors, are:

1. Carbon/metal fiber composites
2. Foamed (aerogel) carbon
3. Activated, synthetic, monolithic carbon
4. Doped conducting polymer films on carbon paper
5. Mixed metal oxides.

The present status of each of these technologies is assessed and projections are made of future developments.

INTRODUCTION

Studies of high energy density, electrochemical capacitors (ultracapacitors) for use in electric drivelines have been underway since 1989 as part of the Electric and Hybrid Vehicle Program of the United States Department of Energy (DOE). These studies (References 1-4) have shown that the use of ultracapacitors in electric and hybrid vehicle drivelines to load level the battery significantly reduces the peak power requirement for the battery and affords the opportunity to design batteries that are optimized for energy density and cycle life with much less attention being given to the peak power density. In the case of hybrid electric vehicles, a study (Reference 4) has shown that load leveling the engine in a hybrid vehicle can improve fuel economy by 50 to 75% over that of conventional ICE-powered vehicles of comparable weight and road load. Driveline schematics of electric and hybrid electric vehicles using ultracapacitors are shown in Figure 1. Other applications of ultracapacitors in light duty vehicles include use as the energy source for electrically heated catalysts (Reference 5) and as the power source for the engine starter motor and other vehicle auxiliaries, such as power steering and brakes, which require intermittent high power.

DOE has initiated a program to develop ultracapacitors for these various automotive applications and to evaluate the devices (deliverables) from the various contractors and commercial sources. In this paper, the goals of the DOE ultracapacitor program are reviewed and the technologies under development are identified and briefly discussed. In addition, the present status (as of the end of 1993) of the different ultracapacitor technologies is summarized based, when possible, on available test data. Projections are also made of future developments for each of the technologies.

THE DOE ULTRACAPACITOR DEVELOPMENT PROGRAM

PROGRAM GOALS - Two sets of program goals have been identified. As shown in Table 1, both near-term and advanced goals have been defined. These goals were developed, as discussed in Reference 3, using simulation results for various possible vehicle designs on the FUDS driving cycle. The simulation results indicated how much energy storage (Wh) was required in the capacitor to load level the battery and it was assumed that the weight and volume of the capacitor could be, at most, 15-20% of that of the main energy

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electrolyte cells and 20 V bipolar stacks at moderate discharge rates are 1 to 1.5 Wh/kg and 1.6 to 2.4 Wh/L and those of the organic electrolyte cells are 5 to 7 Wh/kg and 8 to 9 Wh/L. The resistance of the aqueous electrolyte cells is about 0.2 ohm-cm^2 and that of the organic cells is 1.5 ohm-cm^2. The discharge characteristics of cells using aqueous and organic electrolytes are given in Figures 8 and 9 and a summary of test data for the cells is given in Table 2 and 3. Charge/discharge curves for a 20 V bipolar stack of 1 V cells are given in Figure 10 and a summary of the bipolar stack test data is given in Table 4.

Foamed Aerogel Carbon (Livermore National Laboratory) - Livermore National Laboratory has been investigating the use of foamed (Aerogel) carbon for the substrate of capacitors. The use of aerogel carbon in capacitors is discussed in References 14 and 15. The sol-gel polymerization processes for preparing the foamed carbon are discussed in References 16-18. The monolithic foamed carbon has a surface area of 500-850 m^2/gm and a density of 0.3 to 0.8 gm/cm^3 making it well suited for the capacitor application. Capacitor cells fabricated from substrates prepared from thin slices of foamed carbon have been assembled and tested at Livermore Lab. Contact between the component parts of the cell and the current collector plates was maintained by clamping pressure. Cells have been assembled using both aqueous and organic electrolytes. The energy densities of the aqueous cells (1 V) were reported in Reference 14 and 15 to be 2.5 Wh/kg and 4 Wh/liter and those of the organic cells (3 V) were 8 Wh/kg and 11 Wh/L.

Several single cell (1 V) and bipolar stack (5 V) devices (Figures 11 and 12), fabricated by Livermore National Laboratory using aerogel carbon, were delivered to INEL for testing in October 1993. Screening tests of the devices indicated that there was a significant variation in their performance. The best of the single cell and 5 V bipolar devices were tested over a range of constant currents and powers and on the PSFUDS cycle. The results of the tests are given in Table 5a and 5b. The device weights used to determine the energy and power densities are somewhat uncertain as they were calculated, not measured, based on configuration and material characteristicinputs from Livermore Lab (Reference 19). As indicated in Tables 5, the energy densities measured at INEL were much lower than those stated in Reference 14,15 for aerogel capacitors. The reason for this is that the devices delivered to INEL were not fabricated from disks cut from a monolith aerogel, but were fabricated from disks of particulate aerogel carbon and a polymer binder. This change in fabrication technique resulted in a significant decrease in device performance (Reference 19).

Activated, Synthetic, Monolithic Carbon(Sandia National Laboratory) - DOE has funded a program at the Sandia National Laboratory to investigate various approaches to improving the specific capacitance of carbons through surface charge transfer reactions. Sandia Lab is now working with cellulosic carbon particulate that is pressed into a disk and then activated in place to form a monolithic carbon substrate. The carbon is then chemically treated to increase its specific capacitance. Specific capacitances as high as 200 F/cm^3 have been measure using AC impedance techniques (References 20, 21). Two small (2.25 cm^2) single cell, 1 V devices were delivered to INEL for testing. These devices weighed 28 mgm and were completely sealed. The devices were tested at constant currents up to 0.9 A and constant powers up to 0.45 W (1875 W/kg). In addition, the devices were tested on the PSFUDS cycle with a maximum power step of 300 W/kg. The devices performed very well for all the tests. For a 0.1 A charge and discharge, the devices had a effective capacitance of 3.2 Farads between 0-1 V, a resistance of 0.2 Ohms, and an energy density of 2.0 Wh/kg in charge and 1.4 Wh/kg in discharge. The significant difference between the energy densities in charge and discharge is probably due to the asymmetry of the voltage dependence of the specific capacitance of the positive and negative electrodes in the cells. This results in lower voltages during discharge than in charge at the same state-of-charge of the cell. The test results are summarized in Table 6.

Doped Polymer Layers on Carbon Paper(Los Alamos National Laboratory) - Los Alamos National Laboratory has been investigating the use of doped, porous conducting polymers as a substrate material for high energy density capacitors. The results of the work as of December 1993 are summarized in References 22-24. A key feature of the work is that the Los Alamos Lab has discovered how to form electrochemically n-doped and p-doped conducting polymer layers on the fibers of carbon paper. In 1992, cyclic voltamogram and charge-discharge tests of laboratory cells using various combinations of doped polymer substrates were performed to determine the specific capacitance and useable voltage ranges of the substrate materials (Reference 23). The test results indicated that capacitor cells having energy densities between 10 to 40 Wh/kg based on the weight of the active polymer material alone could be designed depending on the substrate materials used in the cells. It is expected that if the weight of the carbon paper, electrolyte, and separator were included the energy density would be about a factor of two lower. Work in 1993 (Reference 24) was concerned with designing and fabricating sealed single cell devices and showing that the cells could be cycled more than 100,000 times with minimal degradation in performance. No devices of the doped polymer type have been independently tested as yet at INEL, but it is expected they will be tested during 1994.

Mixed Metal Oxides (Pinnacle Research Institute) - Pinnacle Research Institute (PRI) has been developing ultracapacitors using mixed metal oxides as the active material in the substrates for about ten years (References 25-27). The work has been funded over much of that time by DOD on a DARPA contract. Initially the work was directed toward space defense applications. More recently the PRI work has become of interest for automotive applications, such as electric and hybrid vehicle drivelines and electrically heated

TESTING OF ULTRACAPACITORS AT THE INEL

A number of high energy density capacitor devices have been tested over the last several years in the Battery Test Laboratory at the INEL. A summary of the test procedures and results are given in References 10, 29-31. As discussed in previous sections of this paper, testing is continuing on various capacitor devices and modules as they become available. The capacitors most thoroughly tested have been the 3 V, 500 F power capacitors that can now be purchased from Panasonic. Photographs of the device and a 12 V module assembled from twelve of the 3 V devices are shown in Figures 13 and 14. Recently a capacitor pack (Figure 15) consisting of fourteen (14) of the 12 V modules was assembled and characterized. The capacitor pack was cycled on the PSFUDS cycle for up to 8 hours without difficulty. It will be used with the Solectria interface electronics unit to test an 144 V pack of Sonnenschein 8GU1 lead-acid batteries on the DST cycle.

ULTRACAPACITOR TECHNOLOGY (PRESENT STATUS-1993 and FUTURE PROJECTIONS)

A summary of ultracapacitor technology – status as of 1993 and future projections – is given in Table 9. Explanations of the most important findings given in the table are discussed in the following sections.

PRESENT STATUS-1993 - Ultracapacitor technology has continued to improve in the past year and in addition, more detailed information/data are available on which to base technology assessments. High energy density power capacitors are available as a commercial product from Panasonic, which now markets 3 V, 500 F and 1500 F devices. Both devices, which have been tested extensively 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 mohm 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 the 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 for those using organic electrolytes efficiencies of 85 to 88%. Life cycle testing of various capacitors has indicated that achieving greater than 100,000 cycles is possible. Tests of bipolar stacks have indicated that stacking capacitor cells should not prove difficult as minimum difficulty with cell imbalance has been encountered with both the carbon-based and mixed-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 in the devices 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 good 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.

Dramatic improvements in packaging of mixed-oxide capacitors (Reference 27) at Pinnacle Research Institute (PRI) have reduced the cell thickness from 8 mils to 2 mils and increased the energy density to 4-5 Wh/kg in small (several cm^2) bipolar (up to at least 100 V) devices. PRI is presently scaling up their small devices to 80 to 200 cm^2 bipolar devices. Delivery to INEL of these larger devices for testing is expected during 1994. There remain serious questions regarding the affordability of the mixed metal oxide devices for automotive applications, but an evaluation of the cost questions is presently underway as part of the DOE contract with PRI.

FUTURE PROJECTIONS - The major questions regarding ultracapacitor technology are concerned with energy density and cost. As indicated in Table 1, the 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. Carbon-based substrates using an organic electrolyte
2. Mixed metal oxides with 10-20 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, of course, cycle life and cost goals must also be met. Results of a simple analysis of the carbon-based technologies are shown in Tables 10 and 11 for the case of a carbon loading of 1 gm C/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.

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Table 4. Charge/discharge characteristics of a 20 V bipolar stack of 1 V Maxwell carbon/metal fiber composite cells using KOH as the electrolyte.

Test Charge = C Discharge = D		Charge Current = A	Discharge Current = A	(W/kg)av	Time (sec)
(1)	C	1.4	–	133	37.6
	D	–	2	190	25.8
(2)	C	1.4	–	–	37.7
	D	–	4	380	11.8
(3)	C	1.4	–	–	37.9
	D	–	8	760	5.0
(4)	C	1.4	–	–	38.1
	D	–	10	950	3.8
(5)	C	1.4	–	–	38.3
	D	–	12	1140	2.8

Test Charge = C Discharge = D		A-sec	W-sec	Resistance/cell (ohm)	(Wh/kg)
(1)	C	52.6	548	0.0135	1.55
	D	51.5	406	0.0150	1.13
(2)	C	52.7	549	0.0135	–
	D	47.4	328	0.0142	0.91
(3)	C	52.9	550	0.013	–
	D	40.4	226	0.013	0.63
(4)	C	53.1	554	0.0129	–
	D	38.5	206	0.0135	0.57
(5)	C	53.4	557	0.0127	–
	D	33.8	191	0.0132	0.53

Device weight = 5.2 gm/cell x 20 cells = 104 gm
Cell area = 20 cm^2

Table 5b. Summary of test data for the 5 V Lawrence Livermore Laboratory stack.

Test Charge = C Discharge = D	Charge Current = A	Discharge Current = A	Time (sec)	A-sec
(1) C	1	–	21.75	21.68
D	–	1	22.8	22.7
(2) C	2	–	10.1	20.2
D	–	2	11.0	22.0
(3) C	5	–	3.6	18.1
D	–	5	4.1	20.7
(4) C	5	–	3.4	17.1
D	–	10	1.9	19.6

Test Charge = C Discharge = D	W-sec	Resistance/cell (ohm)	Wh/kg	(W/kg)/av
(1) C	71.8	0.010	0.86	108
D	62.1	0.0114	0.75	108
(2) C	69.5	0.0098	0.84	216
D	57.8	0.0115	0.70	216
(3) C	67.9	0.0097	0.82	541
D	49.3	0.0105	0.59	541
(4) C	65.3	0.0096	0.79	541
D	38.7	0.0104	0.46	1082

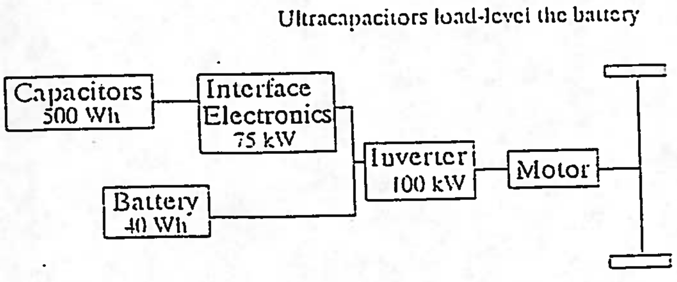
Device weight: 23.1 gm, 58 cm^2, 5 V (five cells in series)

Table 7. Interface circuit evaluation summary (taken from Reference 28).

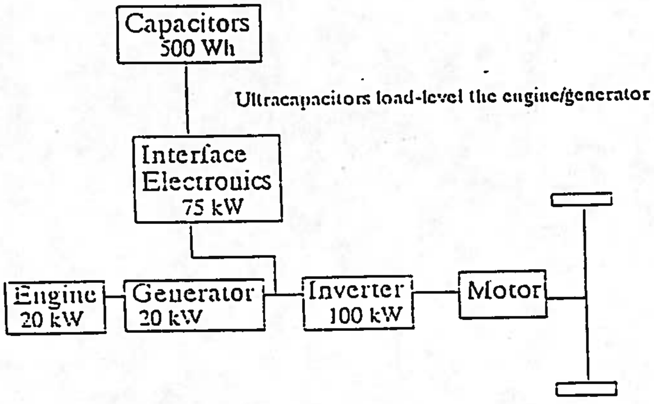
	Hard Switching	Soft Switching
Rated input/output voltage range (V)	120/250	120/250
Input voltage range Vin (V)	80 - 350	50 - 350
Output voltage range (V)	Vin + 5 - 355	Vin + 50 - 400
Rated power (kW)	30	30
Switching frequency (kHz)	10	35
Input current ripple (A) (peak to peak)	30	<1
Weight (pu)*	1.6	0.76
Volume (pu)*	0.66	0.37
Cost (pu)*	0.95	0.70
Efficiency (%)**	93 - 67%	95 - 85%
* 1 pu = equivalent measure of EV2000-75 drive with a 66 kW input capacity from battery		
** Efficiency values are "one-way" efficiencies		

Table 8. Projected characteristics of the Ecostar driveline using ultracapacitors (taken from Reference 28).

	Weight (kg)	Volume (L)	Cost ($)
CONVENTIONAL AC DRIVELINE			
NaS Battery (40 kWh, 56 kW)	450	361	6,000(1)
Motor Controller Electronics	24	39	1,000(2)
Total	474	400	7,000
Incremental Parameters for Ultracapacitor System			
Ultracapacitors (500 Wh)			
Near-term(3)	100	50	500(5)
Advanced(4)	50	25	500(6)
Interface Electronics			
30 kW	18	14	700
60 kW	36	28	1400
Ultracapacitor & Interface Electronics Near-Term Ultracapacitor			
30 kW	118	64	500 + 700
60 kW	136	78	500 + 1400
Ultracapacitor & Interface Electronics Advanced Ultracapacitor			
30 kW	68	39	500 + 700
60 kW	86	53	500 + 1400
(1) Battery cost goal $150/kWh			
(2) Motor controller electronics cost goal, (10,000+ quantity), $1,000 for 56 kW unit			
(3) Near-term ultracapacitor goal 5 Wh/kg, 10 Wh/L			
(4) Advanced ultracapacitor goal 10 Wh/kg, 20 Wh/L			
Capacitor cost goal $1/Wh			



Electric vehicle drive using ultracapacitors



Engine-electric hybrid driveline using ultracapacitors

Figure 1. Electric drivelines using ultracapacitors.

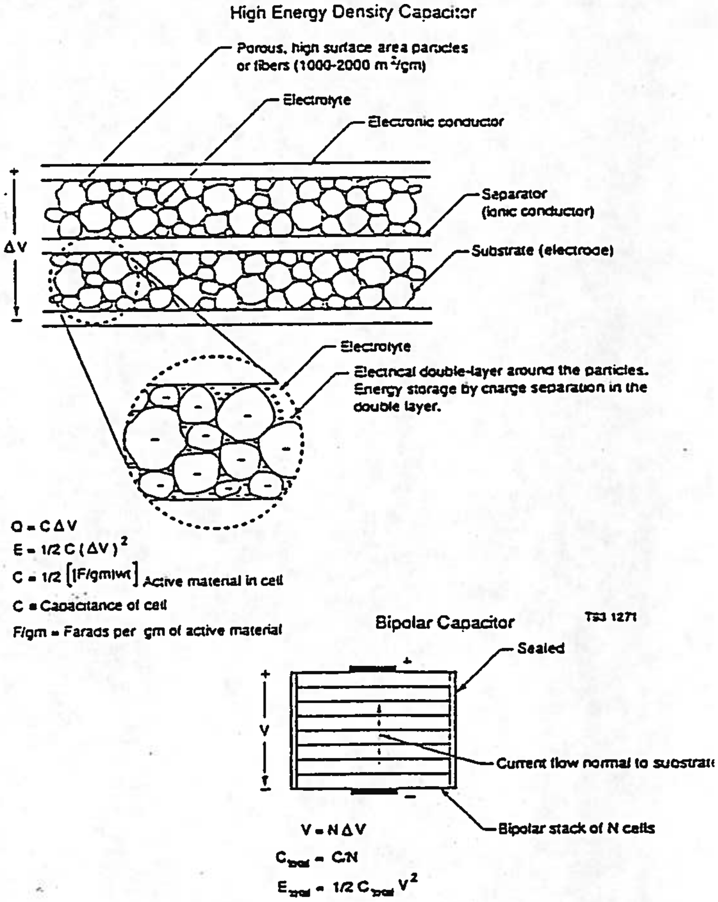


Figure 2. Bipolar ultracapacitor cells and stack.

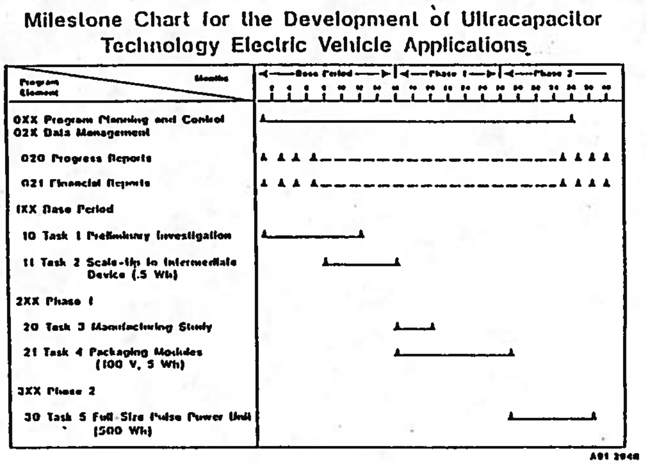


Figure 3. The schedule for the Maxwell/Auburn Program.

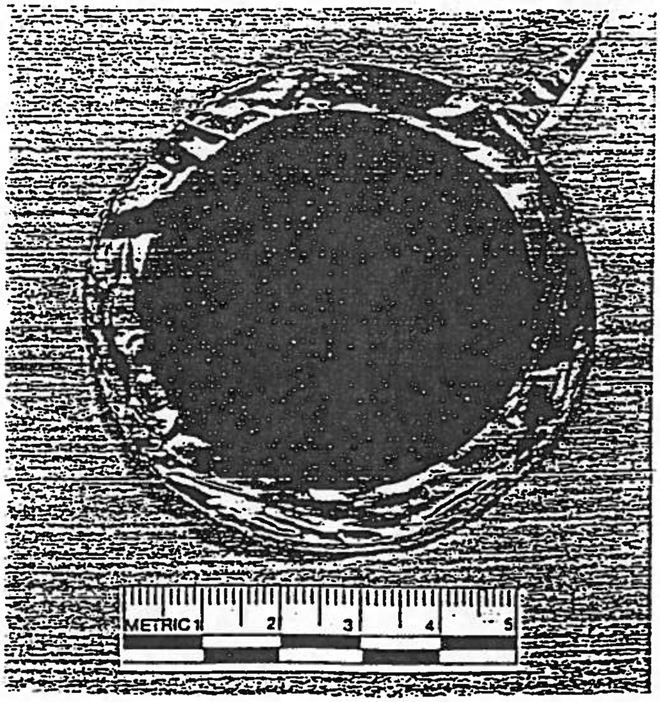


Figure 4. A carbon/metal fiber composite substrate.

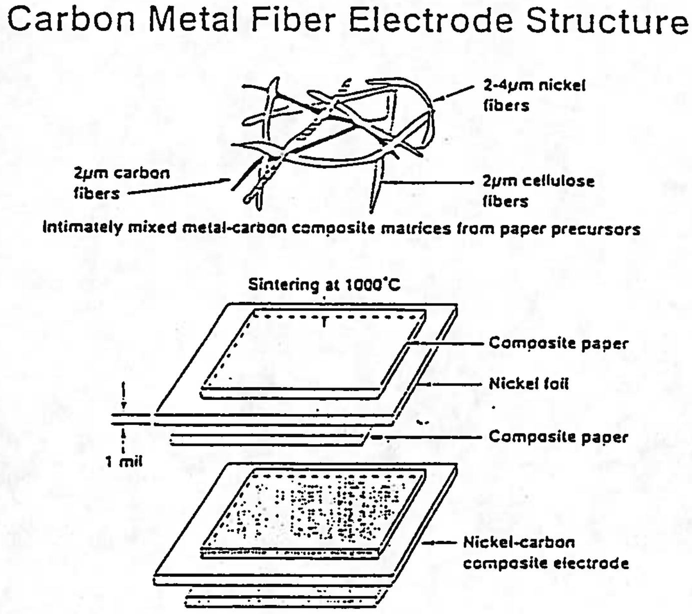


Figure 5. The carbon/metal fiber composite substrate schematic.

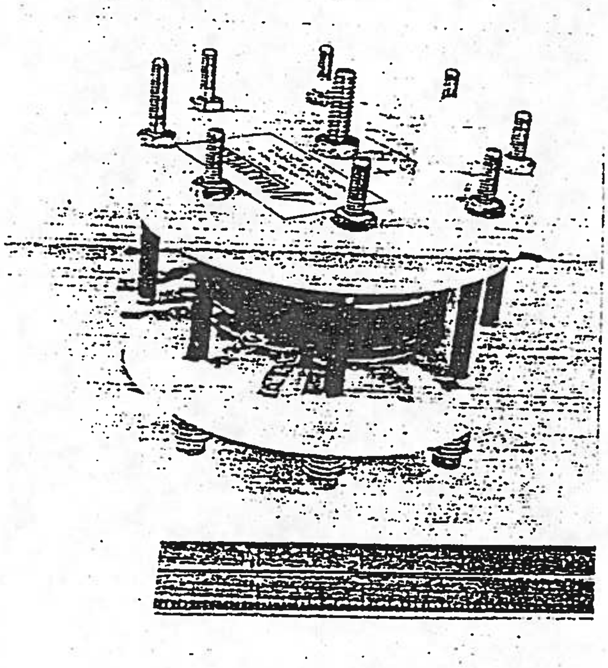


Figure 6. The 20 V Maxwell bipolar stack.

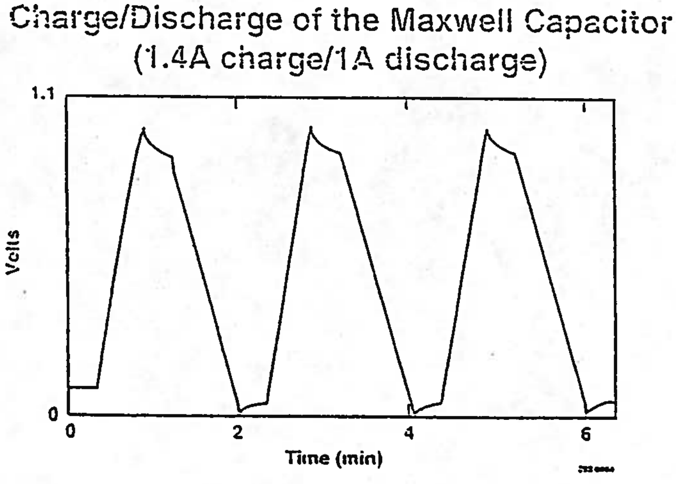


Figure 7. Charge/discharge curves for the Maxwell 1 V cell.

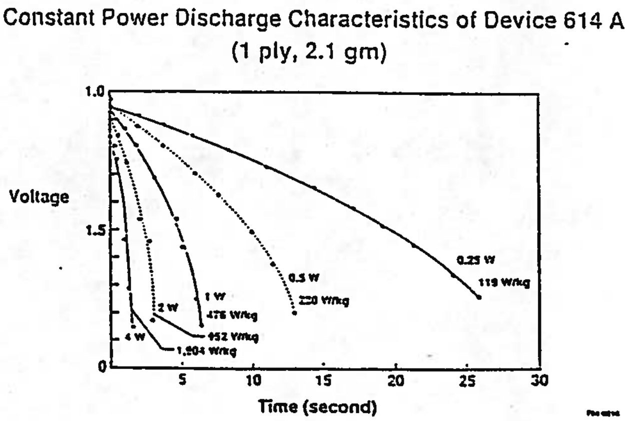


Figure 8. Constant power discharge curves for the Maxwell 1 V cell.

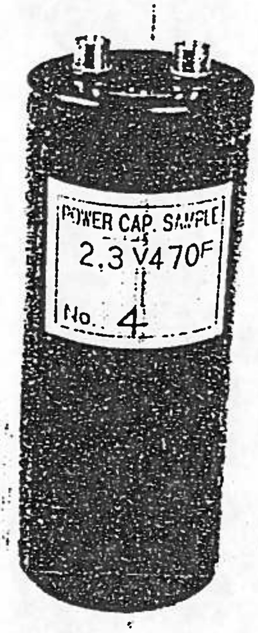


Figure 13. The 3 V, 500 F Panasonic power capacitor.

Figure 14. The 12 V module of 3 V, 500 F Panasonic power capacitors.

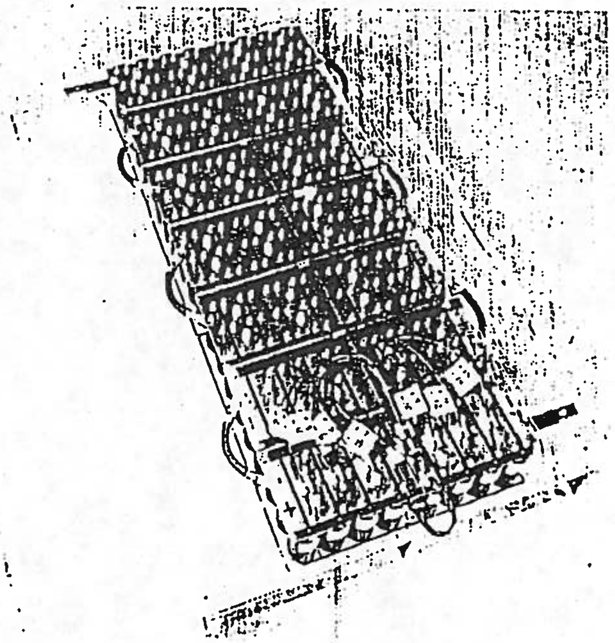


Figure 15. The 168 V pack of fourteen 12 V modules of 3 V, 500 F Panasonic power capacitors.