SYMPOSIUM PROCEEDINGS

RP-35-94 Burke, Andrew
Electrochemical Capacitors for
Electric Vehicles - Technology
Update and Implementation
Considerations

Volume 1, Sessions 1A-2D
Poster Sessions

THE 12TH INTERNATIONAL ELECTRIC VEHICLE SYMPOSIUM (EVS-12)

and Electric Vehicle Exposition

Presented by

Electric Vehicle Association
of the Americas (EVAA)

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Edison Electric Institute
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EVS-12

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Electrochemical Capacitors for Electric Vehicles-Technology Update and Implementation Considerations

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Abstract

Electrochemical capacitor (ultracapacitor) technology for electric vehicles is reviewed. Data is presented for single cell and bipolar devices showing energy densities of 1–2 Wh/kg for 1V, aqueous electrolyte devices and 5–7 Wh/kg for 3V, organic electrolyte devices. Tests have been performed on the devices at constant powers up to 3 kW/kg. Barriers to the availability of these devices in quantities and costs suitable for vehicle testing are discussed as well as the need for interface electronics between the capacitor and the battery if the capacitor is to satisfactorily load level the battery.

Introduction

As the power capability of electric vehicle drivelines (motors and controllers) has steadily increased in recent years, a major problem has been how to design batteries that can provide the peak power they require. Batteries are presently being developed with high peak power capability (peak power density as high as 500–700 W/kg), but it is not yet known what trade–offs in energy density, cycle life, and cost will result from the need to attain that high power density. Another approach to meeting the high power requirement of the energy storage system in the vehicle applications is to use a pulse power unit in conjunction with the battery (Figure 1). The pulse power unit provides the peak power and the battery provides the average power and the required energy storage. Electrochemical capacitors (ultracapacitors) are a promising candidate for the pulse power unit. In this paper, the design specifications for electrochemical capacitors are summarized and the present status of the technology is reviewed and its future potential assessed. Barriers to the implementation of the technology in vehicles are discussed, including scale–up and limited production of devices and the need for interface electronics between the capacitors, battery, and motor controller.

Capacitor/Battery Energy Storage Systems

Driveline Configurations

Electrochemical capacitors can be used to load level the battery (Figure 1) or the fuel cell (Figure 2) in electric vehicles or the engine/generator in engine–electric hybrid vehicles (Figure 3). In all these driveline configurations, the capacitors provide high power (peak kW) during acceleration of the vehicle and recover energy during regenerative braking. The capacitors are sized by a load–leveling energy storage requirement (Wh), which is dependent on the driving cycle on which the vehicle is expected to operate. The weight and volume of the capacitor then depends on its energy density (Wh/kg, Wh/l). It is generally assumed that for the vehicle applications (Figures 1–3), the peak power density (W/kg) of the capacitor is sufficiently high that the weight and volume of the capacitor needed to meet the energy storage requirement(Wh) can provide the peak power required (kW).

Device Specifications

The results of a study of ultracapacitor specification requirements for various vehicle applications are given in Reference 1. As with batteries, it is expected that devices can be developed with a range of characteristics – that is energy density and peak power density. Previous work (Reference 2) indicated that the minimum energy density that would permit packaging capacitors in vehicles was about 5 Wh/kg, 10Wh/l. Clearly higher energy density would be advantageous if, as discussed in Reference 1, the peak power density of the capacitor is also increased. Table 1 summarizes the specification requirements for capacitors with energy densities of 5 and 10 Wh/kg. Figure 4 shows the requirements graphically as a Ragone plot. These same specifications are applicable for all the vehicle drivelines shown in Figures 1–3. Of special note are the high cycle requirement of 100,000 cycles, which results from the frequent charge and discharge of the capacitor as it load levels the battery, fuel cell, or engine–generator, and the closely related requirement of a high round–trip efficiency of 95% for the charge/discharge cycle. As the energy density of capacitors is increased, it will be possible to store more than a near– minimum amount of energy and the cycle life can thus be reduced accordingly.

Capacitor Technology Update

Electrode Materials

The United States Department of Energy (DOE) initiated an ultracapacitor development program in mid–1992 (Reference 3). Both the Europeans and the Japanese are known to have similar programs, but much less is known about their programs, especially as they relate to high energy density devices suitable for vehicle applications. The distinguishing characteristic of each program is the material being used for the electrodes. The materials being considered include the following:

- Carbon/metal fiber composites
- Foamed (aerogel) carbon
- Carbon particulate with a binder
- Doped conducting polymer films on carbon cloth
- Mixed metal oxide coatings on metal foil

The general approach in all the programs is to develop a very high surface area electrode material (>500 m2/gm) having low electronic resistance and high specific capacitance (>150 F/gm) in which energy is stored as charge–separation and/or surface charge transfer in the many small pores of the material (see Figure 5 for a schematic of a bipolar ultracapacitor device). For best performance, the macro–porosity of the electrode material should be 50% or less and the diameter of the micro– pores should be 40–60 A – sufficiently large for the electrolyte ions to diffusion in and out of the pores as the capacitor charges and discharges at high rates. Discussions of the various technologies can be found in References 4 through 10. Most of the technologies are at the small laboratory prototype stage (20 cm2 or smaller). Single cell and bipolar stack devices (Figure 6) have been fabricated in small numbers. Devices using both aqueous (1V/cell) and organic (3V/cell) electrolytes have been assembled by various groups and a number of the devices have been tested at the Idaho National Engineering Laboratory (INEL) as reported in References 3,11–14. Test results for several of the technologies are discussed 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, 3V single cell configuration. Panasonic now markets 70F, 500F, and 1500F devices. All these devices have been tested at the INEL and found to have energy densities of 2.3 Wh/kg and 2.9 Wh/l for charging to 3V (Reference 12–14). The resistance of the 500F device is 3–4 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 (Figure 7), but their energy densities are not high enough for packaging in electric vehicles.

Laboratory tests of single cell and bipolar stacks of devices fabricated by Maxwell Laboratories as part of the DOE Ultracapacitor Development Program have been performed at the INEL. Tests of single cell devices have shown energy densities of 1 to 2 Wh/kg (Table 2) for devices using aqueous electrolytes and 5 to 7 Wh/kg (Table 3) using organic electrolytes. All the single cell devices exhibited linear constant current discharge characteristics (Figure 8) even at very high discharge rates. The resistances of the 1V cells using the aqueous electrolyte (KOH) are in the range of .2 to .5 ohm–cm2 and for the 3V cells using an organic electrolyte, the range is 1 to 2 ohm–cm2. PSFUDS testing (see Reference 11 for a discussion of the test cycle) of the cells using the aqueous electrolyte has shown round–trip efficiencies of 90 to 92% and for those using the organic electrolyte, the efficiencies were 85 to 88%. Constant power testing of the cells was performed at powers as high as 2Kw/kg for the aqueous electrolyte cells and as high as 4 kW/kg for the organic electrolyte cells (Table 3).

Three 20 V bipolar stacks (Figure 6) of 1V aqueous electrolyte cells (20cm2) from Maxwell Laboratories were tested at INEL. The stacks were assembled using bipolar carbon/metal fiber electrodes with cell–to–cell sealing in the stack done using viton rings with aluminum tabs between cells to track the cell–to–cell variability of the voltage during charge/discharge cycles. The bipolar stacks functioned very well with no sign of degradation over the time of the testing which included constant current, constant power, and PSFUDS cycling. The energy density and resistance of the stacks were consistent with the previously discussed characteristics of the single cells indicating that the bipolar electrodes were functioning in a true bipolar manner. The cell–to–cell variability in voltage was relatively small and stable over many charge/discharge cycles permitting routine testing of the stack at a charge voltage of 19V. Leakage current tests showed the stack to have leakage current characteristics similar to that of single cells. Recently three completely sealed 8V bipolar stacks of 1V cells were delivered to INEL by Maxwell Laboratories for testing. The added weight of the sealing materials was about 15% of the package weight. Initial constant current and constant power tests of the sealed bipolar devices showed performance consistent with the single cell characteristics up to a rated voltage of 8V. After the initial performance evaluation was completed, leakage current tests of the devices were initiated with the devices to be held at 8V for three hours. During this period, all the sealed devices developed major leaks of the electrolyte forcing termination of the tests. The failure of the sealing was likely due to a build–up of pressure in one or more of the cells in the stack as it was held at 8V for a long period. With the sealed stack package, it was not possible to track cell–to–cell voltage variations as was possible with the 20V stack using the viton rings. The 20V stack had been leakage current tested without difficulty to a charge voltage of 19V.

The test results for the carbon/metal fiber composite electrode devices from Maxwell indicate that it will be very difficult, if at all possible, to reach the DOE near–term goal of 5 Wh/kg with that electrode technology using an aqueous electrolyte. However, test results for single cell devices indicate that the near–term goal can be meet using a carbon composite electrode using an organic electrolyte. Maxwell is now concentrating on the fabrication of sealed bipolar stacks using an organic electrolyte with the expectation that those devices will have an energy density in excess of 5 Wh/kg with a power capability of at least 2kW/kg.

Projections of Future Development Potential

The major questions regarding the potential for the development of ultracapacitors are concerned with energy density (Wh/kg) and cost ($/Wh). The energy density goals of the DOE development program are 5 Wh/kg for the near–term and 15 Wh/kg for the long–term. The cost goal is $.50/Wh to $1.0/Wh for pulse units storing 300–750 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, carbon–based substrates (>1 gmC/cm3) using an organic electrolyte

2. Doped polymer substrates with an organic electrolyte

3. Mixed metal oxides with 10 to 20 micron thick substrates with an aqueous or organic electrolyte

For electric and hybrid vehicle applications, it is necessary to meet the energy density goal and at the same time have a sufficiently low resistance that the capacitor can be discharged at a power density of at least 1.5 kW/kg. In addition, the cycle life and cost goals of 100,000 cycles and $1/Wh, respectively, must also be met.

With the limited information available on the various technologies, it is most straight–forward to assess the potential of the carbon–based technologies, because of the relative simplicity of the carbon designs and the associated double–layer energy storage mechanisms. The key parameters in assessing the energy density of the carbon–based capacitors are the carbon loading (gmC/cm3) in the electrodes, the specific capacitance of the carbon (F/gmC), and the cell voltage, which depends primarily on the electrolyte used in the capacitor. Since the capacitor consists mostly of carbon, the cost of carbon dominates the capacitor cost. The results of simple calculations of capacitor energy density and cost for capacitors having a carbon loading of 1 gmC/cm3 are given in Tables 4 and 5. These results show the difficulty of meeting the near–term goal of 5Wh/kg with 1V cells (aqueous electrolytes) and the considerable promise of exceeding the long–term goal of 15 Wh/kg using organic electrolytes (3V/cell or higher). Meeting the cost goal of less than $1/Wh also requires relatively high cell voltage and consequently an organic electrolyte. One disadvantage of carbon as an electrode material is its low gravimetric density compared to the mixed oxides. This results in carbon–based device densities of 1.2–1.5 kg/L and as a result, volumetric energy densities (Wh/L) not much higher than the gravimetric energy density (Wh/kg). From the packaging point–of–view, Wh/L is at least as important as Wh/kg.

Capacitor Implementation Considerations

Scale–up and Small Quantity Production

As discussed in the previous section of the paper, capacitor cells having energy densities as high as 6 Wh/kg have been fabricated and tested. These cells are relatively small (20cm2) and store only very small amounts of energy (75 w–sec) at low voltage (1 to 3V) compared to what is needed in vehicle applications. Hence much larger cells are required and many of the larger cells must be put in series–parallel arrangements to form units to be tested with batteries and in vehicles. Work is presently in progress to design, fabricate, and test bipolar stacks of the smaller cells in preparation for scale–up to larger modules. Scale–up of bipolar stacks to larger size cells is not expected to present great technical difficulty after the packaging techniques for the smaller cells are proven, but it will require electrode material fabrication and cell/module assembly on a much larger scale than has been done by any of the capacitor developers in the United States to date. This will require a much greater investment in product engineering and processing equipment than is presently being made or contemplated at the present time.

Continued rapid progress in the fabrication of high energy density (>10 Wh/kg), bipolar capacitor stacks in the laboratory can be anticipated in the next few years, but unless much greater investment is made in commercializing the technology, it is not likely that affordable devices and energy storage units large enough for use with or testing in vehicles will become available in that time period. An effort comparable in size to that of the USABC nickel–metal hydride battery program is required to develop ultracapacitors for electric vehicle applications. As noted in Reference 15, there are large potential markets (engine starting and electrically heated catalysts) associated with conventional ICE vehicles, which could themselves justify such a large program.

Interface Electronics

In the driveline schematics shown in Figures 1–3, interface electronics are placed between the capacitor unit and the batteries to control the power split between the two energy storage units and to limit the rate at which the battery recharges the capacitor during periods of low vehicle power demand. When the batteries and capacitors are connected in parallel without the interface electronics, the requirement that the two units are at the same voltage at all times results in the capacitor providing or accepting a significant fraction of the power only during times in which the battery voltage is changing rapidly. This occurs during the first few seconds of a vehicle acceleration or deceleration. After the initial surge of current to or from the capacitor, the battery is essentially unaffected by the presence of the capacitor. The test data shown in Figure 9 for a battery and capacitor connected directly in parallel for the DST test cycle shows this clearly and indicates that the capacitor does not satisfactorily load level the battery in the absence of interface electronics. SIMPLEV simulation results for battery power for the Coconni CRX on the SFUDS79 driving cycle with the battery and a 300Wh capacitor in parallel are compared in Figure 10 with results for the same capacitor controlled to load level the battery. Since capacitor resistance is neglected in the present version of SIMPLEV, the results shown in Figure 10 are for an ideal capacitor. Hence, for a real capacitor having a resistance, the calculated effect of the capacitor directly in parallel with the battery would be even smaller than that shown in Figure 10. Also shown is Figure 10 is the battery power vs. time on the SFUDS79 cycle for the CRX with the battery only. Both the experimental data and the SIMPLEV simulation results show the importance of the interface electronics in allowing the capacitor to load level the batteries. Thus development of interface electronics should be included as part of any ultracapacitor program for electric and hybrid vehicles. The weight, volume, and cost of the interface electronics must be considered, however, in evaluating the attractiveness of driveline systems utilizing capacitors as was done in Reference 16.

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Acknowledgment

The work presented in this paper was performed while the author was employed at the Idaho National Engineering Laboratory and was supported by the U.S. Department of Energy, Idaho Operations Office, Contract DE–AC07–76ID01570. E.J. Dowgiallo, DOE Washington, Hybrid and Electric Vehicle Propulsion System Division was the technical program manager at DOE.

Table 1

Design Specifications for Pulse Power Units

Pulse Power Unit		
	(Wh/kg) Pulse Unit	
	5	10
Volumetric energy density (Wh/L)aver.	10	20
Discharge rate (W/kg)average	100	200
Useable peak power (W/kg) maximum[a] Efficiency[b]	900 >95%	1700 >95%
Recharge rate (W/kg) average (W/kg) maximum	100 400	200 800
Cycle life[c]	100,000	100,000
Cost ($/Wh)	1	1

a. Maximum discharge rate at which the useable energy is 75% of that for discharge at $(W/kg)_{av}$

b. Efficiency = $1 - I^2 \cdot R/P_{max}$ at $(W/kg)_{max}$

c. 10-year life, >100,000 mi, discharge/charge at $(W/kg)_{av}$

Table 2

Constant Current Discharge Characteristics of the 1V Maxwell Cells

		Charge		Discharge				
Cap No.	Wght* (gm)	Time (sec)	Capacitance (F)	Time (sec)	Capacitance (F)	Resistance** (Ω)	Energy Density*** (Wh/kg)	Ω-cm²
614B	1.844	14.96	15.7	13.61	15.2	0.0141	1.17	0.28
614A	2.101	15.25	15.8	14.4	15.8	0.0102	1.05	0.20
615A	2.147	15.96	16.6	14.8	16.4	0.0117	1.07	0.23
624A	5.189	54.44	56.9	52.07	55.7	0.0118	1.51	0.23
617A	5.214	49.65	52.2	46.93	51.6	0.0126	1.38	0.25
621A	5.302	56.73	59.2	55.13	58.8	0.0116	1.55	0.23

* Weight of all active materials, 20 cm²

** Calculated from IR step at beginning of charge and discharge

*** Based on 1 V

Table 3

Constant Current Discharge Characteristics of the 3V Maxwell Cells

Discharge Current (A)	Capacitance (F)	Discharge Time (sec)	Resistance (ohm)	Energy Out (J)	Wh/kg	Wh/L	(W/Kg)av
1	12.5	37.6	0.08	55	6.8	8.1	666
3	11.6	11.6	0.67	49	6.1	7.2	2000
5	10.7	6.4	0.076	41	5.1	6.1	3333

Discharee: 3 V to 0 V

Device Characteristics:

Weight	2.25 gm
Area	20 cm²
Volume	1.88 cm³

Table 4

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

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

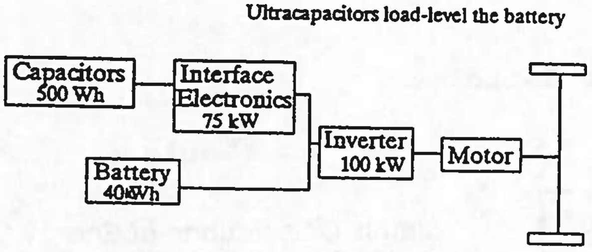
Carbon loading 1 gm/cm3

Table 5

Simple Calculations of Cost (Carbon-Based Ultracapacitors)

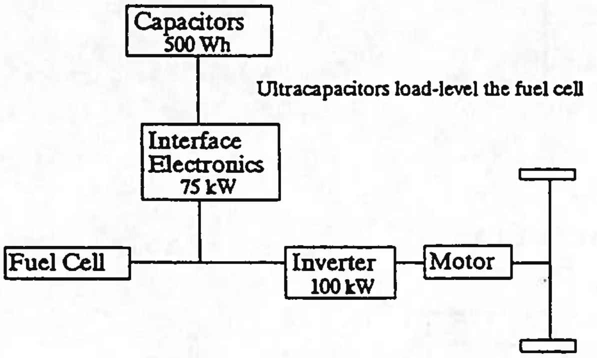
	$/Wh			
$/lbC	5 Wh/kg	10 Wh/kg	20 Wh/kg	30 Wh/kg
2	0.59	0.30	0.15	0.10
5	1.47	0.74	0.37	0.25
10	2.9	1.45	0.73	0.49

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



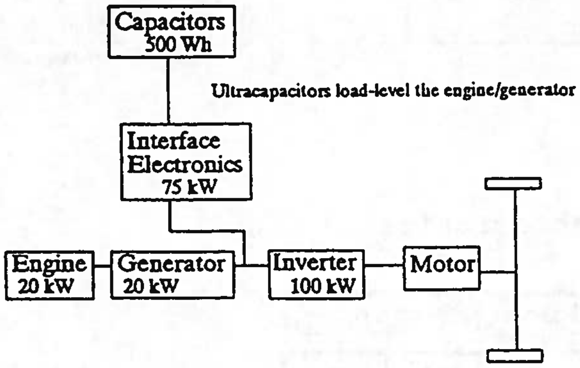
Electric vehicle drive using ultracapacitors

Figure 1



Fuel cell-electric hybrid driveline using ultracapacitors.

Figure 2



Engine-electric hybrid driveline using ultracapacitors

Figure 3

Energy-Power Requirements for Energy Storage Technologies

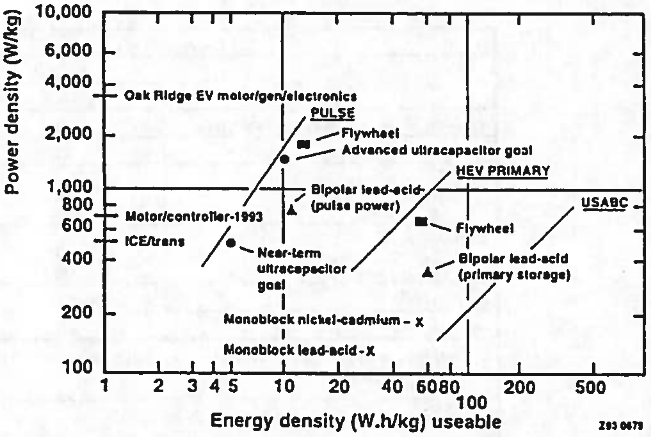


Figure 4

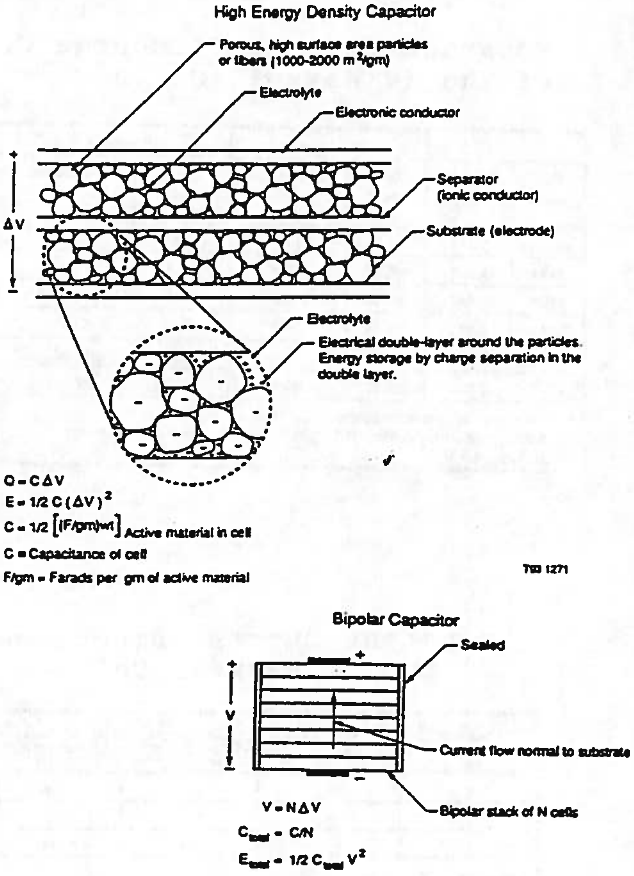


Figure 5

The Maxwell 20V Bipolar Device

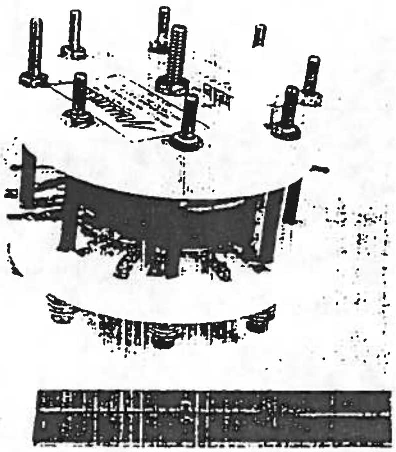


Figure 6

The 168V Panasonic Capacitor Bank

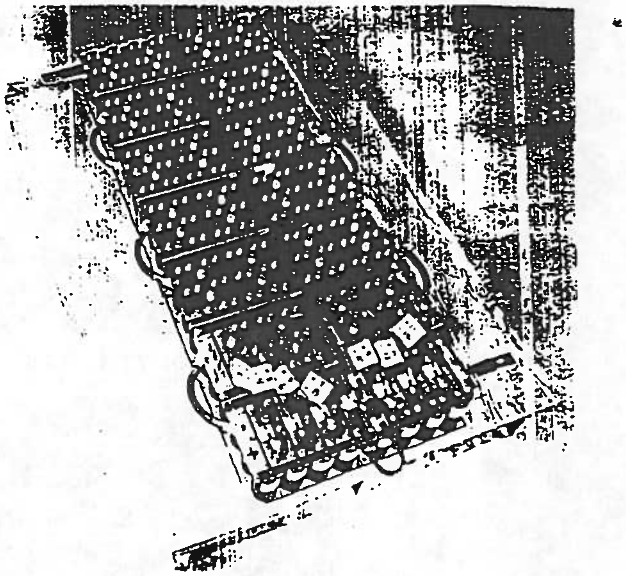


Figure 7

Discharge Characteristics of a Maxwell Ultracapacitor

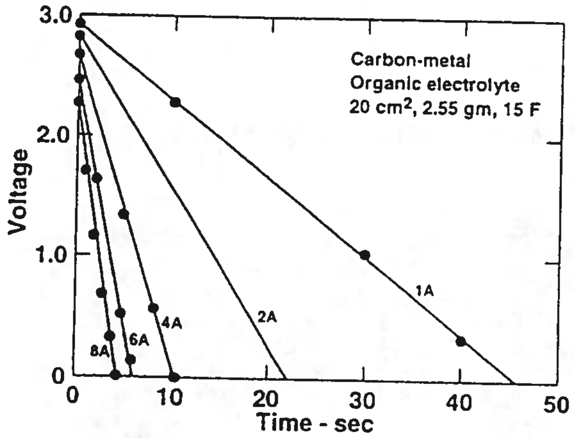


Figure 8

Capacitor/battery in Parallel without Electronics

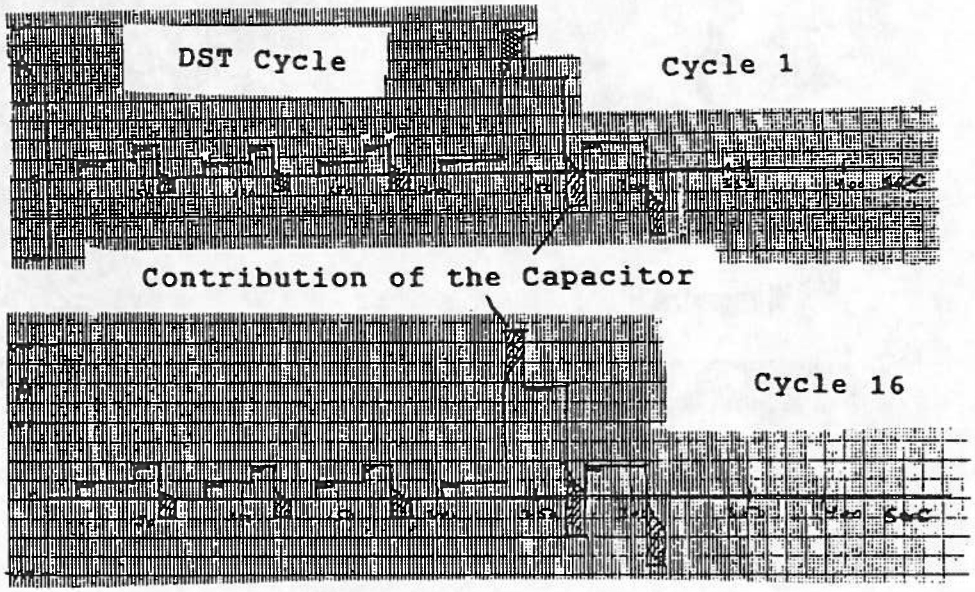


Figure 9

SIMPLEV Simulation Results with and without Interface Electronics

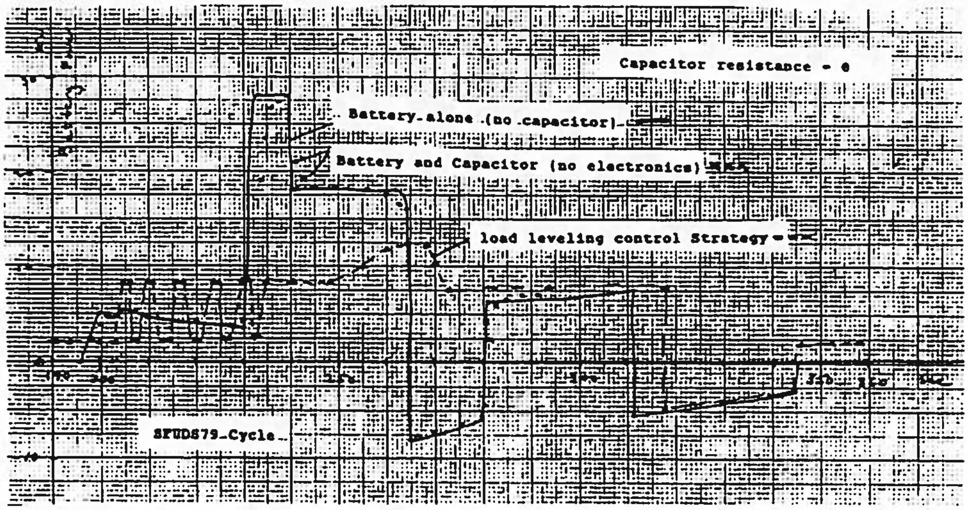


Figure 10