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TEST PROCEDURES FOR HIGH ENERGY DENSITY, ELECTROCHEMICAL CAPACITORS

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ABSTRACT

The testing of ultracapacitors has evolved over the last 4-5 years as devices have become available and it was necessary to determine their characteristics relative to the requirements for electric and hybrid vehicle applications. It is widely recognized in the ultracapacitor community that there is a need for a consistent set of test procedures that can be used by the various groups involved in ultracapacitor device development. In this paper, the test procedures that have been used to evaluate the deliverables from the United States Department of Energy's Ultracapacitor Development Program are reviewed and typical data obtained are presented to illustrate the behavior of state-of-the-art devices. Procedures for both large signal dc and small signal ac impedance testing are discussed as they relate to ultracapacitor research and development. The large signal dc tests make use of equipment and test approaches common to battery testing. The ac impedance tests make use of a programmable potentiostat and the associated software commonly used by electrochemists to evaluate electrodes and small battery cells. The test procedures and data analysis methods are also related to both dc and ac modeling of the ultracapacitors.

1. Introduction

The testing of ultracapacitors has evolved over the last 4-5 years as devices have become available and it was necessary to determine the characteristics of the devices relative to the requirements for electric and hybrid vehicle applications. In addition, it became necessary to characterize materials and electrodes as components in ultracapacitors. Much of the initial testing and the development of the test procedures have been done at the Idaho National Engineering Laboratory (INEL) as part of the

United States Department of Energy's (USDOE) ultracapacitor program (References 1,3).

It is widely recognized in the ultracapacitor community that there is a need for a consistent set of test procedures to evaluate the performance of ultracapacitors, especially for those intended for use in electric drivelines as pulse power devices. Test procedures currently available (Reference 4) were developed to characterize capacitors to be used in electronic circuits (high frequency charge and discharge) or in low power applications (memory backup). Those procedures are not suitable for testing the high power devices to be used in electric drivelines that are charged/discharged in 5 to 100 seconds at high rates. The initial documentation of the test procedures used in the USDOE program is given in Reference 2. That test manual forms the basis for much of the material given in this paper.

The initial testing (Reference 1) of ultracapacitors evolved from battery testing and made use of the same equipment when possible. The charge and discharge times of the ultracapacitors were, of course, much shorter than that of batteries, but the control and response times and sampling rate capabilities of several of the programmable battery testers were compatible with the short (5 to 100 second) test times for the ultracapacitors. In some instances, it was necessary to change the current shunts in the testers when testing small devices to increase the accuracy of the current measurement. All the testing was done at 1 second or smaller sampling times. One of the testers (a Maccor) had the capability of .1 second sampling times when needed and in addition, had an automatic feature that it would take data at that maximum rate whenever a sudden change in voltage occurred as at the start of a charge or discharge step.

The tests performed on the ultracapacitors were in most cases much like those performed on batteries - constant current and constant power charges and discharges and variable power transient cycle tests. These tests will be referred to as large signal dc measurements. As for batteries, the current and power levels for the tests of a particular ultracapacitor device are set based on its energy storage capacity and/or weight. As the ultracapacitor development program progressed and a better understanding of the electrochemistry and circuit characteristics of the devices evolved, it became apparent that information on device and material characteristics that could be extracted from small signal ac impedance data would also be valuable. That type of testing (Reference 5) is familar to most electrochemists, but it is not widely used in battery testing. Ac impedance techniques are now an important element in ultracapacitor testing for electrode, cell, and stack evaluation. Hence procedures for both large signal dc and small signal ac impedance testing are discussed in this paper as they relate to ultracapacitor research and development.

2. Circuit Models of Ultracapacitors

2.1 DC Behavior

Ultracapacitors used in electric drivelines experience large non-steady (transient) discharge currents, much like a battery in an electric vehicle, except that they are subject to short, frequent periods of charging to keep them at a high state-of-charge. They do not, however, experience changes in polarity even though the direction of the current to/from the device changes frequently. Hence, the ultracapacitors function as dc devices. In simplest terms, they can be modeled as a capacitor (C) and a resistance (R) in series.

$$V_0 - V = IR + (Q_0 - Q)/C$$

where

Q - charge on the capacitor
V - Voltage on the capacitor
V_0, Q_0 - Voltage and charge at full charge

For an ideal capacitor, C and R are constants independent of state-of-charge and charge/discharge rate. The intent of the large signal dc testing is to determine the effective values of R and C and the extent to which the behavior of the ultracapacitors in vehicle applications can be described in this simple manner.

2.2 AC Behavior

A more complete understanding of the electrical energy storage and circuit characteristics of ultracapacitors can be attained by treating them as ac devices and studying their response as a function of the frequency of an applied sinusoidal voltage. This is done in ac impedance testing, in which sinusoidal voltage signals of small amplitude, usually only a few millivolts, are applied to the device at frequencies from a fraction of a Hz to many kiloHz. To model the ultracapacitor over this wide range of frequency, it is necessary to use a much more complex circuit (Figure 1) than the simple series connection of a capacitor and resistance cited previously as a dc model. As discussed in the next section, ac impedance data can be used to both determine the R and C for the simple dc model and to select the circuit elements for an ac representation of the ultracapacitor.

3. Test Procedures and Typical Data

3.1 DC testing

As with batteries, the simplest tests of ultracapacitors are done with constant current charging and discharging. In that case, the charge on the capacitor is proportional to the test time and for an ideal device (C = constant), the voltage would be linear with time and departures from ideal behavior become clearly evident from the data (see Figure 2). The average, as well as the instantaneous, capacitance of the device can be calculated from the voltage vs. time data using the relationships: $Cav = Q/V$ or $C(t)=I/dV/dt$. The dc resistance of the device can be determined from the IR step at the beginning of the charge/discharge steps as shown in Figure 3. The data shown in Table 1 and Figure 4 indicate that the simple representation of the dc behavior of ultracapacitors discussed in Section 2.1 are consistent with the constant current test data over a wide range of temperature.

Constant power discharge tests of ultracapacitors are also straightforward to perform using battery test equipment and they yield data that are of considerable interest for vehicle applications. These tests should be run over a range of power density, usually between 100 and 2000 W/kg depending on the power capability of the device being tested. Unlike constant current discharge tests that can be run to zero voltage if desired, the minimum voltage for constant power discharge tests must be sufficiently high that the current required at the constant power of the test does not exceed the maximum current limit of the tester. The ultracapacitor cut-off voltage for constant power discharge tests is often set at one-half the rated voltage of the device, which means that at most about 75% of the energy stored in the device at the rated voltage can be extracted during the constant power discharge. The voltage vs. time curves for constant power discharges are not linear even for ideal capacitor behavior because the current increases during the discharge as the voltage decreases. The energy density of ultracapacitors can best be determined from constant power tests as that type of discharge more closely approximates how the devices are used in vehicles than constant current discharge tests. Typical constant power discharge results are shown in Figure 5. As with batteries, the energy density of an ultracapacitor decreases with discharge rate, but the decrease begins at a much higher power density than for batteries (Figure 6).

Testing of an ultracapacitor should also include transient power cycle tests intended to simulate the use of the capacitor to load level a battery in a vehicle being driven on an urban driving cycle. A test cycle for this type of testing has been designated in Reference 2 as the PSFUDS cycle. As in the case of the SFUDS battery test cycle, the PSFUDS cycle is given as a series of power-time steps involving both charge and discharge of the device being tested. The power levels and length of time for each step is specified such that the test cycle is applicable to different size and performance capacitors. A generalized version of the PSFUDS cycle is given in Table 2, where the power for each step is normalized by a maximum value appropriate for the device being tested. Note that the device is charged back to its rated voltage at the end of each cycle, so that each cycle starts and ends with the device fully charged. The maximum power value should correspond to a power density of at least 500 W/kg. The time shown for each step is appropriate for devices having an energy density of at least 5 Wh/kg. For devices having an energy density less than 5 W/kg, the times for each step should be reduced by the ratio of the energy density of the device to 5Wh/kg. Data from the PSFUD cycle are used to evaluate the transient behavior of an ultracapacitor device in charge/discharge conditions. The round-trip efficiency of the device is calculated as the ratio of the energy taken from it during discharge steps of the cycle to the energy stored in the device during charge steps. The coulombic efficiency can be calculated in a similar manner using the charges taken from and put into the device in the discharge/charge steps of the cycle. For ultracapacitors, the coulombic efficiency should be unity within experimental error. A typical voltage vs. time curve for a device on the PSFUDS cycle is shown in Figure 7. The round-trip efficiency for the data shown is 90% .

Ultracapacitors can also be tested for their leakage current and self-discharge. The leakage current is the current required to maintain the capacitor at its rated or working voltage. It is time- dependent and only approaches a constant value after the voltage has been applied to the capacitor for several hours. Leakage currents arise in part from charge-transfer reactions at the electrodes and often result in gas formation and pressure build-up which can lead to breaching the seals of the capacitor if the leakage current test is done near the limit voltage of the electrolyte. To determine the leakage current characteristics of a device, it is necessary to measure the current to the capacitor over a relatively long time (up to three hours). This can be done using a standard battery tester if it is sufficiently stable and has the capability to measure small currents (down to a fraction of a mA for small devices). Otherwise, it is necessary to use a stable power supply and
a shunt resistor in series with the capacitor being tested.

The self-discharge test is performed to measure the self-dissipation of the ultracapacitor and is an indicator of the extent of the occurrence of non-ideal energy storage/transfer mechanisms at the electrodes. In this test, the capacitor is charged to its rated voltage and held at that voltage for a reasonable period (30 minutes). It is then placed on open-circuit and the voltage measured over a period of 72 hours. Typical self-discharge data are shown in Figure 8. The voltage decreases relatively rapidly over the first hour (or less), after which the decrease is much slower for the remainder of the test.

3.2 AC Impedance Testing

Many important characteristics of ultracapacitor electrodes, cells, and stacks can be determined using ac impedance testing. The tests are done using a programmable potentiostat/galvanostat. Computer software is now commercially available that executes the testing over a specified frequency range and collects and analyzes the data to determine the complex impedance (R and X) of the device being tested at selected frequencies. For ultracapacitors, the tests should be performed at frequencies between .001 Hz and several kiloHz (above the self-resonance frequency of the device). The amplitude of the applied sinusoidal voltage should be set at 5-10 mV per cell. If needed, separate series of tests can be done for a range of base voltages between zero and the rated voltage of the cell or stack to study the effect of voltage level on capacitor characteristics. Typical data for the real and imaginary parts (R and X) of the complex impedance as a function of frequency are shown in Figure 9. As discussed in the next sections, this data can be used to determine the capacitance and resistance characteristics of ultracapacitors and electrodes.

3.2.1 Capacitance and Resistance

The complex impedance (Z) is expressed as

$$Z = R - iX, X = \frac{1}{2}\pi f C$$

$$\mathrm{Abs}(Z) = \sqrt{R^2} + \frac{1}{\left(4\pi^2 f^2 C^2\right)}$$

$$\tan\phi = \frac{-1}{2\pi f R C}$$

where

R = resistance of the capacitor (ohms)
C = Capacitance of the capacitor (farads)
f = frequency of the test (Hz)
ϕ = phase angle

It is evident from Figure 10 that both the capacitance and resistance increase with decreasing frequency (longer discharge times). An approximate relationship between the ac frequency and the dc charge/discharge time is given by

$$t_{cd} = .25 * 1/f$$

For vehicle applications involving charge/discharge times of 2-100 seconds, the corresponding frequency range is .001 to .1 cycles/sec (1-100 mHz). The complex impedance data (R,X) can be analyzed to determine R and C as a function of frequency as shown in Table 3 for one of the Maxwell composite carbon electrode devices. Note that for this device R and C are relatively constant over much of the frequency range of interest for vehicle applications, but change markedly at higher and lower frequencies (shorter and longer discharge times). Hence it appears necessary to evaluate the frequency characteristics of each ultracapacitor design using ac impedance testing.

3.2.2 Electrode and Material Characteristics

Applications of ac impedance testing to determine material and electrode characteristics are discussed in References 6,7. This approach is one of the few direct methods of relating the pore characteristics of the electrode material to the performance of the ultracapacitor. This is done by studying the frequency dependencies of the capacitance and resistance of electrodes and/or cells and relating them to the electrode material characteristics, including pore radius and depth, surface area, and volume and the ionic conductivity of the electrolyte used in the device. In Reference 7, it is shown that the impedance of the pores as a function of frequency can be expressed as follows:

$$Z_p = \frac{1-i}{2\pi_p \sqrt{r_p^3 k\omega C_{dl}}} \operatorname{Coth}\left[l_p \sqrt{\frac{\omega C_{dl}}{k_{rp}}} \left(1+i\right) \right]$$

At high freqencies, Equation (1) reduces to the form

$$Z_p = \frac{1-i}{2\pi n_p \sqrt{r_p^3 k\omega C_{dl}}}$$

At low frequencies, Equation (1) reduces to the form

$$Z_p = \frac{-i}{2\pi r_p \, n_p \, l_p \, \omega c_{dl}}$$

In the complex impedance plot (R vs. X), Equation (2) represents a 45 degree line with respect to the R axis with an intercept at the high frequency limit of R, at which the contribution of the pores to the resistance is essentially zero. Equation (3) represents a vertical line parallel to the X axis. The intersection of the two lines (Figure 11) yields the value of the resistance (R'p) occurring at a frequency (ω rad/sec) equal to the reciprocal of the RC time constant of the device tested. Note that as shown in Figure 10, R'p is only the portion of the total resistance due to the pores and is obtained by subtracting the high frequency dc resistance from the total resistance. R'p is inversely proportional to number of pores in the electrode so that the pore resistance will be less in thick than thin electrodes of a particular electrode material. The pore depth l_p can be calculated from the pore resistance using the expression
This is the same expression used in Appendix II to calculate the contribution of the pores to the resistance of the

electrode. Since the product $V_p{*}R'_p$ is independent of n_p and thus the electrode thickness, l_p becomes purely an electrode material property as is the pore radius, which is given by

$$r_p = 2\ V_p/\ S_p$$

The number (np) of pores in the electrode can be determined from

$$n_p = S_p/\ 2\ \ r_p\ l_p$$

Unfortunately, the pore surface area Sp and pore volume Vp of the electrode material must be known from a source independent of the ac impedance testing before the impedance data can be used to determine np, lp, and rp. Sp and Vp are not easily determined for materials for which most of the surface area is in micropores. Thus impedance testing alone does not yield the electrode material characteristics as would be most desirable.

Acknowledgement

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Table I : Capacitance and resistance of the 1500F Panasonic Power Capacitor at various temperatures

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 4 = 1 sec
(6) Voltage at t = 4 sec

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

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

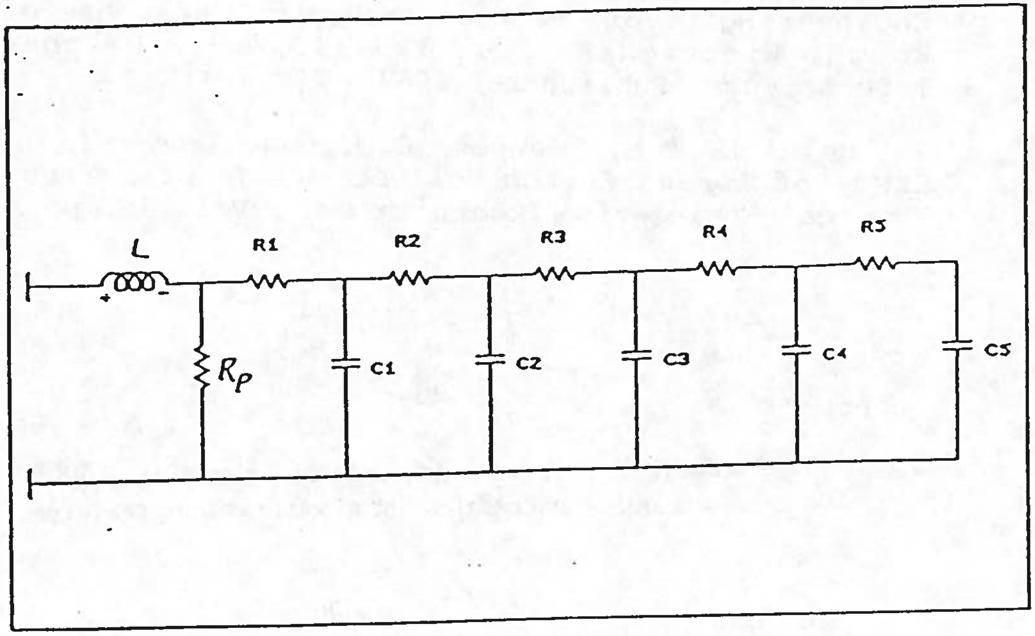

Figure 1 **: Equivalent circuit for an ultracapacitor applicable to a large range of frequency**

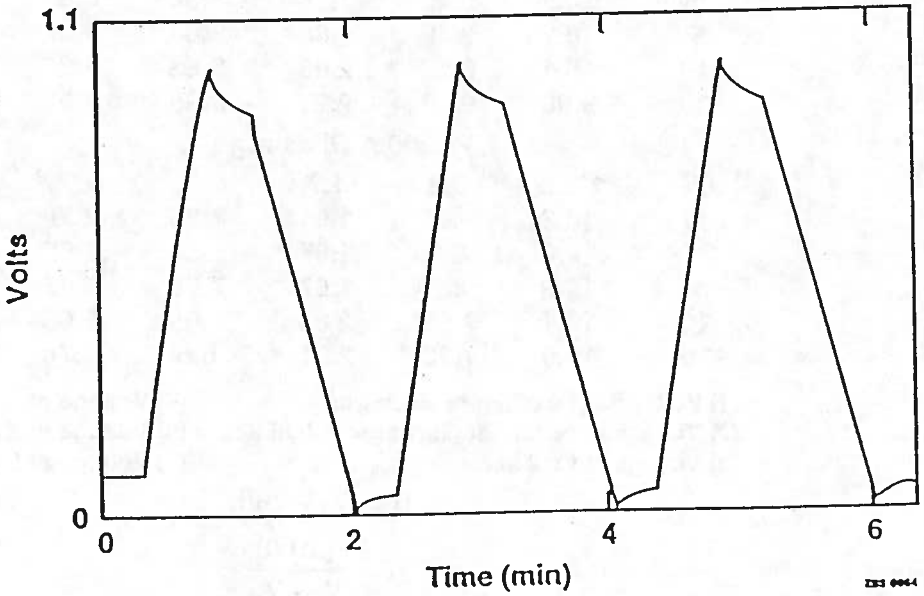

Figure 2 **: Typical charge/discharge voltage vs. time traces for a double-layer capacitor**

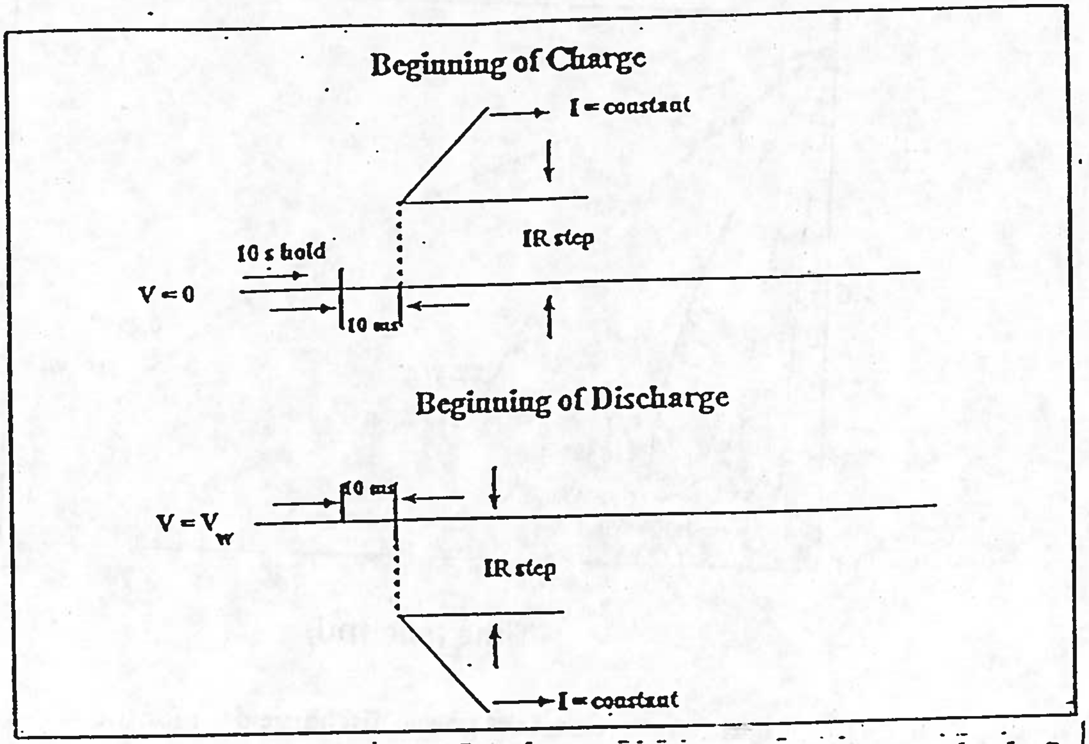

Figure 3: Graphical description of the method for the calculation of capacitro resistance from the IR Step

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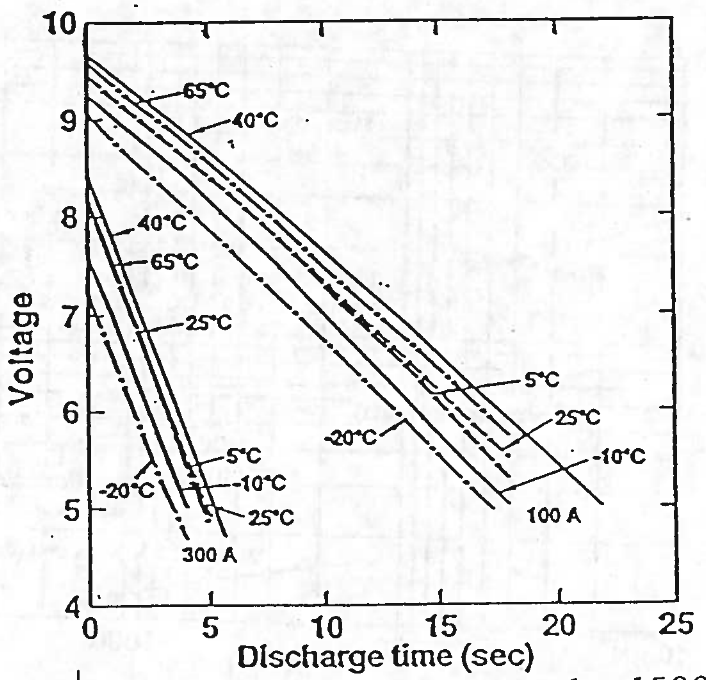

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Figure 4: Voltage vs. time data for the 1500F Panasonic Capacitor (3 devices in series) for 100A and 300A at various temperatures

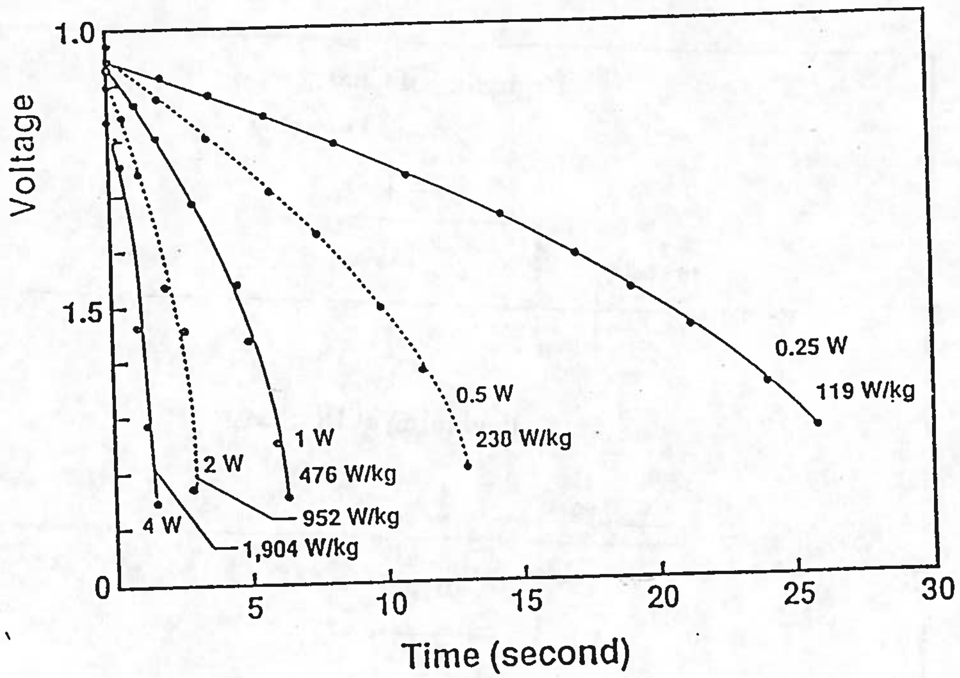

Figure 5 : Constant power discharge data for the IV Maxwell Capacitor

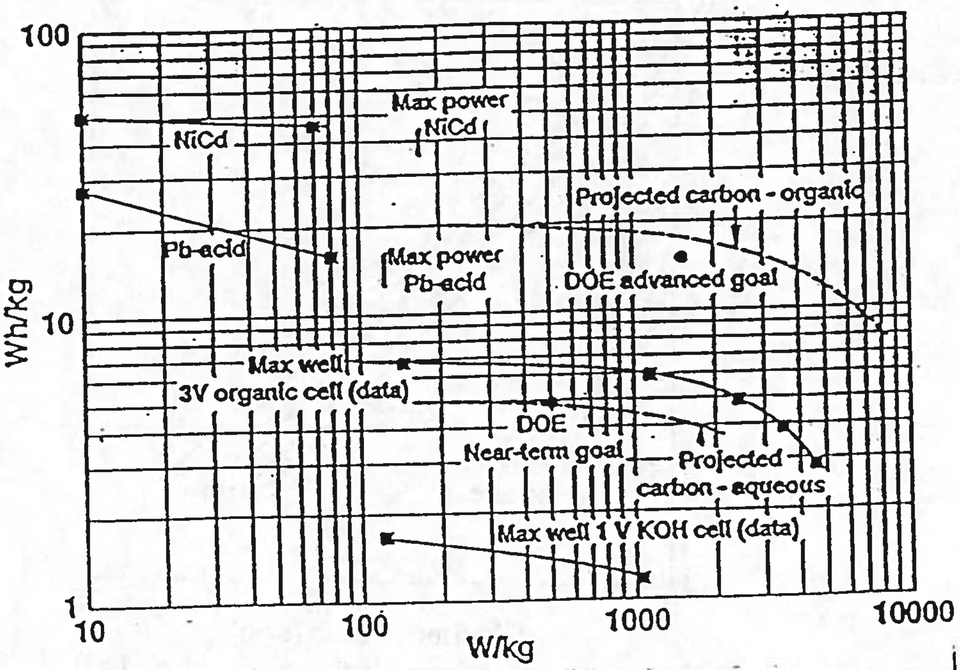

Figure 6: A Ragone Plot for batteries and ultracapacitors

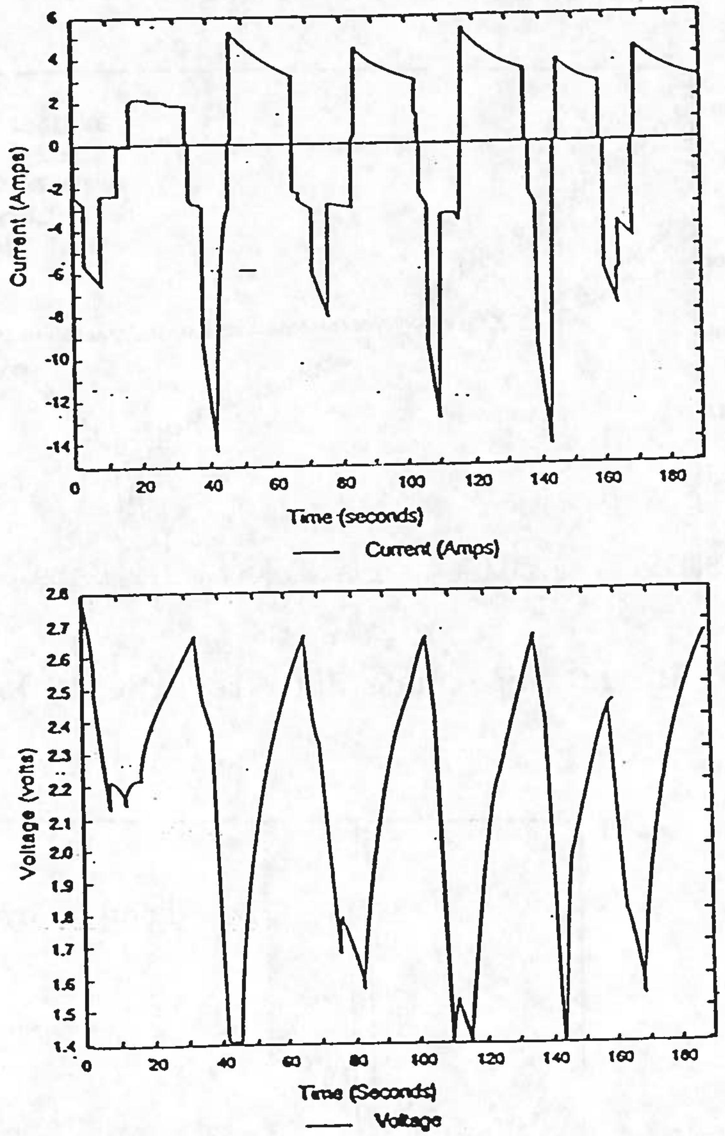

Figure 7: Voltage and current vs. time traces for the 500F Panasonic Capacitor on the PSFUDS cycle

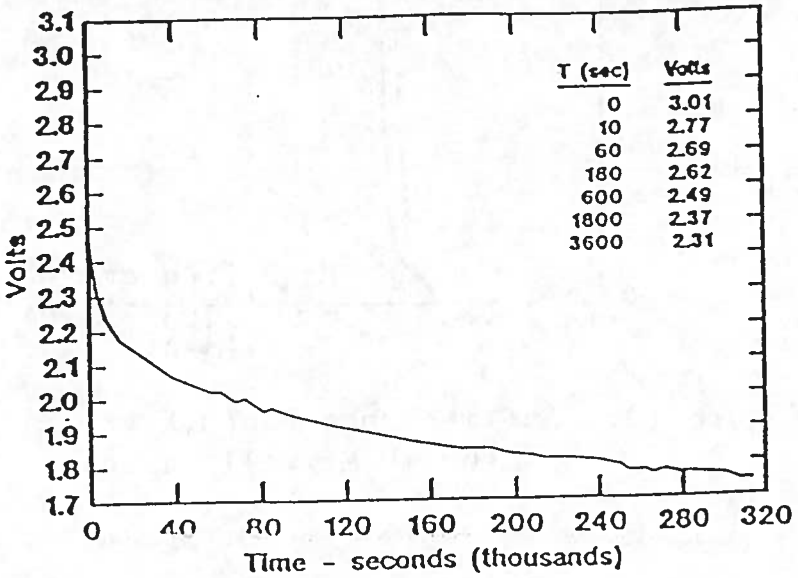

Figure 8: Self-discharge data for the Panasonic 3V,

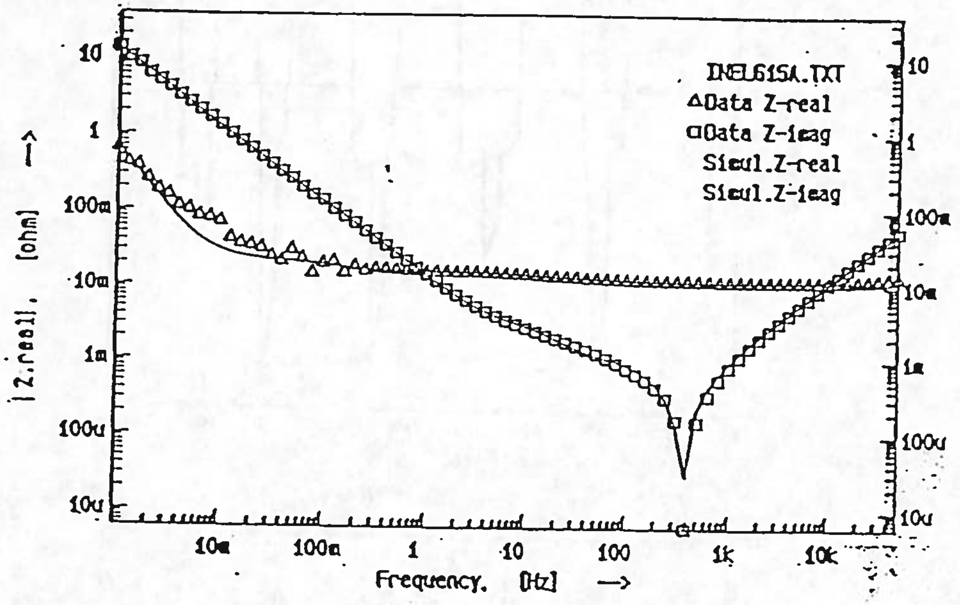

Figure 9: AC Impedance data for the 1V Maxwell Capacitor

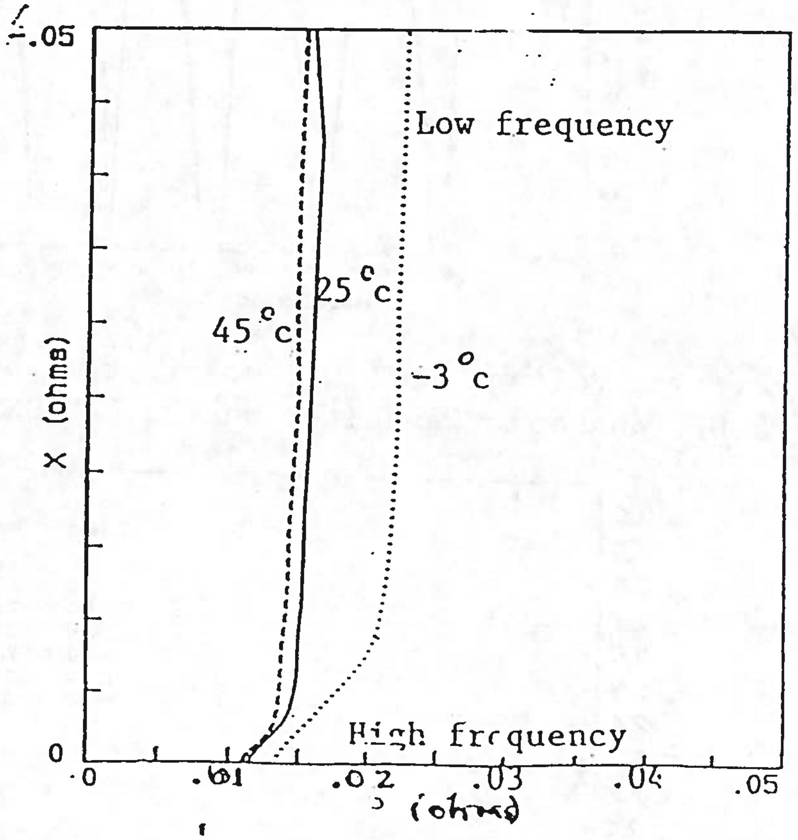

Figure 10: An Impedance Plot (X vs. R) for the 1V Maxwell Capacitor