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FreedomCAR Ultracapacitor Test Manual

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FOREWORD AND ACKNOWLEDGEMENTS

This manual was prepared for the FreedomCAR Electrochemical Energy Storage Technical Team, with the support of the U.S. Department of Energy's Office of FreedomCAR and Vehicle Technologies. It is based on the general testing approach established for FreedomCAR energy storage development programs, and some of the procedures in this manual are specifically intended to evaluate ultracapacitor performance against the FreedomCAR ultracapacitor goals. However, it is anticipated that all the procedures will have utility for characterizing capacitor energy storage device behavior over a range of possible uses.

A continuing need to improve these procedures is expected. Suggestions or comments should be directed to one of the following:

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A number of persons were instrumental in the development of this manual. Consultants John R. Miller (JME, Inc.) and Susan Butler (JME, Inc.) assisted greatly in the preparation of the original draft and in consultations about testing methods. Laboratory engineer David K. Jamison (INEEL) performed much of the testing used to illustrate the various tests. Chet Motloch (INEEL) provided technical guidance and review for the various iterations of the manual. Gary Hunt (INEEL) rewrote the original and final drafts in accordance with guidance provided by the FreedomCAR Ultracapacitor Task Force. The Task Force is chaired by Cyrus Ashtiani (Daimler Chrysler) with technical input from various other task force members representing Ford, General Motors, Daimler Chrysler, the U.S. Department of Energy and various DOE national laboratories.

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ACRONYMS

ASI	area-specific impedance
BOL	beginning of life
DOD	depth of discharge
EIS	electrochemical impedance spectroscopy
EOL	end of life
ESR	equivalent series resistance
HEV	hybrid electric vehicle
HPPC	Hybrid Pulse Power Characterization
INEEL	Idaho National Engineering and Environmental Laboratory
OCV	open-circuit voltage
OSPS	Operating Set Point Stability
RPT	reference performance tests
SDLF	self discharge loss factor
SOC	state of charge
UC	ultracapacitor

TESTING GLOSSARY

5C Rate - the constant current corresponding to discharging a device from V_{MAX} to V_{MIN} in a 12 minute (0.2-hour) discharge. The 5C rate (in amperes) is fixed for a device based on its measured capacity at the start of testing. (See the Scaling Section 2.1.4 and the Reference Capacity Test Section 2.2.1.)

Available Energy –the discharge energy available over the DOD range where both the FreedomCAR discharge and regen pulse power goals for a given application are precisely met. For capacitors this energy is measured using a 1 kW constant current discharge rate, and the limiting power conditions are calculated using a procedure defined in this manual.

Available Power –the discharge pulse power at which the usable energy is equal to the Available Energy goal for a given application.

Average Discharge Power - average power over a specified discharge is the product of the average current and average voltage over this discharge.

Beginning of Life (BOL) - the point at which life testing begins. A distinction is made in this manual between the performance of a capacitor at this point and its initial performance, because some change may take place during early testing before the start of life testing. Analysis of the effects of life testing is based on changes from the BOL performance.

Capacity Fade - the change in measured capacity from the BOL value to the value determined at some later time, expressed as a percentage of the BOL value.

Charge - any condition in which energy is supplied to the device rather than removed from the device. Charge includes both recharge and regen conditions.

C rate (or C_1/1 rate) - a current (in amperes) equal to the device's capacity (in ampere-hours) divided by the length of time (in hours) that it would take to discharge the device from a fully charged state to the minimum operating voltage (one hour for the C_1/1 rate).

Cycle - A series of operations (discharge and charge) that changes the capacitor voltage. A cycle typically begins and ends at specified capacitor voltages.

Depth of Discharge (DOD) - the percentage of a device's (nominal or measured) capacity (in ampere-hours or coulombs), removed by discharge relative to a fully charged condition, normally referenced to a constant-current discharge at the 5C rate. The device capacity is defined over the operating voltage range V_{MAX} to V_{MIN}.

Device - a cell, module, or capacitor pack, depending on the context. The generic term "device" is normally used in test procedures except where a specific type of device is meant. (Most test procedures are intended to apply to any of these types.)

Discharge – any condition in which energy is removed from the device rather than supplied to it.

Efficiency - The ratio, in percent, of the energy delivered by a capacitor to the energy that was supplied to it during a specified discharge/charge cycle, provided that the beginning and ending SOC values for the cycle are identical. Also called Energy Efficiency or Round-Trip Energy Efficiency.

End of Life (EOL) - a condition reached when the device under test is no longer capable of meeting some specified level of performance (e.g., FreedomCAR performance goals).

End of Test - a condition where life testing is halted, either because criteria specified in the test plan are reached, or because it is not possible to continue testing.

Energy Fade - the change in Available Energy from the beginning of life value to the value determined at some later time, expressed as a percentage of the BOL value.

Equivalent Series Resistance (ESR) or R_s - The value of the resistance element when a capacitor is modeled as a series RLC circuit as described in Appendix B. ESR, or R_s, can be measured using current interrupt methods or AC impedance techniques. It contributes to dynamic losses in the capacitor, that is, losses experienced only during charge or discharge. ESR is a lumped element value that arises from the electrical leads, current collectors, electrodes, separators, contacts, and other resistance elements.

Fully Charged - the condition reached by a device when it is subjected to the manufacturer's recommended recharge algorithm, or when it is at the Maximum Operating Voltage V_{MAX} in a stable state. This state is defined as 100% State of Charge, or 0% Depth of Discharge.

Hybrid Pulse Power Characterization (HPPC) Test - a test procedure whose results are used to calculate the device's pulse power and energy capabilities.

Ideal Stored Energy (E_w) - The ideal value of the electrical energy stored in a capacitor, based on the first-order model of a capacitor (i.e., an ideal capacitor). For a capacitor whose operating voltage range is V_{MAX} to V_{MIN}, it is equal to $E_w = (1/2)C\bullet V_{MAX}^2[1 - (V_{MIN}/V_{MAX})^2]$. For the normal case where $V_{MIN} = 0.5\ V_{MAX}$, $E_w = (0.375)C\bullet V_{MAX}^2$. In some instances the total Ideal Stored Energy may also be of interest, i.e., the energy corresponding to the voltage range between V_{MAX} and 0; in this case $E_w = (1/2)C\bullet V_{MAX}^2$.

Impedance (Z) - The ratio V/I of a capacitor where V is a voltage (periodic in time) applied to the component, and I is the resultant current. Z is a complex quantity, having real and imaginary parts. It represents the opposition to current flow for an applied time-dependent voltage.

Initial Reference Capacity – the capacity (in ampere-hours) of a device (normally at 30 °C), measured using the Reference Capacity Test at the start of testing. This (constant) value is used for scaling test currents for various tests, including later iterations of the Reference Capacity Test itself. This value is used in lieu of a "rated" capacity, which is often not defined for capacitors.

Initial Reference Energy – the energy (in watt-hours) of a device (normally at 30 °C), measured using the Reference Capacity Test at the start of testing. This (constant) value is using for scaling test powers for various tests.

Leakage Current (I_L) - The steady-state current drawn by a device after being charged. It is responsible for static energy losses and may be time-dependent. The leakage current can be modeled by adding a resistance element Rp in parallel with the capacitor to a series RLC model.

Maximum Operating Voltage (V_{MAX}) – the maximum voltage to be used for testing a given capacitor. In most cases, this is equal to the rated Working Voltage. However, in some cases it may be necessary to de-rate the Working Voltage for testing due to life or other considerations, such as operation of multiple devices in series. The analysis of test results is based on the Maximum Operating Voltage, however defined.

Maximum Pulse Voltage (V_{pulse}) – the maximum voltage to be applied to a capacitor under pulse conditions. If the manufacturer specifies a value of V_{pulse} that is greater than V_{MAX}, it may be used as a testing limit during pulse test conditions only.

Maximum Rated Current (I_{MAX}) - the maximum discharge current that a manufacturer will permit to be sustained by a device on a continuous basis. (This value need not be achievable at all DOD values.) The manufacturer may also specify a maximum pulse current, whose duration is limited to a few seconds; such a value will be used as a test limit but will not generally determine the scaling of a given test.

Minimum Operating Voltage (V_{MIN}) – the minimum voltage to be used for testing a given capacitor. For purposes of this manual, this is generally defined as 0.5 V_{MAX} (or the manufacturer's minimum allowable operating voltage, if it is greater than 0.5 V_{MAX}.) Other (e.g., more restrictive) values can be applied if a potential application warrants such change. Analysis of test results is based on Minimum Operating Voltage, however defined. This is *not* the same as the manufacturer's rated minimum voltage, which may be zero volts in many cases.

Power Fade - the change in Available Power from the beginning of life value to the value determined at some later time, expressed as a percentage of the BOL value.

Profile - a connected sequence of pulses used as the basic "building block" of many FreedomCAR test procedures. A test profile normally includes discharge, rest, and charge steps in a specific order. Each step is typically defined as having a fixed time duration and a particular (fixed) value of current or power.

Rated (Working) Voltage – see Working Voltage.

Recharge - any device charge interval corresponding to the sustained replenishment of energy stored in the device by a continuous power source (such as an engine-generator or off-board charger.)

Reference Capacity – the discharge capacity (in Ah) measured under specified conditions at any point in the life of a device, using the Reference Capacity Test (Section 2.2.1 of this manual).

Reference Energy – the discharge energy (in Wh) measured under specified conditions at any point in the life of a device, using the Reference Capacity Test. (See *Reference Capacity*.)

Regen - any device charge interval corresponding to the return of vehicle kinetic energy to a device (typically from braking). Because of physical limitations, regen can only persist for a few seconds at a time.

State of Charge (SOC) - the available charge capacity in a device expressed as a percentage of (nominal or measured) capacity. For ultracapacitors a desired SOC is typically established on the basis of OCV rather than actually measuring the available charge.

Usable Energy - a value (calculated from HPPC test results) that represents the discharge energy available over the maximum DOD range where specified pulse power capabilities are available for discharge and regen pulses. This energy is measured using a reference discharge (e.g., a 5C constant-current rate). *Usable Energy is not based on pre-defined performance goals but is an arbitrary quantity that can be used to measure device degradation during life testing, typically based on beginning of life capabilities.*

Usable Power - the discharge pulse power corresponding to a specified Usable Energy value. Note that this value is only meaningful if the ratio of maximum discharge pulse power to maximum regen pulse power is also specified.

Operating Voltage Range - the range in voltage over which the device is tested and for which results are reported. For this manual this is defined as the range from V_{MAX} to V_{MIN}, where V_{MAX} and V_{MIN} are the Maximum and Minimum Operating Voltages respectively as defined in this Glossary. V_{MAX} is *typically* the manufacturer's rated working voltage, and V_{MIN} is *typically* $V_{MAX}/2$, but more restrictive values may be defined for specific devices.

Ultracapacitor – generic term used in this manual to designate electrochemical capacitors. (This is only one of a number of labels used now and previously for such devices, including double-layer capacitors, supercapacitors, and others.)

Working Voltage (V_w) - the maximum (rated) voltage that can be continuously applied to a capacitor. V_w depends on temperature and factors relating to the capacitor's design, life, and reliability. This voltage is usually specified by the manufacturer, often with temperature de-rating factors.

FreedomCAR Ultracapacitor Test Manual

1 PURPOSE AND APPLICABILITY

This manual defines a series of tests to characterize aspects of the performance or life behavior of ultracapacitors for hybrid electric vehicle (HEV) applications.[a] Tests are defined based on the general approach used for all FreedomCAR energy storage testing; however, it is anticipated that these tests may be generally useful for testing capacitors for hybrid electric vehicle or other uses. Most tests are considered applicable to cells, modules, or complete capacitor energy storage systems. This manual does not include special tests for characterizing system behavior, because these are necessarily application-oriented.

The procedures in this manual are intended to characterize device performance over a range of performance parameters that should encompass likely HEV uses. The test procedures described here are modeled on the tests used to evaluate batteries for FreedomCAR programs [1] and also on a previous electric vehicle capacitor test procedures manual [2]. The battery test procedures have been modified as necessary to be applicable to electrochemical capacitors, for example, to account for the voltage droop associated with a capacitor discharge.

In general, the manufacturer of the device must supply certain information to permit proper test conduct. The most important pieces of information required from the manufacturer are the working voltage V_w and the maximum allowable current I_{MAX}. The working voltage in particular influences the values of all the properties that are subsequently measured including energy stored and power delivered by the device. The working voltage used for cell evaluations must be a value specified by the manufacturer as appropriate for operation when the cell is part of a multi-cell string or full-size pack; it should not be the value for operation of a single isolated cell.

Operation at HEV system voltages will require the use of many series-connected cells. As with all electrochemical devices, maintaining uniform voltage among the cells in a series string is critically important for reliability and safe operation. Voltage de-rating is one approach used to prevent cell over-voltage conditions, although this requires additional cells in the string with their added cost, weight, and resistance. Generally, temperature and the level of applied voltage are the two factors causing the most stress, i.e., which most strongly affect operational life. Thus, average cell voltages may need further reduction to assure adequate cycle and calendar life.

1.1 Capacitor Parameters of Interest

This manual is designed to permit evaluating the performance of ultracapacitors over broad (but limited) ranges for those parameters that are judged to be of most interest for potential HEV applications. The performance parameters that are addressed in this manual are listed in Table 1, along with some expected ranges of interest for these parameters. Potential applications that fall outside the limitations of this manual may require different testing methods. For example, if

[a] Further information about the nature and limitations of ultracapacitors for HEV use is detailed in Appendix A. Note that this manual uses “ultracapacitor” as a general designation in place of “electrochemical capacitor” (EC), “double-layer capacitor” (DLC) and various other labels such as “supercapacitor”, all of which have been used for such devices.

ultracapacitors are considered for direct replacement of batteries in a Power Assist application, the existing FreedomCAR Power Assist Battery Test Manual should be used for such testing. [1]

Table 1. Ultracapacitor Parameter Ranges of Interest

Parameter of Interest	Units (normalized)	Likely Range of Interest for Testing	
		Minimum	Maximum
Pulse Discharge Power	W/kg, W/L	Pulse powers scaled to device energy, limited by I_{MAX}	
(pulse durations)		~0.5 s	<10 s
Pulse Regen Power	W/kg, W/L	Pulse powers scaled to device energy, limited by I_{MAX}	
(pulse durations)		~0.5 s	<10 s
Energy at Constant-Power	Wh/kg, Wh/L	≤0.1 of max Power	Power limited by I_{MAX}
Capacity and Energy at Constant-Current	Ah/kg, Ah/l, Wh/kg, Wh/L	≤0.1 of max Current	Current up to I_{MAX}
Energy Efficiency	%	(A) continuous, (B) pulse discharge/charge (cycling); (C) regen acceptance	
Leakage / Stand Loss	A	Hours	Days (≤7)
Cold Cranking	W	Test conditions dependent on device energy	
Temperature Performance (cold)	ºC	-30	0
Cycle Life	Cycles	Using prototypical test profiles scaled to device energy	
Calendar Life	years	At nominal 30 ºC	

It should be noted that this list of parameters does not include capacitance. The capacitance of a device does determine its stored energy, but for FreedomCAR applications, the energy itself (specifically the energy available under various load conditions over the operating voltage range) is the quantity of interest, not the capacitance. The rated capacitance of a device is used only as a starting point for finding the reference current used in testing, while the effective capacitance is determined as a by-product of some tests.

1.2 FreedomCAR Ultracapacitor Goals

FreedomCAR has established a preliminary set of performance and life goals for ultracapacitors based on three potential HEV application areas. This list is not intended to be exhaustive, and it is subject to change. These preliminary goals are detailed in the table in Appendix F. A subset of the procedures in this manual, identified as “core automotive tests”, is designed for comparing device performance with these application-specific goals.

2 TEST PROCEDURES

2.1 General Test Conditions and Scaling

FreedomCAR energy storage testing is divided into three broad categories: (1) characterization, (2) life, and (3) reference performance testing. Characterization testing establishes the baseline performance and may include static (reference) capacity, pulse power characterization, leakage current, self-discharge, cold cranking, temperature performance, and efficiency tests. Note that some of these tests are designated as "core" tests and are required if performance is to be compared to FreedomCAR goals, while other tests provide more general characterization data. In this manual, the desired initial state of charge for a characterization or reference performance test may be (a) fully charged, (b) a state of charge (SOC) value, or (c) a depth of discharge (DOD) value. (a) and (b) are achieved as described in Section 2.1.6. A target DOD value is reached by removing the appropriate fraction of the Initial Reference Capacity from a fully charged device (normally at a 5C constant-current discharge rate).

Life testing establishes behavior over time at various temperatures, states of charge and other stress conditions and includes both cycle-life and calendar-life testing. Reference Performance Tests establish changes in the baseline performance and are performed periodically during life testing, as well as at the start and end of life testing. A generic test plan for FreedomCAR ultracapacitor testing is outlined in Appendix D. This outline can be used as a starting point for device-specific test plans.[b]

2.1.1 Nameplate Data (Manufacturer Ratings)

Certain information is needed about the ratings and limitations of a device before it can be subjected to the tests defined in this manual. The following information must be provided by the device manufacturer or developer in order for the tests to be scaled and conducted properly.

- Rated maximum working voltage, V_W (volts)
- Rated capacitance, C_{RATED} (farads)
- Rated maximum continuous discharge current, I_{MAX} (amperes)
- Maximum operating temperature, T_{MAX} (degrees C)

The following additional ratings or limitations may be provided if applicable to a particular device.

- Minimum operating voltage (volts) [if not zero]
- Maximum continuous charge current (amperes) [if different from I_{MAX}]
- Maximum voltage under pulse conditions (volts, 5 s or less) [if greater than V_W] [c]

2.1.2 Operating Voltage Range

Unless otherwise specified in a device-specific test plan, the Operating Voltage Range for all tests in this manual shall be from the Maximum Operating Voltage (V_{MAX}) to the Minimum

[b] Note that the convention for all procedures in this manual is that discharge current and power values are represented by positive numbers, while regen and charge current and power values are negative.

[c] Note that this pulse voltage could be achieved up to a million or more times during cycle-life testing, so the life implications of such a rating should be considered carefully.

Operating Voltage (V_{MIN}), where V_{MIN} is nominally 0.5 V_{MAX}. No testing will be conducted outside this range, except that pulse voltages are allowed to reach, but not exceed, the Maximum Pulse Voltage V_{pulse} (if defined to be other than V_{MAX}). V_{MAX} is normally set equal to V_W, the manufacturer's rated working voltage. If a value less than V_W is used for V_{MAX}, this should be noted and explained in a device-specific test plan. Use of a value of V_{MIN} other than 0.5 V_{MAX} should also be noted and explained.

2.1.3 Temperature Control

Unless otherwise specified in a device-specific test plan, the ambient temperature for all tests shall be controlled at a default nominal temperature of +30 ºC with a tolerance not to exceed ±2 ºC. This means that each complete test (not necessarily each test segment) should begin within this tolerance band. (But see special instructions below regarding the Constant Current and Constant Power test procedures.) For testing conducted at temperatures other than 30 ºC, the ±2 ºC tolerance around the nominal test temperature should be observed at the start of the test.

Once a test begins, the manufacturer's temperature limits must be observed. In addition, to the extent possible, all testing should be conducted using temperature controlled environmental chambers. As a general practice, a rest period should be observed after each complete test and subsequent recharge before proceeding with further testing, to verify that the device has reached a stable voltage and temperature condition.

Both the Constant Current (Section 2.2.2) and Constant Power (Section 2.2.3) tests include multiple series of three charge/discharge cycles at each of several currents. For test consistency, it is important that each cycle begin within the nominal temperature band. This will typically require that the open circuit rest period after each charge/discharge cycle be extended for a length of time sufficient to return the device within the allowable range. This can be done in one of two ways, depending on test equipment capability.

a. If the test equipment is capable of terminating a test step based on measured temperature, the rest period can simply be extended under program control until the device temperature is within the range, at which point the next cycle can begin.

b. Otherwise, perform a pre-test consisting of a single charge/discharge cycle at the highest current (or power) level planned for the test followed by a rest at open circuit voltage (OCV). Observe the time required for the temperature to return within the allowable range. This (fixed) time is then added to the rest interval after each charge/discharge cycle regardless of the current (or power) rate used.

2.1.4 Scaling of Performance and Cycle-Life Tests

Because test devices may vary over a wide range of size and capacity, it is necessary to establish values and limits for test current and/or power for each device. The same test scaling approach followed by other FreedomCAR test manuals is generally used for scaling the core automotive tests. In brief, this involves establishing a Capacitor Size Factor (CSF) that is the minimum number of devices that would be required to meet all the applicable FreedomCAR goals over life. Power levels for the core automotive tests are then scaled using the CSF. (See Section 2.2.6.4 for detailed information on determining and using the CSF.)

Other generic test procedures in this manual are scaled based on a combination of two factors, independent of any possible application: (1) the initial (actual) device capacity measured using a Reference Capacity Test, and (2) the manufacturer's rated Maximum Rated Current (I_{MAX}). The specifics of test scaling are addressed in the individual test procedures.

Conduct of the Reference Capacity Test is described in Section 2.2.1 following, because this test is also part of the general performance characterization sequence for all devices. This manual establishes a 5C discharge current as the reference discharge current for measurement of device capacity. This value is considered more appropriate for likely ultracapacitor applications than the C/1 value used for Power Assist and other FreedomCAR HEV battery testing or the C/3 value previously used for electric vehicle testing.[d]

The reference 5C discharge current is established at beginning of life using the Reference Capacity Test. When this test is first performed, the actual device capacity is unknown, so the 5C rate is calculated (estimated) at first from the rated device capacitance (in farads) as follows. The theoretical usable charge for the capacitor is calculated using the fundamental relationship Q = CV as defined in Appendix A, but expressed in the form of Equation 1,

$$Q = \frac{C\left(V_{MAX} - V_{MIN}\right)}{3600} \tag{1}$$

where C is the capacitance in farads, ($V_{MAX} - V_{MIN}$) is the operating voltage range used for testing, and Q is the resulting charge in ampere-hours. This value of Q multiplied by 5 is the 5C rate.[e] Note that value for the 5C rate from Equation 1 is used *only* for the first Reference Capacity Tests. After the test has been performed and a stable capacity is determined, the 5C rate for all further testing is fixed based on the actual measured device capacity at this point, i.e., it is simply 5 times the initial measured device capacity in ampere-hours.

The Rated Maximum Current (I_{MAX}) is normally specified by the device manufacturer or developer. Every effort should be made to obtain a realistic value for this parameter from the supplier. If this is simply not possible, a default value of I_{MAX} can be established as the smaller of the following: (a) the current required to cause an immediate (i.e., <0.1 s) 20 % voltage drop in a fully charged device at 30 ºC, or (b) the current required to discharge the device from V_{MAX} to V_{MIN} in 2 s.

Note that in some cases the scaled test current based on I_{MAX} may exceed the capabilities of available test equipment. (This is likely to be the case for devices whose I_{MAX} is much greater than 500 A.) This may require some alterations to test procedures at points noted in this manual, but in general, such a limitation does not change the value of I_{MAX}, even though it may change the test conditions actually achievable.

2.1.5 Pre-Test Conditioning (Break-In)

If a device is not properly conditioned prior to the start of testing, its behavior may vary during initial testing, leading to 'noisy' results and erroneous conclusions about device performance. Both the performance characterization and life tests described in the following

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[d] Note that the reference discharge rate for energy measurements for comparison with the FreedomCAR goals in Appendix F is a 1 kW (scaled) constant current discharge rather than a 5C rate. However, this reference rate is required only in connection with selected core automotive tests (specifically the HPPC test.)

[e] For example, for a capacitor rated at 5000 F, the charge on the capacitor over a voltage range of 2.5 V to 1.25 V would be (5000 F)(2.5 V – 1.25 V) / 3600 coulombs/Ah = 1.736 ampere-hours. The 5C rate for this capacitor would be (5)(1.736 amperes) = 8.681 amperes corresponding to a nominal 1/5 hour (12 minute) discharge.

sections assume that the device has reached a stable state before the start of such testing. FreedomCAR considers it the responsibility of the device manufacturer or developer to assure that a device is stable before testing begins, and in general no allowance is made for the potentially adverse effects of such variability. If there is reason to believe that this has not been done (or done properly), a series of break-in or conditioning discharge/charge cycles can be performed before any other testing is done. A specific test for device break-in is not defined in this manual.

2.1.6 Device Recharging and State of Charge (SOC) [f]

For test repeatability purposes, most of the tests in this manual begin with a fully charged device, i.e., a device at voltage V_{MAX} under stable conditions. This fully charged state is achieved in one of two ways:

1. Charge the device using the manufacturer's recommended charge algorithm, if known, until a stable charge condition is reached.
2. In the absence of a manufacturer-recommended charge method, charge the device to V_{MAX} using a 5C constant-current charge rate. Then clamp the voltage at V_{MAX} until a stable charge condition is reached.

For purposes of this manual, a stable charge condition is defined as (a) the point where the charge current under clamp conditions decreases to less than 1% of the nominal value (e.g., <0.05C for a 5C charge current), limited to one hour at the clamp voltage condition, or (b) for open-circuit conditions, a voltage rate-of-change corresponding to less than 1% per hour, measured over at least 5 minutes. If either of these criteria requires measurement resolution better than the measurement channel is capable of providing, the usable lower limit of the measurement is used rather than an arbitrary percentage.[g]

If the desired SOC condition is something other than full charge, determine the voltage corresponding to the target SOC condition. Then charge the device to this voltage as in (2) above (or if the device SOC is already above the target value, discharge it to the target condition using a 5C constant-current discharge rate and clamp as above.)

2.1.7 Non-Testing (Storage) Periods

As a general rule, devices that are not undergoing tests for a substantial period of time (more than a day or two) should be stored at moderate temperatures (not to exceed 30 ºC, with lower temperatures being preferable) to avoid unplanned adverse effects on life. It is recommended that device voltage should be left between 0.8 V_W and 0.5 V_W, or at V_{MIN} and checked periodically to assure that the voltage is not lower than the manufacturers' minimum voltage limit. The device can also be left at a value less than maximum voltage at the completion of any test until the next test, as long as this precaution is observed.

2.2 Characterization Tests

2.2.1 Reference Capacity Test

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[f] Note that in this manual the term SOC really refers to a known (usually initial) test condition based on OCV rather than an actual numerical measure of remaining charge.

[g] For example, if a 500 A tester has a minimum current measurement resolution of 0.1 A where the 1 % criterion requires the current to drop to 50 mA, the revised criterion would require the measured current to approach 0.1 A instead. This may require some engineering judgment to determine that the current is actually approaching a stable value.

The Reference Capacity Test consists of a single discharge from V_{MAX} to V_{MIN} at a 5C constant-current rate. The 5C rate for a particular device is the current that would (nominally) result in discharging the device from V_{MAX} to V_{MIN} in 0.2 hour (12 minutes) at the default ambient temperature of 30 ºC. This 5C rate is defined as 5 times the ampere-hour capacity measured with this test at the beginning of testing, as soon as it has been determined that the device capacity is stable. (See Section 2.1.4.)

This test is performed at least three consecutive times at the start of testing to verify that the device capacity is stable at least on a short-term basis. (See Section 2.1.5.) It may be repeated as needed to verify device capacity at any point in life. The capacity and energy of a device measured by this test at the start of testing (at 30 °C) are defined as the Initial Reference Capacity and the Initial Reference Energy and are used for scaling test currents and powers for some other tests.[h]

The outline of this test procedure is as follows:

1. Bring the device to a fully charged state at V_{MAX} at 30 °C. (See Section 2.1.6.) An OCV rest period sufficient to show a stable voltage and temperature condition should be observed prior to the start of discharge.
2. Discharge the device from V_{MAX} to V_{MIN} at a 5C constant-current rate.
3. Rest the device in an open circuit condition for one hour (or as required to reach a stable voltage condition).
4. Fully recharge the device (see Section 2.1.6), or if additional tests are not planned for some time, the device can be left in an intermediate charge state (see 2.1.7.)

Data Collection Requirements: Data should be acquired during the discharge (Step 2) at a rate of once per second. Data collection during open circuit (rest) and charge steps should be at a rate sufficient to assure that at least 100 data points will be acquired during each step.

2.2.2 Constant-Current Discharge and Charge Test

This procedure specifies a method for determining the constant-current charging and discharging characteristics of the capacitor, by executing a sequence of discharge/charge cycles at increasing currents. Data collected from this test are used to determine the charge and discharge capacitance of the capacitor over a defined voltage range, the constant-current discharge/charge energy efficiency, and, if applicable, these and other properties at various cell temperatures. The test can also be used to determine values for the charge and discharge equivalent series resistance (ESR) as a function of constant-current charge/discharge current. Results of this test are commonly used for modeling the behavior of a device over a range of continuous discharge/charge conditions.

The capacitor's rated values for minimum voltage (which is not necessarily equal to V_{MIN}), maximum working voltage, V_W, and the maximum rated discharge current, I_{MAX} should be supplied by the vendor. The allowed maximum and minimum temperatures should also be known if temperature tests are to be conducted. This test is conducted between V_{MAX} and V_{MIN} as defined in Section 2.1.2 for all current rates used.

The number of different charge/discharge currents to be used (within the allowable operating range of the capacitor) is nominally set at six values in a fixed ratio, although these may

[h] Because current FreedomCAR ultracapacitor energy goals are not based on a 5C rate, this test is not used in the Hybrid Pulse Power Characterization (HPPC) test sequence as the basis for determining Usable Energy.

vary depending on the information required and any test constraints. For some capacitors, the maximum charging current is limited by the construction of the capacitor and may be different from the maximum discharge current. The charge and discharge currents should be matched to the extent possible, so that the energy efficiency can be determined as a function of charge/discharge current.

In the absence of other constraints, the current values to be used for this test are specified fractions of I_{MAX} as shown in the "Normal Test Currents" column of Table 2. In some cases, test equipment limitations may restrict testing to less than this full range of currents. In this case, the maximum available current becomes the maximum test current and the sequence of test current values is then as shown in the "Test Equipment Limited" column of Table 2.

If the maximum allowable charging current is less than the maximum discharge current, the preferred approach is to match the discharge and charge currents up to the highest value possible and then use the maximum charging current with all higher discharge currents. For example, if the maximum allowable charging current was 0.5 I_{MAX}, the discharge and charge currents would be those shown in the right-hand columns of Table 2.

If the capacitor's maximum allowable temperature is reached at any point during this test, the test must be interrupted. The preferred approach is to allow a temperature stabilization (OCV rest) interval after each set of cycles at a given rate (or if necessary each individual cycle) such that complete cycles can be performed without interruption. Any such alterations to the base test procedure must be reported with the test results.

Table 2. Constant-Current Discharge and Charge Current Test Values

	Normal Test Currents (Discharge & Charge)	Test Currents Test Equipment Limited to $I_{TEST} < I_{MAX}$ (Discharge & Charge)	Test Currents *Example* Charge Current Limited to 0.5 I_{MAX}	
			Discharge	Charge
Minimum Test Current	5C	5C	5C	5C
Other Test Currents	0.1 I_{MAX}	0.1 I_{TEST}	0.1 I_{MAX}	0.1 I_{MAX}
	0.25 I_{MAX}	0.25 I_{TEST}	0.25 I_{MAX}	0.25 I_{MAX}
	0.5 I_{MAX}	0.5 I_{TEST}	0.5 I_{MAX}	0.5 I_{MAX}
	0.75 I_{MAX}	0.75 I_{TEST}	0.75 I_{MAX}	0.5 I_{MAX}
Maximum Test Current	I_{MAX}	I_{TEST}	I_{MAX}	0.5 I_{MAX}

The test is conducted in accordance with the following outline: [i]

1. Fully charge the device to V_{MAX}. (This may involve a clamp voltage interval as part of the normal charge algorithm. See Section 2.1.6.)
2. Discharge the device to V_{MIN} at the lowest test current. (See Table 2.)

[i] The use of clamp voltage intervals during this test has been minimized (i.e., limited to the beginning and possibly the end of each 3-cycle sequence) to reduce the effects of these clamp intervals on efficiency determination and the modeling of constant-current behavior. This also has the effect of shortening the overall duration of the test.

3. Place the device in an open circuit condition for 10 seconds to observe the voltage behavior.
4. Charge the device to V_{MAX} at the lowest test current. (See Table 2.)
5. Place the device in an open circuit condition for 10 seconds, and (if required) for any additional time needed for the device to return within the allowable temperature range. (See Section 2.2.1 for details.)
6. Repeat Steps 2 through 5 for two more iterations (3 cycles total).
7. (Optional) If additional information is needed regarding the complete recharge profile at this current, the voltage can be clamped at V_{MIN} until a stable charge condition is reached before the final recharge in this 3-cycle sequence. (See Section 2.1.6.) Note that doing this may prevent an accurate determination of charge/discharge efficiency at this rate, since only the middle cycle will start and end at the same SOC point.

Repeat the entire sequence of Steps 1 through 7 for each test current as shown in Table 2. Each of the 6 test current sequences should begin at a fully charged, stable state within the normal temperature limits (i.e., 30 ± 2 °C for an ambient temperature test).

If off-nominal temperature tests are to be conducted, the tests at all six test current values should be completed at one temperature, then the temperature changed and the capacitor allowed to equilibrate before the tests are repeated at the new test temperature.[j]

Data Collection Requirements: As a general rule, data acquisition rates should be set such that 100 data points or more will be acquired during each discharge or charge step. (1000 points or more per step may be desirable for modeling purposes.) However, the ability to do this at high currents may be limited by the short duration of the test steps; in such cases the data acquisition interval should be 0.1 s if possible. Data acquisition during rest or clamp voltage intervals is not so critical, but at least 100 data points per step should still be acquired where practical.

2.2.3 Constant-Power Discharge Test

This procedure specifies a method for determining the constant-power discharge characteristics of the capacitor. The major performance parameters determined by this test are the specific energy and energy density (on a weight and volume basis, i.e., Wh/kg and Wh/L, respectively), and the specific power and power density (on a weight and volume basis, i.e., W/kg and W/L, respectively) of the capacitor. It also permits the measurement of the device efficiency using a constant-power discharge and constant-current recharge. If desired, these properties can also be determined at various temperatures.

The capacitor's rated values for the maximum working voltage, V_W, and the maximum discharge current I_{MAX} and maximum charge current (which may be different from I_{MAX}) should be supplied by the capacitor's vendor. The allowed maximum and minimum temperatures should also be known if temperature tests are to be conducted. This test is conducted between V_{MAX} and V_{MIN} as defined in Section 2.1.2 for all power rates used.

[j] For the conduct of this test (Section 2.2.2) at off-nominal temperatures, both charging and discharging are done at the target test temperature. For the constant-power test (Section 2.2.3), charging (for the normal test) or discharging (for the alternative test) is permitted to be done at the test temperature unless there is reason to believe the device will not reach full charge (or discharge) repeatably at off-nominal temperatures.

This test is conducted similarly to the Constant-Current Discharge and Charge Test (Section 2.2.2), in that it is a sequence of 3-cycle discharge/charge iterations performed at fixed fractions of a maximum test power. However, *all recharge steps for this test are conducted using a single constant-current charge rate,* nominally 5C. The maximum power to be used for this test (P_{MAX}) is normally based on the Maximum Rated Current, I_{MAX}. In the absence of other constraints, this is determined using Equation 2 as follows:

$$P_{MAX} = I_{MAX} V_{MIN} \tag{2}$$

If the test equipment to be used is limited to a maximum current I_{TEST} less than I_{MAX}, then the maximum test power must be determined using Equation 3 instead.

$$P_{MAX} = I_{TEST} V_{MIN} \tag{3}$$

The minimum test power is calculated using Equation 4.

$$P_{MIN} = (5C\ rate) V_{MIN} \tag{4}$$

In either case, the nominal sequence of test power values is as follows:

P_{MIN}, 0.1 P_{MAX}, , 0.25P_{MAX}, 0.5 P_{MAX}, 0.75 P_{MAX}, and P_{MAX}

The test is conducted in accordance with the following outline:

1. Fully charge the device to V_{MAX}. (See Section 2.1.6.)
2. Discharge the device to V_{MIN} at the lowest test power. (See list above.)
3. Place the device in an open circuit condition for 10 seconds to observe the voltage behavior.
4. Charge the device to V_{MAX} at the designated constant-current recharge value (nominally 5C).
5. Place the device in an open circuit condition for 10 seconds, and (if required) for any additional time needed for the device to return within the allowable temperature range. (See Section 2.1.3 for details.)
6. Repeat Steps 2 through 5 for two more iterations (3 cycles total).

Repeat the entire sequence of Steps 1 through 6 for each test power as shown in the sequence above. Each of the 6 test power sequences should begin at a fully charged, stable state within the normal temperature limits (i.e., 30$\pm$2 °C for an ambient temperature test).

If off-nominal temperature tests are to be conducted, the tests at all six test power values should be completed at one temperature, then the temperature changed and the capacitor allowed to equilibrate before the tests are repeated at the new test temperature.

Data Collection Requirements: Data acquisition rates for this test are the same as for the Constant-Current Discharge and Charge Test, except that data collection during the recharge intervals can be relaxed for most repetitions because all the steps are identical (at a given temperature.)

2.2.3.1 Alternative Constant-Power Charge (Regen Efficiency) Test

If high rate charging is of special interest for a device (e.g., regen capture), this test can be performed in an inverted form, using the defined sequence of constant-power rates to *charge* the device along with a single (nominal 5C) constant-current *discharge* rate. This form of the test permits the characterization of device efficiency as a function of recharge rate, which cannot be easily determined using either 2.2.2 or 2.2.3.

2.2.4 Leakage-Current Test

The leakage-current test is one means of measuring the losses in a device that is not being exercised. The test determines the leakage current $I_L(t)$ as the current required to maintain the capacitor at a specified voltage, V_{LC}, which is usually set to the maximum operating voltage V_{MAX}. The leakage current is time dependent and only approaches a constant value after the voltage V_{LC} has been applied to the capacitor for, generally, a number of hours. The nominal test temperature is 30 ^oC, although the test can be conducted at different temperatures to determine the effect of temperature on the leakage current. Lower test temperatures typically result in smaller leakage currents.

The test is conducted in accordance with the following outline:

1. Bring the capacitor to a stable operating temperature (30 $^\circ C$ for the default test conditions.)
2. Charge the capacitor to the test voltage V_{LC}, which is normally V_{MAX}.
3. Maintain this voltage for at least 72 hours, or until the current required to maintain the test voltage approaches a stable value. Depending on temperature, this may require up to 7 days. The test equipment used should generally have a current measurement sensitivity of 0.1 mA or better. (If modules are being tested and they include cell-balancing circuitry, the test duration may need to be altered to measure the effect of such circuitry.)

Data Collection Requirements: Voltage and current should be recorded at 1 minute or shorter intervals during the first 24 hours of this test. If the test extends beyond 24 hours, data collection intervals can be increased to up to 10 minutes.

2.2.5 Self-Discharge Test (Stand Test) (CORE AUTOMOTIVE TEST)

The self-discharge test measures the time dependence of the self-dissipation of the capacitor, i.e., the rate of those internal processes that cause the capacitor to discharge when not connected to a load. The goal of the test is twofold: (1) to measure (directly) the energy lost over the test interval; and (2) to measure the decrease of the capacitor's voltage during the test, which allows the associated energy loss to be calculated as a function of stand time. Note that the voltage measuring instrumentation used for this test should have high input impedance to minimize its effects on the capacitor discharge.

The Self-Discharge Test is conducted according to the following outline, where all steps except (possibly) Steps 4 and 5 should be performed at the default nominal temperature of 30 °C to assure consistent capacity measurements.[k]

1. Perform a single iteration of the Reference Capacity Test (Section 2.2.1).
2. Fully charge the capacitor. (See Section 2.1.6.)
3. (Optional) If the test is to be performed at some charge condition other than full charge, discharge the device at the constant-current discharge rate used in Step 1 (normally 5C) to the voltage corresponding to the target charge condition and record the energy removed in reaching this condition. (Do *not* use a clamp voltage interval here.)[l]
4. (Optional) If stand loss is to be measured at a temperature other than 30 °C, bring the device to the target temperature as quickly as practicable.
5. Leave the device at open circuit conditions and measure the voltage of the capacitor over the stand time duration. The stand time is typically 72 hours, but it can be extended to 7 days or more for low loss devices. (The time should be selected such that the percentage of capacitor usable energy lost during the test is 5 % or more.) Return the device to 30 °C if necessary.[m]
6. Discharge the device to V_{MIN} at the constant-current discharge rate (5C rate) used in Step 1 and record the residual energy discharged.
7. Repeat the Reference Capacity Test (Section 2.2.1).

If off-nominal temperature tests are to be conducted, Steps 1 and 7 (which are done at 30 °C regardless) need not be repeated for each temperature. Instead, Steps 2 through 6 can be repeated for each new test temperature, and Step 7 can be performed after the complete series of tests has been done. (However, if the device capacity changes substantially over this series of tests, it will not be possible to attribute this change to any particular test.)

Note that the presence of cell-balancing circuitry may have a significant effect on the stand loss measured for some capacitor modules. In such cases the test duration should be selected to assure that these (potentially intermittent) losses are accounted for in the test data.

Data Collection Requirements: Fast data collection rates are not required for this test. Generally, measurements are made at 1 minute intervals, although an even slower rate (e.g., 10-minute intervals) is acceptable for tests longer than 72 hours.)

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[k] For high leakage rate devices, or as a time saving measure, the entire test sequence can be performed at off-nominal test temperatures, including recharge steps. The result of such a test will be interpreted somewhat differently from that obtained with the standard test, but the difference may not be significant for many devices.

[l] For comparison to FreedomCAR self-discharge goals, this test should always be performed for at least 72 hours starting with the device charged to V_{MAX}, but measuring self-discharge under other conditions may be of interest for some applications.

[m] If the loss rate is such that the device voltage drops to V_{MIN} before the planned end of the stand period, terminate this step and do not perform step 6. The actual stand time (duration of steps 4 and 5) will be used for analysis of the results.

2.2.6 Hybrid Pulse Power Characterization Test (CORE AUTOMOTIVE TEST)

The Hybrid Pulse Power Characterization (HPPC) Test is used to determine dynamic power and energy capability over the capacitor's voltage range using a test profile that incorporates both discharge and regen pulses. The primary objective of this test is to establish, as a function of depth of discharge (DOD): (a) the V_{MIN} discharge power capability at the end of a discharge current pulse, and (b) the V_{MAX} regen power capability at the end of a regen current pulse. These power capabilities are then used to derive other performance characteristics such as Usable Energy and Usable Power, and to evaluate device performance against the FreedomCAR pulse power and energy goals.

2.2.6.1 Ultracapacitor Hybrid Pulse Power Characterization Profile

This profile is designed for the determination of discharge pulse and regen pulse power capabilities at various depths of discharge (DOD) values over pulse durations considered likely to be most useful for capacitor applications. The pulse durations for this version of the HPPC test have been adjusted downward to 5 seconds from the 10 second values used for most hybrid battery testing, both in recognition of the generally lower energy density of capacitors and to allow for higher pulse currents within the normal procedure outline.[n]

The normal test protocol uses constant-current (not constant-power) at levels derived from the manufacturer's maximum rated charge and discharge currents. (These values may not necessarily be the same, especially for the asymmetric-hybrid capacitors). The characterization profile is shown in Table 3 and Figure 1.

Table 3. FreedomCAR Ultracapacitor Pulse Power Characterization Profile

Time Increment (seconds)	Cumulative Time (seconds)	Relative Currents
5	5	1.00
50	55	0
5	60	-0.75

Note that the current values are relative, not absolute. The actual current values for testing a particular device are determined as defined in the following section.

[n] The 10 second pulse durations used for battery testing would limit capacitor pulse currents to rates less than about 140C, which could prevent pulse characterization testing from being conducted in the region most likely to show utility for capacitors. If a comparison with battery performance goals is needed, the battery version of the HPPC test can be performed in addition to or in lieu of the Minimum HPPC Test.

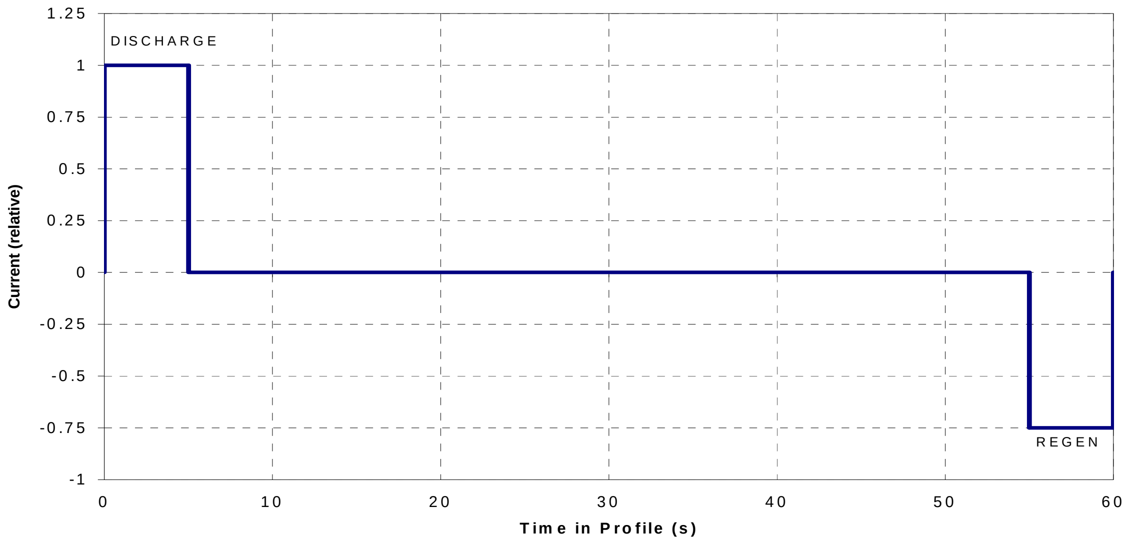

Figure 1. Ultracapacitor HPPC Test Profile

2.2.6.2 HPPC Test Current Scaling

For performance characterization purposes, the HPPC test is normally conducted at two different levels of test scaling. These are designated the Minimum HPPC Test and the Maximum HPPC Test. Either or both of these tests may also be used as Reference Performance Tests during later life testing (if conducted.) The base discharge current during the net 10 % DOD steps (Procedure Step 3) is a 5C constant current rate for either level of the test.

The actual pulse current values used for the two levels of the HPPC test are scaled based on the manufacturer's maximum rated discharge current I_{MAX}. The nominal (default) values are shown in Table 4.

Table 4. Ultracapacitor HPPC Test Currents

Test Level	Discharge Pulse Current	Regen Pulse Current
Minimum HPPC Test	0.25 I_{MAX}	0.1875 I_{MAX} (75% of discharge pulse rate)
Maximum HPPC Test	0.75 I_{MAX} (limit $\leq$280C rate)	0.5625 I_{MAX} (limit $\leq$210C rate) (75% of discharge pulse rate)

If the discharge or charge current values computed using Table 4 for the Minimum HPPC Test are less than the 5C rate, it is not appropriate to test the device using this procedure. If the nominal Regen Pulse Current for the Maximum HPPC Test exceeds the manufacturer's maximum allowable charge current, this test current will have to be adjusted to stay within manufacturer limits. This in turn will affect the results to be reported later for regen power capability.

If the test equipment to be used is not capable of achieving the pulse currents defined for the Maximum HPPC test, the test can still be performed at the maximum available currents. However, this will be reported as a non-standard HPPC test.

Note that the limit of 280C in Table 4 is designed to restrict the maximum charge removed during a single pulse profile to slightly less than 10% of the device capacity. This avoids the possibility of having to return charge to the device to reach the target DOD for the next pulse profile, with any accompanying asymmetry in the voltage behavior. This is typically not a concern for the Minimum HPPC Test because of the lower current levels.

2.2.6.3 HPPC Test Procedure Description

The HPPC test uses the pulse power characterization profile as defined in the previous section, with constant-current steps in the ratios listed in Table 3 and pulse currents as defined in Table 4. The test is made up of single repetitions of this profile, separated by ~10% DOD (depth of discharge) constant-current 5C discharge segments. Each pulse profile and 5C discharge is followed by a rest period of up to 1 hour with the voltage at OCV to allow the cell to reach a temperature and charge (voltage) equilibrium condition before applying the next profile.

If a voltage limit is reached during the actual pulse profile, discharge or regen steps shall be voltage-clamped to stay within limits, and the test sequence shall continue if the 5C constant-current discharge rate can be sustained to the next 10% DOD increment.

The HPPC Test is conducted according to the following outline:

1. (Pre-Test). Perform a 1 kW constant power discharge, i.e., discharge the fully charged device at a CSF-scaled 1 kW constant-power rate from V_{MAX} to V_{MIN}, rest one hour, and then fully taper-recharge the device to V_{MAX}. at the CSF-scaled constant-power recharge rate given in Table F-1 (Appendix F) for the intended application.[o] Place the device in an open circuit condition until the voltage is stable, for a time not to exceed one hour.[p],[q]
2. Perform the Pulse Power Characterization test profile.[r]
3. Discharge at a 5C constant-current rate to remove an amount of charge equal to 10% of the device Initial Reference Capacity in Ah (including the net charge removed by the pulse profile.)
4. Rest at OCV for a period not to exceed one hour, until the voltage reaches a stable condition.
5. Repeat steps 2, 3 and 4 for 9 additional times, or until the voltage reaches V_{MIN} during one of the 5C constant-current discharge steps, whichever comes first.

The beginning of the HPPC test sequence is shown in Figure 2, and the overall test sequence is illustrated in Figure 3. These graphs are for illustration only; in practice the duration of

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[o] See Section 2.2.6.4 for a discussion of how CSF is determined

[p] The duration of all rest periods during the HPPC test is nominally one hour. However, this duration may be shortened to any period sufficient to reach a stable voltage and temperature condition, in order to reduce capacitor self-discharge during the rest periods.

[q] If the test results are not intended for comparison with the FreedomCAR pulse power and energy goals, this Pre-Test can be performed as a single iteration of the Reference Capacity Test (Section 2.2.1) instead. This avoids the need to determine a CSF for generic characterization testing. (See Section 2.2.6.4 for more information.)

[r] This step performs the first HPPC pulse profile at full charge (i.e. 0 % DOD) rather than at 10 % DOD as is done in all battery versions of the test. This is done for better characterization of the complete operating range. Because the first discharge pulse removes more charge than the following regen pulse returns, and the voltage of a capacitor drops as a direct function of charge removed, a capacitor may have significant regen power capability at this point.

the various rest steps and the initial recharge may be variable, and the ratio of the 5C constant-current discharge steps to the pulse values depends on which version of the test is being run.

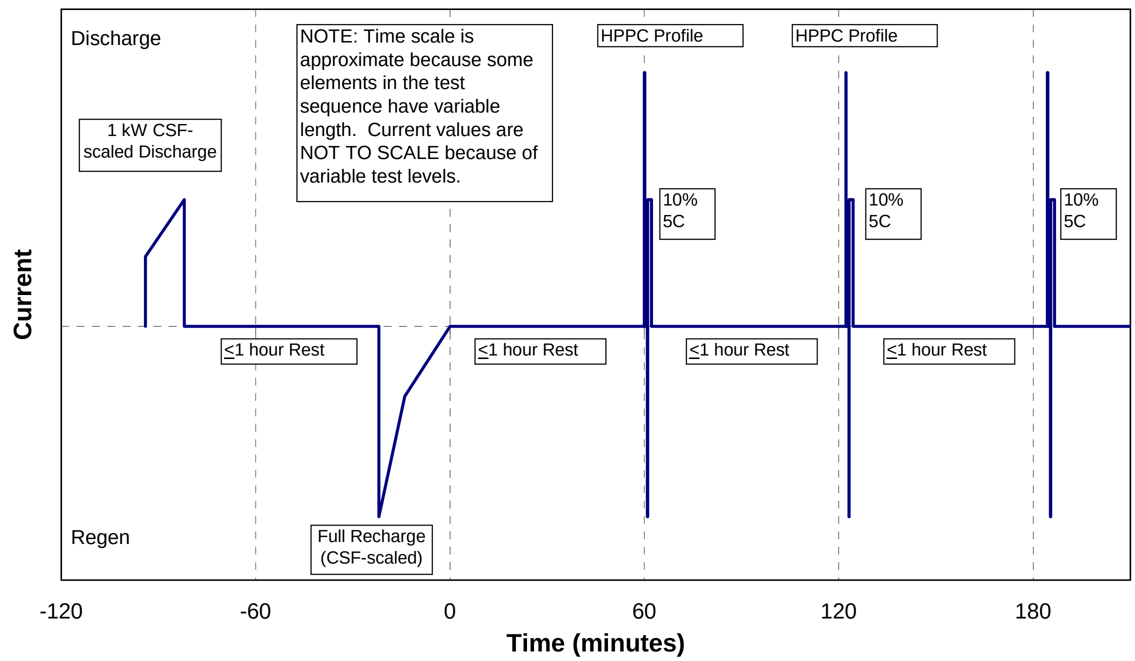

Figure 2. Start of HPPC Test Sequence

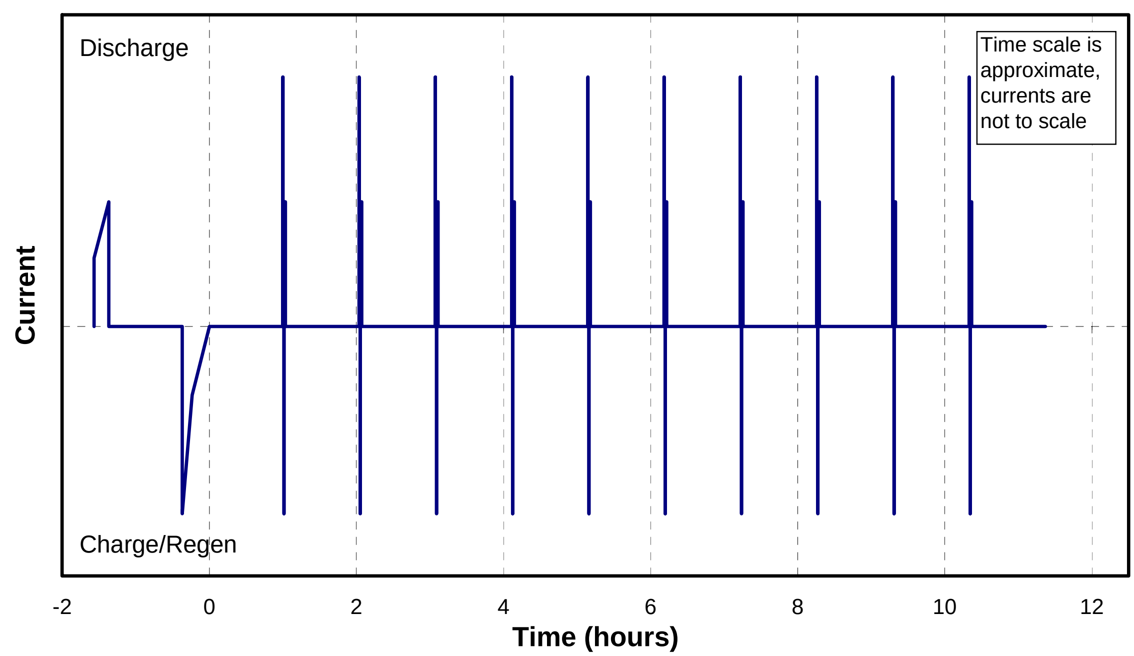

Figure 3. Complete HPPC Test Sequence

Data Collection Requirements: Data requirements for the Pre-Test (Reference Capacity Test) are defined in Section 2.2.1. Data should be acquired during the discharge and regen pulses at intervals of 0.1s (i.e., 10 samples/second), and during the profile rest step and the 5C discharge step at 1 s intervals. Data collection rates are not critical during the Step 3 OCV rest period; a rate of once per minute or faster is suggested.

2.2.6.4 Use of the Capacitor Size Factor

Normally a Capacitor Size Factor (CSF) is expected to be provided by the device manufacturer, because the intent is that the CSF provides whatever Beginning of Life (BOL) power and energy margins the manufacturer deems necessary for the FreedomCAR goals to be met over life, and these margins necessarily interact with non-testable constraints such as system cost. For testing purposes, the CSF is driven by performance requirements. This means that the pulse power, available energy and cold cranking requirements must be met even if the resulting CSF would cause weight, volume or cost constraints to be exceeded.

In those cases where the CSF is not known in advance, a size factor can be determined experimentally from the results of a generic HPPC test (i.e., one which uses a 5C constant-current Pre-Test) using the analysis method outlined in Section 3.2.6.9.

The resulting CSF is used for scaling the test power levels and the power and energy results of core automotive tests where required. This applies specifically to (a) the constant-power discharge and recharge rates during the HPPC Pre-Test; (b) the test power for the Cold Cranking Test; and (c) the reported results of these tests, all of which are expressed at the system level based on the CSF.

Note that that the base (net 10% DOD) discharge steps during the actual HPPC test are performed at a 5C constant-current rate. Although this is similar to the way this test is done for batteries, it departs slightly from the usual practice for FreedomCAR testing because this is *not* the rate on which the FreedomCAR energy goals for capacitors are based. As shown in Appendix F, the FreedomCAR Available Energy requirements for capacitors assume a 1 kW constant power discharge rate.

Energy measurements are in fact made at this (scaled) 1 kW rate during the HPPC Pre-Test step. The use of 5C steps during the HPPC sequence assumes that the DOD vs energy relationships measured at a 5C rate and a 1 kW rate are the same for analysis purposes. This assumption should be validated for a given device by comparing the results of a Reference Discharge Test and a 1 kW constant-power discharge. If necessary, the 10% DOD HPPC steps can be performed at a 1 kW CSF-scaled constant-power rate. Note that the actual test power corresponding to this rate will be different for each of the three FreedomCAR capacitor application areas, because the CSF will be different for each application.

2.2.7 Cold Cranking Test (CORE AUTOMOTIVE TEST)

The Cold Cranking test is intended to measure power capability at low temperature (normally –30 ^{o}C) using a test profile that simulates engine-starting behavior. The test is normally conducted starting from full charge (0% DOD.) Two variations of the test are defined: a Core Automotive Test that is performed at the FreedomCAR capacitor goal power, and a generic version that is designed to remove an amount of energy equal to one third of the (30 ^{o}C) Initial Reference Energy of the device during the test profile. Devices whose energy is greatly reduced at cold temperatures may drop below V_{MIN} during this test but must not be allowed to go below the manufacturer's minimum voltage rating.

The Cold Cranking Test profile is defined as a sequence of three 2-second pulses at 12-second intervals (i.e., 10 seconds between pulses.) The profile is defined in Table 5 and illustrated in Figure 4 following. All three pulses have the same duration and power level. The test power is defined in one of two ways, depending on whether the test results are intended for comparison with the FreedomCAR cold cranking goals.

FreedomCAR Test Power (Core Automotive Test): the test power is the appropriate Cold Cranking Pulse requirement of Table F-1 (Appendix F) scaled (i.e., divided) by the CSF. For example, a device which has a CSF of 15 for the 42V Start-Stop application would be tested at a power of 8 kW divided by 15, or 533 W.

Generic Cold Cranking Test Power: The test power is the constant value that would remove one third of the Initial Reference Energy of the device in the 6 seconds of pulses (ignoring losses), based on the measured capacity at 30 °C. For example, a device having an Initial Reference Energy from V_{MAX} to V_{MIN} (as measured in Section 2.2.1) of 1.0 Wh would be tested using 200 W pulses, calculated using Equation 5.

$$Test\ Power\ (W) = \frac{Initial\ \text{Reference Energy (J)}}{(3)(6\ s)} \tag{5}$$

For this example, the device energy (converted to joules or watt-seconds) is 3600 W-s, and the resulting pulse power is one-third of this energy divided by 6 s total pulsing, or 200 W.

If the calculated test power would exceed the maximum current at the test minimum voltage V_{MIN}, the test power must be reduced to stay within the current limit. For example, if the device described above also has I_{MAX} = 100 A and V_{MIN} = 1.25 V, then the cold cranking test power could be limited to a value of (100 A) times (1.25 V) = 125 W. It may also be necessary to reduce the calculated test power in order to stay within the capability of the available test equipment. Any such deviations from the test procedure must be prominently noted in the reported test results. [s]

Table 5. Cold Cranking Test Profile.

Step Duration (seconds)	Cumulative Time in Profile (seconds)	Test Power (Relative)	Test Power (*Example* for generic 1 Wh Device)
2	2	1.0	200 W
10	12	0	0
2	14	1.0	200 W
10	24	0	0
2	26	1.0	200 W

[s] Without this provision, it is not possible to conduct the entire test at a constant power level, and the analysis of results is more difficult.

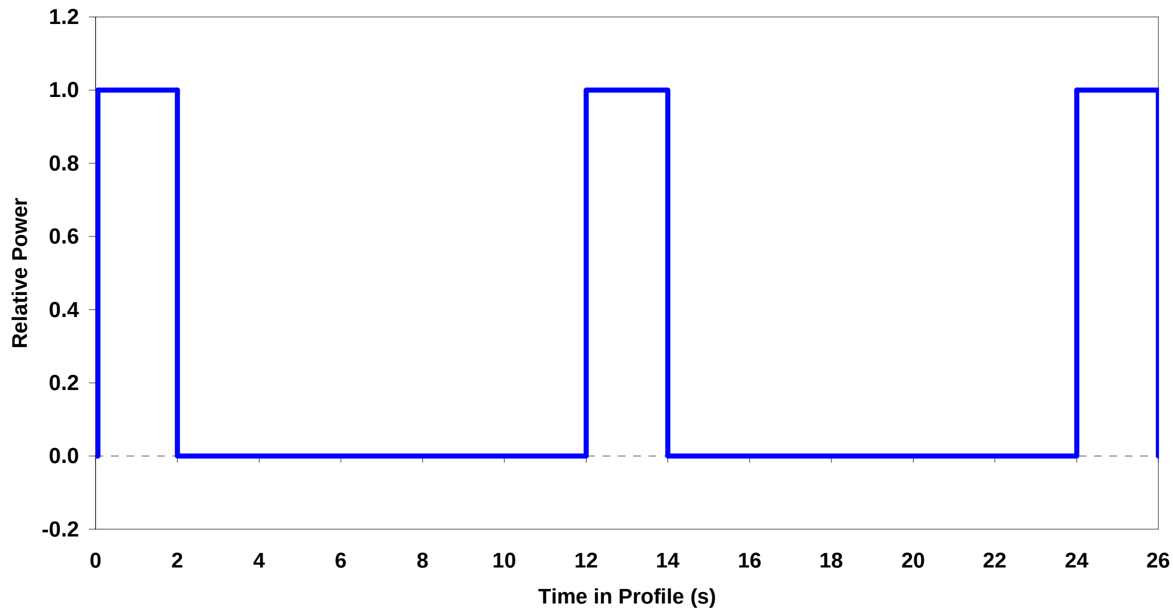

Figure 4. Cold Cranking Test Profile

The Cold Cranking Test is conducted according to the following outline:

1. Fully charge the device at normal ambient temperature (nominally 30 °C).
2. Reduce the ambient temperature to –30 °C, and soak the device at OCV for a period of time adequate to ensure it has reached thermal equilibrium at this temperature.[t]
3. Perform a single iteration of the Cold Cranking Test profile using a pulse power as defined above. Do not allow the device to be discharged below the manufacturer's minimum allowable voltage, or to go below 0 V (i.e., experience voltage reversal) under any circumstances.
4. Return the device to normal ambient temperature

The manufacturer may specify a different minimum discharge voltage for cold cranking testing. This voltage, if specified, will be used for test control, but the test power will still be based on either the CSF or the measured reference energy as described above. The subsequent calculation of cold cranking power capability may also be based on this voltage, provided that it does not exceed the voltage swing allowed in Table F-1 for a particular FreedomCAR application. The profile pulses must be performed for the full 2-second duration even if the test power has to be limited to stay within the manufacturer's minimum voltage.

Data Collection Requirements: Data collection during charge (Step 1), open circuit cool down and soak (Step 2) and the return to ambient temperature (Step 4) is not critical but should be at a rate sufficient to assure that at least 100 data points will be acquired during each step. During the actual pulse profile (Step 3), data should be acquired at a rate of 10 samples per second (0.1 s sampling interval).

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[t] Thermal equilibrium is more important than self-discharge concerns for this test. Most devices of interest will have low self-discharge at such low temperatures, and thus an extended soak time is not an issue.

2.2.8 Temperature Performance Testing

The effects of environment (ambient temperature) on device performance will be measured as needed by performing normal characterization tests (e.g., the Reference Capacity Test, Constant-Current Discharge and Charge Test, Constant-Power Discharge Test, Leakage-Current Test, Self-Discharge Test, HPPC Test and/or Cold Cranking Test) at various temperatures within the appropriate application temperature range. (For FreedomCAR this is typically -30 ^{o}C to +52ºC.) In addition to characterizing the performance of the technology as a function of temperature, this data is also useful to bound the likely constraints on thermal management needs for modules and full-size systems.

Unless otherwise specified in a device-specific test plan, initial charging should be performed at 30 °C during temperature performance testing.[u] This implies a typical test sequence as follows:

1. Charge the device to V_{MAX} at 30 °C.
2. Raise or lower the cell ambient temperature to the target value. Maintain device voltage at V_{MAX}.
3. Wait a suitable soak period for thermal equalization, typically 4 to 8 hours. (The soak time is dependent on device geometry, packaging, and materials and is difficult to specify generically.)
4. Execute the desired performance test.

When the HPPC test is performed at off-nominal temperatures, it may sometimes be necessary to adjust the 1 hour rest intervals to ensure that thermal stability as well as voltage equilibrium is reached before each repetition of the pulse power characterization profile.

Data collection requirements for temperature performance tests are generally the same as for the corresponding ambient temperature characterization tests.

2.2.8.1 Default Temperature Performance Test Regime

No specific temperature performance tests are always expected to be required. However, the following set of tests is generally recommended for characterizing the off-nominal temperature performance of a particular technology or design against the FreedomCAR goals, with others to be added based on potential application needs.

- HPPC Test (+10, -10, -30 °C)
- Self-Discharge Test (+10, +50 °C)
- Energy Efficiency Test (+50, +10, -10, -30 °C)

2.2.8.2 Alternative Self-Discharge Test at Off-Nominal Temperature

The standard Self-Discharge test measures energy loss during an extended OCV stand period by comparing the results of a reference discharge with and without the stand period. When this test is done at off-nominal temperatures as described in Section 2.2.5, it measures the fraction

[u] The constant-current discharge and charge test is an exception to this practice, because it is intended to characterize both charge and discharge behavior at the test temperature.

of the Reference Energy (i.e., the 30 °C energy as measured by the Reference Performance Test) which is lost during the stand period at the test temperature. Depending on how the results of this test are to be used, it may be desirable to perform the entire Self-Discharge test sequence (i.e., steps 1 through 7 of Section 2.2.5) at the test temperature, including reference discharges and device recharge. This alternative test measures the fraction of the energy available *at the test temperature* that is lost due to the OCV stand period.

2.2.9 Energy Efficiency Test (CORE AUTOMOTIVE TEST)

Round-trip efficiency is determined by calculation from a charge-balanced pulse profile, i.e., one whose initial and final SOC states are the same while repetitive cycling is in progress. This manual uses a very simple test profile that has been constructed for use in both efficiency and cycle-life testing.

The test profile consists of a discharge pulse and a charge pulse separated by OCV rest intervals. The discharge pulse is performed at a 100C current rate, and the charge pulse is done at the same rate except as limited by manufacturer ratings. The duration of the discharge pulse is fixed at 3.6 s based on 10 % of the Initial Reference Capacity (as measured in Section 2.2.1) at the beginning of testing.[v] For example, if the Initial Reference Capacity of the device is 1 A-h, the nominal discharge pulse would be 100 A for a duration of 3.6 seconds.

The charge pulse is done at the same 100C current (or the maximum rated charge current, if this is less than 100C), with the pulse terminated at a fixed target voltage (nominally V_{MAX}). Charge and discharge pulses are separated by rest intervals of the same 3.6 s length as the discharge pulse. Thus for a device capable of 100C recharge, the total profile length (neglecting losses) is 14.4 seconds. This nominal test profile is defined in Table 6 and shown in Figure 5 following.

Table 6. Ultracapacitor Energy Efficiency and Life Test Profile

	Step Duration (seconds)	Cumulative Time in Profile (seconds)	Test Current (C-rate)
Discharge	3.6	3.6	100
Rest 1 (OCV)	3.6	7.2	0
Charge	Terminates when V_{TARGET} is reached (nominal 3.6 s at 100C)	10.8 nominal	100 (or maximum rated charge current)
Rest 2 (OCV)	3.6	14.4 nominal	0

[v] Because the 100C rate and the discharge pulse duration are related through the Initial Reference Capacity, the discharge pulse duration will always be 3.6 s to remove 10% of the Initial Reference Capacity. The charge pulse duration will be at least 3.6 s but is variable because the charge pulse is terminated when the voltage reaches V_{TARGET} (under load) regardless of the time required.

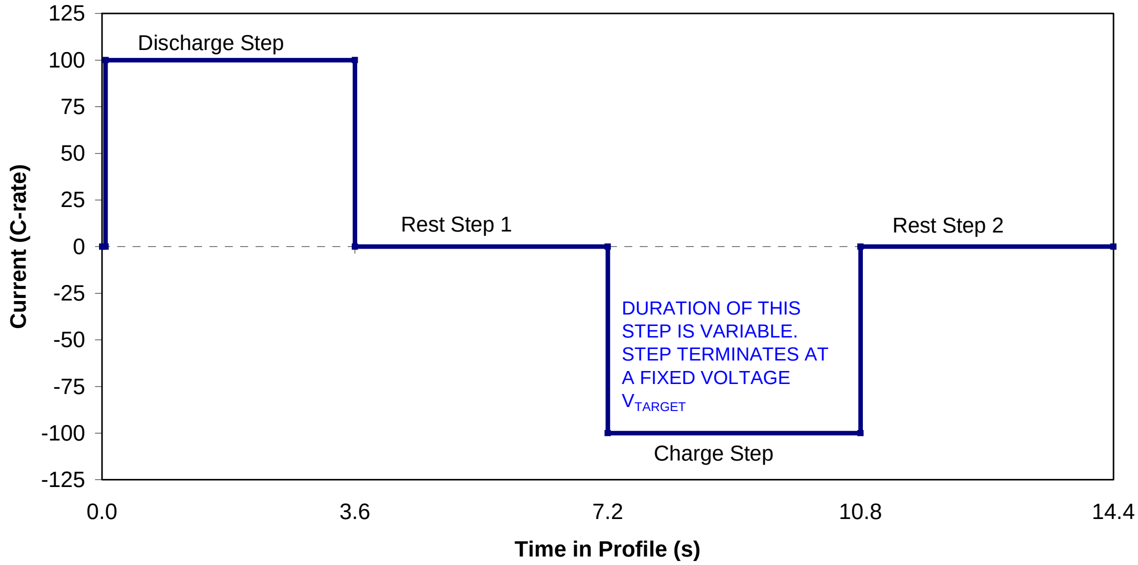

Figure 5. Ultracapacitor Energy Efficiency and Life Test Profile

The target voltage V_{TARGET} to be used for efficiency testing and/or life cycling is fixed based on the capacitor maximum operating voltage and the desired SOC range for cycling. For efficiency testing, V_{TARGET} is normally set equal to V_{MAX} so that discharging takes place in the upper portion of the usable energy range.

The Energy Efficiency Test is performed in accordance with the following outline:

1. Bring the cell to the specified target voltage V_{TARGET} and rest at OCV for one hour or until a stable temperature is observed.
2. Perform 400 efficiency test profiles as defined in Table 6 and Figure 5, or a number adequate to reach a stable cycling condition. Because the profile always reaches the same voltage during the charge step, stable cycling generally means a stable device temperature from profile to profile. Device temperature is considered stable during cycling if the (smoothed) rate of change of temperature is less than one degree C per hour determined over at least 20 test profiles.
3. During Step 2, if the device temperature reaches a pre-determined limit during cycling (typically 5 to 10 °C less than the manufacturer-specified maximum operating temperature) without stabilizing, stop the test. Alter the test profile by extending Rest Step 2 (only) to a value that will stabilize the temperature within 5 to 10 °C below the limit.[w] Repeat Steps 2 and 3 as necessary until a stable cycling condition is reached within the temperature limit.
4. Stop the cycling at the end of a complete test profile (i.e., after Rest Step 2) and observe the voltage during a 1 hour OCV rest. Verify that the final open circuit voltage is acceptably close to V_{TARGET} for this cycling interval. (If not, this can be adjusted by changing V_{TARGET} appropriately [within allowable pulse voltage limits] and repeating the test.)

[w] This is necessarily done by trial and error, although it should be possible to estimate the change needed from the temperature rise and the calculated profile energy loss rate if the temperature excursion is not excessive.

Data collection requirements: During Step 1, data can be acquired at a minimal rate (e.g., 2 or more points per minute) solely for verification that the device temperature is stable before cycling begins. During actual cycling (Step 2), data should be acquired at a rate of 1 sample per second or faster during the four profile steps of all profiles performed.

2.2.9.1 Alternative Coulombic Efficiency Measurement

In some cases it may be desirable to measure the coulombic efficiency of a device, typically to provide a better understanding of its contribution to overall energy efficiency. Coulombic efficiency can be calculated directly from the Energy Efficiency Test as defined here, but it can also be done (with perhaps improved measurement resolution) using a slight modification of this test.

If the test profile is modified such that the charge step has a fixed duration of 3.6 s (rather than terminating at a fixed voltage), then each profile will be charge-neutral. The device can then be cycled for a fixed number of profiles starting from a fully charged condition. Any charge losses during a single profile will be amplified by the number of profiles performed, and a residual capacity discharge at the end of cycling (at the reference 5C rate) will indicate the total charge lost. (See Section 3.2.9 for more information.) Note that this modified test is not suitable for determining energy efficiency because the beginning and final charge states are not the same.

2.2.10 Electrochemical Impedance Spectrum Measurements

For cells, it may be useful to measure ac impedance values at various points during their life. These measurements are generally made with the cell at open-circuit conditions, i.e., not under load. Thus, they are not considered *tests* in the sense commonly used in this manual, but are instead treated as special measurements. No standard measurement procedures are defined for this use. However, the following measurement practice is recommended, especially for cells that are to be life-tested:

A. An initial measurement should be made when a cell is received for testing, as a gross check on the condition of the device. This measurement can be taken at the state of charge at which the device is received, so that it can be done before the cell's installation in a testing station. A simple 1 kHz ac impedance meter can be used for this measurement.

B. A full-spectrum complex impedance measurement scan should be made before the start of life testing and then repeated when life testing is concluded. This measurement will not normally be performed during life testing because it requires disconnecting the device from the testing equipment. However, this can be required in a device-specific test plan if data are needed for a particular use.

A further detailed discussion of electrochemical impedance spectroscopy (EIS) is included in Appendix C.

2.3 Life Testing

2.3.1 Operating Set Point Stability (OSPS) Test

This test is a special case of the cycle-life testing regime to be applied to a given device. The sole purpose of the OSPS test is to verify that stable cycling will occur at the desired target SOC conditions, and to adjust test conditions if necessary to ensure that this will be the case. The default cycle-life SOC test regime exercises the device over at least 10% of its beginning of life (BOL) capacity starting near full charge. A different operating range can be specified if needed in a device-specific test plan based on projected use of the device. The OSPS test is normally performed immediately before the beginning of cycle-life testing, and successful performance of the OSPS constitutes readiness to begin life cycling.

The OSPS test is conducted identically to the Energy Efficiency Test (Section 2.2.9) with one exception. It consists of 400 repetitions of the Energy Efficiency and Life Test profile, with each profile charge step terminated at V_{TARGET}. For the OSPS test and subsequent life testing, the test profile itself is *not* altered if the device temperature limit is approached. If the test temperature limit is reached, cycling is suspended until the device temperature returns to within $\pm$2°C of the nominal target test temperature (nominally 30 °C), at which point continuous cycling resumes.

If the initial Energy Efficiency Test is successful (i.e., a stable temperature is achieved without altering the length of the test profile, and the final SOC after cycling is near the desired target value), this test is equivalent to the OSPS test and the OSPS test need not be repeated. If the final SOC value at the end of cycling is not sufficiently close to the target SOC value (typically within 5% of the desired value), then V_{TARGET} is altered (within allowable pulse voltage limits) and the test is repeated.

Data collection requirements: There are no reportable results from the OSPS test. However, evaluation of whether the test is successful typically requires several data points during each pulse of each profile performed, so a rate of 1 sample per second is recommended during actual cycling. A slower rate (once per 10 seconds or even once per minute) can be used during any periods when cycling is suspended due to thermal limits.

2.3.2 Cycle-Life Test (CORE AUTOMOTIVE TEST)

Cycle-life testing is performed using the Energy Efficiency and Life Test profile defined in Section 2.2.9 in Table 6 and Figure 5. Cycle life testing is performed by repeating the test profile at a fixed state of charge (i.e., the profile is charge-balanced). Control of the state of charge during cycle life testing in this manual is based on termination of a charge step at a fixed voltage V_{TARGET}. The test profile is performed at fixed pulse current values determined at the beginning of testing based on the Initial Reference Capacity (in ampere-hours) of the device to be tested.

Cycle-life testing is performed in accordance with the following outline:

1. The following three values must be known prior to cycle-life testing: (a) the 100C pulse current, calculated from the Initial Reference Capacity for the device; (b) the temperature limit (T_{LIMIT}) to be observed during cycling; and (c) the voltage V_{TARGET} corresponding to the target SOC for cycling. (These are discussed further in Section 2.2.9.)
2. Determine end-of-test criteria for cycle-life testing. These are normally specified in a device-specific test plan. A default (and generally mandatory) end-of-test condition is

reached when the test profile cannot be executed within the voltage limits, e.g., the 100C discharge pulse current cannot be sustained for the defined pulse duration. At this point, the device capability at the target SOC is less than that required by the test profile.

Another default end-of-test condition occurs if performance degrades to a point where the HPPC reference test yields insufficient information to show further degradation. This would normally be the point where valid discharge and regen data are obtained at less than three DOD values using the HPPC test.

End-of-test may also be chosen to occur when a pre-defined number of cycles (e.g., the value corresponding to the FreedomCAR life goal for the target application) have been performed.

3. Select the desired operating state of charge for cycle-life testing and perform the Operating Set Point Stability Test (Section 2.3.1) to verify stable operation at the selected SOC point. Make any needed adjustments to the test operating conditions.
4. Perform the test profile the number of times specified in Table 8 or a device-specific test plan.
5. If the temperature limit T_{LIMIT} is reached during cycling, suspend cycling at the end of the charge pulse in the present test profile and place the device in a rest (OCV) state while monitoring the temperature. When the device temperature returns within the nominal control band (i.e., 30$\pm$2 °C for ambient temperature cycling), resume cycling.
6. After the specified number of test profile repetitions, suspend cycling. If cycling is being done at other than 30 °C, return the cell to 30 °C.[x] Observe the open-circuit voltage after a 1 hour rest. Remove the residual capacity at a 5C constant-current rate to verify the cycling depth of discharge, and perform the Reference Performance Tests to determine the extent of degradation in capacity and/or power capability. The reference tests are listed in Table 8. The nominal intervals between repetitions of these reference tests are also specified in Table 8, though these will be affected if cycling is suspended due to thermal limits.[y]
7. If the residual capacity measured in Step 5 indicates an unacceptable change in DOD during cycling (due to changes in device capacity), repeat Step 3 to re-establish the target cycling condition.
8. Repeat Steps 4, 5 and 6 until an end-of-test condition is reached.

Data collection requirements: Data should be acquired at 1 sample per second or faster during the first and last 100 test profiles of each cycling interval (i.e., between Reference Performance Tests), and for 1 complete profile of each 100 between these points. If the device thermal behavior is such that T_{LIMIT} will be reached during cycling, at least one data point should be recorded during each profile as a record of temperature behavior. Data should be acquired at a rate of 1 sample per minute during any periods when cycling is suspended due to thermal limits.

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[x] If characterization testing indicates that the device pulse resistance is significantly affected by temperature (e.g., more than ~0.25% per degree C at 30°C), it may be necessary to perform an HPPC pulse profile at the cycling SOC before the device is returned to 30°C. This data can be used to determine the temperature sensitivity of the subsequent RPT results, so that they can be corrected for the actual temperature at the time of the RPT test. (See Reference [3] for more information.)

[y] For test convenience, the time between RPTs can be fixed if desired. However, accumulating the total cycle count and device throughput over life will be more complex if cycling suspension intervals occur.

2.3.3 Calendar-Life Test (CORE AUTOMOTIVE TEST)

This test is designed to permit the evaluation of cell degradation as a result of the passage of time with minimal usage. It is not a pure shelf life test, because the device under test is maintained at or near a target state of charge during the test. The device must also be periodically subjected to reference discharges to determine the changes (if any) in its performance characteristics.

In general, calendar-life testing is performed using multiple cells over a range of test conditions. It is commonly done at elevated temperatures in order to shorten the time required for obtaining useful results. Cells to be tested may be included in a matrix of test variables such as temperature and state of charge. This matrix may in turn be part of a larger cycle-life test matrix where calendar-life testing is considered a limiting cycle-life test, i.e., one in which the state of charge swing during cycling is zero. The design of experiments for such a test matrix is not described in this manual. The calendar-life test procedure assumes that the target test conditions for each cell or group of cells have been defined, typically in a device-specific test plan. The planning, conduct and analysis of calendar-life testing for production-ready FreedomCAR energy storage technologies is now described in detail in Reference [3]. This section provides a simplified approach derived from (but not identical to) Reference [3] for testing devices still under development.

2.3.3.1 Calendar-Life Test Procedure

The calendar-life test procedure defined for ultracapacitors is similar (but not identical to) that used for Technology Life Verification Testing of FreedomCAR energy storage technologies in Reference [3]. The outline of this test procedure for a particular cell is as follows:

1. Characterize the cell using the Reference Performance Tests defined in Section 2.4.
2. Discharge or charge the cell to the target DOD/SOC value at 30 °C as described in Section 2.1.6.
3. Apply a single iteration of the Calendar-Life Test Profile defined in Section 2.3.3.2. The nominal discharge current to be used for this profile is equal to the peak discharge current for the Minimum HPPC Test (i.e., 0.25 I_{MAX}).
4. Bring the cell to the target temperature at open-circuit condition and wait for the ambient temperature and voltage to stabilize.
5. Apply a single iteration of the Calendar-Life Test profile defined in Section 2.3.3.2 at the same current level defined in Step 3. The device is then placed in an open-circuit state and the test continues at the target conditions.
6. Once every 24 hours, and immediately before beginning Step 7, repeat Step 5. Note that data acquisition requirements during this pulse profile execution will be similar to those for HPPC tests, even though other data may be required only infrequently during the 24 hour intervals.[z]
7. At intervals as specified in Table 8 or a device-specific test plan, return the cell to nominal temperature (e.g., 30 °C), observe its open-circuit voltage after a 1 h rest, and

[z]. Intermittent charge increments may be required to compensate for self-discharge to keep the state of charge within an acceptable range until the next reference test. The method to be employed for doing this should be specified in a device-specific test plan. One suggested method is to clamp each device after the once-per-24 hours profile at its elevated-temperature OCV (as measured in Step 4) for a specified duration or until the voltage is stable at the target temperature.

apply a single iteration of the Calendar-Life Test profile before discharging its remaining capacity at the 5C rate. Conduct a single iteration of the required periodic Reference Performance Tests, and then return the cell to its test temperature.

8. Repeat this test sequence until the cell reaches an end-of-test condition. Default end-of-test conditions generally include the following: (a) the Calendar-Life Test profile cannot be performed within the voltage limits; (b) the periodic Reference Performance Test yields insufficient information to show further degradation; or (c) sufficient data is acquired to project calendar life at the test conditions with a predetermined degree of confidence.

2.3.3.2 Calendar-Life Test Profile

This test profile, which is identical in form to that used for FreedomCAR battery calendar-life testing, is intended for once-per-day execution during calendar-life testing at the target temperature and state of charge. The data provide daily information regarding the extent and rate of cell degradation during the intervals between periodic reference tests. This test profile is not intended for continuous execution; instead, it is executed once during each 24 hour period while the cell under test is maintained at the target temperature and state of charge. The pulse profile is shown in Table 7 and illustrated in Figure 6.

Table 7. Calendar-Life Test Profile.

Step Time (s)	Cumulative Time (s)	Relative Current (Ratio)	Relative Net Charge (A-s/A)
9	9	1.0	9.0
60	69	0	9.0
2	71	-1.0	7.0
2	73	0	7.0
47	120	-0.149	0

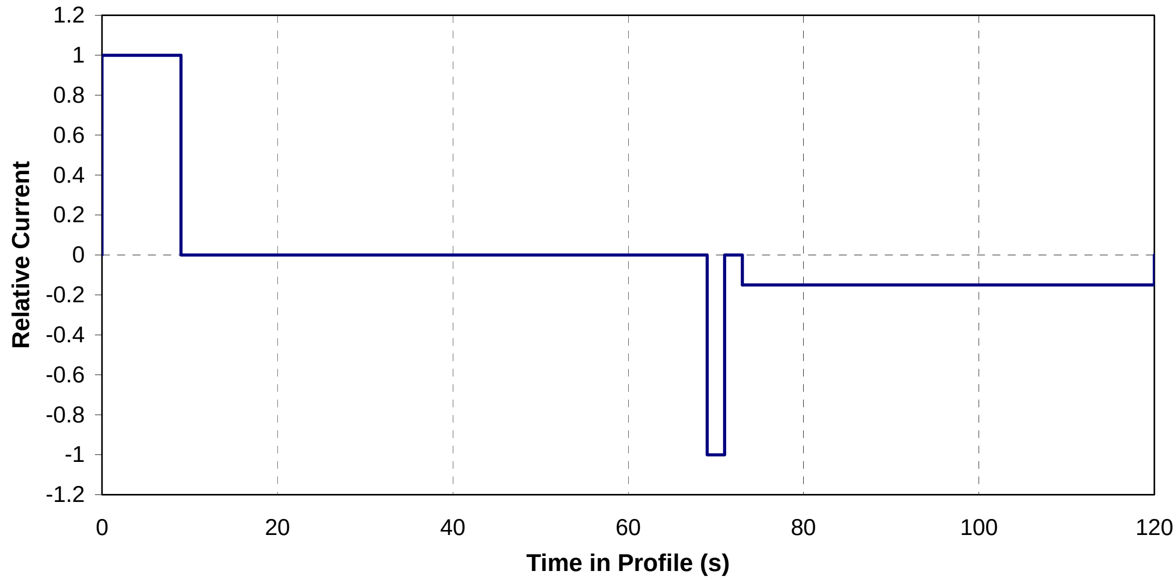

Figure 6. Calendar-Life Test Profile

2.3.3.3 Alternative Calendar-Life Test

In some cases calendar-life testing may be conducted without using the once-per-24 h Calendar-Life Test profile. One reason for this could be a shortage of continuously available test channels for the number of devices to be tested. (If the 24 h pulse profile is not performed, a test channel is required only for the periodic Reference Performance Tests and possibly for occasional charge increments.) The earlier procedure can be used in this fashion by omitting the daily performance of the test profile specified in Step 6 of the procedure. If testing is performed in this fashion, the device open-circuit voltage should be checked every 24 to 48 hours to verify that the state of charge remains in an acceptable region, and an HPPC pulse profile should be performed at the target SOC and temperature before the device is returned to 30 °C for periodic reference testing.

2.4 Reference Performance Tests

Reference Performance Tests (RPTs) are a set of tests performed at periodic intervals during life testing to establish the condition and rate of performance degradation of devices under test. Except as modified by a device-specific test plan, the tests specified in Table 8 should be performed: (a) prior to the start of life testing; (b) at defined periodic intervals; and (c) at end of testing, for all devices undergoing either cycle-life testing or calendar-life testing. The default Reference Performance Test iteration consists of one repetition of the HPPC Test, which includes the appropriate Reference Capacity or 1 kW discharge test. Periodic testing at off-nominal temperatures is not included in the RPT regime except as noted in Section 2.3.3.3.

Where performance is strongly dependent on temperature, it is desirable to measure accurately the actual temperature of the test device during the RPTs and adjust the performance results using the data from the Temperature Performance Tests (Section 2.2.8) and/or pulse data acquired at the end of each test interval to estimate the present performance at the nominal 30 °C temperature. (See Reference [3] for more information on how this is done.)[aa]

Table 8. Reference Performance Tests and Test Intervals for Life testing.

Type of Life Testing	Test Interval Between RPTs	Reference Performance Tests
Cycle-Life Testing	135,000 cycle-life profiles nominal (25 days)	Minimum HPPC Test (includes 1 kW constant-current or Reference Capacity Test as appropriate)
Calendar-Life Testing	Approximately 25 days (600 hours)	

Table 8 also lists typical intervals for reference tests during cycle-life and calendar-life testing. In practice, these intervals may have to be adjusted somewhat to synchronize reference testing for groups of multiple cells, especially where calendar life and cycle life cells are being tested in the same temperature chamber. Note that the cycle-life test profile defined in this manual may have variable length, and non-cycling intervals may occur due to thermal limits. This can affect the time required to perform the specified number of cycles, and it may be desirable to fix the interval between RPTs based on calendar time rather than number of profiles.

[aa] Note that performing such an adjustment is only sensible if the accuracy (or at least the test-to-test stability) of the temperature measurements is better than the device temperature variations to be corrected. Otherwise the correction simply introduces another source of variability in the calculated results. Also note that this can be done using either ambient temperature or device temperature, because the correction is done using the temperature measured just before a reference discharge pulse, when the device is at thermal equilibrium at a zero power condition.

3 ANALYSIS AND REPORTING OF TEST RESULTS

3.1 General

For purposes of test reporting consistency (particularly between multiple testing organizations), a required set of information, based on the procedures in this manual, has been compiled for FreedomCAR testing and is tabulated in Appendix E. This is not intended to limit the reporting of other test results where appropriate. The intent is rather to ensure that important test results are reported in a fashion that allows them to be compared to test results on devices tested at various locations and stages of development.

Note that the results of many of these tests involve the use of quantities of charge (e.g., ampere-hours) or energy (Wh) removed from or returned to the device over specific parts of a test. It is generally assumed that the test equipment used will report these values directly as a result of internal integration. In rare cases, it may be necessary for the user to derive them by manually integrating current data (for charge) or the product of current and voltage (for energy) over test segments. In such cases, careful attention must be given to the test data collection requirements in Section 2 to assure that reasonable accuracy is preserved during transient portions of the tests.

All the figures shown in this section that are based on actual test data are for illustration only and are not necessarily representative of any specific ultracapacitor technology.

3.2 Characterization Tests

3.2.1 Reference Capacity Test

The fundamental results from the Reference Capacity Test are the discharge capacity (in ampere-hours) and the discharge energy (in watt-hours) measured over the operating voltage range from V_{MAX} to V_{MIN}. Energy removed (watt-hours) is also reported as a function of depth of discharge (in percent of the Initial Reference Energy). These data are used for the later calculation of usable energy, and examples of the results are shown in Section 3.2.6 on the Hybrid Pulse Power Characterization Test.

Ampere-hours and watt-hours returned (and the corresponding overall charge/discharge efficiencies) are also reported for the corresponding recharge.[bb]

For devices subjected to life testing, the change in reference capacity from the beginning-of-life value (measured just prior to the start of life testing) to some later point in time is to be reported periodically as Capacity Fade (for either charge capacity or energy), expressed as a percentage of the original (BOL) capacity as shown in Equation 6.

$$Capacity\ \ Fade(\%) = 100\left(1 - \frac{Capacity_{t1}}{Capacity_{t0}}\right) \tag{6}$$

where *t0* refers to the time of the initial (BOL) RPT and *t1* refers to the time of the later RPT where capacity fade is to be determined.

[bb] Note that the recharge begins at the DOD reached at the end of the discharge to V_{MIN}, which is not exactly equal to the SOC corresponding to V_{MIN}. The recharge terminates with the device fully charged so that efficiency can be determined, using the same equation defined in Section 3.2.9.

3.2.2 Constant-Current Discharge and Charge Test

Results to be reported from this test are itemized in the following list and further described in subsequent sections.

a. Discharge and charge capacity (Ah) and energy (Wh), both removed and returned, is reported for each discharge and charge cycle of the test between V_{MAX} and V_{MIN}, at each current level.

b. Capacitor voltage as a function of charge removed (in Ah) at each test current level is reported for both discharge and charge steps.[cc]

c. Capacitor voltage is also reported as a function of energy removed (in Wh) and of % DOD (based on the Initial Reference Capacity.)

d. The effective capacitance of the device is calculated for each test condition (current rate), along with the Equivalent Series Resistance (ESR) and the charge/discharge efficiency.

e. If the test is performed at other temperatures in addition to the nominal 30 °C condition, the results of these tests are similarly reported along with the 30 °C results.

3.2.2.1 Capacitor Voltage as a Function of Charge, Energy and DOD Removed

Figures 7 and 8 illustrate the cell voltage as a function of charge removed and energy removed for an example ultracapacitor for constant-current discharge tests performed using test currents from 10 A to 400 A in both discharge and charge modes.

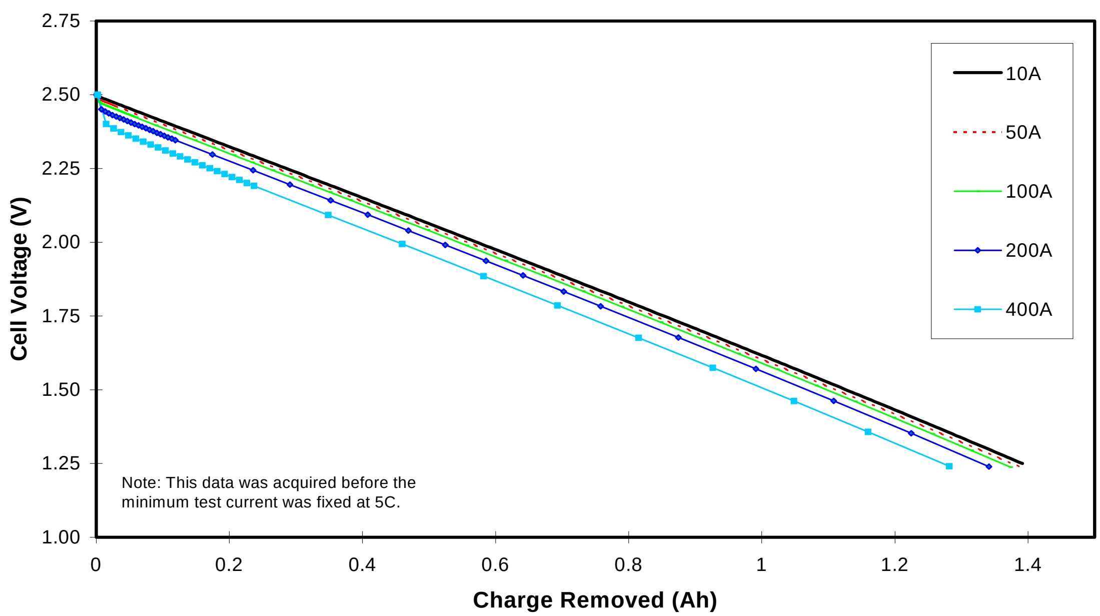

Figure 7. Cell voltage as a function of charge removed for a series of constant-current tests.

[cc] If device or equipment limitations prevent using the same currents for charge and discharge, the charge and discharge currents must be clearly stated when presenting all results from this test, including the charge/discharge capacitance, ESR, and energy efficiency.

This example capacitor was rated at 3600 F with a working voltage of 2.5 V, and its reference capacity (from 2.5 to 1.25 V) was about 1.38 Ah. The test C-rates for these data thus ranged from ~7C to ~290C. The ESR induced drop in the cell voltage at the onset of the discharge is visible in these figures, although it is somewhat obscured by the available data for this test.

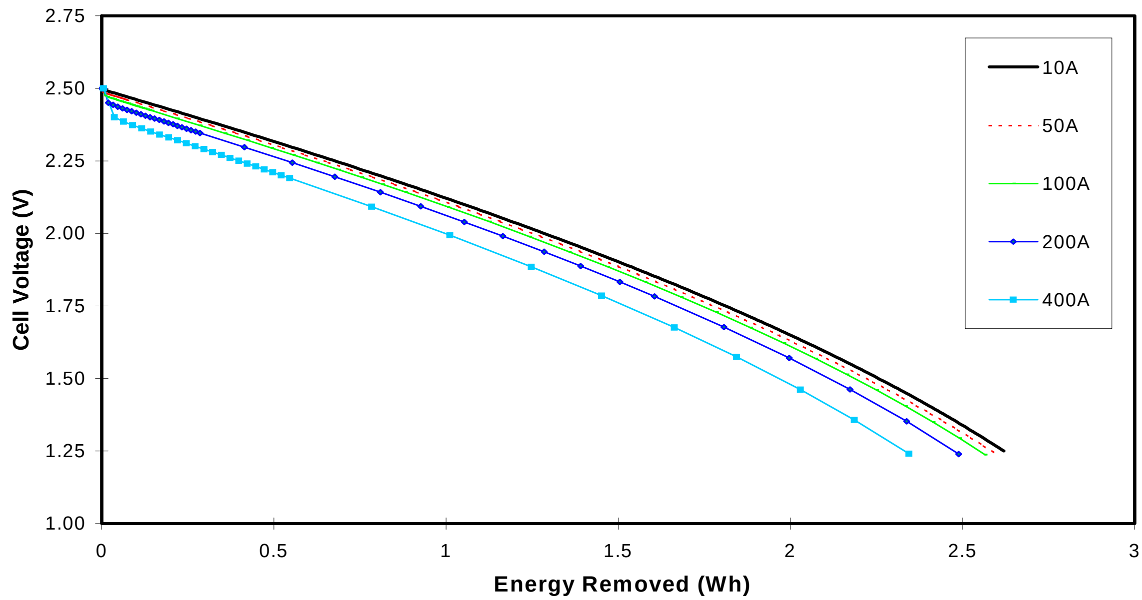

Figure 8. Cell voltage as a function of the energy removed for a series of constant-current tests.

3.2.2.2 Calculation of Device Capacitance, Efficiency and ESR

For an ideal capacitor, the curve of device voltage versus charge removed is a straight line, where the inverse slope of this line is equal to the capacitance (in farads, if charge is expressed in coulombs rather than Ah). This linear relationship only holds true if the capacitance is not a function of the device voltage (or charge level), which may not be true for a real device. (See the curves in Figure 7 for an illustration of this nonlinearity.) Consequently the value of capacitance to be reported from this test series is computed as the ratio of the total charge removed (or added) in a discharge (or charge) between V_{MAX} and V_{MIN}, divided by the change in voltage as shown in Equation 7.

$$C_I = Q_I / (V_{MAX} - V_{MIN}) \tag{7}$$

where C_I is the effective capacitance at current I, and Q_I is the charge removed (between V_{MAX} and V_{MIN}) at current I.

Note that the discharge and charge steps performed during this test do not use clamp voltage intervals to force the capacitor's beginning or ending SOC exactly to the values corresponding to V_{MAX} and V_{MIN} (except at the start of each 3-cycle series at a given test current). The capacitance derived from each step of this test does not correspond to the total charge that could be available between V_{MAX} and V_{MIN} at *any* rate. Rather it corresponds to the charge available at the tested current (either discharge or charge), and it should be labeled as "effective capacitance".

The fundamental definition of energy efficiency for an energy storage device is expressed in Equation 21 in Section 3.2.9. This equation can be used to calculate round-trip energy efficiency for any series of discharge and charge steps that result in the same initial and final state of charge, by taking the ratio of the discharge energy to the charge energy (expressed as a percentage). In this case, it can be used to calculate efficiency at each constant-current test value. This is most accurately done using the middle cycle of each 3-cycle series, although it may also be of interest to do the calculation for the entire 3-cycle series (i.e., total discharge energy over 3 cycles divided by total charge energy over 3 cycles).

During the constant-current discharge and charge tests, the current is suddenly changed at the beginning and end of each discharge and charge step. The equivalent series resistance (ESR) is calculated at these points using Equation 8.

$$ESR = \Delta V / \Delta I \qquad (8)$$

where ΔV is the voltage change that occurs due to the change in current ΔI at the beginning (or end) of a constant-current charge or discharge step. The beginning calculation should be done using measurements at a time very close to (i.e., immediately before and after) the onset of the constant-current step. This time interval is necessarily tester dependent. An alternate method of determining the ESR at the beginning of a current step is to plot the value of the voltage after the step begins as a function of time and extrapolate the curve back to zero time to obtain the value of ΔV. Another method for calculating the ESR at the end of a time step is done by using the final voltage during the step and the voltage 5 s after the step ends where the capacitor is at OCV.[dd]

Figure 9 shows the effective (discharge) capacitance, (discharge) ESR and efficiency values calculated from the test results of Figures 7 and 8. The values are shown for all 3 cycles at each test current, although some markers overlap on the graph.

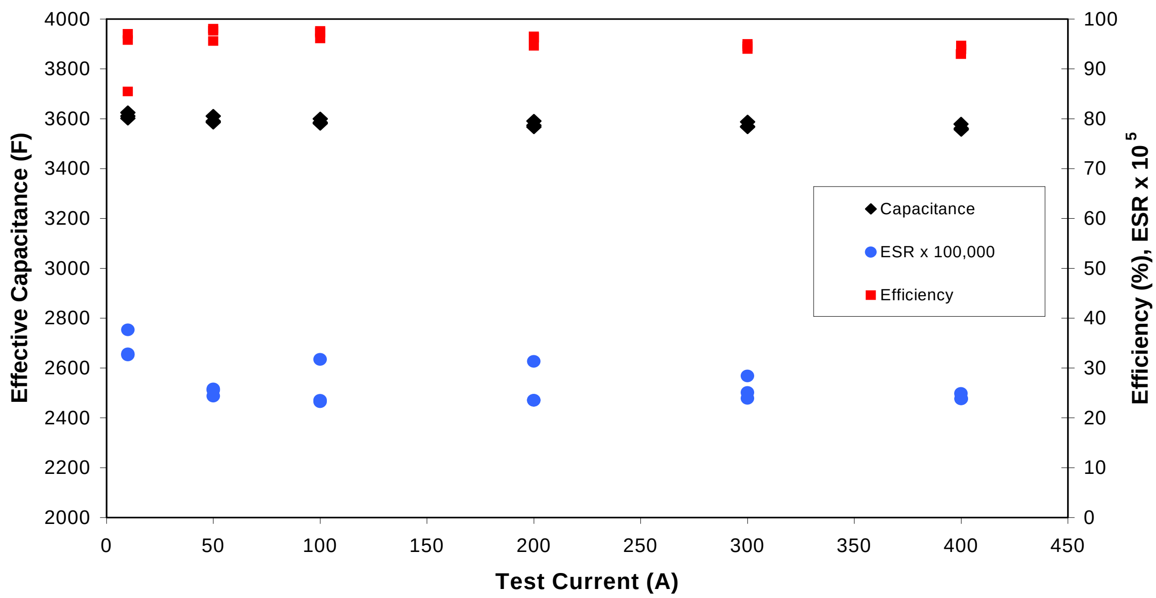

Figure 9. Cell discharge ESR, effective capacitance and efficiency for a series of constant-current tests.

[dd] This 5 s value is used for repeatability and for comparison with a similar result reported by some capacitor manufacturers. It will give a somewhat different result for ESR than the "instantaneous" calculation, but this is true of any two of the numerous methods for calculating ESR.

ESR is defined based on a transition between a fixed current step and a rest interval, so more consistent results will be obtained if the voltage is stable (i.e., at an equilibrium value) during the rest interval. The rest periods in this test may not be long enough to assure this condition at all test conditions, except for the first discharge step in each 3-cycle sequence at a given test current.

The ESR value is given in ohms, and is generally found to vary with the constant-current charge or discharge currents (as well as the test temperature). The degree of variation of the ESR is highly dependent on the construction and materials used in the assembly of the capacitor.

3.2.3 Constant-Power Discharge Test

The primary results from the Constant-Power Discharge Test are (a) the capacitor voltage as a function of test time and/or energy removed at each constant-power level during the test; and (b) a Ragone plot of specific energy versus specific power, based on the actual weight of the device tested. It is also possible to calculate energy efficiency as a function of discharge power from this test. Note that this test focuses on discharge behavior; all recharging is done at a single, relatively low constant-current rate (usually the 5C rate).

The voltage versus energy removed relationship can be plotted directly from the raw test data, as illustrated in Figure 10. The example data is from a capacitor rated at 3600 F over the operating voltage range of 1.25 V to 2.5 V.

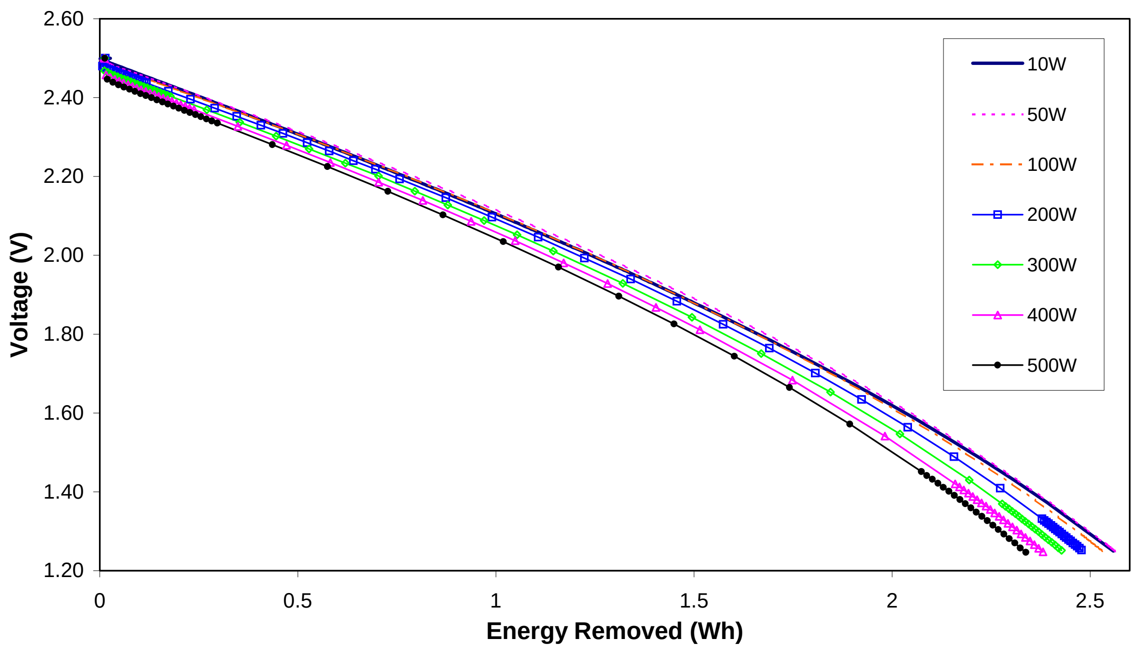

Figure 10. Cell voltage as a function of energy removed for a series of constant-power discharge cycles.

The specific energy versus specific power relationship is generally reported in graphical form. At each tested discharge power value, the corresponding energy (in watt-hours) discharged from the device between V_{MAX} and V_{MIN} is determined from the test data, along with the actual test power (in watts). The energy and power values are converted to specific energy and specific power by dividing by the tested device weight (0.76 kilograms for this example), and the resulting values are plotted against each other on a single curve, as illustrated in Figure 11.[ee]

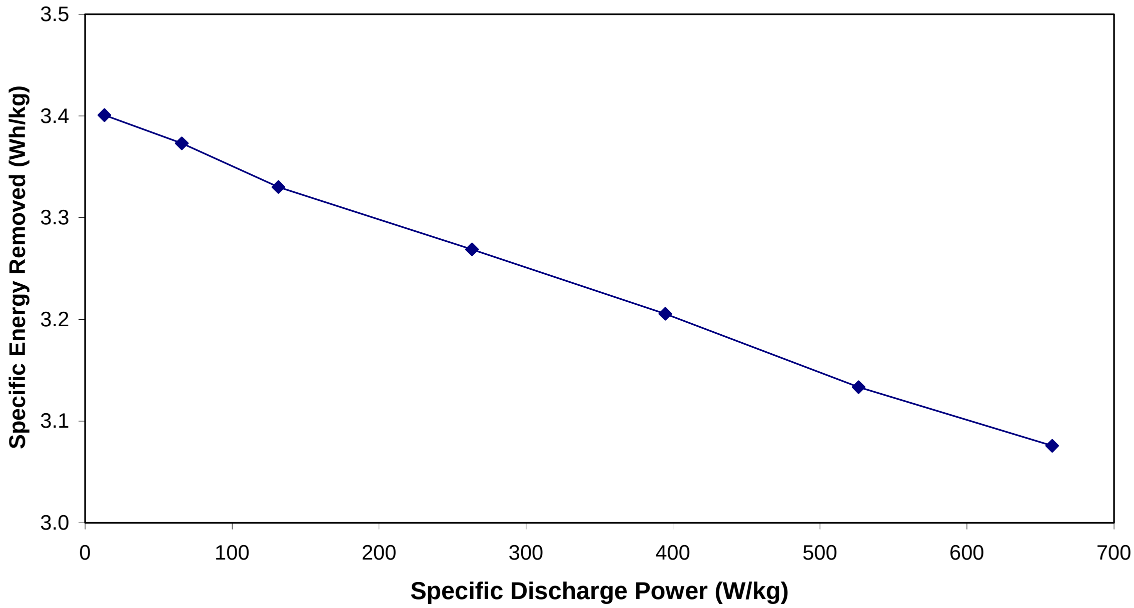

Figure 11. Specific Energy versus Specific Power for a Representative Ultracapacitor

Energy efficiency can be calculated from the results of the constant-power tests using the same basic equation from Section 3.2.9. In this case the data from the second cycle in each 3-cycle sequence (or the combined second and third cycles) should be used. This gives an energy efficiency at each test discharge power for a combined constant-power discharge/constant-current charge cycle. The resulting efficiency values can be plotted versus discharge power to show how efficiency is affected by variations in discharge power (only).

3.2.3.1 Alternative Constant-Power Charge (Regen Efficiency) Test

If the constant-power charge version of this test is performed, the results to be reported are exactly the same, except that all are presented in terms of charge power (and charge energy) rather than discharge power and energy. For example, the resulting plot of energy efficiency versus charge power shows how efficiency is affected by variations in charge power (e.g., regen) only, with all discharging done at the single (relatively low) reference constant-current (normally 5C) rate.

3.2.4 Leakage-Current Test

The primary results of the leakage-current test are presented as two graphs: (a) a plot of the measured leakage current as a function of time; and (b) a plot of the corresponding inferred leakage resistance. Example current data from a leakage-current test is shown in Figure 12 for three

[ee] A similar plot can be prepared for energy density versus power density by dividing the test power and energy values by the volume of the tested device (in liters). This is not illustrated here. Note that it is generally not appropriate to use cell-level plots in this form for a direct comparison with target system performance or goals, because they do not address packaging and system auxiliary weight and volume considerations.

different test temperatures. This example data is from a double-layer capacitor with symmetric carbon/carbon electrodes and organic electrolyte, rated at 3600 F. The capacitor voltage in this example is being held at 2.5 V.

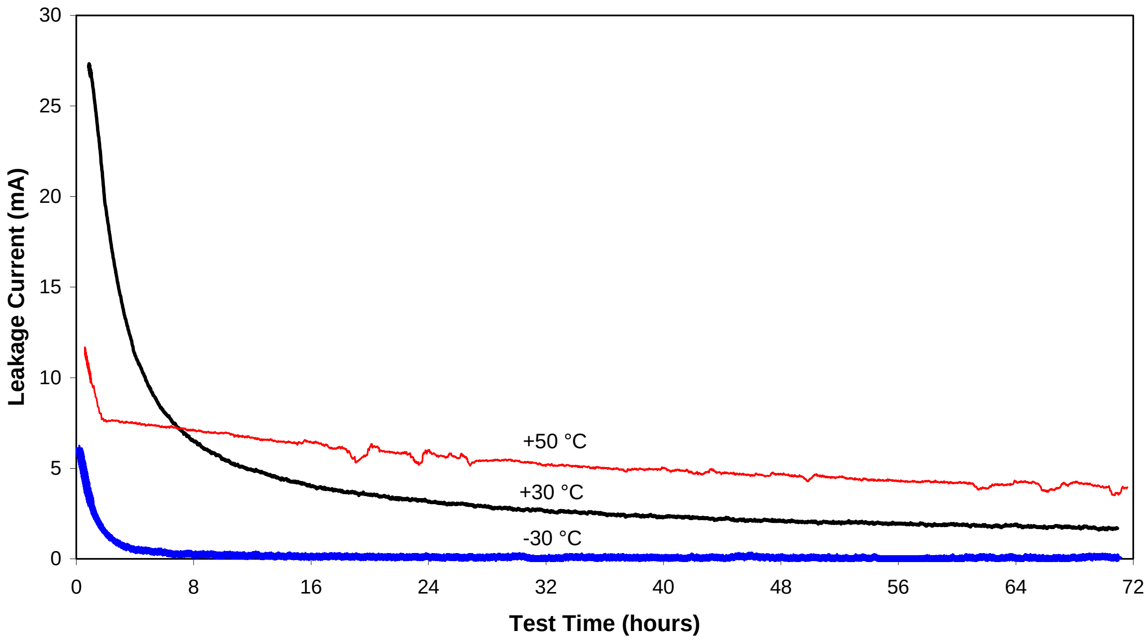

Figure 12. Leakage current measured on a capacitor at three temperatures.

Leakage-current test data can be used to determine the value of the implied parallel resistor, R_p, sometimes referred to as the leakage resistance, in the simple circuit model of the capacitor found in Appendix B and described by Equation 9.

$$R_p(t) = V_{TEST} / I(t) \tag{9}$$

where V_{TEST} is the initial voltage on the capacitor, and $I(t)$ is the measured time-dependent current required to maintain the voltage at its initial value. The value commonly reported for R_p is determined when $V_{TEST}/I(t)$ has reached a relatively constant value. The actual time dependence of $R_p(t)$ is also reported in graphical form as illustrated in Figure 13.

Leakage current data can also be used to estimate the energy required to maintain the device at the test voltage over time. This 'leakage energy' is calculated by integrating the product of the leakage current and the device voltage during the test as shown in Equation 10.

$$Energy_{Leakage} = \int_0^t V_{TEST} I(t)\, dt \tag{10}$$

where V_{TEST} is the constant voltage at which the test is conducted.

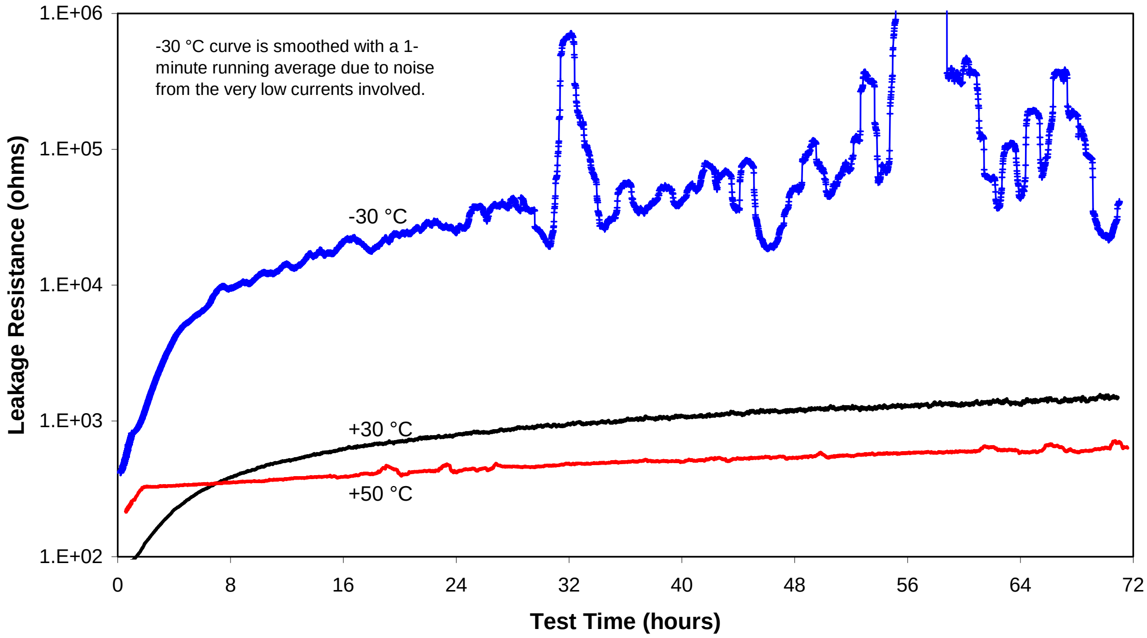

Figure 13. Leakage resistance determined from data in Figure 12 for a capacitor at three temperatures.

An example of the resulting leakage energy, calculated by numerical integration of the ambient temperature data of Figure 12, is shown as Figure 14. Note that the leakage current typically approaches an asymptote as the test progresses; but the leakage energy continues to increase indefinitely because the current does not go to zero.

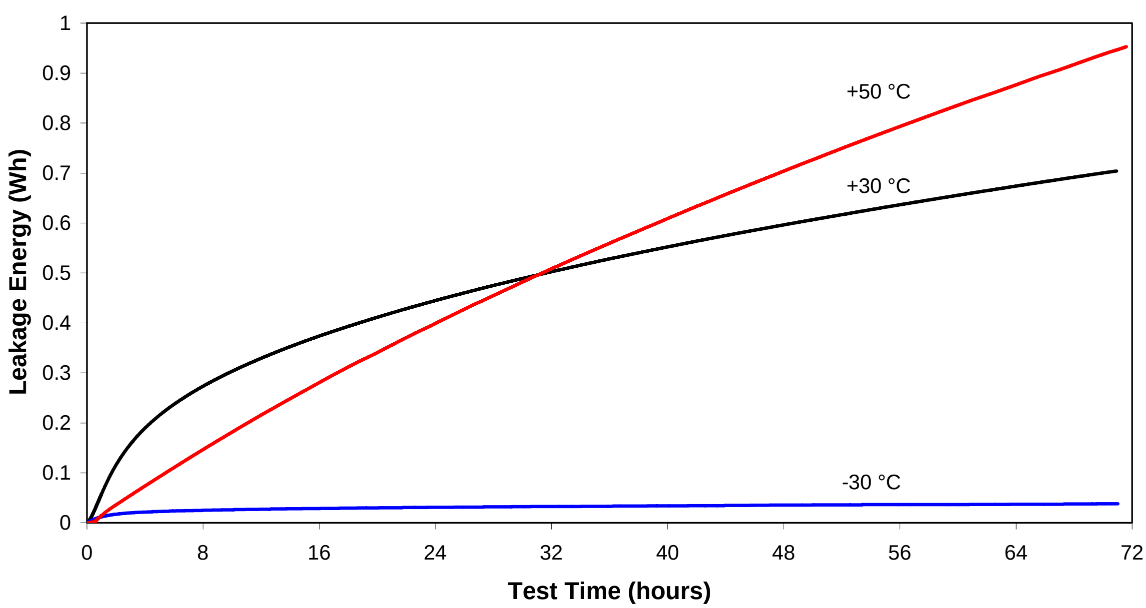

Figure 14. Integrated leakage energy for the data of Figure 12.

3.2.5 Self-Discharge Test (Stand Test)

The basic result of the self-discharge test is a single quantity: the fraction of the reference energy that is lost during the device stand period. This energy loss is computed (as in all FreedomCAR test manuals) as the difference between the pretest (reference) energy and the sum of the energies in the partial discharges before and after the stand period. This value is then divided by the reference energy and reported as average loss in percent over the stand period as shown in Equation 11.

$$\text{Self Discharge} = \frac{\text{Reference Energy} - (Wh_{\text{step3}} + Wh_{\text{step 6}})}{\text{Reference Energy}} \times 100 \tag{11}$$

where the Reference Energy is measured during Step 1 of the test, and Wh_{step3} and Wh_{step6} are the discharge energies measured during the partial discharges in procedure Steps 3 and 6. (Wh_{step3} will be zero if the device is tested starting at the fully charged condition.) This value can also be divided by the length of the stand period and converted to average loss in percent per day.

The voltage measured as a function of stand time during a Self-Discharge Test is also reported graphically, as illustrated in Figure 15 for an example capacitor at various temperatures. This data is from a double-layer capacitor with symmetric carbon/carbon electrodes and organic electrolyte, rated at 3600 F. The initial voltage for the test was 2.5 V at all tested temperatures.

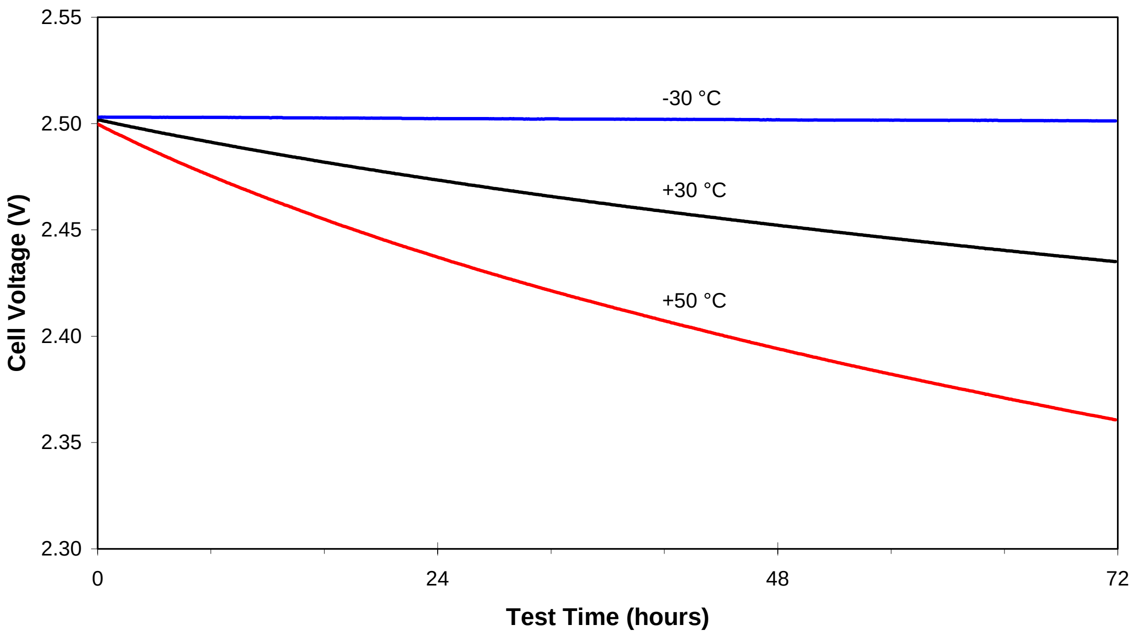

Figure 15. Cell voltage during a Self-Discharge Test measured at several temperatures.

Note that capacitor modules may include cell-balancing circuitry that can cause continuous or intermittent losses that are not attributable to the cells themselves. If possible, these losses external to the cells should be quantified separately during this test. If this is not practical, the presence of such circuitry, any external power and energy required for its operation, and any effects observed in the measured data should still be reported.

The voltage measured over time during the open circuit stand period can be used to calculate the Self-Discharge Energy Loss Factor, *SDLF(t)*, which represents the fraction of the total theoretical energy of the device (down to zero voltage) that is lost as a function of time based on Equation 12.

$$SDLF(t) = 1 - \left(\frac{V(t)}{V_0}\right)^2 \tag{12}$$

where V_o is the initial voltage on the capacitor.

Note that this is not the same as the fraction of the energy over the operating voltage range that has been lost, i.e., it cannot be compared to the results of the stand loss measurements. The more comparable (but still theoretical) result in this case is given by Equation 13.

$$SDLF_{OVR}(t) = 1 - \left(\frac{V^2(t) - V_{MIN}^2}{V_0^2 - V_{MIN}^2}\right) \tag{13}$$

where $V_{MIN} \leq V(t) \leq V_0 \leq V_{MAX}$. This represents the fraction of the original energy between V_0 and V_{MIN} that is lost as a function of time, and if V_0 is equal to V_{MAX} (as is typical), it is the lost fraction of the energy over the operating range V_{MAX} to V_{MIN}.

Figure 16 illustrates the values of SDLF(t) calculated over the operating voltage range of 2.5 to 1.25 V from the self-discharge test data shown in Figure 15. Both figures show the large reduction in energy loss rate at lower temperatures that is to be expected from capacitors.

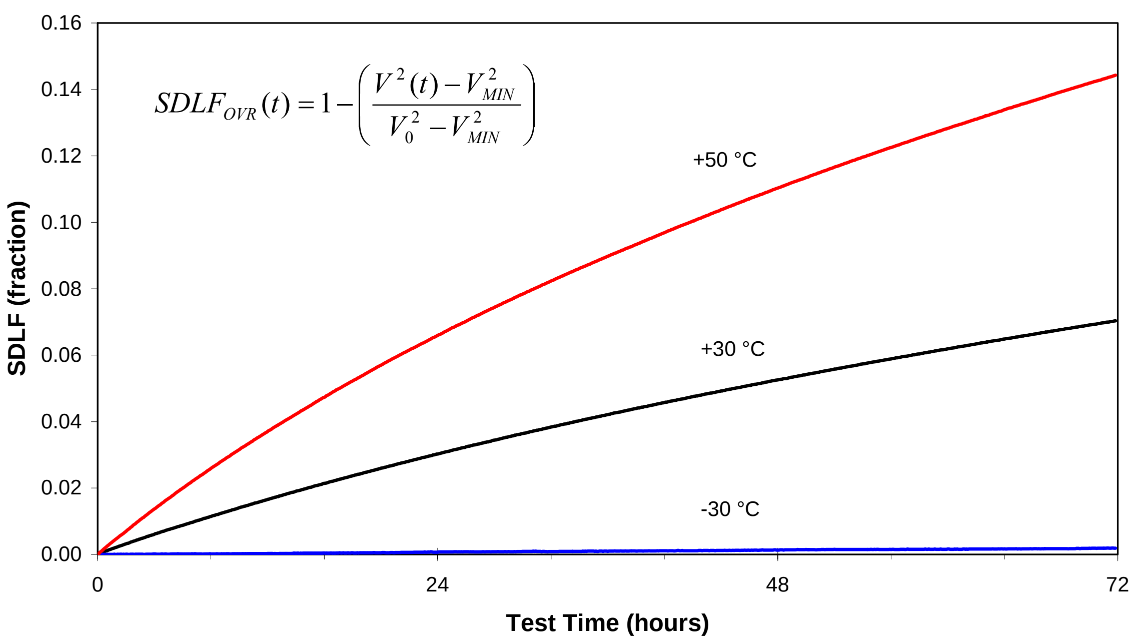

Figure 16. Self-Discharge Energy Loss Factor calculated from the data of Figure 15.

Note that even though the Leakage Current and Self-Discharge tests indicate generally similar behavior, the calculated energy values in Figures 14 and 16 are quite different at all temperatures. This is probably due to the different test conditions but may also be affected by measurement errors at these very low currents. Because of the different conditions and measurement limitations of the tests, the energy loss of interest must be carefully defined and the test must be conducted for a duration long enough to give meaningful results. In general the credibility of the results should be ranked as follows (from highest to lowest): (1) total loss measured by the Self-Discharge Test (for measured values of at least 5 percent); (2) the SDLF calculated from the Self-Discharge Test; and (3) the integrated energy from the leakage current measurements.

An independent estimate of the energy loss (in watt-hours) during the test can be computed by using Equation 14.[ff]

$$\textit{Energy Loss(t)} = \frac{0.5}{3600} C \left[V_0^2 - V^2(t) \right] \tag{14}$$

where C is the effective capacitance of the device over the operating voltage range from V_{MAX} to V_{MIN}. The value of C is not generally known under the test conditions. As a first approximation for C, the current-dependent capacitance (found by constant-current discharge testing) can be extrapolated to its value at a discharge current of zero for use in Equation 14. The degree of agreement between the self-discharge loss measured directly by the test and the energy loss estimated by Equation 14 is some measure of how much the device resembles an ideal capacitor, although it also depends on the measurement uncertainties inherent in both the test results and the capacitance.

3.2.6 Hybrid Pulse Power Characterization Test

The results of the HPPC test are used to compare the present performance of a device to the FreedomCAR goals. The HPPC test can also be used: (a) to permit comparison of the performance of various capacitors to each other; and (b) to monitor changes in the performance of a particular device during life testing. Results are scaled by the Capacitor Size Factor (CSF) for comparison to FreedomCAR goals. For other potential applications, the results are typically scaled relative to the weight and/or the volume of the device.

The results of most interest to be derived from the HPPC test are the pulse resistance, pulse power capability (for discharge and regen) and energy available as a function of depth of discharge (DOD). The analysis and interpretation of HPPC results is based on the following assumptions.

a. Pulse power capability is calculated using resistance and OCV behavior during the HPPC test.
b. Energy performance is determined from a separate reference discharge, either a 1 kW constant-power test for comparison with FreedomCAR capacitor goals or a 5C constant current discharge for generic testing.
c. The measured DOD values (i.e., as fractions of the Initial Reference Capacity) are assumed to be equivalent for these two tests. This assumption permits the energy measured in (b) to be compared to the pulse capability found in (a).[gg]

[ff] This value is independent of the stand loss measured over the test duration; it is based only on the theoretical energy in the capacitor.

3.2.6.1 Voltage Behavior

Computation of the device pulse power capability requires knowledge of the open circuit voltage (OCV) as a function of depth of discharge. This voltage behavior is determined from the voltage measured at the end of each OCV rest period during the HPPC test itself, i.e., at 11 points from 0% to (nominally) 100% DOD based on the Initial Reference Capacity. A curve can be fitted through these points for use in determining the OCV corresponding to intermediate DOD values, or the corresponding voltages can simply be interpolated between the actual data points.

These voltage results are reported in graphical fashion for information. (Since this curve is a straight line for an ideal capacitor, any deviation from linearity in the data is due either to non-ideal device behavior or to measurement errors.) An example graph of cell voltage versus time during a test is illustrated in Figure 17 for a representative device, and the resulting plot of OCV versus DOD is shown as Figure 18.

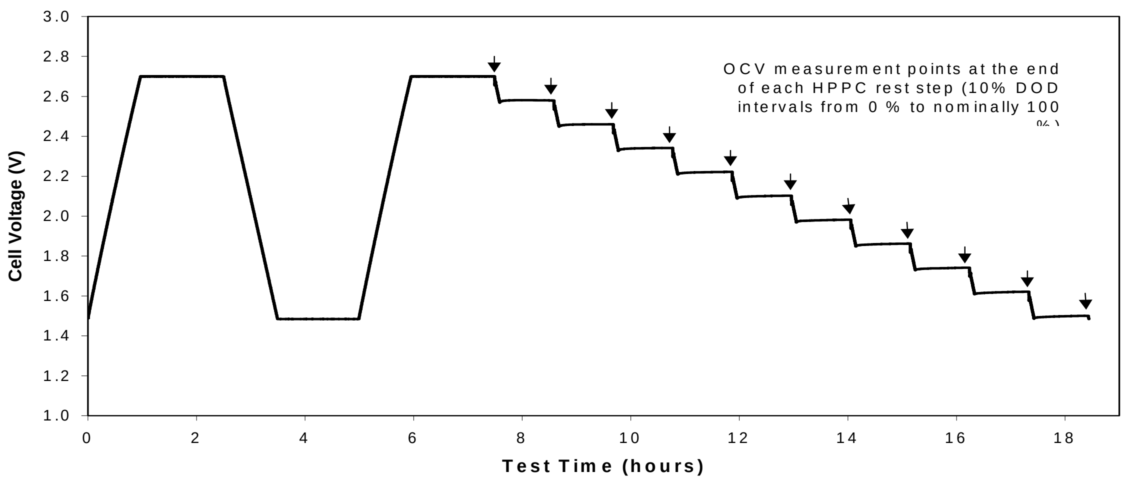

Figure 17. Capacitor Voltage versus Time for an Example HPPC Test

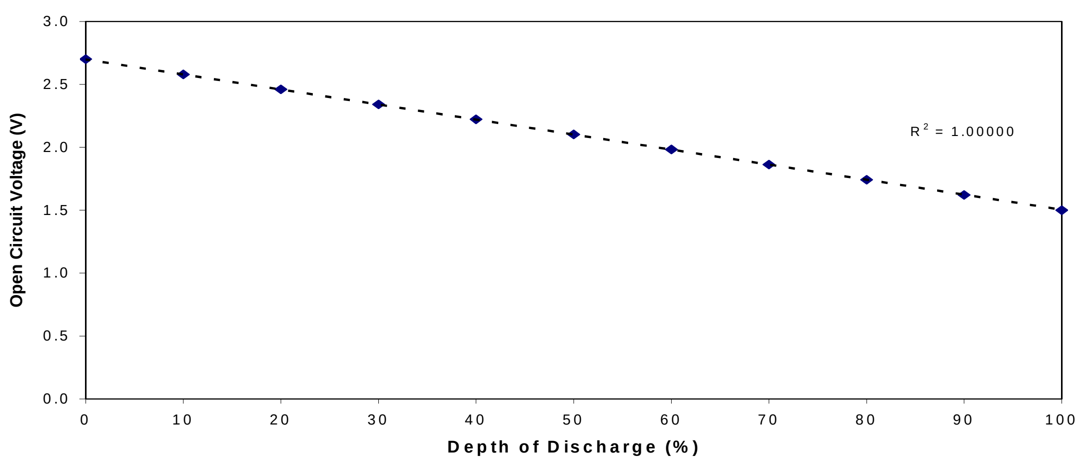

Figure 18. Open Circuit Voltage versus DOD for an Example HPPC Test

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[gg] This assumption is not strictly true due to pulse-related or other rate-dependent losses in a device, but in practice the difference is acceptably small for technologies of interest to FreedomCAR. For those applications for which goals have been defined, this assumption is effectively built into the goals themselves.

3.2.6.2 Energy versus Depth of Discharge

The energy of interest for the HPPC test is actually that measured during the Pre-Test step of the procedure. This is reported versus DOD for use in later calculations of usable energy as a function of pulse power capability. The results can be reported graphically as illustrated in Figure 19 for a representative device, although the actual detailed watt-hour and ampere-hour data are normally used for the calculations. The capacitor whose behavior is illustrated here was a symmetric device with carbon/carbon electrodes and organic electrolyte, rated at 2700 F over an operating voltage range of 2.7 to 1.485 V; the data has been fitted with a cubic polynomial.

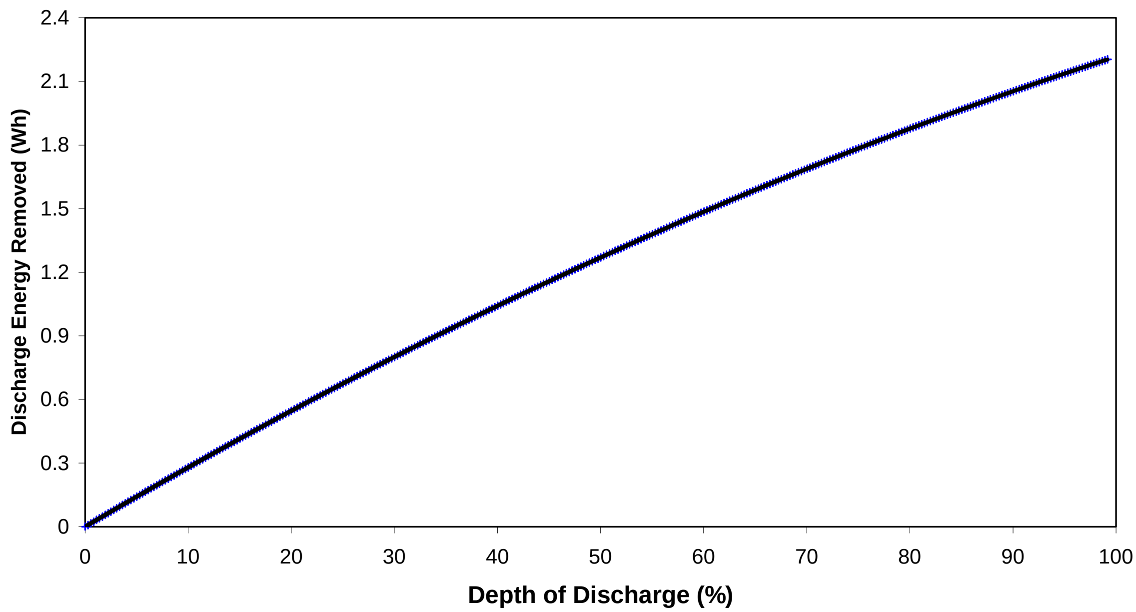

Figure 19. Energy from the Reference Discharge Test for a Representative Capacitor

3.2.6.3 Calculated Resistance Characteristics as a Function of Depth of Discharge

Calculated resistance characteristics as a function of depth of discharge are derived from the pulse profile test data just prior to and at the end of each discharge and regen pulse. There are normally 10 pulses of each type, from 0 to 90% DOD nominal at 10% increments. Each pulse resistance is plotted at the actual % DOD where the pulse begins, which means that DOD values for regen pulses must be determined (interpolated) from the HPPC discharge (Ah) data.

Discharge and regen resistances are determined using an $R = \Delta V/\Delta I$ calculation for each iteration of the test profile, in accordance with Equations 15 and 16. Figure 20 shows the calculation points in the HPPC pulse profile. Resistances are normally only calculated for completely unabated test profile pulses, i.e., those with full duration and amplitude.[hh]

[hh] Because the HPPC test is required to continue to 100% DOD (or until the constant-current or constant-power discharge rate cannot be sustained), some data may be acquired during pulses where current limiting was encountered. While this current-limited data may be useful as an indication of device behavior, it should not be used for direct comparisons to the other data points.

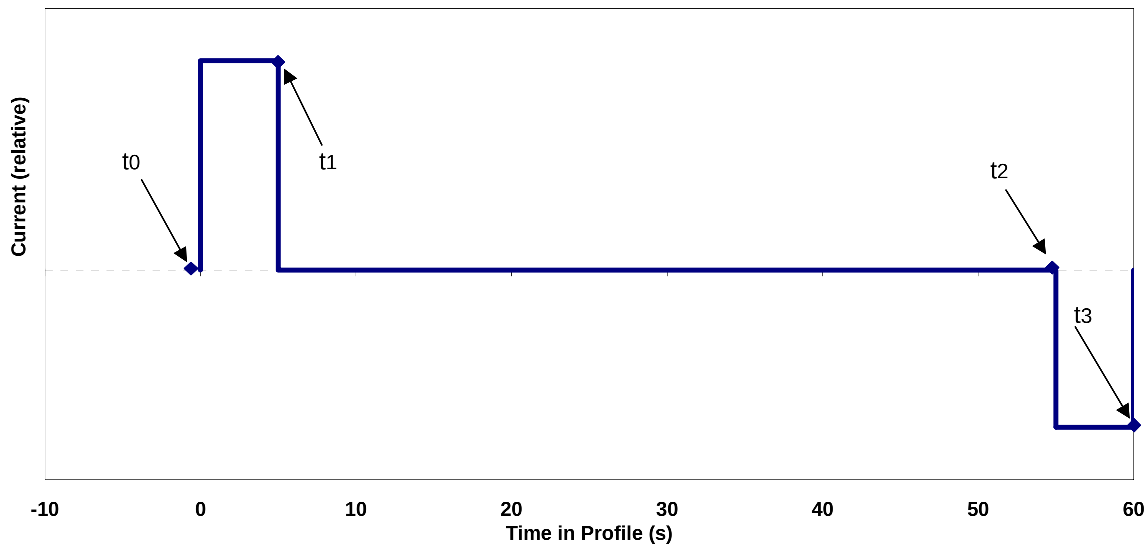

Figure 20. Resistance Calculation Points for HPPC Pulse Profile

$$Discharge\ \ Resistance = \frac{\Delta V_{discharge}}{\Delta I_{discharge}} = \left| \frac{V_{t1} - V_{t0}}{I_{t1} - I_{t0}} \right| \qquad (15)$$

$$Regen\ Resistance = \frac{\Delta V_{regen}}{\Delta I_{regen}} = \left| \frac{V_{t3} - V_{t2}}{I_{t3} - I_{t2}} \right| \qquad (16)$$

where t0, t1, t2 and t3 are the corresponding time points shown in Figure 20. These discharge and regen resistances are plotted as a function of depth of discharge as shown in Figure 21 for the same representative device used for Figure 19.

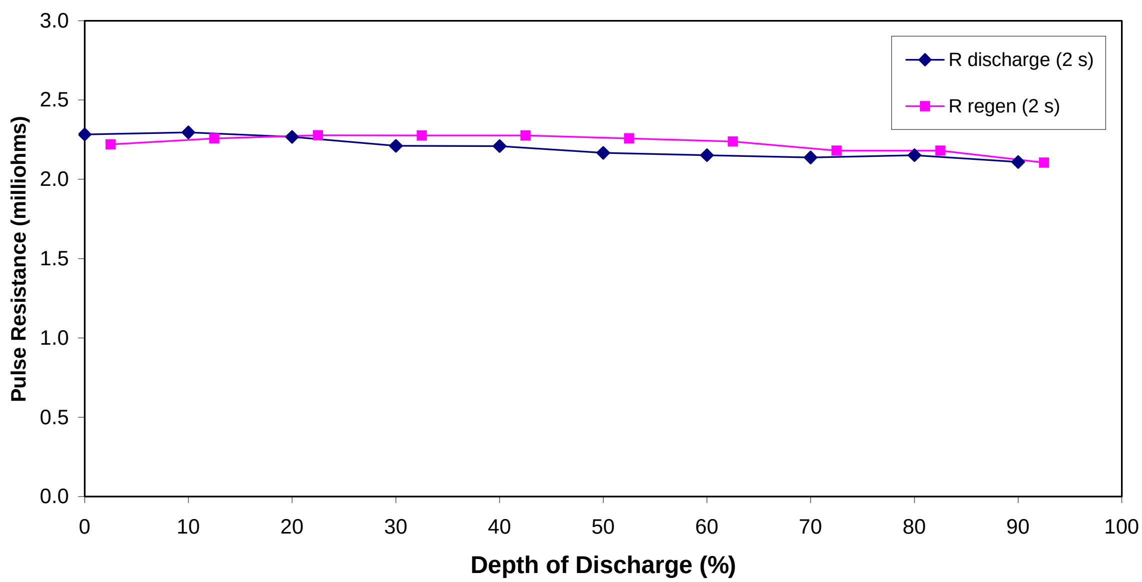

Figure 21. Discharge and Regen Pulse Resistances for an HPPC Test

Note that these pulse resistances are not the same as the ESR calculated in Section 3.2.2.2, even though they are based on the same equations, because the test conditions are different. These resistances are computed based on the full pulse duration (or a defined fraction of it) rather than on an instantaneous voltage response to a step current change.

If pulse resistance and power capability values are desired for pulse durations shorter than the full HPPC pulse values, time points t1 and t3 can be adjusted to the corresponding values after the start of the pulses. For example, a 2 s pulse power capability (typical for the FreedomCAR capacitor requirements in Appendix F) is computed by using the voltage and current values 2 seconds after the start of a pulse. The corresponding measurement points for this example are shown in Figure 22. (The results of Figure 21 are actually calculated on this basis.)

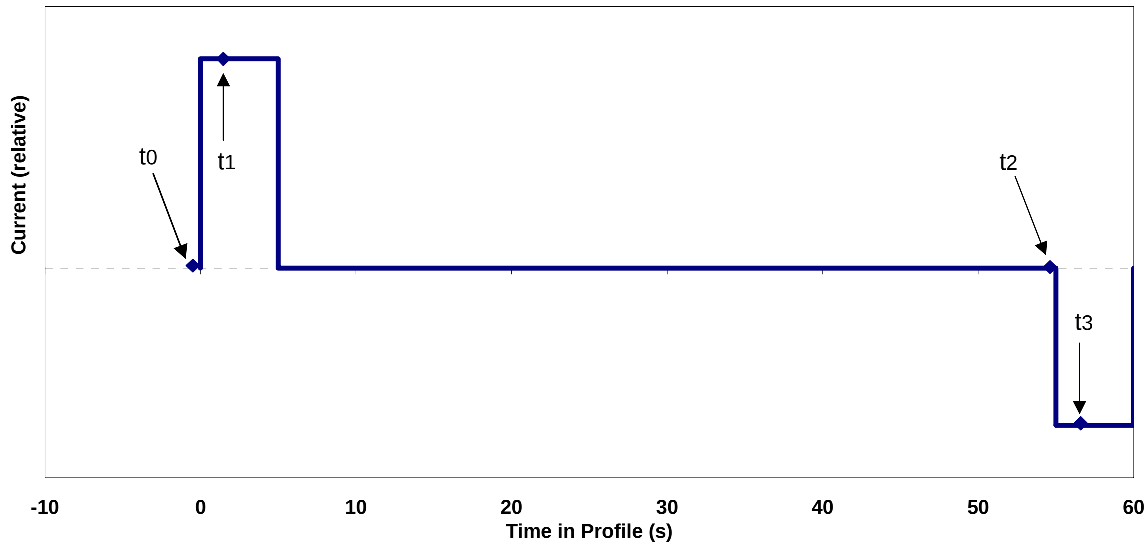

Figure 22. Resistance Calculation Points (2 s Pulse Capability Example)

Also, an alternative measure of discharge ESR can be calculated using the instantaneous change in voltage and current at the end of each discharge pulse. (ESR values, however obtained, are not to be used for the normal pulse power calculations.)[ii]

3.2.6.4 Pulse Power Capability

Pulse power capability is calculated and plotted from the voltage and resistance characteristics, showing the discharge capability above V_{MIN} and the regen capability below V_{MAX} at each DOD tested.[jj]

Discharge and regen pulse power capability is calculated at each available DOD increment from the open-circuit voltage and resistance determined for that DOD using Equations 17 and 18. An example of the resulting graph is shown in Figure 23.

[ii] ESR and pulse resistance are not interchangeable in this manual. ESR is an instantaneous resistance value, whereas pulse resistance represents the apparent resistance over a defined (non-zero) pulse duration.

[jj] For clarity it is assumed here that the maximum allowable pulse voltage is equal to V_{MAX}. For devices where a higher pulse voltage is allowed, this maximum value can be used in place of V_{MAX} for calculating regen pulse power capability. Such a margin is not used for V_{MIN}.

$$\text{Discharge Pulse Power Capability} = \frac{V_{MIN}\left(OCV_{dis} - V_{MIN}\right)}{R_{discharge}} \tag{17}$$

and

$$\text{Regen Pulse Power Capability} = \frac{V_{MAX}\left(V_{MAX} - OCV_{regen}\right)}{R_{regen}} \tag{18}$$

where $R_{discharge}$ and R_{regen} are the discharge and regen pulse resistances computed in the previous section, and OCV_{dis} and OCV_{regen} are the open circuit voltages (measured and interpolated respectively) at the beginning of the discharge and regen pulses.

These power capability values are used to determine the depth of discharge and energy swing that can be used (within the operating voltage range) for specified discharge and regen power levels. Note that profile charge removal has to be accounted for in determining the DOD for regen pulses, so the regen power values are slightly displaced from the even 10 % DOD increments. (Plotted DOD values always represent the beginnings of their respective discharge or regen pulses.)

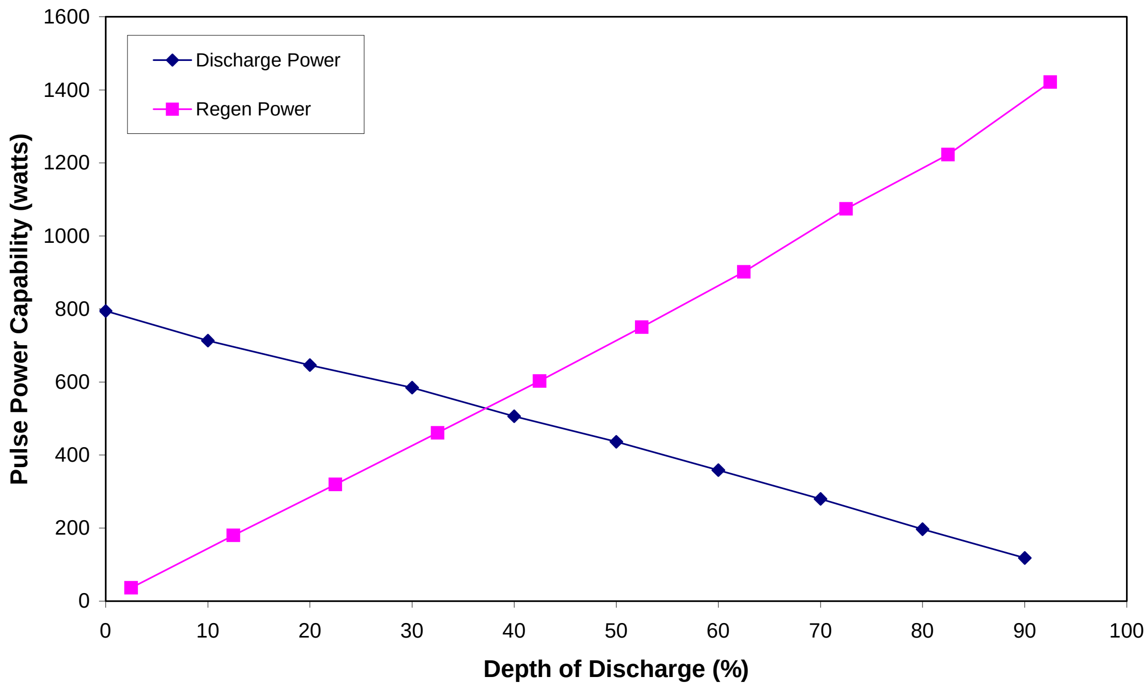

Figure 23. Example Pulse Power Capability Results from an HPPC Test

3.2.6.5 Usable Energy versus Power Capability

The fundamental result of the HPPC test is the relationship between the energy available at the reference discharge rate and the desired pulse power capability. Results are expressed in one or more of the following ways:

(a) actual device power and energy capability of the tested device (in W and Wh),
(b) for FreedomCAR reporting purposes, power and energy scaled by the established Capacitor Size Factor (CSF) (also in W and Wh), or
(c) specific power and energy (i.e., normalized to device weight, in W/kg and Wh/kg) and energy and power density (i.e., normalized to device volume, in W/L and Wh/L).

The ground rules and assumptions given in Table 9 are used for the default analysis and reporting of ultracapacitor HPPC data.

Table 9. HPPC Analysis and Reporting Ground Rules and Assumptions

Testing against FreedomCAR Goals	Generic Characterization Testing
Pulse power capability is computed at the pulse duration specified in the FreedomCAR goals (i.e., 2 s) as described in Section 3.2.6.3.	Pulse power capability is computed at the maximum duration of the HPPC pulses used for testing (i.e., 5 s).
All power and energy values are reported as scaled system-level values (in W and Wh) based on the established CSF for the target application,.	All power and energy values are reported as actual device values (in W and Wh), and also as normalized to the actual weight of the device (reported in units of W/kg and Wh/kg).
Available Energy and Available Power are computed and reported at the scaled system level (in Wh and W). (See Section 3.2.6.6)	There are no single-valued power and energy parameters corresponding to Available Energy and Available Power (because there are no corresponding specific goals for these parameters). Consequently, the final result to be computed is a curve of usable energy as a function of discharge pulse power capability.
The ratio of required discharge to regen pulse power specified in the Appendix F goals table is used for calculating Available Energy and Available Power for the intended application. (See Section 3.2.6.7)	By default, the ratio of discharge and regen pulse powers is assumed to be unity, i.e., equal discharge and regen pulse power values. (If this assumption is known to be untrue for a prospective application, the results are computed by scaling the regen power capability curve by the ratio of discharge pulse power to regen pulse power. See Section 3.2.6.7 for more information.)

Usable Energy is defined (see the Glossary) as the discharge energy available over the maximum DOD range where specific pulse power capabilities are available for discharge and regen pulses.

Determining available energy consists of the following steps:

1. Establish the relationship between HPPC pulse power capability and reference (1 kW or 5C as appropriate) discharge energy as a function of DOD.

2. For various values of pulse power capability within the range of both the discharge and regen capability curves, determine the corresponding minimum and maximum DOD values over which these powers are possible.

3. Calculate the usable energy over the discharge region corresponding to these minimum and maximum DOD values, and plot the result against the corresponding power capability.

HPPC power capability and reference energy values are related by assuming that the corresponding measured DOD values in a pair of such tests are equivalent. With this assumption, Figure 23 can be transformed to a power-versus-energy plot by replacing each DOD value from the HPPC data with the energy value at that DOD from the corresponding reference test. Figure 24 illustrates the resulting HPPC power versus reference energy plot for the cell-level data shown in Figures 19 and 23.[kk]

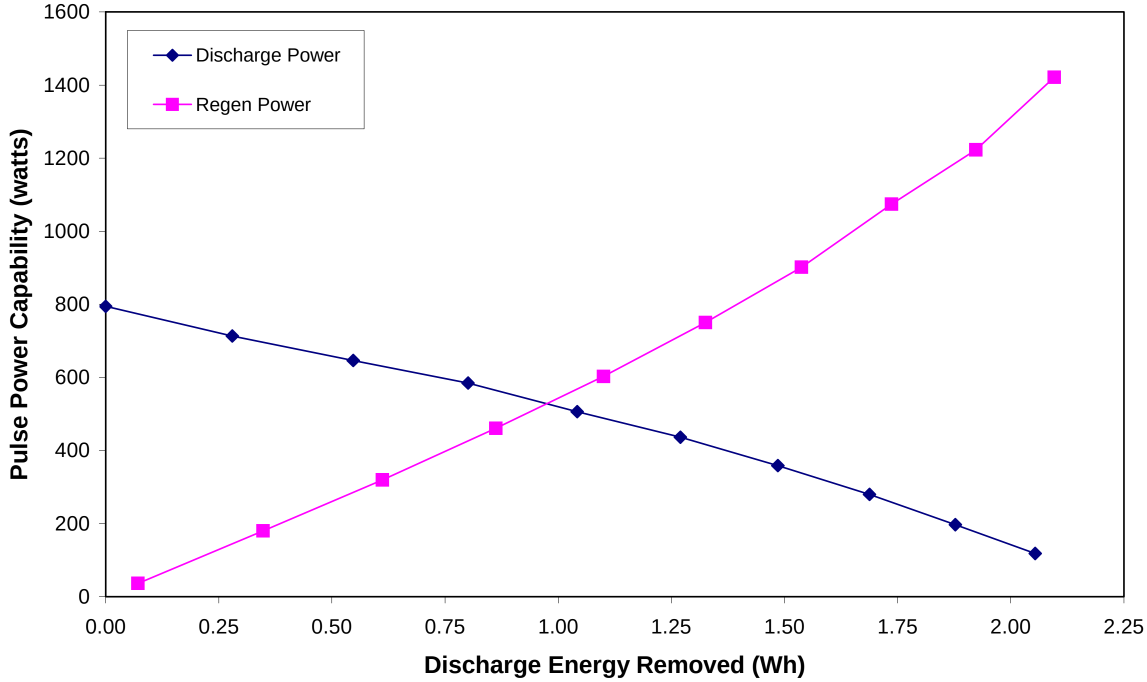

Figure 24. HPPC Power Capability versus Energy Removed for the data presented in Figures 19 and 23 (unscaled).

This power-versus-energy data plot can also be normalized (a) to specific power versus specific energy by dividing all cell-level power and energy values by the weight of the tested device, or (b) to FreedomCAR system power and energy levels by multiplying all cell-level power and energy values by the appropriate Capacitor Size Factor. Any version of the resulting graph can be used to determine the usable energy at any pulse power demand (within the device capabilities) by drawing a horizontal line across the graph at the pulse power value of interest. The part of this line between the two power curves is the usable energy at this power level.

Figure 25 illustrates the result of scaling by weight for the same data used for the previous figures, where it can also be seen that the usable (specific) energy at a pulse power demand of 500 W/kg is 1.09 Wh/kg for this device, which had a weight of 0.724 kg. Note that a similar result can be computed from the unscaled version of Figure 24. The only difference between the results of Figures 24 and 25 is the scaling factor.

CSF scaling is normally used for comparing results to the FreedomCAR capacitor goals. Weight specific scaling is commonly used for comparing the performance of different devices across a range of sizes or technologies. The raw (unscaled) results are more easily usable for

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[kk] In Figure 24 and the following figures, the data markers continue to correspond to data taken at 10% DOD intervals.

application-oriented studies. To avoid confusion, all the graphs in this section of the manual except for Figure 25 present unscaled results based on the raw device performance.

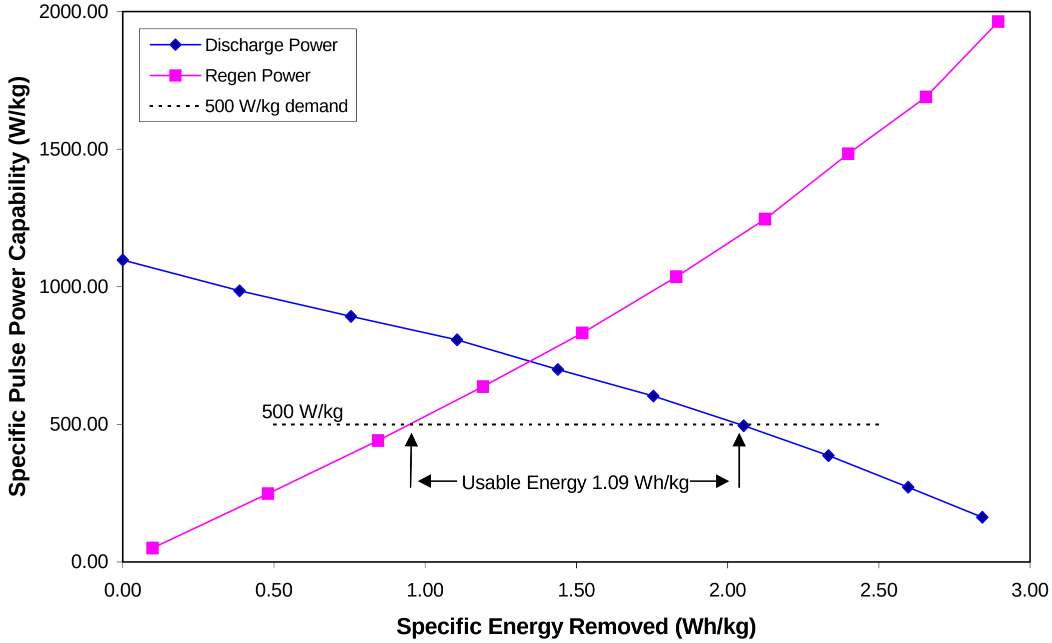

Figure 25. Specific Energy versus Specific Pulse Power Capability for an Example Ultracapacitor, showing Usable Energy at 500 W/kg

These results can be converted to a clearer representation of the energy-versus-power relationship by evaluating Usable Energy over the entire range of possible pulse power capabilities (i.e., the power region below the intersection of the discharge and regen pulse power capability curves) and plotting the result. Such a plot of usable energy is illustrated in Figure 26 for the results of Figure 24.

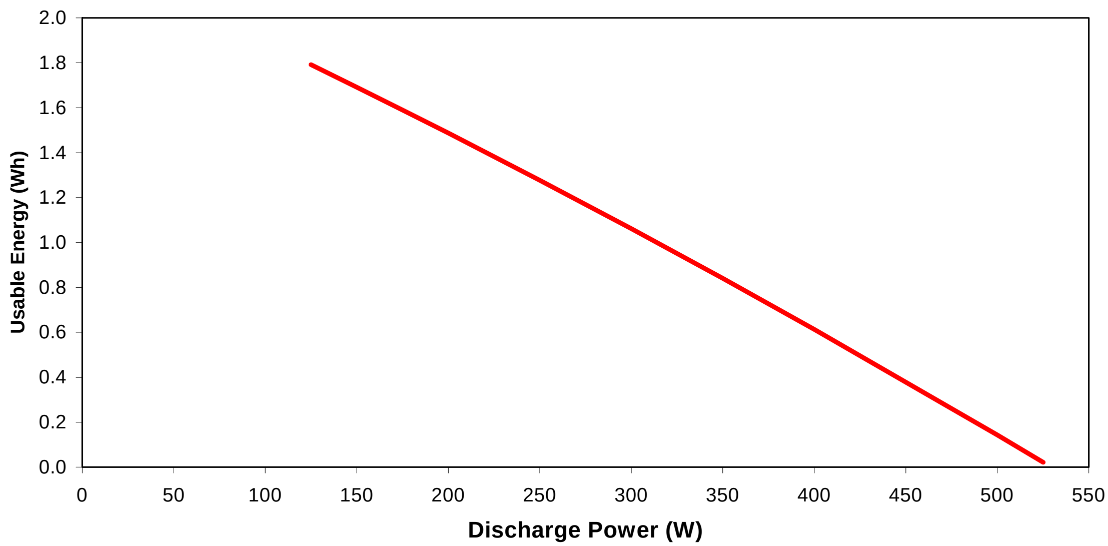

Figure 26. Example Usable Energy versus Discharge Pulse Power Capability for an Example Capacitor (Unscaled)

3.2.6.6 Usable Power and Available Power and Energy

Usable Power can be defined as the discharge pulse power capability for which the usable energy is equal to some specific target value. The determination of Usable Power is illustrated for an arbitrary usable energy value in Figure 27. This example shows that the usable power is 314 W for a target usable energy of 1.0 Wh. Usable Power at a target energy value and Usable Energy at a target pulse power demand represent two complementary aspects in the performance of a capacitor at any point in time; either can be though of as a point on the overall Usable Energy versus Pulse Power curve.

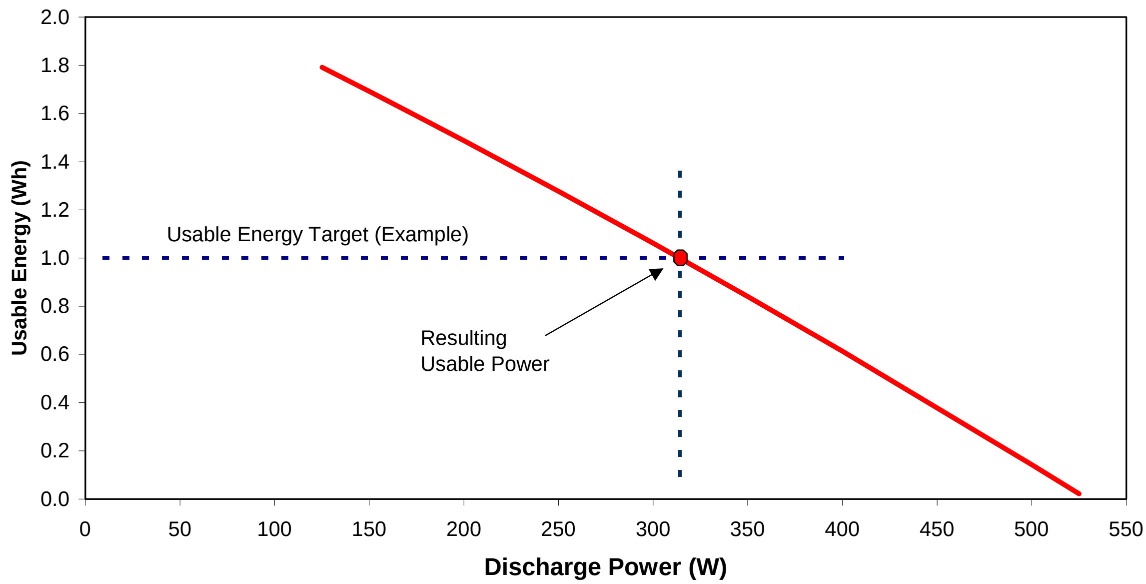

Figure 27. Determination of Usable Power at a Selected Usable Energy Target

This same Usable Energy versus Pulse Power relationship is used to determine Available Energy and Available Power for comparison with FreedomCAR performance goals. (In this context, Available Power is the value of Usable Power corresponding to the FreedomCAR Available Energy goal, and Available Energy is conversely the value of Usable Energy corresponding to the FreedomCAR Pulse Power goal.) The only change necessary in the analysis process is to scale the results by the Capacitor Size Factor and use the appropriate goal power or energy as input. For example, Figure 28 shows this same curve scaled for a CSF of 24 with an Available Energy requirement of 30 Wh as input. The resulting Available Power is 6.15 kW. Conversely, if a pulse power capability of 6.15 kW is required, this same graph shows that the corresponding Available Energy is 30 Wh.

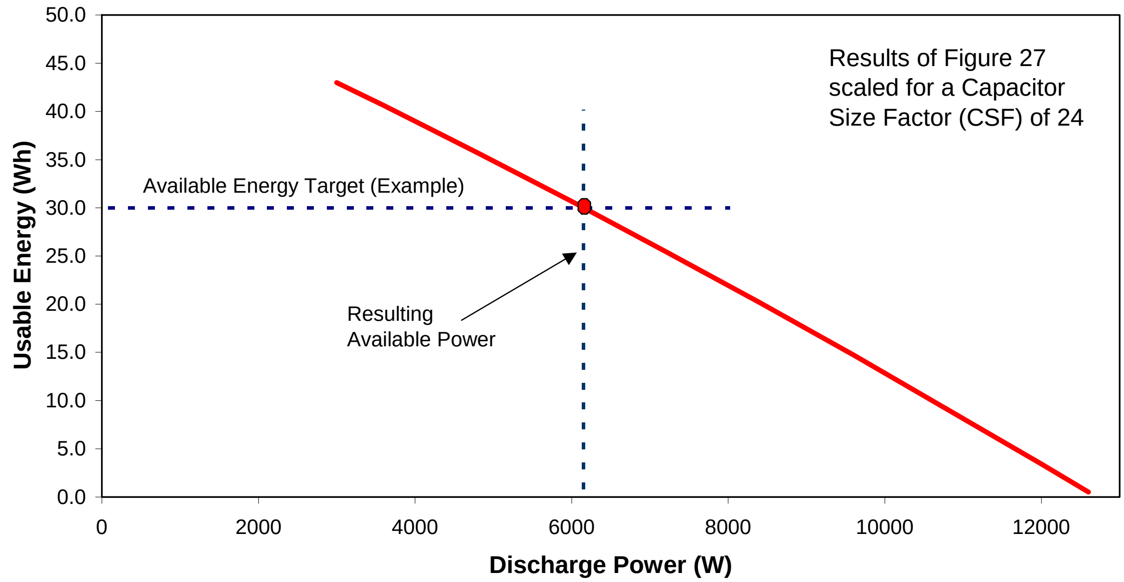

Figure 28. Determining System Available Power for a System Available Energy Goal of 30 Wh with CSF = 24

3.2.6.7 Effect of Non-Equal Discharge and Regen Pulse Power Requirements

The usable energy curve is affected by the ratio of the needed discharge and regen pulse powers. Three cases may be encountered:

a. *Discharge and regen power requirements are equal.* (All the figures in this manual are based on this case.)

b. *Discharge and regen power requirements are different*. (This is typical of FreedomCAR energy storage requirements.) In this case, the recommended analysis approach is to re-scale the regen pulse power versus energy curve (as shown in Figure 24, for example) by the ratio of discharge to regen power. The rescaled values are then used for all further analysis. (See Reference [1] Section 4.3.4 for a more extensive discussion of this.)

c. *There is no regen power requirement.* (This is the case for some of the FreedomCAR capacitor application targets in Appendix F.) In this case, the regen power results need not be computed, and the Usable Energy curve is simply the inverse of the discharge pulse power versus energy curve (i.e., the entire energy region beneath the discharge pulse power curve is available.)

In all three cases, the analysis method is exactly the same once the appropriate pulse power versus energy relationship is determined.

3.2.6.8 Power and Energy Fade

For devices subjected to life testing, the changes in Usable Energy versus Power Capability from the beginning of life values (measured just prior to the start of life testing) to later points in time are to be reported periodically. This can be done graphically, by plotting the original (BOL) Energy versus Power curve and the curve from the most recent HPPC test on the same graph to show the extent of the degradation in energy versus power capability. It can also be evaluated numerically by computing Power Fade or Energy Fade, in either case expressed as a percentage of the original (BOL) value as shown in Equation 19 or 20.

$$Power\ Fade_i\ (\%) = 100 \times \left(1 - \frac{Available\ Power_i}{Available\ Power_{BOL}}\right) \tag{19}$$

where $Available\ Power_{BOL}$ is the usable power for the FreedomCAR goal energy at BOL (i.e., the RPT performed before the start of life testing) and $Available\ Power_{,i}$ is the usable power computed for the *same* Available Energy goal based on the *i*th (presumably most current) RPT data.

$$Energy\ Fade_i\ (\%) = 100 \times \left(1 - \frac{Available\ Energy_i}{Available\ Energy_{BOL}}\right) \tag{20}$$

where $Available\ Energy_{BOL}$ is the usable energy for the FreedomCAR goal power at BOL and $Available\ Energy_i$ is the usable energy computed for the same power goal based on the *i*th RPT data .

For testing not conducted against the application-specific FreedomCAR capacitor goals in Appendix F, it is possible to use any value of energy or pulse power within the capabilities of the device for monitoring power fade or energy fade over life. However, the following guidelines are recommended for choosing a target value.

- If Power Fade is to be the monitored parameter, the reference value of usable energy should be less than one-half of the maximum (energy) value on the energy versus power curve at BOL. Using higher values may result in the inability to determine power fade at this energy value late in life.
- If Energy Fade is to be the monitored parameter, the reference value of usable power should be less than one-half of the maximum value (power) on the energy versus power curve at BOL.

3.2.6.9 Determining Capacitor Size Factor When Not Supplied By Manufacturer

Section 2.2.6.4 discusses the special case where the device manufacturer is unable to supply a Capacitor Size Factor in advance of testing. In this case, the minimum Capacitor Size Factor is calculated directly from the initial Minimum HPPC test results. The method for doing this is effectively an inversion of the available energy calculation process described previously, with steps as follows:[ll]

1. Establish the relationship between HPPC power and reference discharge energy, both as functions of DOD, and plot this relationship as shown in Figure 24.

2. Rescale the regen power by the ratio of the discharge power and regen power goals and re-plot the results as in Figure 24 (without a Capacitor Size Factor applied).

3. Develop the Usable Energy versus discharge pulse power capability using the method described in Section 3.2.6.5 with a result as depicted in Figure 26, again without applying a CSF multiplier to the results. Figure 29 illustrates such a graph along with the results of the following steps.

[ll]. This process is most accurately done using an automated analysis tool. However, it is described graphically here for an understanding of the calculational method, and the graphical result may be accurate enough if done carefully.

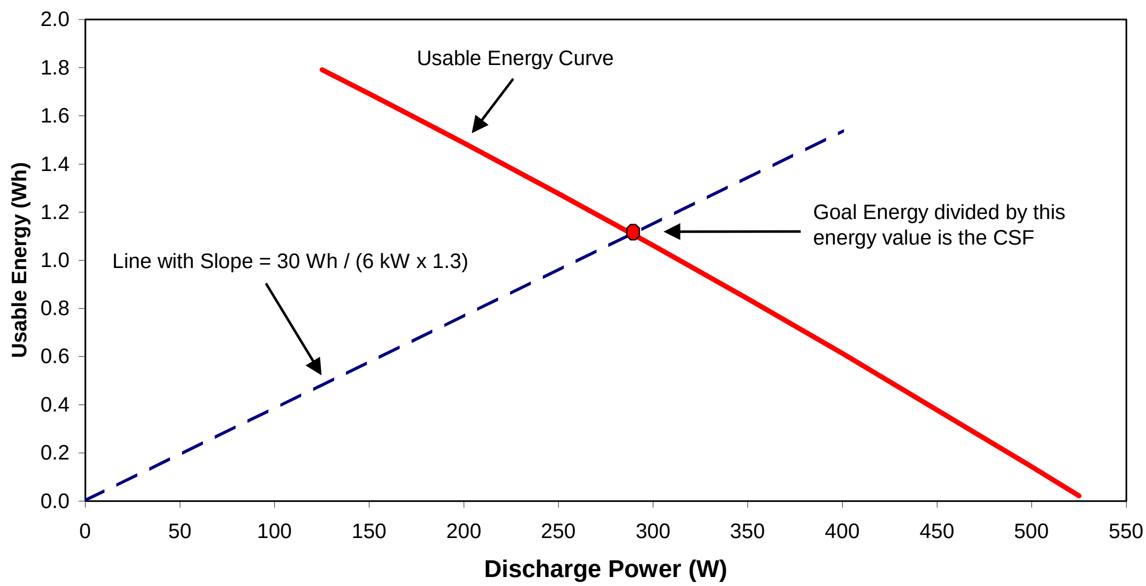

Figure 29. Finding a Capacitor Size Factor Using Device-Level Results.

4. On the Usable Energy graph, draw a line from the origin having a slope equal to the ratio of the energy goal to the discharge power goal with a 30% power margin. For the 42V Start-Stop application goals, for example, this slope would be 30 Wh ÷ [6000 W x 1.3].[mm, nn]

5. Determine the value of energy at the point where this line intersects the Usable Energy curve (about 1.11 Wh for this example).

6. Divide this energy value into the energy goal. The result is the Capacitor Size Factor. For the graph shown in Figure 29 and an energy goal of 30 Wh, the resulting CSF would be about 27 cells.[oo]

7. Verify that this Capacitor Size Factor is expected to give round-trip efficiency values within the FreedomCAR goals at end of life. This can be done by executing the Efficiency Test at a power level scaled at 130% of the normal value (i.e., test power = full system power divided by CSF and multiplied by 1.3.) [pp] However, the efficiency can

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[mm] This 30% BOL power margin is arbitrary but is a typical maximum value allowed for FreedomCAR energy storage applications. It will not necessarily increase the available energy margin at beginning of life by 30%, due to the accompanying increase in power capability of the larger size device. The power-to-energy (P/E) ratios corresponding to exactly meeting the goals are fixed for a given application, but the P/E function for a given device may be highly nonlinear. Thus, the effect of this 30% power margin may be a change of much more or much less than 30% in available energy, depending on where the resulting device powers fall on the P/E curves.

[nn] Note that the curves in Figures 24 through 29 have not actually been adjusted for the 42V Start-Stop discharge-to-regen power ratio; the goal numbers are used here only as an illustration of the CSF determination.

[oo] The CSF is not constrained to be an integer, especially where the value is small. Non-integer CSF values do imply that a different cell size is required for eventual system design, but this will commonly be true for optimizing voltage operating ranges as well. Note that the CSF is not influenced by either device or system voltage; it is a power and energy multiplier.

[pp]. The logic behind this approach is to increase the testing "stress level" (power) by a percentage equal to the BOL power margin, to give results that approximate those expected at end of life when the power margin has declined to zero.

also be estimated using the analytical process described in Reference [1] Appendix D. If the applicable efficiency goal(s) are not met using this scaling factor, the multiplier must be increased appropriately.

8. The Capacitor Size Factor resulting from this process is used for all future testing. (A single typical or average value can be used for testing a group of identical devices.)

3.2.7 Cold Cranking Test

The fundamental result of the Cold Cranking Test is the power capability over the three 2-second discharge pulses in the pulse profile performed at –30 °C. Because the test is conducted at an arbitrary power based on either a FreedomCAR goal or device capacity, the actual power achieved during the test does not necessarily represent the maximum power capability; it merely shows whether the device was able to perform the test at this power. The maximum power capability may be calculated in a manner analogous to the normal pulse power capability as follows:

1. Calculate the discharge pulse resistance values using the voltage and current values at three pairs of time points [(t0, t1), (t2, t3), and (t4, t5), illustrated in Figure 30, using the same ΔV/ΔI calculation used for discharge resistance in Section 3.2.6.3.

2. Calculate the discharge pulse power capability for each of the Cold Cranking Test pulses as in Section 3.2.6.4. The current limitations of the device must be observed in the calculation as well. If comparison to the FreedomCAR goals is intended, the V_{MAX}/V_{MIN} ratio implied by the Cold Cranking requirements of Table F-1 (Appendix F) must be used to determine V_{MIN}. If the manufacturer specifies a more restrictive minimum discharge voltage specifically for cold cranking, this voltage will be used for the calculation in place of the normal value.

3. Report the calculated power values as both unscaled results (W) and CSF-scaled power values (W), or for generic testing, specific power values (W/kg, obtained by dividing each of the three pulse power capability values by the device weight).

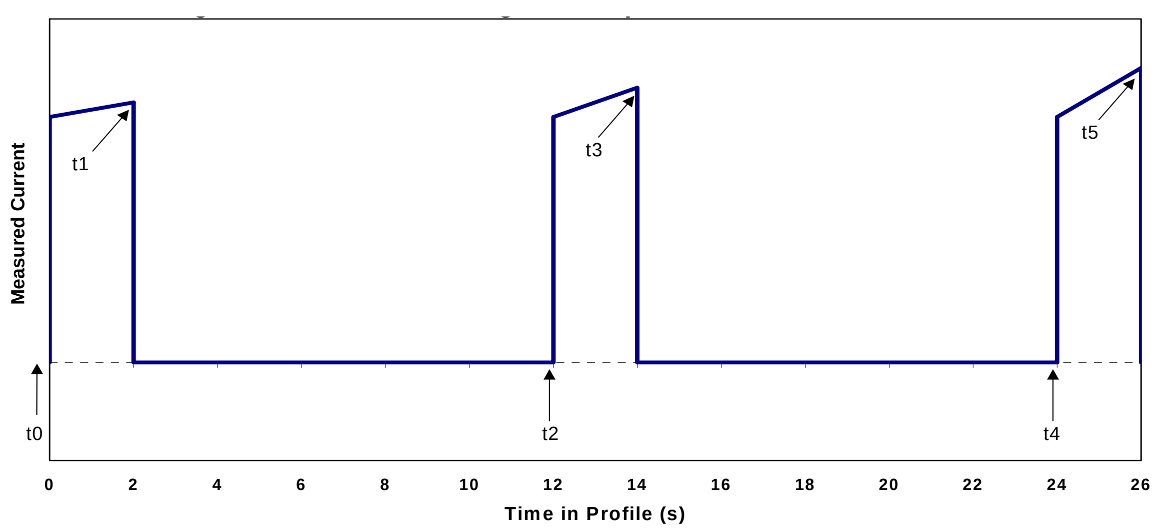

Figure 30. Cold Cranking Resistance Calculation Points

Figure 31 shows the discharge current and the cell voltage during an example Cold Cranking Test on a representative capacitor. (This example test was not performed at V_{MAX}.)

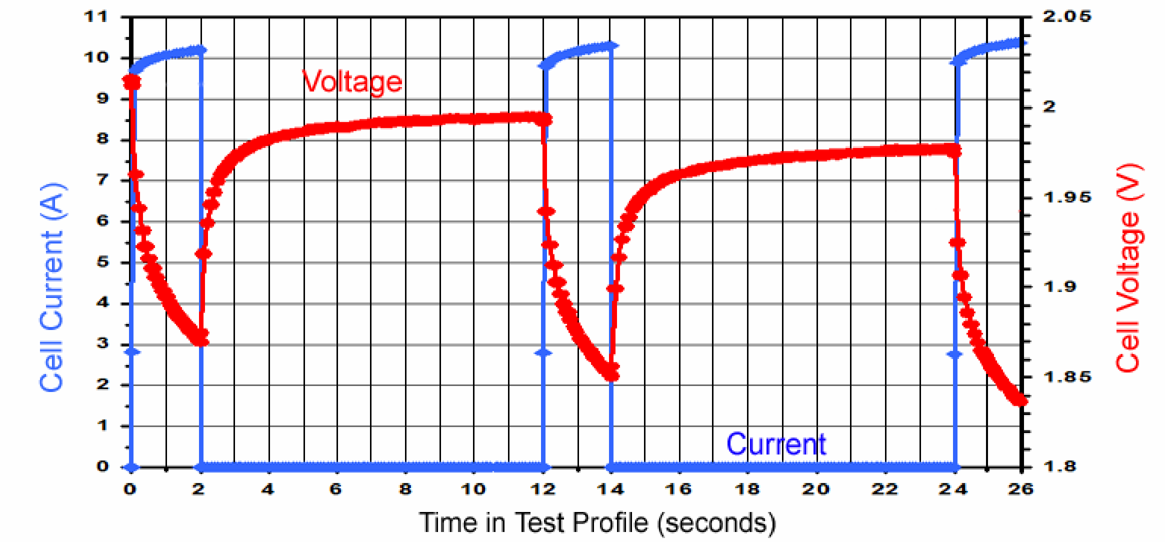

Figure 31. Example Cold Cranking Discharge Current and Voltage

3.2.8 Temperature Performance Tests

For those tests conducted at off-nominal temperatures, the test results are reported exactly as for the corresponding ambient temperature tests, except for the following additional requirements:

- Results should also be compared to the default 30 °C values, preferably by presenting the values for multiple temperatures on the same plot where practical.
- The test temperature(s) used must be clearly noted on all data tables and graphs.

3.2.9 Energy Efficiency Test

Round trip energy efficiency is calculated from an integral number of test profiles of the Efficiency Test. The preferred approach is to use a group of 10 or more consecutive test profiles, both to reduce the impact of small profile-to-profile variations and to minimize numerical round-off effects. The calculation is performed as follows:

1. From an examination of the Efficiency Test data, choose a group of consecutive test profiles where the cell average SOC (as implied by temperature and peak voltage behavior) is stable, normally at the end of the cycling period. The amount of time to reach this condition varies but will commonly be an hour or more after the start of cycling.

2. Calculate both the charge (ampere-hours) and power (watt-hours) for the discharge and regen intervals of these profiles (separately.) Verify that the discharge ampere-hours and the regen ampere-hours are equal (within 1%). If this condition is not satisfied, either: (a) the cycling conditions were not sufficiently stable, or (b) the cell is not 100% coulombically efficient at the cycling conditions. In the first case, the test must be

repeated using additional test profiles. In the second case, if a review of the data indicates that voltage and temperature conditions were stable and the charge measurements are not in error, the results are reported but the charge imbalance must be noted. (See Section 3.2.9.1in this case.)

3. Calculate the round-trip efficiency as the ratio of discharge energy removed to regen energy returned during the profiles, expressed in percent as shown in Equation 21.

$$Round\text{-}trip\ efficiency = \frac{watt-hours\,(discharge)}{watt-hours\,(regen)} \times 100 \tag{21}$$

Round-trip efficiency may also be calculated if desired over a longer period of time (e.g., during life cycling) using any integral number of repeated test profiles for which the state of charge is stable, e.g., an entire block of up to several thousand profiles may be used instead of a small group. (The Energy Efficiency Test and Cycle-Life Test profiles are identical, so Cycle-Life Test data are directly usable for efficiency calculations.)

3.2.9.1 Coulombic Efficiency Calculation

If coulombic losses are a significant contribution to overall energy efficiency (which is typically not the case for capacitors), it may be desirable to quantify and report such losses. This can be done from the Efficiency Test data using the same calculation as above for charge rather than energy.

$$Coulombic\ efficiency = \frac{ampere-hours\,(discharge)}{ampere-hours\,(regen)} \times 100 \tag{22}$$

If the alternative test for coulombic efficiency measurement described in Section 2.2.9.1 is performed, coulombic efficiency can be calculated as follows.

$$Coulombic\ efficiency = \left(1 - \frac{Reference\ Capacity - Residual\ Capacity}{Reference\ Capacity \times No.of\ Cycles}\right) \times 100 \tag{23}$$

3.2.10 Electrochemical Impedance Testing

See Appendix C for more information about such testing. There are no specific requirements for test analysis or reporting of EIS tests defined in this manual, although there are some recommended results described in Appendix E.

3.3 Life Testing

3.3.1 Operating Set Point Stability Test

No results are reported specifically from this test. The current, voltage, and residual capacity data are reviewed to determine that state of charge and other conditions are stable (and at their target values) for continuous cycle life testing, but otherwise this test is treated as part of cycle life testing.

3.3.2 Cycle Life Tests

For the selected life test profile, both the cumulative number of test profiles executed and the cumulative discharge energy throughput up to the most recent Reference Performance Tests are reported, along with any performance changes measured by these Reference Performance Tests. If testing is terminated due to the inability of the cell to perform the programmed test profile within the voltage limits or some other end-of-test condition, this is reported. Detailed results of the reference tests are reported over life as described under these specific tests, including both uncorrected results as well as the corrected values based on the actual RPT temperature. In addition, degradation of reference capacity, reference energy, pulse power capability, usable energy or power, and cold cranking power capability as a function of life (i.e., number of test profiles performed) should be reported graphically.

Note that the total number of cycle-life profiles performed should not be reported as the "cycle life" of the device. For FreedomCAR testing, end-of-life occurs at the point where the device is no longer capable of meeting one or more of the performance goals, and the point where this occurred during life testing will probably have to be interpolated (or extrapolated) from performance data acquired at end-of-test. Furthermore, FreedomCAR cycle life goals are typically based on nominal temperature operation. Results from accelerated life tests should be analyzed using the methods of Reference [3] to determine the projected device life.

3.3.3 Calendar-Life Test

Summary-reported results of this testing include: (a) calendar life in months versus test temperature, (b) capacity versus calendar time and temperature as measured by the periodic reference tests, and (c) cell discharge and regen resistance versus calendar time and temperature as measured by the periodic HPPC tests. The corresponding values of the pulse power capability, usable energy, and cold cranking power capability (all scaled by the CSF or the device weight or volume as appropriate) are also reported versus calendar time and temperature.

FreedomCAR analytical methods for predicting life in service as a function of temperature, state of charge, or other factors are defined in Reference [3]. However, these are primarily aimed at technologies which are approaching a production-ready status. They generally assume that the form of the life degradation function is known for a technology and that only the coefficients of this life model need to be determined from testing. This is unlikely to be the case for ultracapacitors as yet. Consequently the primary goal of ultracapacitor calendar-life testing is to acquire data which can be used to model the life behavior of the devices as a function of various stress factors. The test planning section of Reference [3] should be used for guidance in this area.

3.4 Reference Performance Tests

The standard Reference Performance Tests for ultracapacitors consist of periodic repetitions of the HPPC test, which also includes the 1 kW constant-power or 5C reference capacity test. Reporting requirements for these tests are generally defined in Sections 3.2.1 and 3.2.6, with additional information on the reporting of results over life as noted in Sections 3.3.2 and 3.3.3.

4 REFERENCES

1. *FreedomCAR Battery Test Manual for Power-Assist Hybrid Electric Vehicles*, DOE/ID-11069, October 2003.

2. *Electric Vehicle Capacitor Test Procedures Manual, Revision 0*, J. R. Miller and A. F. Burke, DOE/ID-10491, October 1994.

3. *FreedomCAR Battery Technology Life Verification Test Manual*, INEL/EXT-04-01986, to be published.

Appendix A

Discussion of Various Electrochemical Capacitors

Appendix A

Discussion of Various Electrochemical Capacitors

The energy E that is stored in an ideal capacitor for a voltage range of V_w (the maximum working voltage) to V_{min} (the minimum voltage) is equal to:

$$\mathbf{E = (1/2)C[V_w^2 - V_{min}^2]} \tag{1}$$

In addition, the maximum power that can be delivered by an ideal capacitor is

$$\mathbf{P_{max} = V_w^2/(4R_s)} \tag{2}$$

where R_s is the series resistance (ESR). Both the stored energy and the maximum power increase as the square of the applied voltage. When charged or discharged at a constant current, the voltage of the ideal capacitor rises or falls linearly with time. When charged or discharged at a constant power, the stored energy rises or falls linearly with time. These equations for energy and power and the linear change in voltage for a constant current charge or discharge describe an ideal capacitor. (The ideal capacitor is further discussed in Appendix B.)

Electrochemical capacitors (ECs) exhibit non-ideal characteristics beyond those represented by the circuit model shown in Figure A-1. The non-ideality results primarily from the porous material used to form their electrodes. This causes the resistance and capacitance to be distributed, and creates a multiple-time-constant response. Capacitor non-ideality is discussed in more detail in Appendix C describing electrochemical impedance measurements for capacitors.

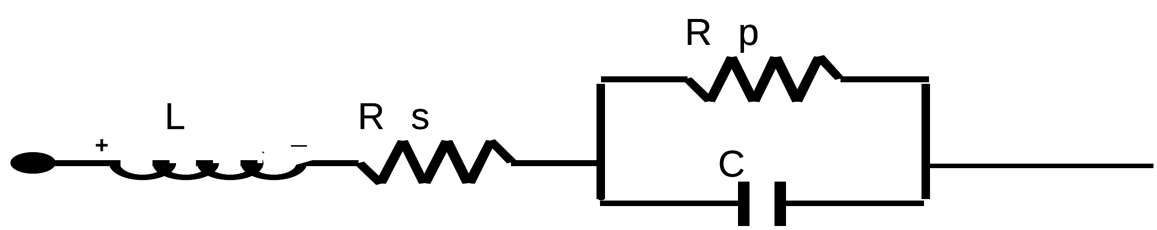

Figure A-1. The first-order circuit model of a capacitor. Each of the four circuit elements is ideal.

In the first type of EC developed, a single capacitor cell was formed from two identical high-surface-area carbon electrodes positioned on opposite faces of a thin micro-porous separator, all wetted with an aqueous solution of sulfuric acid (H_2SO_4). This assembly was sealed within an insulating rubber envelope having thin conductive-rubber face plates held against the rear surface of each carbon electrode. Its voltage rating was approximately one volt. Six or more of these cells were stacked together to form a bipolar capacitor stack that was finally placed in a metal package and crimped closed. This first product design is referred to as a Generation I electrochemical capacitor. Its essential features are: 1) symmetric construction, and 2) an aqueous electrolyte. Symmetric construction means that both electrodes are of the same material and that each has approximately the same mass.

Soon after the Generation I products were introduced, a new electrochemical capacitor product appeared, one having identical carbon electrodes (symmetric construction), but with a non-aqueous electrolyte. This Generation II product allowed higher unit cell operating voltages than possible with the aqueous electrolyte that generally limits the operating voltage to ~1.2 V due to the electrolysis of the water in the electrolyte.

The Generation II capacitor provided a step-increase in energy density over the Generation I products. This arose primarily because of the higher unit cell operating voltage, for instance ~2.5 instead of ~0.9 V, which leads to a theoretical greater than seven-fold increase in energy density due to the quadratic dependence of stored energy on voltage. This energy density increase factor is not fully observed in practice since the specific capacitance of the high-surface-area carbon is usually lower with the organic electrolyte.

It is interesting to examine the operation of Generation I and II capacitor cells during charging, as shown in Figure A-2. With zero applied charge Q, the electrodes of each cell will be at the same potential, and thus have zero volts between them. Their rest potentials, however, will probably be different for a given carbon material due to electrolyte differences. When charged, one of the Generation I electrodes increases in potential while the other decreases by an equal amount, since each has approximately the same capacitance. Moreover, the Generation II electrodes show a similar sort of behavior, except that the magnitudes of the slopes are greater since electrode capacitance is generally lower with the organic electrolyte. Maximum cell operating voltages V_I and V_{II} are reached when one of the electrodes reaches a stability limit, shown by the horizontal lines and established by the electrolyte/electrode system.

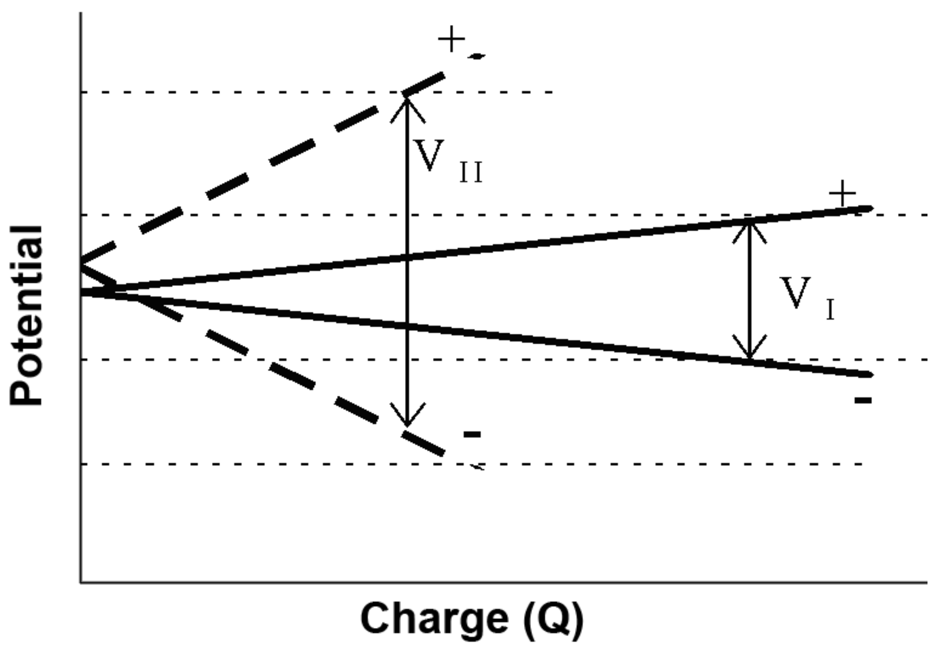

Figure A-2. Electrode potentials for an aqueous symmetric Generation I (solid) and an organic symmetric Generation II (dashed) electrochemical capacitor during application of charge Q.

In 1997, an asymmetric capacitor with aqueous electrolyte was described. This capacitor design is referred to as a Generation III electrochemical capacitor. It is asymmetric because one of its electrodes has ~three- to ~ten-times more capacity than the other. Essential features of the Generation III electrochemical capacitor are 1) asymmetric construction, and 2) an aqueous electrolyte. Both NiOOH positive electrodes and lead oxide positive electrodes have been used in this design with a standard high-surface-area carbon negative electrode in an aqueous potassium hydroxide (with the NiOOH) or sulfuric acid (with the lead oxide) electrolyte. The positive electrode is essentially the same type found in NiCd and NiMH batteries, or in lead acid batteries. The capacity of this electrode is much larger than the negative electrode that limits its depth-of-discharge, which then creates the situation needed for a high-cycle-life capacitor. Further, for a given carbon negative electrode, the device provided two times the capacitance that would be obtained if it were used in a Generation I device. This is explained below.

Referring to Figure A-3, the Generation III device (solid lines) has a voltage, with zero applied charge Q, similar to a discharged battery. With charge applied, the negative electrode potential decreases linearly with charge while the positive electrode remains at essentially the same potential, as expected for a high-capacity battery electrode. Thus, the voltage change of the device for a given amount of applied charge is one-half that obtained for the symmetric design like that shown in Figure A-2. Consequently, the device capacitance of a given carbon electrode is two times larger in the asymmetric design than in the symmetric design. Note that the maximum operating voltage V_{III} is reached during charge when the capacitor electrode reaches its lower stability limit.

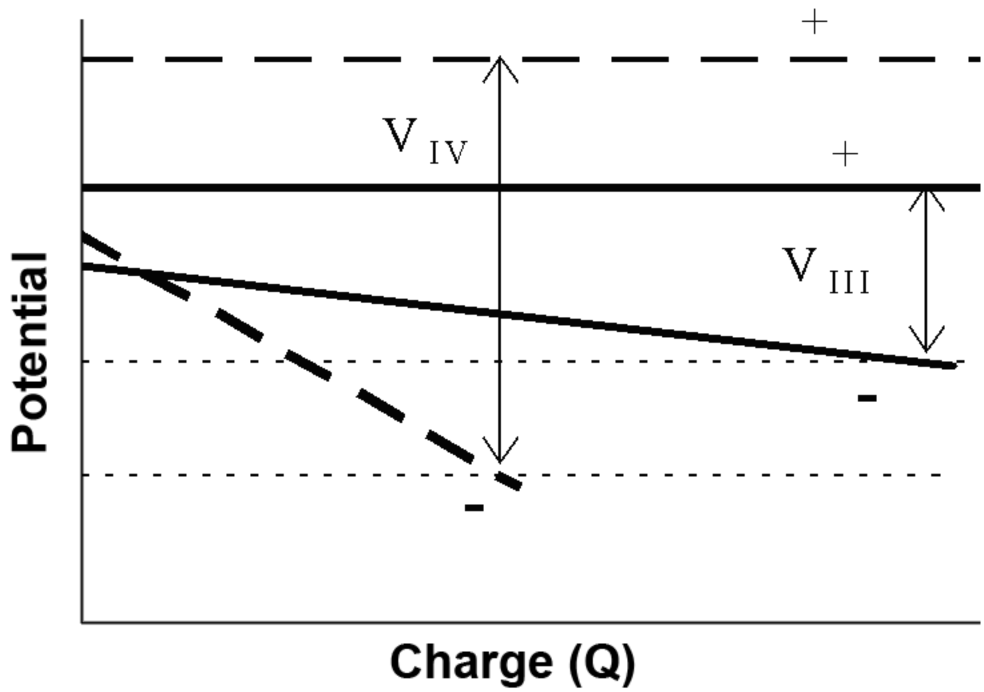

Figure A-3. Electrode potentials for a Generation III (solid) and Generation IV (dashed) electrochemical capacitor during application of charge Q.

Another important advantage of the aqueous electrolyte Generation III capacitor is that it can reliably operate above 1.2 V without gas evolution. For example, commercial cells operate as high as 1.6 V; almost doubling the stored energy compared with the Generation I devices operating below 1.2 V. This over-voltage operating condition is possible because the reaction kinetics for electrolyte decomposition are slow, the same reason that lead-acid batteries can operate at 2.05 V per cell with an aqueous electrolyte.

Another extremely important practical advantage of Generation III capacitor cells is their ability to self-balance in voltage when series connected in strings. Leakage current is characterized by a strong, single, voltage dependent mechanism that gives rise to oxygen-cycle operation like observed in sealed NiCd or valve-regulated lead acid batteries (VRLA batteries operate on the principle of oxygen recombination, using a “starved” or immobilized electrolyte. The oxygen generated at the positive electrode during charge can, in these battery designs, diffuse to the negative electrode, where it can react, in the presence of sulfuric acid, with the freshly formed lead. The VRLA design reduces gas emission by over 95% as the generation of hydrogen is also suppressed.) Thus, higher voltage cells in the capacitor string become pinned in voltage during charging while the others continue to rise in voltage. This self-balancing feature is extremely important for reliability in high-voltage systems, where hundreds of cells are series-connected.

Generation IV capacitors, characterized as asymmetric organic electrolyte capacitors, are only now starting to appear. Referring to the dashed lines in Figure A-2, this design operates exactly like Generation III devices, but with a non-aqueous electrolyte. Thus, the operating voltage can be much higher. One system under investigation is $C/AN/Li_4Ti_5O_{12}$. Here the high-capacity electrode is a lithium intercalation material and the electrolyte solvent is acetonitrile (AN), CH_3CN.

There are fundamental differences between batteries and electrochemical capacitors. Batteries have nearly constant voltage during most of their discharge. ECs exhibit a decrease in voltage during discharge, linear decrease for an ideal capacitor, and the voltage of a capacitor uniquely defines its state of charge (SOC) and state of energy (SOE). Generation III and IV electrochemical capacitors might be called batteries because one of their electrodes is a battery electrode. However, device characteristics are clearly capacitive with a sloping charge and discharge behavior defined by capacitor-like equations. Further, these devices can have a cycle life that is very high. Finally, the power performance of such devices can be quite high. Thus, classifying these components as capacitors is justified and useful.

There is a second fundamental difference between batteries and symmetric ECs. Some aqueous batteries can be subjected to conditions that might lead to over-voltage, but they do not actually rise in voltage. Instead, the high voltage causes the evolution of oxygen gas at the positive electrode of the cell. The gas travels to the negative electrode and recombines to form water. This mechanism is in fact used in recombinant lead-acid batteries as well as in sealed nickel cadmium (NiCd), and sealed nickel metal hydride (NiMH) batteries. In contrast, when gas is generated due to over-voltage in a symmetric electrochemical capacitor there is essentially no means for recombining the generated gas. The over voltage condition, if allowed to persist for long times, generally leads to failure due to loss of electrolyte or mechanical failure (package swelling), each creating an open circuit condition.

Aqueous asymmetric ECs react to over-voltage in much the same way as some aqueous batteries. The high voltage causes evolution of oxygen gas at the positive electrode of the cell with recombination into water at the negative electrode. This operation helps to maintain voltage balance in asymmetric type capacitor cells connected in a series string. When the series string is charged with a controlled current, cells that first reach over-voltage conditions start to evolve oxygen. They do not rise in voltage while the lower-charge cells “catch up.” This sequence continues until all of the cells reach full voltage. Provided the rate of oxygen generation is not too high compared to the rate of gas recombination, there is no loss of electrolyte and the cells in the string are self-leveling in terms of voltage.

Generation III cells can be operated at their rated voltage when series connected, in contrast, Generation I, II, and IV cells generally require voltage de-rating when connected in long series-strings. Alternatively, or perhaps in combination, active or passive voltage balance is used.

MISCELLANEOUS CAPACITOR TERMINOLOGY

Capacitor – a capacitor is an arrangement of two conductors in the same vicinity which are given equal, but opposite amounts of electric charge.

Capacitance - The capacitance, C, of a capacitor is defined as the ratio of the charge, Q, on either conductor to the potential difference V_{ab} between the conductors:

$$C = Q/V_{ab}$$

The unit of capacitance is the farad, which is equal to 1 coulomb/volt.

The capacitance of a parallel plate capacitor located in a vacuum is of plate area A, separated by a distance d is

$$C = Q/Vab = \varepsilon_o(A/d)$$

where ε_o is the permittivity of the vacuum. Since ε_o, A, and d are constants for a given capacitor, the capacitance is a constant independent of the charge on the capacitor, and is directly proportional to the area of the plates and inversely proportional to their separation.

Most capacitors have a (solid or liquid) nonconducting material or dielectric between their plates. In this instance, the capacitance is equal to

$$C = K\varepsilon_o(A/d)$$

where K is the dielectric constant of the material.

Capacitance of capacitors connected in parallel - for capacitors connected in parallel with capacitances C_i, the total capacitance is calculated as

$$C = C_1 + C_2 + C_3 + \ldots + C_i$$

Capacitance of capacitors connected in series - for capacitors connected in series with capacitances C_i, the total capacitance is calculated as

$$1/C = 1/C_1 + 1/C_2 + 1/C_3 + \ldots + 1/C_i$$

Appendix B

Circuit Analysis of an Ideal Capacitor

Appendix B

Circuit Analysis of an Ideal Capacitor

"Capacitance is a measure of the ability of a device, a capacitor, to store energy in the form of separated charge or as an electric field."

A capacitor stores electrical energy in the form of an electric field created by separated charge. The capacitance, C, of a capacitor is defined as the ratio of the charge difference, Q (in units of coulombs, the charge on an electron $1e^- = 1.602 \times 10^{-19}$ coulombs/electron), between two spatially separated conductors to the potential difference, V (in volts), between the conductors as given by the general relation:

$$C = Q/V \qquad (1B)$$

The unit of capacitance is the farad defined as one coulomb per volt. A farad is also defined to be one ampere-second/volt, where an ampere is defined to be 1 coulomb/second.

The type capacitor most suited for the FreedomCar hybrid electric vehicle (HEV) energy storage application is the electrochemical capacitor (EC). ECs have the highest energy density and the lowest cost of any type of capacitor. Energy is stored in a separation of charge called the electric double-layer, which forms when a voltage exists at the interface between an electrolyte and a solid. A previous test capacitor test manual was prepared by Burke and Miller in 1992 [B1]. A very thorough treatment of electrochemical capacitors can be found in Conway's book on the subject [B2].

The circuit schematic shown in Figure 1A represents the first-order model for an electrochemical capacitor. It is comprised of four ideal circuit elements, which include a capacitor C, a series resistor R_s, a parallel resistor R_p, and a series inductor L. R_s is called the equivalent series resistance (ESR) and contributes to energy loss during capacitor charging and discharging. R_p simulates energy loss due to the capacitor's self-discharge. R_p is often referred to as the leakage-current resistance. The inductor, L, results primarily from the physical construction of the capacitor and is usually small. It can be neglected in most applications.

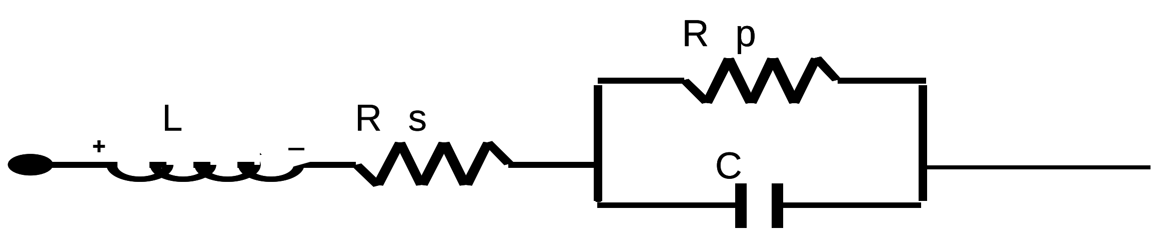

Figure 1A. The first-order circuit model of a capacitor. Each of the four circuit elements is ideal.

For a series RC-circuit (neglecting R_p and L), and for an ideal capacitor that has a constant capacitance, C, which does not depend on the capacitor voltage or charge, the voltage measured across the RC-circuit as a function of time can be expressed as:

$$[V_o \pm IR_s] - V(t) = [Q_o - Q(t)]/C \qquad (2B)$$

where V_o is the initial voltage across the capacitor, Q_o is the initial charge on the capacitor having a capacitance C. The capacitance can also be labeled with the subscript "c" or "d" to distinguish the case where the charging capacitance, C_c, may be different from the discharging capacitance, C_d. Q(t) is the charge on the capacitor at time t (in seconds), I is the current (in amperes) flowing in the circuit and R_s is the series resistance. (Note that the series resistance for the charge and discharge cycles are not necessarily the same, nor are they constants independent of the charge/discharge current or the temperature. This has been observed in experimental studies on capacitors.) The sign in front of IR_s corresponds to a voltage "jump" that occurs at the initiation of charging of the capacitor, a "+" sign, and a voltage "drop", a "-" sign, that occurs at the initiation of the discharging of the capacitor.

During a constant-current charging test, $I = I_c$ = constant is set by the test during charging. $V_o = 0$ (or $= V_{min}$ if the capacitor's minimum voltage is not zero) if the capacitor is totally discharged, or $V_o = V_o$ if the capacitor has been charged to a voltage V_o. R_s will be replaced by R_c to distinguish the charging ESR that may be different from that measured during discharge. For $Q_o = 0$, then $Q(t) = I_c t$, or if Qo = Qo then $Q(t) = Q_o + I_c t$ so that the voltage as a function time during charging, $V_c(t)$ is:

$$\mathbf{V_c(t) = (V_o + I_cR_c) + (I_c/C_c)t} \qquad (3B)$$

From Equation (3B) it can be seen that a plot of the capacitor voltage, $V_c(t)$, versus the test time (t) should be a straight line with an intercept at t = 0 equal to $(V_o + I_cR_c)$. This relation will allow the determination of the equivalent series resistance for charging, R_c, i.e., $R_c = (\text{Intercept}_c - V_o)/I_c$. The slope of the straight line should be positive and equal to (I_c/C_c) that permits the determination of the capacitor's charging capacitance: $C_c = I_c/\text{Slope}_c$. In practice, "real-world" capacitors are observed to deviate from the ideal-capacitor model in that the capacitor voltage as a function of charging time during a constant-current charge is nonlinear. This can be attributed to a voltage (i.e., charge) dependent capacitance. Depending on the voltage dependence of the capacitance, this can cause positive and/or negative deviations from the linear relationship expressed in Equation (3B).

During a constant-current discharge test $V(t = 0) = V_o$, and R_s is redefined to be R_d for discharging. I_d = constant is set by the test, and $I_d t$ corresponds to the amount of charge removed from the capacitor over a time period, t, so that $Q(t) = Q_o - I_d t$ resulting in the expression:

$$\mathbf{V_d(t) = (V_o - I_dR_d) - (I_d/C_d)t} \qquad (4B)$$

As was the case for the constant-current charge test, a plot of the capacitor voltage, $V_d(t)$, as a function of the constant-current discharge test time, t, should result in a straight line with an intercept at t=0 equal to $(V_o - I_dR_d)$ from which the equivalent series resistance for discharging, R_d, can be determined by $R_d = (V_o - \text{Intercept}_d)/I_d$. The slope of the straight line should be negative and equal to $-(I_d/C_d)$. This permits the determination of the capacitor's discharging capacitance buy using $C_d = -I_d/\text{Slope}_d$.

The relationships expressed by Equations (3B) and (4B) permit the determination of whether or not the capacitance is constant or if it depends on the voltage (charge) on the capacitor. Deviations of the charge or discharge voltages as a function of the charge or discharge test time from a straight line relationship would be indicative of a non-constant charge or discharge capacitance. Similarly, Equation (1B) would also enable this determination.

The simple RC-series circuit used to model the capacitor during a constant-current charge cycle shows that the experimentally measured voltage, V_c, across the RC-circuit is:

$$\mathbf{V_c = V_{cap,c} + I_cR_c} \qquad (5B)$$

where $V_{cap,c}$ is the actual voltage across the capacitor during charging. Therefore, the voltage on the capacitor during charging is:

$$\mathbf{V_{cap,c} = V_c - I_cR_c} \qquad (6B)$$

i.e., due to the voltage jump at the start of the charge cycle, the actual voltage across the capacitor is equal to the experimentally measured voltage minus the I_cR_c voltage jump. The charge on the capacitor during charging, Q_c, is equal to $Q_c = Q_o + Q(V_c \text{ or } t)$ where Q_o is the initial charge on the capacitor, and $Q(V_c$ or t) is the charge added to the capacitor as a function of time (or as a function of the measured voltage, V_c) during the charging cycle. Thus, the capacitance as a function of the voltage on the capacitor is:

$$\mathbf{C_c(V_c \text{ or } t) = [Q_o + Q(V_c \text{ or } t)]/[V_c - I_cR_c]} \qquad (7B)$$

It should be noted that if the charging cycle is not started when $Q_o = 0$, i.e., the voltage and charge on the capacitor are not zero, then the total charge on the capacitor, $[Q_o + Q(V_c \text{ or } t)]$, may not be known and the capacitance as a function of the measured voltage cannot accurately be determined. Experimentally, the most accurate determination of the capacitance of the capacitor would be for those measurements where the charge cycle starts at zero volts (or V_{min} for asymmetric devices where the electrodes are different), i.e., no charge on the capacitor, and ends at the specified maximum voltage, V_w, of the capacitor. Similarly, the discharge cycle should begin at the specified maximum voltage, V_w, of the capacitor and end at zero volts (or V_{min}). (It should be noted that for some capacitor designs, particularly the asymmetric electrode devices, this voltage range to zero volts is not possible. In this instance the voltage range used should be explicitly stated, i.e., V_{min} to V_w.)

For the simple RC-series circuit, the experimentally measured voltage, V_d, across the RC-circuit during a constant-current discharge cycle is:

$$\mathbf{V_d = V_{cap,d} - I_dR_d} \qquad (8B)$$

where $V_{cap,d}$ is the actual voltage across the capacitor during discharge. Therefore, the voltage on the capacitor during discharging is:

$$\mathbf{V_{cap,d} = V_d + I_dR_d} \qquad (9B)$$

i.e., due to the voltage drop at the start of the discharge cycle, the actual voltage across the capacitor is equal to the experimentally measured voltage plus the I_dR_d voltage drop. The charge on the capacitor during discharging, Q_d, is equal to $Q_d = Q_o - Q(V_d \text{ or } t)$ where Q_o is the initial charge on the capacitor, and $Q(V_d$ or t) is the charge removed from the capacitor as a function of time (or as a function of the measured voltage, V_d) during the discharge cycle. Thus, the capacitance as a function of the voltage on the capacitor for discharge is:

$$\mathbf{C_d(V_d \text{ or } t) = [Q_o - Q(V_d \text{ or } t)]/[V_d + I_dR_d]} \qquad (10B)$$

It should be noted that the initial charge on the capacitor is that amount of charge added during the charging cycle. In order to accurately determine Q_o, the charge on the capacitor before the start of the discharge should be known and the experimental charging voltage range should be the same as the discharge voltage range.

As mentioned above, the terms ($V_o + I_cR_c$) for constant-current charging and ($V_o - I_dR_d$) for constant-current discharging can be used to calculate the Equivalent Series Resistance (ESR) during charging and discharging of the capacitor. This is known as the IR_{step} method that monitors the voltage on the capacitor immediately after the current to/from the capacitor has been changed. In practice, depending on the test equipment used, the first measurement data point is several to several tens of milliseconds after the start of the constant-current charge or discharge step. This may or may not be accurate enough for the determination of the ESR value as will be discussed later.

Energy and Power Supplied by a Capacitor

For a capacitor having a capacitance C, and charged to an initial voltage, V_o, which is then discharged to a final voltage V_f, the energy E_d, (in joules) extracted is:

$$\mathbf{E_d = (1/2)CV_o^2\ [1 - (V_f/V_o)^2]} \qquad (11B)$$

This equation assumes that the ESR of the capacitor is zero. For example, if the capacitor is discharged to 1/2 of its initial voltage, $V_f = (1/2)V_o$, then the energy withdrawn is 3/4 (i.e., 75%) of the maximum energy available, i.e.,

$$\mathbf{E_d = (3/4)(1/2)CV_o^2} \qquad (12B)$$

(For the case where the minimum voltage, V_{min}, is not zero, then $V_f \geq V_{min}$.) Similarly, the total energy initially stored in the capacitor is, when $V_f = 0$ or V_{min}:

$$\mathbf{E_T = (1/2)CV_o^2[1 - (V_{min}^2/V_o^2)]} \qquad (13B)$$

Equations (11B) to (13B) have not taken into account that the capacitance may not be a constant, but may depend on the voltage (charge) on the capacitor, and also that the voltage (charge) dependence of the capacitance during charging may be different from that during discharging.

If the influence of the equivalent series resistance is taken into account (assuming a series RC-circuit), then upon initiation of a constant-current discharge the actual voltage of the capacitor is reduced by the IR-drop due to the series resistance:

$$\mathbf{V_{o,d} = V_o - I_dR_d} \qquad (14B)$$

where V_o is the initial voltage of the capacitor immediately before the initiation of the constant-current discharge of magnitude I_d ,and the capacitor has a constant-current discharge ESR equal to R_d. The discharge energy expression, Equation (11B), then becomes:

$$\mathbf{E_d = (1/2)C_d(V_o - I_dR_d)^2\ \{1 - [V_f/(V_o - I_dR_d)]^2\}} \qquad (15B)$$

with $V_f \lesssim (V_o - I_dR_d)$. When $V_f = V_{min} \geq 0$ then the total usable energy that can be extracted from the capacitor, E_T, is, from Equation (13B), equal to:

$$\mathbf{E_{T,extractable} = (1/2)C_d(V_o - I_dR_d)^2\{1 - [V_{min}/(V_o - I_dR_d)]^2\}} \qquad (16B)$$

This relation shows the importance of having as low as possible a discharge ESR, R_d, in order to extract the maximum amount of energy that was initially stored in the capacitor. The capacitance has been defined to be the discharge capacitance, C_d, to show that the discharge capacitance may be different from the charge capacitance, C_c.

Power, P [in watts, where 1 watt = (1 ampere)(1 volt) = (1 coulomb/second)(1 joule/coulomb) = 1 joule/second], is defined to be equal to the energy, in joules (1 joule = 3600 watt-hours), which is expended over a time interval Δt (in seconds):

$$\mathbf{P = E/\Delta t} \quad (17B)$$

The discharge power for a constant-current discharge, P_d, can also be expressed as:

$$\mathbf{P_d = I_d\Delta V = I_d(V_{o,d} - V_{min})} \quad (18B)$$

where I_d is the constant-current discharge current, and $(V_{o,d} - V_{min})$ is the initial voltage on the capacitor prior to initiation of the discharge minus the lower voltage limit of the discharge that may be the minimum rated voltage, V_{min}, or to some other voltage $V_f \geq V_{min}$. Equation (14B) is also relevant as the initial voltage of the capacitor is reduced by the I_dR_d loss so that (polarization losses have not been included in this relation as is discussed by Conway [B2]):

$$\mathbf{P_d = I_d\Delta V_o - I_d^2R_d} \quad (19B)$$

This again illustrates that a low discharge ESR of the capacitor is very desirable to maximize the useable power.

Conway [B2] and Miller [B3, B4] have discussed several issues pertaining to the energy and power capabilities of capacitors. Their discussions will be reproduced and expanded upon in the following treatment. Using Equation (19B), the maximum power attainable during a constant-current discharge can be derived by differentiating this equation with respect to I_d, setting the expression equal to zero, and then solving for I_d in terms of V_o and R_d:

$$\mathbf{dP_d/dI_d = 0 = \Delta V_o - 2I_dR_d} \quad (20B)$$

then,

$$\mathbf{I_{d,max} = \Delta V_o/(2R_d) = (V_o - V_{min})/(2R_d)} \quad (21B)$$

Upon substitution of this current into Equation (19B), the maximum useable discharge power for a constant-current discharge, $P_{d,max}$, can be found:

$$\mathbf{P_{d,max} = \Delta V_o^2/(4R_d) = (V_o - V_{min})^2/(4R_d)} \quad (22B)$$

Since from Equation (13B) the total energy initially stored in the capacitor is equal to $(1/2)C_dV_o^2[1 - (V_{min}/V_o)^2]$, it then follows that $V_o^2[1 - (V_{min}/V_o)^2] = (V_o^2 - V_{min}^2) = 2E_T/C_d$. This result leads to the relation that $\Delta V_o^2 = (V_o - V_{min})^2 = (2E_T/C)^2/(Vo + V_{min})^2$. $P_{d,max}$ is then given by:

$$\mathbf{P_{d,max} = [E_T/(2R_dC_d)]^2/(V_o + V_{min})^2} \quad (23B)$$

The maximum discharge energy that can be extracted from the capacitor during a constant-current discharge that corresponds to this maximum discharge power is found by substituting $I_{d\,max}$ [Equation (21B)] for I_d in Equation (16B) [B2]:

$$E_{d\ at\ Pmax} = [C_d(V_o + V_{min})^2/8][1 – (V_{min}/(V_o + V_{min}))^2] \quad (24B)$$

From Equation (13B), $E_{d\ at\ Pmax}$ is equal to $(1/4)E_T$ if $V_{min} = 0$. This energy would correspond to a discharge over a voltage range of V_o to $1/4 = [1 – V_f^2/V_o^2]$, or V_o to $(3/4)^{1/2}V_o = (0.866)V_o$.

Expressions (22B) and (23B) also illustrate the point that in order to have the capacitor provide the maximum amount of power, then the discharge ESR, and the (ESR)(Capacitance) product, i.e., the R_dC_d time-constant of the capacitor (discussed further below), should be as low as possible.

According to Miller [B3], the situation where $P_{d,max}$ is the maximum power that can be delivered to a load resistor, R_L, occurs when this resistance is equal to the discharge ESR of the capacitor, R_d, a so-called “matched load”. With this load, the capacitor’s voltage immediately drops from V_o to $V_o/2$ when the discharge begins. That this is the case can be seen from the usual relation $P = IV = V^2/R$, where if $V = V_o/2$ then $P = V_o^2/(4R)$ which is relation (22B) when $V_{min} = 0$. This result can also be derived by using Equation (19B) and substituting for I_d the current flowing through the series connected load, R_L, and the discharge ESR of the capacitor, R_d, i.e., $I_d = V_o/(R_L + R_d)$:

$$P = V_o^2/(R_L + R_d) - V_o^2R_d/(R_L + R_d)^2 \quad (25B)$$

$$dP/dR_L = 0 = V_o^2[-(R_L + R_d)^{-2} + 2R_d (R_L + R_d)^{-3}] \quad (26B)$$

then,

$$R_L = R_d \quad (27B)$$

This yields Equation (22B) when this result is substituted into Equation (25B), even for the case when $V_{min} \geq 0$.

The concept of an RC time-constant, as discussed above, also enters into situations where a simple series RC-circuit is short-circuited. In this case, a capacitor with a capacitance C that is initially charged to a total charge of Q_o and having an initial voltage V_o is connected across a resistor having a resistance R_s (for example, the equivalent series discharge resistance, R_d, of the capacitor). This situation causes the capacitor to discharge as a function of time. The time dependence of the charge, voltage, and current flowing across the series connected resistor, R_s, are expressed by the relations:

$$Q = Q_o \exp[-t/(R_sC)] \quad (28B)$$

$$V = V_o \exp[-t/(R_sC)] \quad (29B)$$

$$I = I_o \exp[-t/(R_sC)] \quad (30B)$$

where t is the time in seconds for an RC-series circuit with a resistor, R_s, in ohms, and a capacitor of capacitance, C, in farads. The initial current is $I_o = Q_o/(R_sC) = V_o/R_s$. The time duration for Q, V, and I to decrease to half their initial values (i.e., to $Q_o/2$, $V_o/2$ and $I_o/2$) is $R_sC[\ln(2)] = (0.6932)R_sC$ seconds. From Equation (29B), the time it takes for the voltage to decrease to a voltage V_f ($V_o > V_f > 0$) would be $t = RC[\ln(V_o/V_f)]$. Expression (29B) also pertains to the situation where the capacitor can be modeled with a resistor, R_p, in parallel with the capacitor in addition to the series resistor R_s (R_p is generally much greater than R_s). This situation would be relevant for the self-discharge of the capacitor, where even under open-circuit conditions, the capacitor would discharge due to the parallel resistor.

The energy and power weight and volume densities (usually referred to as the specific energy density and the specific power density, respectively) corresponding to the above expressions can be obtained by dividing, respectively, by the weight (in kg), or volume (in liters) of the capacitor.

There is also interest in the efficiency with which a capacitor can be used to supply energy and power to a load. The energy efficiency of a capacitor, Eefficiency, for a constant-current charge of current I_c, followed by a constant-current discharge of current I_d where the capacitor has a charge ESR equal to R_c and a discharge ESR equal to R_d is from Equation (16B) with $V_f \geq V_{min} \geq 0$:

$$\mathbf{Eefficiency = Edischarge/Echarge}$$

$$\mathbf{= \{(1/2)C_d[(V_o - I_dR_d)^2 - V_f^2]\}/\{(1/2)C_c[V_o^2 - V_f^2]\}} \quad (31B)$$

If the charge capacitance, C_c, = discharge capacitance, C_d, = C, $I_d = I_c$, and $R_d = R_c$ then the energy efficiency is given by:

$$\mathbf{Eefficiency = [(V_o - IR)^2 - V_f^2]/(V_o^2 - V_f^2)} \quad (32B)$$

where as before, V_o is the final voltage to which the capacitor is charged. The voltage to which the capacitor is discharged for this case is V_f volts. The initial voltage of the capacitor before the constant-current charge is also assumed to be the same final voltage of the constant-current discharge, i.e., V_f. It should be noted that R_c and R_d are not necessarily equal and are often a function of the constant-current charge and discharge current. With these assumptions, Equation (32B) can be solved for the product of the constant-current charge/discharge current, I, and the constant–current charge/discharge resistance, R, resulting in the relation:

$$\mathbf{IR = Vo \pm [EefficiencyV_o^2 + (1 - Eefficiency)V_{min}^2]^{1/2}} \quad (33B)$$

Substituting this relation for the IR product in Equation (16B) where $V_f \geq V_{min} \geq 0$, then the extractable energy from the capacitor as a function of efficiency is given by:

$$\mathbf{Eextractable = (1/2)CV_o^2[1 - V_f^2/V_o^2](Efficiency)}$$

$$\mathbf{= (Eefficiency)(E_T)} \quad (34B)$$

This equation then implies that the total energy extractable from a capacitor is directly proportional to the efficiency at which it is extracted.

For the case of a <u>constant-power charge</u> followed by a <u>constant-power discharge</u>, the energy efficiency, E'efficiency, would be given by the relation (with $V_f \geq V_{min} \geq 0$):

$$\mathbf{E'efficiency = I_d(V_d - V_f - I_dR_d)/[I_c(V_c - V_f)]} \quad (35B)$$

Assuming that $V_o = V_d = V_c$, $I_d = I_c$, and that $R_d = R_c$, then

$$\mathbf{E'efficiency = (V_o - V_f - IR)/(V_o - V_f)} \quad (36B)$$

Solving this expression for the discharge current, I:

$$\mathbf{I = (1\text{-}E'efficiency)(V_o - V_f)/R} \quad (37B)$$

Substituting this relation into the energy expression, Equation (16B), then the efficiency dependence of the extractable energy during a constant-power charge/discharge cycle, Eextractable constant power, would be:

$$\mathbf{Eextractable\ constant\ power = [(C/2)(V_o - V_f)(E'efficiency)][(2\text{-}\ E'efficiency)V_o + (E'efficiency)V_f]} \quad (38B)$$

If $V_f = V_m = 0$, then the extractable energy from a constant-power charge discharge would be given by:

$$\mathbf{Eextractable\ constant\ power = (CV_o^2/2)[E'efficiency(2\text{-}E'efficiency)]} \quad (39B)$$

Or, in terms of the energy stored in the capacitor for $V_f = V_{min} = 0$:

$$\mathbf{Eextractable\ constant\ power = [E'efficiency(2\text{-}E'efficiency)]E_T} \quad (40B)$$

If the efficiency is zero the extractable energy would be zero as expected. If the efficiency were unity, i.e., 100%, then the extractable energy would be the total energy stored in the device, i.e., $E = (1/2)C(Vo^2 - V_f^2)$. For the power efficiency, using Equation (19B) with the substitution for IR given above, then:

$$\mathbf{Pconstant\text{-}power = I(V_o - V_{min}) - I^2R} \quad (41B)$$

or,

$$\mathbf{Pconstant\text{-}power = (E'efficiency)(1 - E'efficiency)(V_o - V_{min})^2/R} \quad (42B)$$

In this instance, if the efficiency is zero, the power available from the system is zero also. For the particular case of an efficiency of 0.5 (i.e., 50%) then the available power would be:

$$\mathbf{Pconstant\text{-}power = (V_o - V_{min})^2/(4R)} \quad (43B)$$

This result is consistent for the discharge of the capacitor into a matched load as given earlier in Equation (22B).

Equation (42B), can be maximized with respect to E'efficiency to determine the maximum power available, i.e.,

$$\mathbf{[dP/dE'efficiency] = 0 = 1\text{-}2(E'efficiency)} \quad (44B)$$

or,

$$\mathbf{[E'efficiency]_{max} = 0.5} \quad (45B)$$

The maximum power available, therefore, occurs when E'efficiency = 0.5, or 50% efficiency and is equal to:

$$\mathbf{Pconstant\ power\ at\ maximum\ efficiency = (V_o - V_{min})^2/(4R)} \qquad (46B)$$

This discussion of efficiency is important from the point of view of designing commercial systems that use capacitors as energy storage devices. The efficiency enters into discussions dealing with the energy and power supplied to the integrated system in that in order to use the capacitor in an optimum manner, considerations must be made as to how efficiently the capacitor can be used. These considerations can have a major impact on the actual energy and power supplied by the capacitor to the integrated power/energy system.

An additional topic that is of interest regarding the energy and power capabilities of capacitors is the time dependence of the energy stored in the capacitor, and the time dependence of the power produced by the capacitor under various combinations of resistive loads during a constant-current discharge. For the case where the capacitor is modeled using only a series resistor, R_d, to represent the discharge ESR of the capacitor, then from Equations (13B), (18B), (29B), and (30B) the energy stored in the capacitor, $E_{cap}(t)$, and the power produced by the capacitor, $P_{cap}(t)$, as a function of discharge time are given by (the capacitor has been charged to a voltage V_o; thus, $E_T = (1/2)CV_o^2$):

$$\mathbf{E_{cap}(t) = (1/2)CV^2 = [(1/2)CV_o^2]\ exp[-2t/(RC)]}$$

$$\mathbf{= [E_T]\ exp[-2t/(RC)]} \qquad (47B)$$

For Equation (47B), if R and C are given in ohms and farads respectively, then time is in seconds. The time it takes $E_{cap}(t)$ to decrease to 1/2 of its initial value is given by $t_{1/2} = (1/2)RC[\ln(2)] = (0.3466)RC$ seconds. The time it takes for the energy to decrease to $E = (1/2)CV_f^2$, where V_f is the final voltage on the capacitor, is given by $t = RC[\ln(V_o/V_f)]$.

It was shown previously in Equations (41B) to (46B) that when the maximum deliverable power is given by $P_{max} = V_o^2/(4R)$, then the voltage on the capacitor is $V_o/2$ and the current through the series resistor (ESR) shown in Figure 1A, is by Ohm's Law $[Vo/(2R_s)]$. If a series connected load resistance, R_L, is added to the circuit shown in Figure 1A, then the power delivered to the load is given by:

$$\mathbf{P_L = I^2R_L} \qquad (48B)$$

The current flowing in this circuit is given by:

$$\mathbf{I = V/(R_s + R_L)} \qquad (49B)$$

Therefore:

$$\mathbf{P_L = V^2[R_L/(R_s + R_L)^2]} \qquad (50B)$$

Using $V(t) = (V_o)[\exp(-t/RC)]$, Equation (29B), and the fact that the total resistance is $R = R_s + R_L$, then:

$$\mathbf{P_L(t) = V_o^2[R_L/(R_s + R_L)^2][exp(-2t/(C(R_s + R_L)))]} \qquad (51B)$$

Using $P_{max} = V^2/(4R_s)$, Equation (46B), and the substitution of a relative resistance $r = R_L/R_s$, and $\tau = t/(RC)$, then the power delivered to the load is given by the relation:

$$P_L(\tau) = \{4P_{max})[r/(1 + r)^2]\}[\exp(-2\tau/(1 + r))] \qquad (52B)$$

This equation was previously derived by Miller [B2, B4], but his equation has been corrected as given by Equation (52B). If $R_L = R_s$, then the power delivered into the load as a function of time is given by $P_L = Pmax[\exp(-t/(R_sC))] = [V_o^2/(4R_s)][\exp(-t/(R_sC))]$. This is the case for a "matching" load discussed previously. In this case, the voltage across the capacitor would immediately drop from V_o to $V_o/2$ when the discharge was initiated. The delivered energy would then be zero for any voltage limit lower than $V_o/2$ [B3]. It is usually the case, however, that $R_L >> Rs$. In this instance, the power delivered to the load would be:

$$P_L(t) =[V_o^2/R_L][\exp(-2t/(R_LC))] \qquad (53B)$$

If an additional resistor, R_L', is connected in parallel with resistor R_L, then the influence of this additional resistor can be determined by substituting $R_L \equiv [R_LR_L'/(R_L + R_L')^2]$ in Equations (48B) through (53B).

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B2. B. E. Conway, "Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications", Kluwer/Plenum Publishers, (New York, Boston, Dordrecht, Moscow), 1999.

B3. B. E. Conway and J. R. Miller, "Fundamentals and Applications of Electrochemical Capacitors", manual for an Electrochemical Society Short Course, May 4, 1997.

B4. J. R. Miller, "Optimization of Electrochemical Capacitors for High-Power Applications", Proceedings of the 4th International Seminal on Double Layer Capacitors and Similar Energy Storage Devices, December 12-14, 1994, Volume 4.

Appendix C

Electrochemical Impedance Spectroscopy

Appendix C

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS), also known as "ac impedance" or "complex impedance" measurement, is a powerful measurement tool for electrochemical devices. Using small signals, this approach measures device characteristics with minimum perturbation to the system's equilibrium. In effect, the device is "tickled" by a sinusoidal voltage of amplitude V_0 and angular frequency ω, and the current response to this stimulation I(t) is recorded. Figure 1C shows the experimental arrangement for an EIS measurement. Device impedance Z(ω) is calculated as the ratio of the applied signal V(t) to the measured current I(t). It usually is a complex number that changes with frequency, since the current and voltage are not in phase. This relationship is Ohm's law in the limit of zero frequency, i.e. under dc conditions.

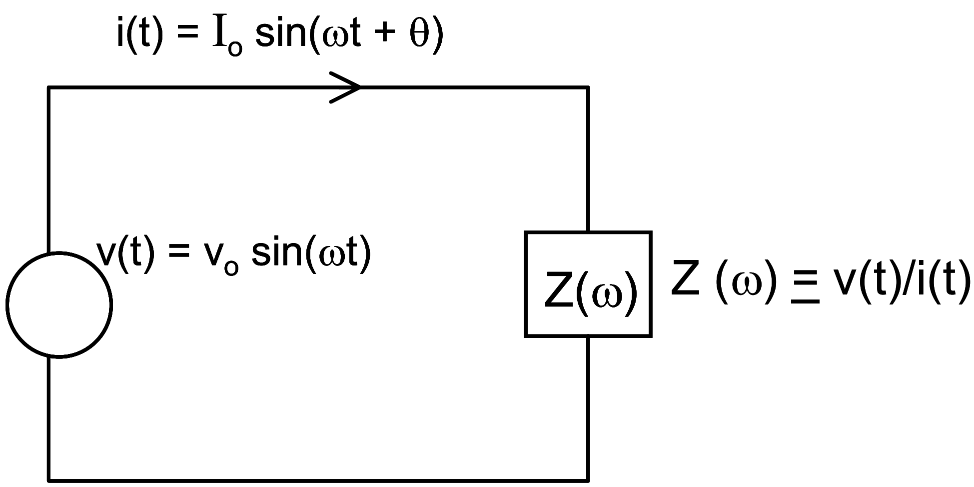


Figure 1C. Experimental setup for EIS measurements.

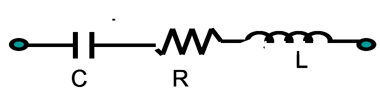
Impedance values for the circuit elements are listed in Table 1C. The resistor has an impedance equal to its resistance value R, the capacitor has an impedance equal to 1/(jωC) where j is equal to $\sqrt{-1}$, and the inductor L has an impedance equal to jωL. Note that a capacitor and an inductor each have 90^o phase shifts, and the resistor no phase shift. (The variable ω can be converted from angular frequency to Hertz by dividing by 2π.)

Table 1C. Impedance values for circuit elements.

Element	Z(ω)
Resistor (R)	R
Capacitor (C)	1/(jωC) where j = $\sqrt{-1}$
Inductor (L)	jωL

A simple equivalent circuit model for any two-terminal device is a series-RLC circuit, shown in Figure 2C. The impedance of this series circuit is the sum of the individual impedances. Thus, the impedance is Z = R + 1/(jωC) + jωL = R + j(ωL – 1/ωC). Note that Z is a real number when ωL – 1/ωC = 0, which is when $\omega = 1/\sqrt{LC}$, which is the self-resonance frequency of the device. At this, and only this frequency, the impedance is equal to the value of the series resistance. At all other frequencies the impedance is complex, which means it must be represented by a pair of numbers, in Cartesian coordinates as a real and an imaginary part (Z’,Z”) or in polar coordinates as a magnitude with a phase angle (|Z|, θ). Both representations are useful.

Series RLC Circuit



$$Z = R + \frac{1}{j\omega C} + j\omega L = R + j(\omega L - \frac{1}{\omega C})$$

$$|Z| = \sqrt{R^2 + (\omega L - \frac{1}{\omega C})^2}$$

$$\Theta = Tan^{-1}\left[\frac{\omega L - \frac{1}{\omega C}}{R}\right]$$

When ωL – (1/ωC) = 0 is the self-resonant frequency ω_o defined by

$$\omega_O = \frac{1}{\sqrt{LC}}$$

Figure 2C. Series RLC circuit model for a two terminal device.

Figure 3C shows the magnitude of the impedance versus frequency (log-log scale) for a series-RLC circuit. At low frequencies, capacitive reactance dominates and gives a straight line with a slope of -1, while at high frequencies inductive reactance dominates and gives a straight line with a slope of +1. The series-resistance R is independent of frequency, and only has strong influence near the self-resonance frequency. The magnitude of the impedance is the square root of the sum of the squares of resistance and the dominant reactance, as graphically shown in the figure.

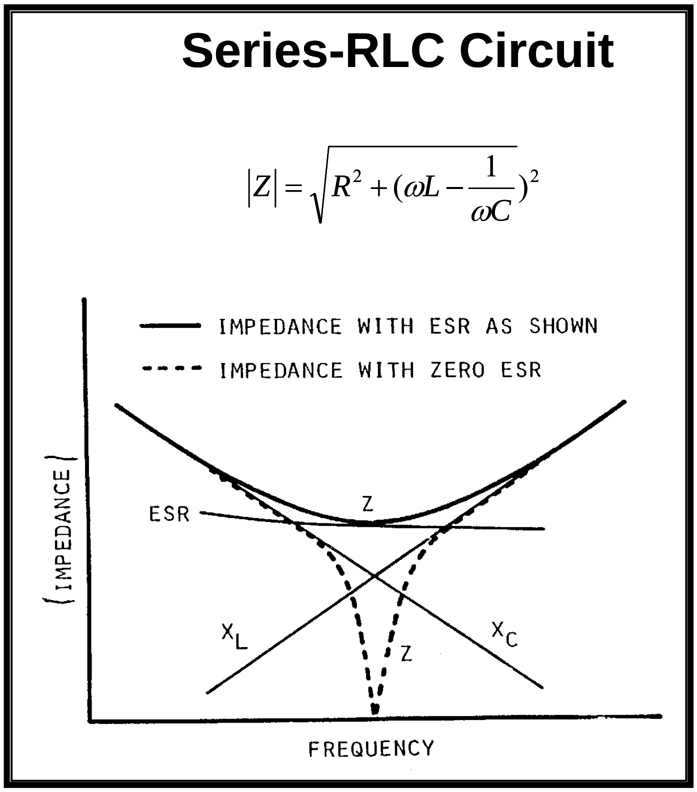


Figure 3C. Magnitude of the impedance as a function of frequency.

Thus, the equivalent series resistance (ESR) of a device is its impedance value at the self-resonance frequency, or equivalently, at the frequency where the phase angle θ = 0. This frequency is generally less than 100 Hz for many of the large electrochemical capacitors being considered for the FreedomCAR application. This low frequency arises because of very large capacitance values, not because of the inductance. For example, a 1000 F capacitor having a 1 microH series-inductance will have a self-resonance frequency at ω = 31.6 radians/s = 5 Hz. Thus, the 1 kHz measurement frequency that is typically specified and used for small electrochemical capacitors is very inappropriate for large devices. Most practical devices, because of their distributed resistance and capacitance, do not show sharp resonance behavior. *Nevertheless, relying on a 1 kHz measurement to determine the ESR can result in a serious error.*

The typical frequency range for EIS measurements is from approximately one decade above the self-resonance frequency down to a frequency at which the device shows clear capacitive behavior, for instance, to a phase angle less than -80^{o}. For capacitors appropriate for FreedomCAR applications, this may be to 10 mHz or less, depending on the technology. It is useful to make five or more measurements within each decade of frequency that is measured. Impedance measurement from 1 mHz to 10 Hz at six points per decade would involve 24 measurement frequencies. Since the SOC of the capacitor may affect its impedance behavior, it is important to make measurements consistently. The suggested measurement is at a 70% SOC.

The frequency response of electrochemical capacitors is very different from other types of capacitors, primarily because of their porous electrodes. This means that a simple series-RLC circuit is not adequate for describing the response of the device. A better equivalent circuit model is a RC ladder network. This multiple-time-constant model comprised of resistors and capacitors emulates the charge stored in the porous network.

Several practical considerations must be kept in mind when making EIS measurements. The first is that the amplitude of the signal must be kept small to not disturb the device equilibrium. Typical amplitudes are 5 mV or less. A second consideration is the need to use a true four lead measurement. Typical ESR values for electrochemical capacitor cells under consideration for this application are in the mΩ range, so lead resistance must be totally eliminated. A third consideration is to use equipment that has adequate current delivery capability. For example, a device with a minimum impedance value of 1 mΩ when measured by equipment with a 5 mV amplitude signal will need to supply 5 A. Some large commercial electrochemical capacitor cells have ESR values of just a fraction of a milliohm, clearly making this issue important.

EIS data should be graphed in a complex plane representation as in Figure 4C, which shows the real part of the impedance versus the negative of the imaginary part of the impedance. Features to note in this representation include the intersection of the data with the real axis (phase angle of zero). This provides the ESR value for the device.

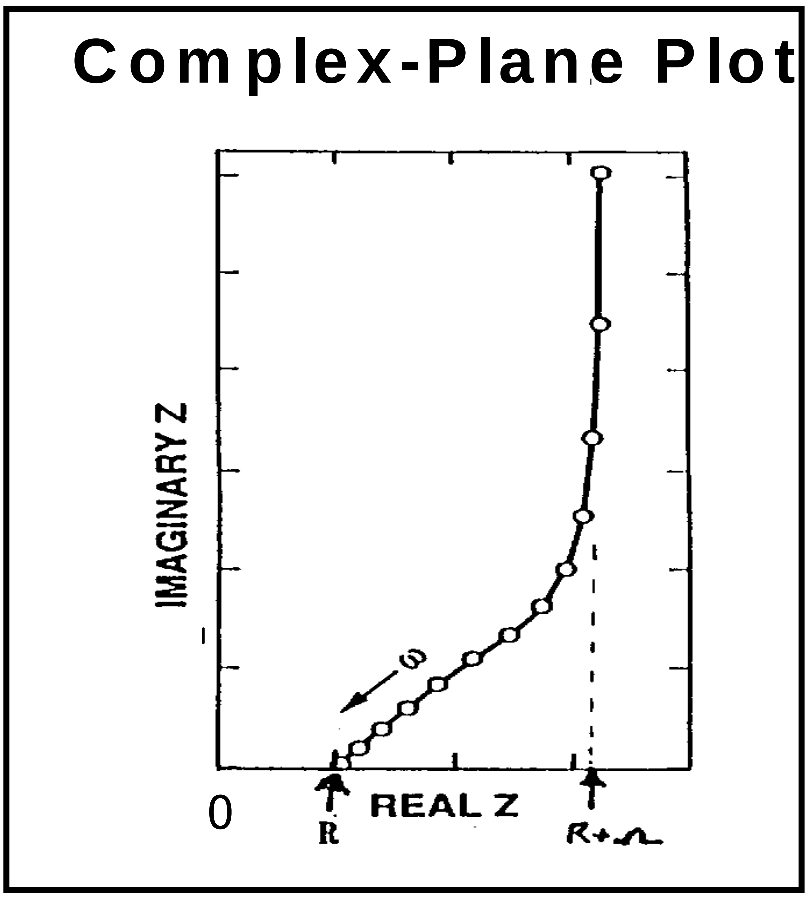


Figure 4C. Graphical representation of EIS data.

The second feature is the ionic resistance Ω. Ionic resistance is an inherent characteristic of a device that uses porous electrodes. It is estimated by extending a straight line from the low-frequency data to the real axis. The intersection point is R+Ω. This is shown as the dashed line. Ionic resistance causes energy dissipation in exactly the same way as does the ESR. Its relative size compared with the ESR value depends on the construction technology, and on the temperature. Generally, the ESR and Ω are comparable in size at room temperature, with the value of Ω increasing faster and in a greater amount at low temperatures than the ESR. Thus, it is useful to examine the relative sizes of these two loss factors for estimating cycle efficiency and its direct impact on thermal management issues.

Appendix D

Generic Test Plan Outline for FreedomCAR Testing

Appendix D

Generic Test Plan Outline for FreedomCAR Testing

Information in italics is generally intended as guidance for the user of this appendix and should be deleted or replaced by appropriate information in an actual device-specific test plan.

1.0 Purpose and Applicability

This section should describe the intent of the testing and the general nature and type of the devices to be tested.

2.0 References

2.1 *FreedomCAR Capacitor Test Manual,* (this document with the proper reference)
2.2 *Other references may be included as appropriate*

3.0 Equipment

3.1 General description of any specific requirements or limitations that the test equipment used for this test plan must satisfy.

3.2 Except where specifically noted otherwise, all testing will be performed within a temperature chamber capable of controlling the chamber temperature to within $\pm 2^{o}C$.

3.3 *Requirements for cooling systems or other ancillary equipment required for proper operation of the specific devices to be tested should be included here.*

4.0 Prerequisites and Pretest Preparation

4.1 A notebook for the devices should be started, and both the manufacturer and laboratory identification numbers should be recorded.

4.2 Actual weights and open-circuit voltages of the cells as delivered should be recorded.

4.3 In addition, an EIS measurement can be made on each device at the "as received" state of charge to verify device condition. This measurement must span the frequency range from above self-resonance to near capacitance saturation, as described in Appendix C.

4.4 Before the start of testing, a test readiness review should be conducted that may include the laboratory manager, the person responsible for writing the test plan, and/or the test engineer.

4.5 *Any other conditions necessary for the start of testing should be described.*

5.0 Ratings, Test Limitations, and Other Test Information

Items in bold print are required for the test laboratory to establish test conditions for certain tests. Those items in Section 5.1 in bold print should be obtained from the device manufacturer whenever possible. Other items (not in bold print) should also be provided by the manufacturer for the protection of the device(s) under test as necessary.

5.1 Ratings of the Device as Supplied by the Manufacturer

Rated maximum working voltage, V_W ______ **(volts)**
Rated capacitance, C_{RATED} ______ **(farads)**
Rated maximum continuous discharge current, I_{MAX} ______ **(amperes)**
Maximum operating temperature, T_{MAX} ______ **(degrees C)**

The following additional ratings or limitations may be provided if applicable to a particular device.

Minimum operating voltage ______ (volts)
[if not zero]
Maximum continuous charge current ______ (amperes)
[if different from I_{MAX}]
Maximum voltage under pulse conditions ______ (volts, 5s or less)
[if greater than V_W]
Minimum Discharge Voltage for Cold Cranking: _______ (volts)
[2 seconds at –30°C]

Other temperature range limitations (if any)
______ -°C to ______ °C charge
______ °C to ______ °C storage
______ °C to ______ °C extended storage

5.2 Nominal Values (Information Only)

Cell Nominal Weight: ___________ kg (analysis use only)

Cell Nominal Volume: __________ liter (analysis use only)

5.3 Operating Voltage Range for this Test Plan

Maximum Operating Voltage, V_{MAX} ______ (volts) [normally same as V_W]
Minimum Operating Voltage, V_{MIN} ______ (volts) [normally $V_{MAX}/2$]

In general all measured performance will be reported over this operating voltage range. *If either V_{MAX} or V_{MIN} is defined as different than the nominal values for this device specific test plan, an explanation and justification must be provided here.*

5.4 Capacitor Size Factor (CSF)

IF SUPPLIED BY MANUFACTURER:
CSF Value to be used for testing ______ (cells or modules)
IF CSF IS TO BE DETERMINED BY TEST:
Beginning of Life Power Margin to be used for calculation ______ (%)

5.5 Life Test Criteria

Nominal DOD value for life testing ______ (%)
Device voltage corresponding to this DOD ______ (volts)

5.6 End-of-Test Criteria for Life Testing

Tthe following default end-of-test criteria should be considered:

1. The test profile (either cycle-life or calendar-life) cannot be executed within the voltage limits, e.g., the 100C cycle-life discharge pulse current cannot be sustained for the defined pulse duration. At this point, the device capability at the target SOC is less than that required by the test profile.
2. Performance degrades to a point where the HPPC reference test yields insufficient information to show further degradation. This would normally be the point where valid discharge and regen data are obtained at less than three DOD values using the HPPC test.
2. A pre-defined number of cycles (e.g. the FreedomCAR cycle life goal) or a predetermined amount of time on test has been reached.
3. As defined by the FreedomCAR program manager.
4. (Calendar-Life testing only.) Acquisition of calendar-life data that is adequate to predict the device calendar life at the test temperature with a 90% confidence level that the true value will be no less than 90% of the mean predicted value. (See the FreedomCAR TLVT manual, reference [3] in this manual, for more information.)

6.0 Safety and Health (requirements may be test laboratory-specific)

6.1 Hazard Identification

The checklist below provides a listing of potential hazards that may be encountered during the normal conduct of the tests. Exclusive of unanticipated upset conditions, but including handling of the capacitors, construction of test setup, and the use of peripheral supporting equipment (e.g., cooling systems), check for any hazards to which personnel may be exposed to, or for any anticipated hazardous activities.

Table 6.1. Checklist of potential hazards to be considered

Check if applicable to planned tests	**Hazard**
	Flammable materials (flash point < 100°F or 38°C)
	Combustible materials (flash point < 200°F or 93°C)
	Handling of corrosives (pH<2 or pH>12)
	Toxic materials (used as a pure substance or >1% in mixture)
	Carcinogenic materials (used as a pure substance or >0.1% in mixture)
	Pyrophoric or reactive materials
	Cryogenic materials
	Compressed gasses
	Rotating equipment (exclusive of hand tools)
	Welding, soldering, brazing

	Irritants or sensitizers
	Dust, mists, aerosols, ashes
	Use of fume hood, elephant trunk, glove box, etc.
	Pressurized system of components (>30 psi)
	High temperature sources or surfaces (>125°F or 52°C)
	Low temperature sources or surfaces (< 32°F or 0°C)
	Exposed electrical contacts (≥ 50 V)
	High currents (>50 mA DC or 10 mA AC)
	Heavy Lifting (>50 lbs)
	Stored energy devices other than test items (batteries, capacitors, springs, hydraulic accumulators, etc.)
	Other hazards. Please specify:

Although not a specific hazard, the following items may present hazards that need to be considered in the execution of the planned testing activities. Check all that apply.

Table 6.2. Other activities of potential concern

Check if applicable to planned tests	**Testing Activity includes:**
	Disposal of hazardous waste
	Working alone
	Unattended operation or testing
	Purchasing, use, or storage of chemicals
	Other activities

6.2 Hazard Mitigation

For each checked item above, describe the nature and magnitude of the hazard, exposure, or activity. If unknown, so state. Describe any extraordinary recommended actions (e.g. safe handling precautions, personal protective equipment required and when it should be worn).

Describe any other recommended precautions that should be taken during the conduct of this testing (such as storage conditions, or other manufacturer recommendations)

6.3 Lessons Learned

Describe or reference any known failures and/or upset conditions experienced with this, or similar, type of capacitor. The cause, consequences, and lessons learned resulting from the failure(s) should be described. All test personnel before commencement of testing activities, must review this reference material.

6.3 Emergency Response

Describe any initial actions or actions in addition to laboratory standard operating procedures that are to be taken in the event of a credible failure of the test item and/or supporting system(s). This should include known failure mechanisms resulting from unintended abuse of the test item.

6.4 Device-Specific Handling Precautions

Describe any precautions specified by the device manufacturer for the particular devices to be tested under this plan.

7.0 Tests to be Performed Under this Test Plan

The devices to be tested under this test plan will be subjected to the characterization test sequence in Table 7.1. Cycle-life and calendar-life testing will be conducted in accordance with the test sequences in Tables 7.2 and 7.3 respectively. Unless otherwise specified, the ambient device temperature for all tests shall be 30 ± 2ºC. Depth of Discharge (DOD) for HPPC tests will be determined by removing a percentage of the Initial Reference Capacity from a fully charged device at a 5C rate. See manual Section 2.1.6 for information on establishing initial states of charge other than full charge. The device will be tested in temperature chambers unless this becomes unfeasible, in which case the responsible program or project engineer should be notified before testing continues.

This section should identify the number of groups of devices, and the number of devices in each group, to be tested under this test plan. *The list of tests in Tables 7.1, 7.2, and 7.3 is intended to be comprehensive; not all tests may be required for any given device. In addition, the specific information in these tables regarding particular tests is illustrative only. If only some devices are to be subjected to a given test, criteria must be provided for choosing the specific devices (either here or in the specific table entries*.) Note that all section references in Tables 7.1, 7.2, and 7.3 (shown in italics) refer to the *FreedomCAR Capacitor Test Manual*, in this test plan.

Table 7.1. Characterization test sequence.

Test Item	Sequence of Characterization Tests for All Cells	Number of Iterations
1	**Reference Capacity Test** *(Section 2.2.1)* This test must be conducted on all devices. The first performance of this test (at the start of testing) is a single-constant 5C discharge based on the rated capacitance, with the rate calculated as defined in Section 2.1.4 of the manual. (Initial 5C rate is calculated at ______ amperes.) All subsequent Reference Capacity tests are conducted using a reference 5C rate based on the actual ampere-hour capacity measured in the first test. All tests are to be conducted between V_{MAX} and V_{MIN} as defined in Section 5.3. * Repeat discharge if necessary until measured capacity is stable within 2% for three successive discharges (maximum 10 discharges without project engineer concurrence)	*
2	**Constant-Current Discharge and Charge Test** *(Section 2.2.2)* *(Specify* as *desired. This test is normally conducted as part of a full device characterization*, generally at –30, +30 and +50 °C.*)*	1
3	**Constant- Power Discharge Test** *(Section 2.2.3)*	1

	(Specify as *desired. This test is normally conducted as part of a full device characterization*. It is commonly performed either in addition to or in place of the Constant-Current test at –30, +30 and +50 °C for thermal performance characterization*.)*	
4	**Leakage Current Test** *(Section 2.2.4)* *Specify as desired. This test is normally conducted as part of a full device characterization. It may also be conducted at +10, +30 and +50 C for thermal performance characterization.)* Conduct this test on all specified devices for a ____-day stand interval with the voltage clamped to ______ volts (normally done at V_{MAX}). Note: If the final measured Reference Capacity is significantly less than the pretest value, contact the Program Engineer before beginning life testing.	1
5	**Self-Discharge Test** *(Section 2.2.5)* *Specify as desired. This test is normally conducted as part of a full device characterization. The test is normally conducted at +10, +30 and +50 C for thermal performance characterization.)* Conduct this test on all specified devices for a ____-day open circuit stand interval (3-day minimum for FreedomCAR testing) at _____ %DOD, corresponding to a voltage of ______ volts (normally done at V_{MAX}). Note: If the final measured Reference Capacity is significantly less than the pretest value, contact the Program Engineer before beginning life testing.	1
6	**Hybrid Pulse Power Characterization Test** *(Section 2.2.6)* This test must be performed on all devices at two current levels. The Minimum HPPC Test is performed at a peak discharge current of ____A (normally 25% of I_{MAX}). The Maximum HPPC Test is performed at a peak discharge current of ____ A (normally 75% of I_{MAX}, which is _____ A, with an allowable upper limit of a 280C rate.) A CSF-scaled Pre-Test discharge power of ______ W (for FreedomCAR testing, corresponding to 1 kW system power) A CSF-scaled Pre-Test recharge power of ______ W (corresponding to system recharge power requirement of ____ W) Pulse Power Capability will be computed for all devices over the operating voltage range of V_{MAX} to V_{MIN} as defined in Section 5.3.	2

7	**Cold Cranking Test** *(Section 2.2.7)* *(Specify as desired. This test is normally conducted as part of a full device characterization.)* Conduct this test on all specified devices at -30°C at a pulse power of ______ W and a DOD value of ______ %, corresponding to a voltage of _____ volts. (Normally done at V_{MAX}.) For this test plan, the cold soak time at -30 °C before pulse testing shall be _____ hours.	1
8	**Thermal Performance Testing** *(Section 2.2.8)* *(Specify any planned thermal performance testing here. A default minimum thermal performance test regime is outlined in Section 2.2.8.)*	As Required
9	**Energy Efficiency Test** *(Section 2.2.9)* *(Specify as desired. This test is normally conducted as part of a full device characterization. If cycle-life testing is to be performed, the efficiency test and the OSPS test are essentially equivalent.)* Perform this test on all specified devices using the Efficiency and Cycle-Life Test profile. *Specify target DOD values here for each device. (Default value is V_{MAX}.)*	
10	**EIS Measurements** *(Section 2.2.10)* *(Specify as desired. EIS measurements will typically be made on devices as part of initial characterization and again at end-of-testing.)* Perform this test on all specified devices at _____ % state of charge (equivalent to open circuit voltage _____ volts). Special considerations for this testing are listed in Section 7.1	As specified

Table 7.2. Cycle-Life test sequence.

<table>
<tr><th>Item</th><th>Sequence of Tests for All Cells to be subjected to Cycle-Life Testing</th><th>No. Iterations</th></tr>
<tr><td>1</td><td> Reference Performance Tests (Section 2.4) Perform the Reference Performance Tests required by FreedomCAR Capacitor Test Manual Table 9 before the start of cycle-life testing. During cycle-life testing, repeat the required Reference Performance Tests at the intervals required by FreedomCAR Capacitor Test Manual Table 9. The 1 kW (or 5C Reference Capacity, for generic testing) Pre-Test discharge data should be included in the same data file with the HPPC results. At completion of cycle-life testing, perform the required Reference Performance Tests as above. Also, repeat any EIS measurements specified in Table 7.1 No. 10 as part of characterization testing. </td><td>As Required</td></tr>
<tr><td>2</td><td> Operating Set Point Stability Test. (Section 2.3.1) Conduct this test on all specified devices at the target DOD given in Section 5.6 of this test plan. List devices and target DOD values here. This test is conducted at the beginning of cycle-life testing using the same test profile(s) and conditions required for cycle-life testing. </td><td>As required</td></tr>
<tr><td>3</td><td> Cycle-Life Testing (Section 2.3.2) For all specified devices, perform the number of test profiles specified in FreedomCAR Capacitor Test Manual Table 9, after which the Reference Performance Tests of No.1 are repeated. Devices and target DOD values are the same as for the OSPS test.. </td><td>Per Table 3.1</td></tr>
</table>

Table 7.3. Calendar-Life Test Sequence

Item	**Sequence of Tests for All Devices to be subjected to Calendar-Life Testing**	No. Iterations
1	**Reference Performance Tests** *(Section 2.4)* Perform the Reference Performance Tests required by *FreedomCAR Capacitor Test Manual Table 9* before the start of calendar-life testing. During calendar-life testing, repeat the required Reference Performance Tests at the intervals required by *FreedomCAR Capacitor Test Manual Table 9.* The 1 kW (or 5C Reference Capacity, for generic testing) Pre-Test discharge data should be included in the same data file with the HPPC results. At completion of calendar-life testing, perform the required Reference Performance Tests as above. Also, repeat any EIS measurements specified in Table 7.1 No. 10 as part of characterization testing.	Periodic
2	**Calendar-Life Tests** *(Section 2.3.3)* *Identify required calendar-life test conditions and associated devices here.*	N/A

7.1 Impedance Spectrum Testing Considerations

The following conditions should be defined and controlled when performing Electrochemical Impedance Spectroscopy (EIS) measurements to assure consistent results. (Suggested default conditions are listed in brackets.)

a. Location of measurements, i.e., in situ or in a special controlled environment such as a Faraday cage. [Except in unusual circumstances, this testing is recommended to be done in situ in the normal test setup.]

b. State-of-charge [70% or as specified in the test plan]

c. Temperature [30°C or specified nominal device operating temperature]

d. Recovery/soak time after SOC and temperature conditions are established [1 hour minimum, 8 hour maximum; highly dependent on design of capacitor device]

e. EIS signal amplitude [<5 mV]

f. EIS frequency range [nominally 0.001 Hz to 100 kHz or to self-resonance frequency (Appendix B).

g. A true four-lead measurement method is needed to minimize error from leads (Appendix B).

8.0 Measurement and Reporting Requirements

8.1 Measurements

For each group of devices subjected to a common test regime at a given temperature, the ambient temperature for this device group should also be measured and included in the data for the first (lowest numbered) device in that group. For data consistency, this should normally be the last recorded variable for that particular device. This ambient temperature measurement is in addition to the measured temperature of the device itself.

Detailed data acquisition and reporting requirements for the characterization and cycle-life tests are as specified for the applicable test procedures in the *FreedomCAR Capacitor Test Manual*.

8.2 Data Recording Intervals

During all pulse profiles for HPPC, Cold Cranking and Efficiency tests, and once-per-day Calendar-Life pulse profiles, data should be acquired at a periodic rate as suggested in the *FreedomCAR Capacitor Test Manual.* Data acquisition rates for all tests are discussed in connection with each procedure in the manual. These data rates may have to be changed depending on the data acquisition rates of the testers to be used.

In general, specified rest periods should be treated as part of the associated test with respect to data acquisition and archiving; voltage and temperature data should be acquired during these periods.

8.3 Data Access (typical for test laboratory)

Describe requirements for data protection or archiving here. Data may or not be required to be treated as CRADA Protected and marked as "Protected Information". *[Applies to government test labs only.]* Access to these data will be restricted to program personnel and to the manufacturer and FreedomCAR representatives listed in Section 11, unless written authorization for other persons is provided by the responsible Program Engineer or Department Manager.

8.4 Data Files (typical for test laboratory)

Individual HPPC tests should be archived as a single data file. It is recommended that this HPPC file should also include the associated 1 kW or 5C Pre-Test portions of the test. This file may or may not include the charge before the start of the test. For Self Discharge (Stand) Tests, the initial partial discharge, and stand period should be included in a single data file where possible. Cycle-life test data should generally be separated into no more than three data files for each testing interval: the initial profiles required to be recorded, the final profiles required to be recorded, and all other data acquired between these two groups of profiles. At the completion of testing, the characterization and RPT results should be transcribed to a compact disk or other storage medium and sent to the FreedomCAR Technical Contact as well as other specified groups.

Anticipated Results

Briefly, summarize general or specific results that are desired or expected from testing.

8.2 Testing Deliverables

Describe required periodic or final reporting along with any data deliverables due to FreedomCAR technical team or program management.

9.0 Post-Test Examination and Analysis

Describe any required post-test examination or analysis here.

10.0 Contact Persons *(typical for government test labs only)*

Laboratory Program Manager:
Name:____________________________
Phone:____________________________
Fax:______________________________
Email:____________________________

Laboratory Program Engineer:
Name:____________________________
Phone:____________________________
Fax:______________________________
Email:____________________________

Laboratory Project Engineer:
Name:____________________________
Phone:____________________________
Fax:______________________________
Email:____________________________

Manufacturer Technical Contact:
Name:____________________________
Phone:____________________________
Fax:______________________________
Email:____________________________

USABC/FreedomCar Program Manager:
Name:____________________________
Phone:____________________________
Fax:______________________________
Email:____________________________

DOE/FreedomCAR Test Manager:
Name:____________________________
Phone:____________________________
Fax:______________________________
Email:____________________________

DOE Program Manager
Name:____________________________
Phone:____________________________
Fax:______________________________
Email:____________________________

Appendix E

Minimum Test Reporting for FreedomCAR Testing

Appendix E

Minimum Test Reporting for FreedomCAR Testing

The following information should be reported for each capacitor tested, for each of the following tests when conducted. (This list does not imply that all tests listed will or should be performed.) Test conditions are tabulated first, followed by test results.

General

Manufacturer Serial Number _______________
Test Lab Reference Number _______________
Device Weight _______________ (kg)
Device Dimensions_______________ (cm)
Device Volume _______________ (liter)
Device Electrode Area (if known) _______________ (cm^2)

Rated Capacitance, C_{RATED} _______________ (F)
Rated Maximum Working Voltage, V_W _______________ (V)
Maximum Discharge Current, I_{MAX} _______________ (A)
Maximum Operating Temperature, T_{MAX} ____________ (degrees C)

Minimum Operating Voltage ______________ (V, if not equal to zero)
Maximum continuous charge current ____________ (A, if different from I_{MAX})
Maximum voltage under pulse conditions ___________(V, 5s or less, if greater than V_W)

Cold Cranking Discharge Voltage Limit (for 2 s at -30°C) ____________ (V, if specified)
Minimum Pulse Discharge Voltage for 5 Seconds _____________ (V, if specified)
Maximum Pulse Regen Voltage for 5 Seconds _____________ (V, if specified)
Equivalent Series Resistance ___________ (ohms, if specified)

Manufacturer-Specified Recharge or Discharge Algorithm (describe if provided; otherwise a 5C constant current charge to V_{MAX} followed by a clamp voltage interval is assumed)

Reference Capacity (5C) Test (at 30°C nominal)

Measured Capacity _______________ (Ah)
Delivered Energy _______________ (Wh)
(Both from V_{MAX} to V_{MIN})
Discharge/Recharge Efficiency _______________ (%, coulometric)
_______________ (%, energy)
(Using manufacturer-specified recharge algorithm if provided)

Energy versus %DOD (Wh vs. %DOD) *(plot)*

Constant-Current Discharge and Charge Test

(All reported values are from V_{MAX} to V_{MIN})
Discharge and charge capacity (Ah) removed and returned for each cycle at each test current *(tabulation)*

Effective discharge and charge capacitance (farads), discharge and charge ESR (ohms) and energy efficiency (%) at each test current rate *(tabulation)*
Capacitor voltage versus charge removed (Ah and % DOD) at each test current *(plot)*
Capacitor voltage versus energy removed (Wh) at each test current *(plot)*

Constant-Power Discharge Test

Capacitor voltage versus energy removed at each test power *(plot)*
Specific energy (Wh/kg) versus specific power (W/kg) *(Ragone plot)*
Energy efficiency versus test discharge power *(plot)*

If the alternative Constant-Power Discharge Test is conducted, the reporting requirements are the same except that performance is reported in terms of charge power and energy rather than discharge.

Leakage Current Test

Clamp voltage used for test ________ (V)
Test temperature _________ (°C)
Leakage current versus test time *(plot)*
Calculated leakage resistance versus test time *(plot)*
Integrated leakage energy (Wh) versus test time *(plot)*

Self-Discharge Test

Stand % DOD _______________ (%)
Corresponding voltage for stand __________ (V)
Stand Time _______________ (days or hours) (minimum 72 hours for FreedomCAR)
Stand Temperature(s) _______________ (°C)
Total Energy Loss _______________ (Wh)
Stand Loss _______________ (% over 72 hours, or stand time if longer)
Voltage versus test time *(plot)*
Self-Discharge Energy Loss Factor (%) versus time (plot)

Hybrid Pulse Power Characterization Test (at 30°C nominal)

Peak Discharge Test Current (Low) _______________ (A)
Peak Discharge Test Current (High) _______________ (A)
Minimum FreedomCAR Discharge Voltage Used for Calculations _______________ (V_{MIN})
Maximum FreedomCAR Regen Voltage Used for Calculations _________________ (V_{MAX})
Minimum Voltage used for test conduct (if different from V_{MIN}) _______________ (V)
Pulse durations used for power calculations:
Discharge _______ (s)
Regen _______ (s)

Open-Circuit Voltage versus % DOD *(plot)*
Discharge and Regen Resistance versus % DOD *(plot)*

Pulse Power Capability (discharge and regen) versus % DOD and energy removed *(plots)*
Usable Energy versus Discharge Pulse Power *(plot)**

- These results should be presented in units of cell performance (Wh, W). For FreedomCAR testing, they should also be presented in CSF-scaled values (Wh, W at system level). For generic testing, they may also be presented in terms of specific energy and specific power (Wh/kg, W/kg) or energy and power density (Wh/L, W/L)

FreedomCAR Testing Only:
Capacitor Size Factor (CSF) ____________ (cells or modules)
CSF Basis _______Manufacturer-Supplied ______ calculated by test
CSF-Scaled Available Energy ________ (Wh) at goal power of ______ (W)
CSF-Scaled Available Power ________ (W) at goal energy of ______ (Wh)
Power Margin at goal energy ______ (%)
Actual Pre-Test Discharge Power (derived from CSF) ______ (W)
Actual Pre-Test Recharge Power (derived from CSF) ______ (W)

Cold Cranking Test

Test Temperature _______________ (°C) (nominal –30°C)
Test %DOD _______________ (%) (nominal V_{MAX})
Pulse Power Level Used for Test _______________ (W)
Minimum Allowed Cold Cranking Voltage _______________ (V)
Minimum Measured Cold Cranking Voltage _______________ (V)
Calculated Pulse Power Capability:
Pulse 1 ______ (W)
Pulse 2 ______ (W)
Pulse 3 ______ (W)

FreedomCAR Testing Only
CSF-Scaled Cold Cranking Pulse Power Capability:
Pulse 1 ______ (W) Pulse 2 ______ (W) Pulse 3 ______ (W)

Thermal Performance Tests

Reporting requirements for thermal performance testing are the same as for tests conducted at the nominal temperature, except that the test temperature must be clearly identified along with all results.

Efficiency Test

Efficiency Test Power Level _______________ (W)
Round Trip Energy Efficiency _______________ (%) (Note what part of the data was used to calculate the efficiency.)

Operating Set Point Stability Test

No reporting requirements

Cycle-Life Tests

Test Profile Discharge Power Used _______________ (W)
Nominal Depth-of-Discharge Used _______________ (% DOD)

Test Profile Recharge Power Used _______________ (W) (if not equal to discharge)

Total Profiles Tested _______________ (Number of test profiles achieved)
Energy Throughput (cumulative energy and number of test profiles per RPT interval) *(plot)*
FreedomCAR CSF-Scaled Energy Throughput (cumulative energy at system level) *(plot)*
End-of-Test Condition _______________ (if reached, e.g. inability to perform profile, etc.)

Reporting requirements for the periodic Reference Performance Tests are the same as for the Reference Capacity and HPPC tests, with the following additions:

Reference Capacity (Ah) and Capacity Fade (%) versus life (# test profiles) *(plot)*
Available Energy versus. Power over life (Wh vs. W at RPT intervals) *(plot)*
Discharge and Regen Resistance versus life (ohms versus # test profiles) *(plot)*
Average cycling temperature versus life (degrees C versus RPT intervals

Additionally, one of the following single-valued parameters can be reported over life as a simple measure of life degradation:

Energy Fade versus life (% fade at RPT intervals, based on a target power selected at beginning of life testing) *(plot)*
Power Fade versus life (% fade at RPT intervals, based on a target energy selected at beginning of life testing) *(plot)*

Calendar- Life Test

Storage Temperatures (tabulate device ID vs. °C)

Total Time at Temperature (to date) _______________ (at each test temperature)

Projected Calendar Life at test temperature _______________ (years, if available)
Basis for projected calendar life (calculations/explanation/statistical basis)

Results of periodic reference tests have the same reporting requirements as above, with the following additions:

Reference Capacity (Ah) and Capacity Fade (%) versus life (time at test temperature) *(plot)*
Available Energy versus. Power over life (Wh vs. W at RPT intervals) *(plot)*
Discharge and Regen Resistance versus life (ohms versus # test profiles) *(plot)*

Additionally, one of the following single-valued parameters can be reported over life as a simple measure of life degradation:

Energy Fade versus life (% fade at RPT intervals, based on the target power for a selected application at beginning of life testing) *(plot)*
Power Fade versus life (% fade at RPT intervals, based on the target energy for a selected application at beginning of life testing) *(plot)*

Impedance Spectrum Measurements

Magnitude Value as Received _______________ (ohms) (1 kHz or other single frequency only; repeat values at other times if measured)

Beginning-of-Life *(Plot of complex impedance)*

End-of-Testing *(Plot of complex impedance)*

Electrochemical Impedance Spectroscopy (EIS) Measurements (Recommended Results)

Initial Voltage ____________ (V), or SOC _______________

Self-Resonance Frequency _______________ Hz (initial measurement)
_______________ Hz at 70% SOC initial
_______________ Hz at 70% SOC end of testing

Frequency with -45˚ Phase Angle _______________ Hz initial measurement
_______________ Hz at 70% SOC initial
_______________ Hz at 70% SOC end of testing

ESR at Self-Resonance Frequency _______________ Ω (initial measurement)
_______________ Ω at 70% SOC initial
_______________ Ω at 70% SOC end of testing

%SOC for the following plots can be specified as being different than those given:

Complex plane plots of Impedance at 70% SOC (Initial measurement)
Complex plane plots of Impedance at 70% SOC at end of testing
Bode plots (|Z| vs. frequency, and θ vs. frequency at 70% SOC) (Initial measurement)
Bode plots (|Z| vs. frequency, and θ vs. frequency at 70% SOC) at end of testing

Appendix F

FreedomCAR Ultracapacitor Requirements

FreedomCAR Ultracapacitor Requirements

The following table defines preliminary performance and life requirements developed by the FreedomCAR Ultracapacitor Task Force and approved by the USABC Management Committee in June 2004 for three potential HEV application areas. No detailed definition of the characteristics of these prospective applications has yet been made available at the time of publication of this manual.

Table F-1. FreedomCAR Ultracapacitor (End of Life) Requirements

System Attributes	12V Start-Stop (TSS)		42V Start-Stop (FSS)		42V Transient Power Assist (TPA)	
Discharge Pulse	4.2 kW	2s	6 kW	2s	13 kW	2s
Regenerative Pulse	N/A		N/A		8 kW	2s
Cold Cranking Pulse @ -30°C	4.2 kW	7 V Min.	8 kW	21 V Min.	8 kW	21 V Min.
Available Energy (CP @1kW)	15 Wh		30 Wh		60 Wh	
Recharge Rate (kW)	0.4 kW		2.4 kW		2.6 kW	
Cycle Life / Equiv. Road Miles	750k / 150,000 miles		750k / 150,000 miles		750k / 150,000 miles	
Cycle Life and Efficiency Load Profile	UC10		UC10		UC10	
Calendar Life (Yrs)	15		15		15	
Energy Efficiency on Load Profile (%)	95		95		95	
Self Discharge (72hr from Max. V)	<4%		<4%		<4%	
Maximum Operating Voltage (Vdc)	17		48		48	
Minimum Operating Voltage (Vdc)	9		27		27	
Operating Temperature Range (°C)	-30 to +52		-30 to +52		-30 to +52	
Survival Temperature Range (°C)	-46 to +66		-46 to +66		-46 to +66	
Maximum System Weight (kg)	5		10		20	
Maximum System Volume (Liters)	4		8		16	
Selling Price ($/system @ 100k/yr)	40		80		130	