

Test and Evaluation of an Asymmetrical Electrochemical Capacitor

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Electrochemical capacitors (EC) have come a long way in a relatively short period of time for being able to serve as a viable energy storage technology in a variety of applications. (In this context, ECs refer to all energy storage devices operating on the basis of double-layer capacitance and/or pseudocapacitive charge storage mechanisms.) In fact, a number of large ECs are now commercially available, in both single-cell and multi-cell packages, and most commercially available devices have energy densities in the 4 to 14 W-h/kg range. And although these energy densities are significantly less than those of commercially available batteries, the higher cycle life, better power performance, and higher round-trip efficiencies of ECs could make them the preferred option for some utility applications, such as short-duration energy storage for transmission and distribution support.

Despite this promise, there have been several pitfalls in the road to development and application of ECs. The most prominent among these is the confusing array of specifications and testing regimes used in the EC community. A number of figures of merit are commonly used, some of which have little meaning in the application world.

For example, the cost-per-unit-capacitance (\$/F) is commonly used to show that ECs are cheaper per farad than conventional capacitors. However, this comparison makes little sense since conventional capacitors are usually used in AC applications and are rarely used for DC storage, while ECs are principally a DC device and do not have the frequency response characteristics to operate in most AC applications. Worse, cost-per-unit-capacitance cannot be directly used to compare the relative merit between two EC designs since the operating voltage ranges of the designs must also be considered and used to derive a comparative figure of merit, namely the cost-per-unit-energy (\$/W-h).

On the other hand, there are figures of merit for EC products that are useful in developing applications. These include energy density (in J/L or W-h/L), power density (in W/L), specific energy (in J/kg or W-h/kg), specific power (W/kg), cost per energy (\$/J or \$/W-h), and cost per power (\$/W). Here the same problem arises in a different form: that is, the method by which these figures are calculated sometimes do not match the way the devices would be used in the application.

By way of example, the specific energy for symmetric ECs is typically based on a discharge from the maximum cell voltage down to zero. While this is a perfectly legitimate method for making this determination, for most utility applications this approach is somewhat misleading. The reason being that few applications can actually use energy delivered at very low voltage. In addition, in many systems, the maximum operating voltage is set somewhat below the rated maximum in order to avoid overvoltage conditions in cell strings.

Another problem arises in the way that these figures are determined and which is often dependant on manufacturer. For example, when calculating the specific energy, some manufacturers include the mass of the terminals and packaging, and others do not. Testing methodology also changes depending on the manufacturer, and further complicating this issue is the fact that there is often no easy way to find out how a figure of merit is determined for a specific product.

The lack of convention has limited the value of specification data for application engineers and has lead to the general conclusion that specified data cannot be relied on when considering a product for a system. Furthermore, application engineers have no easy way of setting targets for performance that EC developers must meet in order to match their application since each developer follows a different standard.

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One solution to this situation is the development of a standard testing protocol for EC devices. In order to meet this need EPRI PEAC and Sandia National Laboratories initiated a joint testing and evaluation program for electrochemical capacitors that has included the development of a standardized test protocol based on projected use applications. This protocol includes standardized test conditions, such as ambient temperature, as well as standardized test procedures for commonly used metrics such as capacitance and power capability. Suggested procedures for conducting characterization tests, such as AC impedance testing and self-discharge measurement for different temperatures, are also included. Application-specific testing, applying only to certain applications or classes of applications, also form a part of the protocol. This protocol includes characterization tests and application testing to support the development of utility applications for these and similar electrochemical capacitor devices. In particular, the testing is designed to research the problem of unbalanced cell voltages, and has included the characterization of individual EC cells, as well as series strings of cells, for variations in parameters such as leakage current, self-discharge rates, and sensitivity to the use of an active leveling circuit. To aid in the development of this protocol as well as to help us evaluate its overall utility, we have included test and evaluation of commercially available ECs as described more fully below.

The test protocol is intended to be fairly flexible, and is being designed to allow evaluation of ECs at every state of development, from single cells to modules to entire systems. Our preliminary work with an EC from ESMA was carried out at the module level, and it soon became clear that cell level testing of the module elements would provide us with a better understanding of the behavior observed at the module level. We subsequently initiated cell level evaluation of two different types of 30-cell modules.

The first application of the protocol was designed around a transmission stabilization application. This application uses EC as energy storage in conjunction with a Flexible AC Transmission System (FACTS) device. This combination allows the injection of pulses of active power in addition to reactive power compensation on a power transmission system to increase the dynamic stability of the system. This effectively increases the power transfer limits of the transmission system, as well as improving power quality on the line.

An ESMA 30EC502 module was selected as the building block for the demonstration FACTS and energy storage system because of its suitability in applications requiring brief pulses of power, as demonstrated in simulations. The testing to be carried out was intended to validate the simulation and confirm that the module was suitable for this application, as well as to identify any other pitfalls in integration.

The test protocol for this application included the following components:

- **Initial capacity test:** The capacity test is conducted by charging each cell at 5 A up to 1.5 V, allowing the cell to rest for five minutes at open circuit, and then discharging at 5 A until the voltage reaches 0.75 V and again resting at open circuit for five minutes. This charge/discharge cycling is repeated 10 times, and the average value for discharge capacity is used for reporting purposes.
- **Initial AC impedance test:** The AC impedance test is performed on each cell in the test modules. Each cell is charged at 5 A to 1.5 V, and held at 1.5 V for 24 hours. The cell is then left open circuit for at least one hour, and the open-circuit cell voltage recorded. The complex impedance of each cell is then measured over the frequency range of 10 Hz to 10 MHz using a Parr potentiostat and power booster in a four-lead configuration with minimal lead length.
- **Cell leakage current tests:** Each cell is charged at 5 A until it reaches 1.5 V. The cell is then placed on float charge at 1.5 V for 12 hours. The charge current is measured throughout this period. (It should be noted that this measurement of leakage current diverges from the methods of most manufacturers, who typically use 72 hours as the leakage current measurement time.)
- **Cell self-discharge test:** Each cell is charged at 5 A until it reaches 1.5 V. The cell is then left open-circuit for 10 days at room temperature while continuing to monitor the cell voltage. At the end of 10 days the cell is discharged to 0.75 V to measure remaining capacity in the cell.
- **Cycling with voltage stabilization charge/discharge profiles:** The entire EC module is cycled according to a 5-step profile, as shown in Figure 1. These five steps are:

1. Charge stack at rate I_1 until stack voltage reaches V_1 .
2. Keep stack voltage at V_1 for a time t_1 .
3. Discharge at rate I_2 for time t_2 .
4. Recharge at rate I_1 until stack voltage reaches V_1 .
5. Repeat steps 2 through 4 for at least 30 cycles.

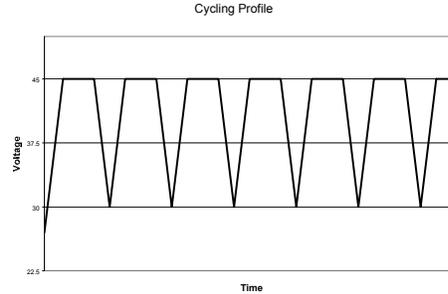


Figure 1: Transmission Stabilization Profile

The definitions for the parameters are as follows:

$$\begin{aligned}
 I_1 &= 40A \\
 V_1 &= 45V \\
 t_1 &= 10 \text{ minutes} \\
 I_2 &= 150A \\
 t_2 &= 10 \text{ seconds}
 \end{aligned}$$

During the entire test, module voltage, individual cell voltages, module current, ambient temperature, and cell temperatures are recorded.

- **Final capacity and AC impedance tests:** The capacity and AC impedance tests are repeated at the end of the test regime.

The testing protocol was submitted to the manufacturer for review, and was considered acceptable. The results from some of these tests follow.

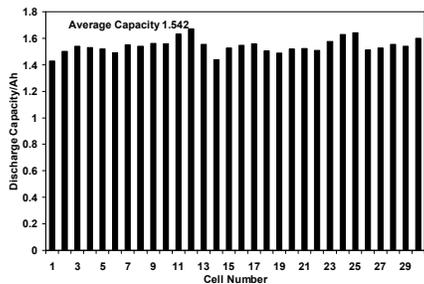


Figure 2: Comparison of Discharge Capacity

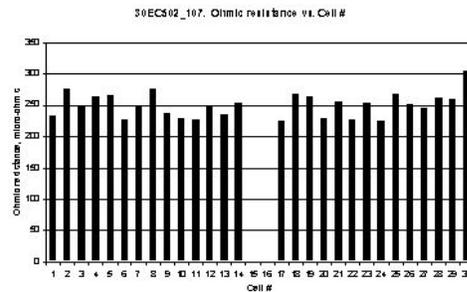


Figure 3: Ohmic resistance for cells in a module

Figure 2 shows a comparison of discharge capacity across the cells in a single 30EC502 module. The average capacity of the cells is 1.54 Ah, and range between 1.4 Ah and 1.6 Ah with a statistical deviation of 0.0542 Ah. This shows that the cells in a single module show some variation in capacity, which can lead to divergence in capacity level during operation.

Figure 3 shows the resistance of cells in a single module. These resistances represent the x-intercept on the Nyquist plot from AC impedance spectroscopy on each individual cell, performed by the procedure above.

Impedance was not measured for cells 15 and 16 due to lack of space for connecting leads to the cells. The impedance values vary between 225 and 305 microohms.

Figures 4 and 5 show data from AC impedance spectroscopy performed on a single cell. In Figure 4 the cell has been tested at varying states of charge. The angle of the impedance curve seems to decrease with decreasing cell voltage. The angle of the impedance curve when using isotropic axes is usually related to the self-discharge rate of the cell, and a smaller angle would indicate a greater self-discharge rate. The data would suggest that the self-discharge rate increases at lower states-of-charge, which runs counter not only to experimental data and the theory that the self-discharge rate is higher at higher voltages. Some researchers have said that the slope of this curve is more dependent on the recent activity of the cell than on the state-of-charge – so that a recently charged cell, for example, would have a smaller angle than a cell that has been sitting open-circuit [1].

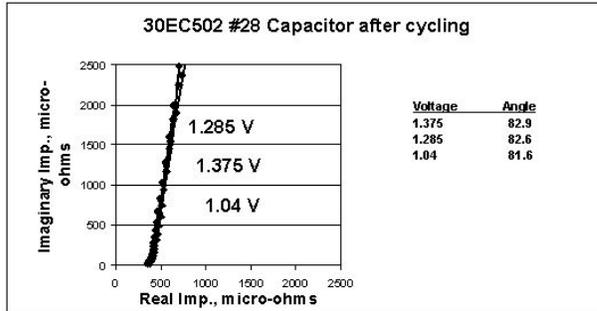


Figure 4: AC Impedance Sweeps at Varying Voltage

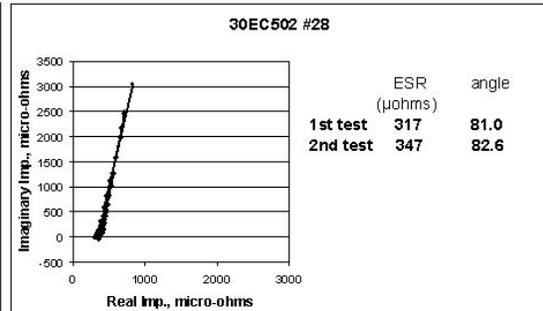


Figure 5: Changes in AC Impedance over a period of time

Figure 5 shows data from multiple AC impedance sweeps conducted on the same cell at the same state-of-charge, with a period of time between them. This data shows that the AC impedance characteristics do change with periods of open-circuit stand, although it is difficult to say from this data whether this is a result of porous electrode behavior or a result of self-discharge over the time between the two tests.

Figure 6 shows the results from the leakage current testing. It was found that at the end of 12 hours, the leakage current was still not stable, and changed considerably for each individual cell. Figure 6 shows the average leakage current over the last 6 hours of the 12 hour taper-charge period. This shows that 12 hours is not sufficient time for the EC module to stabilize, and other ways of calculating leakage current should be investigated.

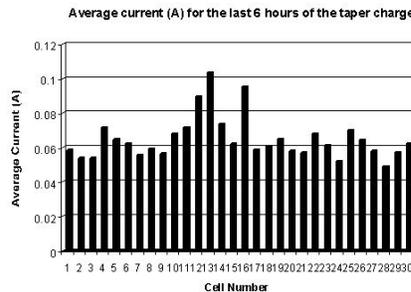


Figure 6: Average Cell Currents during Taper Charging

Figures 7 and 8 show the results of the 10-day open-circuit stand test. As seen by the data in Figure 7, there are significant drops in voltage for all cells during this time. In addition, most of this voltage drop occurs early during the stand, and the voltage stabilizes somewhat by the end of the 10 day period. It is also seen that while many of the cells exhibit similar behavior, there are few outliers, and depending on how the cells are configured in the module, i.e. series/parallel configuration, these outliers may ultimately limit the overall module behavior.

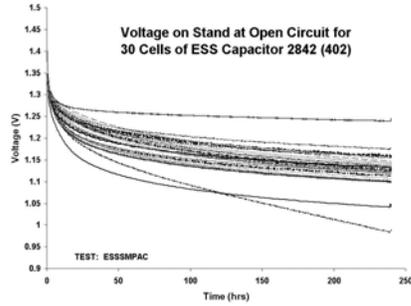


Figure 7: Voltage decay during open-circuit stand

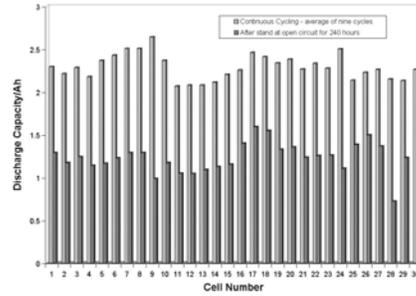


Figure 8: Remaining Charge after 10 days

Figure 8 shows the charge remaining after the 10-day stand in relation to the average capacities determined in the initial capacity tests. As expected from the drop in voltage on stand, the capacity fell significantly in all cells during stand. In addition, the capacity loss appears to be independent of the initial capacity of the cell.

The remainder of the test protocol is currently in progress, and results will be reported in future papers.

Several broad conclusions can be drawn from these tests and results. Many of these results are useful in determining the application envelope for these types of EC devices. Perhaps more importantly, however, these tests are invaluable in determining the validity of the testing protocol itself. It is evident from many of these results that the protocol is still a work in progress, and requires some fine-tuning before it is a useful tool in evaluating ECs. One example of a procedure that requires further work is the AC impedance measurement, which perhaps requires a closer definition of the state-of-charge and open-circuit time of the capacitors during testing. Another example is the leakage current testing, which requires more than 12 hours to test. These conclusions and others lessons learned in the course of this effort will be used in the further development of this protocol.

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References:

1. Nelms, R.M., and Taturchuk, B.J. (2003) "Modeling Double-Layer Capacitor Behavior Using Ladder Circuits." *IEEE Transactions on Aerospace and Electronic Systems* **39**, 2 (April 2003) 430 – 438.

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