Best practice methods for determining an electrode material's performance for ultracapacitors

Meryl D. Stoller and Rodney S. Ruoff*

Ultracapacitors are rapidly being adopted for a wide range of electrical energy storage applications. While ultracapacitors are able to deliver high rates of charge and discharge, they are limited in the amount of energy stored. The capacity of ultracapacitors is largely determined by the electrode material and as a result research to improve the performance of electrode materials has dramatically increased. While test methods for packaged ultracapacitors are well developed, it is often impractical for the materials scientist to assemble full sized, packaged cells to test electrode materials. Methodology to reliably measure a material's performance for use as an ultracapacitor electrode is not well standardized with various techniques yielding widely varying results. In this manuscript, we review and validate best practice test methods that accurately predict a material's performance, yet are flexible and quick enough to accommodate a wide range of material sample types and amounts.

Introduction

Ultracapacitors based on electrochemical double-layer capacitance (EDLC) are electrical energy storage devices that store and release energy by nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte.[1] While the charge storage mechanism of EDLCs is based on the interfacial double-layer of high specific area carbons, another class of capacitors is based on pseudocapacitance, and thus associated with electrosorption and surface redox processes at high surface area electrode materials such as metal oxides and conducting polymers. Hybrid capacitors are the combination of a faradic battery-type electrode coupled with a capacitive electrode in a two-electrode module (termed an asymmetric capacitor).[2] While the energy density of ultracapacitors is very high compared to electrostatic and electrolytic capacitors, it is still significantly lower than batteries and fuel cells. Coupling ultracapacitors with batteries (or another power source) is still required for supplying energy for longer periods of time. Thus,

there is a strong interest as enunciated, *e.g.*, by the US Department of Energy, for increasing the energy density of ultracapacitors to be closer to the energy density of batteries.[3]

The electrode material is a key component that determines an ultracapacitor's capacity and the most definitive test for a new electrode material is how it performs in a full scale, commercial ultracapacitor. However, it is not always practical to use a full sized, packaged cell, especially when dealing with minute quantities of material and/or a large number of different types of samples to be tested. The goal of this manuscript is to review experimental procedures that accurately evaluate a material's performance, yet are flexible and rapid enough to accommodate a large number of samples over a wide range of material types and quantities. In addition, test results should be repeatable and match those from other locations and research groups. At this time, the measurement methods for determining a material's performance are not well standardized and as a result it is difficult to assess the true performance reported in the literature, which in our opinion is hindering progress in this field.

Methodology for electrode material testing can be grouped into *test fixture configuration* and *measurement procedures*. Test fixture configuration includes the *test fixture type* along with guidelines for *electrode mass* and *thickness*, and other cell

Department of Mechanical Engineering and the Texas Materials Institute, The University of Texas at Austin, One University Station C2200, Austin, Texas, 78712-0292, USA. E-mail: r.ruoff@mail.utexas.edu

---

Broader context

Without advances in electrical energy storage (EES), important alternative forms of energy cannot be fully realized. Secondary batteries and electrochemical double-layer capacitors (EDLCs or ultracapacitors) are the two main types of EES devices. Ultracapacitors based on electrochemical double-layer capacitance are electrical energy storage devices that store and release energy by nanoscopic charge separation at the electrochemical interface between an electrode and an electrolyte. The capacity of an ultracapacitor is largely determined by the electrode material and as a result research to improve the performance of electrode materials has dramatically increased. While test methods for packaged ultracapacitors are well developed, it is often not feasible for the materials scientist to assemble full sized, packaged cells to test electrode materials. Methodology to reliably measure a material's performance for ultracapacitor electrode use is not well standardized with the different techniques currently being used yielding widely varying results. In this manuscript, we demonstrate best practice test methods that accurately predict a material's performance, yet are flexible and quick enough to accommodate a wide range of material sample types and amounts.

components including the *electrolyte*, *separator*, *current collectors*, and *binder*. Measurement procedures include *electrochemical measurements and parameters* along with the *computations to reduce the data to the desired metrics*.

Test fixture configuration

A typical ultracapacitor unit cell is comprised of two electrodes that are isolated from electrical contact by a porous separator.[1] Electrodes often contain conductive, low surface area additives such as carbon black to improve electrical conductivity. Current collectors of metal foil or carbon filled polymers are used to conduct electrical current from each electrode. The separator and the electrodes are impregnated with an electrolyte, which allows ionic current to flow between the electrodes while preventing electronic current from discharging the cell. A packaged ultracapacitor module, depending upon the desired size and voltage, is constructed of multiple repeating unit cells.

A test fixture configuration that closely mimics the unit cell configuration will more closely match the performance of a packaged cell. Two-electrode test fixtures are either available commercially or can be easily fabricated from two stainless steel plates as shown in Fig. 1.[4] Three-electrode electrochemical cells are commonly used in electrochemical research and consist of a working electrode, a reference electrode, and a counter electrode. *Three-electrode cells differ from two-electrode test and packaged cells in several important aspects*. With the three-electrode configuration, only one electrode, called the working electrode, contains the material being analyzed and the applied voltage and charge transfer across the single electrode are markedly different than with a two-electrode cell configuration. For a three-electrode cell, the voltage potential applied to the working electrode is that shown on the *X*-axis of the cyclic voltammogram (CV) chart (and on the *Y*-axis of the constant current diagram) and is with respect to the particular reference electrode used. In a symmetrical two-electrode cell, the potential differences applied to each electrode are equal to each other and are one-half of the values shown on the *X*-axis of the CV chart. Therefore, for a given potential range on the *X*-axis of the CV, the working electrode of a three-electrode cell has twice the potential range applied as is applied to the electrodes in a two-electrode cell and this results in a doubling of the calculated capacitance. There are other differences as well. The potential across the other electrode (counter electrode) in a three-electrode cell is not controlled or measured, and is an order of magnitude or more lower (in the typical case that the counter electrode is
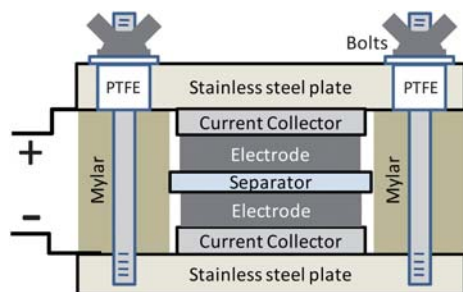
larger than the reference electrode) or can be approximately equal (in the case that the working and counter electrodes are of the same size and material.) The point of zero charge location (PZC) on the CV also varies for each reference electrode/electrolyte/material combination and unless the location is experimentally determined and used as the minimum voltage during a CV scan, the working electrode can actually reverse polarizations during cell operation. Khomenko *et al.* reported the dependence of measured capacitance values on test cell configuration.[5] Composite electrodes comprised of multiwalled carbon nanotubes (MWCNTs) and two conducting polymers, polyaniline (PANI) and polypyrrole (PPy), were measured using both two-electrode and three-electrode cell configurations. Fig. 2 shows the CVs for three- and two-electrode configurations using such PANI/MWNT electrodes. In the case of three-electrode cell measurements, values of 250 to 1100 F g^{-1} were measured. For the same materials in a two-electrode cell, values of 190 to 360 F g^{-1} were measured. Table 1 lists the specific capacitance results for two different materials, PPy and PANI, as measured with each cell type. As seen from the table, the three-electrode cell yields values approximately double those of the two-electrode cell. While valuable for analyzing the faradic reactions and voltages at a single surface, *the heightened sensitivity of the three-electrode configuration can lead to large errors when projecting the energy storage capability of an electrode material for ultracapacitor use.*
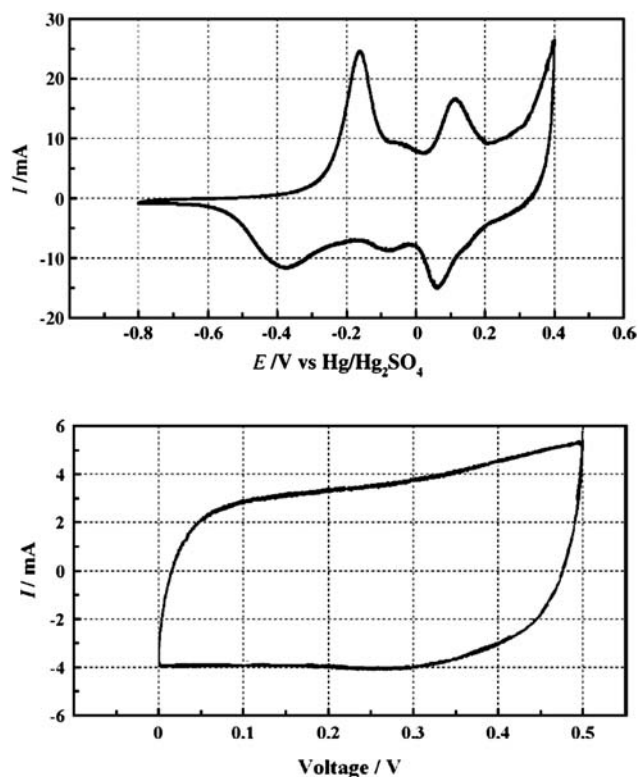

Fig. 2 (Top) CV of PANI/MWNT electrodes using a three-electrode cell and (bottom) using a two-electrode cell. Reprinted from V. Khomenko *et al.*, *Electrochim. Acta*, 2005, **50**, 2499–2506 with permission from Elsevier.[5]

Fig. 1 Two-electrode test cell configuration.[4]

This journal is © The Royal Society of Chemistry 2010

Energy Environ. Sci., 2010, **3**, 1294–1301 | 1295

Table 1 Values of specific capacitance (F g^{-1}) depending on cell type. Reprinted from V. Khomenko *et al.*, *Electrochim. Acta*, 2005, **50**, 2499–2506 with permission from Elsevier[5]

ECP in the composite electrode	Three-electrode cell		Two-electrode cell	
	CV	Galvanostatic discharge	CV	Galvanostatic discharge
PPy	506	495	192	200
PANI	670	650	344	360

Table 2 Graphene-based electrode performance by electrolyte and measurement method[4]

Electrolyte	Galvanostatic discharge		Cyclic voltammogram average	
	10 mA	20 mA	20 mV s^{-1}	40 mV s^{-1}
KOH	135	128	100	107
TEABF$_4$/PC	94	91	82	80
TEABF$_4$/AN	99	95	99	85

The mass of the active material and thickness of the electrodes also influence the measured results. Depending upon whether an ultracapacitor is constructed to optimize energy density or power density, commercial cell electrode thicknesses range from about 10 μm thick (high power density) to several hundred microns thick (high energy density). Test electrodes should be of comparable thicknesses *and ones that are extremely thin and/or contain very minute amounts of material can lead to an over-statement of a material's performance*. Signal to noise is also a concern. The capacitance of the active material in the electrodes should be significantly higher than that contributed by other cell components such as the electrode support surface, collector, and other conducting surfaces within the test fixture. In addition, mass measurement errors can be significant when handling and weighing microgram sized electrodes. For reliable measurements, a test cell should have a capacitance of 0.25 or more farads with the mass of the active material on the order of 10 or more milligrams. Hu *et al.* demonstrated the dependence of mass and thickness on measured results.[6] Fig. 3, from the supporting information of the referenced manuscript, shows specific capac-itances for four different mass loadings for electrodes con-structed of single-walled carbon nanotube (SWCNT) paper and measured in a two-electrode test cell.[6] The graph shows that, with aqueous electrolyte, as the mass loading was increased from 72 μg cm^{-2} to 1.33 mg cm^{-2}, the specific capacitance at a reported current density of about 2 A g^{-1} decreased from about 200 to 85 F g^{-1} respectively. For the same electrolyte and mass loading increase, the specific capacitance at a current density of 5 A g^{-1} decreased from about 175 to 75 F g^{-1}. The reported electrode

thickness for the 1.33 mg cm^{-2} mass loading was 14 μm.[6] The electrodes with a mass loading of 72 μg cm^{-2} thus have a thick-ness of about 0.75 micron, an order of magnitude thinner than commercial ultracapacitor electrodes. It is important to use appropriate electrode thicknesses and masses for any meaning to be attached to reported values of specific capacitance and energy density.

The most common organic electrolytes are tetraethylammo-nium tetrafluoroborate (TEABF$_4$) in either propylene carbonate (PC) or acetonitrile (AN). Common aqueous electrolytes include 5M KOH and H$_2$SO$_4$. Since energy stored is related to the square of voltage, organic electrolytes are currently used in commercial ultracapacitors due to their wider electrochemical window (about 2.7 volts) as compared to about 1 volt for aqueous electrolytes. Ionic liquid electrolytes are also being adopted due to their increased electrochemical windows and improved thermal stability. A material's performance with an aqueous electrolyte will typically yield higher specific capacitances and does not indicate its performance with an organic or IL electrolyte. Fig. 3 shows SWCNT paper electrodes of equal mass measured with aqueous (paper : H$_2$SO$_4$, 1 V : 72 μg cm^{-2}) and organic (paper : organic, 3 V : 72 μg cm^{-2}) electrolytes.[6] The values for aqueous electrolytes are consistently 40–50% higher than with the organic electrolyte over a wide range of current densities. The presence of faradic charge storage or pseudocapacitance specific to acidic mediums can also inflate the measured capacitance relative to organic electrolytes. The performance disparity for different electrolytes also depends upon material type and morphology. Table 2 shows specific capacitances for electrodes composed of chemically modified graphene material.[4] For this material, the specific capacitance differences due to the electrolyte have in our work ranged from about 20 to 25 percent higher for the aqueous electrolyte. Other cell components such as binders, current collectors, and separators also have an effect upon cell perfor-mance. However, when from a commercial source, their impact upon measured values is relatively small.

Measurement procedures

Charging rates, voltage ranges, and methods for calculation of metrics also affect the reported results and should closely match currently established and accepted procedures used for packaged cells. The primary performance metrics for packaged ultra-capacitors include gravimetric energy and power densities, and life cycle testing.[7–10] In turn, an ultracapacitor's energy density (W h kg^{-1}) is primarily determined by the cell's electrode material and electrochemical voltage window. With energy density currently the primary limitation for ultracapacitors, the most
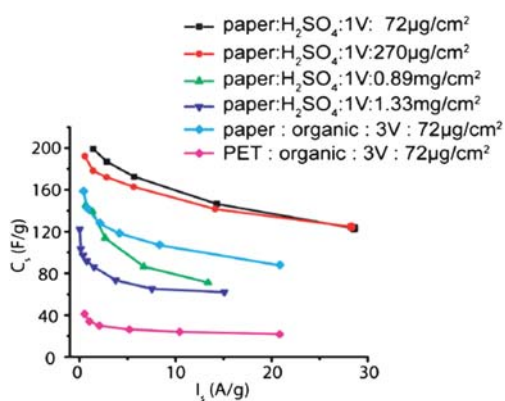

Fig. 3 Measured capacitance decrease with an increase of electrode mass. Reprinted from L. B. Hu *et al.*, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 21490–21494.[6]

important metric for an electrode material is thus its specific capacitance (F g^{-1}). An ultracapacitor's power scales with the square of voltage divided by its equivalent series resistance (ESR).[11] The measured ESR of a test cell, as well as that of a full scale packaged capacitor, is due to all cell components (leads, current collectors, electrodes, electrolyte, and separator) and therefore only a portion of the measured resistance can be attributed to the electrode material itself. Other metrics, such as an electrode material's energy and power density, also do not correlate directly to those of a packaged cell and must include information such as package dimensions and the mass of the other cell components to be meaningful.

Specific capacitance is the capacitance per unit mass for one electrode (eqn (1))

$$C_{sp} \ (F \ g^{-1}) = 4 \times C/m \tag{1}$$

where C is the measured capacitance for the two-electrode cell and m is the total mass of the active material in both electrodes. The multiplier of 4 adjusts the capacitance of the cell and the combined mass of two electrodes to the capacitance and mass of a single electrode. If volume is more important for the targeted application, the electrode material's volume may be substituted for mass. Cell capacitance is best determined from galvanostatic or constant current (CC) discharge curves using eqn (2) with I the discharge current and

$$C = I/(dV/dt) \tag{2}$$

dV/dt calculated from the slope of the CC discharge curve. Galvanostatic discharge is the accepted measurement method for determining capacitance for packaged ultracapacitors in the ultracapacitor industry and correlates more closely to how a load is typically applied to an ultracapacitor in the majority of applications. The same voltage range should be used for testing should match that used for commercial cells and should reflect the electrolyte's electrochemical window—from 0 V to approximately 1 V for aqueous electrolytes and from 0 V to 2.5–2.7 V for organic electr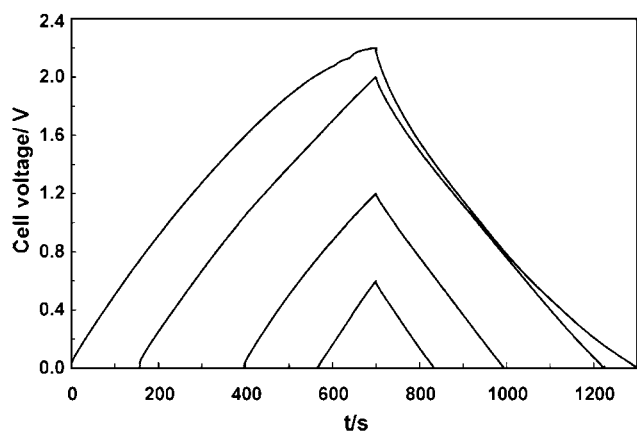olytes. Maximum voltages for hybrid cells will depend upon electrode materials and electrolytes. The initial portion of a discharge curve exhibits an *IR* drop due to internal resistance and the rest of the curve will typically be linear for non-faradic materials. Pseudocapacitive and hybrid systems can exhibit large deviations in linearity based upon varying capacitance with voltage. Fig. 4 shows CC charge–discharge curves (100 mA g^{-1}) of an asymmetric manganese oxide/activated carbon ultracapacitor in 2 mol L^{-1} KNO$_3$ electrolyte cycled at different maximum cell voltages.[12] When the maximum voltage is at 2.2 V, the CC curve is no longer symmetric indicating non-capacitive behavior. Fig. 5 shows, for the same cell, the coulombic efficiency and specific capacitance (F g^{-1}) *vs.* maximum voltage.[12] While the specific capacitance continues to increase with increasing voltage range, the coulombic efficiency decreases dramatically when cycled above 2 V. Driving a cell above its true maximum operating voltage can lead to an overestimation of specific capacitance and cells operated at these levels will have shortened lifetimes and poor efficiencies due to the non-reversible reactions within the cell. Significant errors can also be introduced by the method used to calculate the slope (dV/dt). As stated previously, capacitance varies with voltage, especially for hybrid and pseudocapacitive cells, and it is important to calculate capacitance using the typical operating voltage range for the application that the device will be used. Most ultracapacitors will be operated in the range of V_{max} to approximately $\frac{1}{2}V_{max}$ and the recommended method is to use two data points from the discharge curve with $dV/dt = (V_{max} - \frac{1}{2}V_{max})/(T_2 - T_1)$. *Including the lower half of the voltage range in the calculations can distort the apparent capacitance above that which is practically realizable for an actual application.*

Very low rates of discharge also lead to large errors, especially when coupled with small electrode masses, with the current from cell leakage, capacitance from other cell components, and faradic reactions contributing an increasing percentage of the signal as discharge rate and electrode mass are decreased. Charge and discharge rates should be specified in units of current per
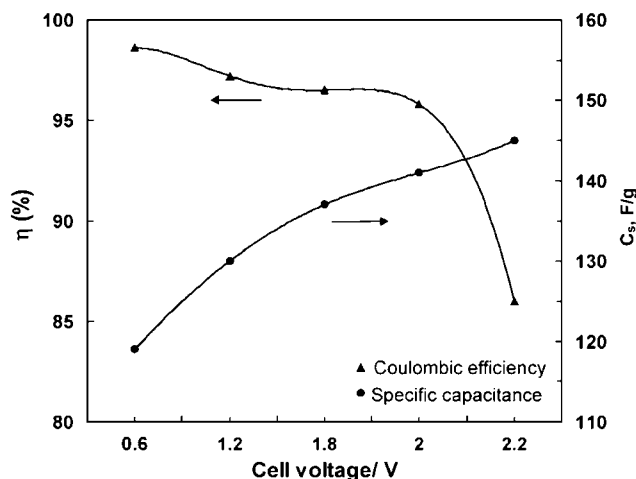

Fig. 4 CC charge–discharge curves (100 mA g^{-1}) of an asymmetric manganese oxide/activated carbon ultracapacitor in 2 mol L^{-1} KNO$_3$ electrolyte. Reprinted from V. Khomenko *et al.*, *J. Power Sources*, 2006, **153**, 183–190 with permission from Elsevier.[12]

Fig. 5 Coulombic efficiency and specific capacitance (F g^{-1}) of an asymmetric manganese oxide/activated carbon ultracapacitor in 2 mol L^{-1} KNO$_3$ electrolyte *vs.* the cell voltage. Reprinted from V. Khomenko *et al.*, *J. Power Sources*, 2006, **153**, 183–190 with permission from Elsevier.[12]

electrode mass with the duration of charge and discharge corresponding to typical ultracapacitor applications. Current should be adjusted to provide charge and discharge times of approximately 5 to 60 seconds.[11] For example, a test cell with two 10 mg electrodes composed of 100 F g^{-1} specific capacitance material will have a capacitance of 0.5 F. With a discharge current of 40 mA, corresponding to a discharge density of 4 A g^{-1}, discharge time from 2.7 to 0 volts will be approximately 34 seconds. Fig. 3 shows the dependence of specific capacitance on the rate of discharge and electrode mass loading.[6] For the electrode labeled "paper : H$_2$SO$_4$, 1.33 mg cm^{-2}" with reported electrode thickness of 14 μm,[6] the measured specific capacitance varies significantly (from over 120 F g^{-1} to about 85 F g^{-1}) for discharge rates of less than 2 A g^{-1}. This effect is most pronounced with the thicker electrode highlighting the importance of using electrode thicknesses that match packaged cells.

While the use of CC data is recommended, CVs may be used to calculate capacitance. Using eqn (2) and CV data, I is the average current during discharge (from V_{max} to zero volts) and dV/dt is the scan rate. As with CC curves, capacitance depends on scan rate, voltage range, and computation method. The cell should be cycled for 20 or more cycles prior to recording the data and should only be cycled from 0 volts to the maximum voltage. Fig. 6 shows two CVs, one cycled from 0 V to 1 V (top) and the second is the same cell cycled from −1 V to 1 V (bottom). The first (blue) and the 20th (red) cycles are shown on each CV. When a cell is first cycled or when it is cycled from a negative to positive voltage, there are increased current levels due to reversing the polarity of the cell. This demonstrates the importance of determining the point of zero charge when using a three-electrode cell
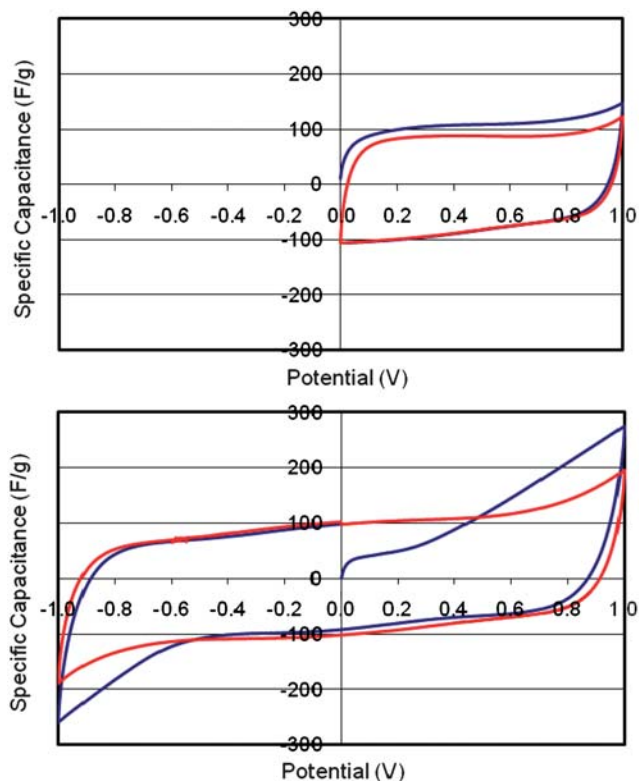

Fig. 6 CVs from 0.0 V to 1.0 V (top) and from −1.0 V to 1.0 V (bottom). The first cycle is shown in blue and 20th cycle is shown in red for each CV.

Table 3 Comparison of methods to calculate specific capacitance from CV curves

Method that current was determined	C_{sp}/F g^{-1}
Maximum current 1st scan (CV from −1 to 1 V)	268
Maximum current 20th scan (CV from −1 to 1 V)	179
Maximum current 1st scan (CV from 0 to 1 V)	128
Current at zero V 20th scan (CV from −1 to 1 V)	102
Ave discharge current 20th scan (CV from −1 to 1 V)	97
Ave discharge current 20th scan (CV from 0 to 1 V)	77

and ensuring electrode polarization is not reversed during testing. Table 3 shows the results of various calculation methods for different ranges of I from the two CV curves with over a 300 percent difference in values of specific capacitance. *As with CC curves, the discharge rate should reflect that of a typical ultracapacitor application. Voltage scan rates of at least 20 to 40 mV s^{-1} are needed to maintain discharge times on the order of a minute and adequately reflect a material's performance.*

Secondary material performance metrics

A packaged cell's specific power and cycle life depend upon all components within the cell as well as the cell architecture. The main indicator for the power capability for a packaged cell is based upon its direct current resistance or ESR. Methods for determining cell resistance include measuring the IR drop at the initiation of a constant current discharge, measuring the bounce back of voltage at the end of a constant current discharge, or using AC impedance spectroscopy. For packaged cells, ESR is typically determined from the CC tests using the *IR* drop at the beginning of the discharge curve and the same method is recommended for test cells. The ESR is the value calculated from the change in voltage (*IR* drop) divided by the total change in current applied. Typically the initial current is set close to zero to stabilize the voltage prior to initiating discharge. In the case that the current is switched directly from full charge to full discharge, the resulting voltage drop should be divided by twice the current applied. The reader is referred to Burke[11] and Zhao *et al.*[10] for a detailed description. ESR is inversely proportional to cell size and if reporting ESR, the capacitance of the test cell should also be reported. Cell life also depends upon all cell components and a simple constant power or constant current cycle is adequate for an initial gauge of a material's stability. One should note that since degradation of a material–electrolyte system occurs primarily at higher voltage, any life cycle testing should include the maximum rated voltage in each cycle. Again the reader is referred to Burke[11] for more detailed methods of testing packaged cells.

Validation of test methods

To validate the best practice test method recommendations, a commercial packaged cell was first measured, then

disassembled into individual components for testing in two and three-electrode test cells. The commercial cell (Cooper Bussmann PowerStor B Series) consisted of a cylindrical, can type package with two spirally wound electrodes connected to radial lead terminals, and had a nominal capacitance of 1 farad with an operating voltage rating of 2.5 volts. Electrodes consisted of carbon coated onto one side of the current collectors. Each electrode measured approximately 11.4 cm long, 0.5 cm wide and 0.012 cm thick. When assembled in the metal can, the electrodes were isolated electrically from each other and the package by separators about 0.8 cm wide and 57 µm thick. Organic electrolyte, TEA/BF$_4$ in PC (the packaged cell electrolyte was also based on PC), was used in all test cells. For two-electrode cell testing, a 2.5 cm length was cut from each electrode and assembled with each of two different separator materials, the first consisting of a short length of separator material taken from the package, the second was from a commercial manufacturer (Celgard 3501). The text fixture used for two-electrode cell testing is shown in Fig. 1. Three-electrode tests were performed in a beaker type cell using a 1.4 cm length of the carbon electrode for the working electrode and Pt wire and Pt mesh for the reference and counter electrodes, respectively. Volumetric specific capacitance (F cm^{-3}) is reported instead of gravimetric since accurately determining the mass of the active material in the electrodes required removing the electrolyte from the carbon. The mass of the carbon was, however, estimated to ensure that current levels used for constant current charge/discharge tests are in line with those recommended. To eliminate effects of thickness variation along the length of the electrodes and ensure accurate comparison between cells, electrodes for all cells were weighed and mass ratios were used to verify the relative amounts of carbon for each cell as compared to the package cell. A voltage range of 0 to 2.5 volts was used for testing the packaged ultracapacitor and the two-electrode test cells. The three-electrode cell was cycled both from −1.25 to 1.25 and from 0 to 1.25 V with reference to Pt. Specific capacitance calculations for the three-electrode cell were taken from the CV and CC curves cycled from 0 to 1.25 volts.

Table 4 shows results for each cell configuration. Specific capacitance values calculated from galvanostatic discharge (CC curves) from both two-electrode test cells are within 5% of the packaged cell values for each current level. The three-electrode cell measurements, however, yield up to double the values of the packaged cell at lower current levels, but gave lower values at higher currents. Values based on CV curves show the same trend

with two-electrode cell values closely matching those of the packaged ultracapacitor with three-electrode cell values again diverging from the other cells. The two-electrode cell based on the Celgard separator gives slightly higher values than either the packaged cell or the two-electrode cell with the separator material taken from the package. This may be attributed to the thickness difference between the two separator materials; the Celgard material at 25 µm in thickness is less than half that of the material used in the packaged device. A major contribution to internal resistance of a cell is conductivity of the electrolyte and so internal resistance of an ultracapacitor is very sensitive to electrode spacing. The three-electrode cell has an even larger spacing between electrodes (on the order of mm) and the corresponding high ESR likely explains the dramatic decrease in
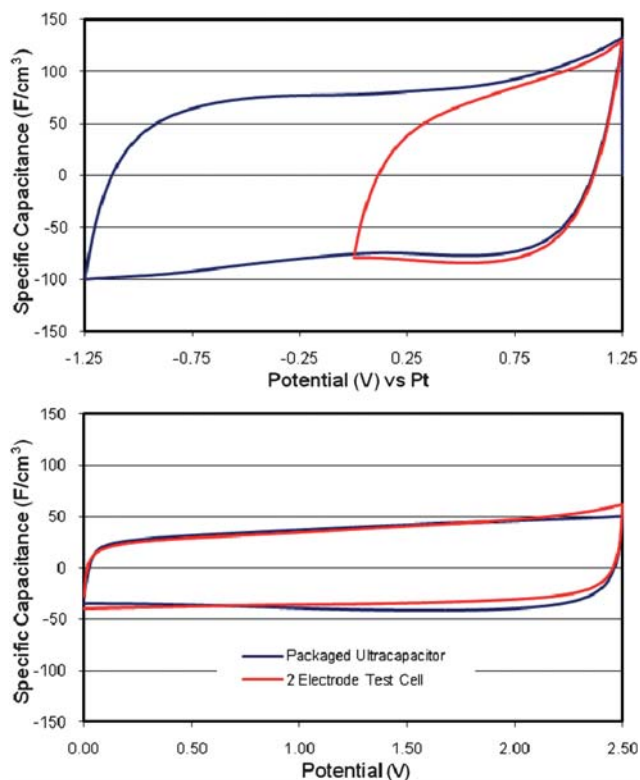

Fig. 7 (Top) CV curves for three-electrode test cell and (bottom) packaged ultracapacitor and two-electrode cell. Scan rates for all curves was 10 mV s^{-1}.

Table 4 Specific capacitance (F cm^{-3}) as measured with various cell configurations

Cell configuration	Galvanostatic discharge				Cyclic voltammogram			
	0.25 A g^{-1}	0.5 A g^{-1}	1.0 A g^{-1}	2.0 A g^{-1}	10 mV s^{-1}	20 mV s^{-1}	40 mV s^{-1}	100 mV s^{-1}
Packaged ultracapacitor[a]	42.2	41.2	39.3	37.4	36.9	36.0	33.6	28.3
Two-electrode test cell (package separator)	40.8	39.3	38.4	36.9	32.6	34.1	33.6	31.2
Two-electrode test cell (Celgard separator)	43.2	41.7	40.8	39.3	33.1	35.5	35.5	32.6
Three-electrode test cell	85.4	69.5	35.0	—	60.0	42.2	—	—

[a] Commercial cell (Cooper Bussman PowerStor) as described in the text.

This journal is © The Royal Society of Chemistry 2010

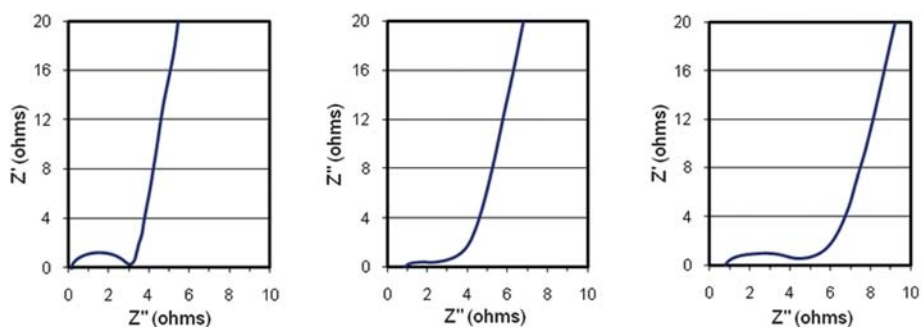*Energy Environ. Sci.*, 2010, **3**, 1294–1301 | 1299

Fig. 8 Nyquist plots for: (left) packaged cell, (middle) two-electrode test cell with Celgard separator, and (right) two-electrode cell with separator material from package.

measured values as current loadings (or scan rates) are increased. Fig. 7 shows CV curves for the three-electrode cell scanned over two potential ranges (top) and two-electrode and packaged cell (bottom). All CVs shown were scanned at 10 mV s^{-1}. The two-electrode test cell closely matches the packaged ultracapacitor while the three-electrode configuration yields values approximately twice that of the other cells. For three-electrode cell measurements to approximate those of the packaged cell, equation 1 should be modified to $C_{sp} = C/m$ where m is the mass of the active material in the working electrode. As stated previously, the voltage scan range for a three-electrode configuration should be adjusted to approximately half that of the packaged cell and should not pass through the PZC.

The internal resistance (ESR) was calculated for each cell configuration using the IR drop from the CC curves. The values were 3.1, 4.6, 6.2, and 79.4 ohms for the packaged cell, two-electrode test cell with Celgard separator, two-electrode cell with separator from the package, and three-electrode cell, respectively. Nyquist plots also give an indication of internal resistance. Fig. 8 shows Nyquist plots for the packaged cell (left), two-electrode test cell with Celgard separator (middle) and two-electrode cell with separator from the package (right). Since the *X*-axis of the Nyquist plot is the real component of impedance (ohms), a higher series resistance results in a shift to the right. Extrapolating the curve on the Nyquist plot to intersect the *X*-axis typically yields values that correspond reasonably well to the calculated ESR values from the CC curves. ESR is inversely based on cell size as well as other factors such as electrode spacing, electrolyte, package type, *etc.* The capacitance of the packaged cell was approximately 4 times that of the two-electrode cell yet the ESR was only half. Impedance analysis using two-electrode test cells is useful for comparing materials and cell components (it does show lower resistance for the thinner separator material); however, other techniques should be used to predict the ESR (and power) for a packaged cell. It should be noted that while a three-electrode cell configuration with closely spaced electrodes can have ESR values on the order of the other cells, this configuration will still yield capacitance values approximately double the other cells due to the doubled voltage applied to the working electrode.

Summary of recommendations

While a three-electrode cell is valuable for determining electrochemical-specific material characteristics, a two-electrode test cell mimics the physical configuration, internal voltages and charge transfer that occurs in a packaged ultracapacitor and thus provides the best indication of an electrode material's performance. For good signal to noise and to minimize measurement errors, the test cell should have a capacity of over 0.25 farad with the mass of the active material on the order of 10 or more mg. Electrode thicknesses should be on the order of packaged commercial cells (at least 15 μm thick) and should be tested with the same electrolytes that would be used in an actual capacitor. Charge and discharge rates (on the order of 2 A g^{-1} and 20 mV s^{-1}) and operating voltages (at least 2.5 V for organic electrolytes) should match that of typical ultracapacitor applications. Calculations for capacitance and ESR should match those currently recommended for commercial ultracapacitors.

At the packaged cell level, energy density (W h kg^{-1}) and power density (W kg^{-1}) are the key parameters. These parameters are not appropriate for material level performance reporting since they depend upon package specific parameters such as the mass of the dead components and cell architecture. Thus, any reporting of energy and power densities should be done in the context of a full sized, packaged ultracapacitor and calculations should include the mass of all components including the package. As electrode thickness and spacing affect measured performance, ESR measurements should only be performed using test electrodes with the same thicknesses and spacing of commercial cells. Test cells do not accurately predict the ESR of a packaged cell and as a result, power capability cannot be accurately estimated using test cell measurements. Lifetime testing should be performed using a cycle that includes the maximum rated voltage.

Conclusion

Measurement methods for determining a material's performance for use as an ultracapacitor electrode are not well standardized with various techniques currently being employed leading to wide variations in reported results. The various experimental procedures were reviewed and best practice methods were recommended that effectively simulate a packaged, commercial cell, yet are flexible and rapid enough to accommodate a large number of samples with a wide range of material types and quantities. We believe adoption of these measurement practices will enable the more accurate determination and reporting of an electrode material's performance.

Acknowledgements

References

1 B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Plenum Publishers, New York, 1999.

2 B. E. Conway and W. G. Pell, Double-Layer and Pseudocapacitance Types of Electrochemical Capacitors and Their Applications to the Development of Hybrid Devices, *J. Solid State Electrochem.*, 2003, **7**, 637–644.

3 J. Goodenough, *Basic Research Needs for Electrical Energy Storage: Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, April 2–4, 2007*, Office of Basic Energy Sciences, DOE, July 2007.

4 M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, Graphene-Based Ultracapacitors, *Nano Lett.*, 2008, **8**(10), 3498–3502.

5 V. Khomenko, E. Frackowiak and F. Beguin, Determination of the Specific Capacitance of Conducting Polymer/Nanotubes Composite Electrodes Using Different Cell Configurations, *Electrochim. Acta*, 2005, **50**, 2499–2506.

6 L. B. Hu, J. W. Choi, Y. Yang, S. Jeong, F. La Mantia, L. F. Cui and Y. Cui, Highly Conductive Paper for Energy-Storage Devices, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 21490–21494.

7 J. R. Miller and A. F. Burke, *Electric Vehicle Capacitor Test Procedures Manual*, Idaho National Engineering Laboratory, Report No. DOE/ID-10491, 1994.

8 R. B. Wright and C. Motloch, *Freedom CAR Ultracapacitor Test Manual*, Idaho National Engineering Laboratory, Report No. DOE/NE ID-11173, 2004.

9 *Maxwell Representative Test Procedure for Customer Evaluations*, Maxwell Web, 2002.

10 S. Zhao, F. Wu, L. Yang, L. Gao and A. Burke, A Measurement Method for Determination of dc Internal Resistance of Batteries and Supercapacitors, *Electrochem. Commun.*, 2010, **12**, 242–245.

11 A. Burke, *Testing of Supercapacitors: Capacitance, Resistance, Energy, Energy and Power Capacity*, Institute of Transportation Studies, University of CA, Davis, Research Report UCD-ITS-RR-09–19, 2009.

12 V. Khomenko, E. Raymundo-Pinero and F. Beguin, Optimisation of an Asymmetric Manganese Oxide/Activated Carbon Capacitor Working at 2 V in Aqueous Medium, *J. Power Sources*, 2006, **153**, 183–190.