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ORIGINAL PAPER

Using coin cells for ultracapacitor electrode material testing

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Abstract The effects of compressive force and the addition of conductive fillers on ultracapacitor electrode performance measurements were studied. We have shown that the force exerted by typical battery coin cell components is inadequate, resulting in erroneous measurements of electrode performance. We further demonstrated that with modest modifications, coin cell measurements can equal those of specialized test fixtures and of packaged cells.

Keywords Ultracapacitors · Electrode testing · Energy storage · Coin cell

1 Introduction

Coin cells are widely recognized as the standard test platform for lithium ion battery electrode research. In addition to batteries, ultracapacitors constitute another type of electrical energy-storage device, and ultracapacitor research has been rapidly increasing in recent years. Ultracapacitors share the same physical configuration as batteries, consisting of a stack of two collectors, two electrodes, and a separator, all wetted with an electrolyte. However, ultracapacitors have different requirements for electrode testing than batteries do. A primary difference is that ultracapacitors charge and discharge 1–2 orders of magnitude faster than batteries, and the internal resistance of the coin cell influences the measured performance of the electrode material. Many researchers may wish to utilize their existing battery coin cell equipment, and this study demonstrates how coin cells can be adapted for testing ultracapacitor electrode materials.

The primary performance metrics for packaged ultracapacitors include gravimetric energy and power densities. In turn, an ultracapacitor's energy density (W h kg^{-1}) is primarily determined by the cell's electrode material capacity and electrochemical voltage window. With energy density currently the primary limitation for ultracapacitors, the most 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) [1]. 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. It is therefore important that cell components contribute as little ESR as possible. Since batteries are charged/discharged on the order of hours compared to 1–2 minutes for ultracapacitors, current densities for testing batteries are 1–2 orders of magnitude lower than that of ultracapacitors. As a result, coin cells intended for battery testing are not optimized to minimize ESR.

The ESR can be reduced through improved physical contact between the electrodes and current collectors [2]. For a packaged ultracapacitor, force is applied during assembly and testing to insure good contact between cell components. If a test fixture contributes to the high electrical resistance, then the measured values of specific

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capacitance will be depressed in addition to giving higher ESR values.

Battery coin cells have many advantages that have driven their widespread adoption for battery materials research [3, 4]. Coin cell components and equipment to assemble them are commercially available, and their use is widespread and well accepted in the battery industry. Once a coin cell is assembled, it remains hermetically sealed from the environment and is easily transported for testing. Since battery test equipment typically has multiple channels, this enables many samples/cells to be assembled concurrently and tested for cycling without requiring multiple test fixtures. However, for ultracapacitor material testing, coin cells have one major drawback—the internal force pressing the cell stack together, though adequate for batteries, cannot be precisely controlled and will significantly affect the internal ESR and ultimately the measured capacitance. Controlled pressure on the cell stack is required for accurate testing of ultracapacitor electrodes. One solution for ultracapacitor electrode material testing is the use of specialized, two-electrode test fixtures that have been shown to accurately predict an electrode material's performance [5]. This study shows how existing coin cells can be adapted to apply increased force on the cell stack and give similar results to the specialized test fixtures.

2 Experimental

First, the influence of pressure on measured electrode performance was studied along with ways to lessen the need for the exact application of force. These included optimizing electrode thickness and the addition of conductive fillers. Second, experiments were performed to determine how to adapt coin cells using existing components to deliver the optimum pressure.

2.1 Influence of pressure on measured performance

To measure the effect of pressure, the ultracapacitor cell stack was placed between two stainless steel plates, and increasing pressure was applied. Two commercial activated carbons, Norit DLC30 with a specific surface area of 1406 $m^2\ g^{-1}$ and Fuzhou Yihuan YEC7 with a specific surface area of 1830 $m^2\ g^{-1}$, were used for the study. The compression ratio is used as a metric to control the amount of force applied to the electrode stack. The compression ratio is the initial thickness of the ultracapacitor stack (collectors, electrodes, and separator) divided by its thickness at each pressure. A compression ratio of exactly 1 is no pressure applied, and a ratio of 1.1 indicates that the applied pressure has compressed the stack from a thickness of 200 μm to a thickness of 182 μm. In the test fixture, once the optimum compression ratio is known, it is replicated for subsequent samples by inserting PET film spacers between the stainless steel plates—the spacer thickness is simply determined by dividing the un-compressed cell stack by the desired compression ratio. Using compression ratio as a metric instead of force eliminates the need for more specialized load-measuring equipment as part of the test cell assembly. In the experiment, the thickness of the cell stack at each pressure was determined by measuring the overall thickness of the assembly and then subtracting the plate thicknesses. The use of a carbon black conductive filler and optimizing electrode thickness were also investigated.

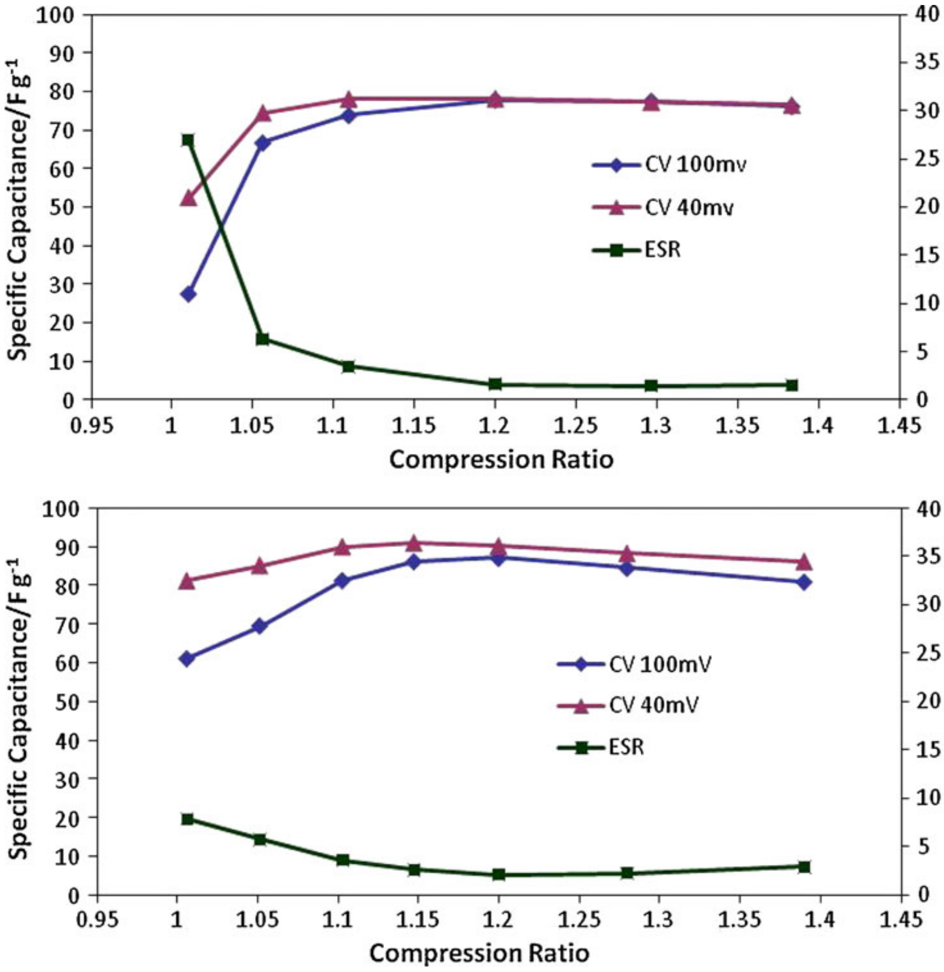
2.2 Coin cell pressure optimization

The typical coin cell consists of a two piece metal case, two metal spacers, and a spring. The capacitor stack is positioned between the two spacers and consists of an anode, a cathode, and a separator. The spring insures that the capacitor stack (electrodes, collectors, and separator) is held together and electrical contact is made. The case edges are crimped by using a die press, and a polymer seal prevents leakage of the electrolyte and keeps oxygen and moisture from entering the cell.

Owing to the enclosed nature of a fully assembled coin cell, it is not possible to accurately measure the amount of force the assembly is exerting upon the ultracapacitor stack or to accurately measure how much the stack is being compressed. However, by assembling a coin cell and comparing the measured performance to the results from Sect. 2.1 (Figs. 1, 2), an estimation of the compression of the stack can be made. Coin cells were assembled with DLC30 electrodes at the optimum electrode thickness (80 μm) and with 10 wt% conductive filler. Even with the optimized electrode thickness and the addition of conductive filler, the measured performance for the DLC30 (71 $F\ g^{-1}$ at 10 $mV\ s^{-1}$, 57 $F\ g^{-1}$ at 10 $mV\ s^{-1}$, and 16.1 ohm ESR) showed that the stack pressure being exerted by the coin cell with one spring corresponded to a compression ratio of less than 1.05. Therefore, increased spring force was still necessary to yield similar performance results to the standard two-cell ultracapacitor test fixture.

Coin cells can be assembled in several configurations. Variables include number of springs, spring orientation, and location. Spacer thickness is also a variable, however making spacers too thin can result in deformation of the spacers resulting in uneven contact between electrodes, current collectors, and the case. The easiest method to increase internal pressure is using additional springs during cell assembly. However, adding more springs does not linearly add more force. For each additional spring, the

Fig. 1 Performance versus compressive force for DLC30 (*top*) and YEC7 (*bottom*)



spacing within the case is reduced and the distance the springs are compressed is increased. If springs are compressed past their yielding point, the force from each spring will be reduced. Adding too many springs will actually result in less force on the ultracapacitor stack. Another variable was the flexing of the coin cell case—as more springs were added, the case bowed outward increasing the area inside the case and partially offsetting the reduced spacing because of the additional springs.

To determine the optimum number of springs, the force required to compress each spring for various displacements was measured. Coin cells were then assembled to determine the actual displacement that the springs are subjected to inside the cell for the various spring configurations. As more springs were added to the cell, the greater internal force from the additional springs resulted in the cell case deforming or "bowing" outward. The distance that the springs were compressed for each configuration was calculated by measuring the outside thickness of the assembled coin cell and subtracting the thickness of the internal cell components as measured prior to assembly. Finally, the force exerted by the spring(s) was calculated for each configuration based on the number of springs, the distance the spring(s) were compressed, and the force exerted by each spring from the spring load displacement curves. Coin cell ultracapacitors with 2, 3, and 4 spring configurations confirmed the calculated data.

2.3 Electrode assembly and instrumentation

The activated carbons were assembled into electrodes by mixing with 5 wt% polytetrafluoroethylene binder (PTFE 60% dispersion in H_2O, Sigma-Aldrich). The mixture was homogenized in an agate mortar, formed into electrodes by rolling the activated carbon/PTFE mixture into sheets of the desired thickness, and finally by punching out 1.6 cm diameter disks. The two electrode test cell assembly is made of two current collectors, two electrodes, and a porous separator (Celgard 3501). The collector material was from Intelicoat Technologies—a 13-μm-thick aluminum foil with a conducting carbon coating. The compression tests used a cell assembly that was supported in a test fixture consisting of two stainless steel (SS) plates fastened together using threaded bolts. Spacers (PET, McMaster

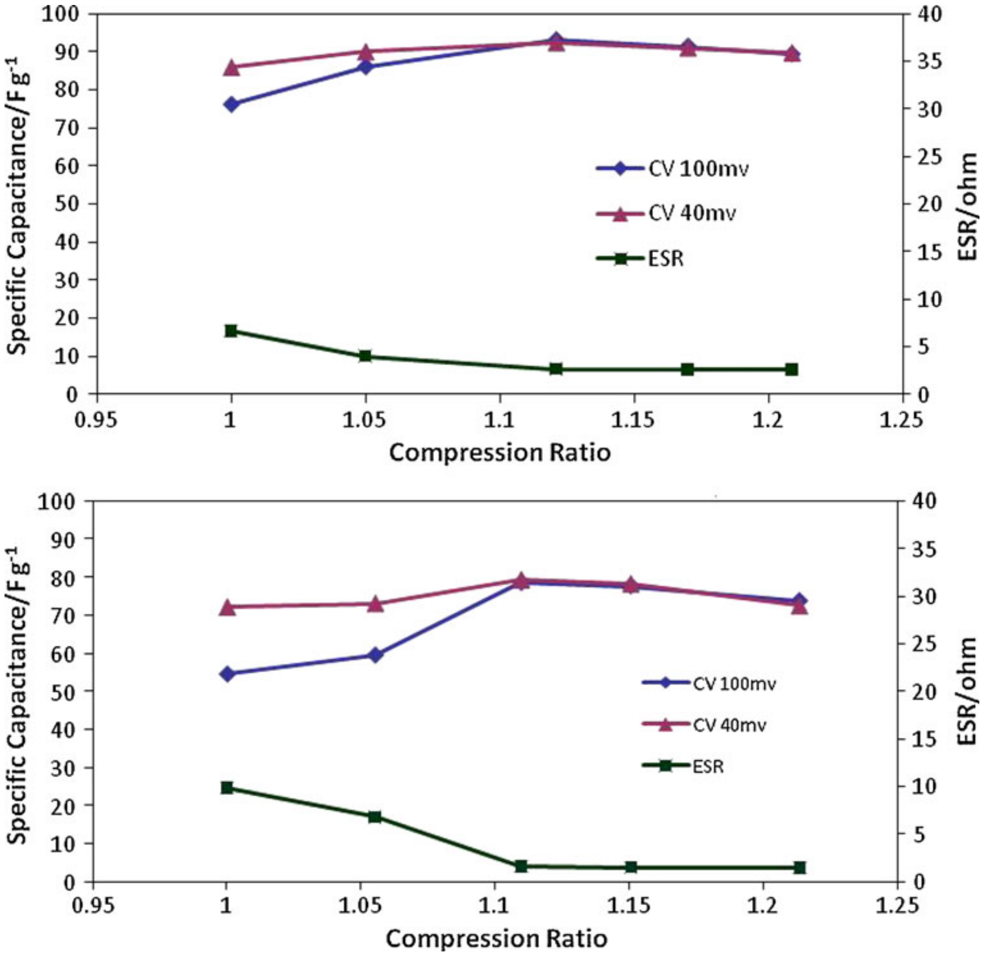


Fig. 2 Performance versus compressive force for YEC7 40-μm-thick electrodes (*top*) and DLC30 with 10% carbon black (*bottom*)

Carr) were placed between the SS plates to electrically isolate the plates, provide a hermetic seal, and maintain a consistent, even compression on the cell stack. A micrometer (Mititoyo, 1 μm resolution) was used to measure the distance of the assembly to determine cell thickness during compression testing. Electrolyte was prepared using 1 M Tetraethylammonium tetrafluoroborate (TEA BF_4, electrochemical grade $> 99\%$, Sigma-Aldrich) in acetonitrile (anhydrous, 99.8%, Sigma-Aldrich).

Cyclic voltammetry (CV) curves and galvanostatic charge/discharge testing was done with an Eco Chemie Autolab PGSTAT100 potentiostat equipped with the FRA2 frequency response analyzer module and GPES/FRA software. CV curves were scanned at voltage ramp rates of 40 and 100 mV per second. EIS was done using a sinusoidal signal with mean voltage of 0 V and amplitude of 10 mV over a frequency range of 500 kHz to 0.01 Hz. Capacitance values were calculated for the CV curves by dividing the current by the voltage scan rate, $C = I/(\mathrm{d}V/\mathrm{d}t)$. Specific capacitance reported is the capacitance for the carbon material of one electrode (Specific capacitance = capacitance of single electrode/weight of activated carbon in a single electrode), as per the normal convention.

BET specific surface area was measured by nitrogen adsorption using a Quantachrome Instruments Nova 2000. Spring load displacement testing was performed on a Deben Microtest MTEST300 tensile loading stage from Gatan USA fitted with a 200 Newton (N) load cell. CR2032 coin cell cases were used for all testing and are nominally of 20-mm diameter by 3.2-mm thickness.

3 Results and discussion

Figure 1 shows how the measured performance of a two-electrode ultracapacitor cell varies with pressure for the two carbons. The graphs show that, in general, the measured ultracapacitor performance increases (specific capacitance increases and ESR decreases) as pressure is applied up until approximately a ratio of 1.2–1.3 upon which additional pressure causes the specific capacitance to begin decreasing. This could be due to the electrode material collapsing making it increasingly more difficult for the electrolyte to access the pores [2], or due to the separator material distorting and preventing good ionic conduction of the electrolyte. At less than optimum

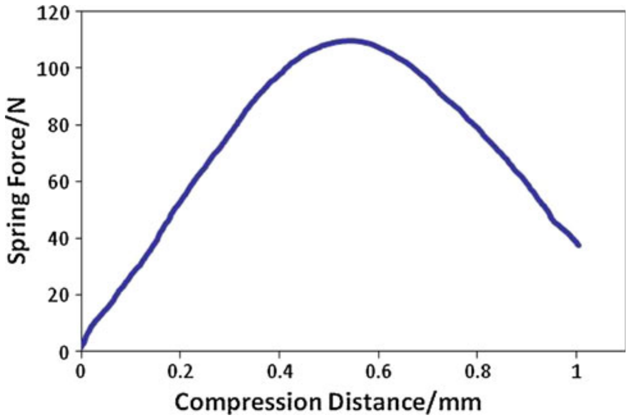


Fig. 3 Spring force displacement curve

pressure, measured specific capacitance is lowered by more than 50%, especially for the less conductive DLC30 carbon. As expected, for low pressures (and higher ESRs) the drop in measured capacitance is more pronounced at the higher scan rate. The addition of conductive carbon can reduce the overall ESR within the electrode and will help reduce measurement errors because of inadequate pressure exerted upon the cell. Figure 2 (bottom) shows DLC30 activated carbon with 10 wt% carbon black added to the electrode. Both ESR and specific capacitance are dramatically improved at the lower compression ratios with the addition of conductive fillers and electrode thickness optimization. Our tests showed that the optimal electrode thickness was specific to each carbon and was 80 µm for DLC30 and 40 µm for YEC7. The reason for the dependence of optimum electrode thickness may be due to particle size and distribution, conductivity, etc., and will be the subject of a separate study. Figure 2 (top) shows YEC7 activated carbon with 40-µm-thick electrodes. As with the addition of conductive fillers, the thinner electrode showed less degradation in measured performance at lower cell pressures. The results show that optimized electrode thickness and adding conductive fillers changes the optimum compression ratio from over 1.2 to approximately 1.1. The application of these strategies are very important when using test fixtures such as coin cells that lack the ability to control and exert adequate force upon the ultracapacitor cell stack.

Table 1 Calculated force for each spring configuration

Number of springs	Spring displacement (mm)	Force per spring (N)	Total force (*N*)
1	0.77	87	87
2	0.52	109	218
3	0.75	93	279
4	0.87	64	256

Table 2 Measured performance for each spring configuration for DLC30

Number of springs	Specific capacitance (F g^{-1})		ESR (ohm)
	40 mV s^{-1}	100 mV s^{-1}	
1	71	57	16.1
2	73	64	11.2
3	78	73	3.7
4	70	63	3.8

Without modification, coin cells do not provide the necessary force for accurate ultracapacitor measurements. Our testing does show that pressure can be improved in the coin cells by using additional springs. Figure 3 shows force (N) exerted to compress each spring (displacement in mm). From the graph, Hooke's law is observed up to a displacement of approximately 0.5 mm. Above 0.5 mm, the spring exceeds its elastic limit with decreasing force required for additional compression. This shows it is important to not over-compress the springs. or the result will actually be a reduction rather than an increase in force. The results from calculating the internal force (Table 1) show that the cell configuration with three springs exerts the highest total force upon the cell stack. Finally, the actual, measured results of DLC30 with conductive filler (Table 2) show that indeed, three springs give the best measured performance, correlating to the predicted results from the spring force measurements. The measured results using the optimized coin cell configuration are comparable to measurements using the specialized ultracapacitor test fixture.

4 Conclusion

Owing to increasing electrical energy-storage needs, ultracapacitor research has dramatically increased in recent years. Coin cells have long been used for battery electrode testing, and many research groups would like to apply their existing equipment and cell components for ultracapacitor research. However, ultracapacitor testing has different requirements than batteries, which in turn places different requirements upon test components. The primary difference is the rate of charge/discharge, which in turn requires a low internal resistance within the test cell for ultracapacitor testing. Increased pressure upon the cell stack is one method of controlling the resistance between cell components, as well as the addition of conductive fillers to electrodes. We have shown that the force exerted by typical battery coin cell components is not sufficient, resulting in inaccurate electrode performance measurements. However, with only modest modifications, in this case by increasing the number of springs, the addition of conductive fillers, and optimizing electrode thickness, coin cell measurements can match those of specialized test fixtures and of packaged cells.

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