

Characteristics and performance of 500 F asymmetric hybrid advanced supercapacitor prototypes

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Abstract

Nonaqueous asymmetric hybrid electrochemical supercapacitors using a nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode and an activated carbon cathode were built. Thin prismatic prototypes were made in the same technology as plastic Li-ion batteries. The 500 F devices had a usable packaged specific energy of 11 Wh/kg, with a specific power of 800 W/kg at 95% efficiency, and a matched impedance power of 4000 W/kg. The cycle-life ranged between 10,000 and 100,000 cycles depending on cycling conditions. The appropriateness for automotive applications was evidenced by the study of several typical examples.

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1. Introduction

Global warming, oil dependency and urban pollution are just a few examples of the urgent need to shift from an oil-based economy to an electricity-based civilization. Transforming natural energy such as wind, tides and solar energy can generate large amounts of electricity. However, man has limited control over natural phenomena, and therefore, needs to store the generated electricity for future use. In some instances, a large amount of energy can be released in a very short time, so the energy storage device must be able to absorb that energy fast and with good efficiency. At the same time, there is a need for mobile power sources that are lighter and smaller than batteries, while capable of delivering high-power. Carbon/carbon double-layer capacitors (supercapacitors) are already a proven solution to complement batteries. However, their energy density is still considered as too low for applications such as automotive. For instance, the US Department of Energy has set a goal of 7.5 Wh/kg at 625 W/kg for its PNGV power assist program. Although, supercapacitors can meet the power goal without difficulty, none of them has yet reached the energy goal, with the best commercial cells storing about 3.5 Wh/kg of useful energy

[1]. Telcordia Technologies has created a nonaqueous asymmetric hybrid supercapacitor that has three to four times the energy density of carbon/carbon supercapacitors. This was made possible by replacing the activated carbon anode by a newly developed nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ intercalation active material [2] that combines fast intercalation capability and long cycle-life, the latter due to the material's zero strain behavior upon lithium intercalation [3]. A variant of the device may also include the use of a pseudocapacitive conductive polymer cathode such as poly(fluorophenylthiophene) [4]. The energy density improvement (both gravimetric and volumetric) results from two effects: the average voltage of the device is raised from 1.5 to 2.25 V due to the flat low voltage profile of the anode material. Also, the anode is lighter and thinner than an activated carbon anode of same capacity, and requires the use of a smaller amount of electrolyte. The result is an asymmetric hybrid supercapacitor with about half the thickness and half the electrolyte content of the same capacity carbon/carbon supercapacitor, because it contains only one activated carbon positive electrode. The concept, already demonstrated at the fundamental level, is now in its development and commercialization phase. For demonstration purposes, large prototypes have been developed at Telcordia, and the present paper will present their full characteristics, covering the practical aspects of their manufacturing, as well as their behavior in a wide range of conditions.

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2. Experimental

Commercial nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (recently released by FMC) was mixed with Super P conductive carbon (MMM), poly(vinylidene-hexafluoropropylene) (Atofina), propylene carbonate (Aldrich) and acetone. The slurry (~ 2 l) was homogenized in an air-driven mixer, and cast on a Pereny caster, using a Mylar carrier film. For preparation of the cathode, activated carbon was used instead of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. After acetone evaporation, the electrodes were stored on a 12" wide roll. Current collectors were aluminum foils and expanded grids, etched in NaOH solution and painted with commercial adhesive coatings (Acheson Co.), aimed at reducing the impedance and improving the electrode-collector bond. Electrodes with their PC plasticizer were bonded to the aluminum current collectors by hot-lamination under pressure. From the electrode-collector laminates, 6" \times 4" anode and cathode pieces were cut and bonded to 25 μm thick surface-modified microporous polyolefin separators (Celgard) by hot-lamination under pressure. The bicell structure was used, e.g. two cathodes shared one anode and its current collector, thus saving the weight of one current collector. The cell assemblies were dipped for 30 min in ether for plasticizer extraction, dried in a 60 °C oven for 1 h, checked for shorts, then connected in parallel using an Amtech Ultraweld ultrasonic welding machine. External nickel current collectors were ultrasonically welded to the aluminum tabs. The cells were then packaged in multilayer nylon/Al/PE housing (Dai Nippon), and further dried for 12 h at 75 °C under vacuum in the antechamber of an He-filled glove-box (VAC). Under inert He atmosphere, CH_3CN , LiBF_4 2 M electrolyte (Ferro,

<20 ppm H_2O) was injected in the cells, followed by sealing them. Formation and testing of the cells was performed on a Maccor battery cycler. After formation, cells were degassed and labeled. Impedance analysis was done with a Solartron SI 1260 analyzer and Zplot software.

3. Results and discussion

3.1. Prototype description

Most of the cells described in this study were 500 F 1.9 mm thick prismatic units of 6" \times 4" made of two bicell plates connected in parallel, such as the one shown on Plate 1. Their product datasheet is summarized on Table 1.

The discharge voltage profile of a prototype cell at currents ranging from 4 to 40 A is shown on Fig. 1. The insert shows that the capacitance is not constant during discharge. The 500 F is the average on the whole voltage range, while the maximum capacitance measured at 2.5 V is around 1000 F. The internal resistance of the device also increases during the course of the discharge, due to the delithiation of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode that becomes less conductive. Therefore, although the cycle-life and power capabilities are in the range of supercapacitors, the electrochemical response is closer to that of a battery.

3.2. Formation and higher voltage limits

The maximum voltage of the device was determined in order to maximize its energy and power density, while

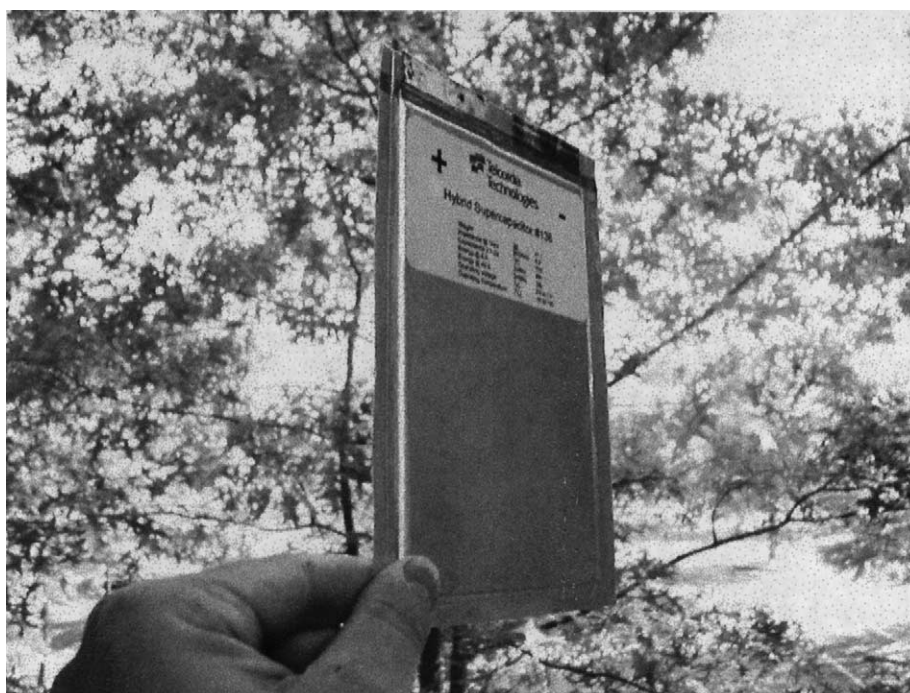


Plate 1.

Table 1
Physical and electrochemical characteristics of the 500 F Telcordia asymmetric hybrid prototypes

Device	Telcordia hybrid
V_{rated}	2.8
C (F)	500
ac R (m Ω) @ 1000 Hz	7.7
dc R (m Ω)	11
RC (s)	5.5
Wh/kg ^a	10.4
W/kg (95%) ^b	793
Matched impedance power (W/kg)	4173
Weight (kg)	0.043

^a Energy density at 400 W/kg constant power, $V_{\text{rated}} = (1/2)V_{\text{rated}}$.

^b Power based on $P = 9/16(1 - EF)V(2/R)$, EF = efficiency of discharge.

minimizing its impedance increase and gas generation. The activated carbon positive electrode may undergo electrolyte oxidation at high voltages, due to its large BET specific surface area. This results in gas byproducts, and the formation of a resistive film on the carbon, causing impedance increase. In order to determine the maximum voltage of the device, cells were held for 20 h at 2.7, 2.8, 2.9 and 3.0 V. The impedance values at 1000 and 0.1 Hz were plotted as a function of the voltage. There was no noticeable impedance increase up to 2.8 V, but impedance at 1000 and 0.1 Hz increased for 2.9 and 3.0 V (Fig. 2). In another set of experiments, four cells were held for 4 h at 2.7, 2.8, 2.9 and 3.0 V. Their Ragone energy versus power characteristic was then measured, and this procedure was repeated several times. It was observed that up to 2.8 V, the Ragone curves

remained the same, while for 2.9 and 3.0 V, the energy and power gradually decreased after each cycle of holding the cells at constant voltage (Fig. 3). From these two sets of experiments, 2.8 V was set to be the maximum voltage for the hybrid device and this type of carbon, ensuring a better stability of the impedance over time. Thus, newly made cells were subjected to a formation cycle, which consisted in holding them at 2.8 V until the leakage current was <5 mA. This usually occurred within few hours. Cells that remained at a higher than 5 mA leakage current were rejected. The kinetics of self-discharge was recorded for cells having <5 mA leakage current, and after 200 h of open-circuit, cells still retained 60% of their original capacity, measured by fully discharging them (Fig. 4).

3.3. Energy and power

There are several ways to measure the energy and power of a supercapacitor, and it is always important to specify in which conditions those measures are taken. In particular, constant current and constant power discharges can give different results. Also, the rate of charge may affect the discharge energy, and of course, the voltage limits have a direct effect on the values measured.

In the case of the hybrid device, the formula $E = (1/2)CV^2$ cannot be used, because the capacitance is not constant during the whole discharge. Another important consideration is the effect of packaging: the weight fraction of packaging material is a function of packaging technology, and also device size, where larger size devices use a lower weight fraction of packaging material. Ambiguity can be

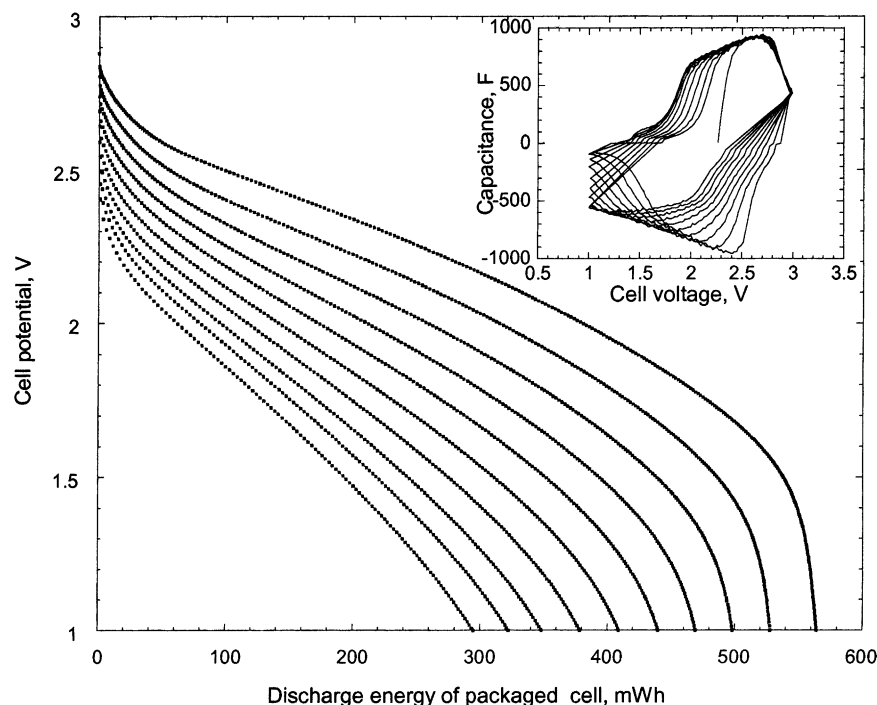


Fig. 1. Discharge voltage profile vs. energy and differential capacity vs. voltage (insert) for a 500 F hybrid cell discharged at currents ranging from 4 to 40 A.

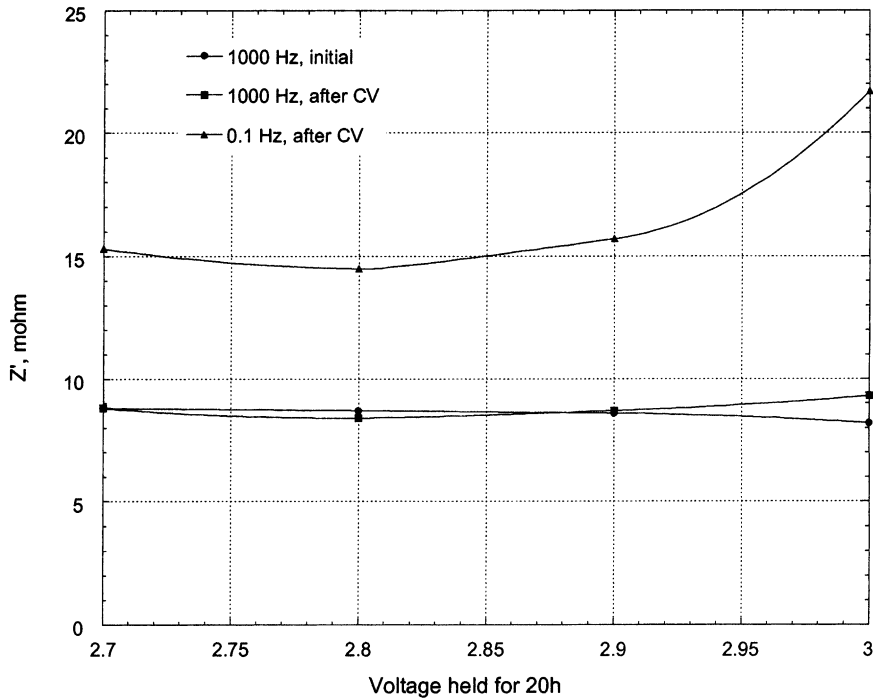


Fig. 2. Impedance changes after holding hybrid cells at various constant voltages for 20 h.

avoided giving energy and power values for both packaged and bare cells. To improve the energy density of packaged prototypes, we packaged two bicell plates. Fig. 5 indicates how the energy density of a 6" × 4" device increases when the number of packaged bicell plates increases. In the most favorable case, e.g. a voltage window of 3–1 V, a slow

constant current discharge and an unpackaged cell, the measured energy is 17 Wh/kg. If measurements are done at constant power, such as recommended by Burke [5], in a voltage window of 2.8–1.4 V, based on the total weight of a device containing two bicells, the measured energy is 11.8 Wh/kg at 669 W/kg (Fig. 6). A commercial carbon/

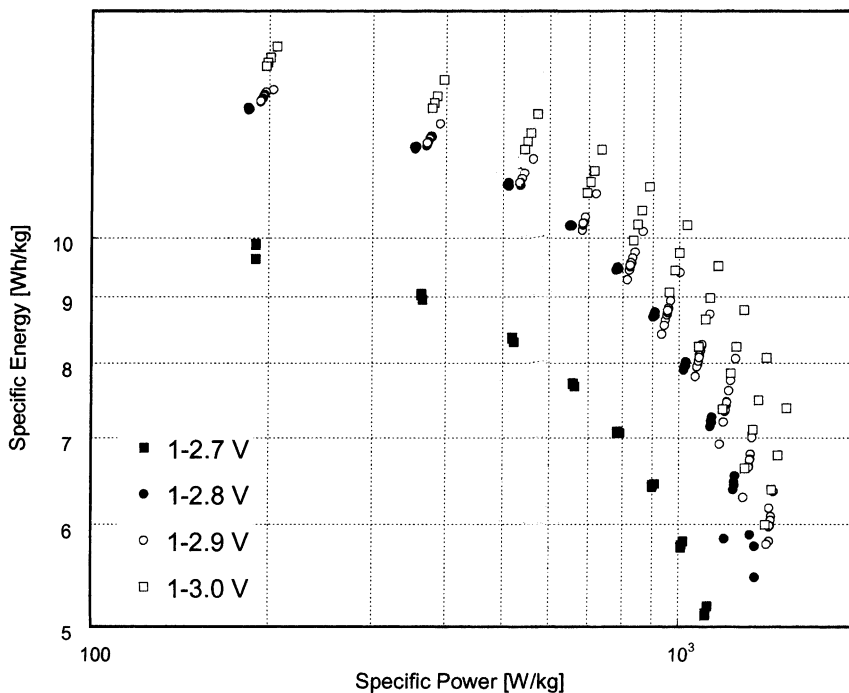


Fig. 3. Ragone plots of hybrid cells repeatedly held for 4 h at various voltages.

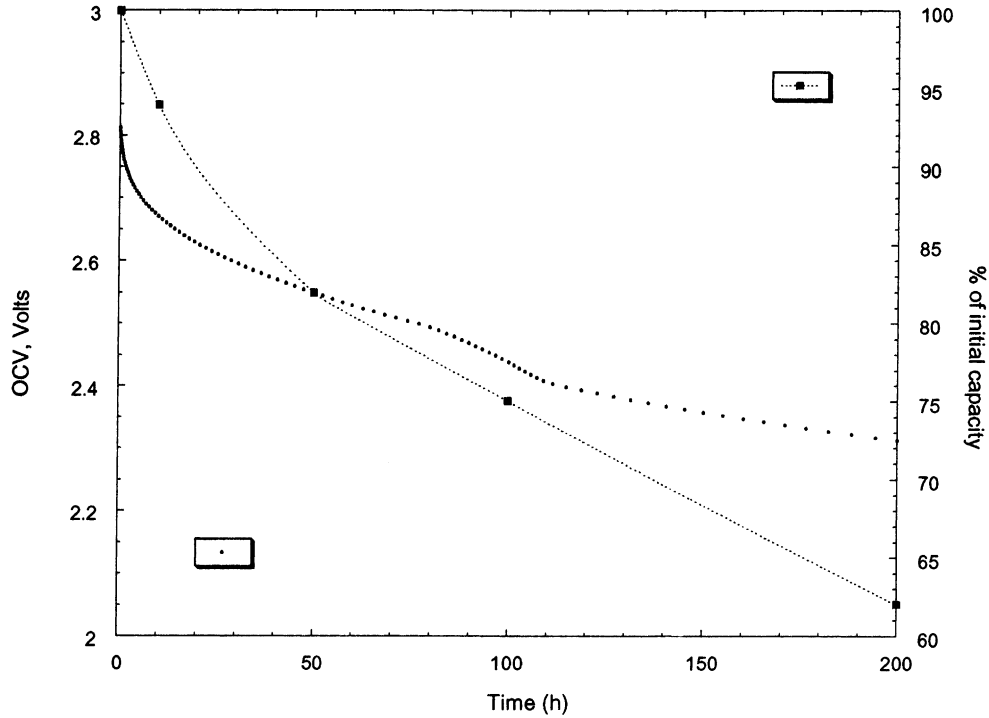


Fig. 4. Capacity change of hybrid cells after various times of open-circuit storage.

carbon supercapacitor would give 2–3.5 Wh/kg of energy if measured under the same conditions. In general, we found that decreasing the electrode thickness did not significantly improve the power capability, but rather lowered the energy density. However, for low temperature operation, where ionic diffusion in the electrodes becomes the limiting factor,

it is advantageous to have thin electrodes. This results in less energy and power losses when operating at low temperature. For instance, a hybrid device made with thin electrodes and delivering 7.5 Wh/kg at 1000 W/kg and 20 °C still delivers 6 Wh/kg at 1000 W/kg and –30 °C (Fig. 7). Also important is the effect of charging rate. As opposed to carbon/carbon

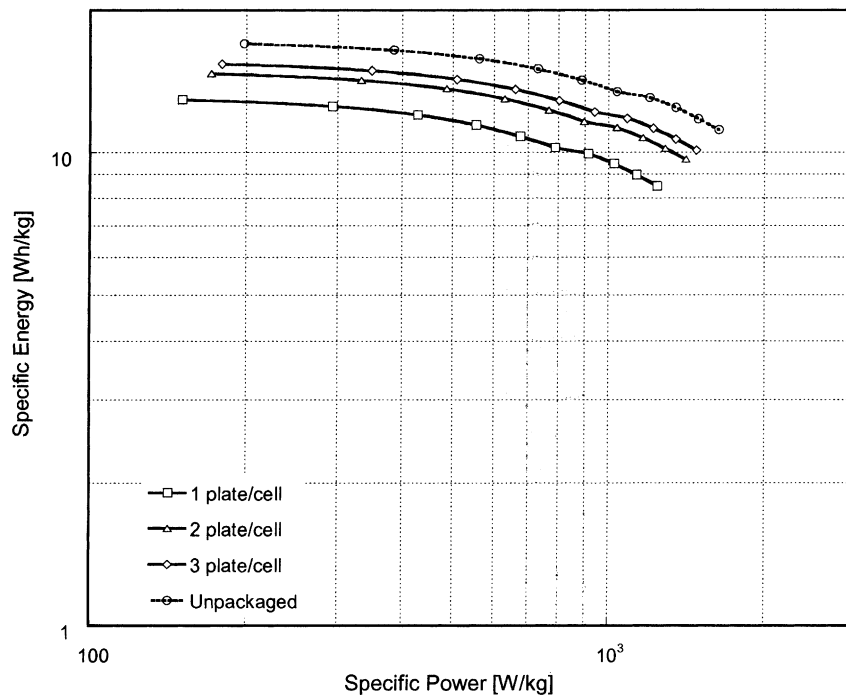


Fig. 5. Ragone plot at constant current discharge (between 1 and 3 V) as function of the number of packaged bicell plates.

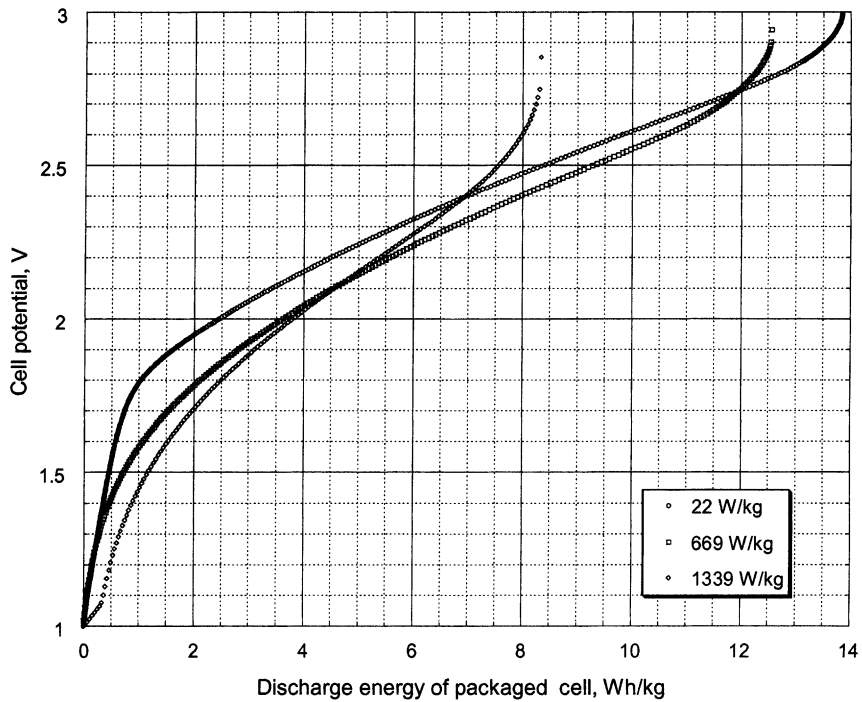


Fig. 6. Specific energy of hybrid cells as function of maximum voltage at various discharge powers.

supercapacitors, the asymmetric hybrid device cannot be charged as fast as it can be discharged. This is because during charge, the intercalation of lithium in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode is diffusion limited, while its deintercalation during discharge is not. Fig. 8 shows the effect of charging fast and

discharging slowly, as opposed to charging slowly while discharging fast. For the same charging rate, we consistently found that the discharge energy was slightly lower at constant power than at constant current (Fig. 9). A similar effect has been observed in carbon/carbon supercapacitors.

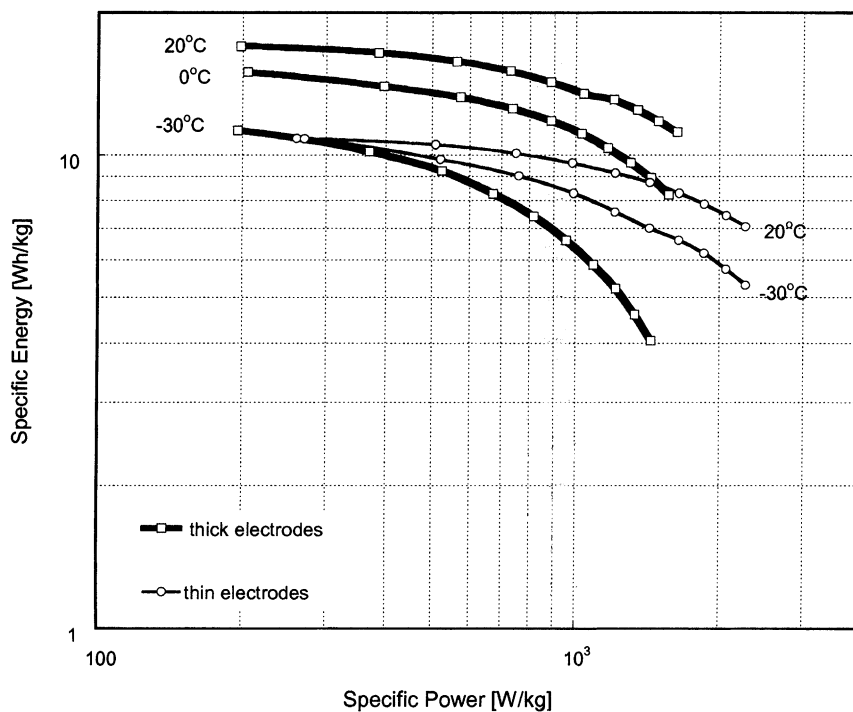


Fig. 7. Ragone plots (between 1 and 3 V) of hybrid cells made of thick or thin electrodes (250 F vs. 500 F cells) at various temperatures.

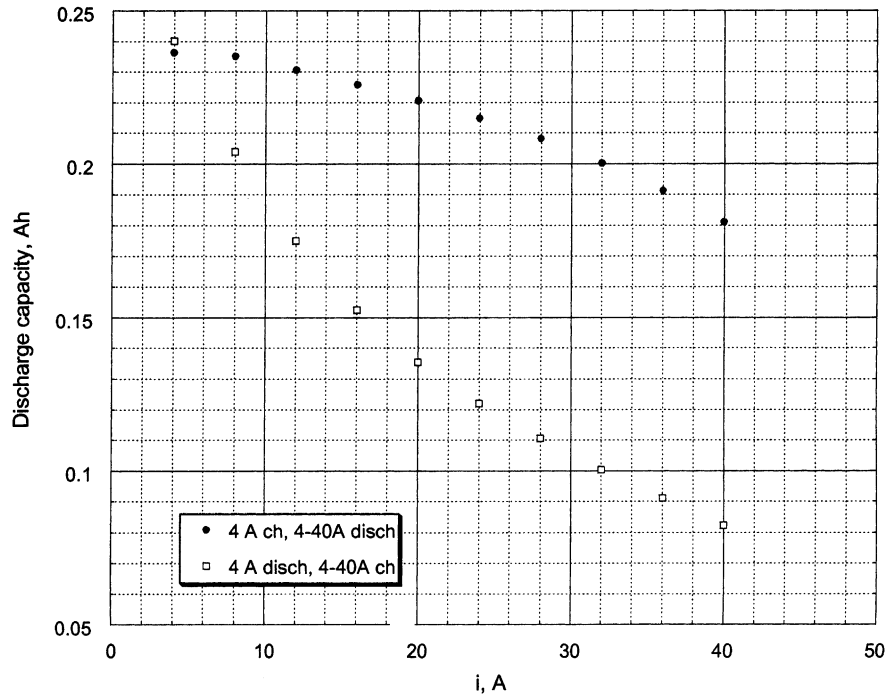


Fig. 8. Hybrid device capacity at constant charge and increasing discharge currents, or constant discharge and increasing charge currents.

3.4. Automotive application

The introduction of 42 V system in automobiles was made necessary by the adoption of new power-hungry devices aimed at increasing comfort and decreasing pollution caused by automobiles. One good example is the integrated starter-

alternator, which in one mode of operation automatically stops and restarts the engine at every stoplight or when the vehicle is at rest. This requires an energy source capable of fast recharge, long cycle-life, and high-power delivery over a very short time. Supercapacitors are best suited for this type of operation. Knowing their time-constant τ , voltage swing

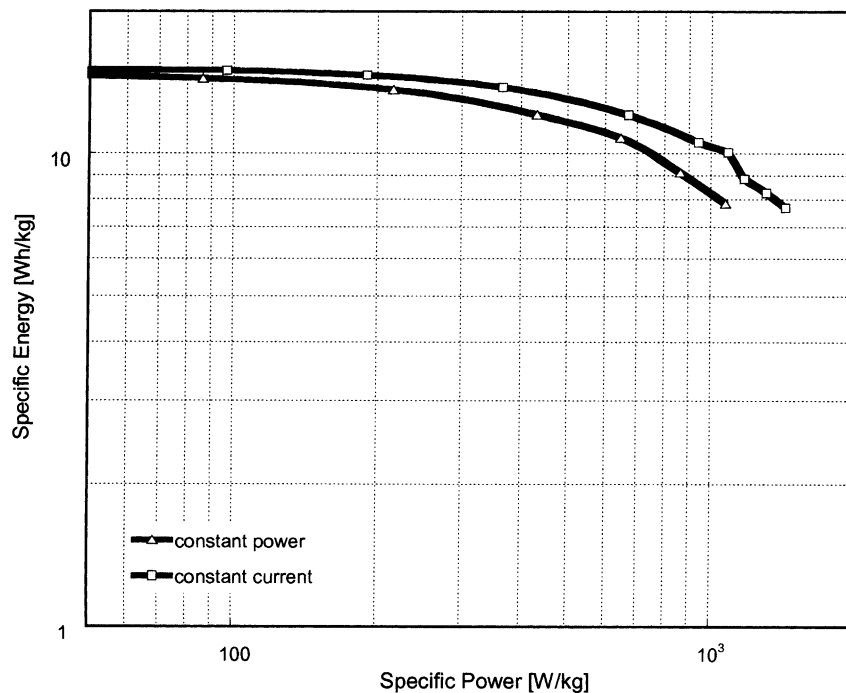


Fig. 9. Ragone plot (between 1 and 3 V) of same device charged at constant current, discharged at either constant current or constant power.

dU and resistance R , the capacitance C required for a given pulse of average current i can be calculated from the following equation:

$$dU = \left(\frac{i}{C} dt \right) + Ri = \frac{i}{C} (dt + \tau) \tag{1}$$

For instance, restarting an automobile engine could require a 5 kW pulse for a duration of 4 s. Assuming an allowable voltage swing of 42–30 V for the system, the average current would be 143 A, and the energy consumed by the pulse 5.6 Wh. We can compare the weight needed using either a 3.5 Wh/kg carbon/carbon supercapacitor having a 1 s RC time-constant, or roughly estimate the weight of a 10.4 Wh/kg hybrid having a 5.5 s RC time-constant, in order to make a 42 V pack capable of delivering the required power:

	Voltage/ cell	Wh/kg	RC (s)	F/pack	Pack weight (g)	#Cells
Carbon/ carbon	2.5	3.5	1	60	3228	17
Hybrid	2.8	10.4	5.5	113	1202	15

The use of the hybrid would therefore allow very significant weight saving, as well as volume saving and a lower number of cells required to be connected in series. Furthermore, the actual savings may be even better, because the

formula used here only applies to ideal capacitors having a constant value of the capacitance. In the case of the Hybrid, the capacitance required for the pack is an average, meaning that the peak capacitance of the pack may be twice that average. Thus, the weight calculated to deliver the pulse is the worst case scenario. To illustrate this, we calculated the duration of discharge for a 500 F carbon/carbon supercapacitor, considering an RC time-constant of 1, 5, 10 and 15 s. This was done for discharge powers of 10, 20, 40 and 50 W. The real data measured from discharging a 500 F hybrid device in the same range of constant powers was also plotted. It can be seen that the values calculated by (Eq. (1)) underestimate the real time of discharge (Fig. 10). However, for very short discharge times (<10 s), it appears that carbon/carbon devices would be more efficient, due to their lower time-constant. So, the hybrid device, in its present state of development, fits best for high-power applications that require discharge times ranging from several minutes to 10 s. This is perfectly suited for acceleration of the vehicle, or 10 cranking of the engine without recharge latency. Furthermore, lower time-constants can simply be achieved by decreasing the thickness of the electrodes.

3.5. Cycle-life

Cycle-life, as energy and power, is a function of temperature, maximum and minimum voltage, and rate of charge–discharge. In a first set of experiments, hybrid cells were cycled at constant current, with a maximum voltage of

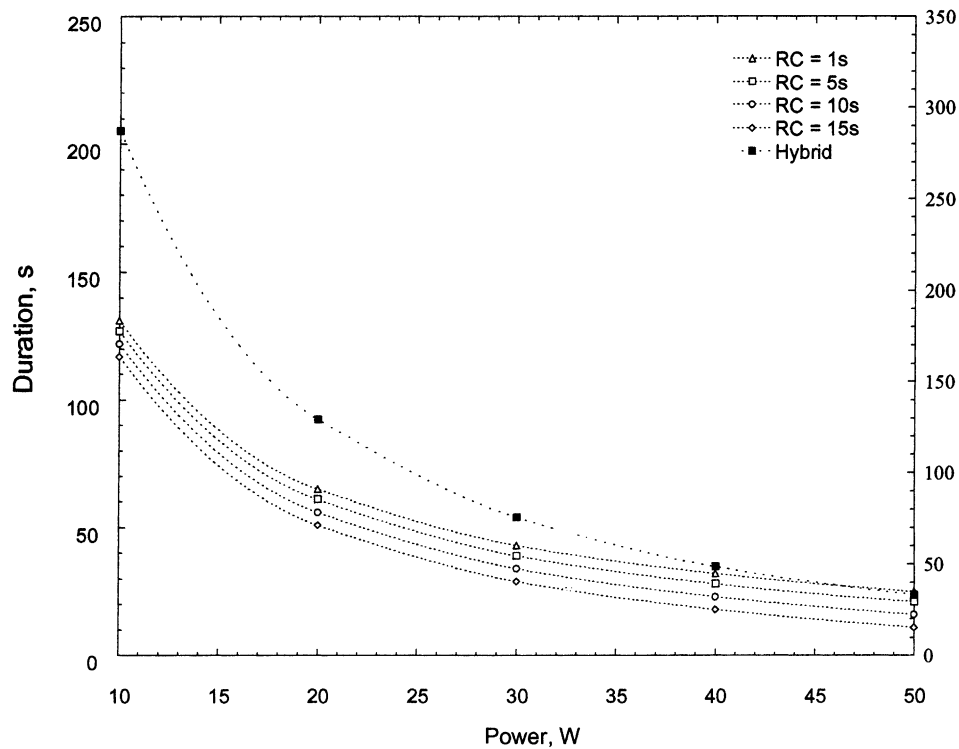


Fig. 10. Discharge time vs. discharge power calculated for 500 F carbon/carbon supercapacitors of various RC time-constants, and experimental data from a 500 F hybrid device.

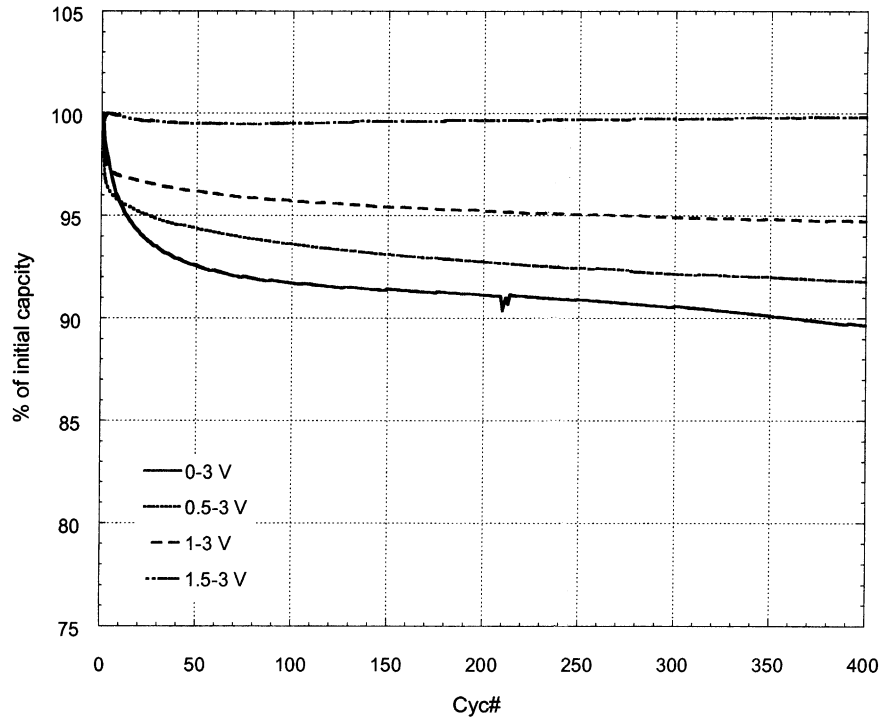


Fig. 11. Cycling of hybrid device at 3.0 V maximum voltage and various minimum cutoff voltages.

3.0 V, and a minimum voltage of 0, 0.5, 1.0 or 1.5 V. It was observed that some capacity fade appeared when the cutoff voltage was lower than 1.5 V, and increased when the cutoff voltage decreased (Fig. 10). From this study, a minimum voltage of 1.0 V was set for the hybrid device operation. At

low to moderate discharge power (<500 W/kg), we found a capacity loss to be quasi null, and a predictable cycle-life superior to 100,000 cycles (Fig. 11).

In more strenuous conditions, e.g. 120 s and tapering at 2.8 V charge and 625 W/kg discharge, some capacity fade

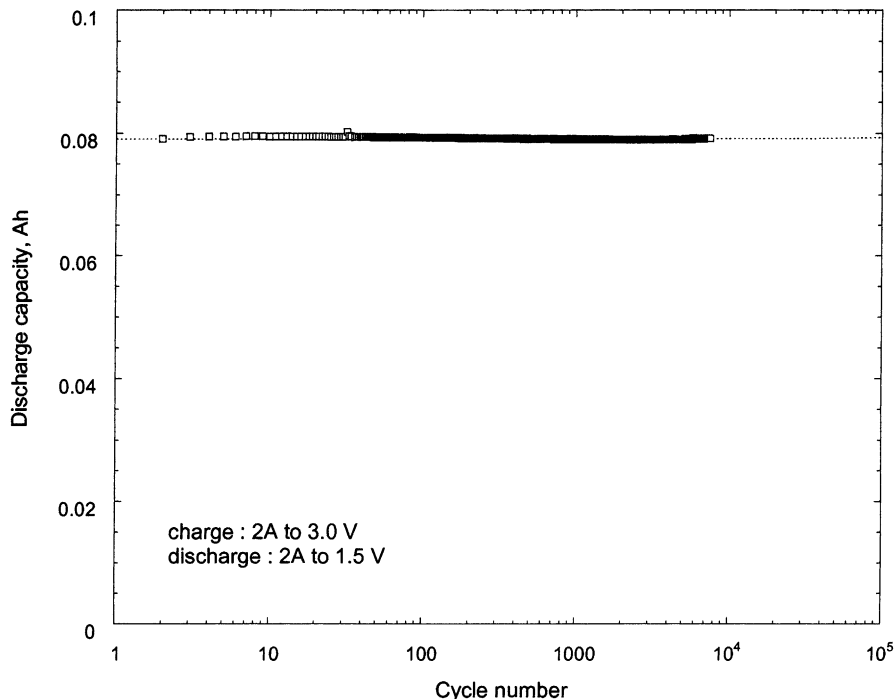


Fig. 12. Long-cycling of a 80 mAh hybrid prototype, at 2 A charge and discharge currents, between 3.0 and 1.5 V.

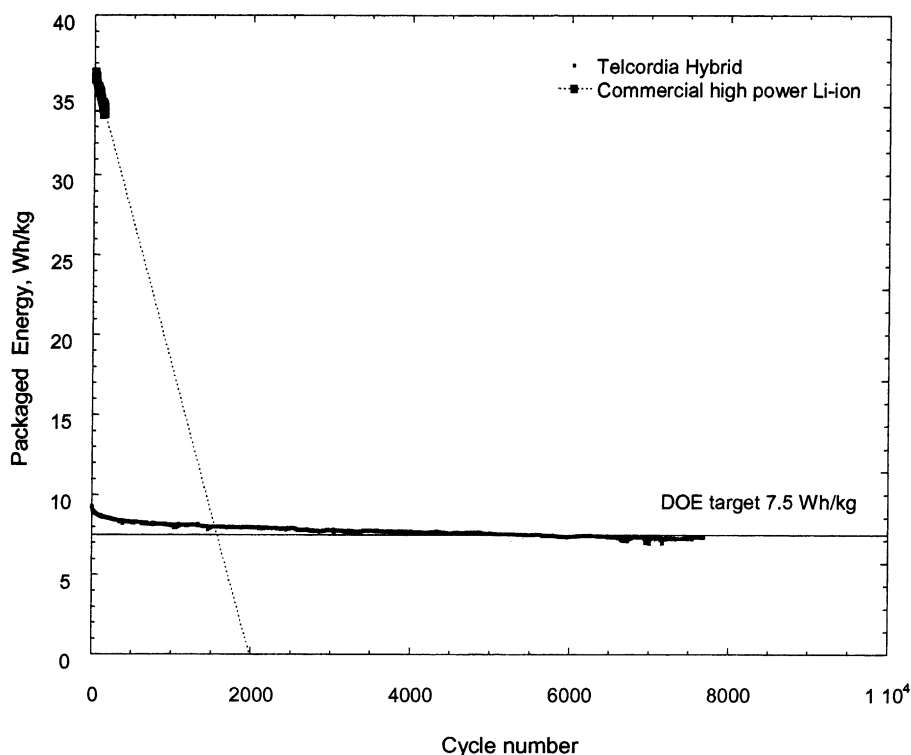


Fig. 13. Long-cycling of a 500 F hybrid prototype at 10 A then 2.8 V to 0.2 A charge, 625 W/kg to 1.4 V discharge.

was observed, and the observed cycle-life was 10,000 cycles. It should be noted however that the initial gravimetric and volumetric specific energies of 9.3 Wh/kg and 13 Wh/l were higher than those required by the US Department of Energy in the Partnership for New Generation of Vehicles (PNGV, now referred to as FreedomCAR) (Figs. 12 and 13). Those requirements, of 7.5 Wh/kg and 9.38 Wh/l at 625 W/kg, are easy to outperform with the present hybrid prototypes. The use of thinner electrodes would result in a better cycle-life, while still meeting those goals. For comparison, the cycle-life of a high-power Li-ion cell is also reported. The cell was also fully discharged at 625 W/kg, but had to be charged at slower rate than the hybrid cell (1 C). If the initial energy is higher (around 37 Wh/kg at this high discharge rate), it can be seen that the rate of energy fade is greater than in the case of the hybrid device. Basically, the energy of the Li-ion cell would be the same as the hybrid after only 1500 cycles.

4. Conclusions

The concept of a nonaqueous asymmetric hybrid device utilizing intercalation and double-layer electroactive mate-

rials was scaled to 500 F plastic matrix bonded prototype devices to evaluate its performance as an energy storage device. The prototypes demonstrated energies of 10.4 Wh/kg that outperform three to four times those of carbon/carbon commercial supercapacitors, while maintaining similar power densities. Cycle-life is higher than Li-ion batteries, approaching that of supercapacitors thereby dispelling the preconceived notion of the limited cycle-life for intercalation compounds. Although in its infancy, the technology presents a solid foundation opening a pathway to improved performance through advancements in electroactive materials, engineering, and design.

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