Use of Reticle Carbon in Supercapacitors

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ABSTRACT

Supercapacitors can be used to augment chemical batteries, in rapid-pulse battery rechargers, with fuel cells, electric motors, turbines, computers and in many other applications. Inasmuch, Reticle Carbon, an inexpensive, high surface area carbon, may lead to a resurgence of interest in electric double-layer (EDL) supercapacitors. Reticle Carbon is a unique, consolidated material that has low electrical resistivities (0.04-0.130 Ω-cm), demonstrated high surface areas (1250-1750 m^2/g), and the highest reported specific capacitance (200-310 F/g). It is produced by consolidating granular activated carbon that has been selected for its properties. The manufacturing process is single-stage in which parameters can be varied to tailor the properties to make the perfect supercapacitor material. This paper shows the wide range of properties that the material possesses with the underlying theory to store energy in the massive available surface area of the material. We have demonstrated the energy storage and discharge capability of the material in leveling the electric load of a small electric motor.

Keywords: supercapacitors, carbon electrode, energy storage, load leveling

1 BACKGROUND

Capacitors are fundamental devices used in electric and electronic circuits. In their simplest form, capacitors use two plates separated by a distance. The concept is simple, just charge the plates and the energy is stored. The capacitance (C), a quantitative measure of energy storage capacity, has the standard unit known as a farad (F). Capacitors typically have high power densities in small bursts, they recharge and discharge very quickly (often in seconds), they can be cycled over 300,000 times without loss of capacity, and they cannot be overcharged.

As an example of the utility of these devices, let's look at electric motors. Engineers size a motor to the peak power output required for start-up, when the power demand to create momentum from a dead stop is greatest. After this initial surge requirement, the power draw is significantly lower to maintain the inertia. So what if you could attach a power supply on the side that could give that boost of energy required at start-up, but then shut off when not needed? The motor could be sized to the lower load—a concept known as load-leveling.

This is not a new idea, but the methods for supplying the extra energy for motor startups vary. Some use chemical batteries, while others use auxiliary motors that "kick in" when needed. Recently, the idea of large capacity energy storage devices (supercapacitors) has appeared as a logical solution.

While the load leveling concept for a motor is understandable, the same theory applies for any electrical or electronic device. For instance, computer hard drives and screens, CD-ROM drives, cell phones, DVD players, fans in furnaces and air conditioners, and refrigerator compressors are examples of things that operate in an 'on-off cycle' which could use this same type of energy storing device. Placing a small capacitor in computers, for instance, would reduce the high peak draw on the battery, which would extend its charge-life. On a larger scale, supercapacitors can augment solar panels, wind turbines or other intermittent power generation systems. Supercapacitors could be used to store this energy until peak demand (when most sources are not generating power.) Now all we need are reliable, high-capacity materials in capacitors that can store large amounts of energy. That is where Reticle Carbon can make a sea change in the technology.

2 RETICLE CARBON—THE ADVANTAGE OF SURFACE AREA

The unique properties of Reticle Carbon are the result of the patented manufacturing process and the precursor carbon properties. Reticle Carbon is manufactured from any granular activated carbon in a simple, one-step consolidation process. The process can be tailored to give Reticle Carbon unique properties, such as macroporosity ranging from 10-40%, electrical resistivity ranging from 0.04 – 0.13 Ω·cm, and thermal conductivity measured at a low 0.1 $^{W}/_{m\cdot K}$. However, the most unique property of the material is the demonstrated high surface areas, ranging from 1250 to over 1750 m^2/g. Compared with other activated carbon materials, this is an exceptionally high surface area range.

Samples of Reticle Carbon have been used to investigate improvements to capacitive energy storage, as well as many other applications. Laboratory and pilot-scale experiments have been performed using the material to desalinate, or deionize water, as well as recover metal from electrolytes. For these tests, several different samples of Reticle Carbon have been made with a wide range of surface areas as determined by BET method [1].

Table I shows the range of properties of Reticle Carbon compared with the properties of other materials being used in supercapacitors—Aerogel carbon (from Lawrence

Specific Attribute	Reticle Carbon Properties	Aerogel Carbon Properties [3-4]	Carbon Nanotube Properties [5-7]
Surface Area (m^2/g)	950 – 1750	100 – 800	125 – 250
Specific Capacitance (F/g)	80-390	100-180	30-90
Bulk Density (g/cm^3)	0.75 – 1.0	0.78	1.3 – 1.4
Est. Mfg. Cost	<$100/kg	$250/kg	>$10,000/kg

TABLE I: Range of properties of Reticle Carbon as compared with Aerogel Carbon and Carbon Nanotubes

Livermore National Laboratory) and carbon nanotubes (as those being studied at MIT). Although the performance of the carbon material is dependent on many properties, the surface area is the standard metric used to differentiate between the samples. Notice that Reticle Carbon has significantly higher proven surface areas than the other "best-in-class" materials, and at significantly lower estimated cost.

The importance of surface area can be illustrated by considering the electric double-layers formed at the solid-liquid interface [1]. The only way to increase the amount of ions in diffuse double-layers would be to (a) increase the charge of the solid (as by an applied potential), or (b) increase the surface area of the interface between the electrolyte and the solid. Both of these are easily accomplished with Reticle Carbon, which has the highest reported surface area and the highest electrical conductivity (inverse resistivity) reported for any activated carbon material.

Let's try to quantify this impact. Capacitance is defined by Equation (1) as:

$$C = \frac{\varepsilon}{4\pi d} \qquad (1)$$

where, C = capacitance per unit area (F/cm^2)
ε = dielectric constant of the medium
d = thickness of the double layer (cm)

Using typical values [2], Equation (1) can be used to calculate an average specific capacitance:

$$C = \frac{8}{4\times\pi\times(4\times10^{-8})}\times\left(\frac{10^6\,\mu F/F}{9\times10^{11}\,esu}\right) = 17.6\ \mu F/cm^2$$

This is in agreement with the reported range of 10 and 20 $\mu F/cm^2$ for carbon materials. Consider just 1-g of Reticle Carbon with more than 1250 m^2 of available interfacial surface area, or 12,500,000 cm^2. A simple capacitor with this material will have 220 F of total capacitance. One-gram of the 1750 m^2/g carbon will have over 300 F!

That is precisely the level of capacitance we have found in Reticle Carbon. Table II shows the properties of three Reticle Carbon samples manufactured from the same granular activated carbon precursor. Notice that the specific surface areas range from 930 to 1240 m^2/g (66-90% of the precursor area), while the specific capacitance of the material varied from 80 to 212 F/g. If we combine these values, the average specific capacitance was 15$\mu F/cm^2$, which demonstrates that nearly all of the available surface area contributed.

We have made and tested capacitors with Reticle Carbon (as diagramed in Figure 1). These simple devices are just sandwiches of the Reticle Carbon electrodes with an electrolyte permeating the space between them. The electrolyte can be any aqueous solution or conductive organic electrolyte. A glass wool separator is used to keep the electrodes from contacting each other. Graphite was the current collector used to attach the leads to the power source. We have measured 53 F/g specific capacitance in capacitors made from the Sample I carbon. This is outstanding considering the previous best-in-class Aerogel carbon electrodes have reported a 40 F/g specific capacitance [3]. Even higher capacitances will be achieved when we incorporate Reticle Carbon that has 1750 m^2/g. The capacitor was not optimized to minimize the overall weight, so we anticipate even better performance with higher surface areas and lower weight capacitors.

	Surface Area (m^2/g)	Mass Specific Capacitance (F/g)	Porosity (%)	Bulk Density (g/cm^3)	Electrical Resistivity (Ω·cm)
Sample I (light consolidation)	1238 ± 21	212	31.0	0.75	0.134
Sample II (moderate consolidation)	1026 ± 20	160	16.8	0.94	0.060
Sample III (heavy consolidation)	931 ± 15	80	11.9	1.05	0.047
Raw carbon (as received)	1400 ± 22	-	19.8	0.66	-

Table II: Range of properties of Reticle Carbon made from a single precursor carbon, demonstrating the flexibility of the manufacturing process.

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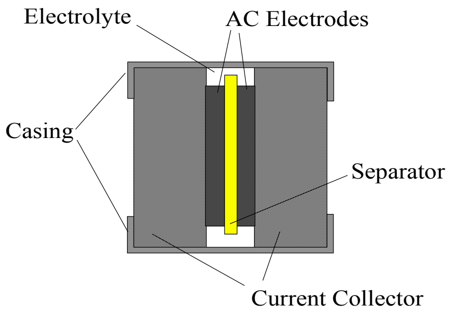

Figure 1. Schematic of the Supercapacitor Using Reticle Activated Carbon (AC) Electrode Material.

To understand the importance of this discovery, we can use the basic principles. The energy stored in a capacitor is defined in Equation (2):

$$w_c(t) = \int_{-\infty}^{t} v \cdot i \, d\tau \qquad (2)$$

Keep in mind that the voltage (v) and current (i) both vary with time in these cells. In fact, Equation (3) represents the time interdependence of both:

$$i = C\frac{dv}{dt} \qquad (3)$$

Combining (2) and (3), and assuming the capacitor is initially uncharged (that is, at t = -∞, v(t) = 0), we get the following:

$$w_c(t) = \frac{1}{2} C v^2(t) \qquad (4)$$

If the capacitance (C) is in farads, and voltage (v(t)) is in volts-DC, then the total energy stored ($w_c(t)$) will be in Joules. As shown in Equation (4), as the voltage changes (an implied current change will also occur, as well), the energy stored changes. But once the capacitor is charged at a specific voltage, the energy will not dissipate until the capacitor is connected to a resistance or load.

So for example, if we have a 1-F capacitor at 10-V, the energy stored would be:

$$w_c(t) = \frac{1}{2}(1)(10)^2 = 50\text{ J}$$

That means that this capacitor will store up to 0.014 W-hr of energy. Now let's look at 1-g of Reticle Carbon, with 212 F of capacitance and 1.5-V potential:

$$w_c(t) = \frac{1}{2}(212)(1.5)^2 = 238.5\text{ J} = 0.068\text{ Wh}$$

In other words, we have the potential for energy densities of 68 W-hr/kg of Reticle Carbon. If 1-g of graphite is used to make the current collectors, and 1 ml of aqueous electrolyte is used, the overall energy density of the entire device will be over 20 W-hr/kg of electrode, which is quite high. Because capacitors discharge their stored energy rapidly (often less than 3 sec), the estimated power density of these small units would be:

$$\frac{20\text{ Whr}}{3\text{ sec}}\left(\frac{3600\text{sec}}{\text{hr}}\right) = 24\text{ kW per kg of capacitor.}$$

Improvements to our capacitors will improve the amount of energy stored. Aqueous electrolytes are an obvious first target, although they are low cost, safe, available, and are adjustable with minor changes to salt concentrations. But it has an electrochemical restriction—at relatively low electrical potentials (above 1.5-V) water decomposes into gaseous hydrogen and oxygen. However, capacitors in series could handle much larger voltages and energy loads. If we could double the voltage to 3-V, we would have a four-fold increase in the energy density for the same material. There are many commercially available organic electrolytes that have relatively high decomposition potentials (>5-V) that may be considered. We have performed preliminary experiments and have not as yet found an organic that has sufficiently high ionic strengths to meet requirements of our capacitors. However, the possibilities for improvement are certainly endless for the energy storage of supercapacitors.

In a qualitative test, we incorporated a set of supercapacitors in a toy electric car (shown in Figure 2) to demonstrate load leveling of batteries. As you will notice, six "AA" batteries are required to operate the car under normal conditions—that's 9-V from the batteries in series.

As discussed earlier, the power required for starting the motor is significantly higher than the power required for constant driving conditions. So to show how our supercapacitor provides the "kick" at start up, we attached a supercapacitor rated at 4-V in parallel with the battery bank of the toy car as shown in Figure 3. The capacitor was actually two capacitors in series, to avoid generating hydrogen or oxygen under charge.

Figure 2. The battery powered car used for the load leveling tests with Reticle Carbon supercapacitors.

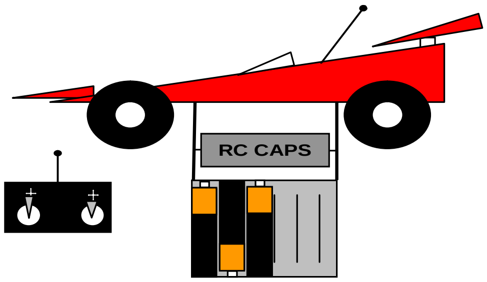

Figure 3. Schematic of the Reticle Carbon supercapacitor attached in series with half of the required batteries to operate a toy car.

For this test, we removed half of the batteries. Three batteries (4.5-V) alone did not provide enough power to get the car started. The current draw from the batteries was so great, that the batteries potentials dipped to meet the sudden demand for power. The drop in the potential shown in Figure 4 was the actual voltage response of the batteries in the car at startup. (Notice that the batteries we used only provided 4.0-V of potential instead of the 4.5-V expected from fresh batteries.) However, the capacitor provided the boost to the motor to get the car started with only a moderate voltage drop observed in the batteries. The batteries then supplied enough power to operate the car normally. As the car stopped, the current from the batteries was slow to respond, and quickly recharged the capacitor, readying it for the next start. Incorporating the capacitor provided the power required to start the motor, but allowed us to reduce the number of batteries required. It also helps save battery life by minimizing the voltage drop when the load is applied!

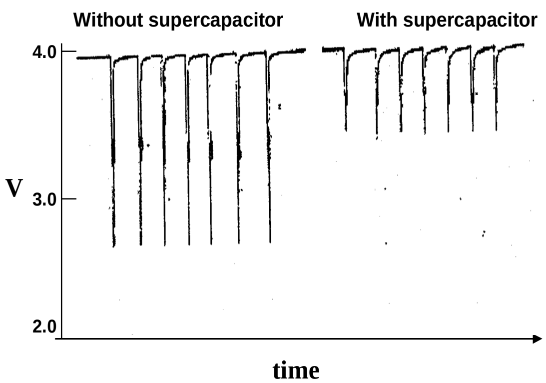

Figure 4. Battery response at the start of the toy electric car with and without Reticle Carbon supercapacitor. The car would not run without the capacitor.

3 SUMMARY

Reticle Carbon has unique properties that allow it to be an efficient electrode material in supercapacitors. The material has surface areas as high as 1750 m^2/g, which give the material a specific capacitance of 300 F/g. Supercapacitors made with material with just 1240 m^2/g had energy densities of 23 Wh/kg and peak power densities of 8 kW/kg. With modification and design optimization these levels will be exceeded in next generation Reticle supercapacitors.

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