Practical aspects & hurdles in the development of low-cost high-performance supercapacitors

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Introduction

In the class of electrochemical capacitors, those based on carbon are most likely to lead the uptake of the technology into the market. Among the many characteristics that electrochemical capacitors must posses in order to enter the market, low cost and high energy and power are perhaps the most important. These characteristics are especially required in the telecommunications, motive (eg hybrid vehicle) and industrial applications. Because the energy of a capacitor scales with the square of the voltage, the high energy requirement can probably only be attained through the use of non-aqueous electrolytes which have at least double the voltage rating and hence 4 times the energy of aqueous systems. Aqueous electrolytes are, however, better suited to providing high power capability and so there will always be a trade-off between energy density and power density. The discussion and results below are limited to carbon based supercapacitors using non-aqueous electrolytes.

The maximum power deliverable from a capacitor is proportional to the square of the maximum voltage and inversely proportional to the effective series resistance (esr):

$$P=V^2max/4.esr$$

ie, for constant weight, an increase in power is achieved by operating at a higher voltage, and/or decreasing the esr. Some of the factors affecting the operating voltage and esr are discussed below.

Design criteria

There are only 2 basic ways of assembling large carbon electrochemical capacitors, spiral wound and prismatic, and each have their own advantages and disadvantages. Some of these are given in Table 1. Prismatic design also facilitates the use of bipolar construction, in which one electrode is both anode and cathode of adjacent cells, and may be useful in high voltage stacks. Bipolar construction however is much more challenging because of the need for a perimeter seal around each single layer cell. Very large capacitors are more easily made using spirally wound construction.

Table 1 Advantages and Disadvantages of Prismatic and Spiral Construction

Spiral Wound		Prismatic	
advantages	disadvantages	advantages	disadvantages
established technology	clumsy series connection of cells	easy series connection of cells	difficult to incorporate large electrode areas
high compression achievable	poor packing density of cells	good packing density of cells	may require bulky pressure housing
very large electrode areas achievable	electrode connections	amenable to bipolar construction	larger perimeter seal
			gas venting awkward

Carbon

Carbon characteristics play a key role in the performance and cost of electrochemical capacitors. The most critical of these are:

available surface area & pore size distribution.

To a broad approximation, the specific capacitance is directly proportional to the surface area (Figure 1), however highly microporous carbons, such as those produced by KOH activation, may have a significant fraction of electrolyte inaccessible surface due to the very small pore dimensions. This is much more of a problem when non-aqueous electrolytes are used because of their larger ion sizes. Some of the newer carbons, such as the Aerogels (1) and nanotubes (2) provide a narrower pore size distribution than traditional chemically activated carbons.

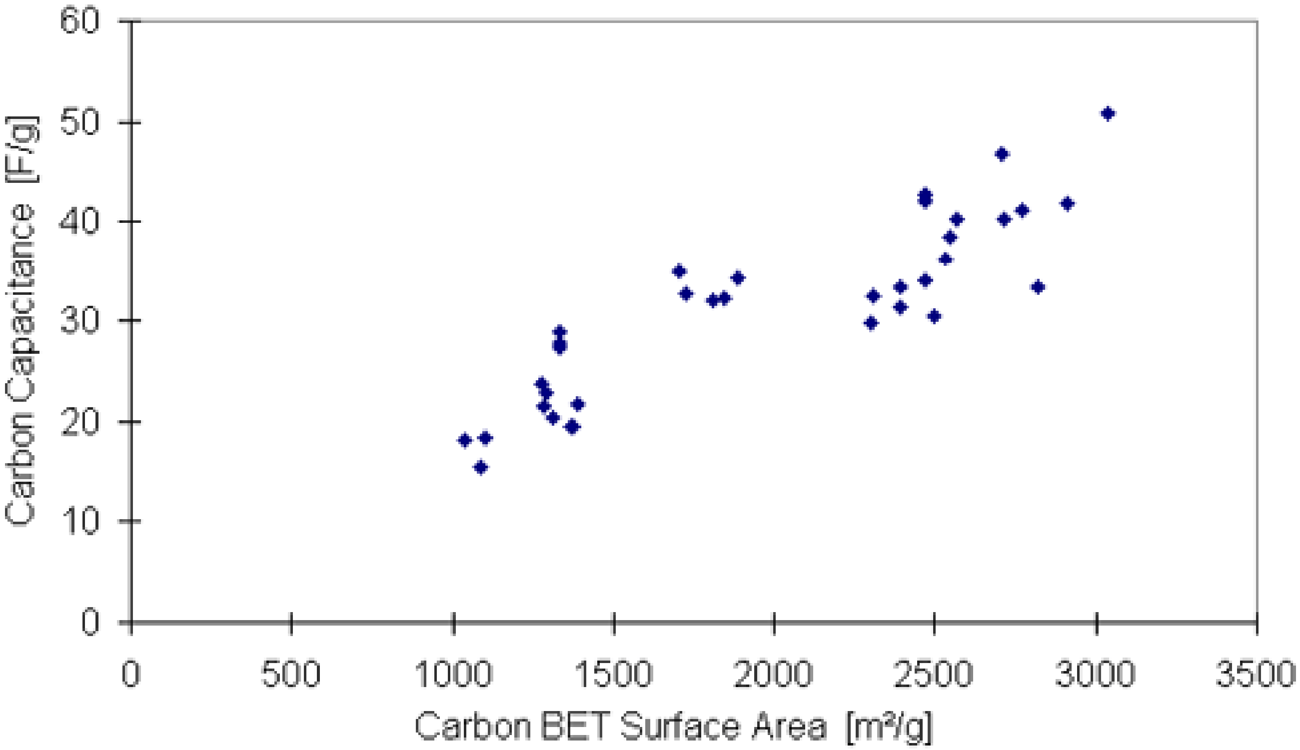

Figure 1 Relationship between device capacitance and carbon surface area

electrochemical stability

One of the main advantages of carbon as an active material in electrochemical capacitors is its electrochemical stability (3). However it appears that high surface area carbons have a lower operating voltage than less activated carbons (4), at least in their native form. As a comparison, an increase in operating voltage from 2.5 to 3.0 V is equivalent in energy to increasing the surface area (and hence the capacitance) by 44%, but also to increasing the power by 44%. This decrease in operating voltage for highly microporous carbons may be a result of carbon breakdown in the ultrathin pore walls of these carbons due to the very high electric fields present. Electrochemical stability at 3.0 V and above is a challenge that must be met for energy densities to reach 10 Wh/kg in a packaged device.

electrical conductivity

Good electrical conductivity of the active carbon is required to minimise the esr, however for chemically activated carbons, the electrical conductivity generally decreases as the surface area increases, due to a disruption of the electronic conduction bands and physically less carbon in the pore walls. Thus a trade between power and energy is frequently made, nevertheless some of the newer carbons can provide very low resistivity with high surface area (1500-2000 m^2/g). The resistivity of some custom made and commercially available high surface area carbons is shown in Table 2. These values were measured using the technique of Espinola (5) under a pressure of 4000 kPa.

Table 2 Resistivity of selected carbons considered for use in supercapacitors

carbon	ρmΩ.cm	type*
SCB248	6	Graphite
SCA115	9	Graphite
SCB223	17	CB
SCA209	21	CB
SCA117	27	AC
SCA233	27	AC
SCB222	27	CB
SCB243	28	CB
SCB234	30	AC
SCA15	30	AC
SCB259	30	AC
SCA208	31	CB
SCB244	31	CB
SCB233	35	AC

SCA234	36	AC
SCA26	40	CB
SCA22	40	AC
SCA5	40	AC
SCA17	40	AC
SCB242	41	AC
SCB232/1	41	AC
SCA407	41	AC
SCB241	59	AC
SCA1	60	AC
SCA4	80	AC
SCA6	90	AC
SCA21	360	AC
SCA16	380	AC
SCA118	367	AC
AC; activated carbon CB; carbon black		

cost

The cost of carbons suitable for electrochemical capacitors can vary over 2 orders of magnitude - from as little as $US 1/kg to over $US 200/kg depending on their characteristics. For large capacitors, eg >1000 F this carbon cost can be significant. Cheaper carbons usually contain from 2-10% mineral impurity and may have up to 10% oxygen. The mineral impurities are not necessarily a problem unless electroactive ions can be leached from them but they do contribute extra mass and decrease the energy density.

Electrolyte

Electrolyte choice is particularly important in high performance supercapacitors as it will be the limiting factor in achieving high power capability, and may contribute the most to weight and cost of these supercapacitors. High conductivity is essential, as is voltage and chemical stability. Quaternary ammonium salts dissolved in cyclic carbonates are the staple for these capacitors. However with costs above US$200/kg they need to be used sparingly. As an example, in our experience, a 1000 F capacitor will require between $4 and $13 of electrolyte depending on the salt and bulk pricing.

The cyclic carbonate solvents are hygroscopic and particularly prone to hydrolysis requiring extra care during electrolyte storage and addition. Moisture content of the electrolyte must be kept below 50 ppm to keep gas generation and leakage current low. The selection of electrolyte and solvent depends very much on the power density required, and there is scope to tailor the solvent and electrolyte for the application.

Separator

In the first instance, the impedance of the separator in electrolyte is proportional to its thickness and inversely proportional to its porosity. Therefore the key characteristics for a membrane separator are high porosity, high strength and ultrathin manufacture. Paper has traditionally been used for electrolytic capacitors and is a cheap and convenient separator, however the finest papers are still more than twice the thickness of the best polymer membranes. In our experience, very thin papers also suffer from shorting due to carbon penetration, and thicker papers significantly increase the weight of capacitors because of their very high porosity. There are a number of very good polymeric separators now available, and although expensive, provide low impedance and high strength with a thickness of 20-40 ?m. A comparison of the esr of capacitors using 3 different separators is given in Table 2. It is clear that thickness and porosity alone are not sufficient to determine the esr contribution, but that other characteristics such as tortuosity and wetability also need to be taken into account.

Table 3 Effect of separator porosity and thickness on esr

separator	thickness (μm)	% porosity	esr Ω*
#1	25	75	0.23
#2	40	80	0.13
#3	90	90	0.25
* 25 cm^2 electrode area, 1.0 M TEATFB/PC, discharge			

Conclusion

Successful market uptake of carbon supercapacitors will rely heavily on the ability of manufacturers to tailor-make products for particular applications. Careful selection of carbon formulation, solvent, electrolyte, separator and design will be necessary to provide the required performance at an acceptable cost. It is difficult to provide high power and high energy density together in one device, but this is what will be required in some applications.

Acknowledgments

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