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R&D considerations for the performance and application of electrochemical capacitors

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Abstract

Research and development (R&D) of electrochemical capacitors is discussed in terms of material characteristics and device performance and testing. Various chemistries and technologies being developed are identified and the status of and problems associated with each of the technologies are discussed. The technologies considered include those using various types of carbon and pseudo-capacitive materials such as metal oxides. What is needed to make the various electrochemical capacitor technologies cost competitive with batteries for different applications and markets is also considered.

Electrochemical capacitors (especially double-layer capacitors) are intrinsically high power devices of limited energy storage capability and long cycle life; batteries are basically energy storage devices, which can be designed and used as relatively high power devices with a sacrifice in useable energy storage capacity. Both electrochemical capacitors and high power batteries are designed with thin electrodes, materials having nano-scale characteristics, and a minimum resistance. Much of the research on electrochemical capacitors is concerned with increasing their energy density with the minimum sacrifice in power capability and cycle life for deep discharges. Of special interest has been the development of advanced carbons with specific capacitance (F/g) significantly greater than the present values of 150–200 F/g in aqueous electrolytes and 80–120 F/g in organic electrolytes. Cost continues to be a major obstacle to the development of large markets for electrochemical capacitors particularly for vehicle applications. The development of lower cost carbons appropriate for use in electrochemical capacitors is underway by several speciality carbon suppliers. The goal is to reduce the cost of the carbon to $10–15/kg.

Keywords: Electrochemical capacitors; Carbon; Energy density; Power density; Cost

1. Introduction

The development of electrochemical capacitors for high power applications started about 1990. Early work [1] in the 1970s had been done to develop similar devices for low power applications such as backup for uninterruptible power supplies and memory in computers. That work recognized the potential of using high surface area carbons to achieve capacitance in devices much greater than achievable using thin film dielectric materials; the carbon electrodes were made by compressing the carbon into relatively thick layers resulting in devices with high resistance and low power. In the United States, much of the first work [2,3] on electrochemical capacitors (supercapacitors or ultracapacitors) was started and supported by the United States Department of Energy as part of their electric and hybrid vehicle programs. From the outset of this work, the twin goals were to achieve an energy density of at least 5 Wh/kg for high power density (at least 500 W/kg) constant power discharges. The life cycle goal was at least 500,000 deep discharge cycles. The overall goals of increasing energy density with minimum sacrifice in power density and cycle life have remained central to electrochemical capacitor R&D up to the present time (2006).

In order to justify the development of electrochemical capacitors as a distinct technology separate from high power batteries, it is critical that their power and life cycle characteristics be significantly better than the high power batteries because it seems clear that the energy density of the capacitors will be significantly less than that of batteries. In this paper, past, present, and future research and development on electrochemical capacitors is discussed in terms of material characteristics and device performance and testing. This is done by identifying the various chemistries and technologies being developed and discussing the status of and problems associated with

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each of the technologies. The technologies considered include those using various types of carbon and pseudo-capacitive materials such as metal oxides. The intent of this paper is not to review each of the technologies in depth, but rather to present general considerations, which should guide the R&D needed to develop electrochemical capacitors, which will be attractive to their potential users. A short discussion is also given of how the various technologies may be made cost competitive with batteries for different applications and markets.

2. Electrochemical capacitors versus high power batteries

2.1. Performance and design

Electrochemical capacitors and high power batteries are significantly different in terms of both performance and design. Electrochemical capacitors are intended to be charged and discharged in a few minutes or less (60–120 s is typical) and to cycle energy in and out at very high efficiency (90–95% or higher) even at high power density (greater than 1000–1500 W/kg). High power batteries in contrast are intended to be charged/discharged in many minutes (at least 10–15 min) rather than in seconds and are designed primarily as energy storage devices with power capability as a secondary consideration. The power characteristics of high power batteries, such as lithium-ion, are significantly less than that of electrochemical capacitors when one specifies that the discharge/charge must be made at high efficiency. In addition, in most applications, it is common that only a relatively small fraction (less than 10%) of the energy capacity of the high power battery is used in order to achieve high cycle life (100,000–200,000 cycles). Capacitors are designed with very thin electrodes having very low resistance (less than $1.0\,\Omega\,\mathrm{cm}^2$ even using organic electrolytes). In addition, electrochemical double-layer capacitors (EDLC) using activated carbon have no intrinsic open-circuit voltage and symmetric charge/discharge power capability over the complete range of operation (maximum rated voltage to near zero). Thus carbon/carbon capacitors can be utilized over the complete voltage range without damage for at least 500,000 cycles. Batteries operate in a relatively narrow range having a well-defined open-circuit voltage and a minimum discharge voltage below which the cell will be damaged. The chemistry of high power batteries is Faradaic with reactions occurring primarily in the bulk of the electrode materials with the power limited by diffusion of the reactants even when the electrodes are thin and the particle size of the electrode material nano-scale. The power capability of the battery is not symmetric for charge and discharge unless the battery is maintained at a specified partial state-of-charge (typically 60–70%).

In summary, it seems clear that electrochemical capacitors (especially double-layer capacitors) are intrinsically high power devices of limited energy storage capability and long cycle life; batteries are basically energy storage devices, which can be designed and used as relatively high power devices with a sacrifice in useable energy storage capacity. Both electrochemical capacitors and high power batteries are designed with thin electrodes, materials having nano-scale characteristics, and a minimum resistance. Nevertheless, the intrinsic differences between the basic chemistry of the two devices remain and the differences can be only partially eliminated by available design trade-offs.

2.2. Test procedures

There are similarities and differences in the test procedures [4–6] for electrochemical capacitors and high power batteries. It is customary to perform constant current and constant power tests of both types of devices. From the constant current tests, the charge capacity (capacitance (Farads) and Ah) and resistance of the devices are determined. From the constant power tests, the energy storage characteristics (Wh/kg versus W/kg—the Ragone curve) are determined. The currents and powers to be used in the testing are selected such that the charge and discharge times are compatible with the capabilities of the devices being tested. In the case of the capacitors, the test discharge times are usually in the range of 5–60 s and for the batteries several minutes to a significant fraction of an hour even for high power batteries. The differences in the recharge times for the devices are also large. For example, the capacitors can be fully charged in 5–10 s without difficulty, but the high power batteries require a minimum of 5–10 min for a complete charge even when the initial charge current is set at a maximum value.

In addition to the constant current and constant power tests, the capacitors and batteries are tested using charge/discharge pulses of 5–15 s. For these tests, the current and power levels for the capacitors and high power batteries are comparable (on a normalized basis). The test cycles [4,5] consist of a sequence of charge and discharge pulses (power density for a specified time) are meant to simulation how the devices would be used in particular applications. The power steps for the PSFUDS (Pulsed Simple Federal Urban Driving Schedule) are given in Table 1. This cycle was initially intended to show how a capacitor would respond if used to load level the battery in an electric vehicle in stop-and-go city driving. However, it has proven to be a useful cycle for testing high power devices in general. The relative performance of the electrochemical capacitors and power batteries can be directly assessed from the pulse power tests since both types of devices are capable of high power pulses even though the battery is not intended to be charged/discharged for long periods at these high power levels. The pulse testing of the battery is usually done at a specified partial state-of-charge as only a small fraction of the energy stored in the battery is used in the cycle tests. Of particular interest in the pulse tests is the round-trip efficiency of the devices. This is determined from the ratio of the energy out compared to the energy into the devices during the test cycle. This efficiency is determined primarily by the relative resistances of the devices.

3. Chemistries for electrochemical capacitors

There are a number of chemistries (electrode materials and electrolytes) being developed for electrochemical capacitors [7–15]. The dominant electrode material is microporous

Table 1
Time–power steps for the PSFUDS test cycle

Step number	Time step duration (s)	Charge/discharge (C/D)	$P/P_{\max}$, $P_{\max} = 500$ W/kg
1	8	D	0.20
2	12	D	0.40
3	12	D	0.10
4	50	C	0.10
5	12	D	0.20
6	12	D	1.0
7	8	D	0.40
8	50	C	0.30
9	12	D	0.20
10	12	D	0.40
11	18	D	0.10
12	50	C	0.20
13	8	D	0.20
14	12	D	1.0
15	12	D	0.10
16	50	C	0.30
17	8	D	0.20
18	12	D	1.0
19	38	C	0.25
20	12	D	0.40
21	12	D	0.20
22	≥50	Charge to V_0	0.30

activated carbon, which appears to be an ideal material for use in double-layer electrochemical capacitors (EDLC). Activated carbon can be used with either aqueous or organic electrolytes. Recently considerable research [9,10] is being done on other forms of carbon in which intercalation and/or surface adsorption processes are thought to be responsible for the charge storage in the electrodes. There has also been development of devices that use carbon in one electrode and a battery-like Faradic (pseudo-capacitive) material in the other electrode. A few devices have been studied that utilize pseudo-capacitive materials, usually metal oxides, in both electrodes. These non-double-layer devices exhibit charge/discharge characteristics more like batteries than EDLC [12,13].

The performance of an electrochemical capacitor is rather simply related to the characteristics of the electrode material and the electrolyte used in the device. The relationship for the energy density (Wh/kg) can be expressed as:

$$\mathrm{Wh/kg} = \frac{1}{8}(\mathrm{F/g}) \times V_0^2/3.6 \tag{1}$$

where F/g is the specific capacitance of the electrode material and V_0 is the cell voltage dependent primarily on the electrolyte used in the device. The weight of the materials in the cell other than carbon are neglected in Eq. (1). The power characteristics of a cell are proportional to V_0^2/R where R is the DC resistance of the device. Estimation of the resistance of a cell, including the contribution of ion diffusion in the pores and the effects of current transients in the electrodes, is not simple as shown in Refs. [14,15]. However, a first approximation for the resistance can be written as:

$$R = \frac{2}{3}t \times \frac{r'}{A_x} \tag{2}$$

where "t" is the electrode thickness, "r'" the resistivity (Ω cm) of the electrolyte, and A_x is the geometric area of the electrode. Eqs. (1) and (2) show the effect of key geometric parameters and material properties on cell performance. The electrode materials and electrolytes used in the various types of electrochemical capacitors are discussed in the following sections.

3.1. Carbon electrode material

The electrodes in the capacitors are in general thin coatings applied to a metallic current collector. The active material is mixed with a binder to form a slurry that can be applied at a controlled thickness, rolled, and dried to form a thin, porous electrode. The thickness of the electrode is generally in the range of 100–300 μm and it has a high porosity of 65–75%. In order to achieve a low resistance, the contact resistance between the active material coating and the current collector must be very low. This requires special attention to preparing the surface of the current collector before applying the electrode coating [16,17]. As noted previously, a key electrode material property is its specific capacitance (F/g). The capacitance of an electrode of known geometric dimensions (t, A_x) can be calculated directly with good accuracy from its specific capacitance and density ($C = (\mathrm{F/g}) \times \text{density} \times t \times A_x$).

As indicated in Table 2, the specific capacitance of activated carbon can vary over a wide range (100–220 F/g) depending on how it is processed and the electrolyte used in the cell. The density of the carbon can vary from 0.4 to 0.8 g/cm^3. The specific capacitance of the carbon depends on its surface area (m^2/g), pore size distribution, and true surface double-layer capacitance (μF/cm^2). The maximum specific capacitance of a particular carbon can be estimated using the following relationship:

$$(\mathrm{F/g})_{\max} = (\mathrm{m^2/g}) \times (\mu\mathrm{F/cm^2}) \times 10^{-2}$$

Table 2
Specific capacitance for various electrode materials

Material	Density (g/cm^3)	Electrolyte	F/g	F/cm^3	Reference
Carbon cloth	0.35	KOH	200	70	
		Organic	100	35	[19]
Activated carbon		KOH	160	112	
	0.7	Organic	100	70	[19]
Aerogel carbon	0.6	KOH	140	84	[19]
Particulate carbon from SiC	0.7	KOH	175	122	[20]
		Organic	100	70	
Particulate carbon from TiC	0.5	KOH	220	110	[20]
		Organic	120	60	
Advanced carbon	0.7	Organic	180	126	[9,10]
Anhydrous RuO_2	2.7	Sulfuric acid	150	405	[30]
Hydrous RuO_2	2.0	Sulfuric acid	650	1300	[30]
Doped conducting polymer	0.7	Organic	450	315	[31]

Table 3
Effect of current density on the specific capacitance (F/g)

I (A)	mA/cm^2	*C* (F)	*R* (Ω)	Ω cm^2	F/g (dry, electrode)
0.2	66	5.72	0.123	0.37	163
0.3	100	5.58	0.151	0.45	159
0.5	167	5.3	0.120	0.36	151
0.75	250	4.96	0.144	0.43	142
1.0	333	4.80	0.164	0.49	153

Lab cells, area, 3 cm^2, sulfuric acid electrolyte, electrode thickness 200 μm, Ref. [15].

For example, if the surface area were 1500 m^2/g and μF/cm^2 = 20, the maximum estimated specific capacitance would be 300 F/g. As indicated in Table 2, the measured specific capacitance of activated carbon is much lower than the calculated maximum value. There are several possible explanations for the difference. There is uncertainty regarding both the effective surface area of the carbon and the true specific capacitance in the small pores of the material. It is well known that the BET method of measuring surface area overestimates the surface area and that the electrolyte ions cannot access the smallest pores for charge storage. Nevertheless, in order to optimize materials for electrochemical capacitors, control of both the surface area and the pore size distribution is critical to achieving high specific capacitance. The physical process by which the ions diffuse in and out of the pores is not well understood, but it is thought that the pore diameters should be in the range of 10–20 Å to be effective for capacitors using organic electrolytes. Smaller pores are effective in devices using aqueous electrolytes like sulfuric acid and KOH. The concentration (mol/L) of the ions in the electrolyte is selected to yield high ionic conductivity and to provide sufficient numbers of ions to form the double-layer in the pores without reducing the conductivity of the electrolyte during the charge and discharge of the electrode.

The specific capacitance of the various types of electrode materials listed in Table 2 will vary significantly depending on how the materials are prepared [18–20]. The values shown in the table are given primarily to indicate representative values of specific capacitance of the various electrode materials. The specific capacitance of the electrode materials can also vary significantly with current density (A/cm^2). Hence in evaluating materials for electrochemical capacitors, the specific capacitance of the active material should be measured for current density up to at least 300 mA/cm^2 using relatively thin electrodes (less than 200 μm). The most direct method for evaluating active materials is to form thin electrodes from the material and perform constant current tests of small cells assembled from the electrodes. Test data [15] for a carbon/carbon cell are shown in Table 3. The carbon material in the test cell was prepared as described in Ref. [20].

Experience has shown that when data like that shown in Table 3 are available for the electrode material, the capacitance of electrochemical capacitors can be calculated with good accuracy. Specific capacitance data at very low current densities (10–20 mA/cm^2) commonly overestimate the performance of carbon materials and can lead to overly optimistic predictions of capacitor performance using the materials.

3.2. Electrolytes

The capacitance of an electrochemical capacitor is dependent primarily on the specific capacitance (F/g) of the electrode material, but the cell voltage and resistance is primarily dependent on the electrolyte used in the device. Three types of electrolytes have been used in electrochemical capacitors: aqueous (sulfuric acid and KOH), organic (propylene carbonate and acetonitrile), and recently ionic liquids. Salts are added to the organic electrolytes to provide the ions that move in and out of the double-layers formed in the micropores of the carbon. The characteristics of these electrolytes are given in Table 4. Detailed discussions of various combinations of electrolyte solvents and salts are given in Refs. [21,22].

There are large differences in the ionic resistivity and cell voltage (useable electrochemical window) of the electrolytes. These differences lead to corresponding large differences in the performance of devices using the various electrolytes. Since the energy density is proportional to the square of the cell voltage, increasing the cell voltage is a key objective of electrochemical capacitor research. Using activated carbon, the cell voltage is 2.3–2.7 V using organic electrolytes and 0.8–1.0 V/cell using aqueous electrolytes. The cell voltage is also dependent to a limited extent on the carbon used in the device. Cell voltages up to 3.5 V/cell have been reported with structured carbons [9,10]. The differences in the ionic resistivity of the electrolytes have a large effect on resistance and consequently the power capability of a device. Note from Table 4 that the resistivity of propylene carbonate is about a factor of three higher than that of acetonitrile. For this reason, electrochemical capacitors with the best performance (highest energy density and power capability) use acetonitrile as the electrolyte. There is a continuing controversy [23,24] concerning the safety of acetonitrile especially in vehicles because of its toxicity and flammability. There has been much research effort to develop a low resistivity, non-toxic electrolyte to replace acetonitrile, but to date that work has not succeeded. Electrochemical capacitors are being marketed that use propylene carbonate and their performance [25,26] is satisfactory for some applications.

Research [27] is being done to develop electrochemical capacitors using ionic liquid electrolytes. These electrolytes are attractive for several reasons. First, they can be thermally stable for temperatures as high as 300 °C with near zero vapor pressure and are non-flammable with very low toxicity. Further the useable electrochemical window is large leading to cell voltages as high as 4 V with some carbons. The major difficulties

Table 4
Properties of various electrolytes

Electrolyte	Density (g/cm^3)	Resistivity (Ω cm)	Cell voltage
KOH	1.29	1.9	1.0
Sulfuric acid	1.2	1.35	1.0
Propylene carbonate	1.2	52	2.5–3.0
Acetonitrile	0.78	18	2.5–3.0
Ionic liquid[a]	1.3–1.5	125 (25 °C)	4.0
		28 (100 °C)	3.25

[a] Data taken from Ref. [27].

with the ionic liquids are their relatively high ionic resistivity at near room temperature and high cost. The resistivity of an ionic liquid is strongly temperature sensitive and requires a temperature of about 125 °C to have a resistivity comparable to that of acetonitrile. In addition, as indicated in Table 4, the voltage window of the ionic liquid decreases markedly at high temperature. Blending ionic liquids [x] with acetonitrile can greatly reduce the flammability of the electrolyte with only minor changes in room-temperature conductivity and the voltage window. However, acetonitrile-free blends, which are both non-flammable and non-toxic, show large increases in resistivity and a 0.5–1.0 voltage reduction in the voltage window.

4. Status of the electrochemical capacitor technologies

4.1. Carbon/carbon double-layer devices

There are presently commercially available carbon/carbon devices (single cells and modules) using activated carbon from several companies [25,26]. These devices are suitable for high power industrial and vehicle applications. The performance of the various devices is given in Table 5. The energy densities (Wh/kg) shown correspond to the useable energy from the devices based on constant power discharge tests from V_0 to $(1/2)V_0$. Peak power densities are given for both matched impedance and 95% efficiency pulses. For most applications with electrochemical capacitors, the high efficiency power density is the appropriate measure of the power capability of the device. For the large devices, the energy density for the available devices is between 3.5 and 4.5 Wh/kg and the 95% power density is between 800 and 1200 W/kg. Test results in Table 5 for a proto-type cell using an advanced carbon [9,10] show an energy density of 8 Wh/kg.

4.2. Hybrid capacitors

As indicated in Refs. [11–15], there has been considerable development of electrochemical capacitor devices that have at least one of the electrodes that utilize non-double-layer mechanisms for electrical charge storage. Most of these devices use carbon in one electrode and pseudo-capacitive or Faradaic materials in the other electrode. The performance characteristics of several hybrid technologies based on tests at UC Davis [7,8] are given in Table 6. These devices are not commercially available and are in varying stages of development. In general, the energy densities of the hybrid devices are significantly higher than the carbon/carbon devices and their power densities are somewhat lower. The presence of the battery-like, Faradaic electrode results in an increase in energy density of the hybrid devices for two reasons. First, the carbon electrode is able to operate over double the voltage range experienced in the simple double-layer C/C capacitor—thereby doubling the charge stored in the hybrid device for the same weight of carbon. Second, the battery-like electrode biases the voltage of the hybrid cell around that of its electrochemical potential. The net result is a more than doubling of the energy density compared to the carbon/carbon cells. However, the energy densities of the hybrid devices are more rate dependent than those of the carbon/carbon devices.

The major concerns about the hybrid devices are cycle and calendar life. Further development of the hybrid devices is needed to show that W/kg power density capability and cycle life comparable to carbon/carbon devices and significantly higher than batteries are achievable. Otherwise the hybrid devices will be low energy density devices with characteristics not too different than higher energy density batteries. Hence simply achieving higher energy density than carbon/carbon

Table 5
Summary of the characteristics of various electrochemical devices

Device	V rated	C (F)	R (mΩ)	RC (s)	Wh/kg[a]	W/kg (95%)[b]	W/kg matched impedance	Weight (kg)	Volume (L)
Maxwell[c]	2.7	2,800	0.48	1.4	4.45	900	8,000	0.475	0.320
Maxwell	2.7	650	0.80	0.52	2.5	1281	11,390	0.20	0.211
Maxwell	2.7	350	3.2	1.1	4.4	1068	9,492	0.06	0.05
Ness	2.7	1,800	0.55	1.00	3.6	975	8,674	0.38	0.277
Ness	2.7	3,640	0.30	1.10	4.2	928	8,010	0.65	0.514
Ness	2.7	5,085	0.24	1.22	4.3	958	8,532	0.89	0.712
Asahi Glass (propylene carbonate)	2.7	1,375	2.5	3.4	4.9	390	3,471	0.210 (estimated)	0.151
Panasonic (propylene carbonate)	2.5	1,200	1.0	1.2	2.3	514	4,596	0.34	0.245
Panasonic	2.5	1,791	0.30	0.54	3.44	1890	16,800	0.310	0.245
Panasonic	2.5	2,500	0.43	1.1	3.70	1035	9,200	0.395	0.328
EPCOS	2.7	3,400	0.45	1.5	4.3	760	6,750	0.60	0.48
LS Cable	2.8	3,200	0.25	0.80	3.7	1400	12,400	0.63	0.47
Power Sys. (activated carbon, propylene carbonate)	2.7	1,350	1.5	2.0	4.9	650	5,785	0.21	0.151
Power Sys. (advanced carbon, propylene carbonate)	3.3	1,800	3.0	5.4	8.0	825	4,320	0.21	0.15
ESMA–Hybrid (C/NiO/aqueous electrolytes)	1.3	10,000	0.275	2.75	1.1	156	1,400	1.1	0.547
Fuji Heavy Industry-hybrid (C/metal oxide)	3.8	1,800	1.5	2.6	9.2	1025	10,375	0.232	0.143

[a] Energy density at 400 W/kg constant power; V rated, $(1/2)V$ rated.

[b] Power based on $P = (9/16) \times (1 - \mathrm{EF}) \times V_2/R$, EF = efficiency of discharge.

[c] Except where noted, all the devices use acetonitrile as the electrolyte.

Table 6
Comparison of the energy density (Wh/kg) of various carbon/carbon and hybrid devices as a function of power density (W/kg)

Power density (W/kg)	AC/PbO_2, 2.25–1.0 V	AC/metal oxide, 2.8–1.0 V	Metal oxide/metal oxide, 3.35–1.4 V	AC/Li^+C, 3.8–2.2 V	Small AC/AC, 2.7–1.35 V	Large AC/AC, 2.7–1.35 V
100	10.5	10.7	13.8	–	4.12	3.96
200	10.3	10.7	13.7	–	4.10	3.98
400	9.7	10.5	13.0	10.7	4.14	3.82
600	9.3	9.7	12.1	10.2	4.14	3.67
800	8.7	8.8	11.0	–	4.14	nt
1200	–	7.3	8.9	9.2	4.14	nt
1500	–	6.2	7.2	–	4.14	nt
1700	–	5.8	6.5	–	nt	nt
RC (s)	2.8	5.4	6.2	2.9	0.63	1.3
Reference	[15]	[12]	[28]	[13]	[25]	[25]

AC, activated, microporous carbon.

devices is not attractive unless the devices maintain the primary power and life cycle advantages of double-layer capacitors.

5. Projected future progress

Continued research on carbon/carbon and hybrid capacitors can be expected to improve their performance. These improvements will result from the utilization of better materials, more optimum design, and changes in assembly techniques. In the case of the carbon/carbon devices, the primary improvements will be the use of carbon with higher specific capacitance (F/g), a cell voltage of at least 3 V, and thinner electrodes and current collectors. Prototype devices using activated carbon [25,29] have been tested at UC Davis. As shown in Table 7, the devices have energy densities of 5.0–5.5 Wh/kg and power density of 3–8 kW/kg (95% efficiency) for a rated voltage of 2.7 V. All the electrochemical capacitor developers claim to know how to increase the energy density of their devices from about 4 to 5 Wh/kg, but they are currently concentrating their efforts on reducing the cost of the devices rather than improving performance. Hence it seems likely that the useable energy density of commercially available carbon/carbon capacitors will be increased to 5 Wh/kg or higher in the near-future.

Estimating the improvement likely for non-double-layer electrochemical capacitors (hybrid devices and those using advanced carbons for which the mechanisms for charge storage are still unclear) is more uncertain than for the double-layer devices using activated carbons in both electrodes. For the advanced devices, an analytical method [15] was used to calculate the performance characteristics of devices for specified device geometry and assumed material properties of the electrodes and electrolyte. The results of the calculations are given in Table 8. Also shown in the table are calculated results for carbon/carbon devices using both sulfuric acid and acetonitrile as the electrolyte. All the advanced capacitor devices have higher energy density than the carbon/carbon devices and comparable power capability. Note from Table 8 that the devices using aqueous electrolytes, especially sulfuric acid, have higher power capability than comparable devices using an organic electrolyte. This results from the much lower ionic resistivity of the aqueous electrolytes. The major uncertainties regarding the advanced devices are their cycle and calendar life. It is highly unlikely that

Table 7
Characteristics of prototype carbon/carbon devices

Company	V	F	R (mΩ)	RC (s)	Wh/kg	Wh/L	W/kg, 95%	Reference
APowerCap	2.7	55	4.0	0.22	5.0	7.0	8300	[29]
Skeleton	2.7	1422	0.35	0.50	5.3	7.8	2929	[25]
Ness	2.7	3600	0.30	1.1	4.2	5.3	928	Table 5
Maxwell	2.7	2800	0.48	1.4	4.45	6.5	900	Table 5

Table 8
Calculated energy density and power density characteristics of various electrochemical capacitor technologies

Type	V	Wh/kg	Wh/L	$\Omega\,cm^2$	RC (s)	kW/kg (95% efficiency)
Activated carbon/PbO_2/sulfuric acid	2.25–1.0	15.7	39.2	0.12	0.36	8.9
Activated carbon/NiOOH/KOH	1.6–0.6	13.9	31.5	0.16	0.71	4.0
$Li_4Ti_5O_{12}$/activated carbon/acetonitrile	2.8–1.6	13.8	24	1.0	0.73	3.8
Advanced carbon/advanced carbon/acetonitrile[a]	3.3–2.0	13.7	19	1.0	1.5	1.9
Activated carbon/activated carbon/sulfuric acid	1.0–0.5	1.72	2.2	0.17	0.29	1.2
Activated carbon/activated carbon/acetonitrile	2.7–1.35	5.7	7.6	0.78	0.18	6.4

[a] Effective specific capacitance 180 F/g.

Table 9
Material costs for a 2.7 V, 3500 F electrochemical capacitor for various carbon and other material unit costs

Carbon (F/g)	g C/dev.	$/kg	Electrolyte CAN ($/L)	Salt ($/kg)	Device (total material cost, $)	Unit ($/kg)	Costs ($/Wh)	$/kW	Ct./F
75	187	50	10	125	17.0	29	6.4	29	.48
120	117	100	10	125	15.5	26	6	26	.44
75	187	5	2	50	3.6	6.0	1.3	6	.10
120	117	10	2	50	2.5	4.2	.93	4.2	.07

Table 10
Comparisons of the weight, cost, and power capability of electrochemical capacitors of various Wh sizes assembled with carbon/PbO_2 and carbon/carbon electrodes

Wh	C/PbO_2 hybrid			Carbon/carbon		
	Weight (kg)	kW (95% efficiency)	Cost ($)	Weight (kg)	kW (95% efficiency)	Cost ($)
50	3.7	13	17	12.5	12.5	125
100	7.4	26	33	25	25	250
200	14.8	52	66	50	50	500
300	22.2	78	100	75	75	750
400	29.6	104	133	100	100	1000
1000	74.1	259	334	250	250	2500
2000	148	Greater than 500	666	500	500	5000

C/PbO_2: 13.5 Wh/kg, 3500 W/kg, $4.5/kg; C/C: 4 Wh/kg, 1000 W/kg, $10/kg.

the devices using battery-like electrodes will have a cycle life comparable to the carbon/carbon devices (greater than 500,000 cycles) for deep discharges. However, a cycle life of 100,000 deep cycles seems possible by proper design of the battery-like electrode. For some applications, this reduced cycle life would be sufficient.

6. Cost and marketing considerations

In comparing the attractiveness of electrochemical capacitors and batteries for various applications, the cost of the capacitors is the central issue as it is recognized that the power and life cycle characteristics of the capacitors are superior to those of high power batteries. In terms of power characteristics, only lithium-ion batteries have a power capability close to that of the capacitors. The cost of an energy storage device can be expressed as $/Wh, $/kW, or $/kg. The $/Wh cost of batteries is always lower than that of capacitors because of the large difference in the energy densities of the two types of devices. However, because of the superior power capability of the capacitors, their $/kW cost can be lower than that of batteries.

The major material costs for carbon/carbon capacitors are the carbon, the organic electrolyte, and the salt added to the electrolyte to provide the ions. These costs must be reduced in the future if electrochemical capacitors are to be marketed in large volumes. Hence cost considerations should be included in determining what electrode materials and electrolytes are evaluated in research projects for the capacitors. A key issue is the unit cost ($/kg) of the carbon in combination with its specific capacitance (F/g). In the case of the electrolyte, both the cost of the solvent (acetonitrile in most cases) and the salt (TEATFB) are relatively expensive. The total material costs for carbon/carbon devices of specified design can be calculated rather simply and the effect of the unit costs of the component materials on the device costs determined. The results shown in Table 9 indicate that the material cost of the capacitors can be expected to decrease markedly as the unit material costs become lower. For low cost carbon ($5/kg), a total material cost of less than 0.1 cent/F appears to be possible. The importance of developing low cost carbon having good performance (specific capacitance of 75–120 F/g) is evident from Table 9.

The costs of the electrochemical capacitors using a battery-like electrode can be related to the cost of the batteries that use the same electrode material and similar electrolyte. As an example, consider the case of the C/PbO_2 device, whose manufacture is closely related to that of lead acid batteries [15]. Discussions with several lead acid battery manufacturers have indicated that the cost of lead acid batteries is $2–4/kg. Assuming an energy density of 13.5 Wh/kg and unit cost of $4.5/kg for the carbon/$PbO_2$ device, one can calculate the weight and cost of devices as a function of the Wh stored. The results of such a calculation are shown in Table 10. Also shown is the peak power (kW) for each of the devices. For comparison purposes, the cost of a carbon/carbon device with a unit cost of $10/kg is shown in Table 10. Using a cell voltage of 2.7 V/cell for the carbon/carbon device, the $10/kg cost corresponds to about 0.2 cents per Farad, which is well below the 0.5 cent per Farad often quoted as reasonable for carbon/carbon devices using acetonitrile as the electrolyte. The cost advantage of the carbon/PbO_2 devices is readily apparent in the table.

7. Summary

In this paper, past, present, and future research and development on electrochemical capacitors is discussed in terms of material characteristics and device performance and testing. This done by identifying the various chemistries and technologies being developed and discussing the status of and problems associated with each of the technologies. The technologies considered include those using various types of carbon and pseudo-capacitive materials such as metal oxides. A short discussion is also given of how the various technologies may be made cost competitive with batteries for different applications and markets.

Research to date has shown that electrochemical capacitors (especially double-layer capacitors) are intrinsically high power devices of limited energy storage capability and long cycle life; batteries are basically energy storage devices, which can be designed and used as relatively high power devices with a sacrifice in useable energy storage capacity. Both electrochemical capacitors and high power batteries are designed with thin electrodes, materials having nano-scale characteristics, and a minimum resistance. Nevertheless, the intrinsic differences between the basic chemistry of the two devices remain and the differences can be only partially eliminated by design trade-offs. Much of the research on electrochemical capacitors is concerned with increasing their energy density with the minimum sacrifice in power capability and cycle life for deep discharges. Of special interest has been the development of advanced carbons with specific capacitance (F/g) significantly greater than the present values of 150–200 F/g in aqueous electrolytes and 80–120 F/g in organic electrolytes.

Research and development is being performed by a number of groups world-wide on the use of battery-like materials in one or both electrodes of electrochemical capacitors in order to increase the energy density of the devices. Cells with energy densities in the 10–15 Wh/kg range have been assembled and tested, but those cells exhibit longer RC time constants and greater sensitivity to discharge power density than carbon/carbon devices. It is also expected that the cycle life of the hybrid cells will be significantly less than that of the double-layer carbon devices.

Electrochemical capacitors using both aqueous and organic electrolytes have been assembled and tested. Most of the commercially available devices use either acetonitrile or propylene carbonate as the electrolyte with a maximum cell voltage of 2.5–2.7 V. Devices using acetonitrile have significantly higher energy density and power capability than those using propylene carbonate due to the lower ionic resistivity of acetonitrile. Limited research has been done on devices using ionic liquid electrolytes, which are particularly attractive for high temperature applications.

Cost continues to be a major obstacle to the mass marketing of electrochemical capacitors particularly for vehicle applications. The development of lower cost carbons appropriate for use in capacitors is underway by several speciality carbon suppliers. The goal is to reduce the cost of the carbon to $10–15/kg.

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