UC Davis
Recent Work

Title
Ultracapacitors: Why, How, and Where is the Technology

Permalink
https://escholarship.org/uc/item/9n905017

Author
Burke, Andrew

Publication Date
2000-11-01

Ultracapacitors: why, how, and where is the technology

Andrew Burke [*]

Institute of Transportation Studies, University of California-Davis, Davis, CA 95616, USA

Abstract

The science and technology of ultracapacitors are reviewed for a number of electrode materials, including carbon, mixed metal oxides, and conducting polymers. More work has been done using microporous carbons than with the other materials and most of the commercially available devices use carbon electrodes and an organic electrolytes. The energy density of these devices is 3–5 Wh/kg with a power density of 300–500 W/kg for high efficiency (90–95%) charge/discharges. Projections of future developments using carbon indicate that energy densities of 10 Wh/kg or higher are likely with power densities of 1–2 kW/kg. A key problem in the fabrication of these advanced devices is the bonding of the thin electrodes to a current collector such the contact resistance is less than 0.1 Ω cm^2.

Special attention is given in the paper to comparing the power density characteristics of ultracapacitors and batteries. The comparisons should be made at the same charge/discharge efficiency. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ultracapacitors; Hybrid capacitor; Electrical energy storage

1. Introduction

Electrical energy storage is required in many applications — telecommunication devices, such as cell phones and pagers, stand-by power systems, and electric/hybrid vehicles. The specifications for the various energy storage devices are given in terms of energy stored (W h) and maximum power (W) as well as size and weight, initial cost and life. A storage device to be suitable for a particular application must meet all the requirements. As power requirements for many applications become more demanding, it is often reasonable to consider separating the energy and power requirements by providing for the peak power by using a pulse power device (capacitor) that is charged periodically from a primary energy storage unit (battery). For applications in which significant energy is needed in pulse form, traditional capacitors as used in electronic circuits cannot store enough energy in the volume and weight available. For these applications, the development of high energy density capacitors (ultracapacitors or electrochemical capacitors) has been undertaken by various groups around the world. This paper considers in detail why such capacitors are being developed, how they function, and the present status and projected development of ultracapacitor technology.

2. Why are ultracapacitors being developed?

The most common electrical energy storage device is the battery. Batteries have been the technology of choice for most applications, because they can store large amounts of energy in a relatively small volume and weight and provide suitable levels of power for many applications. Shelf and cycle life has been a problem with most types of batteries, but people have learned to tolerate this shortcoming due to the lack of an alternative. In recent times, the power requirements in a number of applications have increased markedly and have exceeded the capability of batteries of standard design. This has led to the design of special high power, pulse batteries often with the sacrifice of energy density and cycle life. Ultracapacitors are being developed as an alternative to pulse batteries. To be an attractive alternative, ultracapacitors must have much higher power and much longer shelf and cycle life than batteries. By "much" is meant at least one order of magnitude higher. Ultracapacitors have much lower energy density than batteries and their low energy density is in most cases the factor that determines the feasibility of their use in a particular high power application. For ultracapacitors, the trade-off between the energy density and the RC time constant of the device is an important design consideration. In general, for a particular set of materials, a sacrifice in energy density is required to get a large reduction in the time constant and thus a large increase in power capability.

[*] Tel.: +1-530-752-9812; fax: +1-530-752-6572.

This paper is concerned with the development of ultracapacitors having relatively high energy density and not devices in which the requirement for high power has resulted in a large reduction in energy density.

The characteristics of a number of ultracapacitors and pulse batteries are given in Table 1. Two approaches to the calculation of the peak power density of the batteries are indicated in the table. The first and more standard approach is to determine the power at the so-called matched impedance condition at which one-half the energy of the discharge is in the form of electricity and one-half is in heat. The maximum power at this point is given by

$$P_{mi} = V_{oc}^2/4R_b,$$

where V_{oc} is the open-circuit voltage of the battery and R_b is its resistance. The discharge efficiency at this point is 50%. For many applications in which a significant fraction of the energy is stored in the energy storage device before it is used by the system, the efficiency of the charge/discharge cycle is important to the system efficiency. In those cases, the use of the energy storage device should be limited to conditions that result in high efficiency for both charge and discharge. The discharge/charge power for a battery as function of efficiency is given by

$$P_{ef} = EF * (1 - EF) * V_{oc}^2/R_b,$$

where EF is the efficiency of the high power pulse. For EF = 0.95, $P_{ef}/P_{mi} = 0.19$. Hence, in applications in which efficiency is a primary concern, the useable power of the battery is much less than the peak power (P_{mi}) often quoted by the manufacturer for the battery.

In the case of ultracapacitors, the peak power for a discharge between V_o and $V_o/2$, where V_o is the rated voltage of the device, is given by

$$P_{uc} = 9/16 * (1 - EF) * V_o^2/R_{uc},$$

where R_{uc} is the resistance of the ultracapacitor. The expression shown above accounts for the reduction of voltage during the discharge of the device. Peak power values are shown in Table 1 for both matched impedance and high efficiency discharges of the batteries and ultracapacitors. It is apparent that in nearly all cases, the power from the ultracapacitors is much higher than that from the batteries. Note that it is not correct to compare the high

Table 1
Comparison of the performance characteristics of various ultracapacitors and high power batteries

	Voltage (V)	A h	Weight (kg)	Resistance (mΩ)	W h/kg	(W/kg)$_{max}$	
						95% Discharge efficiency	Matched impedance discharge
Ultracapacitor device							
Maxwell ultracapacitor							
2700 F	3	2.25	0.85	0.5	4.0	593	5294
1000 F	3	0.83	0.39	1.5	3.1	430	3846
Panasonic							
800 F	3	0.67	0.32	2.0	3.1	392	3505
2000 F	3	1.67	0.57	3.5	4.4	127	1128
Superfarad (250 F)	50	3.4	16	20	5.4	219	1953
Saft (mfg. data)							
Gen 2 (144 F)	3	0.12	0.030	24	6.0	350	3125
Gen 3 (132 F)	3	0.11	0.025	13	6.8	775	6923
PowerStor (10F)	3	0.0083	0.015	10	833	1680	15 000
Batteries							
Panasonic NiHD	7.2	6.5	1.1	18	42	124	655
	12.0	98	17.2	8.7	68	46	240
Ovonic NiHD	13.2	88	17.0	10.6	70	46	245
	12.0	60	12.2	8.5	65	80	420
	12.0	20	5.2	11.0	46	120	628
	7.2	3.1	0.522	60	43	79	414
Varta NiHD (mfg. data)	1.2	4	0.18	3.5	29	109	571
	1.2	17	0.58	1.5	38	79	414
Sanyo Li-ion (mfg. data)	3.6	1.3	0.039	150	121	105	553
Hawker Pb-acid	2.1	36	2.67	0.83	27.0	95	498
	12	13	4.89	15	29.0	93	490
Optima Pb-acid (mfg. data)	6	15	3.2	4.4	28	121	635
Horizon Pb-acid	2.1	85	3.63	0.5	46	115	607
Bolder Pb-acid	2.1	1.05	0.083	5.7	25	442	2330

efficiency power density for the ultracapacitors with the matched impedance power density for the batteries as is often done. The power capability of both types of device is primarily dependent on their resistance and knowledge of the resistance is key to determining the peak useable power capability. Hence, measurement of the resistance of a device in the pulsed mode of operation is critical to an evaluation of its high power capability.

In addition to high power capability, the other reason for considering ultracapacitors for a particular application is their long shelf and cycle life. This is especially true of ultracapacitors using carbon electrodes. Most secondary (rechargeable) batteries, if left on the shelf unused for many months will degrade markedly and be essentially useless after this time due to self-discharge and corrosion effects. Ultracapacitors will self-discharge over a period of time to low voltage, but they will retain their capacitance and thus be capable of recharge to their original condition. Experience has shown that ultracapacitors can be unused for several years and remain in nearly their original condition. Ultracapacitors can be deep cycled at high rates (discharge times of seconds) for 500,000–1,000,000 cycles with a relatively small change in characteristics (10–20% degradation in capacitance and resistance). This is not possible with batteries even if the depth of discharge is kept small (10–20%).

Hence, relative to batteries, the advantages of ultracapacitors as pulse power devices are high power density, high efficiency, and long shelf and cycle life. The primary disadvantage of ultracapacitors is their relatively low energy density (W h/kg and W h/l) compared to batteries limiting their use to applications in which relatively small quantities of energy are required before the ultracapacitor can be recharged. Ultracapacitors can, however, be recharged in very short times (seconds or fraction of seconds) compared to batteries if a source of energy is available at the high power levels required.

3. How do ultracapacitors store energy?

The most common electrical energy storage devices are capacitors and batteries. Capacitors store energy by charge separation. The simplest capacitors store the energy in a thin layer of dielectric material that is supported by metal plates that act as the terminals for the device. The energy stored in a capacitor is given by $1/2\ CV^2$, where C is its capacitance (Farads) and V is the voltage between the terminal plates. The maximum voltage of the capacitor is dependent on the breakdown characteristics of the dielectric material. The charge Q (coulombs) stored in the capacitor is given by CV. The capacitance of the dielectric capacitor depends on the dielectric constant (K) and the thickness (th) of the dielectric material and its geometric area (A).

$$C = KA/\text{th}$$

In a battery, energy is stored in chemical form as active material in its electrodes. Energy is released in electrical form by connecting a load across the terminals of the battery permitting the electrode materials to react electrochemically with the ions required in the reactions to be transferred through the electrolyte in which the electrodes are immersed. The useable energy stored in the battery is given as VQ, where V is the voltage of the cell and Q is the electrical charge (It) transferred to the load during the chemical reaction. The voltage is dependent on the active materials (chemical couple) of the battery and is close to the open-circuit voltage (V_{oc}) for those materials.

An ultracapacitor, sometimes referred to as an electrochemical capacitor, is an electrical energy storage device that is constructed much like a battery (see Fig. 1) in that it has two electrodes immersed in an electrolyte with a separator between the electrodes. The electrodes are fabricated from high surface area, porous material having pores of diameter in the nanometer (nm) range. The surface area of the electrode materials used in ultracapacitors is much greater than that used in battery electrodes being 500–2000 m^2/g. Charge is stored in the micropores at or near the interface between the solid electrode material and the electrolyte. The charge and energy stored are given by the same expressions as cited previously for the simple dielectric capacitor. However, calculation of the capacitance of the ultracapacitor is much more difficult as it depends on complex phenomena occurring in the micropores of the electrode.

It is convenient to discuss the mechanisms for energy storage in ultracapacitors in terms of double-layer and pseudo-capacitance separately. The physics and chemistry of these processes as they apply to electrochemical capacitors are explained in great detail in Ref. [1]. In the following sections, the mechanisms are discussed briefly in terms of how they relate to the properties of the electrode materials and electrolyte.

3.1. Double-layer capacitors

Energy is stored in the double-layer capacitor as charge separation in the double-layer formed at the interface between the solid electrode material surface and the liquid electrolyte in the micropores of the electrodes. A schematic of an ultracapacitor is shown in Fig. 1. The ions displaced in forming the double-layers in the pores are transferred between the electrodes by diffusion through the electrolyte. The energy and charge stored in the electrochemical capacitor are $1/2\ CV^2$ and CV, respectively. The capacitance is dependent primarily on the characteristics of the electrode material (surface area and pore size distribution). The specific capacitance of an electrode material can be written as

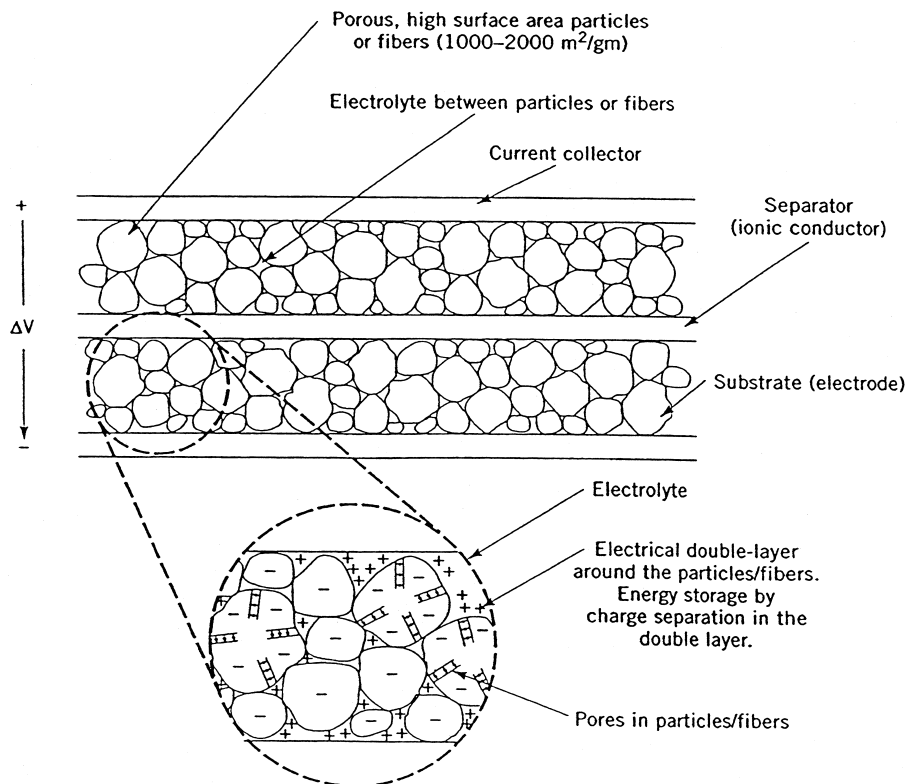$$C/g = \left(F/cm^2\right)_{act} * \left(cm^2/g\right)_{act},$$

Fig. 1. Schematic of a double-layer ultracapacitor.

where the surface area referred to is the active area in the pores on which the double-layer is formed. In simplest terms, the capacitance per unit of active area is given by

$$(F/cm^2)_{act} = (K/thickness\ of\ the\ double\text{-}layer)_{eff}.$$

As discussed in Ref. [1], determination of the effective (eff) dielectric constant K_{eff} of the electrolyte and the thickness of the double-layer formed at the interface is complex and not well understood. The thickness of the double-layer is very small (a fraction of a nm in liquid electrolytes) resulting in a high value for the specific capacitance of 15–30 $\mu F/cm^2$. For a surface area of 1000 m^2/g, this results in a potential capacitance of 150–300 F/g of electrode material. As indicated in Table 2, the

Table 2
The specific capacitance of selected electrode materials

Material	Density (g/cm³)	Electrolyte	F/g	F/cm³
Carbon cloth	0.35	KOH	200	70
		organic	100	35
Carbon black	1.0	KOH	95	95
Aerogel carbon	0.6	KOH	140	84
Particulate from SiC	0.7	KOH	175	126
		organic	100	72
Particulate from TiC	0.5	KOH	220	110
		organic	120	60
Anhydrous RuO₂	2.7	H₂SO₄	150	405
Hydrous RuO₂	2.0	H₂SO₄	650	1300
Doped conducting polymers	0.7	organic	450	315

measured specific capacitances of carbon materials being used in ultracapacitors are in most cases less than these high values being in the range of 75–175 F/g for aqueous electrolytes and 40–100 F/g using organic electrolytes, because for most carbon materials a relatively large fraction of the surface area is in pores that cannot be accessed by the ions in the electrolyte. This is especially true for the organic electrolytes for which the size of ions is much larger than in an aqueous electrolyte. Porous carbons for use in ultracapacitors should have a large fraction of their pore volume in pores of diameter 1–5 nm. Materials with small pores (< 1 nm) show a large fall-off in capacitance at discharge currents greater than 100 mA/cm^2 especially using organic electrolytes. Materials with the larger pore diameters can be discharged at current densities of greater than 500 mA/cm^2 with a minimal decrease in capacitance.

The cell voltage of the ultracapacitor is dependent on the electrolyte used. For aqueous electrolytes, the cell voltage is about 1 V and for organic electrolytes, the cell voltage is 3–3.5 V.

3.2. Electrochemical capacitors utilizing pseudo-capacitance

For an ideal double-layer capacitor, the charge is transferred into the double-layer and there are no Faradaic reactions between the solid material and the electrolyte. In this case, the capacitance (dQ/dV) is a constant and

independent of voltage. For devices that utilize pseudo-capacitance, most of the charge is transferred at the surface or in the bulk near the surface of the solid electrode material. Hence, in this case, the interaction between the solid material and the electrolyte involves Faradaic reactions, which in most instances can be described as charge transfer reactions. The charge transferred in these reactions is voltage-dependent resulting in the pseudo-capacitance ($C = \mathrm{d}Q/\mathrm{d}V$) also being voltage-dependent. Three types of electrochemical processes have been utilized in the development of ultracapacitors using pseudo-capacitance. These are surface adsorption of ions from the electrolyte, redox reactions involving ions from the electrolyte, and the doping and undoping of active conducting polymer material in the electrode. The first two processes are primarily surface mechanisms and are hence highly dependent on the surface area of the electrode material. The third process involving the conducting polymer material is more of a bulk process and the specific capacitance of the material is much less dependent on its surface area although relatively high surface area with micropores is required to distribute the ions to and from the electrodes in a cell. In all cases, the electrodes must have high electronic conductivity to distribute and collect the electron current. An understanding of the charge transfer mechanism can be inferred from $C(V)$, which is often determined using cyclic voltammetry.

For assessing the characteristics of devices, it is convenient to use the average capacitance (C_{av}) calculated from

$$C_{av} = Q_{tot}/V_{tot},$$

where the Q_{tot} and V_{tot} are the total charge and voltage change for a charge or discharge of the electrode. This permits a determination of the specific capacitance (C_{av}/g) of the material for the electrolyte of interest. As shown in Table 2, the specific capacitance of pseudo-capacitance materials is much higher than that of carbon materials. It is thus expected that the energy density of devices developed using the pseudo-capacitance materials would be higher.

3.3. Hybrid capacitors

Ultracapacitors can be fabricated with one electrode being of a double-layer (carbon) material and the other electrode being of a pseudo-capacitance material (see Fig. 2). Such devices are often referred to as hybrid capacitors. Most of the hybrid capacitors developed to date have used nickel oxide as the pseudo-capacitance material in the
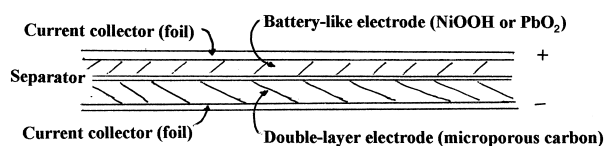
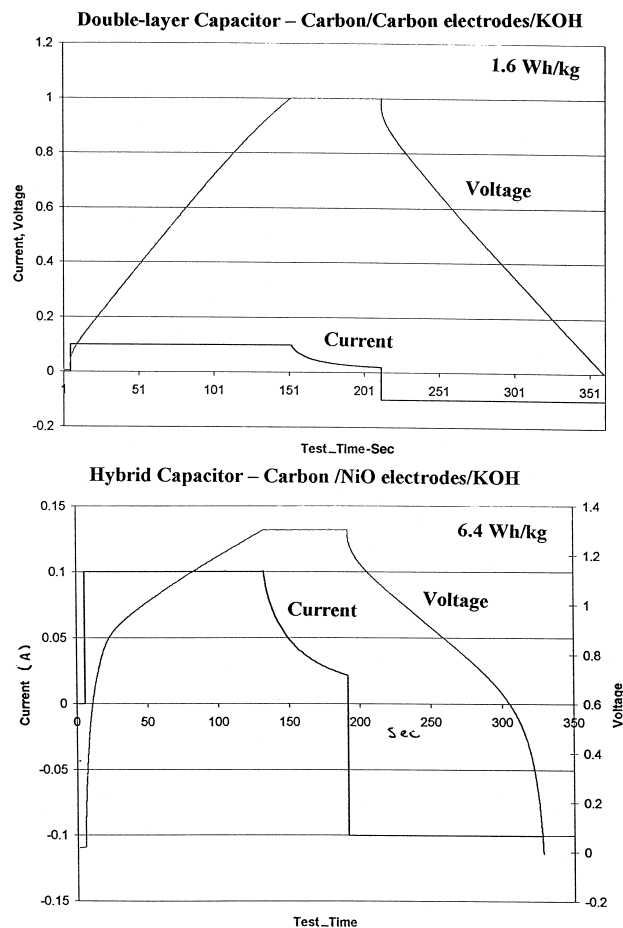Fig. 2. Schematic of a hybrid ultracapacitor.

Fig. 3. Charge/discharge characteristics of double-layer and hybrid ultra-capacitors.

positive electrode. The energy density of these devices can be significantly higher than for double-layer capacitors, but as shown in Fig. 3, their charge/discharge characteristics (V vs. Q) are very non-ideal (nonlinear). Hybrid capacitors can also be assembled using two non-similar mixed metal oxide or doped conducting polymer materials.

4. What is the present and projected status of ultracapacitor technology?

There is currently research and development on ultracapacitors underway in the United States, Japan, and Europe. Much of this work is directed toward electric and hybrid vehicle applications, but some of work is for medical and consumer electronics applications. A summary of ultracapacitor research and development around the world is given in Table 3. It is clear from the table that devices using a wide range of materials and construction approaches have been fabricated. Only a few of the devices have progressed to the point that they are ready or near ready for commercialization and even fewer are available for purchase even in small quantities.

In the following sections, the present status of the technology is reviewed for carbon double-layer capacitors,

Table 3
World-wide research and development activities on ultracapacitors

Country	Company or lab	Funding	Description of the technology	Device characteristics	Energy density (W h/kg)	Power density (W/kg)	Status/availability
Carbon particulate composites							
Japan	Panasonic	Private	Spiral wound, particulate with binder, organic electrolyte	3 V, 800–2000 F	3–4	200–400	Commercial
France/US	Saft/Alcatel	US DOE/private	Spiral wound, particulate with binder, organic electrolyte	3 V, 130 F	3	500	Packaged prototypes
Australia	Cap xx	Private	Spiral wound and monoblock, particulate with binder, organic electrolyte	3 V, 120 F	6	300	Packaged prototypes
Japan	NEC	Private	Monoblock, multi-cell, particulate with binder, aqueous electrolyte	5–11 V, 1–2 F	0.5	5–10	Commercial
Russia (Moscow)	ELIT	Russian Government/private	Bipolar, multi-cell, carbon with sulfuric acid	450 V, 0.5 F	1.0	900–1000 > 100,000 cycles	Commercial
Carbon fiber composites							
United States	Maxwell	US DOE/private	Monoblock, carbon cloth on aluminium foil, organic electrolyte	3 V, 1000–2700 F	3–5	400–600	Commercial
Sweden/Ukraine	Superfarad	Private	Monoblock, multi-cell, carbon cloth on aluminum foil, organic electrolyte	40 V, 250 F	5	200–300	Packaged prototypes
Aerogel carbons							
United States	PowerStor	US DOE/private	Spiral wound, aerogel carbon with binder, organic electrolyte	3 V, 7.5 F	0.4	250	Commercial
Conducting polymer films							
United States	Los Alamos National Lab	US DOE	Single-cell, conducting polymer (PFPT) on carbon paper, organic electrolyte	2.8 V, 0.8 F	1.2	2000	Laboratory prototype
Mixed metal oxides							
United States	Pinnacle Research Institute	US DOE/private	Bipolar, multi-cell, ruthenium oxide, on titanium foil, sulfuric acid	15 V, 125 F 100 V, 1 F	0.5–0.6	200	Packaged prototypes
United States	US Army, Fort Monmouth	US DOD	Hydrous ruthenium oxide, bipolar, multi-cell, sulfuric acid	5 V, 1F	1.5	4000	Unpacked lab prototype
Hybrid							
United States	Evans	Private	Double-layer/electrolytic, single cell, monoblock, ruthenium oxide/ tantalum powder dielectric, sulfuric acid	28 V, 0.02 F	0.1	30,000	Packaged prototype
Russia (Moscow)	ESMA	Russian Government/private	Double-layer/Faradaic, monoblock, multi-cell modules, carbon/nickel oxide/KOH	1.7 V cells/17 V modules/20 A h (50,000 F)	8–10	80–100 (95% discharge effic.) cycle life 10–20 K cycles	Commercial

Table 4
Typical performance characteristics of small ultracapacitors

Device	Voltage (V)	Capacity (F)	Resistance (mΩ)	RC (s)	W h/kg	(W/kg) (95% efficiency)	Weight (g)
Superfarad	1.4	114	20	2.3	2.5	324	8.5
Maxwell	3	10	100	1.0	1.75	444	6.6
PowerStor	3	2.5	40	0.1	0.57	1150	5.5
Cap xx	3	120	26	3.1	5.8	374	26
Cap xx	3	30	7.4	0.22	1.5	1368	25
Cap xx	3	10	8.1	0.08	0.74	1838	17

electrochemical capacitors utilizing pseudo-capacitance, and hybrid capacitors. For each type, the present status is summarized first and then prospects for future development are discussed.

4.1. Carbon double-layer capacitors

4.1.1. Present status

Double-layer capacitor electrodes have been fabricated using carbon black and aerogel particulate and carbon cloth. Ultracapacitor devices have been assembled using such electrodes using both aqueous and organic electrodes. The capacitance of the devices has varied from a few Farads to several thousand Farads per cell. The characteristics of some of the small devices are summarized in Table 4 and those of some of the large devices in Table 5. Most of the devices utilize an organic electrolyte with a cell voltage of about 3 V. The highest energy densities are 5–6 W h/kg with a strong correlation between the energy density and RC time constant with the high energy density devices having a time constant of at least 2 s. Devices with a RC time constant as low as 0.1 s are available, but these devices have an energy density of less than 1 W h/kg even though they use an organic electrolyte and have a cell voltage of 3 V. As expected, the power capability of the devices with a small RC time constant is greater than the devices with larger time constant. Power densities for a 95% efficient discharge of 1.5–2 kW/kg are calculated for the devices with time constants of about 0.1 s and

about 500 W/kg for the large devices having a time constant of a 1.5–2 s. The corresponding power densities for a matched impedance discharge are 8 and 2 kW/kg, respectively. The primary reason for the higher power and relatively low energy density of the devices with the low RC time constant is that they utilize much thinner electrodes with the result that the inactive components (current collector, separator and packaging) are a much greater fraction of the device weight. Especially using the high resistivity organic electrolytes, it is necessary to use thin (less than 0.1 mm) electrodes to achieve very low cell resistance. This also results in a low F/cm^2 for the device and relatively low capacitance. As illustrated by the Maxwell devices of various sizes (capacitances), the time constants are primarily dependent on electrode technology and not device size. In the case of Maxwell, all their devices use the same carbon cloth and aluminum substrate resulting in a time constant of 1–2 s.

4.1.2. Future projections

In terms of weight and size, the performance of the present generation of ultracapacitors is marginal for passenger car applications. The question is what are the prospects for improving the performance of the ultracapacitors — for example increasing both the energy density and power capability by a factor of two or more. The most direct routes to increasing the energy density are to utilize carbons with higher specific capacitance (F/g) and to reduce the inactive weight of the current collector and the

Table 5
Typical performance characteristics of large ultracapacitors

Device	Voltage (V)	Capacity (F)	Resistance (mΩ)	RC (s)	W h/kg	(W/kg) (95% efficiency)	Weight (kg)
Superfarad (Kiev)	3	4000	1.25	5.0	5.0	203	1.0
Superfarad (F2)	1.4	500	15	7.5	3.3	131	0.028
Panasonic	3	800	2.0	1.6	3.1	395	0.32
	3	2000	3.5	7.0	4.4	127	0.57
Maxwell	3	2700	0.6	1.6	4.2	527	0.80
Saft (Gen 2)	3	130	16.5	2.1	5.1	479	0.032
Cap. xx	3	250	0.77	0.19	1.1	1114	0.295
ESMA	1.3	3200	0.4	1.3	1.5	371	0.32
ECOND (1 V/cell)	60	7	20	0.14	0.36	506	10 (estimated)

material used to bond the carbon to the substrate with minimum contact resistance. Increasing the cell voltage is also a direct route to increasing the energy density. This requires a change in the electrolyte and/or its purity. The most direct route to increasing the power capability is to reduce the specific resistance (Ω cm^2) of the cell such that the RC time constant is also reduced. As noted previously, one certain way to reduce the time constant is to decrease the thickness of the electrodes which both reduces the specific resistance and the F/cm^2 of the cell. The Maxwell ultracapacitors listed in Tables 4 and 5 use a carbon cloth, which is about 0.35 mm thick and has an effective specific capacitance of about 100 F/g. Using particulate carbon with a binder, it is not difficult to reduce the electrode thickness to 50–100 μm (0.05–0.10 mm) and to eliminate the weight of the aluminum sprayed on the cloth to help bond it to the aluminum foil current collector. It is, however, not easy to find carbon particulate with a specific capacitance greater than 100 F/g in organic electrolytes.

As an illustration, assume materials are available with the following characteristics:

Carbon — 125 F/g, 0.7 g/cm^3, porosity 65%, resistivity 0.01 Ω cm;
Electrolyte — organic, resistivity 20 Ω cm, maximum cell voltage 3.5 V.

Assume the electrodes are 100 μm in thickness and contain 10% binder; the separator has a thickness of 10 μm; the current collector is 50 μm aluminum foil with carbon on both sides. For this capacitor, a straightforward calculation results in the following:

14.9 W h/kg, resistance 1.6 Ω cm^2, capacitance 0.39 F/cm^2,
RC = 0.62 s, 4.8 kW/kg for a 95% efficient discharge.

This calculation includes the weights of the carbon, binder, electrolyte, current collector and the resistance of the carbon and electrolyte and excludes the weight of the packaging and resistance of the pores. For a carbon material to be useful for this application, the pore size must be sufficiently large that the pore resistance is small compared to the resistance of the organic electrolyte in the micropores. The calculated results indicate that there is considerable potential for increasing the energy density and maximum power of ultracapacitors using carbon and organic electrolytes from that of the best of the present devices. Design goals of 8–10 W h/kg and 2–3 kW/kg seem to be attainable for fully packaged devices using carbon as the active material.

4.2. Capacitors utilizing pseudo-capacitance

4.2.1. Metal oxide capacitors

4.2.1.1. Present status. Most of the work on ultracapacitors utilizing pseudo-capacitance has been done using mixed metal oxide materials [2,3], but some work has been done using surface treated carbons [4]. The most success has been achieved using ruthenium and tantalum oxides. The high cost of ruthenium has resulted in a search for other metal oxides and nitrides [5,6] for use in ultracapacitor electrodes, but no substitute for ruthenium has been found with a comparable specific capacitance and higher surface area (m^2/g). The most extensive efforts [7,8] to develop ultracapacitors using ruthenium oxide have been done at Pinnacle Research Institute (PRI). The PRI devices utilized a thin (10–50 μm) layer of ruthenium/tantalum oxide on a titanium substrate with sulfuric acid as the electrolyte. PRI fabricated large cells (up to 200 cm^2 in area) and assembled them into bipolar stacks of up to 100 cells. A summary of test results [9,10] for two large PRI devices is given in Table 6. The energy density of both packaged devices is 0.6 W h/kg. The RC time constants for the two devices are quite different being 0.25 s for the 15 V device and 0.06 s for the 100 V device. Even though the configurations of the two devices are very different (one has 110 cells in the bipolar stack and the other, sixteen 15-cell bipolar stacks in parallel), the primary reason for the difference in the time constants is that the cells in the 100 V device have a lower resistance and lower capacitance than those in the 15 V device. The power densities for a 95% efficiency discharge of the two devices are 527 and 2010 W/kg, respectively. Hence, the 100 V device has very high power capability. The energy density of 0.6 W h/kg would be reasonable for a large carbon-based device using an aqueous electrolyte, but for a device using ruthenium, it is considerably lower than would be expected. PRI projected [11] that the energy density of their devices would improve rapidly with further development, but that did not occur primarily because of problems in attaining higher surface area (> 100 m^2/g) and higher specific capacitance (> 150 F/cm^2) for large devices (> 50 cm^2).

Table 6
The characteristics of various RuO$_2$ ultracapacitors

Device	Voltage (V)	Number of cells	Area (cm^2)	Capacity (F)	Resistance (Ω)	RC (s)	W h/kg	W/kg (95% efficiency)	Weight (kg)
PRI-15	15	240	3000	105	2.4	0.25	0.6	527	5
PRI-100	100	110	200	0.6	100	0.06	0.6	2010	1.4
ARL-1	5	5	2.8	1.5	200	0.3	8.5	5800	0.61 g

Tests [9,10] indicated that another difficulty with the PRI devices was that both of them had a high self-discharge rate with the voltage of the 100 V device decreasing from 100 to 50 V in less than 30 min.

The devices discussed in the previous paragraph utilized anhydrous, crystalline ruthenium oxide as the electrode material. In recent papers [12,13], the use of hydrous ruthenium oxide as an electrode material was investigated. It was found that the specific capacitance of the hydrous RuO$_2$ with an aqueous electrolyte (sulfuric acid) was about 750 F/g, which is much higher than ever measured for anhydrous ruthenium oxide. The high specific capacitance is thought to be due to the intercalation of the H$^+$ ions into the bulk of the hydrous oxide making the specific capacitance much less sensitive to surface area than was the case with the anhydrous oxide. In Ref. [14], electrodes were prepared using a mixture of hydrous ruthenium oxide powder and carbon black to increase the porosity of the electrode and thus the power density of devices assembled using the electrodes. Small (2.8 cm^2) devices have been assembled at the US Army Research Lab, Fort Monmouth using this approach. The characteristics of a 5 V device (five 1 V-cells in a bipolar stack) based on the test data given in Ref. [14] are given in Table 6. The performance of the device using the hydrous ruthenium oxide/carbon composite is impressive with an energy density of 8.5 W h/kg and a power density for a 95% efficient discharge of 6 kW/kg. The RC time constant of the device is 0.3 s. For small devices, the weight of ruthenium oxide needed is only a fraction of a gram so that the cost of the materials would be quite low.

4.2.1.2. Future projections. Progress on the use of metal oxides other than ruthenium has been very limited until recently when work was reported [15] using a manganese oxide-based complex metal oxide having a specific capacitance of 200 F/g in an aqueous electrolyte of potassium and sodium salts. Small 8 V bipolar capacitors have been fabricated using the manganese oxide-based material. The devices showed promising performance and relatively long cycle life (over 1000 h on a GSM test cycle). Additional work [16] on ultracapacitors using mixed metal oxide materials was also reported at the 9th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices. No information was given on the chemical composition of the material used in prototype cells that had an energy density of 10–15 W h/kg. These recent results using mixed metal oxide electrode materials indicate that such pseudo-capacitive materials can be promising materials for future ultracapacitor development.

As discussed in the previous section, the use of hydrous ruthenium oxide with activated carbon powders in composite electrodes has shown considerable promise in small, laboratory devices (see Table 6). It can be expected that the development of this technology will proceed to the fabrication and testing of larger devices that could be cost-effective for consumer electronic applications in which the high unit cost (US$/g) of the ruthenium may be acceptable. Such devices would have very high power (at least several kW/kg), but information on their cycle and calendar life and self-discharge characteristics requires future evaluation.

4.2.2. Conducting polymer capacitors

4.2.2.1. Present status. Research on the use of conducting polymers as the active material for ultracapacitors has been in progress at the Los Alamos National Laboratory (LANL) in the United States since 1991 [17–19]. LANL has concerned several design options and is presently focusing their attention on a type III ultracapacitor using poly[3-(parafluorophenyl)thiophene] (PFPT) as the active material. PFPT is an electronically conducting polymer that can be charged both positively (p-doped) and negatively (n-doped). When the capacitor is discharged, both electrodes return to their undoped state as ions from the organic electrolyte (2 M Et$_4$NBF$_4$ in acetonitrile) diffuse into the bulk of the polymer. The microporous active polymer is electropolymerized onto carbon paper that acts as the substrate for the electrode. At the present time, LANL has fabricated and tested small, 1.9 cm^2 cells with a packaged weight of 0.25 g [18]. The discharge performance of a 0.2 F-cell is shown in Fig. 4 for a range of discharge current densities. Note that the voltage vs. time characteristics of the device are more similar to that of a battery than a double-layer capacitor due to the pseudo-capacitive nature of the energy storage. The energy density of the present prototype cell is about 1 W h/kg for a steady power discharge at 1.8 kW/kg. The present cells have limited cycle life and relatively high self-discharge.

4.2.2.2. Future projections. Work is continuing on this technology at LANL to improve the performance of the cells and to scale them up to larger sizes. In a recent paper [19], it was projected that future packaged cells could have an energy density of 8 W h/kg for a constant power discharge at 4 kW/kg.
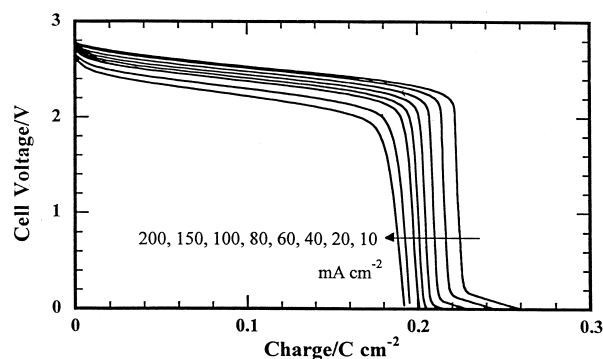

Fig. 4. Discharge characteristics of the LANL ultracapacitor using doped conducting polymer electrodes.

4.2.3. Hybrid capacitors

4.2.3.1. Present status. Most of the work on hybrid capacitors has been done in Russia [20,21] using nickel oxide as the positive, battery-like electrode, but some work has been done using lead oxide [22] as the material in the positive electrode. The negative electrodes in these hybrid capacitors were fabricated using activated carbon cloth. The hybrid capacitors made in Russia are large devices having relatively thick electrodes resulting in capacitances of 3000–15,000 F/cell. The performance of the Russian hybrid devices is more like a battery than an ultracapacitor in that the charge and discharge times in most applications would be 10–20 min and the peak power density for a high efficiency discharge would be about 300 W/kg. In the case of the devices using nickel oxide, the energy density claimed for charge/discharge is dependent on the voltage range, being about 1.5 W h/kg for 0.8–1.3 V and 8–10 W h/kg for 0.8–1.6 with the large difference in energy density being due to pseudo-capacitance in the carbon electrode at the higher voltage. The energy density claimed for the devices using lead oxide for the positive electrode are 10–20 W h/kg for a voltage range of 0.7–1.8 V. Little information is given on the deep discharge cycle life of the Russian devices. The Russian devices appear to be essentially high power batteries having a relatively low energy density rather than more traditional electrochemical ultracapacitors.

4.2.3.2. Future projections. Hybrid capacitors designed using thin electrodes with thicknesses of 10–125 μm can be expected to have charge/discharge characteristics similar to those of double-layer capacitors. In general, the negative carbon electrode will be thicker than that of the positive battery-like electrode, because the capacity per unit volume of the carbon to store charge is much less than that of the positive electrode material. Using aqueous electrolytes, the intent of the design is to permit the carbon to charge/discharge over nearly 1 V (−0.5–+0.5 V) while the battery-like electrode is charged/discharged over a relatively narrow voltage range. Restricting the depth of discharge of the battery-like electrode is key to achieve very high cycle life for the device.

Only limited work has been done to date on the thin-film type of hybrid capacitor. It is of interest, however, to project the characteristics of such devices based on known properties of electrode materials that can be used. The performance of such devices are highly dependent on the details of the design, particularly the thickness of the electrodes. Calculated results are shown in Table 7 for several devices using nickel oxide and lead oxide in the positive electrode. The calculations indicate that the energy densities of the hybrid capacitors can be expected to be 10–20 W h/kg. The power densities are more difficult to estimate with reasonable confidence because of the uncertain contributions of the pore resistance of the carbon and

Table 7
Calculated performance of hybrid capacitor designs

Hybrid capacitor (carbon/PbO_2)

Carbon — negative
Current collector: 25-μm-thick titanium foil coated on both sides
Carbon material: 0.8 gm/cm^3, 200 F/gm, 125-μm-thick
Voltage range: −0.5 to +0.5 V

PbO_2 — positive
Current collector: 25-μm-thick lead foil coated on both sides
PbO_2 material: 50% porosity, 792 A s capacity, 50-μm-thick
Voltage range: 1.1–2.1 V
Separator: 85% porosity, 25-μm-thick
Electrolyte: sulfuric acid

Calculations per cm^2 of device area
Weight: 64 mg
Charge stored: 2 A s
Energy stored: 4.27 W s
Energy density: 18.5 W h/kg, 52 W h/l, not including packaging

Hybrid capacitor (carbon, NiOOH)

Carbon — negative
Current collector: 25-μm-thick nickel foil coated on both sides
Carbon material: 0.8 g/cm^3, 200 F/g, 100-μm-thick
Voltage range: −0.35 to +0.35 V

NiOOH — positive
Current collector: 25-μm-thick nickel foil coated on both sides
NiO material: 50% porosity, 1044 A s capacity, 10-μm-thick
Voltage range: 0.7 to 1.4 V
Separator: 85% porosity, 25-μm-thick
Electrolyte: KOH

Calculations per cm^2 of device
Weight: 42 mg
Charge stored: 1.14 A s
Energy stored: 1.2 W s
Energy density: 7.95 W h/kg, 20.8 W h/l, not including packaging

the contact resistances at the electrode/current collector interfaces to the total resistance of the device. Based on the low resistance of the thin electrodes using aqueous electrolytes, it seems likely that the peak power densities of the devices will be at least several kW/kg. The primary uncertainties concerning the hybrid capacitors are their shelf and cycle life due to the use of battery-like positive electrodes.

5. Key design and cost issues

Research and development of ultracapacitors underway for nearly 10 years has been showing significant progress, but as yet no devices are available that are both technically and economically attractive. For vehicle applications, it is desirable to have devices with high energy density (greater than 5 W h/kg), high power density (that is low resistance), long cycle and shelf life, and reasonably low cost (less than US$2–3/W h). During the past 10 years, the difficulties associated with the development of ultracapaci-

tors meeting these requirements have become evident. In this section of the paper, some of these key design and cost issues are identified and discussed.

5.1. Electrode thickness and material properties

For vehicle applications, high useable power density (greater than 1 kW/kg and a RC time constant less than 1 s) are needed. In order to meet these power requirements, the electrode thickness should be less than 150 μm and a large fraction of the micropores should have a diameter of at least 10–20 Å. A pore size distribution favoring the larger micropores is especially important when organic electrolytes are used as is necessary to achieve the high energy density requirement.

Most of the high surface area, activated carbon materials available for use in ultracapacitors were developed for filtration applications. In those materials, a large fraction of the micropore volume results from pores that are too small to permit the electrolyte ions to freely diffuse in and out. Hence, only a fraction of the surface area is utilized to form double-layer capacitance and a significant fraction of the total electrode resistance is pore resistance. Work is needed to develop special carbons for ultracapacitor applications that have a pore size distribution tailored for that application. A number of particulate activated carbons having relatively high specific capacitance (100–200 F/g on an electrode basis) are available, but to date capacitors using carbon (fiber) cloth have shown the best performance even though the cloth material has a relatively low carbon loading (less than 0.5 g/cm^3). The carbon cloth is expensive (greater than US\$100/kg) resulting in a high capacitor cost (US\$/W h).

5.2. Contact resistance between material particles / fibers

The electronic resistivity of the electrode in an ultracapacitor must be less than 1 mΩ-cm if the resistance of the cell is to be low. This means that the contact resistance between the elements (particles or fibers) in the electrode must be very small. This requirement can be met using a conducting binder or a process that atomically connects the elements, such as sintering. The joining of the particles must be done without adversely effecting the surface area, macroporosity, or micropore structure of the electrode or its constituent elements. Meeting this requirement for electronic resistivity of the electrode has proven to be a problem in many ultracapacitor development programs.

5.3. Bonding the active material to a current collector

In order for the ultracapacitor to have a low resistance, the microporous electrode must be bonded to a current collector such that the effective contact resistance is very small (less than 0.1 Ω cm^2). This requires a very high conductivity adhesive or a bonding process that chemically joins the electrode material to the current collector material, which is usually a metal foil, either nickel or aluminum. For bipolar cell designs, the current collector can be a thin composite carbon/polymer sheet with an electronic resistivity of less than 1 Ω cm. Joining the electrode to a current collector has been a persistent problem in ultracapacitor development.

5.4. Electrolyte resistivity

The resistance of the ultracapacitor cell is strongly dependent on the resistivity of the electrolyte used and size of the ions from the electrolyte that diffuse into and out of the pores of the microporous electrode particles. This is usually not a problem for an aqueous electrolyte, such as potassium hydroxide or sulfuric acid, but is almost always a problem using organic electrolytes based on propylene carbonate or acetonitrile. The resistivity of aqueous electrolytes are much lower (1–2 Ω cm) than that of organic electrolytes (20–60 Ω cm). The pore size requirements for organic electrolytes are also greater (5–10 Å for aqueous and 15–20 Å for organic). The result of these differences in electrolyte properties is that ultracapacitors using organic electrolytes must much thinner electrodes than those using aqueous electrolytes and thus lower capacitance per electrode area. In developing ultracapacitors, the electrode material and electrolyte characteristics should be considered jointly and not separately as is often done.

5.5. Cell / stack configuration

For vehicle applications, an ultracapacitor unit will have a voltage of 200–400 V, resulting in the need to have many cells in series and likely a significant number of modules in parallel. The cell configuration can be bipolar or monoblock. In the case of monoblock, each cell consists of many positive and negative electrodes in parallel so that the effective cross-sectional area of the electrode is much greater than the geometric area of one electrode. In this case the current to each cell is collected/distributed from the multi-electrode plates and current collection is a primary concern in achieving a low cell resistance. The current collector substrate must be metallic and have a very low resistivity. Most devices consisting of interconnected cells use the monoblock configuration. In the bipolar design, each cell consists of two electrodes with the cells stacked in sequence with the current flowing directing from electrode to electrode and cell to cell. Each cell must be electrically separated from the adjoining cell with the bipolar electrodes being the positive for one cell and the negative for the next one. In the bipolar configuration, if one electrode and thus cell in the series is degraded, then the stack performance is also degraded. Most ultracapacitor devices have been built using the monoblock approach, because the quality control required is less demanding and the packaging and assembly are simpler. However, the

resistance of the bipolar design is inherently lower (no current collection voltage drops) and the packaging weight is less than for the monoblock design. High voltage bipolar ultracapacitor stacks have been fabricated [8,23] that functioned well, indicating that it is much easier to design and build bipolar ultracapacitors than bipolar batteries. Self-discharge and cell balancing are much more difficult problems in the bipolar configuration than for monoblock designs.

5.6. Packaging

The major issues involving packaging are weight, inter-electrode connections, venting, and leakage of the electrolyte. In progressing from small laboratory cells to larger, multi-electrode or multi-cell devices, packaging has been a problem in developing ultracapacitors, because of their inherent low energy density and need for very low resistance to have a clear power density advantage compared with batteries. Packaging weight must be kept to a minimum in order to achieve a reasonable energy density and contact and current collection resistances must be minimized if power density targets are to be met. Since ultracapacitors must have very long cycle and shelf life, the devices must be completely sealed with no leakage even when they are charged at very high rates.

5.7. Electrode material and electrolyte purity

Material purity is particularly important for ultracapacitors because it strongly affects both their leakage current and life characteristics. Contamination in either the electrode material or the electrolyte leads to unacceptable leakage current and resultant self-discharge of the ultracapacitor. It is relatively easy to develop devices for which the self-discharge does not significantly affect the performance of the device when it is in use. However, great care must be taken to reduce the leakage currents such that the device can sit unused for many hours or days with only a small change in voltage when it is charged near its rated voltage. Devices with very low leakage current also have a

long life as a low leakage current indicates the absence of low level Faradaic reactions between the electrode material and the electrolyte which over long periods of time result in the degradation of the device (a reduction in capacitance and an increase in resistance).

5.8. Quality and uniformity of fabrication

Quality control in the fabrication of ultracapacitors is extremely important and difficult to achieve. In vehicle applications, an ultracapacitor unit will have many cells/modules in series and parallel. It is essential that the variability between cells/modules be very small. Otherwise the maximum voltage of the unit must be significantly reduced to prevent over-voltage of individual cells due to their lower capacitance or higher resistance. Since the energy stored in the unit is proportional to its voltage squared, reducing the maximum voltage of the unit will have a significant effect on its useable energy density. Variations in the self-discharge of the cells can also lead to imbalance of the voltages in the ultracapacitor unit and subsequent variability in the maximum cell voltages when the unit is charged. This can lead to degradation of the cells and much shortened life. The quality control requirements can be reduced by using balancing resistors between the modules, but this leads to higher cost and greater weight and volume for the ultracapacitor unit. The need for quality control is extreme for the bipolar stack configuration in which it is difficult to design internal balance into the unit.

5.9. Cost of materials

The cost of the ultracapacitors has been a critical issue in attempting to market them for vehicle applications as well as for other applications. Satisfactory performance of the ultracapacitor is not sufficient for its successful marketing. It must be cost-competitive with an alternative solution, which in most cases involves the use of batteries. If the ultracapacitor is to be used with a battery to meet high power requirements, then the cost of the ultracapacitor

Table 8
Summary of present and projected future performance of various ultracapacitor technologies

Type	Electrode/electrolyte	Present status		Future projections	
		W h/kg	kW/kg	W h/kg	kW/kg
Double-layer	Carbon/aqueous	1.0	1.0	1.5	2.0
	carbon/organic	5–6	0.5	8–10	1–1.5
Pseudo-capacitance	Anhydrous RuO_2 aqueous	0.6	0.5–2.0	1.0	2–3
	hydrous RuO_2 aqueous	–	–	8–10	4–6
	mixed metal oxides/aqueous	–	–	1.5	2–3
	doped metal oxides/organic	–	–	8–12	1–2
	doped conducting polymer/organic	1.0	1.8	8	4
Hybrid	Carbon/NiO/aqueous	1.5	0.3	8–10	2–3
	carbon/PbO_2 aqueous	–	–	10–20	2–3

must be competitive with the use of more batteries or a redesigned battery to meet the power requirements of the system. The most critical factor in the cost of the ultracapacitor is the cost of the electrode material, which in many cases is high surface area, speciality carbon particulate or cloth. Such carbon is presently expensive, being US$50–100/kg. In addition, the electrode area in ultracapacitors is very high, leading to a high cost for the separator material. For ultracapacitors using organic electrolytes, the cost of the electrolyte is also high. The simple cost estimate given in Ref. [24] indicates that for large, high energy density ultracapacitors like those needed for vehicle applications, the cost of carbon should be at most US$5–8/kg for the cost of the ultracapacitor to be US$1–2/W h. Some carbons (for example, carbon blacks) are less than US$5/kg, but speciality carbons currently used in ultracapacitors are much higher in price.

6. Summary

The physics/chemistry of how ultracapacitors operate has been reviewed for a number of different electrode materials, including carbon, metal oxides, and doped conducting polymers. The special characteristic that differentiates ultracapacitors from other types of capacitors is their high energy density (W h/kg). As shown in Table 8, ultracapacitors are presently available with an energy density of 5–6 W h/kg and projections of improved performance indicate that future devices could have energy densities of 10–15 W h/kg. Ultracapacitors are inherently high power devices compared to batteries, but as indicated in Table 8, they can have a wide range of power capability from 0.5–2 kW/kg for presently available devices to 1–6 kW/kg in projected future devices. Very high power capability ($\gg 1$ kW/kg) can be achieved by utilizing thin electrodes ($\ll 100$ μm) in the device. The use of the thin electrodes results in a significantly lower energy density than would be attained using the same electrode material and thicker electrodes.

One of the key advantages of ultracapacitors is they are symmetric with respect to charge and discharge throughout their complete operating range of voltage and that they have high round-trip efficiency ($> 90\%$) even when operated at very high rates (> 1 kW/kg). When comparing the power characteristics of ultracapacitors and batteries, the comparisons should be made for the same charge/discharge efficiency. The peak power capability of batteries is often quoted for a discharge at the matched impedance point at which only one-half the energy from the battery is in the form of electrical energy to the load and the other one-half is dissipated within the battery as heat. For ultracapacitors, the peak power quoted is usually for a 95% efficient discharge in which only 5% of the energy from the device is dissipated in heat. For a corresponding high efficiency discharge, batteries would have a much lower power capability.

Ultracapacitor development is continuing worldwide with good progress being made in improving their performance. Except for low power, memory backup capacitors, however, markets for ultracapacitors have not been developed due primarily to their high cost and relatively low energy density. The projected improvement in energy density should open new markets for ultracapacitors if their price can be significantly reduced (by about a factor of 10). Key factors in reducing the price are to utilize lower cost electrode materials and to develop assembly processes that can be automated at reasonable investments. The use of carbon blacks and low cost metal oxides in recent work should result in lower material costs.

References

[1] B.E. Conway, Electrochemical Capacitors: Scientific Fundamentals and Technological Applications, Kluwer Academic/Plenum, 1999.

[2] I.D. Raistrick, R.J. Sherman, Electrical Response of Electrochemical Capacitors based on High Surface Area Ruthenium Oxide Electrodes, Los Alamos National Laboratory, Report No. LA-UR-87-2340, 1987.

[3] I.D. Raistrick, Electrochemical capacitors, in: J. McHardy, F. Ludwig (Eds.), Electrochemistry of Semiconductors and Electronics-Process and Devices, Noyes Publications, 1992, Chap. 7.

[4] F.M. Delnik, D. Ingersoll, D. Firsich, Double-layer capacitance of carbon foam electrodes, Proceedings of the Third International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1994.

[5] S.L. Roberson, D. Finello, R.F. Davis, W. Lui, W. Pell, B.E. Conway, Behavior of molybdenum nitrides for electrochemical capacitors, Proceedings of the 7th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, December 1997.

[6] P. Kurzweil, O. Schmid, A. Loffler, Metal oxide supercapacitors for automotive applications, Proceedings of the 7th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, December 1997.

[7] R.R. Tong et al., Power characteristics of the ultracapacitor, Proceedings of the Ultracapacitor, Proceedings of the 33rd International Power Sources Symposium, Cherry Hill, NJ, June 1988.

[8] M.L. Goodwin, R.L. Keenan, Development of PRI ultracapacitors for SLI and other automotive applications, Proceedings of the 4th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1994.

[9] J.T. Guerin, Ultracapacitors as Peak Power Devices in Electric Vehicles, MS Thesis, University of California-Davis, 1996.

[10] J. DeGaynor, PRI 100 Volts Ultracapacitor Testing (Final Report), Prepared by the AeroVironment, for the California Energy Commission, January 1997.

[11] M.L. Goodwin, Examples of advanced PRI ultracapacitor product development, 2nd International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1992, paper presented.

[12] T.R. Jow, J.P. Zheng, Electrochemical capacitors based on amorphous ruthenium oxide ($RuO_2 \cdot H_2O$), Proceedings of the 4th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1994.

[13] Z. Chen, S.A. Merryman, The performance of thin amorphous $RuO_2 \cdot H_2O$ capacitors, Proceedings of the 9th International Seminar

on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1999.

[14] J.P. Zheng, T.R. Jow, High power and high energy density capacitors with composite hydrous ruthenium oxide electrodes, Proceedings of the 5th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1995.

[15] Y.H. Lee, H.S. Kim, W.K. Seong, S.W. Kim, Electrochemical oxide pseudocapacitor working in a mild aqueous electrolyte, Proceedings of the 9th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1999.

[16] N. Doddapaneni, Z. Hu, S. Denzumi, Development of pulse power systems, 9th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1999, paper presented.

[17] A. Rudge, J. Davey, J. Raistrick, S. Gottesfield, J.P. Ferraris, Conducting polymers as active materials in electrochemical capacitors, J. Power Sources 47 (1994) 89.

[18] S. Zhichao, J. Davey, X. Ren, S. Gottesfeld, Performance of prototype ultracapacitor based on conducting polymer active material, Proceedings of the 8th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1998.

[19] L. Lin, D.C. Loveday, J.P. Feraris, A.B. McEwen, Performance study of electrochemical capacitors based on poly 3-(3,4-difluorphenyl) thiophene, Proceedings of the 9th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1999.

[20] A.L. Beliakov, A.M. Brintsev, Development and application of combined capacitors: double electric layer — pseudocapacity, Proceedings of the 7th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1997.

[21] I.N. Varakin, A.D. Kiementov, S.V. Litvinenko, N.F. Starodubtsev, A.B. Stepanov, New ultracapacitors developed by JSC ESMA for various applications, Proceedings of the 8th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1998.

[22] Y.M Volfkovich, P.A. Shmatko, High energy density supercapacitor, 8th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1998, paper presented.

[23] N. Marincic, F.P. Ortloff, Continuing scale-up of carbon based electrochemical capacitors, Proceedings of the 7th International Seminar on Double-layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, FL, December 1997.

[24] A.F. Burke, Electrochemical capacitors for electric vehicles — technology update and implementation considerations, Proceedings of the 12th International Electric Vehicle Symposium, Anaheim, CA, December 1994.