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Prospects for Ultracapacitors in Electric and Hybrid Vehicles

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ABSTRACT

The prospects for ultracapacitors for use in electric and hybrid vehicles in the near-term (within five years) are discussed based on the present status of the technology world-wide and the characteristics of devices that are available for purchase or in an advanced state-of-development and thus nearly ready to be marketed. The energy density (Wh/kg) of the devices presently available for purchase are too low (2.2 Wh/kg) for most vehicle applications and their price ($100-$300) is too high for even applications requiring only a small energy storage capacity (50-100 Wh). Prototype devices having an energy density of 5-8 Wh/kg are almost ready for marketing from several capacitor/battery companies. The higher energy density capacitors are carbon-based and use an organic electrolyte. They are fabricated using existing production equipment, so their price can be expected to be much lower when they are manufactured in high quantities and there are multiple sources for purchasing them. Projections of the future performance of ultracapacitors were made indicating energy densities of 10-20 Wh/kg are achievable in the relatively near-term using carbon electrode materials having specific capacitances of 150-200 F/gm.

INTRODUCTION

The concept of a high energy density, electrochemical (double–layer) capacitor is relatively recent with the first patent being issued in 1957 and the first attempts to market such devices in 1969 by SOHIO. The first devices were low voltage and very low power. The next attempt to commercialize electrochemical capacitors was by the Japanese company, NEC Corp., in 1978. These devices were also relatively low power. The early electrochemical capacitors used compressed carbon particulate and an aqueous electrolyte resulting in a cell voltage of 1 V. Even though capacitors are traditionally thought of as high power devices, the early double–layer capacitors were intended for low power applications as smaller, longer life replacements for batteries. The first high power, double–layer capacitors were developed by the Pinnacle Research Institute (PRI) starting in the early 1980's for military applications. The PRI devices, which used ruthenium/tantalum oxide electrodes and sulfuric acid as the electrolyte, had low resistance and high power capability (> 10 kW/kg), but an energy density of only about 1 Wh/kg. It was, however, reports of the PRI devices that triggered the studies in 1990 by DOE of the possibility of increasing the energy density of ultracapacitors to at least 5 Wh/kg, while maintaining a power density of 1 kW/kg . Vehicle simulations indicated that such devices could be used to load level the batteries in electric vehicles. The DOE Ultracapacitor Development Program was started in 1992 with the award of a contract to Maxwell Laboratories, San Diego, California for the development of carbon–based, bipolar devices. Since the outset of the DOE program, ultracapacitor development work has started in Europe and Japan using essentially the same goals – that is 5 Wh/kg and 500–1000 W/kg. This paper is concerned with a review of the current status of ultracapacitor research and technology and the prospects for the commercialization of the technology for use in vehicle applications in the near–term (within five years).

REVIEW OF WORLD ACTIVITY

There is currently research and development on ultracapacitors underway in the United States, Canada, Europe, and Japan. The work is directed toward electric and hybrid vehicles, as well as medical and electronic power system. applications. It is convenient to categorize the various R&D projects in terms of the materials used in the electrodes of the ultracapacitors. The materials approaches being pursued in the R&D are listed below.

1. Particulate carbon with a binder
2. Carbon/metal fiber composites
3. Aerogel carbons
4. In–place carbonization of carbon composites
5. Doped conducting polymer films on foils and carbon cloth
6. Carbon electrodes with solid polymer electrolytes
7. Mixed metal oxides (Anhydrous and hydrous)

R&D projects on which there is published information (References 1-3) are listed in Table 1 with each program and its status described briefly.

Projections of Future Developments

In the relatively short time that research and development of high energy density, high power capacitors has been underway, rapid progress has been made in increasing their performance. It is of interest to make projections of what improvements in performance can be expected in the future and what electrode material characteristics are required to achieve them. It is relatively straightforward to relate the performance of ultracapacitors to the characteristics of the materials used to fabricate them and to their internal dimensions. This is especially true of capacitors utilizing a bipolar design as in those cases, current collection is simple with the current flow through the device being essentially one–dimensional (Figure 1). The equations for the energy density (Wh/kg) and the resistance (ohm–cm2) of a cell are given below:

$$\left(\frac{Wh}{Kg}\right)_{cell} = \frac{1}{8}\,\frac{\left(F/gm\right)_{eltde}\;\left(V/cell\right)^{2}/3.6}{\left[1+\epsilon^{eltde}\,\frac{\rho^{eltyte}}{\rho^{eltde}}\right]+\left[\frac{\rho^{ccl}\,t_{ccl}}{\rho^{eltde}\,t_{eltde}}+\frac{\rho^{sep}\,t_{sep}}{\rho^{eltde}\,t_{teltde}}\right]}$$

$$R_{cell}\left(ohm\text{ - }cm^{2}\right) = 2\left[\frac{t_{eltde}}{2}\,k_{eltyte} + R_{pores}\right] + \left[t_{sep}\,k_{sep}\right]$$

where $$R_{pores} = \frac{l_p^{2}\,k_{elytyte}}{t_{eltde}\,V_{fp}}$$

(F/gm)eltde = specific capacitance of the electrode
eltde = porosity of the electrode
eltyte = density of the electrolyte
eltde = density of the electrode
sep = density of the separator, including electrolyte
ccl = density of the current collector
teltde = thickness of the electrode
tccl = thickness of the current collector
tsep = thickness of the separator
keltyte = resistivity of the electrolyte (ohm-cm)
lp = pore depth
Vfp = volume fraction of pores (cm3/cm3)

Calculations have made for ranges of the parameters that make physical sense and appear to be attainable with further development of materials for ultracapacitors. The calculated results for energy density and resistance are given in Figures 2 and 3. The energy density shows a strong dependence on material loading, specific capacitance, and cell voltage and a weaker dependency on electrode thickness. The resistance is primarily dependent on electrode thickness and electrolyte resistivity. All combinations of the parameters will almost certainly not be attainable, but the calculations indicate what ultracapacitor performance would be possible if they were. For example, the simultaneous attainment of a cell voltage of 4V and a specific capacitance of 300 F/gm would result in a very high energy density (60–80 Wh/kg). The 4V cell voltage requires the use of an organic electrolyte, which is expected to lead to a considerable reduction in the high specific capacitance values that have been reported for carbons using aqueous electrolytes. Nevertheless, the energy density projections given in Figure 2 do indicate that there are good possibilities for achieving battery–like energy densities with continuing development of materials for ultracapacitors.

PATHS TO COMMERCIALIZATION

Since electrochemical capacitors have already been commercialized for memory backup applications, this section is concerned with the commercialization of high energy density, high power ultracapacitors needed for electric and hybrid vehicle applications. As discussed below, there are several paths that can be and are being pursued to commercialize power capacitors. Much of this commericialization activity is taking place in Europe and Japan even though most of the impedious for the development of the capacitors started in the United States with the DOE program. As would be expected, it is companies that are presently manufacturing lower power capacitors and sealed batteries that are primarily involved with commercializing the high power capacitors.

The only high power, high energy density capacitors currently available for purchase off– the–shelf are from Matsushita (Panasonic) Electric Industrial Co. (Japan). The Panasonic capacitors (Figure 4) are spiral wound, 3V cells consisting of carbon electrodes and an organic electrolyte. They have an energy density of 2.2 Wh/kg and are available in 70F, 500F, and 1500F sizes at rather high prices – $120 for the 500F device and $300 for the 1500F device. At the present time, the Panasonic capacitors are fabricated in relatively small numbers. It would be expected that the price would be much lower (possibly by a factor of 20–30) if they were manufactured in large quantities like the spiral wound batteries made using some of the same equipment. This example illustrates that one path to the near–term commercialization of high power ultracapacitors for vehicle applications can be through the use of battery manufacturing expertise and equipment. A recent announcement (August 1995) from Alcatel Alsthom (Saft) in France indicates they are close to marketing a device similar to the Panasonic unit. The Saft device is 1800F, 3V packaged as a spiral wound, single cell. The energy density of the device is 2.8 Wh/kg. As was the case with the Panasonic devices, fabrication of the new Saft unit also employs equipment used in the manufacture of spiral wound batteries.

Another power capacitor that will probably be on the market soon (1995–96) is a 470F, 15V unit from NEC, a major supplier of low power "supercapacitors" for memory backup. The NEC capacitor uses carbon electrodes and sulfuric acid as the electrolyte and consists of 18 cells connected in series. The unit has an energy density of 1.3 Wh/kg completely packaged and a useable power density of about 500 W/kg. Asahi Glass Co. in Japan is another supplier of low power electrochemical capacitors that is developing high power capacitors. Asahi Glass has reported that they have prototype 3V devices of 4300F and 3300F utilizing carbon electrodes and an organic electrolyte. These units have an energy density of 6–8 Wh/kg and a power density of 500 W/kg. The approach used by NEC and Asahi Glass to commercialize their high power capacitors is simply to add a new product to an existing product line that meets a consumer need not met by their other products. This is the traditional way of introducing new products that takes maximum advantage of in–house expertise and investment in related products.

Maxwell Laboratories, which has been under contract to DOE to develop ultracapacitors for vehicle applications, has fabricated a completely packaged 2500F, 3V unit of prismatic design having an energy density of 6 Wh/kg and a power density greater than 1 kW/kg. Maxwell would like to market these devices for use in electric/hybrid vehicle drivelines, but they have no manufacturing capability already in place like Panasonic, Saft, NEC, and Asahi Glass and the large new investment required is difficult to justify without a well–defined market. This would be true of any ultracapacitor developer, who does not already have a related product line. One approach to circumventing this problem is to form a joint venture with a larger company that does have manufacturing capability. This is the approach being taken by Pinnacle Research Institute (PRI), Los Gatos, California in their joint venture with the Westinghouse Corporation to manufacture the PRI ultracapacitors for medical and military applications.

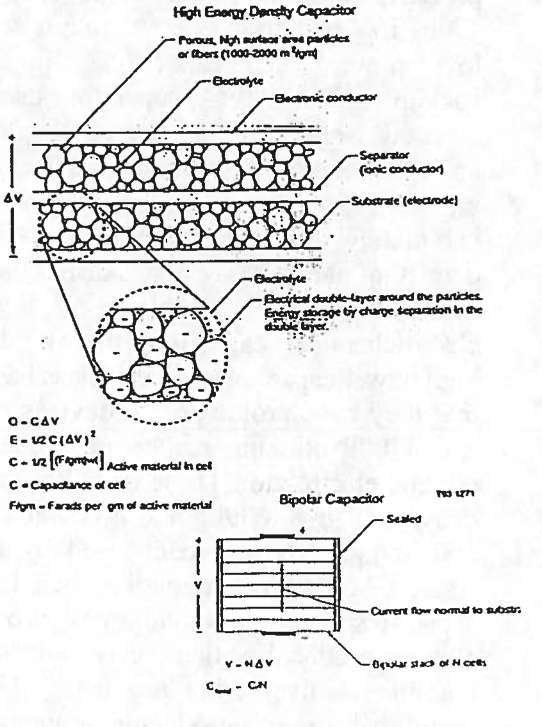

Figure 1: Schematic of an ultracapacitor cell using porous electrodes and a bipolar stack

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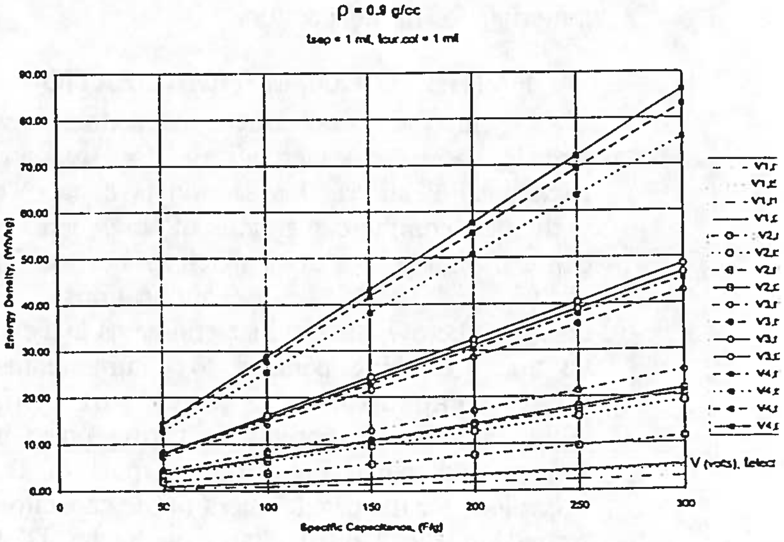

Figure 2: Projections of the energy density of carbon-based ultracapacitors of various design (carbon loading = .9 gm/cm^3)

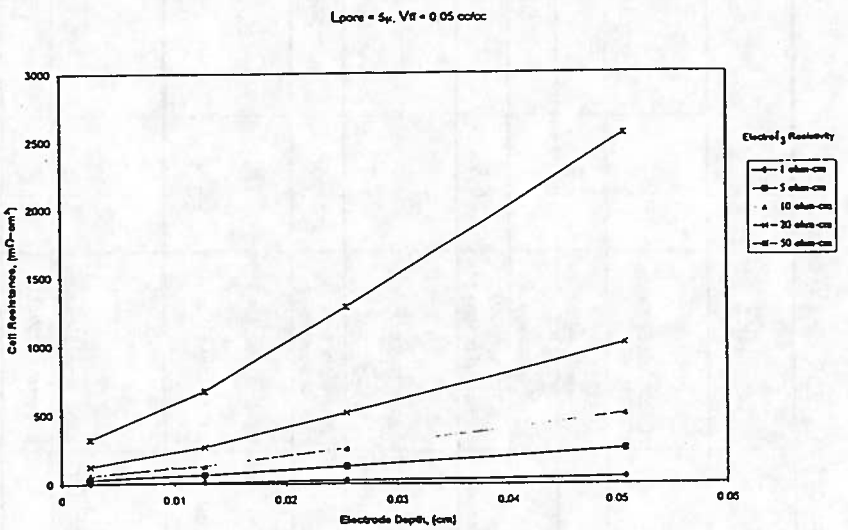

Figure 3: Projections of cell resistance (ohm-cm^2) for various designs as a function of electrode thickness

Figure 4: The Panasonic 1500F, 3V Power Capacitor

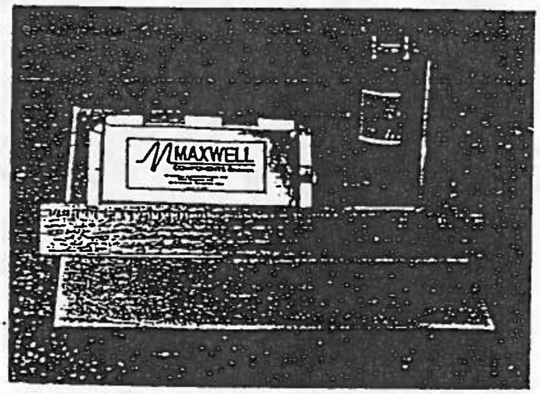

Figure 5: The 2500F, 3V Maxwell Capacitor

Table 1: Summary of Research and Development on Ultracapacitors Around the World

Country	Company or Lab	Sponsor(1)	Project Description	Technical Status	Status	
					Wh/kg	(W/kg)max
Carbon Particulate Composites						
Japan	Panasonic	Private	Spiral Wound, Particulate with binder, 3V, organic electrolyte	Commerical, 3V, 70-1500F	2.2	500-1000
France	Alcatel Alsthom	CEC	same as above	3V, 175F, lab prototype	2.9	1000
Japan	NEC	Private	Monoblock, 15V, activated carbon particulate resin molded composite, sulfuric acid	15V, 470F advanced prototype	1.3	500
Japan	Asahi Glass	Private	Monoblock, activated carbon particulate, carbon black, and binder pressed into sheets, organic electrolyte	2.5-3V, 3000-4000F, advanced prototype	6-8	400
Carbon Fiber Composites						
United States	Maxwell Laboratories	US DOE	Cloth/aluminum composite, organic electrolyte, bipolar	Laboratory devices ($20\ cm^2$), 3V cells, multicell stacks	5-7	2000-3000
United States	Federal Fabrics	US DOE, ARPA	Oriented fibers, sulfuric acid	Laboratory devices, multicell stacks	unreported	unreported
Aerogel Carbons						
United States	Lawrence Livermore National Laboratory	US DOE	Sol-gel polymerization of resorcinol-formaldehyde to form foamed carbon sheets, aqueous electrolytes	Laboratory 1V cells, 5V stacks	1-1.4	1000
Carbons with solid Polymer Electrolytes						
Denmark	Danionics A/S	CEC	Carbon particulate with a polymer binder, solid polymer electrolyte/separator	Laboratory 2V cells	<1	500-700
Japan	Yamaguchi University	---	Carbon cloth with PAN based gel-type solid electrolyte	Laboratory 2V cells	<1	Low
Conducting Polymer Films on Carbon Cloth or Metal Foils						
United States	Los Alamos National Laboratory	US DOE	Conducting polymer, electrochemically grown, p-doped films on carbon cloth or metal foil, liquid electrolytes	Laboratory cells, .75V	<2	500
Mixed Metal Oxide						
United States	Pinnacle Research Inst.	US DOE, US Army, Private	Anhydrous Ruthenium oxide films on Titanium foil, sulfuric acid	Prototype, sealed bipolar stacks, 8-100V, $200cm^2$	.8	1000-2000
United States	US Army, Fort Monmouth Rsch. Lab	US Army	Hydrous ruthenium oxide films on Titanium, sulfuric acid	Laboratory, 1V cells, 55F	10-20	unreported

(1) US DOE - United States Department of Energy
CEC - Commision of European Communities
ARPA - United States Advanced Research Projects Agency