Ultracapacitors for Electric and Hybrid Vehicles - Performance Requirements, Status of the Technology, and R&D Needs

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by

Andrew F. Burke

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The Swedish National Board for Industrial Development (NUTEK)
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Institute of Transportation Studies
One Shields Avenue
University of California, Davis
Davis, California 95616
Tel. 530/752-0247 Fax 530/752-6572
http://www.engr.ucdavis.edu/~its/
e-mail: itspublications@ucdavis.edu

Foreword

One approach to meeting the high power requirements for the energy storage system in electric and hybrid vehicles is to use a pulse power unit in conjunction with or in place of the battery. The pulse power unit provides the peak power during accelerations and recovers energy during braking while the battery provides the stored energy to achieve the desired range of the vehicle.

Electrochemical capacitors, often referred to as ultracapacitors, are being presumed to be promising candidates for the pulse power unit because of their simple design and mode of operation and the ease in which they can be integrated into the electric driveline.

Within the framework of our research programme on Electric and Hybrid Electric Vehicles NUTEK therefore has initiated and funded this state-of-the-art study to clarify the development potential for ultracapacitors as drive line components for EVs and HEVs. The study has been carried out by Dr. A.F. Burke at the University of California, in our opinion in an ideal way.

The opinions and conclusions expressed in this report are those of the author and not necessarily those of NUTEK.

Stockholm in January 1996

Göran Yström
Head of unit

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A.F. Burke
Institute of Transportation Studies
University of California, Davis
Davis, California 95616

ABSTRACT

The development of ultracapacitors for electric and hybrid vehicle applications has been underway since the early 1990s. In this report, those development activities are reviewed and the status of the technology, as of mid-1995, is assessed. It was found that work is being done in the United States, Canada, Europe, and Japan to develop ultracapacitors using various types of carbons, doped conducting polymers, and metal oxides as electrode materials and aqueous, organic, and solid polymer electrolytes. The present state-of-the-art for ultracapacitor cells is 1.5 Wh/kg and 1 kW/kg for devices using an aqueous electrolyte and 5-7 Wh/kg and 2 kW/kg for devices using an organic electrolyte. Prototype multicell units of ultracapacitors having the above characteristics are being developed by capacitor/battery companies in the United States, Europe, and Japan and should be ready for marketing within 1-2 years.

Projections of the future ultracapacitor technology indicate that the development of units with an energy density of 10-15 Wh/kg and a power density of 3-4 kW/kg can be expected in the near-term (within 5 years) and even higher energy and power densities in the longer term (5-10 years). Carbon electrodes and organic electrolytes (3V cells) appear to offer the best opportunities for achieving high energy density and affordable cost for vehicle applications. Key areas of research and development for increasing the energy density of ultracapacitors are identified. These include the development of carbon materials for electrodes having a specific capacitance of 75-100 F/cm^3 and organic electrolytes with resistivities of lower than 30 ohm-cm. Possible synergisms between ultracapacitor, lithium-ion battery, and fuel cell development are indicated as a means of decreasing the time required to commercialize advanced ultracapacitors.

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Table of Contents

1. Introduction

As the power capability of electric drivelines (motors and electronics) has steadily increased in recent years, a major problem has been how to design energy storage systems (batteries in most cases) that can provide the peak power they require. Batteries for electric vehicles are presently being developed with high power capability (peak power density as high as 500 to 700 W/kg), but it is not yet known what trade–offs in energy density, cycle life, and cost will result from the need to attain that high power density. For hybrid–electric vehicles using either an engine/generator or fuel cell for on–board generation of electrical energy, the peak power density (W/kg) desired of the batteries is considerably higher than for an electric vehicle, because the all–electric range of the hybrid vehicle is usually much shorter and the reduced energy storage (kWh) required would result in a relatively small battery <u>if</u> the smaller battery could provide the maximum power required by the electric driveline. Many of these optimum hybrid designs would require batteries with peak power densities greater than 1 kW/kg. One approach to meeting the high power requirements for the energy storage system in electric and hybrid vehicles is to use a pulse power unit in conjunction with or in place of the battery (see Figure 1). In an electric vehicle (Figure 1a), the pulse power unit provides the peak power during accelerations and recovers energy during braking and the battery provides the stored energy to achieve the desired range of the vehicle. The pulse power unit is recharged from the battery during periods when the power demand is less than the average power required by the vehicle. In hybrid vehicles (Figure 1c), the pulse power unit alone can load–level the engine/generator or fuel cell by providing the high power for accelerations and recovering energy during braking. Batteries would be required in hybrid vehicles using pulse power units only if a significant all–electric range is desired. Electrochemical capacitors (often referred to as ultracapacitors or supercapacitors) are promising candidates for the pulse power unit, because of their simple design and mode of operation and the ease in which they can be integrated into the electric driveline.

The United States Department of Energy (DOE) initiated the study of ultracapacitors for electric vehicles in 1990 and the development of ultracapacitor devices with energy densities and power capability suitable for electric and hybrid vehicles in 1992. Most of the earlier work (References 1,2) on capacitors for energy storage was done for uninterruptable power supplies (UPS), which are low power applications. Following the initiation of the DOE program for ultracapacitors for electric vehicles, there is now considerable research and development work underway in Japan and Europe as well as the United States and Canada directed toward meeting the goals (Table 1) of the DOE program. In this report, the world–wide activities on ultracapacitor R&D are summarized and the present status (1995) of the technology and projections of future develpments are discussed. Key areas for the research and development needed to advance the technology to the point that the performance of ultracapacitor units meet the requirements for electric and hybrid vehicles are identified. The Appendices include a summary of analysis/calculation procedures for determining ultracapacitor performance and a discussion of test procedures and typical data for ultracapacitors.

2. Energy Storage and Performance Requirements

2.1 Energy Storage Requirements

The use of ultracapacators in electric and hybrid vehicle drivelines is shown schematically in Figure 1. The advantages of systems using ultracapacitors relative to systems using batteries alone and whether it is even possible to package ultracapacitors in various types of vehicles depend both on the energy storage (kWh) and power (kW) requirements of the vehicle and the characteristics of the ultracapacitors available. A number of studies (References 3–6) of these energy storage considerations for electric and hybrid vehicles from passenger cars to transit buses have been performed. The key factors are the energy (Wh) needed to be stored in the ultracapacitor and its energy density (Wh/kg) and the peak power and energy storage requirements of the electric driveline of the vehicle required to meet its range and acceleration design specifications. Computer simulations of passenger cars and minivans on the Federal Urban Driving Schedule (FUDS) have shown (References 3–5) that the electric and hybrid drivelines in those types of vehicles can be load–leveled with ultracapacitors that store 300–750 Wh. Simulations of electric and hybrid transit buses in city driving (References 6,7) indicate that an ultracapacitor storing about 3000 Wh is needed to load–level the batteries or engine/generator in a 15000 kg bus. The ultracapacitors in all these simulations were maintained above one–half rated voltage (50% state–of–charge) at all times during the driving cycles (see Figures 2 and 3 for typical ultracapacitor simulation results). The ultracapacitors were not sized to provide the energy to climb long grades. Steady gradeability is provided by the batteries, engine/generator, or fuel cell. Somewhat greater energy storage (by maybe 50%) in the ultracapacitors could be provided as a safety margin if that was deemed necessary by the vehicle designer, but in any case, the energy stored in the capacitor would be only 2–10% of that stored in a battery to provide the same power.

It is easily possible to be so conservative in specifying the energy storage requirement of the ultracapacitors that their use in electric /hybrid vehicles would be precluded. Requiring a capacitor with 5 kWh energy storage in a hybrid passenger car or 10 kWh in a transit bus are examples of this degree of conservatism. These ultracapacitors would be so heavy and cost so much that their use would be almost certainly rejected by the vehicle designer. It is much less likely that ultracapacitors would be greatly oversized in electric vehicles, because of the large energy storage available in the battery for use in the event that the energy stored in the capacitor became depleted. In electric vehicles, the primary role of the ultracapacitors would be to protect the battery from short high power pulses during periods of rapid acceleration and deceleration. The effects of load leveling on the initial and life cycle costs of the energy storage system (batteries, ultracapacitors, and interface electronics) in electric and hybrid vehicles as a function of vehicle acceleration and range characteristics were studied in Reference 8 using spreadsheet models that related cycle life, $/kWh, average depth-of-discharge, energy density, battery peak power density, and load leveled battery power density. The load leveling was done using ultracapacitors having an energy density of 10Wh/kg. The spreadsheet results showed that the advantages of load leveling the batteries are largest for hybrid vehicles with relatively short all-electric range (less than 50 km) and for electric vehicles with 0-60 mph acceleration times of 10 seconds or less. The over-riding factor in assessing the operating cost of all the vehicles was battery cycle life and how it was affected by the maximum working power density of the battery and the average daily depth-of-discharge it experiences over its life.

2.2 Performance Requirements

The performance (Wh/kg, Wh/liter, and W/kg) needed for ultracapacitors to be used in electric and hybrid vehicles can be determined from the energy storage (Wh), weight (kg), and volume (liters) allocated for the energy storage unit in vehicle designs and the acceleration specification and thus the maximum power of the vehicle. A study of performance requirements for energy storage systems/components in electric/hybrid vehicles was performed previously for DOE (Reference 9). Electric drivelines utilizing a battery alone to meet both the energy storage (kWh) and power (kW) requirements of the vehicle and drivelines incorporating an ultracapacitor as a stand alone power device in a hybrid vehicle or inconjunction with a battery in either an electric or hybrid vehicle were considered. The results of the study are summarized in Figure 4 in the form of a Ragone curve, which shows that for all applications the peak power required of the energy storage unit must increase as its energy density increases if the potential gain of its improved energy density is to be fully realized in a vehicle design. This indicates that advanced batteries will need to be combined with a pulse power device, such as an ultracapacitor, even in a battery powered vehicle unless the power density of advanced batteries are greater than 200–300 W/kg. For hybrid vehicles, the power density of advanced batteries would need to be greater than 1000 W/kg for them to be used alone without ultracapacitors. The need for increasing the maximum power density of advanced batteries has been recognized by the United States Advanced Battery Consortium (USABC) that has set a goal of 400 W/kg for batteries having an energy density of 200 Wh/kg. Design of advanced batteries having a peak power density of 400 W/kg will likely require life cycle, cost, and safety trade-offs that could be reduced or eliminated by using pulse power devices such as ultracapacitors.

The volume and weight of an ultracapacitor storing 500 Wh and 1000 Wh are shown in Table 2 for various energy densities of the ultracapacitor. The corresponding peak power densities requirements are also shown in Table

2 for use in vehicles with different acceleration capabilities. The results shown indicate that in order for the ultracapacitor to have a relatively small effect on the weight of a passenger car its energy density should be greater than 10 Wh/kg and its power density should be greater than 1 kW/kg. Ultracapacitors with an energy density of 20 Wh/kg and 2 kW/kg would be even smaller and thus could be easily packaged in all types of vehicles from ultralite electric/hybrid vehicles to transit buses. Hence much of the later discussions of ultracapacitors will focus on developing ultracapacitors with energy densities of 10–20 Wh/kg and power densities of 1–2 kW/kg. The corresponding volumetric energy densities (Wh/liter) are expected to be 15–30 Wh/liter.

3. World–wide Research and Development Activities on Ultracapacitors

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. In this study, the vehicle applications will be emphasized. 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 are listed in Table 3 and each program and its status are described briefly. A bibliography of the ultracapacitor literature is given in Appendix I, which is organized, as is Table 3, by electrode material.

Most of the ultracapacitor work related to vehicle applications has been done in the last 3–5 years, but considerable work was done prior to that for lower power applications. Many patents were issued prior to 1990 on capacitors suitable for energy storage. Most of those patents were and continue to be issued in Japan. A survey of the patent literature is given in Reference (10). Considerable work on ultracapacitors is being done that is proprietary and unreported in the literature; however, it is thought that the published work is a good indication of the status of ultracapacitor R&D. The status of the technology will be presented in considerable detail in the next section.

4. A Review of Ultracapacitor Technology

This technlology review will focus on the status and performance of devices fabricated using the various materials approaches cited previously. A detailed discussion of how ultracapacitors work and how they store electrical energy is given in Appendix II. Readers unfamilar with field of ultracapacitors should read Appendix II before reading this review section. Much of the discussion in this section is based on test data. Test procedures for evaluating ultracapacitors are presented in Appendix III for those unfamilar with testing of such devices. Each of the material approaches is considered with aqueous and organic electrolytes. Devices using a solid polymer electrolyte are discussed separately. No attempt will be made to include all the research, which has been done for a given type of ultracapacitor. Only key results that define the present status of each material technology will be presented and discussed.

4.1 Particulate Carbon with a Binder

The most common approach to fabricating electrodes for ultracapacitors is to mix high surface area, activated carbon particulate with a binder and to spread the paste to form a thin layer on a current collector, which is often an aluminum foil. The electrodes are then separated by a microporous sheet of polyethylene and the assembly is spiral wound to form a cell. The cell is then impregnated with an organic electrolyte and sealed in a cylindrical container. The cell voltage is 2.3–3V. Capacitors fabricated using this approach have been on the market from Panasonic since about 1992 (see Figure 5). Panasonic presently has for sale 70F, 500F, and 1500F devices. The Panasonic capacitors have been thoroughly tested at the Idaho National Engineering Laboratory (INEL) over the last several years (References 11,12). Their energy densities are 2.3 Wh/kg and 2.9 Wh/liter. As shown in Figure 6, their charge/discharge characteristics are quite ideal – that is the voltage vs. time curves for constant current charge/discharges are nearly linear. The DC resistance of the 1500F Panasonic device is 1.3 mohms and they have been tested at constant power up to 1000 W/kg. At that high power, about 60% as much energy is extracted from the capacitors as at 100 W/kg. The spiral wound devices are low resistance devices in absolute terms (ohms) because of their high current flow area (many m^2). However, when the resistance is normalized by the area and expressed in terms of ohm–cm^2, one finds the resistance is 5–10 ohm–cm^2. Hence the Panasonic capacitors are not low resistance devices when one looks at the resistance characteristics of the electrodes. Their relatively high resistance is likely due to the presence of the binder between the carbon particles and the contact resistance at the carbon–foil interface. The use of the binder also results in the relatively low energy density for carbon devices using an organic electrolyte. Hence there is reason to expect the performance of the spiral wound devices will improve significantly as they are further developed. In large quantity production, the cost of the spiral wound capacitors should be low as they use low price activated carbon particulate and utilize production facilities already in place to make batteries. If their energy density can be increased to 4–5 Wh/kg, they could then be used at least in the near–term in some vehicle applications. Life cycle tests (Reference 13) of a 500F Panasonic capacitor at INEL showed a cycle life of over 500,000 cycles indicating that cycle life should not be a problem and the devices should last the life of a vehicle.

Recent work (Reference 14) being performed at the Alcatel Alsthom Research Center in France as part of the ultracapacitor development program of the Commission of the European Communities indicates that the performance of spiral wound capacitors is being improved. The energy densities cited for the Alcatel devices are 2.9 Wh/kg and 4.4 Wh/liter for D size 3V cells. This is a significant improvement over that cited for the Panasonic devices of similar design. It is not possible to determine from the available data whether the resistance (ohm–cm^2) of the Alcatel device is improved over that of the Panasonic devices.

4.2 Carbon/Metal Fiber Composites

The ultracapacitor development program in the United States funded by the United States Department of Energy (DOE) has concentrated for the most part on the use of carbon fiber materials for the electrodes of the ultracapacitors. The original goals (Table 1) of the DOE program emphasized both high energy density and the low resistance needed to attain high power density and high round–trip efficiency. Work published in the United States by Auburn University (References 15,16) indicated that carbon fibers interconnected with metal fibers in the electrode would result in the desired low electrical resistance devices. This approach was taken by Maxwell Laboratories, who were the initial industrial contractor for the DOE ultracapacitor program started in 1992. The first Maxwell work used activated carbon and nickel fibers sintered into a composite electrode. These electrodes were utilized to fabricate bipolar cells (Reference 17,18) using an aqueous electrolyte (KOH). Because of the aqueous electrolyte, the cell voltage was limited to 1V. The construction of the electrodes and cells are illustrated in Figure 7 and photographs of a 20 cm^2 electrode and cell stack are given in Figures 8 and 9. The charge/discharge characteristics of the 20 cm^2 cells were quite ideal (Figure 10) and the resistance of the cells was low (.3 ohm– cm^2); however the energy density of the cells was only 1–1.5 Wh/kg, which was much below the program goal of at least 5 Wh/kg. The decision was then made to design and fabricate cells using an organic electrolyte for which the cell voltage could be increased to at least 3V. Since the energy stored in the cell is proportional to the square of the voltage, this was expected to result in a major improvement in energy density. It was also known that the ionic resistance of the organic electrolyte was much higher than that of the aqueous electrolyte, which would result in a much higher cell resistance.

Maxwell Laboratories then proceeded to develop composite electrodes that would be electrochemically compatible with the organic electrolyte and the higher cell voltage. This meant switching from nickel fibers to aluminum fibers in the carbon/metal fiber mix. Sintering carbon and aluminum fibers such that the mechanical strength and electrical resistance characteristics of the composite electrode sheets were suitable proved to be a very difficult problem and no satisfactory solution was found. Hence the sintered carbon/metal fiber approach to forming the composite electrodes was abandoned and a new approach involving the use of carbon cloth and a metal spray was developed. This approach for the fabrication of electrodes for cells using an organic electrolyte has proved to be quite successful. Cells and stacks have been fabricated and tested (References 19,20) that have energy densities of 5–7 Wh/kg meeting the DOE goal of 5 Wh/kg. These cells also have ideal charge/discharge characteristics (Figure 11) and high power capability (Table 4). The DC resistance of the cells using the organic electrolyte is 1–1.5 ohm–cm^2, which is much higher than that of the cells using the aqueous electrolyte. However, as shown in Table 4, the high energy density 3V cells can be discharged at power densities up to 3000 W/kg with only about a 25% decrease in the recoverable energy compared to discharges at much lower power densities. Vehicle simulations (References 5,6) indicate that the round–trip efficiency of the 3V/cell devices, even though their resistance is much higher than the 1V/cell devices, is sufficiently high for vehicle applications. The DOE funded program at Maxwell Laboratories is continuing with the scale–up of the 20 cm^2 cells to 200 cm^2 and the fabrication and packaging of multi–cell bipolar stacks. Completely sealed eight (8) cell stacks of the 20 cm^2 cells have been fabricated having an energy density of 6–7 Wh/kg and a peak power density greater than 2000 W/kg.

The DOE ultracapacitor program at Maxwell Laboratories is directed toward the development of high voltage, bipolar stacks. Maxwell has started an internal program to use the DOE electrode technology to design and fabricate high capacitance, 3V devices that they could marketed before the development of the bipolar, high voltage units is complete. A photograph of a Maxwell 2500F, 3V device, which has energy densities of 5.6 Wh/kg and 8.7 Wh/liter, is shown in Figure 12. Charge/discharge data for that device are shown in Figure 13. Envisioning large quantity production of the Maxwell devices in the near–term is more difficult than for the spiral wound devices previously discussed, because the machinery needed to manufacture the Maxwell devices is not available and in place at Maxwell as was the case for the spiral wound devices at the battery companies. Nevertheless, the progress made by Maxwell in fabricating their 2500F devices indicates that high energy density capacitors can be expected to be available in the relatively near term. Improvements in the carbon loading in the electrode and specific capacitance (F/gm) of the carbon should result in ultracapacitors like the Maxwell 2500F unit having an energy density of at least 10 Wh/kg within several years.

The U.S. DOE also has a contract with Federal Fiber–Fabrics, Andover, Massachusetts for the development of carbon–based capacitors using activated carbon fibers. The goal of that development is to fabricate electrodes and cells with a high carbon loading (greater than 1 gm/cm^3) and with activated carbon having a specific capacitance of at least 200 F/gm. Little has been published on this work, but if successful, it could yield ultracapacitor devices with energy densities of 15–20 Wh/kg for 3V cells. Small (20 cm^2) cells are presently being fabricated, but none of the cells have yet been tested by an independent laboratory to determine their performance..

4.3 Aerogel Carbons

Aerogel (foamed) carbons have been utilized by workers at the Lawrence Livermore National Laboratory (LLNL) to fabricate ultracapacitors (References 21,22). Aerogels can be formed from the sol–gel polymerization of a number of organic substances, but resorcinol– formaldehyde using sodium carbonate as the base catalyst seems to result in the best material for ultracapacitor applications. The initial gel formed is superdried with carbon dioxide and then pyrolyzed at 600–1100 deg C in flowing nitrogen to form the carbon aerogels (References 23,24). The aerogels have an open–cell structure composed of interconnected particles, fibers, and platelets with characteristic dimensions of 100 Angstroms. Carbon aerogels can be formed with densities between .2 and .7 gm/cm^3 having surface areas of 500–700 m^2/gm. The specific capacitance of the aerogel varies with density showing a maximum of 150–160 F/gm in aqueous electrolytes at .6 gm/cm^3. The aerogel material is atomically interconnected so no binder is required to form thin electrode structures and its electronic resistivity is very low (< .01 ohm–cm). Hence most of the electronic resistance of an aerogel electrode is due to the contact resistance at the aerogel–current collector interface.

Ultracapacitor cells have been assembled at the Lawrence Livermore National Laboratory using the aerogel electrodes and KOH as the electrolyte. The 1V cells were 58 cm^2 in area and rectangular in cross-section. The cells were tested at the Idaho National Engineering Laboratory (Reference 25). The test data is summarized in Table 5, where it is seen that the energy density of the devices was 1–1.4 Wh/kg with a resistance of .58 ohm–cm^2. Tests were performed at discharge rates up to 1100 W/kg. The performance of the LLNL devices were comparable to the Maxwell Laboratory devices using an aqueous electrode. The carbon aerogel is a good electrode material and it warrants additional consideration for use with organic electrolytes if it can be manufactured at a low enough cost.

4.4 Insitu–Carbonization of Carbon Composites

High surface area carbon electrodes can be fabricated (References 26–29) by the insitu– carbonization of carbon composites formed by pressing mixtures of activated carbon particulate of various types and phenol resins into thin sheets. The sheets are thermally treated and then carbonized at 900–1000 deg C. The result is an electrode structure with open macropores several microns in diameter and micropores of 30 Angstroms and smaller. The insitu–carbonization not only forms the macropores needed to distribute the electrolyte within the electrode, it also bonds the carbon particles together resulting in a much lower electronic resistivity than is the case with a binder. The composite carbon sheets are then attached to a current collector. Ultracapacitor cells are assembled from two electrodes with a microporous separator between them. Devices have been fabricated using both aqueous and organic electrolytes. Test data (Reference 25) for small (2.25 cm^2) 1V cells fabricated at the Sandia National Laboratory in the United States using cellulose–derived microcellular foam carbon particles and KOH as the electrolyte are shown in Table 6. The energy density of the Sandia cells was about 1.5 Wh/kg with a resistance of .4 ohm– cm^2. The carbon composite electrode approach (Reference 28) is also being used by NEC in Japan to develop a 15V, 470F unit consisting of eighteen 1V cells connected in series. The electrolyte is sulfuric acid. This completely packaged device weighs 11.2 kg and the cell area is about 600cm^2. Its energy densities are 1.3 Wh/kg and 2.2 Wh/liter with a resistance of about .15 ohm–cm^2. The maximum current of 500A corresponds to a power density of 675 W/kg. The NEC unit can be considered state–of–the–art for ultracapacitors using aqueous electrolytes.

A recent paper (Reference 29) describes two power capacitors being developed by Asahi Glass in Japan that utilize carbon sheet electrodes and an organic electrolyte. These are single cell devices with capacitances of 4300F and 3300F. The characteristics of the units are summarized in Table 7 . Using a rated voltage of 3V/cell, the energy densities of the two devices are about 8 Wh/kg and 12 Wh/liter. Data are shown in Reference 29 for the units discharged at 100A, which is a power density of about 500 W/kg. As indicated in Table 7, the resistance of the 4300F unit is 3 mohm and that of the 3300F unit is 1 mohm. It would be of interest to determine the specific resistance (ohm–cm^2) of the units, but Reference 29 does not give the plate area of the units. These high energy density capacitors from Asahi Glass indicate that the state–of– the–art for ultracapacitors is approaching 10 Wh/kg for completely packaged units.

4.5 Doped Conducting Polymer Films on Foils and Carbon Cloth

Research on utilizing doped polymers as the active electrode material for ultracapacitors has been in progress at the Los Alamos National Laboratory in the United States since 1992 (References 30–32). A thin (<100 micron), high surface area layer of a conducting polymer, such as polyaniline, is electrochemically grown on a carbon cloth or metallic foil current collector to form the electrode. During the electrochemical formation process, the electrode material can be p– doped or n–doped. When the electrode is charged or discharged, the dopant ions move in and out of the polymer to the double–layer formed in the micropores of the electrode. In a capacitor cell, the dopant ions move between electrodes as an ionic current in the electrolyte. These devices utilize psuedo–capacitance (charge transfer at the surface in the micropores) rather than simple double–layer charge separation for energy storage. As a result, the specific capacitance of these electrodes is very high (400 to 500 F/gm of active material). The charge/discharge characteristics of the doped polymer devices are not as ideal (see Figure 14) as those of the carbon double–layer devices, but they are capacitor–like (Q is a strong function of V) in character. The electronic resistivity of the polymer film is low (0.01 to 0.1 ohm–cm) and the resistance of the cell is determined primarily by the resistance of the electrolyte in the micropores of the electrode. Hence high power devices can be fabricated using the doped–polymers as the active electrode material.

Recent test results (Reference 32) on p–doped polyaniline devices from the Los Alamos National Laboratory (LANL) indicate they are now fabricating 10 cm^2, sealed 1V cells that have a high capacitance (2.5 F) and can be discharged at high currents (100 ma/cm^2). The energy density of these devices is about 4 Wh/kg based on the weight of the polyaniline in the electrodes. Projections by LANL (Reference 31) are that energy densities as high as 15 to 20 Wh/kg in packaged devices may be possible using n–doped and p–doped electrodes and organic electrolytes in 4V cells. Much work remains to be done to understand the charge and discharge characteristics of the doped polymer electrodes that utilize psuedo–capacitance mechanisms for charge storage and to determine how they differ from batteries in terms of cycle life and peak power density.

4.6 Carbon Electrodes with Solid Polymer Electrolytes

All the ultracapacitor technologies considered thus far involve the use of liquid electrolytes (aqueous and organic) with high surface area, microporous electrodes. The electrolyte must penetrate the small pores of the electrodes and carry the ion current between the electrodes. In order to minimize the resistance of the ultracapacitor, the space between the electrodes should be as small as possible consistent with electronically insulating the two electrodes. Research on utilizing solid polymer electrolytes between the electrodes is now in progress in both Europe and Japan. The results of that work is now starting to be published (References 33–35).

The major consideration in using a solid polymer electrolyte in ultracapacitors in high power applications is its ionic conductivity, which is a major factor in determining the resistance of the cell. The resistance of the solid electrolyte layer alone is simply

$$(\text{ohm–cm}^2) = (\text{thickness})/(\text{conductivity in S})$$

As shown in Figure 15, plasticized solid polymer electrolytes can have conductivites of .004 to .007 S (150–250 ohm–cm) depending on temperature. The resistance of a 100 micron solid electrolyte sheet would then be 1.4 to 2.5 ohm–cm^2, which is comparable to the cell resistance for organic liquid electrolytes. Hence it appears that the conductivity of plasticized solid electrolytes may be sufficiently high for use in ultracapacitors if the electrolyte layer can be made very thin (<100 microns).

Additional considerations in the use of solid polymer electrolytes in ultracapacitors are the specific capacitance (F/gm) and resistance of the electrode active material when the micropores are filled with the solid polymer electrolyte. Test data given in References 33,34 seem to indicate that the specific capacitance of activated carbon material is relatively low in the presence of a solid polymer electrolyte being only 20–40 F/gm. Much higher specific capacitance is needed to develop high energy density ultracapacitors even if cell voltages of 3 to 4V are attainable with solid polymer electrolytes. Projections of ultracapacitor performance with carbon and solid polymer electrolytes are shown in Figure 16 taken from Reference 36. The projections indicate that energy densities of 5–10 Wh/kg and power densities greater than 1000 W/kg appear possible. Very high energy density may be achievable if the high specific capacitance of the porous polymer films being researched at Los Alamos National Laboratory were combined with very thin polymer electrolytes. The packaging of thin film ultracapacitor devices using solid polymer electrolytes should be much simpler than thicker devices using liquid electrolytes.

Some test data are available for ultracapacitor cells fabricated using carbon and plasticized solid polymer electrolytes. Work performed in Denmark (Reference 33) supported in part by the Commission of the European Communities utilized activated carbon particles and the liquid precursor of the polymer electrolyte as the binder to form the electrodes on nickel and aluminum foil current collectors. The solid polymer electrolyte had an ionic conductivity of about .004 S/cm and a thickness of 120 microns. Tests of 2V cells indicated an energy density of about .5 Wh/liter at a power density of 1000 W/liter. The inferred specific capacitance was 40 F/gm based on the carbon in both electrodes. Work performed in Japan on ultracapacitors using solid polymer electrolytes is given in Reference 35. The electrodes in this work were fabricated using activated carbon cloth with aluminum sprayed on the back as the current collector. A Poly(acrylonitrile) – PAN based gel type solid polymer electrolyte was used between and in the pores of the cloth fibers. The spacing between the electrodes was 2mm, resulting in a very low power device. The conductivity of the solid polymer electrolyte was measured to be about .005 S at room temperature. Test of the 2V cells at currents up to 1.5 mA indicated .40 F/cm^2 and 16 F/gm carbon in each electrode. The estimated energy density of the device was .5 Wh/kg. The results of work done in Japan appear to be consistent with that done in Denmark in terms of the solid electrolyte conductivity and the energy densities of the devices. The power capability of the devices fabricated in Denmark was much higher as they used much thinner solid electrolyte separation thicknesses.

4.7 Mixed Metal Oxides (anhydrous and hydrous)

Ultracapacitors using mixed metal oxide materials for the electrodes have been under development for nearly ten years (References 37–40). Most of the work has been done using ruthenium and tantalum oxides, but more recently other metal oxides and nitrides (References 41,42) have recieved attention in order to use precursor materials for electrode formation that are more plentiful and lower cost than ruthenium and tantalum. Thin (10 to 50 microns) layers of oxides can be formed on metallic surfaces by applying ruthenium chloride to the substrate followed by oxidation in air at 300 to 500 deg C. The electrode layers are porous having a surface area of 100 to 200 m2/gm. This is relatively low surface area for a capacitor electrode material. It is generally accepted (Reference 40,43,44) that the dominant charge storage mechanism in the double–layer formed on the metal oxide are redox surface charge transfer reactions resulting in a specific capacitance of 150 to 200 microF/cm^2 of active area compared with 20 to 30 microF/cm^2 of active area for simple charge separation in the double–layer. Capacitance due to surface charge transfer as opposed to charge separation is usually referred to as psuedo–capacitance. The charge transfer to the surface layer of material is highly reversible, but the differential capacitance is voltage dependent unlike charge separation which is independent of voltage. Based on mass, the specific capacitance for the ruthenium oxides can be 150 to 350 F/gm, which led to considerable optimism a number of years ago that high energy density (> 5 Wh/kg) capacitors could be developed using ruthenium oxide electrodes and sulfuric acid as the electrolyte. As indicated in References 11,45, progress has been slower than anticipated due primarily to problems in attaining surface areas much greater than 100 m2/gm and specific capacitances greater than about 150 F/gm for large electrode devices (>50cm^2).

The devices discussed above utilized anhydrous, crystalline ruthenium oxide as the electrode material. In recent papers (References 46,47), the use of hydrous ruthenium oxide as an electrode material was investigated. It was found that the specific capacitance of the hydrous RuO2 with an aqueous electrolyte (sulfuric acid) was 750 F/gm which is much higher than ever measured for anhydrous ruthenium oxide. The hydrous oxide material was amorphous compared to the crystalline form of the anhydrous oxide. The high specific capacitance is thought to be due to intercalation of H+ ions into the bulk of the hydrous oxide making the specific capacitance much less sensitive to surface area than was the case for the anhydrous oxide. Cyclic voltammetry measurements with the hydrous oxide indicate the capacitance of the material is nearly independent of voltage except near 0 V, where it is lower. The electronic resistivity of pellets made from the hydrous oxide is low (about .001 ohm–cm). Hence, the hydrous ruthenium oxide appears to be an excellent material for ultracapacitors. However, only small devices have been fabricated with the material to date and much work remains to be done to better understand the material. In addition, the ruthenium materials are very expensive and probably not affordable for consumer markets.

5. Projections of Future Developments

The technical status of ultracapacitors using various electrode materials and electrolytes was reviewed in the previous section of the report. In this section, projections are made of what improvements in performance can be expected in the future and what electrode material characteristics are required to achieve them. In the first part of this section, the results of a parametric study of ultracapacitor performance is presented to show what material and device characterisitics are needed to achieve specific levels of energy density and resistance. Later sections will consider separately developments for ultracapacators using carbons, mixed metal oxides and solid polymers.

5.1 A Parametric Study of Ultracapacitor Performance

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 and the current flow through the device is essentially one–dimensional (Figure 17). Previous simple analyzes of bipolar ultracapacitors can be found in the literature (References 36,48). The approach taken in this study is more detailed than was done previously especially in the treatment of pore resistance. The analytical basis for the present calculations is given in Appendix II. The equations used to calculate the energy density (Wh/kg) and the resistance (ohm–cm^2) are given below:

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

$$R_{\mathrm{cell}}\left(\mathrm{ohm\text{-}cm}^2\right) = 2\left[\frac{t_{\mathrm{eltde}}}{2}\,k_{\mathrm{eltyte}}\,\epsilon_{\mathrm{eltde}}^{-1.5} + R_{\mathrm{pores}}\right] + \left[t_{\mathrm{sep}}\,k_{\mathrm{sep}}\right]$$

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

where

$(\mathrm{F/gm})_{\mathrm{eltde}}$ = specific capacitance of the electrode
$\epsilon_{\mathrm{eltde}}$ = porosity of the electrode
ρ_{eltyte} = density of the electrolyte
ρ_{eltde} = density of the electrode
ρ_{sep} = density of the separator, including electrolyte
ρ_{ccl} = density of the current collector
t_{eltde} = thickness of the electrode
t_{ccl} = thickness of the current collector
t_{sep} = thickness of the separator
k_{eltyte} = resistivity of the electrolyte (ohm-cm)
l_p = pore depth

V_{fp} = volume fraction of pores (cm^3/cm^3)

The equation for the energy density was derived assuming sufficient ions were available from the electrolyte to charge the double-layer in the micropores of the electrode material. This requires that

$$\left(F/gm\right)_{eltde}\left(V/cell\right) << \frac{n_i\, M_i\, FD/1000}{\rho_{eltde}}\left(\epsilon_{eltde} + \frac{1}{2}\,\frac{t_{sep}}{t_{eltde}}\right)$$

where

FD = Faraday's constant (96,500 coul/mole)
Mi = Molarity of the ionized salt in the electrolyte
n_i = charge number of charge ions

This condition is most likely to be limiting for materials having a high specific capacitance $\left(F/gm > 100\right)$ used with an organic electrolyte (V/cell >2 and M_i near unity). Achieving high energy density (>15 Wh/kg) will likely require high salt concentrations and greater than minimum separator thicknesses. The calculated results for energy density and resistance are given in Figures 18–23. The energy density shows a strong dependency on the active material loading, specific capacitance, and cell voltage and a weaker dependency on electrode thickness. The calculations were made for ranges of the parameters that make physical sense and appear to be attainable with further development of materials for ultracapacitors. 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 300F/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 Figures 18–21 do indicate that there are good possibilities for achieving battery–like energy densities with continuing development of materials for ultracapacitors.

The results of the resistance (ohm–cm^2) calculations are shown in Figures 22 and 23. The resistance of the ultracapacitor cell depends primarily on the electrode thickness, resistivity of the electrolyte, and the characteristics of the mesapores (those of radius 5–50 Angstroms) in the electrode material. The calculations confirm what has been measured in tests of ultracapacitor devices that ultracapacitors can be very low resistance devices especially those using aqueous electrolytes. The resistances shown in Figures 22 and 23 do not include the contribution of the contact resistance between the electrode active material and the current collector, which can be much larger than the resistances taken into account unless special care is taken to minimize it. The calculated results indicate that resistances less than 1 ohm–cm^2 should be attainable in ultracapacitors even in ones using organic electrolyte. Based on the energy density results in Figures 18–21, this should to be possible without suffering a significant penalty in energy density.

The power density of ultracapacitors is analyzed in Appendix II (Sec. II.4). It is shown that the maximum power density (W/kg) at which the capacitor can be discharged with a fractional reduction in energy capacity of less than "fre" is given by

$$\left({}^{W}\!/_{kg}\right)_{max} = 3600 \text{ x} \left(\frac{Wh}{kg}\right)_0 \text{ x} \left({}^{9}\!/_{16}\right) \text{x} \left(1 - \frac{1}{4} f_{re}\right) \text{x } {}^{f_{re}}\!/_{RC}$$

where

$\left({}^{Wh}\!/_{kg}\right)_0$ = energy density for discharge to 0 volts

f_{re} = fractional reduction in energy capacity

RC = time constant of the ultracapacitor (C is capacitance in Farads, R is resistance in Ohms)

The above equation has been evaluated for selected capacitor designs taken from Figures 19 and 22. The results are shown in Table 8. The maximum power density values (W/kg) calculated are higher than one would expect in practice, because the resistance values (ohm-cm^2) given in Figure 22 completely neglect the contact resistance between the electrode and current collector and the energy densities do not include the packaging weight. Nevertheless, the power densities calculated indicate that power densities in the 2-3 kW/kg range for ultracapacitors should be achievable using carbon electrodes and organic electrolytes.

5.2 Carbon–based Technologies

As discussed previously, there are ultracapacitors being developed using a number of carbon–based technologies. In all cases, the objectives of the development are to increase the loading of the active carbon in the devices and its specific capacitance (F/gm) in order to achieve energy densities of 10–20 Wh/kg that are required for vehicle applications. All the work to date indicates that to meet even the minimum goals, it will be necessary to utilize an organic electrolyte so that the cell voltage can be at least 3V. Based on projections given in Figures 18–21, a volumetric specific capacitance of about 90 F/cm^3 (ex. .6gm/cm^3, 150 F/gm)for the electrode in the presence of an organic electrolyte is required to achieve 15 Wh/kg in a device. This level of specific capacitance has already been achieved for activated carbon in an aqueous electrolyte (Reference 27,49), but no data are in the literature at the present time to show it has been reached for carbon using an organic electrolyte. From unpublished data, there are indications that 100 F/cm3 and higher can be achieved in carbon fiber electrodes of density approaching 1 gm/cm^3. If this proves to be the case, then ultracapacitors with an energy density greater than 20 Wh/kg can be developed. The resistance and the power capability (W/kg) of the capacitors would depend primarily on the thickness of the electrode and the resistivity of the electrolyte. Tests of Maxwell Laboratory 3V cells (Reference 19,20) using an organic electrolytes exhibited a peak power in excess of 2kW/kg even for cells with a resistance of about 1.5 ohm–cm^2. With a reduction in cell resistance to less than 1 0hm–cm^2, devices with even higher power density would result (see Table 8). Reasonable mid–term goals for ultracapacitor development appear to be 15 Wh/kg and 3 kW/kg using activated carbon (fibers and particulate) and an organic electrolyte. Significantly higher energy density is possible if carbons with higher than 90 F/cm^3 are developed and packaged into an electrode. This will probably require the use of psuedo–capacitance in addition to the double–layer capacitance that has been dominate in the development of carbon–based ultracapacitors to date.

It can be expected that work will continue on composite, foamed, and fiber carbon electrodes with each approach utilizing carbon with increasing specific capacitance. Packaging of the cell stacks and bonding of the electrode and current collector will have increasing importance on ultracapacitor device performance and cost.

5.3 Solid Polymer Technologies

In making projections of the development of ultracapacitors using solid polymer materials, one should differentiate between the use of the material in the electrode and as the electrolyte/separator. Much less work has been done using polymers in ultracapacitors than activated carbons so projections of advances using polymers are more speculative.

Consider first ultracapacitors using conducting polymers as the electrode material. In this case, the important material properties are the electronic conductivity and specific capacitance of the polymer. The electronic conductivity of conducting polymers is sufficiently high that current collection/distribution in bipolar electrodes should not be a problem when porous p– or n–doped polymers are deposited on carbon cloth or metal foils. The specific capacitance of the doped polymers is much higher than that of the activated carbons primarily because of the psuedo– capacitance of the polymers as opposed to the double–layer capacitance of the carbons. Data available (Reference 32) from the Los Alamos National Laboratory in the United States indicates that specific capacitance in the range of 200–300 F/cm^3 (active area) may be possible using doped polymers as electrode material. If these high specific capacitances are realized, Figures 18–21 indicate that energy densities of at least 15 to 20 Wh/kg would be achievable in ultracapacitors using organic electrolytes (3V cells, .6 gm/cm^3 electrode density). Even higher energy densities (up to 30 Wh/kg) would result for modestly larger electrode densities and cell voltages. The power capability of ultracapacitors using the doped–polymers should be high as long as the resistivity of the organic electrolyte used is comparable to or lower than that of the organic electrolytes currently being used.

Projections of the performance of ultracapacitors using solid polmer electrolytes is difficult, because so little is presently known about several key aspects of their use in ultracapacitors. The major uncertainty concerns the specific capacitance of electrode materials when they are used with plastized solid polymer electrolytes rather than liquid electrolytes. Initial indications from work both in Europe and Japan (References 33–35) are that the specific capacitance of activated carbons are much lower using solid polymer than the liquid electrolytes. A second concern is the ionic conductivity of the solid polymer electrolyte in the macro– and mesa–pores of the electrodes. A solid polymer material with an ionic conductivity of .004 to .007 S is marginally acceptable as an electrolyte/separator in an ultracapacitor cell, but its acceptability for high power ultracapacitors when it is distributed throughout the porous electrode is presently highly uncertain. When more information concerning the specific capacitance and ionic resistance of electrodes using solid polymer electrolytes becomes available, Figures 18–21 can be used to project the performance of bipolar ultracapacitors using them. The ease of packaging and maufacture of ultracapacitors using solid polymer electrolytes is clear and should provide the stimulus for continued research on their application to ultracapacitors.

5.4 Mixed Metal Oxide Technologies

The projection of future developments for ultracapacitors using mixed metal oxide electrode materials is much different than for activated carbons and solid polymers for several reasons. First, there is much less information on the electrode characteristics and specific capacitance of the mixed oxide materials than for the carbon–based materials and there is even some disagreement concerning the mechanisms for energy storage (double–layer vs. psuedo– capacitance). This is the situation because the primary developer of mixed metal oxide ultracapacitors (Pinnacle Research Institute in the United States) has publish very little concerning their work. Second, there are almost no data in the literature on the use of organic electrolytes in ultracapacitors with mixed metal oxide electrodes from which to project future developments. Third, most of the work to date has been done using ruthenium/tantalum oxides and it is widely recognized that other lower cost metal oxides must be substituted if the resultant capacitors are to be affordable in consumer applications. Little work has been published as yet identifying the substitute materials (Reference 40,42) and their properties for ultracapacitor electrodes.

For this reason, the projections here will be made only for mixed oxide–based ultracapacitor using anhydrous and hydrous ruthenium oxides.

In order to make the projections, energy density calculations are needed for higher electrode densities and specific capacitances than were previously done for the carbon–based electrode materials. The density of the porous ruthenium oxide electrode is 2.3 to 2.5 gm/cm^3, corresponding to a porosity of 70-75% for the electrode . The specific capacitance of the anhydrous ruthenium oxide is given in the literature as 350 F/gm, but tests of devices using the material indicate a much lower specific capacitance of 150 F/gm. In Reference 46, a capacitance of 600–700 F/gm is measured for hydrous ruthenium oxide (RuO2*0.5 H2O). Calculated results for the energy density of ruthenium oxide–based ultracapacitors are given in Figure 24. The calculations shown are for an electrode density of 2.3 gm/cm^3, specific capacitances between 100 and 700 F/gm, and electrode thicknesses from 15-500 microns. Cell voltages of 1V and 2V were assumed in the calculations. The projected energy densities shown in Figure 24 cover a wide range from less than 1 Wh/kg to greater than 50 Wh/kg. High energy density seems to be achievable with metal oxide electrodes if the electrodes can be made at least 100 microns thick and the high specific capacitance potential of the metal oxide materials can be realized in practice. For example, for 125 micron thick electrodes, an electrode specific capacitance of 350 F/gm, and sulfuric acid as the electrolyte (1V cells), the projected energy density is 6.9 Wh/kg. The cell density would be 3.2 gm/cm^3 resulting in a volumetric energy density of 22 Wh/liter. The resistance of the cell using ruthenium oxide for the electrode material and sulfuric acid as the electrolyte should be very low, likely less than .025 ohm–cm^2.

6. Key areas of Research and Development

The development of ultracapacitors for vehicle applications has been underway for a relatively short time having been started in 1992. Good progress has been made in that time with the development of small prototype, high power devices with energy densities of 6–7 Wh/kg, but as indicated by the projections presented in the previous section, large improvements in energy density would result from the development of electrode materials having higher specific capacitance than are currently available and electrolytes that would permit the use of cell voltages of 3 to 4V. As shown in Appendix I, a large number of reports and papers on ultracapacitors have been published in the last several years. This body of literature has been used as the basis for the continuing research and development program outlined in this section of the report. The discussion of key research needs is divided into a consideration of materials - electrodes and electrolytes -, electrode fabrication and cell assembly, and stack packaging and sealing. Where appropriate, research needs for the different ultracapacitor technologies are discussed separately.

6.1 Materials Research

The performance of the ultracapacitor is highly dependent on the characteristics of the electrode material and the electrolyte. The energy density of the capacitor and how it changes with charge/discharge rate depends to a large degree on the specific capacitance of the electrode material and its pore size distribution. The resistance and power capability of the capacitor and its efficiency depend on the resistivity of the electrode material and the electrolyte. A detailed quantitative evaluation of the relationships between these material characteristics and ultracapacitor performance for the various capacitor technologies should be an important part of any ultracapacitor research program.

6.1.1 Electrode Materials

Increasing the specific capacitance of the various carbon electrode materials to 200 F/gm and higher will require the utilization of psuedo–capacitance in addition to double–layer capacitance and careful tailoring of the pore size distribution of the porous carbons for use with an organic electrolyte. Larger (40–50 Angstroms) and more uniform size pores than are found in presently available carbons are needed. Optimization of the pore size distribution of the carbons must be done using the electrolyte with which it will be used in the ultracapacitor. The increase in specific capacitance must be realized without sacrificing electronic conductivity. There are many carbon–based materials that can be investigated including aerogels and foamed monoliths, activated fibers and particulates, and doped conducting polymers. The processes for preparing each of these carbons is different and the characteristics of the material are highly dependent on how the process is controlled. Much of the work to date to fabricate ultracapacitors has made use of available carbon materials optimized for other applications (for example, removing pollutants from water or air) and little research has been done as yet to optimize carbons for ultracapacitor applications. The limited work in this area to date (References 27, 50) indicates that much progress in material optimization for capacitors can be expected from future research.

Much less work has been done using conducting polymer materials than activated carbons in ultracapacitor electrodes. Conducting polymers, such as polyaniline and polypyrrole, can be p– doped or n–doped with the dopant ions moving in and out of the polymer matrix as the electrode is charged and discharged. These psuedo–capacitive type materials have a high specific capacitance of around 500 F/gm making them good candidates for ultracapacitor electrodes. Relatively thick (up to several mils) porous layers of this material can be deposited electrochemically on carbon cloth or metal foils. The two electrodes in the ultracapacitor need not be the same for the device to function and it has been proposed (Reference 31) that to reach the maximum energy density with doped conducting polymer electrodes that one electrode be p–doped and the other be n– doped. Continued research on the use of doped polymer electrodes should be pursued as they offer the promise of high energy density (> 20 Wh/kg) using relatively low cost materials. Current data (Reference 32) indicate that the cells using doped polymer electrodes can have a long life approaching 100,000 cycles and high power (>1000 w/kg). Characterization of these devices at various charge/discharge rates is incomplete and their characteristics are uncertain because they are psuedo–capacitive and thus not nearly as ideal as double–layer carbon ultracapacitors. The research in this area is in its infancy and much work needs to be done to assess the potential of doped polymer mateials for ultracapacitors.

Development of ultracapacitors for military applications was started (Reference 37) over ten years ago. Much of that work has involved the use of ruthenium oxide as the electrode material on a titanium foil. That approach was taken, because achieving high power density rather than high energy density was the primary goal of the initial ultracapacitor research. Also the high cost and limited supply of the ruthenium was not a serious concern for the military applications. Work is currently underway to significantly increase the energy density of the ruthenium–based capacitors and to substitute other metal oxides that are much lower cost and more abundant than ruthenium. The energy density of ruthenium–based ultracapacitors has been improved by increasing the thickness of the oxide layer and by utilizing hydrous, rather than anhydrous, oxides in the electrodes. In this work, aqueous sulfuric acid is used as the electrolyte. Efforts to find substitute metal oxides that have high electronic conductivity and high surface area are relatively recent and have met with only limited success. Nickel and Manganese oxides could be good candidates as they have potentially high specific capacitances of about 1000 F/gm (Reference 40). Research on finding substitute oxides and investigating the possibility of using a hydrous form of the oxides with aqueous electrolytes for vehicle applications should be continued. Work on anhydrous metal oxides with organic electrolytes also should be pursued especially if thicker electrodes (at least 100 microns) can be prepared without sacrificing the high electronic conductivity of the electrode. This is more likely to be done by forming the electrodes from pressing oxide particles into a sheet than by the sol–gel or dipping processes now being used in most instances to fabricate ruthenium oxide electrodes.

6.1.2 Electrolytes

Most of the early work on ultracapacitors involved the use of aqueous electrolytes, because achieving very high power was the primary goal of the developments. Aqueous electrolytes, such as sulfuric acid and KOH, are well characterized in the literature and their chemical composition is, of course, well–defined. More recently, the emphasis in ultracapacitor research has shifted to the use of organic electrolytes as a means of increasing the cell voltage from 1V to 3–4 V even though those electrolytes have much higher resistance than aqueous electrolytes. The characteristics of the organic electrolytes are much less well defined than the aqueous electrolytes. In fact, the chemical composition of the organic electrolyte being used in particular ultracapacitor developments is often unknown to anyone except the developer and the ionic conductivity of the electrolyte is usually unreported. Available test data (Reference 19,20) for ultracapacitors using organic electrolytes have indicated higher energy density, lower resistance and higher power capability than was expected based on the properties (surface area and pore size) of the electrode material and the nominal conductivity of the organic electrolyte. Further investigations of the relationships between the capacitance, resistance and power capability of ultracapacitors using organic electrolytes and the properties of the electrode material and the organic electrolyte should be undertaken.

Research should include identification of the ions involved in the formation of the double– layer and those taking part in the redox reactions responsible for the psuedo–capacitance of the electrode material in the presence of particular organic electrolytes (solvent and salt combinations). Study of the diffusion of the ions in the mesapores of the electrode material and how that effects the resistance and power capability (dependence of capacitance on charge/discharge rate) of the ultracapacitor is also important. Establishing cell voltage limits for different combinations of organic electrolyte, electrode material, and current collector (Reference 51) and the effect of impurities on these limits are particularly important, because of the strong dependence of energy density on the maximum useable cell voltage.

Preparing electrolytes with as high an ionic conductivity as possible consistent with cost constraints is key to the development of high energy density, low resistance ultracapacitors. This is true for both liquid organic and solid polymer electrolytes. Since this is a requirement for lithium– based batteries as well as for ultracapacitors, much of the work presently being done on electrolytes for lithium batteries is expected to be applicable to capacitors. That work should be carefully reviewed and utilized in the capacitor research programs when it is applicable. This is especially true for solid polymer electrolytes being studied for thin film lithium polymer batteries for which electrolyte conductivity and electrode interface contact resistance are critical issues. The lithium batteries utilize carbon and mixed metal oxide electrodes as do the capacitors. Hence, much of what is learned in the battery research is likely also to be of importance for ultracapacitors. Much more attention needs to be focused on electrolytes in future ultracapacitor research than has been the case in the past when most of the the cells used aqueous electrolytes.

6.2 Electrode Fabrication and Cell Assembly

The research discussed in the previous section was concerned primarily with preparing and characterizing the electrode materials and electrolytes for the ultracapacitors as a means of determining what capacitor performance could be achieved with the various materials. This section is concerned primarily with identifying and researching the problems associated with the fabrication of electrodes and the assembly of cells and cell stacks using the most promising of the materials in electrode sizes that could be considered building blocks for larger ultracapacitor units. This research would include the development of laboratory processes for forming the electrodes from the different materials, the attachment of the electrodes to the current collectors with low contact resistance, and assembly of the electrodes with a separator into cells and cell stacks. The devices fabricated would then be tested using the test procedures discussed in Appendix III to determine their performance. For each of the electrode material technologies, devices of different internal dimensions and material properties should be fabricated as a means of better understanding the performance and cost trade–offs for that technology and in the process improve and validate the modeling of ultracapacitors. Research on cell variability and imbalance in stacks and the cycle life of stacks will become important as larger stacks are fabricated. These issues are particularly important for stacks of bipolar cells.

6.3 Packaging and Sealing

Packaging of cells into sealed bipolar stacks or monoblock modules without adding significant weight and cost to the units must be achieved before the ultracapacitors can be used in vehicle demonstration projects outside the laboratory and ultimately marketed for use in vehicles. The packaging must be done in ways that do not significantly increase the resistance of the devices or impact their cycle/calendar life. One of the most important aspects of packaging/sealing that must be solved in a cost–effective way for bipolar stacks is the impregnation of the liquid electrolyte into the stack such that the micropores are uniformly wetted and filled and the stack does not leak after the final sealing process. Non–uniform wetting of the cells with the electrolyte can lead to cell imbalances and early stack failure. In the case of ultracapacitors using a solid polymer electrolyte, sealing the stack becomes much simpler and the major issues are the uniformity of the polymer material itself and the interfaces between the solid electrolyte and the electrode materials as they will determine the magnitude of the cell variability and the maximum permissible operating voltage of the ultracapacitor unit.

Each of the material technologies will have different packaging and sealing problems which must be worked on separately. For ultracapacitors using liquid organic or solid polymer electrolytes, there are strong similarities with work being done on the packaging and manufacture of lithium batteries. Every effort should be made to utilize the technology being developed in the battery programs in the development of ultracapacitors as the battery programs are in general much larger and funded at a much higher level. For some companies, it may be possible to make use of equipment for manufacturing ultracapacitors that is available from manufacturing another product, such as is being done by Saft (Alcatel Alsthom) for their spiral wound ultracapacitors (Reference 14). These possibilities should be explored as a means of the early commercialization of ultracapacitors.

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List of Tables

Table 1: Goals of the US DOE Ultracapacitor Development Program

	Near-term	Advanced
Energy Density		
wh/kg	5	15
wh/liter	10	25
Power Density W/kg	500	1600
Round-trip Efficiency (%)	>90	>90
Cycle Life	>100,000	>100,000
Cost ($/wh)	.5-1	.5-1

Table 2: Ultracapacitor Size and Power Density for Various Energy Densities

	500 Wh Storage Energy Density (Wh/kg)				1000 Wh Storage Energy Density (Wh/kg)			
	3	5	10	20	3	5	10	20
Weight (Kg)	166	100	50	25	333	200	100	50
Volume (liters)	110	66	33	16	222	133	66	33
(W/kg) maximum								
(1) 0-96 km/h in 10 seconds	590	980	1960	3920	295	490	983	1960
(2) 0-96 km/h in 15 seconds	301	501	1000	2000	150	250	500	1000

(1) Pmax = 98 Kw for a 1400kg vehicle
(2) Pmax = 50 Kw for a 1400kg vehicle

Table 3: 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

Table 4: Constant Current Discharge Characteristics of the 3V MaxwellCells using an Organic Electrolyte

Discharge Current (A)	Capacitance (F)	Discharge Time (sec)	Resistance (ohm)	Energy Out (J)	W·h/kg	W·h/L	(W/kg)av
1	12.5	37.6	0.08	55	6.8	8.1	666
3	11.6	11.6	0.67	49	6.1	7.2	2000
5	10.7	6.4	0.076	41	5.1	6.1	3333

Discharge: 3 V to 0 V

Device Characteristics:

Weight	2.25 gm
Area	20 cm^2
Volume	1.88 cm^3

Table 5: Summary of Test Data for a 1V Cell Using Aerogel Carbon from the Lawrence Livermore National Laboratory (USA)

Test Charge = C Discharge = D	Charge Current = A	Discharge Current = A	Time (sec)	A-sec
(1) C	1	–	34.8	34.8
D	–	1	35.9	35.8
(2) C	2	–	15.7	31.4
D	–	2	17.0	34.3
(3) C	5	–	5.4	27.0
D	–	5	6.2	31.3
(4) C	5	–	4.7	24.0
D	–	10	2.8	26.3

Test Charge = C Discharge = D	W-sec	Resistance/cell (ohm)	W·h/kg	(W/kg)/av
(1) C	22.9	0.010	1.38	108
D	19.7	0.0126	1.18	108
(2) C	21.5	0.010	1.29	216
D	18.1	0.0125	1.09	216
(3) C	20.2	0.0105	1.21	540
D	15.3	0.0137	0.92	540
(4) C	19.0	0.0127	1.15	540
D	11.7	0.0135	0.70	1082

PSFUD (W/kg)max = 300
(A·h)in = 0.02429, (A·h)out = 0.02393, (W·h)in = 0.01629, (W·h)out = 0.01458, roundtrip efficiency = 89.5%
Device weight: 4.62 gm, 58 cm^2, 1 V cell

Table 6: Summary of Test Data for a 1 V Cell Using Insitu-Activated Carbon from the Sandia National Laboratory (USA)

Test Charge = C Discharge = D	Charge Current = A	Discharge Current = A	Time (sec)	A-sec
(1) C	0.1	–	34.6	3.5
D	–	0.1	32.0	3.2
(2) C	0.2	–	14.8	2.94
D	–	0.2	15.3	3.1
(3) C	0.45	–	5.3	2.40
D	–	0.45	6.0	2.72
(4) C	0.7	–	2.6	1.84
D	–	0.7	3.4	2.40
(5) C	0.9	–	1.7	1.55
D	–	0.9	2.3	2.1

Test Charge = C Discharge = D	W-sec	Resistance/cell (ohm)	W·h/kg	(W/kg)/av
(1) C	–	0.134	2.04	208
D	1.22	0.19	1.4	208
(2) C	1.69	0.17	1.96	416
D	1.11	0.2	1.28	416
(3) C	1.55	0.15	1.79	937
D	0.94	0.18	1.08	937
(4) C	1.30	0.14	1.50	1458
D	0.72	0.18	0.83	1458
(5) C	1.15	0.15	1.33	1875
D	0.65	0.17	0.75	1875
Device Characteristics: 24 mgm, 2.25 cm^2				

Table 7: Characteristics of an Ultracapacitor Device from Asahi Glass Co. (Japan) Using Carbon Particulate and an Organic Electrolyte

Voltage (V)	Capacitance (F)	ESR (mΩ)	Volume (ℓ)	Weight (kg)
2.5	4300	3	0.43	.670
2.5	3300	1	0.43	.700

List of Figures

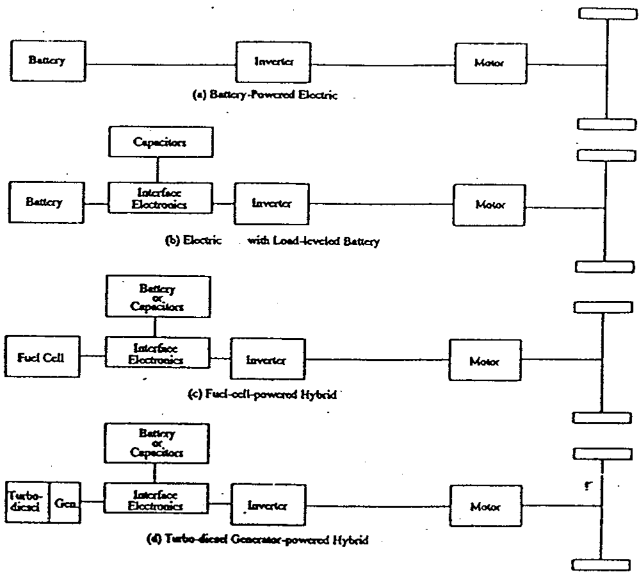


Figure 1: Driveline Schematics for Electric and Hybrid Vehicles using Ultracapacitors

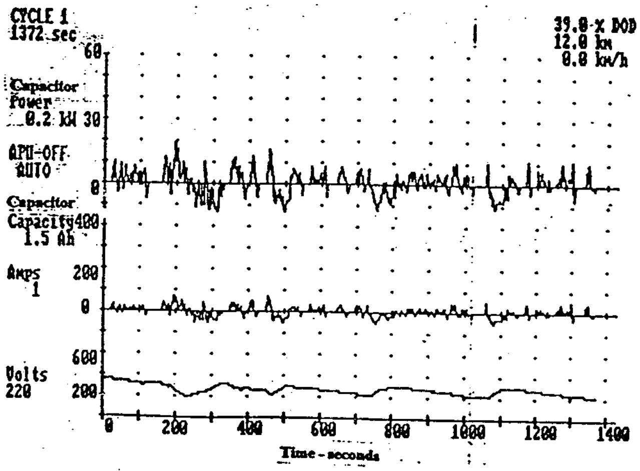


Figure 2: Discharge/charge (simulation) of a 400Wh Ultracapacitor in a Series Hybrid Passenger Car on the Federal (USA) Urban Driving Cycle

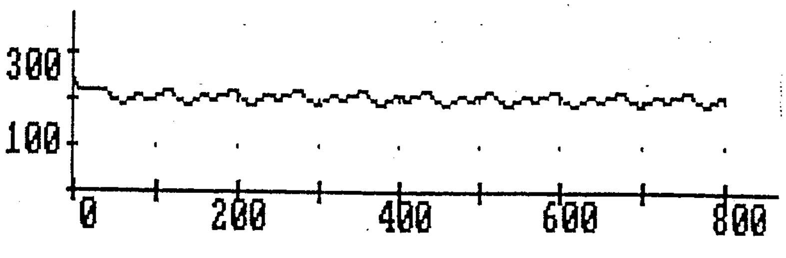


Figure 3: Discharge/charge (simulation) of a 3000Wh Ultracapacitor in a Series Hybrid 15000 Kg Transit Bus on the CBD Driving Cycle

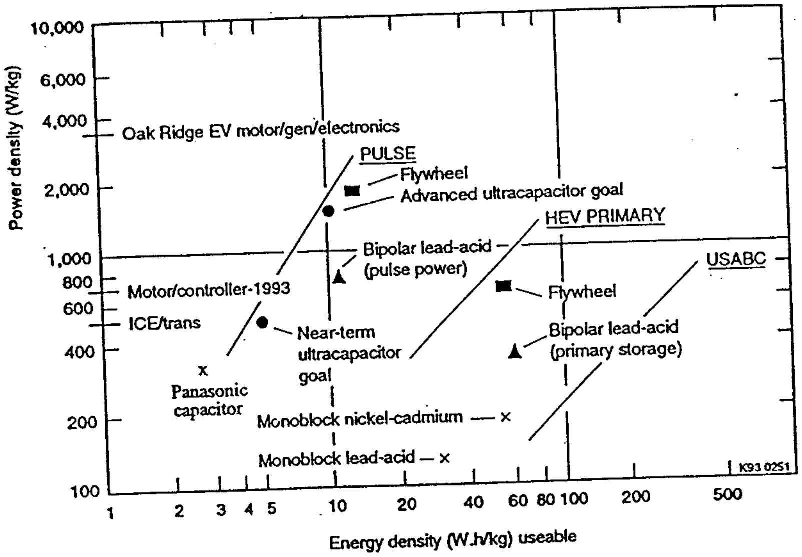


Figure 4: Energy-Power Requirements for Primary-Energy-Storage and Pulse-Power Units for Battery-powered and Hybrid Vehicles

Figure 5: The Panasonic 1500F, 3V Power Capacitor

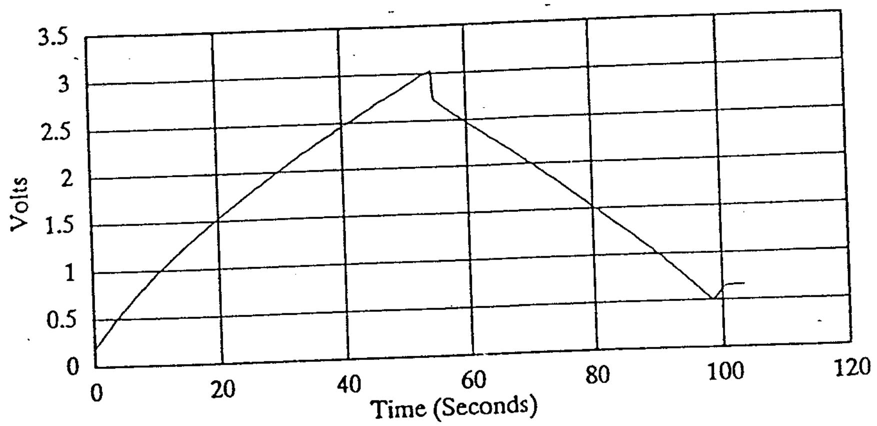
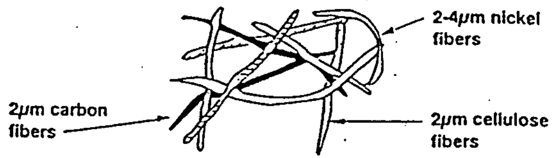


Figure 6: Charge/Discharge, voltage vs. time curves for the 1500F Panasonic Capacitor at 100A



Intimately mixed metal-carbon composite matrices from paper precursors

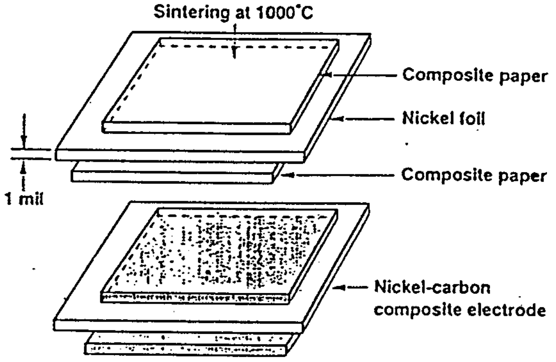


Figure 7: Construction details of the Maxwell Capacitor using carbon-nickel-fiber composite electrodes

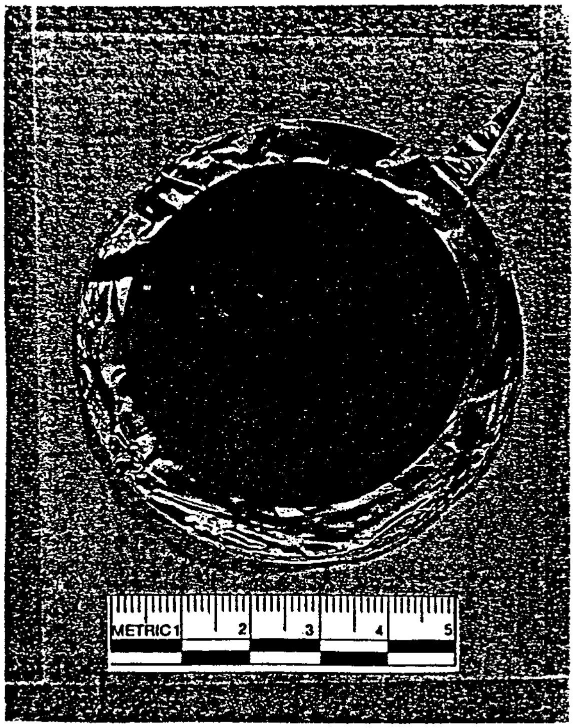


Figure 8: The Maxwell Composite-Fiber Electrode (20 cm^2)

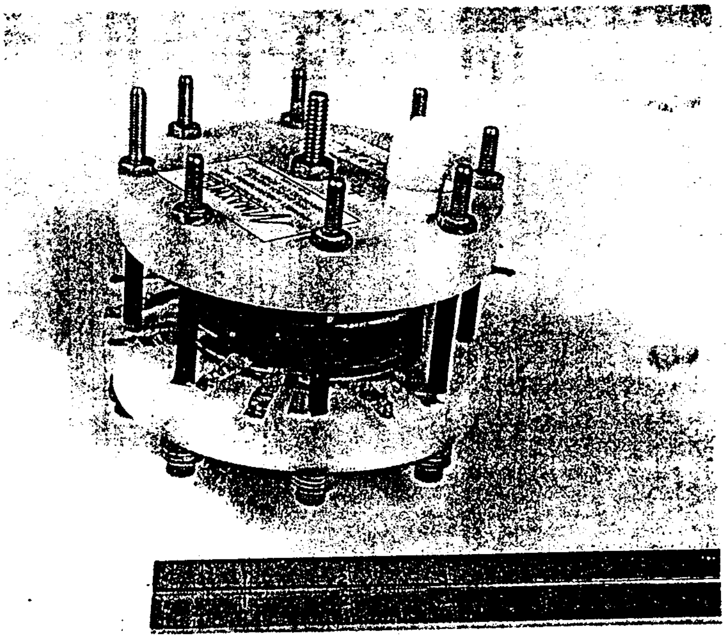


Figure 9: A 20V stack of 1V Maxwell Cells using thin gaskets and voltage tabs between cells

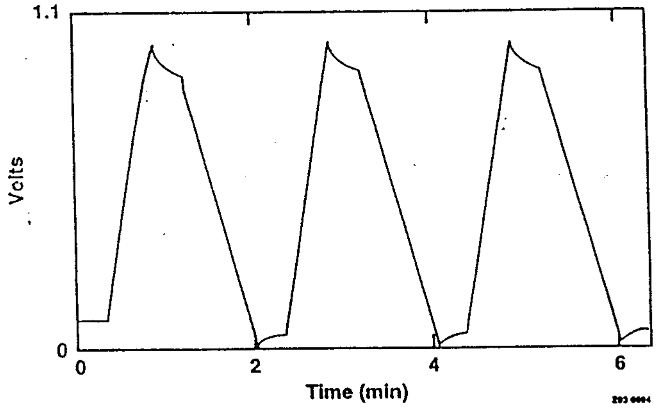


Figure 10: Charge/discharge, voltage vs. time curves (data) of a 1V Maxwell Cell (10 cm^2) at 1A

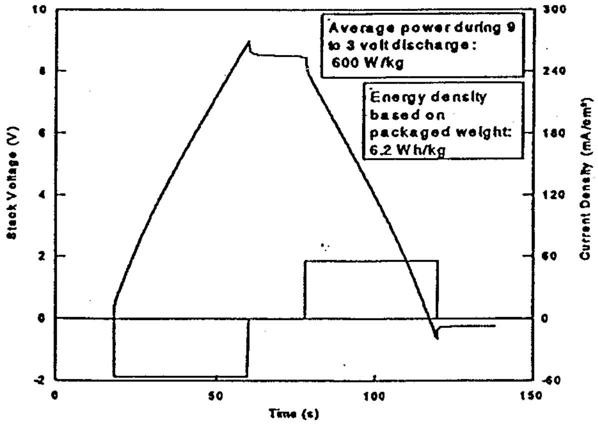


Figure 11: A charge/discharge, voltage vs. time curve (data) of a 3-cell stack of 3V, Maxwell cells (20 cm^2) at 1A

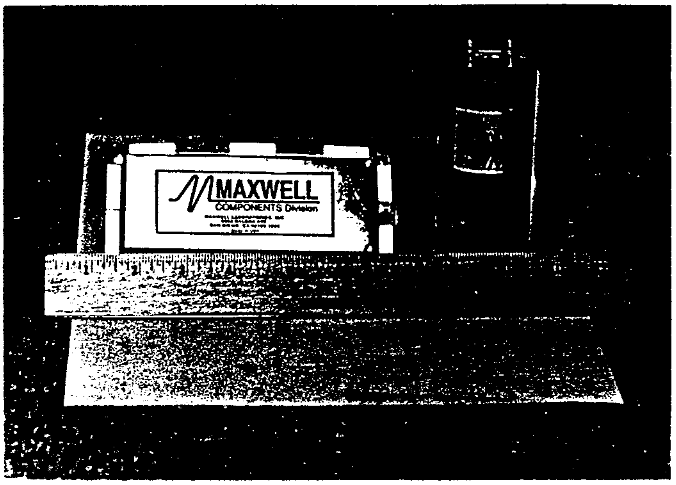


Figure 12: The 2500F, 3V Maxwell Capacitor

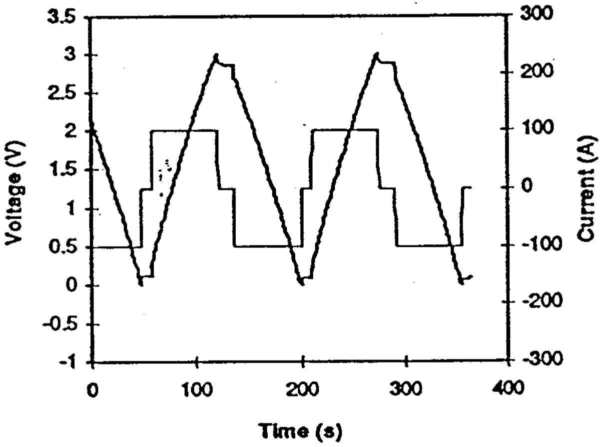


Figure 13: Charge/discharge, voltage vs. time curves (data) for the 2500F Maxwell Capacitor, at 100A

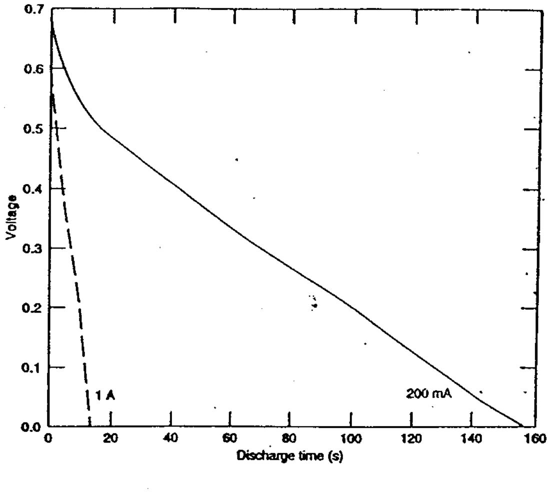


Figure 14: Discharge curves (data) for the .75V, p-doped polyaniline cells (10 cm^2)
from the Los Alamos National Laboratory (USA)

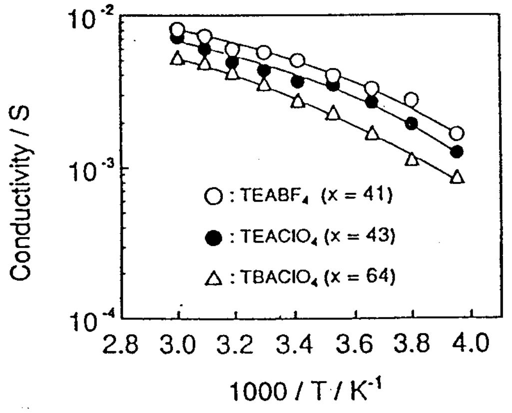


Figure 15: Ionic conductivity of solid polymer electrolytes as a funciton of temperature

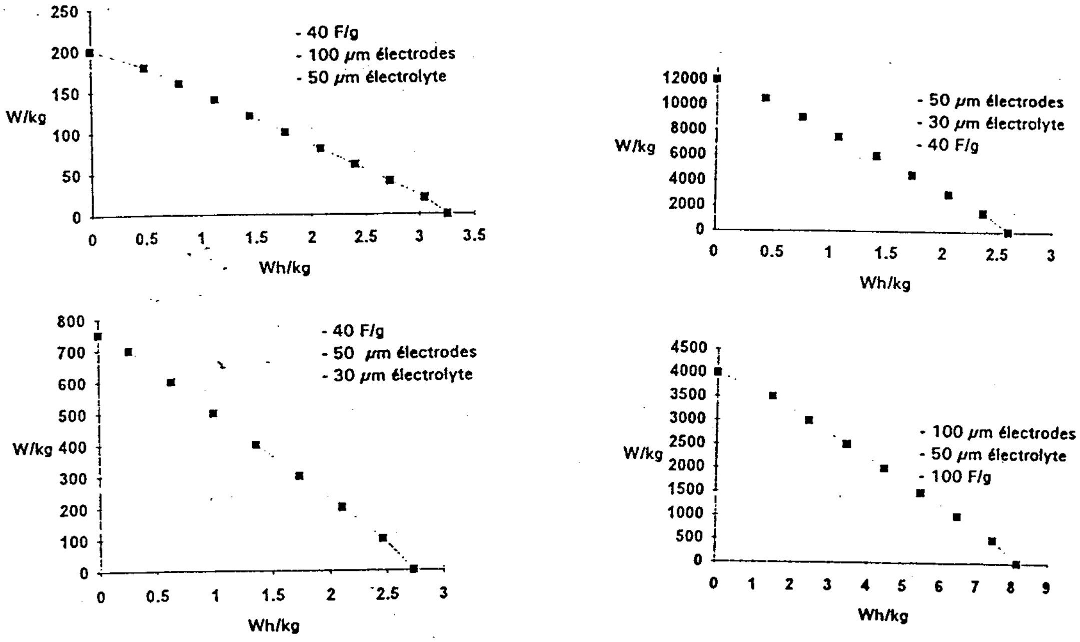


Figure 16: Projections of the energy and power densities of solid polymer ultracapacitors of various designs

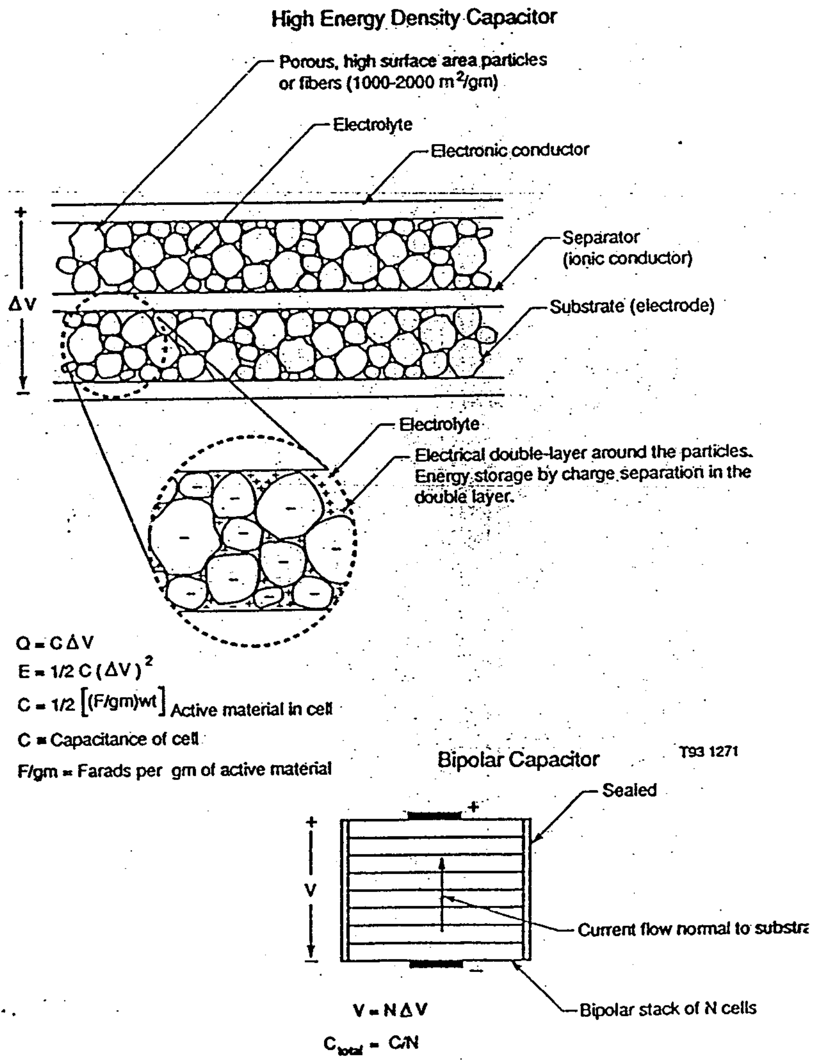


Figure 17: Schematic of an ultracapacitor cell using porous electrodes and a bipolar stack

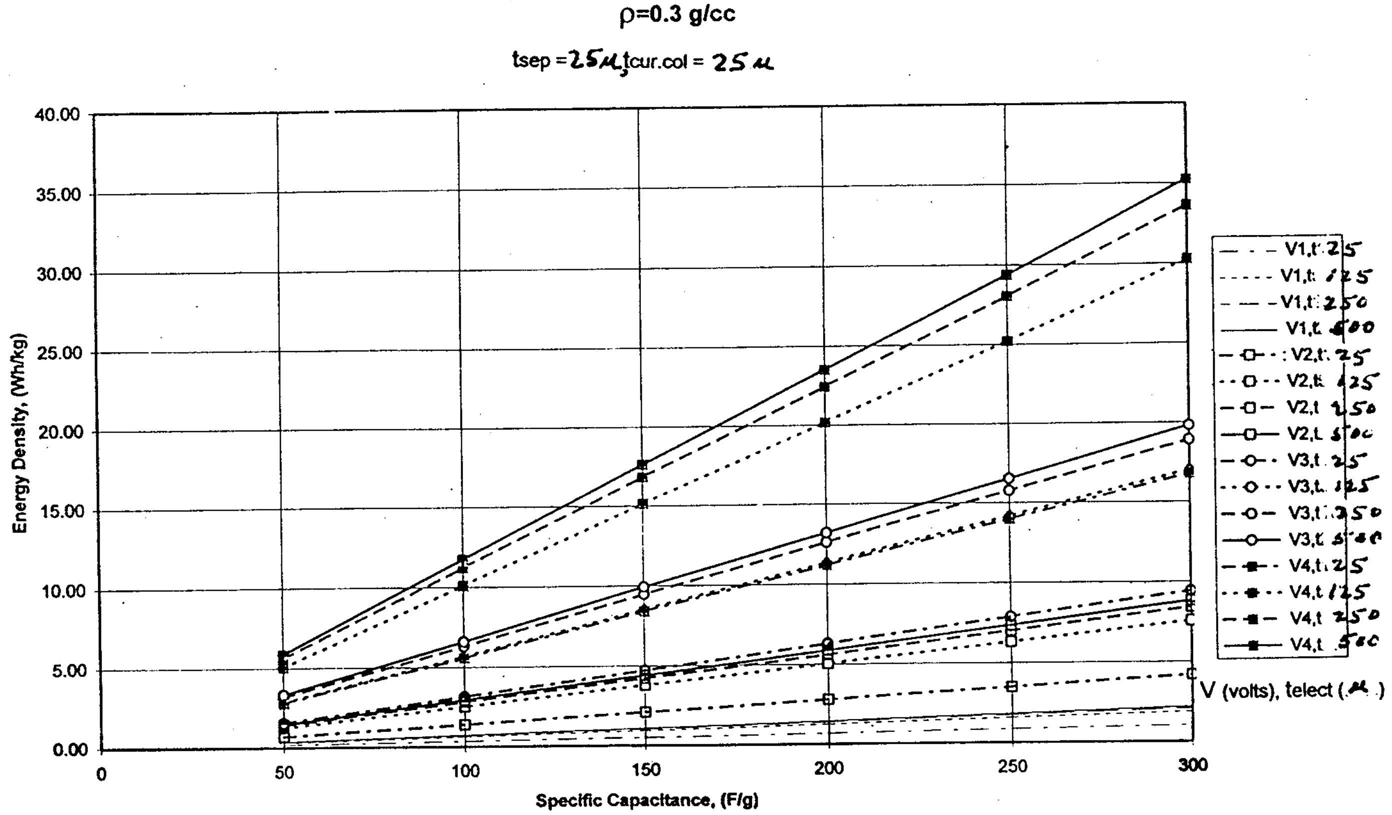


Figure 18: Projections of the energy density of carbon-based ultracapacitors of various design (carbon loading = .3 gm/cm^3)

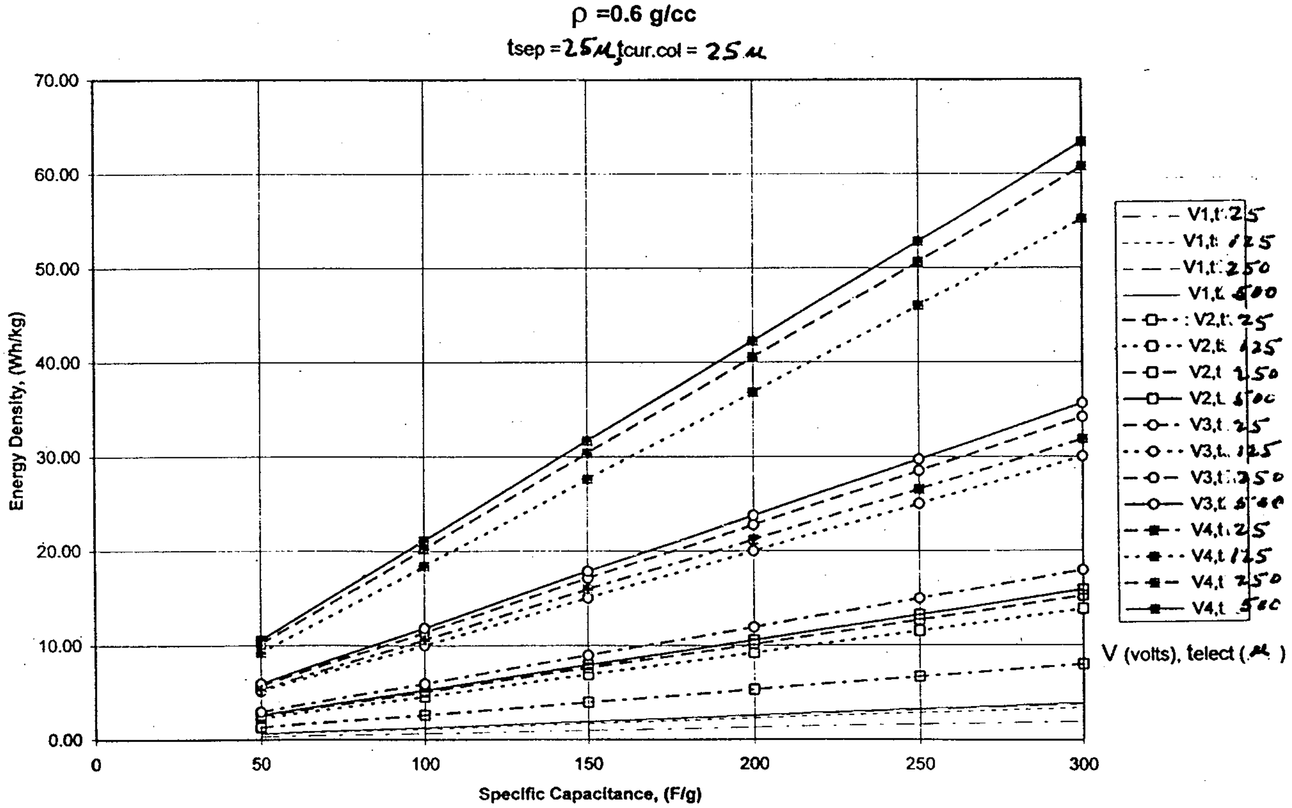


Figure 19: Projections of the energy density of carbon-based ultracapacitors of various design (carbon loading = .6 gm/cm^3)

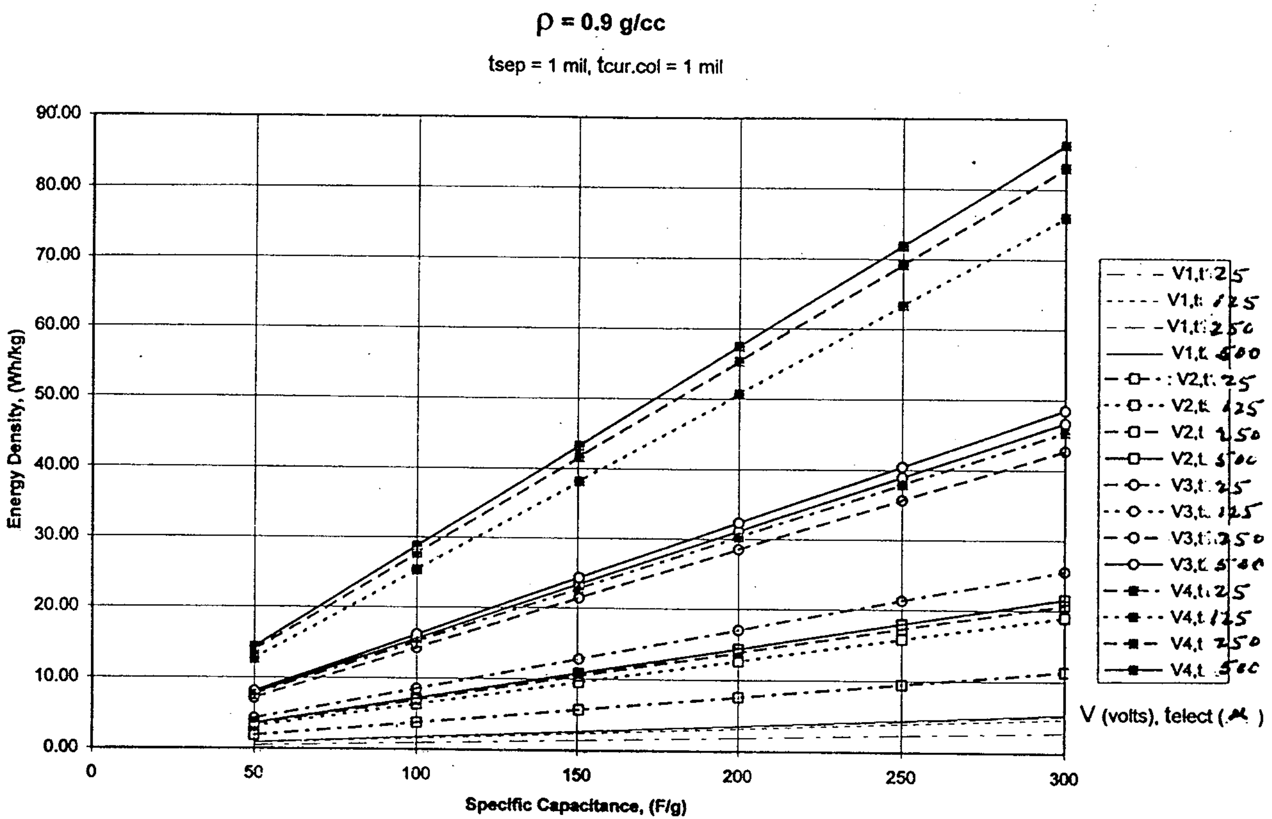


Figure 20: Projections of the energy density of carbon-based ultracapacitors of various design (carbon loading = .9 gm/cm^3)

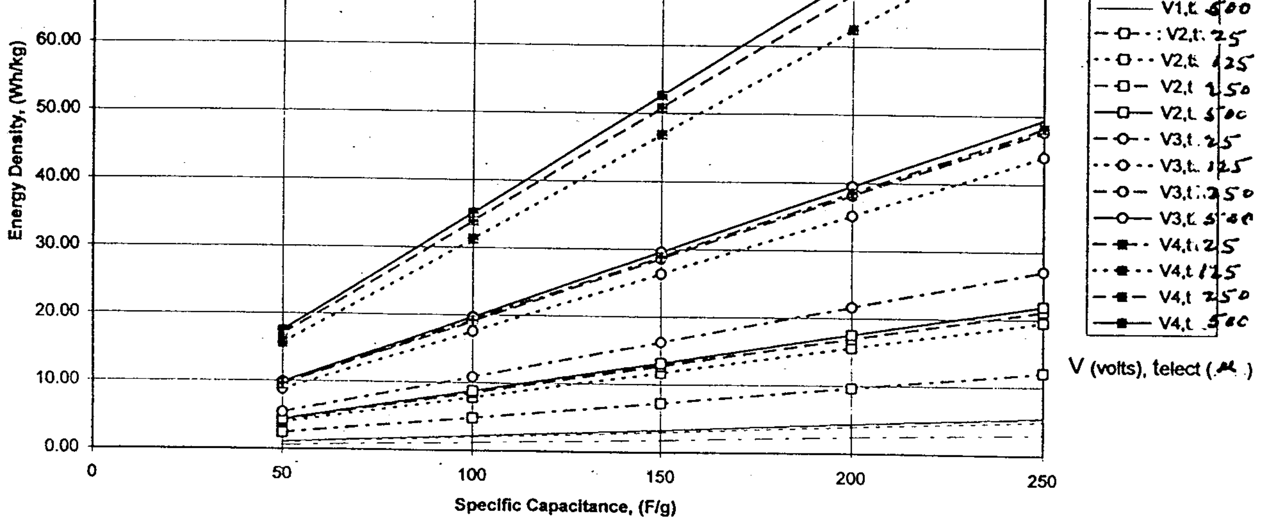


Figure 21: Projections of the energy density of carbon-based ultracapacitors of various design (carbon loading = 1.2 gm/cm^3)

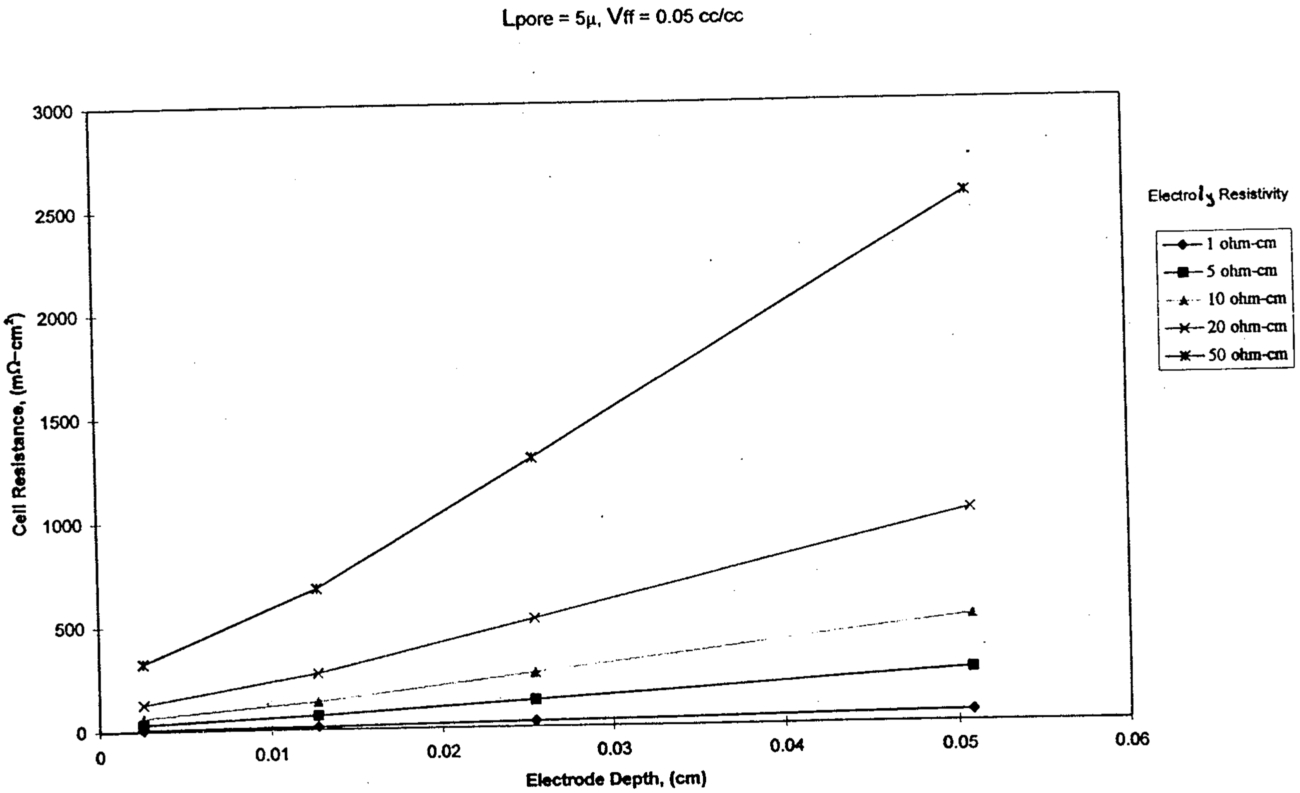


Figure 22: Projections of cell resistance (ohm-cm^2) for various designs as a function of electrode thickness

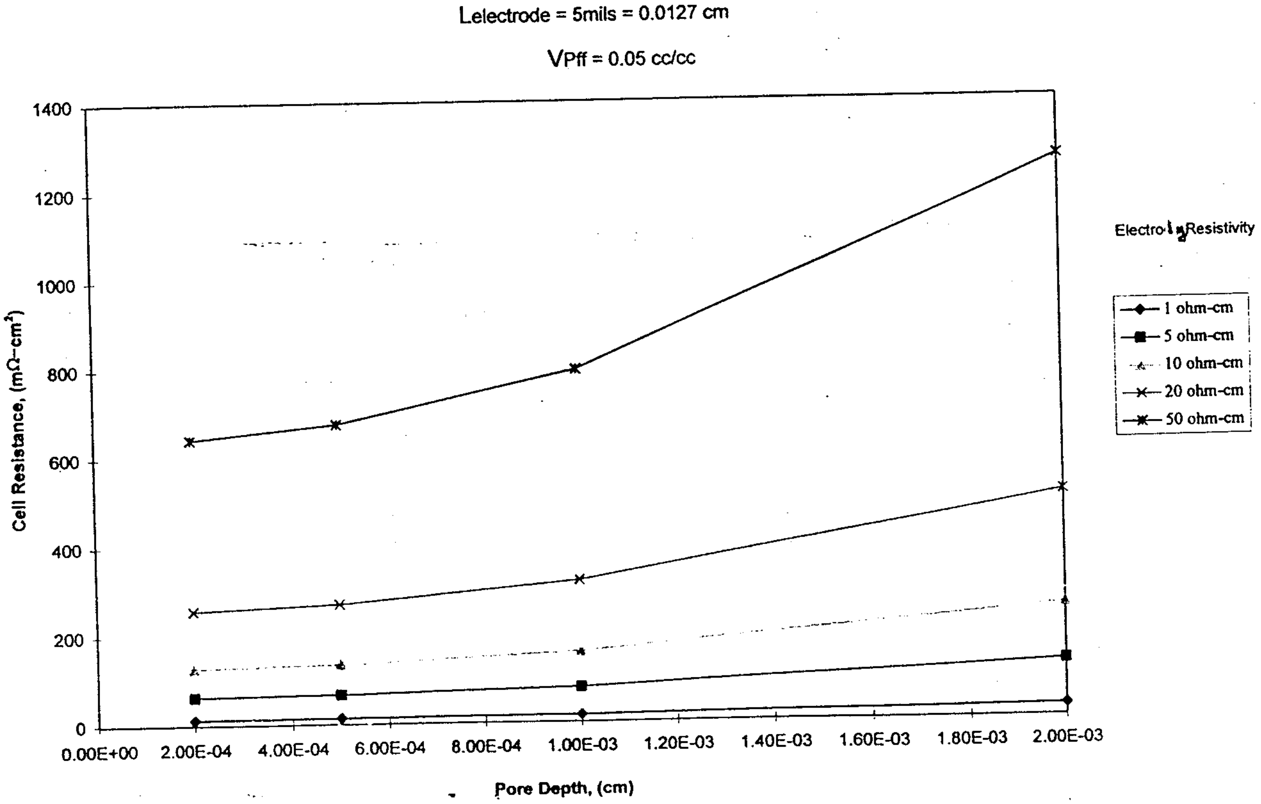


Figure 23: Projections of cell resistance (ohm-cm^2) for various designs as a function of electrode material pore depth

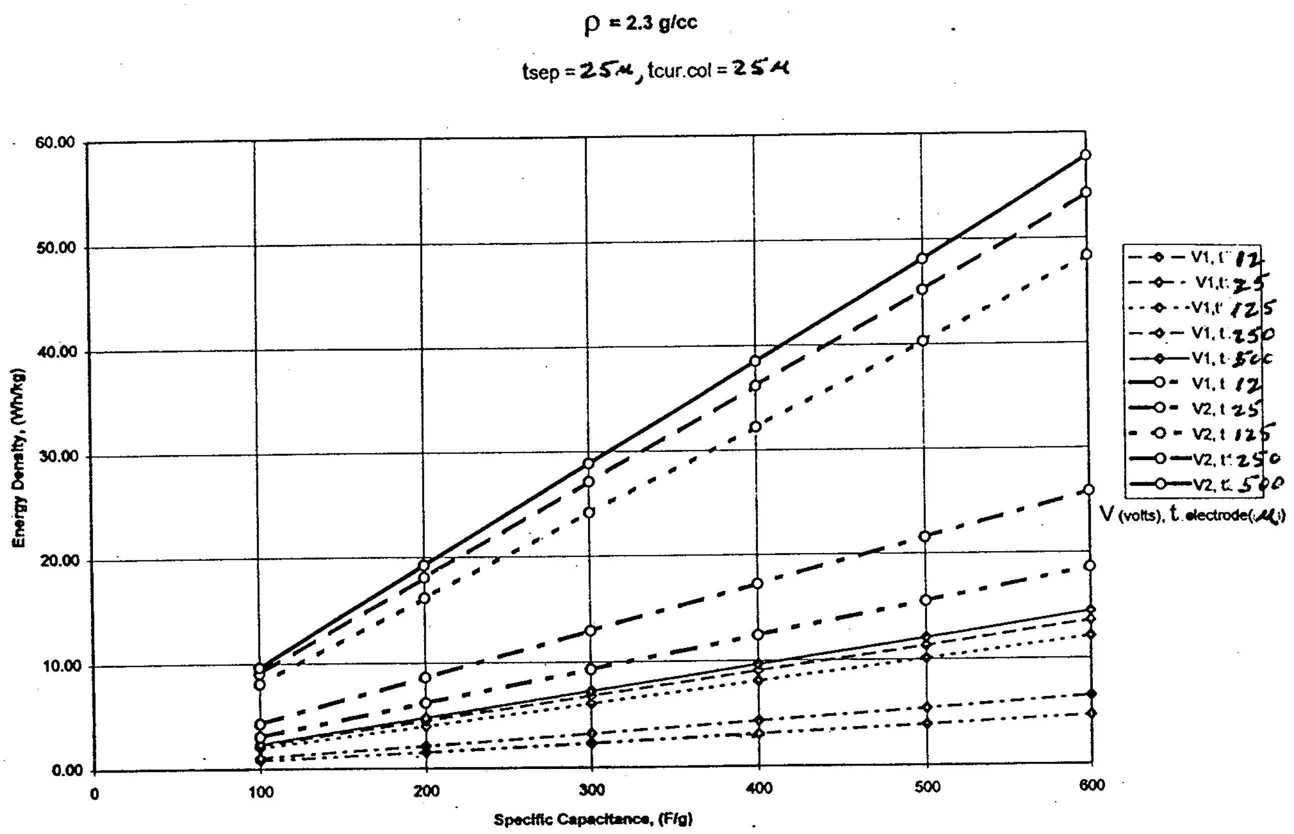


Figure 24: Projections of the energy density of ultracapacitors using mixed metal oxide electrodes for various cell designs

Appendix I:
Bibliography of Ultracapacitor Publications

I.1 General References

a. The most centralized sources of information on ultracapacitors are the proceedings of the international seminars held annually in December at Deerfield Beach, Florida. These references are cited as the "Proceedings of the ——— International Seminar on Double Layer Capacitors and Similar Energy Storage Devices". Seminars have been held in 1991, 1992, 1993, and 1994 and the fifth seminar is scheduled for December 1995.

b. A survey of ultracapacitor technology worldwide was performed in 1993 by Dr. Sumner Wolsky, who organizes the International Seminar in Deerfield Beach. The results of the survey were published as "The International Technology and Market Study of Electrochemical Capacitors" in February 1994. This publication can be purchased from Ansum Enterprises, Inc., Boca Raton, Florida, 33431 (407–338–8727). It is a comprehensive summary of ultracapacitor technology, the specifications for commercially available supercapacitor devices, and a list of applicable patents by date and country issued.

c. There is very little textbook type material available at the present time. The best tutorial material has been written by Professor B. E. Conway of the University of Ottawa, Ontario, Canada and Dr. I. D. Raistrick of Los Alamos National Laboratory in the United States. Prof. Conway has been a contributor each year to the International Seminar series in Deerfield Beach and his articles in the proceedings are excellent tutorial material on ultracapacitors. Material from Dr. Raistrick has been published in a book, "Electrochemistry of Semiconductors and Electronics – Processes and Devices (Chapter 7)", by Noyes Publications in 1992.

I.2 Systems Studies for Vehicles using Ultracapacitors

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Appendix II: Analysis of Ultracapacitor Performance

II.1 Energy Storage in Ultracapacitors

Energy is stored in an electrochemical capacitor (ultracapacitor) by charge separation within the micropores of a very high surface area electrode material (see Figure II-1). The charge separation is distributed throughout the volume of the electrode material in the double layer formed at the liquid - solid interface between the solid electrode material and the liquid electrolyte with which the electrode is impregnated. As shown in Figure II-1, the internal construction of an electrochemical capacitor is much like that of a battery in that it has two electrodes, a separator, and an electrolyte for ion transfer within the cell. In most cases, the two electrodes in the electrochemical capacitor cell are indentical (unlike in a battery where the electrodes are made of the different materials that form the electrochemical couple of the battery). A double layer forms at solid-liquid interfaces in all electrochemical systems and is discussed in all texts on electrochemistry and electrochemical engineering.[II-1,2] The current (electronic or ionic) at any electrode must be accounted for either by Faradaic reactions, surface charge-transfer, or charging of the double layer. In a battery, the faradaic reactions are dominant and the electrode material takes part in the reaction, with the effect of the double layer being minor. In the case of the simplest electrochemical capacitors, usually termed "double layer capacitors," all the current to or from the electrode is due to charging or discharging the double layer. In a double-layer capacitor, the ions from the electrolyte approach the electrode material, but do not react with it or are not absorbed into it. The faradaic current is zero in the case of the double layer capacitor. A more complex situation arises in the double layer if some, or most, of the ions that enter the double layer are absorbed into the surface of the electrode (charge transfer) or are intercalated into the material matrix of the electrode. In this case, the double layer can store much more charge than in the simple case of double-layer capacitance, and the additional capacitance is referred to as pseudo- capacitance. Even in this case, the electrode material, itself, does not take part in the interface reactions, and all the ions being transferred are from the electrolyte. For vehicle applications, the simple double-layer devices are the most attractive as they are expected to have the highest power capability and the longest cycle life. However, it is expected that devices that utilize pseudo-capacitance will have higher energy density.

The capacitance C of the double layer can be expressed as

$$C = \frac{dQ}{dV}$$

where Q is charge stored, and V is voltage across the double layer. The stored (E) is

$$E = \int C d\left(\frac{V^2}{2}\right)$$

In general, C is a function of the voltage. If C is a constant,

$$Q = CV \tag{1}$$

$$E = \frac{1}{2}CV^2 \tag{2}$$

Equations (1) and (2) are often used to describe the performance of simple double+layer capacitors. C can be expressed in terms of the capacitance per unit area of the double layer, $\frac{farads}{cm^2}$:

$$\frac{C}{electrode} = \left(\frac{F}{active\ cm_2}\right)\left(\frac{active\ area}{electrode}\right)$$

The active area per electrode can be expressed in terms of m^2/gm of electrode active material. Hence:

$$\frac{C}{electrode} = \left(\frac{F}{active\ cm_2}\right)\left(\frac{m_2}{gm}\right)\left(\frac{gm}{electrode}\right)$$

It is convenient to introduce the parameter (F/gm), the specific capacitance of the electrode material. Now:

$$\frac{C}{electrode} = \left(\frac{F}{gm}\right)_{electrode\ material}$$
$$x\left(gm\ active\ material\ /\ electrode\right)$$

The mass of the active material in the electrode is simply:

$$\frac{mass}{electrode} = (density\ of\ the\ active\ material)$$

$$\text{x}\ (volume\ of\ the\ electrode)$$

and the capacitance of the electrode can also be written as:

$$\frac{C}{electrode} = \left(\frac{F}{cm^3}\right) electrode\ material\ x\ (\ volume\ of\ the\ electrode\ )$$

Either F/gm or F/cm^3 can be used to express the specific capacitance of an electrode material. A cell consists of two electrodes in series, so the capacitance of the cell is

$$\frac{C}{cell} = \frac{1}{2}\ x\ \frac{C}{electrode}$$

and the energy stored is

$$\frac{E}{cell} = \frac{1}{2}\ x\ \frac{C}{cell}\ x\left(\frac{V}{cell}\right)^2$$

For the case where the two electrodes are identical, the voltage is split about equally between the two electrodes. If the electrodes are different, the charge stored on the two electrodes is the same, and the voltage will split as the ratio of the capacitances of the electrodes. The maximum achievable voltage per cell depends on the electrolyte used in the capacitor. For aqueous electrolytes, the maximum is ≈ 1.2 V due to electrolysis of water at higher voltages. The maximum using organic electrolytes is 3 to 4 V.

II.2 Resistance of Ultracapacitors

The relationships between the electrode material characteristics and the capacitance of a device were discussed in Section II.1. In this section, the relationships between the resistance of a device, the material characteristics, and the dimensions of the device are considered. There are several contributors to the resistance:

1. The electrode electronic resistance
2. The ionic resistance in the micropores of the electrode
3. The ionic resistance of the electrolyte in the macropores of the electrode
4. The interfacial resistance between the electrode and the current collector
5. The ionic resistance of the separator

The most complex and uncertain of these resistances is the ionic resistance in the micropores of the electrode material. The micropore resistance has been analyzed in terms of a simple transmission line model in Reference II-3, and measured using AC impedance methods in References II-4,5. It is shown in Reference 4 that the resistance of the micropores can be expressed as:

$$R_{pores} = \frac{L_{pore} \, x \, k_{electrol}}{2\,\pi \, x \, r^2 \, x \, n}$$

where:

L_{pore} = effective pore length

r = average pore radius

n = number of pores in the electrode

$k_{electrol}$ = specific ionic resistance of the electrolyte $(\Omega\text{-cm})$

The number of pores in the electrode is given by:

$$n = n' x \; (A_x \, x \, L)$$

where:

n' = number of pores per unit volume

A_x = cross-sectional area of the electrode

L = thickness of the electrode

Hence the pore resistance is given by:

$$R_{pores} = \frac{L_{pore} \, x \, k_{electrol}}{(2\pi \, x \, r^2 \, x \, n^1 \, x \, A_x \, x \, L)}$$

$$R_{pores} = \frac{C_1 \, x \, k_{electrol}}{(A_x \, x \, L)}; \; C_1 = \frac{L_{pore}}{(2\pi \, x \, r^2 \, x \, n^1)}$$

C_1 can be determined from AC impedance measurements for a sample electrode. Note that the pore resistance is smaller for thicker electrodes for a given pore geometry (n', r, L_{pore}), because there are more pores to carry the current in parallel.

The total electrode resistance $R(\Omega - cm^2)$ for a bipolar cell can be written as:

$$\hat{R}_{electrode} = \hat{R}_{intf} + \hat{R}_{etd} + \hat{R}_{pores} + \hat{R}_{sep}\ (ohm - cm^2)$$

where:

$$\hat{R}_{intf} \equiv \textit{electrode / current collector interface resistance}$$

$$\hat{R}_{etd} = \left(\frac{L}{2}\right) x\, k_{etd} = \textit{electrode electronic resistance}$$

$$\hat{R}_{electrol} = \left(\frac{L}{2}\right) \mathrm{x}\ k_{electrol}\ \epsilon_0^{-1.5} = \text{electrolyte ionic resistance,}$$

ϵ_0 is the macroporosity of the electrode

$$\hat{R}_{sep} = \left(\frac{L_{sep}}{2}\right) x\, k_{sep} \equiv \textit{separator ionic resistance}$$

It has been assumed that the mean diffusion distance is one-half the element thickness for all the layers. The contribution of the terms that vary with electrode thickness L can be expressed as:

$$\hat{R}_{electrode} = \frac{L}{2} \mathrm{x}\ k_{etd} + \frac{L}{2} \mathrm{x}\ k_{electrol} + \frac{L_{pore} \mathrm{x}\ k_{electrol}}{2\pi r^2 n \mathbb{C} L}$$

For the case in which $k_{eld} << k_{electrol}$, the minimum value of $\hat{R}_{electrol}$ occurs for

$$L_{min} = \sqrt{2 C_1}\ \epsilon_0^{3/4}$$

and

$$\left(R_{\text{electrode}}\right)\min = \sqrt{2\,C_1}\,k_{\text{electrol}}\;\epsilon_0^{-3/4}$$

Hence, making electrode thicker for a fixed cross-sectional area, increases its resistance only after the thickness has exceeded L_{min}. The AC impedance data for most electrochemical capacitor materials show that the specific capacitance and the micropore resistance are frequency-dependent. This means that the charge/discharge characteristics of cells fabricated from particular materials will be rate-dependent, and the optimum designs with those materials will be application-specific.

II.3. Summary of Ultracapacitor Material Properties

A summary of material characteristics for ultracapacitors using the various electrode material technologies are given in Table II-1. Values are given for each of the material properties in Table II-2. In most cases, a range of values is given both because of the present uncertainty in knowledge of the property and differences in the property that are obtained using different processing techniques. The values of the properties shown in Table II-2 can be used in the formulas given in sections II-1 and II.2 to estimate the characteristics of electrodes for ultracapacitors fabricated using the various materials.

II.4 The Maximum Power Density for Ultracapacitors

In other parts of this report, expressions have been given for the energy density and resistance of ultracapacitors in terms of their electrode and electrolyte material characteristics and internal dimensions. The power density of the ultracapacitor is also of considerable interest for most applications. The energy that can be stored or withdrawn from an ultracapacitor is rate dependent and any definition of maximum usable power density should take this into account. Claims have been made of very high power density (Megawatts/kg) for ultracapacitors, but in those cases only a very small fraction of the energy storage capacity of the device can be utilized. In this section, an expression is derived for the maximum power density at which an ultracapacitor can be charged or discharged while attaining a specified fraction of its ideal energy storage capacity ($^1/_2\ CV^2$). Of particular interest are power densities at which the energy capacity of the ultracapacitor is only reduced by 20-25%. The derivation accounts for the resistance of the device (IR voltage drops), but not changes in capacitance C due to limitations on ion diffusion in the micropores of the electrodes.

For the case in which the capacitance C and resistance R of the device are constant, the voltage during discharge is given by

$$V_0 - V = IR + Q_{out} / C$$

For a constant current discharge (I),

$$Q_{out} = I\,t$$

and

$$V = V_0 - IR - I\,t/C$$

t = discharge time (sec)
V_0 = the initial voltage

If the device is discharged from V0 to V0/2, the average voltage and power are given by

$$V_{av} = {}^3/_4\,V_0 - IR/2$$
$$P_{av} = {}^3/_4\,I\,V_0 - I^2\,R/2$$

The discharge time is

$$t = C\,V_0/2\,I - RC$$

The quantity RC is the time constant of the ultracapacitor. The energy recovered during the discharge is given by

$$E_{out} = P_{av} * t = ({}^3/_4\,I * V_0 - I^2 * R/2) * (C * V_0/2I - RC)$$

The fractional reduction (f_{re}) in energy from the capacitor at the high current I compared to an ideal discharge ($E_0 = {}^3/_4 * 1/2\ CV_0^2$) is

$$f_{re} = (E_0 - E_{out})/E_0 = 1 - ((1 - {}^2/_3\,IR/V_0) * (1 - 2\,IR/V_0))$$

Expanding the equation for f_{re}

$$f_{re} = {}^8/_3\,I\,R/V_0 - {}^4/_3\,(IR)^2/V0^2$$

This quadratic equation for I can be solved in closed form to obtain

$$I\,R\,/\,V_0 = 1 - \sqrt{(1 - \tfrac{3}{4}\,f_{re})}$$

and for relatively small values of f_{re},

$$IR/V_0 = {}^3/_8\,f_{re}$$

The average power for the discharge from V0 to V0/2 can now be written as

$$P_{av} = 3/4\ I\ V_0 * (1 - 1/4\ f_{re})$$

Eliminating the discharge current I and introducing the RC time constant of the ultracapacitor device,

$$P_{av} / (\tfrac{1}{2}\ CV_0^2) = (\tfrac{9}{16}) * (1 - \tfrac{1}{4}\ f_{re}) * f_{re} / (RC)$$

and in terms of energy density and power density,

$$(W/kg)max = 3600 * (Wh/kg) * (\tfrac{9}{16}) * (1 - \tfrac{1}{4}\ f_{re}) * f_{re} / (RC)$$

RC is most simply written for a multicell stack as

$$RC = (ohm\text{-}cm^2)cell * (F/cm^2)cell$$

The expression for the power density (W/kg) has been checked with test data for Maxwell devices using both aqueous and organic electrolytes and found to give power density values in good agreement with those measured for "f_{re}" values between .1 and .5. Consider for example, a typical 20 cm^2 3 V cell,

Wh/kg = 6.8, C = 12.5F, R= .08 Ohm

For f_{re} = .2, the calculated power density for the cell is 3235 W/kg. This cell was discharged at 5A (an average power of 3300 W/kg) at the INEL (Reference II.6) and showed as predicted a 25-30% reduction in energy density from low power discharges at .5A. The power density expression derived should prove useful in predicting the power capability of ultracapacitors of various designs.

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Table II-1: List of important ultracapacitor material properties

Summary of electrochemical capacitor material characteristics.

1.	Specific capacitance of the electrode material	F/gm, F/cm^{3}
2.	Surface area of the electrode material	m^{2}/gm
3.	Porosity and pore size distribution	–
4.	Density of the electrode	gm/cm^{3}
5.	Specific electronic resistivity of the electrode material	Ohm-cm
6.	Specific ionic resistivity of the electrolyte	Ohm-cm
7.	Specific electronic resistivity of the current collector material	Ohm-cm
8.	Interface resistance between the electrode material and the current collector	Ohm-cm

Table II-2: Summary of Characteristics of Electrode Material

Summary of the characteristics of electrode materials.

Electrode Material	Specif Capac (F/gm)	Surface Area (m2/gm)	Density (gm/cm3)	Resistivity (ohm-cm)
Carbon/metal composites	100 to 200	1000 to 1500	0.5 to 0.7	< 0.01
Aerogel carbon	120 to 160	500 to 800	0.4 to 0.8	< 0.01
Cellulose-deriv. foamed carbon	70 to 180	500 to 800	0.8 to 1.0	0.015
Doped-polymer (Polyaniline)	400 to 500	200 to 400	0.5 to 0.9	0.01
Anhydrous Ruthenium oxide	100 to 150	100 to 150	2.5 to 3.0	< 0.001
Hydrous Ruthenium oxide	600 to 750	80 to 100	2.3 to 2.5	0.002 to 0.005
Aqueous Electrolytes	–	–	1.18 to 1.24	1.4 to 2.0
Organic Electrolytes	–	–	1.1 TO 1.2	12 TO 17

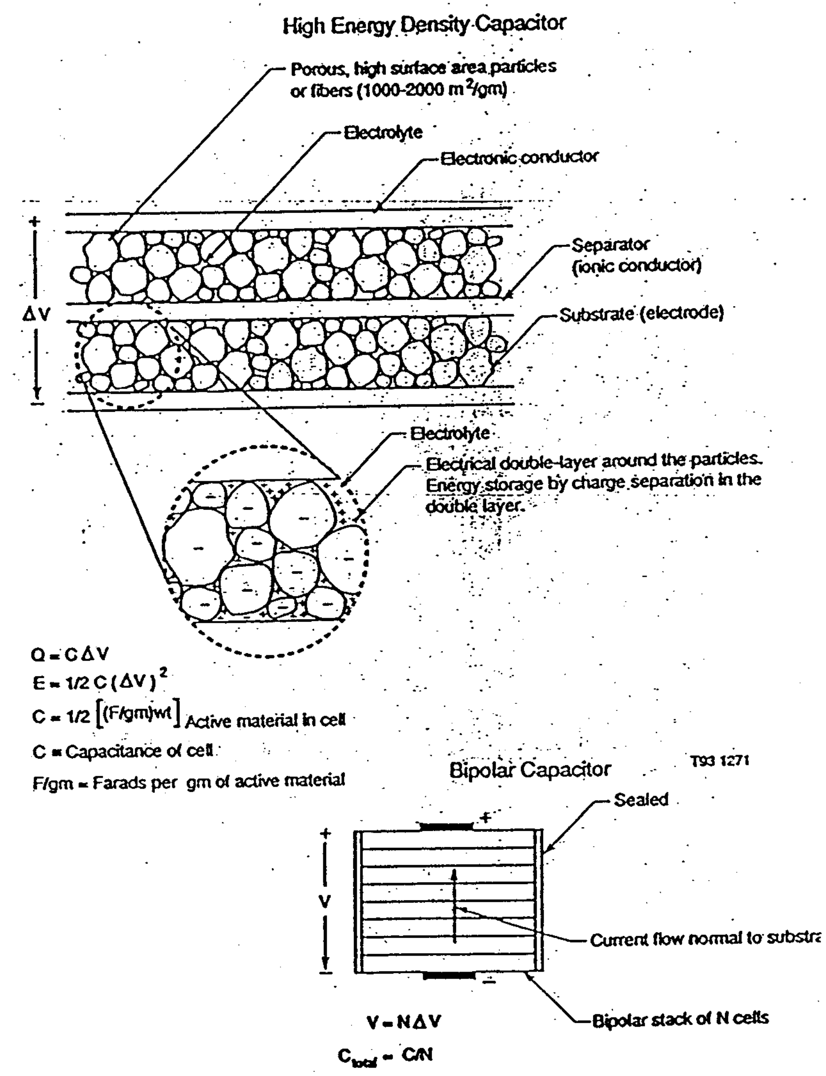

Figure II-1: Schematic of a bipolar ultracapacitor with porous electrodes

Appendix III: Test Procedures for Evaluating the Performance of Ultracapacitors

III.1. Introduction

The testing of ultracapacitors has evolved over the last 4–5 years as devices have become available and it was necessary to determine the characteristics of the devices relative to the requirements for electric and hybrid vehicle applications. In addition, it became necessary to characterize materials and electrodes as components in ultracapacitors. Much of the initial testing and the development of the test procedures have been done at the Idaho National Engineering Laboratory (INEL) as part of the United States Department of Energy's (USDOE) ultracapacitor program (References III-1,3).

It is widely recognized in the ultracapacitor community that there is a need for a consistent set of test procedures to evaluate the performance of ultracapacitors, especially for those intended for use in electric drivelines as pulse power devices. Test procedures currently available (Reference III-4) were developed to characterize capacitors to be used in electronic circuits (high frequency charge and discharge) or in low power applications (memory backup). Those procedures are not suitable for testing the high power devices to be used in electric drivelines that are charged/discharged in 5 to 100 seconds at high rates. The initial documentation of the test procedures used in the USDOE program is given in Reference III-2. That test manual forms the basis for much of the material given in this Appendix.

The initial testing (Reference III-1) of ultracapacitors evolved from battery testing and made use of the same equipment when possible. The charge and discharge times of the ultracapacitors were, of course, much shorter than that of batteries, but the control and response times and sampling rate capabilities of several of the programmable battery testers were compatible with the short (5 to 100 second) test times for the ultracapacitors. In some instances, it was necessary to change the current shunts in the testers when testing small devices to increase the accuracy of the current measurement. All the testing was done at 1 second or smaller sampling times. One of the testers (a Maccor) had the capability of .1 second sampling times when needed and in addition, had an automatic feature that it would take data at that maximum rate whenever a sudden change in voltage occurred as at the start of a charge or discharge step.

The tests performed on the ultracapacitors were in most cases much like those performed on batteries – constant current and constant power charges and discharges and variable power transient cycle tests. These tests will be referred to as large signal dc measurements. As for batteries, the current and power levels for the tests of a particular ultracapacitor device are set based on its energy storage capacity and/or weight. As the ultracapacitor development program progressed and a better understanding of the electrochemistry and circuit characteristics of the devices evolved, it became apparent that information on device and material characteristics that could be extracted from small signal ac impedance data would also be valuable. That type of testing (Reference III-5) is familar to most electrochemists, but it is not widely used in battery testing. Ac impedance techniques are now an important element in ultracapacitor testing for electrode, cell, and stack evaluation. Hence procedures for both large signal dc and small signal ac impedance testing are discussed in this appendix as they relate to ultracapacitor research and development.

III-2. Circuit Models of Ultracapacitors

III.2.1 DC Behavior

Ultracapacitors used in electric drivelines experience large non–steady (transient) discharge currents, much like a battery in an electric vehicle, except that they are subject to short, frequent periods of charging to keep them at a high state–of–charge. They do not, however, experience changes in polarity even though the direction of the current to/from the device changes frequently. Hence, the ultracapacitors function as dc devices. In simplest terms, they can be modeled as a capacitor (C) and a resistance (R) in series.

$$V_0 - V = IR + (Q_0 - Q)/C$$

where

Q – charge on the capacitor
V – Voltage on the capacitor
V_0, Q_0 – Voltage and charge at full charge

For an ideal capacitor, C and R are constants independent of state–of–charge and charge/discharge rate. The intent of the large signal dc testing is to determine the effective values of R and C and the extent to which the behavior of the ultracapacitors in vehicle applications can be described in this simple manner.

III.2.2 AC Behavior

A more complete understanding of the electrical energy storage and circuit characteristics of ultracapacitors can be attained by treating them as ac devices and studying their response as a function of the frequency of an applied sinusoidal voltage. This is done in ac impedance testing, in which sinusoidal voltage signals of small amplitude, usually only a few millivolts, are applied to the device at frequencies from a fraction of a Hz to many kiloHz. To model the ultracapacitor over this wide range of frequency, it is necessary to use a much more complex circuit (Figure 1) than the simple series connection of a capacitor and resistance cited previously as a dc model. As discussed in the next section, ac impedance data can be used to both determine the R and C for the simple dc model and to select the circuit elements for an ac representation of the ultracapacitor.

III.3. Test Procedures and Typical Data

III.3.1 DC testing

As with batteries, the simplest tests of ultracapacitors are done with constant current charging and discharging. In that case, the charge on the capacitor is proportional to the test time and for an ideal device (C = constant), the voltage would be linear with time and departures from ideal behavior become clearly evident from the data (see Figure 2). The average, as well as the instanteous, capacitance of the device can be calculated from the voltage vs. time data using the relationships: $Cav = Q/V$ or $C(t)=I/dV/dt$. The dc resistance of the device can be determined from the IR step at the beginning of the charge/discharge steps as shown in Figure 3. The data shown in Table 1 and Figure 4 indicate that the simple representation of the dc behavior of ultracapacitors discussed in Section 2.1 are consistent with the constant current test data over a wide range of temperature.

Constant power discharge tests of ultracapacitors are also straightforward to perform using battery test equipment and they yield data that are of considerable interest for vehicle applications. These tests should be run over a range of power density, usually between 100 and 2000 W/kg depending on the power capability of the device being tested. Unlike constant current discharge tests that can be run to zero voltage if desired, the minimum voltage for constant power discharge tests must be sufficiently high that the current required at the constant power of the test does not exceed the maximum current limit of the tester. The ultracapacitor cut–off voltage for constant power discharge tests is often set at one–half the rated voltage of the device, which means that at most about 75% of the energy stored in the device at the rated voltage can be extracted during the constant power discharge. The voltage vs. time curves for constant power discharges are not linear even for ideal capacitor behavior because the current increases during the discharge as the voltage decreases. The energy density of ultracapacitors can best be determined from constant power tests as that type of discharge more closely approximates how the devices are used in vehicles than constant current discharge tests. Typical constant power discharge results are shown in Figure 5. As with batteries, the energy density of an ultracapacitor decreases with discharge rate, but the decrease begins at a much higher power density than for batteries (Figure 6).

Testing of an ultracapacitor should also include transient power cycle tests intended to simulate the use of the capacitor to load level a battery in a vehicle being driven on an urban driving cycle. A test cycle for this type of testing has been designated in Reference III-2 as the PSFUDS cycle. As in the case of the SFUDS battery test cycle, the PSFUDS cycle is given as a series of power–time steps involving both charge and discharge of the device being tested. The power levels and length of time for each step is specified such that the test cycle is applicable to different size and performance capacitors. A generalized version of the PSFUDS cycle is given in Table 2, where the power for each step is normalized by a maximum value appropriate for the device being tested. Note that the device is charged back to its rated voltage at the end of each cycle, so that each cycle starts and ends with the device fully charged. The maximum power value should correspond to a power density of at least 500 W/kg. The time shown for each step is appropriate for devices having an energy density of at least 5 Wh/kg. For devices having an energy density less than 5 W/kg, the times for each step should be reduced by the ratio of the energy density of the device to 5Wh/kg. Data from the PSFUD cycle are used to evaluate the transient behavior of an ultracapacitor device in charge/discharge conditions. The round–trip efficiency of the device is calculated as the ratio of the energy taken from it during discharge steps of the cycle to the energy stored in the device during charge steps. The coulombic efficiency can be calculated in a similar manner using the charges taken from and put into the device in the discharge/charge steps of the cycle. For ultracapacitors, the coulombic efficiency should be unity within experimental error. A typical voltage vs. time curve for a device on the PSFUDS cycle is shown in Figure 7. The round–trip efficiency for the data shown is 90% .

Ultracapacitors can also be tested for their leakage current and self–discharge. The leakage current is the current required to maintain the capacitor at its rated or working voltage. It is time– dependent and only approaches a constant value after the voltage has been applied to the capacitor for several hours. Leakage currents arise in part from charge–transfer reactions at the electrodes and often result in gas formation and pressure build–up which can lead to breaching the seals of the capacitor if the leakage current test is done near the limit voltage of the electrolyte. To determine the leakage current characteristics of a device, it is necessary to measure the current to the capacitor over a relatively long time (up to three hours). This can be done using a standard battery tester if it is sufficiently stable and has the capability to measure small currents (down to a fraction of a mA for small devices). Otherwise, it is necessary to use a stable power supply and a shunt resistor in series with the capacitor being tested.

The self–discharge test is performed to measure the self–dissipation of the ultracapacitor and is an indicator of the extent of the occurrence of non–ideal energy storage/transfer mechanisms at the electrodes. In this test, the capacitor is charged to its rated voltage and held at that voltage for a reasonable period (30 minutes). It is then placed on open–circuit and the voltage measured over a period of 72 hours. Typical self–discharge data are shown in Figure 8. The voltage decreases relatively rapidly over the first hour (or less), after which the decrease is much slower for the remainder of the test.

III.3.2 AC Impedance Testing

Many important characteristics of ultracapacitor elctrodes, cells, and stacks can be determined using ac impedance testing. The tests are done using a programmable potentiostat/galvanostat. Computer software is now commercially available that executes the testing over a specified frequency range and collects and analyzes the data to determine the complex impedance (R and X) of the device being tested at selected frequencies. For ultracapacitors, the tests should be performed at frequencies between .001 Hz and several kiloHz (above the self–resonance frequency of the device). The amplitude of the applied sinusoidal voltage should be set at 5–10 mV per cell. If needed, separate series of tests can be done for a range of base voltages between zero and the rated voltage of the cell or stack to study the effect of voltage level on capacitor characteristics. Typical data for the real and imaginary parts (R and X) of the complex impedance as a function of frequency are shown in Figure 9. As discussed in the next sections, this data can be used to determine the capacitance and resistance characteristics of ultracapacitors and electrodes.

III.3.2.1 Capacitance and Resistance

The complex impedance (Z) is expressed as

$$Z = R - iX, X = {}^{1}\!/_{2}\,\pi fC$$

$$\mathrm{Abs}(Z) = \sqrt{R^2} + {}^{1}\!/_{\left(4\pi^2 f^2 C^2\right)}$$

$$\tan\phi = {}^{-1}\!/_{2\pi fRC}$$

where

R = resistance of the capacitor (ohms)
C = Capacitance of the capacitor (farads)
f = frequency of the test (Hz)
ϕ = phase angle

It is evident from Figure 10 that both the capacitance and resistance increase with decreasing frequency (longer discharge times). An approximate relationship between the ac frequency and the dc charge/discharge time is given by

$$t_{cd} = .25^* \, 1/f$$

For vehicle applications involving charge/discharge times of 2–100 seconds, the corresponding frequency range is .001 to .1 cycles/sec (1–100 mHz). The complex impedance data (R,X) can be analyzed to determine R and C as a function of frequency as shown in Table III-3 for one of the Maxwell composite carbon electrode devices. Note that for this device R and C are relatively constant over much of the frequency range of interest for vehicle applications, but change markedly at higher and lower frequencies (shorter and longer discharge times). Hence it appears necessary to evaluate the frequency characteristics of each ultracapacitor design using ac impedance testing.

III.3.2.2 Electrode and Material Characteristics

Applications of ac impedance testing to determine material and electrode characteristics are discussed in References III-6,7. This approach is one of the few direct methods of relating the pore characteristics of the electrode material to the performance of the ultracapacitor. This is done by studying the frequency dependencies of the capacitance and resistance of electrodes and/or cells and relating them to the electrode material characteristics, including pore radius and depth, surface area, and volume and the ionic conductivity of the electrolyte used in the device. In Reference III-7, it is shown that the impedance of the pores as a function of frequency can be expressed as follows:

$$Z_p = \frac{1-i}{2\pi_p \sqrt{r_p^3 \, k\omega C_{dl}}} \; \mathrm{Coth}\left[l_p \sqrt{\frac{\omega C_{dl}}{k_{rp}}} \, (1+i) \right]$$

At high freqencies, Equation (1) reduces to the form

$$Z_p = \frac{1 - i}{2\pi n_p \sqrt{r_p^3 \, k\omega C_{dl}}}$$

At low frequencies, Equation (1) reduces to the form

$$Z_p = \frac{-i}{2\pi r_p \, n_p \, l_p \, \omega c_{dl}}$$

In the complex impedance plot (R vs. X), Equation (2) represents a 45 degree line with respect to the R axis with an intercept at the high frequency limit of R, at which the contribution of the pores to the resistance is essentially zero. Equation (3) represents a vertical line parallel to the X axis. The intersection of the two lines (Figure 11) yields the value of the resistance (R'p) occurring at a frequency (ω rad/sec) equal to the reciprocal of the RC time constant of the device tested. Note that as shown in Figure 10, R'p is only the portion of the total resistance due to the pores and is obtained by subtracting the high frequency dc resistance from the total resistance. R'p is inversely proportional to number of pores in the electrode so that the pore resistance will be less in thick than thin electrodes of a particular electrode material. The pore depth l_p can be calculated from the pore resistance using the expression

This is the same expression used in Appendix II to calculate the contribution of the pores to the resistance of the electrode. Since the product V_p*R'_p is independent of n_p and thus the electrode thickness, l_p becomes purely an electrode material property as is the pore radius, which is given by

$$r_p = 2\, V_p / S_p$$

The number (np) of pores in the electrode can be determined from

$$n_p = S_p / 2 \; r_p \, l_p$$

Unfortunately, the pore surface area Sp and pore volume Vp of the electrode material must be known from a source independent of the ac impedance testing before the impedance data can be used to determine np, lp, and rp. Sp and Vp are not easily determined for materials for which most of the surface area is in micropores. Thus impedance testing alone does not yield the electrode material characteristics as would be most desirable.

References for Appendix III

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III-2. Miller, J.R. and Burke, A.F., Electric Vehicle Capacitor Test Procedures Manual (Revision 0), Idaho National Engineering Laboratory Report No. DOE/ID–10491, October 1994

III-3. Burke, A.F., Electrochemical Capacitors for Electric and Hybrid Vehicles – The DOE Program and the Status of the Technology – 1993, Proceedings of the Annual Automotive Technology Development Contractors' Coordination Meeting (November 1992), Society of Automotive Engineers Publication , SAE P–278, May 1994

III-4. Capacitor Test Procedure DOD–C–29501

III-5. Gileadi, E.,"Electrode Kinetics for Chemists, Chemical Engineers, and Material Scientists", Chapters 25 and 26, VCH Publishers, Inc., New York, N.Y., 1993

III-6. Levie,"Advances in Electrochemistry and Electrochemical Engineering", Vol. 6, Electrochemical Response of Porous and Rough Electrodes, Pg 329–397, P. Delahay, Editor, Interscience Publishers, 1967

III-7. Delnick, F.M., Jaeger, C.D., and Levy, S., AC Impedance Study of Porous Carbon Collectors for Li/SO2 Primary Cells, Chemical Engineering Communications, Vol. 35, pg 23–28, 1985

Table III-1: Capacitance and resistance of the 1500F Panasonic Power Capacitor at various temperatures

Temp °C	V_1[1]	V_2[2]	R/cell mohm	V_3	V_4	C/cell farads
			100 A Discharge			
65	10.25	9.62	1.58	9.0	6.85	1860
40	10.3	9.7	1.50	9.1	7.03	1932
25	10.2	9.45	1.88	8.84	6.65	1826
5	10.2	9.45	1.88	8.84	6.6	1786
-10	10.1	9.28	2.05	8.63	6.26	1688
-20	9.98	9.08	2.25	8.35	6.03	1724
			300 A Discharge			
65	10.25	8.2	1.7	7.58[5]	5.55[6]	1773
40	10.3	8.45	1.54	7.86	5.8	1747
25	10.2	8.2	1.67	7.58	5.55	1773
5	10.2	8.2	1.67	7.58	5.45	1690
-10	10.1	7.65	2.04	7.05	5.03	1782
-20	10.0	7.23	2.31	6.6	4.74	1777

(1) Voltage at t = 0 before discharge
(2) Voltage at t = 0 after discharge is initiated
(3) Voltage at t = 3 sec
(4) Voltage at t = 13 sec
(5) Voltage at 4 = 1 sec
(6) Voltage at t = 4 sec

$$R = (V_1 - V_2/I)$$

$$C = \frac{(\Delta t)\,(I)}{V_3 - V_4}$$

Table III-2: Power-time steps for the generalized PSFUDS cycle for testing ultracapacitors

Time Step (s)	P/P_{max}	Charge (C) or Discharge (D)
8	0.2	D
12	0.4	D
12	0.1	D
50	0.1	C
12	0.2	D
12	1.0	D
8	0.4	D
50	0.2	C
12	0.2	D
12	0.4	D
18	0.1	D
50	0.2	C
8	0.2	D
12	1.0	D
12	0.1	D
50	0.25	C
8	0.20	D
12	1.0	D
38	0.20	C
12	0.4	D
12	0.2	D
≥50	0.25	C to V_w
Total 470 s		

Table III-3: Frequency Characteristics of a IV Carbon-Metal Fiber Composite Ultracapacitor Cell

Frequency (Hz)	Capacitance (F)	Resistance (Λ)
.01	13.3	.06
.03	11.3	.028
.1	10.6	.020
.3	11.3	.016
1.0	10.6	.015
3	10.6	.0133
10	5.5	.0115

List of Figures: Appendix III

Figures - Appendix III

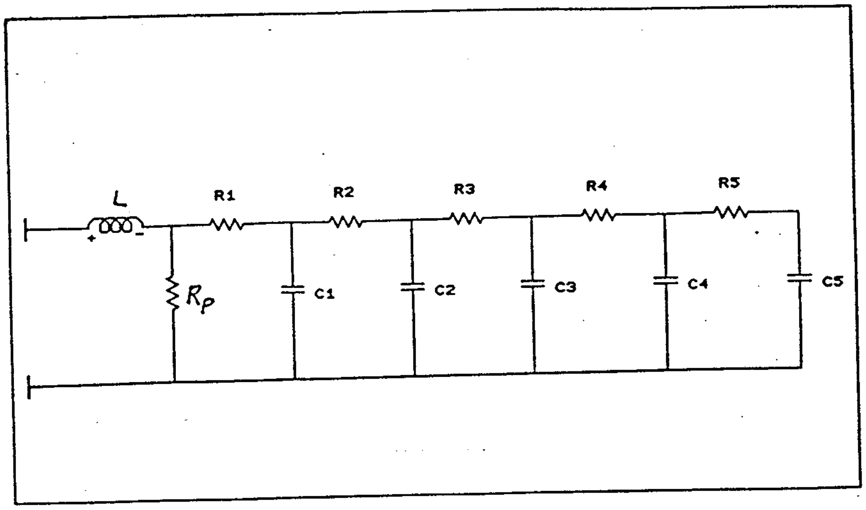

Figure III-1: Equivalent circuit for an ultracapacitor applicable to a large range of frequency

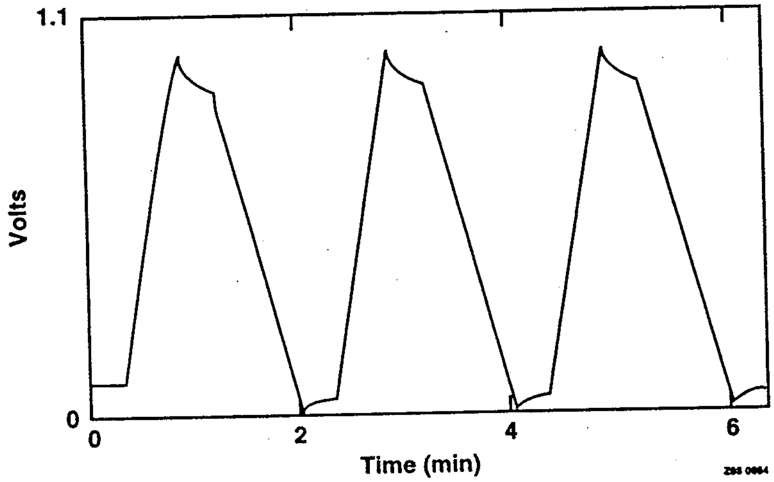

Figure III-2: Typical charge/discharge voltage vs. time traces for a double-layer capacitor

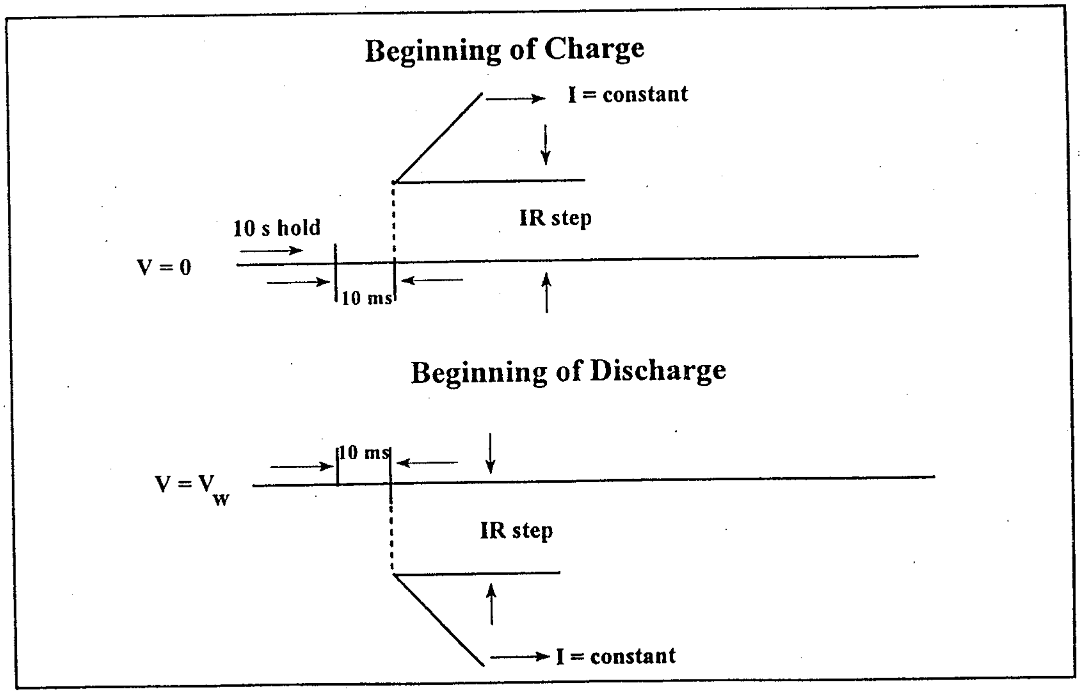

Figure III-3: Graphical description of the method for the calculation of capacitro resistance from the IR step

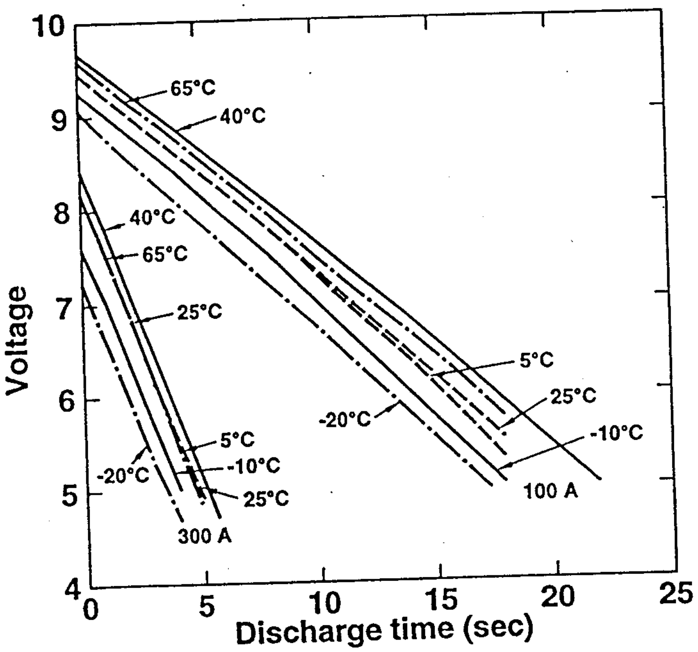

Figure III-4: Voltage vs. time data for the 1500F Panasonic Capacitor (3 devices in series) for 100A and 300A at various temperatures

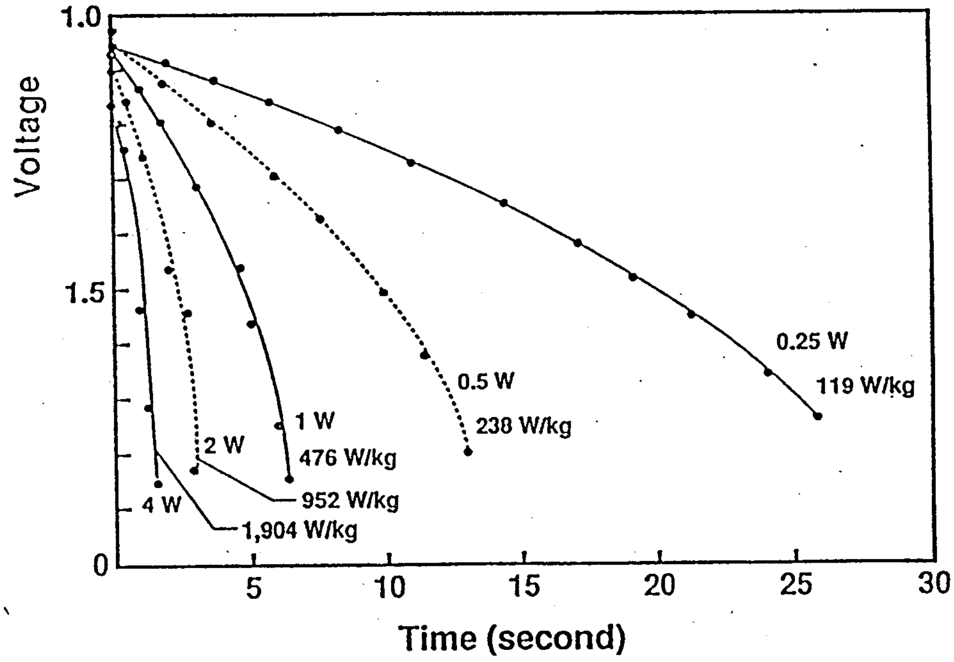

Figure III-5: Constant power discharge data for the IV Maxwell Capacitor

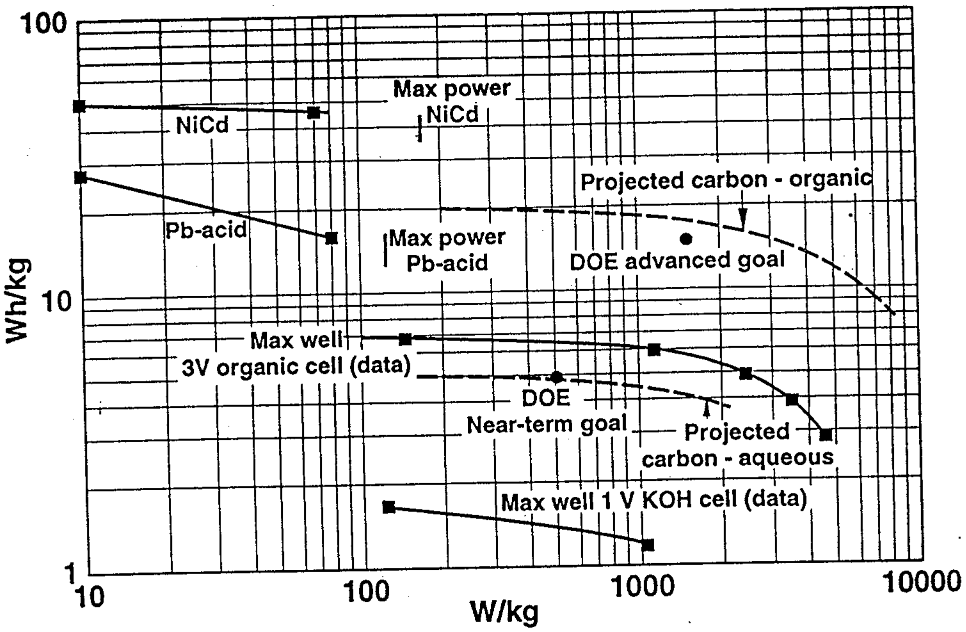

Figure III-6: A Ragone Plot for batteries and ultracapacitors

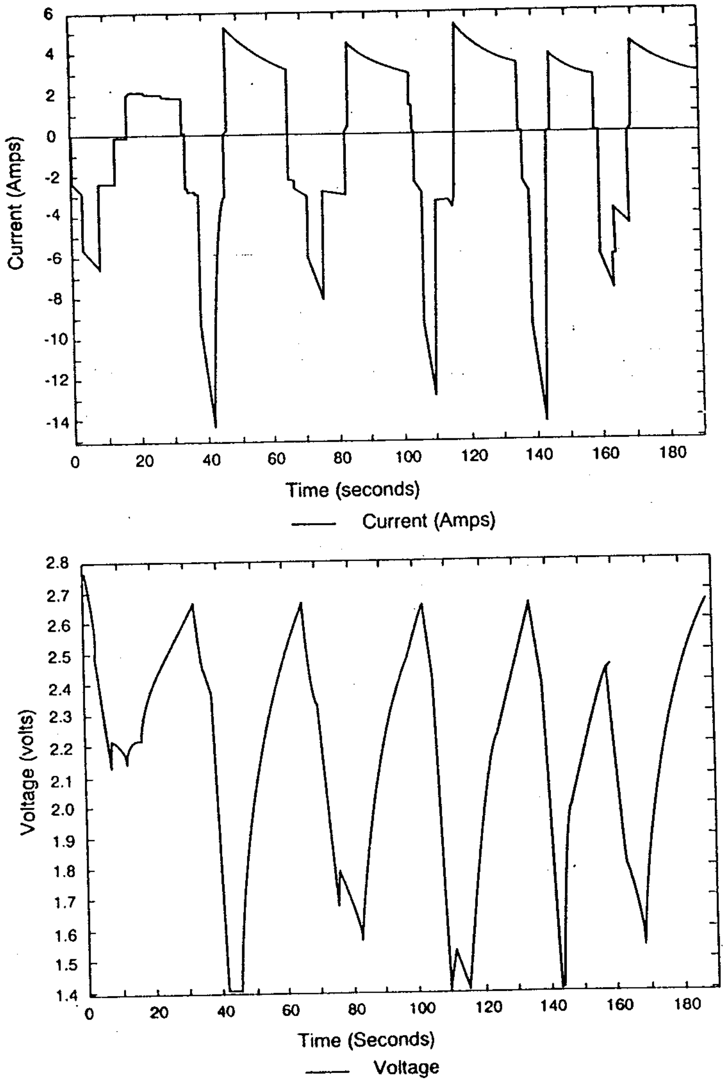

Figure III-7: Voltage and current vs. time traces for the 500F Panasonic Capacitor on the PSFUDS cycle

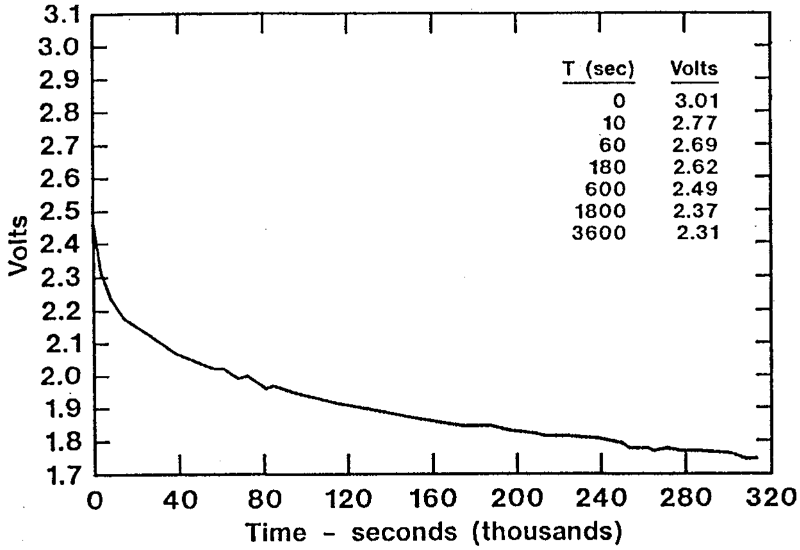

Figure III-8: Self-discharge data for the Panasonic 3V, 500F Capacitor

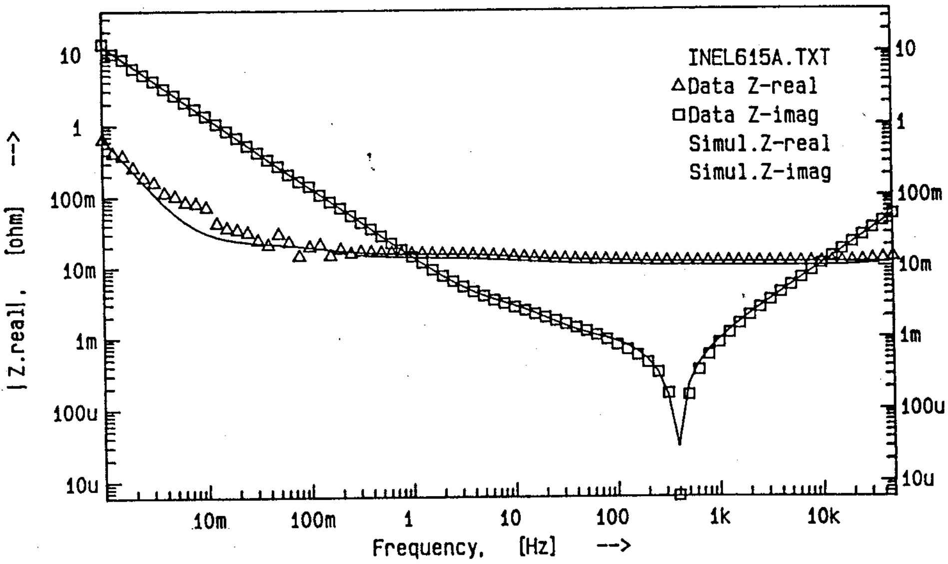

Figure III-9: AC Impedance data for the 1V Maxwell Capacitor