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Advanced Power Conversion Based on the Aerocapacitor™

Contract # DE-FC07-94ID13283

Final Report

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Summary

This report summarizes work performed under contract # DE-FC07-94ID13283 , "Advanced Power Conversion Based on the Aerocapacitors™." Under this contract high power density, high energy density, organic electrolyte Aerocapacitors™ were developed and characterized for power conversion applications. Pilot facilities for manufacturing prototype AA-size Aerocapacitors™ were put in place. The low ESR and good frequency response of these devices show that they are ideal components for high discharge rate and low to moderate frequency (< 10 kHz) applications such as power conversion.

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1. Introduction

This is the final report for TRP Contract "Advanced Power Conversion using the Aerocapacitor™." The goal of this contract was to develop and test Aerocapacitors™ for power supply applications. Contract participants were Power-One, PolyStor Corp., Aerojet and Lawrence Livermore National Lab (LLNL). Power-One's role was to define application requirements and perform application testing. PolyStor's role was to develop and test Aerocapacitors™ for power supply applications. Aerojet's role was to scaleup production of carbon aerogel. LLNL's role was to assist with carbon aerogel scaleup and Aerocapacitor™ development.

This contract has enabled the development of a new Electrochemical Double Layer Capacitor (EDLC) based on carbon aerogel. This new organic-electrolyte EDLC, the Aerocapacitor™, was developed entirely during the course of this contract. (This effort was also partially funded by two ONR contracts.) Without these contracts PolyStor would not have been able to develop these devices in this time frame. The properties of the Aerocapacitor™ are superior to or similar to those of commercially available organic-electrolyte EDLCs. Specifically they have the same voltage rating and a similar capacitance to commercial devices of an equivalent size but have a lower equivalent series resistance (ESR). Low ESR is what differentiates the Aerocapacitor™ from other commercial devices and enables promising applications such as power conversion and battery load leveling.

During the first several months of this project PolyStor was developing aqueous-electrolyte Aerocapacitors™ and organic-electrolyte Aerocapacitors™ in parallel with most of the emphasis being placed on the aqueous device. For reasons which will be explained later in this report, work on aqueous electrolyte Aerocapacitors™ was discontinued in April 1995. Since that time work has focused on organic electrolyte Aerocapacitors™ which is the first type of capacitor product that PolyStor will commercialize.

The remainder of this report is divided into six additional sections. Section two describes project commencement. Section 3 discusses PolyStor's Aerocapacitor™ development strategy. Section 4 describes a marketing strategy developed by Power-One. Organic electrolyte Aerocapacitors™ and aqueous-electrolyte Aerocapacitors™ are discussed in sections 5 and 6, respectively. Conclusions are contained in section 7.

The milestones in this contract can be grouped into the following four topics:

1. Cell chemistry and internal cell design.
2. Packaging specifications and development.
3. Process development, process scaleup and pilot line development.
4. Aerocapacitor™ product performance testing and specifications.

The sections on organic-electrolyte and aqueous-electrolyte Aerocapacitor™ development are subdivided into these areas.

2. Project Commencement

The Aeropacitor project officially began on August 1, 1994, although it had originally been planned to start much earlier, around November 1993: time was needed to establish contractual and patent rights between the participants, and negotiations to arrive at these took over six months. The project began with all the parties signing a cooperative agreement with DOE and each other, in Oakland, CA, on August 4, 1994. Parties signing this agreement were: Aerojet/Gencorp, PolyStor Corporation, Lawrence Livermore Labs (LLNL), and Power-One, inc. While Rockwell International had originally been slated as one of the participants, they ultimately did not sign the cooperative agreement nor participate in the project due to differences over wording in the agreement.

Several issues caused negotiations to proceed for so long, the main one being who had patent-rights, and licensee rights, over the Aeropacitor technology, and at what voltage ranges. LLNL was the legal owner of the technology and patents, while both Aerojet and PolyStor wanted some licensing rights. PolyStor had already been granted an exclusive license to the technology, while Aerojet wanted a non-competitive license for higher voltage applications: in Aerojet's view, this would not infringe on PolyStor's target market, since PolyStor's applications were in the lower voltage ranges. Needless to say, considerable discussion ensued. Meanwhile, Power-One sought a "manufacturing-rights" license from whichever party needed up having the technology, to ensure that manufacturing would continue should the licensed party go bankrupt or otherwise discontinue production of the product.

Negotiations around these and similar issues went on from January 1994 until the cooperative agreement was finally signed on August 1994. Upon signing of the cooperative agreement, all licensing and patent issues had been resolved, and the consortium was ready to proceed with the project and technical work. By this time, PolyStor and LLNL had already began work on some preliminary steps of the project, and by September 1994 all consortium members were fully engaged in the project.

3. Aerocapacitor Development Strategy

PolyStor has formulated a development and commercialization strategy for Aerocapacitors™ based on the market application requirements, the state of technical development of Aerocapacitor™ technology, and synergy with other projects at PolyStor. This strategy is based on the following facts:

1. Until April 1995, PolyStor worked on two types of Aerocapacitors™, organic electrolyte and aqueous electrolyte. PolyStor does not have the resources to develop and commercialize both devices in parallel.
2. There are military and commercial markets for both organic-electrolyte and aqueous-electrolyte Aerocapacitors™ and either type of capacitor is suitable for many applications.
3. There is a great deal of synergy between organic-electrolyte Aerocapacitor™ development and other projects at PolyStor.
4. There is much less synergy between aqueous-electrolyte Aerocapacitor™ development and other projects at PolyStor.
5. PolyStor has the in-house resources necessary to develop the cylindrical packaging for organic-electrolyte Aerocapacitors™.
6. Development of an aqueous electrolyte package is expensive and difficult and PolyStor would need outside help to develop the state-of-the-art package required by military and commercial customers.

Based on these facts, PolyStor's strategy is to first develop and commercialize an organic-electrolyte Aerocapacitor™ in a cylindrical package. After this is complete, PolyStor will shift its resources toward the development of an Aerocapacitor™ with an advanced prismatic package that will address some of the markets not covered by the cylindrical Aerocapacitor™. The electrolyte for the later development has not yet been determined, but it may be either organic or aqueous.

The target specifications were developed for the AA-size, organic-electrolyte Aerocapacitor™:

Table 1

Projected Device Specifications

<u>Property</u>	<u>Specification</u>
Capacitance	10.0 Farads
Maximum Voltage	2.5 V
ESR @ 1000 Hz	< 50 mΩ
Leakage Current	< 25 μA
Maximum Discharge Current	35.0 Amps
Operating Temperature	-40°C to +85°C
Form Factor	Cylindrical

4. Power-One Aerocapacitor Marketing Strategy (See appendix B)

5. Organic Electrolyte Aerocapacitors

For the reasons described above PolyStor has emphasized development of organic electrolyte Aerocapacitors™ for the last half of this contract. This section describes this work. Section 3.1. discusses cell chemistry and internal design. Section 3.2. discusses cell packaging. Section 3.3. discusses process scaleup and pilot line development. Section 3.4. discusses Aerocapacitor™ performance testing and product performance specifications.

5.1 Chemistry and Internal Design

5.1.1 Organic Electrolyte Development

Military and automotive applications specify that the Aerocapacitor™ must operate at -40°C. We have screened several organic solvents and combinations of solvents for their low temperature performance. Results are shown in the following table. The salt was $(C_2H_5)_4NBF_4$. The salt concentration was the lesser of 1.0 mole/liter or the equilibrium solubility limit. When two solvents were used they were present in a 50:50 volume ratio. Conductivity was measured at room temperature and the phase behavior (i.e. liquid or solid) was observed at -40°C. Abbreviations for the various solvents are shown in the footnote.

Table 2¹
Screening of Organic Electrolytes

#	<u>Solvent(s)</u>	<u>Salt</u> <u>Concentration</u> <u>(moles/liter)</u>	<u>Conductivity @</u> <u>Room Temp.</u> <u>(S/cm)</u>	<u>Phase @ -40°C</u>
1	PC	1.0	13	Liquid
2	BL	1.0	18	Liquid
3	PC/DEC	Sol. Limit	6	Liquid +Solid
4	PC/DMC	Sol. Limit	14	Solid
5	PC/BL	1.0	15	Liquid
6	PC/DMF	1.0	20	Liquid
7	PC/MG	1.0	13	Liquid
8	DMF/DEC	Sol. Limit	5	Liquid
9	DMF/DMC	Sol Limit	11	Solid
10	DMF/BL	Sol Limit	22	Liquid
11	DMF/MG	Sol. Limit	10	Liquid

Additional boilerplate capacitor experiments were performed with cells containing PC, BL and DMF based electrolytes. ESRs and capacitances were measured at room temperature and -40°C. Results are shown in Table 3. The general result was that the ESR of cells that contained PC increased by more than those that contained only BL or DMF. We have chosen to concentrate on PC and BL as the electrolyte solvents because they have a larger voltage stability window.

Table 3
Ratio of ESR and Capacitance at -40°C to that at Room Temperature
in Organic Electrolytes

#	<u>Solvent(s)</u>	<u>ESR@23°C/ESR@-40°C</u>	<u>Capacitance@-40°C</u> <u>/Capacitance@23°C</u>
1	BL	0.28	0.75
2	PC/BL	0.17	0.64
3	PC/DMF	0.13	0.47
4	BL/DMF	0.33	0.73

¹ PC=propylene carbonate; BL=γ-Butyrolactone; DEC=Diethyl Carbonate; DMC=Dimethyl Carbonate; DMF=Dimethyl Formamide; MG=Dimethoxyethylene

5.2. Cell Packaging

Organic electrolyte Aerocapacitors™ are being made and packaged in AA-size cylindrical cans. Initially the AA can acted as the negative lead and a battery-type lid was used for the positive lead. These devices are shown in Fig. 1 (appendix E). More recently prototype radial and axial lead packages, Fig. 2 (appendix E), have been tested. Currently, test packages have an axial lead positive connection while the can acts as the negative lead. The process for making these capacitors and their performance characteristics as they relate to projected device specifications are described below.

5.3 Process Scaleup and Pilot Line Development (manufacturing process)

Organic electrolyte Aerocapacitors™ are being made and packaged in AA-size cylindrical cans. A pilot process for making these devices is in place and operating. The process for making these capacitors and their performance characteristics as they relate to projected device specifications are described below.

5.3.1 Pilot Line Capabilities

Pilot line facilities are in place to process aerogel powders and slurries, coat electrode laminate, and wind, flood and seal AA-size Aerocapacitors™. Using this line, we now have the ability to make about 100 cells/month for customer evaluation and internal testing.

5.3.2 Manufacturing Process

AA-size Aerocapacitors™ are made with the following process:

1. Bulk monolithic aerogel is crushed to a fine powder.
2. The aerogel powder is attrited to further reduce the particle diameter.
3. The attrited aerogel powder is sieved.
4. An aerogel "paint" is made from the aerogel powder.
5. The aerogel paint is then coated on both sides of a 1-mil aluminum current collector to produce electrode laminate.
6. The electrode roll is then cut to the desired length and tabs are welded to the Al foil.
7. Two electrodes, a positive and a negative, are then spiral wound with a layer of separator between the electrodes.
8. The electrode jelly roll is inserted into a AA-size can and the positive and negative tabs are welded to the lid and can, respectively.
9. The unsealed device is vacuum dried.
10. The dried Aerocapacitor™ is transferred to a glove box, vacuum impregnated with electrolyte and crimp sealed.
11. The sealed Aerocapacitors™ are then tested.

5.4 Aerocapacitor™ Test Results and Specifications (performance)

5.4.1 Equivalent Series Resistance

High discharge rate and high frequency such as power conversion applications require low equivalent series resistance (ESR) so that polarization losses are small and energy efficiency is high. The equivalent series resistance ESR of the organic-electrolyte Aerocapacitors™ are measured by both AC and DC methods. The AC measurements are made at several frequencies on a Fluke 6304 LCR meter. Typical results are shown in Table 4. The ESR is about 25 mΩ at a frequency of 1 kHz. The DC ESR, as measured from discharge data at 1 Amp, is typically about 75-100 % higher than the AC ESR. Measured ESRs at 1 kHz are less than the target value (< 50mΩ) specified in Table 1.

The Aerocapacitor's™ low ESR compares favorably to that of commercial organic electrolyte EDLCs. Devices made by Panasonic and ELNA have an ESR of 60-70 mΩ at 1 kHz, 160 % greater than that of the Aerocapacitor™, for a device with a volume that is 15 % greater than the Aerocapacitor™.

Table 4

Typical Equivalent Series Resistance of Organic Electrolyte AA-size Aerocapacitor™

<u>Measurement Conditions</u>	<u>ESR (mΩ)</u>
50 Hz AC	25
100 Hz AC	24
1 kHz AC	23
10 kHz AC	24
100 kHz AC	34
DC	42

5.4.2 Capacitance

The capacitance of preformatted AA-size Aerocapacitors™ is presently 8 to 10 F.² For example, Aerocapacitors™ produced from laminate run L090996-1 had a mean capacitance of 9.4 F and a standard deviation of 0.3 F. Thus far little effort has been made to optimize the capacitance. Although this capacitance will satisfy most applications, we believe that by optimizing the slurry formulation and positive electrode to negative electrode mass ratio, and decreasing the current-collector thickness an improvement of about 100% is achievable. Our present capacitance is near the value of 10 F specified in Table 1, especially when the smaller package size is accounted for. We project that the capacitance will be significantly greater than 10 F after these expected capacity improvements are realized.

²Unless stated otherwise capacitance is measured by a DC discharge at 0.343 Amps.

5.4.3 Rate Capability/Maximum Discharge Current

AA-size Aerocapacitors™ have shown excellent rate capability up to a discharge current of 15 Amps. (15 Amps is the maximum current available on our cyclers.) Fig. 3 (appendix E) shows discharge curves for discharge currents from 1A to 15 Amps. The nominal capacity (for the purposes of this figure only) is defined as the measured capacity at a discharge rate of 1A. The capacity at 3 Amps, 7 Amps, and 15 Amps are 94%, 87 % and 71 %, respectively of the nominal capacity. The projected capacity at a discharge rate of 35 Amps is 35 % of the nominal capacity. This rate capability/maximum current density will satisfy all of the customer requirements discussed in Section 2.

5.4.4 Low Temperature Discharge Rate Performance

Organic electrolyte Aerocapacitors™ have also demonstrated very good low temperature performance. Fig. 4 (appendix E) shows voltage discharge curves for an AA-size Aerocapacitor™ discharged at temperatures of room temperature, -20°C, -30°C and -40°C at a discharge current of 2 Amps. The discharge capacities at -20°C, -30°C and -40°C are 88 %, 82 %, and 73 %, respectively of the room temperature capacity. This data demonstrates the minimum operating temperature of -40°C specified in Table 1.

5.4.5 Cycle Life of Aerocapacitors™

Life has been tested with several cycle life regimens and at several temperatures. The longest test, in terms of number of cycles, was done with a cycling regimen wherein the cell was charged at 1.0 Amps to a voltage of 2.5 V and then discharged at 1.0 Amps to 0.0 V. Cycling was done at room temperature. Thirty two thousand cycles were completed before the test was suspended so that the cycling channel could be used for other tests. The results are shown in Fig. 5 (appendix E). The capacity declined relatively fast during the initial cycles but remained almost constant after cycle 10,000. The cell capacity decreased by 17 % between cycle 1 and cycle 10,000, but then only decreased by an additional 2 % between cycle 10,000 and cycle 32,000. Extrapolation of these results predict that 72 % of the original cell capacity will be retained at cycle 100,000 and 50 % of the original cell capacity will be retained at cycle 250,000. In addition to demonstrating long cycle life, this data demonstrates the 2.5 V maximum voltage specified in Table 1.

5.4.7 Leakage Current

Reducing the leakage current has been the major focus of Aerocapacitor™ development and significant progress has been made toward achieving this goal. A new process has been developed that significantly decreases the leakage current and shows promise for achieving the target of 50 μ A. Fig. 6 (appendix E) compares the leakage current, as a function of time, of an experimental cell made with the new process and a control. The leakage currents were made by holding the cell at a potential of 2.5 V for 20 hours. The reported leakage currents are the

average current between 10 and 20 hours. The leakage current of the experimental cell made by the new process was 73 μA whereas the leakage current of the control was 640 μA . The leakage current of the experimental cell was a factor of nine less than that of the control.

5.5 Application Testing (see appendix C)

6. Aqueous Electrolyte Aerocapacitor™

6.1 Aqueous Electrolyte Aerocapacitor™ Chemistry and Internal Cell Design

6.1.1 Separator Optimization

Tests were performed at PolyStor that showed that the micro-glass fiber separator used in early aqueous electrolyte Aerocapacitors™ was not stable in alkaline electrolytes.

PolyStor then performed a survey of commercial available separators to find a replacement. Sample separators were obtained from Hollingsworth and Vose, Daramic Inc., Freudenberg and Hoechst-Celanese. These samples were first screened in boiler plate cells and then a selected group was tested for compatibility with the electrolyte in accelerated high temperature tests. Based on these results one separator was chosen as the baseline material.

The results described in section 6.4 were obtained with cells using this separator. This information was also transferred to LLNL and they also reported improved cell performance with the new separator.

6.1.2 Low Temperature Electrolyte Optimization (-40°C Electrolyte)

Military and automotive applications require that capacitors operate at temperatures of -40°C. The KOH and H₂SO₄ electrolytes frequently used in double-layer capacitors have freezing points near -60°C and thus can operate at -40°C.

PolyStor has a proprietary electrolyte designed to insure good cell voltage balance and prevent gassing in multicell capacitors. This electrolyte freezes between -20°C and -25°C and thus cannot be used in capacitors at temperatures below -20°C.

To address this problem, PolyStor formulated a new electrolyte that can operate at temperatures as low as -40°C while still insuring good cell voltage balance. Fig. 8 (appendix E) compares the impedance of a cell containing the new electrolyte with that of cell containing the old proprietary electrolyte. The impedance of the cell with the new electrolyte increases in a manner similar to the proprietary electrolyte but the new electrolyte does not freeze until the temperature is less than -40°C .

6.1.3 Equivalent Series Resistance Improvement

High discharge rate applications require that ESR be minimized so that polarization losses are small and energy efficiency is high. One goal of this TRP contract was to demonstrate an ESR of $200\text{ m}\Omega\cdot\text{cm}^2$. Previously, ESRs ranging from 300 to $1000\text{ m}\Omega\cdot\text{cm}^2$ were obtained.

We have demonstrated ESRs of 175 to $225\text{ m}\Omega\cdot\text{cm}^2$ in cells. Fig. 3 (appendix E) shows the cycle life curve of one cell. The initial ESR was $220\text{ m}\Omega\cdot\text{cm}^2$ and it remained constant for 1500 cycles at which time the test was terminated. These values were achieved by making the following modifications to the cell design:

1. Replacing the old separator with the new optimized separator.
2. Redesigning the current collector.
3. Optimizing cell compression.

Table 6, shows estimates of the individual component resistances of a button cell AerocapacitorTM. These results show that the electrolyte resistance in the separator is the dominant cell resistance. They also suggest that, although the $200\text{ m}\Omega\cdot\text{cm}^2$ value that we have obtained is starting to approach the lower ESR limit based on existing separator technology, an additional factor of two decrease in the ESR may be obtainable.

Table 6

Component ESR Estimates for Button Cell AerocapacitorsTM

<u>Component</u>	<u>Resistivity³</u> <u>(mΩ cm²)</u>	<u>Resistance</u> <u>(mΩ)</u>
Electrolyte	25	40
Separator	50	80
Connector	0.002	0.003
Endplate	0.01	0.005
Spacers	-	0.01
Leads	-	15
Typical	300-1000	
Target	200	

6.1.4 Improved Carbon Aerogel Electrodes to Current Collector Contacts (see appendix C)

6.2 Aqueous Electrolyte AerocapacitorTM Packaging

Two types of aqueous electrolyte AerocapacitorTM cells were developed during this contract: cylindrical "button cells" and prismatic "epoxy bonded" cells. Button cell development was done at PolyStor and epoxy-bonded cells were developed at LLNL.

Button cell AerocapacitorsTM are packaged in cylindrical cans. These cans are 3.0 cm in diameter and 0.8 cm in height. They are crimp sealed to provide compression for low internal resistance. The cells are assembled in a polyethylene cup that controls the stack compression. The cell stack, eight cells each consisting of two electrodes, a separator, an EPDM seal and a bipolar cell current collector; is then assembled inside this cup. The cup is then slid into the cell can and crimped shut. The height of the cup determines the compression of the cell stack. It thus prevents cell shorts caused by over-compression, and high ESR resulting from under compression. It also makes it easier to properly assemble the many parts in the cell. The electrodes and paper separator are assembled pre-wetted with electrolyte. Once the stack has been assembled, the lid is placed on the can, and is sealed by crimping. The top of the can is then potted with epoxy to insure external electrical isolation, and sealing.

³ Normalized for area only.

6.3 Aqueous Electrolyte Aerocapacitor Electrode Process Development (manufacturing) (see appendix C)

6.4 Aqueous Electrolyte AerocapacitorTM Performance Test Results (performance)

6.4.1 Button Cell Performance

The following data is typical for 7 V button cell AerocapacitorsTM. Five button cells were assembled and tested. The results are shown in Table 5. The cell efficiency is high and the leakage current is low which shows that there is no shorting. The capacitance of these cells averaged 0.65 ± 0.08 F and the ESR was $1.00 \pm 0.28 \Omega$. These results show that button cells of this design can be successfully assembled.

Table 5

Performance of Redesigned AerocapacitorTM Button Cells

<u>Device</u>	<u>ESR</u> <u>(Ω)</u>	<u>Capacitance</u> <u>(F)</u>	<u>Efficiency</u> <u>(%)</u>	<u>Leakage</u> <u>Current (μA)</u>
11227TA	1.26	0.55	99.7	22.3
11297TA	0.76	0.665	99.3	73.1
11307TA	0.90	0.73	99.4	70.8
12027TA	0.85	0.66	99.5	58.8
12037TA	1.23	0.65	99.2	48.4
Mean	1.00	0.65	99.4	54.7
Confid. Limit	0.28	0.08	0.2	25.6

6.4.2 Epoxy Bonded Cell Performance (see appendix C)

6.4.3 Cell Balancing Demonstration

Good cell voltage balancing is necessary in multicell capacitors because poor cell voltage balance results in premature failure. Three-cell boilerplate capacitors were assembled to investigate cell voltage balance, explore failure mechanisms in multicell capacitors, and better understand the failure of button cell capacitors. Boilerplate cells are ideal test vehicles for these

experiments because individual cell voltages, impedances, etc. can be measured in boilerplate cells whereas they cannot be easily measured in button cells.

Experiments were conducted by first characterizing the ESR, capacity, coulombic efficiency, etc. of each individual cell and then testing the entire capacitor. Individual cell data for a typical capacitor is shown in Table 6.

Table 6

Characteristics of Individual Cells in a Three Cell Capacitor⁴

<u>Cell #</u>	<u>Discharge Capacity</u> <u>(mAh)</u>	<u>Coulombic</u> <u>Efficiency</u> <u>(%)</u>	<u>ESR</u> <u>(mΩ)</u>
1	1.044	91	89
2	0.974	94	88
3	1.154	94	79

Next the capacitor was tested with the following regimen:

1. Five cycles to a 2.55 V cutoff at room temperature (cycles 1-5).
2. Twenty-three hours on float at 2.55 V at room temperature.
3. Five more cycles to a 2.55 V cutoff at room temperature (cycles 6-10).
4. Steps 1-3 were then repeated at 50°C.

The discharge capacity and coulombic efficiency at cycle ten were 0.76 mAh and 100.3 %, respectively. These results compare favorably to the values of 0.74 mAh and 98.7 % at cycle 5. The average leakage current during the last ten hours of the float was 10 μ A. The voltages of the three individual cells during the 50°C float period are shown in Fig. 9 (appendix E). The change in the individual cell voltage was less than 20 mV. These results show that temperatures of 50°C did not negatively impact the performance of this capacitor. They further demonstrate that the modest cell capacity and impedance imbalances shown in Table 6 do not have an adverse effect on cell voltage balance and capacitor performance.

⁴ Discharge capacity and coulombic efficiency is for cycle five. The discharge and charge currents are 100 mA to a 1.0 V cutoff and the discharge and charge times are five minutes.

6.4.4 Temperature Testing of Button Cells

Commercial and military applications for the Aerocapacitor™ have wide operating temperature range requirements. The minimum operating temperature is usually between -40°C and -20°C, and the maximum operating temperature ranges from 70°C to 105°C.

To characterize the effect of temperature on Aerocapacitors™, the ESR and capacity of the button cell capacitors were measured at various temperatures, and the results are presented in Figure 8 (appendix D). The ESR is almost constant between 20°C and 100°C, but increases sharply between 20 and -20°C. At temperatures below -20°C the electrolyte freezes. The capacitance is almost constant between -20°C and 100°C.

6.4.5 15 V, 2 F Boilerplate Aerocapacitor™

A 15 V, 2 F boiler plate Aerocapacitor™ was assembled to demonstrate the feasibility of assembling large, high voltage devices. This Aerocapacitor™ consisted of 23 bipolar cells in series. The device ESR was 1.4 Ω . Fig. 10 (appendix D) shows a discharge curve for this device. After initial characterization at PolyStor this Aerocapacitor™ was delivered to Rockwell's Allen-Bradley and successfully tested.

6.4.6 Frequency Response of Aqueous Electrolyte Aerocapacitors™ (see appendix C).

6.4.6 Thermal Modeling of Aerocapacitors™ (see appendix D).

7.0 Conclusions

Organic electrolyte Aerocapacitors™ have been developed and characterized for power supply applications. Pilot facilities have been put in place to manufacture prototype devices in AA packages. The properties of these new EDLCs are equal or superior to that of commercial organic electrolyte EDLCs. Most notably their low ESR makes them ideal for high discharge rate and low to moderate frequency applications (< 10kHz) such as power conversion and battery load leveling.

Appendix A
TRP Milestones Grouped into Categories

1. Cell Chemistry and Internal Cell Design
 - 2.1 Begin development of improved contact methods.
 - 3.1 Continue contact development: flame spraying and electroplated carbon fiber paper.
 - 4.1 Continue contact development: sputter deposition and spot welding.
 - 5.1 Select best contact method.
 - 5.5 Electrolyte parameterization complete.
 - 5.6 Research and test separator materials for lowest available ESR at minimum cost.
2. Packaging Specifications and Development
 - 3.2 Identify packaging material.
 - 4.2 Define packaging methods and materials.
 - 6.2 Develop efficient packaging methods.
3. Process development, process scaleup and pilot line development.
 - 2.2 Begin Batch processing of carbon aerogel.
 - 2.4 Transfer aerogel synthesis to PolyStor.
 - 3.4 Optimize aerogel processing at laboratory scale.
 - 3.5 Laboratory batch processing of carbon aerogel monoliths and composites.
 - 3.6 Initial engineering design for continuous processing carbon aerogel electrode material.
 - 5.7 Materials (carbon aerogel) manufacturing parameterization completed.
 - 5.9 Conceptual development of prototype manufacturing line and cost analysis.
 - 5.10 Demonstration of carbon aerogel electrodes produced continuously or semi-continuously.
 - 6.1 Prototype manufacturing line designed.
 - 7.3 Evaluation of new precursor materials for carbon aerogel electrodes.
 - 7.4 Prototype manufacturing line built.
 - 7.5 Integration of carbon aerogel processing into a continuous or semi-continuous operation.
- 8.3 Demonstrate the manufacture of thin film, carbon aerogel electrodes in a pilot facility.
- 8.6 Evaluation of carbon aerogel electrodes derived from new precursor materials.

4. Sampling, Testing and Product Performance Specification Development, etc.
 - 1.1 Kick-off Meeting.
 - 1.2 Milestone Schedule.
 - 1.3 First sample to Power-One.
 - 1.4 Send Aerocapacitor™ Test Description to Power-One.
 - 1.5 Develop preliminary product specification.
 - 2.3 Product specification with Aerocapacitor™ requirements.
 - 2.5 Evaluation and Testing of early Aerocapacitors™.
 - 4.3 Define test plan and specifications for single cell Aerocapacitors™.
 - 4.4 Review safety plan for single cell Aerocapacitors™.
 - 4.5 Construct single cell Aerocapacitors™ and begin testing.
 - 5.2 Demonstrate 5V bipolar stack.
 - 5.3 Begin long term cycle-testing of 5 V Aerocapacitors™.
 - 5.4 Measurement of frequency response of 5 V Aerocapacitors™.
 - 5.5 First commercial product(s) explored.
 - 6.3 Demonstrate 5V bipolar stack Aerocapacitor™.
 - 6.4 Begin testing on first commercial prototype.
 - 6.5 Establish ripple current ratings.
 - 6.6 Develop a thermal model for the Aerocapacitor™.
 - 7.1 Demonstrate a 10 V Aerocapacitor™.
 - 7.2 Aerocapacitor™ prototype integrated into product.
 - 8.1 Demonstrate a 20V Aerocapacitor™.
 - 8.2 Deliver packaging technology.
 - 8.3 Shipment of alpha product.
 - 8.4 Quantity shipment of beta Aerocapacitors™.
 - 8.5 Evaluation of carbon aerogel electrodes derived from new precursor materials.

Appendix C

Aerocapacitor™ Papers and Technical Articles

Papers on Aerocapacitors™ presented during the TRP contract.

Aerojet's role in this ARPA partnership was to transfer the carbon aerogel sheet stock fabrication methods from the laboratory at LLNL to a process more amenable to pilot production. Material would then be produced and delivered to Polystor for use in fabricating capacitors.

LLNL performed one demonstration lab run at the Aerojet facility. This activity resulted in six sheets approximately 3" x 3" being produced. The method used to produce these by Rick Pekala was to place one sheet of carbon paper on a glass sheet, pour resorcinol formaldehyde sol on the material, place a sheet of exmet on top, layer a second carbon sheet, and pour a layer of sol gel and cover these three layers with a glass plate. Processing then proceeded to cure and pyrolyze the electrodes.

Material resulting from this lab activity was supplied to Aerojet's Electronic Division in Azusa to be fabricated into a capacitor to allow us to develop a "use" test for the material to determine:

- A. Its viability as an electron storage medium;
- B. Reproducibility of material characteristics "batch to batch" in a use test.

About this point in the program, Polystor's design for the capacitor diverged from the use of sheet stock and their new favored configuration relied on the use of some form of powdered material. This new approach was held proprietary to Polystor and LLNL.

Small capacitors were the initial target market chosen by Polystor. Small capacitors can be fabricated using powders. The size of capacitors has been limited by the ability to compress powders. Carbon aerogel sheet stock avoids the need for compression in the design.

Market interest in large capacitors was served by continuing the task of understanding the carbon aerogel sheet stock material manufacturing and processing issues. Therefore, Aerojet proceeded to produce a second batch of 44 sheets that were layered "by hand" in a method similar to that previously detailed.

A third run was conducted which explored some production approaches which would lend themselves to scale-up. Forty 3" x 3" sheets were produced — four sheets to a layer with sol impregnation occurring after the stack process (see Figure 1). This technique was successful and dramatically reduced the labor.

These materials were then evaluated in use test by Aerojet's Electronics Division. Testing of the electrode materials gave very erratic results with the resistance of the aerogel electrodes varying by 3-4 times. Initial problems were

believed to be associated with bubbling between the RF aerogel and the nickel electrode/conductor sheet. Two potential causes were investigated: 1) contamination on the nickel mesh prior to application of the aerogel, and 2) dissolved gas in the initial RF aerogel solution. To address these possible problems, nickel electrodes were cleaned with acetone and the RF solution was degassed using a simple vacuum. These steps somewhat reduced the bubbling/separation of the aerogel and nickel conductor. This problem persists in the processing of aerocapacitor electrodes. Aerojet then began to investigate the potential of heat bonding the aerogel and nickel at approximately 1050°C. Thus far, no reportable success has been demonstrated.

Subsequent to the ARPA program, Aerojet produced six thousand 7" x 7-7/8" carbon aerogel sheets 5 mils in thickness for use by LLNL in assembling a test bed deionization water treatment unit. The fabrication technique which was developed on this ARPA program allowed this material to be produced.

More mechanized production will be necessary when markets for this material are realized. Aerojet believes the production to be commercially feasible and is interested in pursuing its production as requirements materialize.

We have introduced the material at two National Design and Engineering shows and at SAMPE. We have had two large capacitors made and intend to use them in future exhibits.

Major cost drivers to be addressed if commercial production were to be initiated would be:

- Cost of carbon aerogel paper is 160 % of electrode cost
- Sizing on carbon paper is water soluble and results in it having no wet strength. This makes rolling plant-type handling impractical. However, it wets with the resins very well, resulting in minimum bubbling. Further work is required to optimize wet strength (ease of handling) versus wettability (minimum bubbling).

Carbon Aerogel Electrodes Pilot Run: Casting Process

Carbon Aerogel Electrodes Pilot Run: Pyrolysis

Appendix D
Thermal Analysis

POWER-ONE D.C. POWER SUPPLIES

TO: Mark Isaacson (cc. D. Roark, H. El-Attrash, L. Josephs, S. Kunkle, B. Bingham, R. Pakela)
FROM: Dennis Gregory
DATE: 6 July, 1995
SUBJECT: Preliminary thermal analysis on Polystor Aerocapacitor (Button type)

This is an attempt to quantify the maximum permissible ripple current for the 6 Volt, 7 cell, "button" type aerocapacitor. The following are some assumptions:

The maximum hot spot temperature is 85 °C.

The thermal resistance from the hot spot to case is 10 °C/W

The thermal conductivities were supplied by Polystor.

The heat transfer is by natural convection.

The ESR is 177 mΩ calculated at 1 KHz ($200 \Omega\text{-cm}^2/5.06 \text{ cm}^2$ per cell times seven cells)

The device orientation is soldered into a PCB by the leads.

A finite element analysis was run to determine the thermal resistance from the internal "hot spot" to the case of the capacitor. In order to simplify the model, a lumped resistance was used for the cell. The case to hot spot resistance was then plugged into a simple finite difference model to determine the temperature rise for various dissipations. This is a first cut analysis, and should be verified experimentally. If we can get a can, cup, and tabs, we can perform a test.

The final result is a graph of permissible RMS ripple current versus ambient temperature.

If there are any questions please call. Thanks.

Thermal Power Handling Capabilities of Aqueous Electrolyte Aerocapacitors

In any capacitor the predominant internal heat generation can be described by $P_d = I_{rms}^2 * ESR$, where I_{rms} is the AC "ripple" current. The maximum operating temperature is a function of the allowable material limits, physical construction, self-heating, and external surface area. In order to determine the maximum ripple current, a finite element analysis was performed on the 32mm diameter x 7.6 mm high button cell to determine the thermal resistance from the internal "hot spot" to the case of the capacitor. With this known, the device was analyzed to determine the allowable dissipation with the capacitor mounted on a PWB, in natural convection. **Figure XXX** shows the relationship of allowable ripple current to ambient temperature (at 1 KHz.).

PolyStar Aerocapacitor
 7 cell, 6 Volt, 0.6 Farad
 1 Watt Diss., R(hot-spot-case) = 8 C/W

SUVIEWTH 1.08 File:aerog1 95/07/05 16:19 ST 1/ 1 Un= 7 Lo= 145 La= 45 R= 0

Allowable ripple current for an Aerocapacitor

Maximum "hot spot" temperature = 85 °C
 Capacitor ESR = 0.177 Ohms

Ambient	Temp Rise	Pd	Irms
25	60	1.93	3.30
30	55	1.76	3.15
35	50	1.58	2.99
40	45	1.4	2.81
45	40	1.24	2.65
50	35	1.08	2.47
55	30	0.92	2.28
60	25	0.75	2.06
65	20	0.6	1.84
70	15	0.45	1.59
75	10	0.3	1.30
80	5	0.15	0.92
85	0	0	0.00

Aerocapacitor Preliminary Thermal Analysis
6 Volt, 7 Cell, "Button" type construction

1) Constants:

$\rho := 200$ Ohm-cm², area resistivity of one cell (@ 1 kHz)

$area := 5.06$ Cm², superficial surface area of a single cell

$NoCells := 7$ Number of cells per capacitor

2) Calculate resistance of capacitor

$$R_{cell} := \frac{area}{\rho} \quad R_{cell} = 0.025 \text{ Ohms, resistance of single cell}$$

$$R_{cap} := R_{cell} \cdot NoCells$$

$$R_{cap} = 0.177 \text{ Ohms, Equivalent Series Resistance of capacitor}$$

AeroCapacitor composite thermal conductivities:

Thermal conductivities:

$$K_{\text{aero}} := .128 \quad \text{W/in-}^{\circ}\text{C}$$

$$K_{\text{poly}} := .01 \quad \text{W/in-}^{\circ}\text{C}$$

$$K_{\text{Ni}} := 1.5 \quad \text{W/in-}^{\circ}\text{C}$$

$$Z_{\text{aero}} := .01 \quad \text{In.}$$

$$Z_{\text{poly}} := .009 \quad \text{In.}$$

$$Z_{\text{Ni}} := .001 \quad \text{In.}$$

Assume area = 1 In², and $R = L/K \cdot \text{area}$, then $R = L/K$. Find the "Z" axis resistivities:

$$R_{z_{\text{aero}}} := \frac{Z_{\text{aero}}}{K_{\text{aero}}} \quad R_{z_{\text{aero}}} = 0.078 \quad ^{\circ}\text{C/W}$$

$$R_{z_{\text{poly}}} := \frac{Z_{\text{poly}}}{K_{\text{poly}}} \quad R_{z_{\text{poly}}} = 0.9 \quad ^{\circ}\text{C/W}$$

$$R_{z_{\text{Ni}}} := \frac{Z_{\text{Ni}}}{K_{\text{Ni}}} \quad R_{z_{\text{Ni}}} = 0.0007 \quad ^{\circ}\text{C/W}$$

The total "Z" axis resistivity is then:

$$R_{z_{\text{tot}}} := 2 \cdot R_{z_{\text{aero}}} + R_{z_{\text{poly}}} + R_{z_{\text{Ni}}} \quad R_{z_{\text{tot}}} = 1.057 \quad ^{\circ}\text{C/W}$$

The equivalent "Z" axis thermal conductivity is:

$$Z_{\text{tot}} := 2 \cdot Z_{\text{aero}} + Z_{\text{poly}} + Z_{\text{Ni}} \quad Z_{\text{tot}} = 0.03 \quad \text{In.}$$

$$K_z := \frac{Z_{\text{tot}}}{R_{z_{\text{tot}}}} \quad K_z = 0.028 \quad \text{W/in-}^{\circ}\text{C}$$

Calculate "XY" axis areas, assuming $L = 1$, $W = 1$:

$$A_{\text{aero}} := 1 \cdot Z_{\text{aero}} \quad A_{\text{aero}} = 0.01 \quad \text{In}^2$$

$$A_{\text{poly}} := 1 \cdot Z_{\text{poly}} \quad A_{\text{poly}} = 0.009 \quad \text{In}^2$$

$$A_{\text{Ni}} := 1 \cdot Z_{\text{Ni}} \quad A_{\text{Ni}} = 0.001 \quad \text{In}^2$$

Calculate "XY" resistances:

$$R_{xy_{\text{aero}}} := \frac{1}{K_{\text{aero}} \cdot A_{\text{aero}}} \quad R_{xy_{\text{aero}}} = 781.25 \quad ^{\circ}\text{C/W}$$

$$R_{xy_{\text{poly}}} := \frac{1}{K_{\text{poly}} \cdot A_{\text{poly}}} \quad R_{xy_{\text{poly}}} = 1.111 \cdot 10^4 \quad ^{\circ}\text{C/W}$$

$$R_{xy_{\text{Ni}}} := \frac{1}{K_{\text{Ni}} \cdot A_{\text{Ni}}} \quad R_{xy_{\text{Ni}}} = 666.667 \quad ^{\circ}\text{C/W}$$

The total "XY" axis resistivity is then:

$$R_{xy \text{ tot}} := \frac{1}{\left(\frac{1}{R_{xy \text{ aéro}}} \cdot 2 + \frac{1}{R_{xy \text{ poly}}} + \frac{1}{R_{xy \text{ Ni}}} \right)} \quad R_{xy \text{ tot}} = 240.964 \quad ^\circ\text{C/W}$$

The equivalent "XY" axis thermal conductivity is:

$$K_{xy} := \frac{1}{R_{xy \text{ tot}} \cdot Z_{\text{tot}}} \quad \begin{array}{l} \text{*****} \\ K_{xy} = 0.138 \quad \text{W/in-}^\circ\text{C} \\ \text{*****} \end{array}$$

Temp. Rise vs. Pd

Maximum Allowable Ripple Current vs. Temp (Natural Convection)

Appendix E
Final Report Figures and Charts

AERO2.XLS

Allowable ripple current for an Aerocapacitor

Maximum "hot spot" temperature = 85 °C
 Capacitor ESR = 0.177 Ohms

Ambient	Temp Rise	Pd	Irms
25	60	1.93	3.30
30	55	1.76	3.15
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60	25	0.75	2.06
65	20	0.6	1.84
70	15	0.45	1.59
75	10	0.3	1.30
80	5	0.15	0.92
85	0	0	0.00

Maximum Allowable Ripple Current vs. Temp (Natural Convection)

Fig. 2. Organic electrolyte Aerocapacitors™ in radial lead and axial lead packages.

Fig. 1. AA-size, organic electrolyte Aerocapacitors™ in battery type

Fig. 3. Discharge rate capability of AA, organic electrolyte Aerocapacitor at room temperature.

Fig. 4. Low temperature discharge performance of AA, organic electrolyte Aerocapacitors. All discharges are at 2 Amps.

Fig. 5. Cycle life of AA, organic electrolyte Aerocapacitors.

Fig. 6 Leakage Current of Formed and Unformed Cells

Fig. 7. Frequency response of AA, organic electrolyte Aerocapacitor at room temperature.

Fig. 8. Effect of temperature on ESR and capacitance of button cell Aerocapacitors.

Fig. 9. Voltage Balance in a Three-Cell Aerocapacitor™

Fig. 10. Discharge curve for 15V boilerplate Aerocapacitor.