FINAL SCIENTIFIC REPORT

Extreme Temperature P/MWD with Energy Storage and Generation, Enabling Substantial Cost and Risk Reduction in Geothermal Exploration

Award:	DE-EE0005503
Lead Recipient:	FastCAP SYSTEMS Corporation
Project Title:	Extreme Temperature P/MWD with Energy Storage and Generation, Enabling Substantial Cost and Risk Reduction in Geothermal Exploration
Principal Investigators:	Dr. Riccardo Signorelli Dr. John Cooley

1 CONTENTS

2 INTRODUCTION

This report summarizes the work performed by FastCAP Systems Corporation to achieve the technical objectives defined by the award DE-EE0005503. Under this program, FastCAP developed three critical subassemblies to TRL3 demonstrating proof of concept of a geothermal MWD power source. This power source includes an energy harvester, electronics and a novel high temperature ultracapacitor ("ultracap") rechargeable energy storage device suitable for geothermal exploration applications.

The ultracap performs reliably at 250°C and beyond and operates over a wide operating temperature range: -5°C to 250°C. The ultracap has significantly higher power density than lithium thionyl chloride batteries, a non-rechargeable incumbent used in oil and gas drilling today. Several hermetically sealed, prototype devices were tested in our laboratories at constant temperatures of 250°C showing no significant degradation over 2000 hours of operation. Other prototypes were tested at Sandia National Lab in the month of April, 2015 for a third party performance validation. These devices showed outstanding performance over 1000 hours of operation at three rated temperatures, 200°C, 225°C and 250°C, with negligible capacitance degradation and minimal equivalent series resistance (ESR) increase.

The electronics have demonstrated a substantially reduced design cycle time by way of process and material selection innovations and have been qualified for 250°C / 10 Grms for at least 200 hours.

The energy harvester has been developed to provide operational power by harvesting rotational mechanical energy that exists downhole in geothermal drilling. The energy harvester has been tested at 250°C / 10 Grms for 200 hours.

Deployment of these technologies in geothermal drilling and exploration applications could have an immediate and significant impact on the effectiveness and efficiency of drilling processes, particularly with regard to use of advanced logging and monitoring techniques.

3 ENABLING TECHNOLOGY FOR GEOTHERMAL MWD

The ultimate goal of this work is to reduce drilling risk to make geothermal energy more attractive and viable to the customer. Generally speaking, we aim to support the transfer of MWD techniques from oil and gas to geothermal exploration with considerations toward the practical differences between the two.

One of the most significant obstacles to the deployment of advanced drilling and production techniques in the geothermal context are limitations related to the maximum operating temperatures of downhole batteries used to provide power for downhole sensors, steering tools, telemetry equipment and other MWD/LWD technologies. FastCAP's higher temperature ultracapacitor technology will provide power solutions for similar advanced drilling and production techniques, even in the harsher environments associated with geothermal energy production. This ultracapacitor will enable downhole power solutions for the geothermal industry capable of the same reliable and safe operation our team has demonstrated in the oil and gas context. Without batteries, geothermal MWD is left without a downhole power source. Some very high temperature turbines exist but provide unsteady, intermittent power and no power when the flow is off. In high loss formations common to geothermal exploration, it will be auspicious to support air drilling in which case there is no flow to power a turbine at all. In the best case, rechargeable energy storage will help to buffer unsteady power from non-battery power sources and in the worst case it will be needed to store energy from highly intermittent sources to provide a continuously operable power source to the tool.

4 Scientific Approach

FastCAP's proposed solution combines an energy harvester coupled to rechargeable energy storage to provide a high power, buffered power source to the MWD toolstring capable of operating at geothermal temperatures. The three critical subassemblies in this system are the rechargeable energy storage (ultracapacitors), the energy harvester (rotary inertial energy generator), and the interfacing electronics between the two. This solution has been demonstrated to TRL3 as a result of this project.

FastCAP's ruggedized ultracapacitor (Ucap) technology has been proven and commercialized in oil and gas exploration operating to rated temperatures of 150°C. Characteristics of this technology are that it is rechargeable and relatively high power. This technology was the basis for the advancements in rechargeable energy storage under this project.

Similarly, FastCAP's ruggedized electronics have been proven and commercialized in oil and gas exploration operating to rated temperatures of 150°C. This technology was the basis for the advancements in downhole electronics under this project. Principal contributions here focused on design for manufacture innovations that have reduced the prototype build cycle time by a factor of 10x.

Finally, FastCAP has invented a rotary inertial energy generator (RIEG) to harvest various mechanical energy sources that exist downhole. This device is flow-independent and has been demonstrated as a proof of concept to survive geothermal well temperatures under this project.

5 TASK 1 - ELECTRONICS AND ENERGY HARVESTER

5.1 ELECTRONICS

FastCAP has successfully completed all milestones related to the electronics including combined temperature and vibration abuse qualification at 250C and 10Grms while processing 10 or more Watts of power. Since the last report, the electronics have continued to operate at temperature and have exceeded the lifetime predicted by the literature cited here. [1]

FastCAP's principal contribution to the design of geothermal electronics has been the development of processes and material selections that yield substantially faster design cycles as compared to previous approaches. Conventional approaches to geothermal electronics design suffer from prototype cycles ranging from 6 to 12 months. The electronics developed here can be procured and fabricated in 4 weeks. FastCAP has reduced the prototyping cycle time by a factor of about 10x.

Conventional approaches involve ceramic-based PCB substrates, multi-chip modules and very high value and long lead time circuit components along with intricate or exotic fabrication steps that tend to damage the components or require special equipment. Special niche service providers control the design cycle and with little competition they are able to demand prohibitive compensation with exceptionally long lead times. All told, previous approaches placed an unwieldy lower-bound on the design cycle for geothermal electronics at approximately 12 months. Considering practical design iteration needs, especially in an application requiring abuse qualification and iteration, this design cycle can easily multiply several-fold leading to a subassembly design cycle that can occupy several years alone. Through this learning process, FastCAP has identified the design cycle (and associated cost) as a key limiting factor for the viability of geothermal products. Out of necessity, the FastCAP team has innovated across the design from the circuit topology, to the choice of substrate material, bonding material, component choice and fabrication process to develop a design cycle resembling that for more standard commercial electronics. PCB substrates can be purchased through standard suppliers with 2-day turns, eutectics can be shipped overnight and fabrication requires only a standard benchtop reflow oven. Even the circuit components can be procured in a few weeks across the entire BOM and in some cases are entirely stocked for overnight shipping. Design iterations are no longer limited by procurement and prototyping time, but by actual design time. As proof of this new design cycle, we have re-designed, prototyped and qualified a circuit at 250C and 10Grms all during the final quarter. The electronics built with these methods have exceeded a lifetime of 2,000 hours at 250C. This result exceeds predictions based on data found in Watts [1], which predicts a time to failure of high temperature surface mount and through-hole configurations at 250C of 168-336 hours (see Figure 2 below).

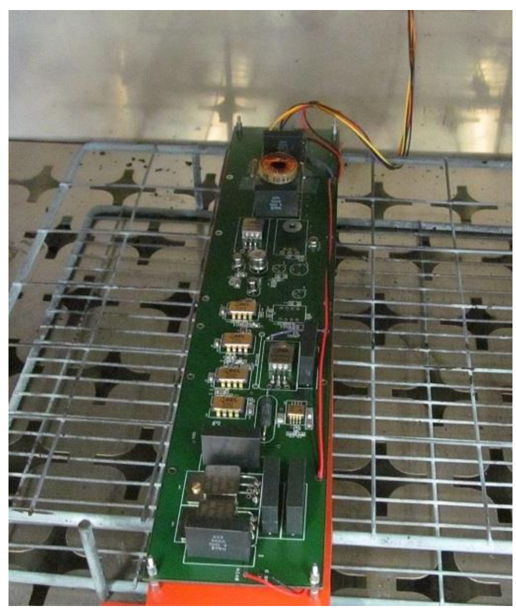


Figure 1: The very high temperature electronics that met the end milestone.

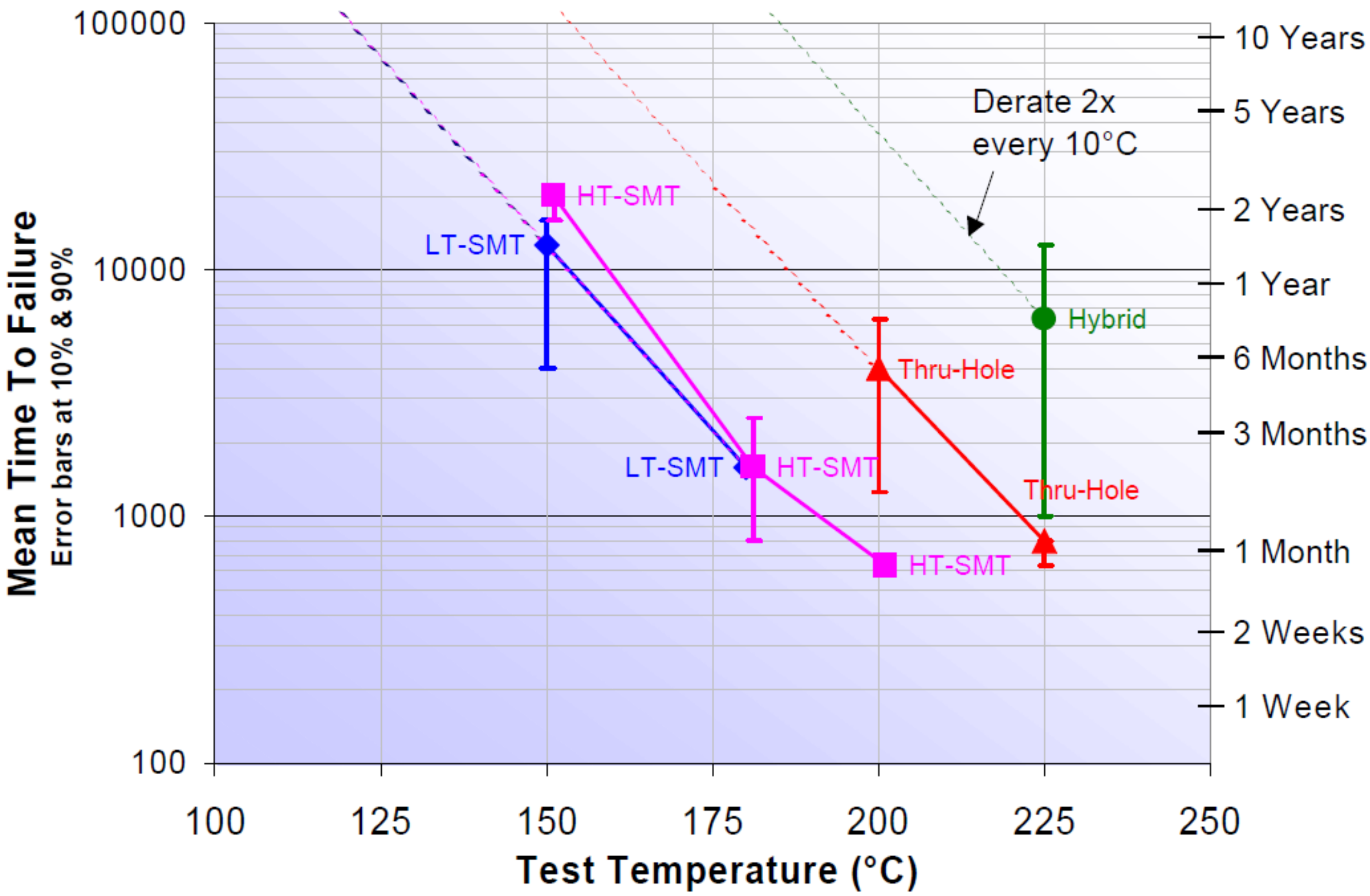


Figure 2: Data from Watts [1]

5.2 Materials and Process

We identified the need to resolve a process and material selection that would accelerate the prototype cycle time and reduce cost substantially. The following design narrative content is adapted from the design documentation of the design that met the final milestone.

5.2.1 PCB Design

This revision of the buck converter addressed several issues related to PCB failures observed in the previous revision. The root cause of the failures observed in the previous revision was likely due to a combination of copper spacing and board deformation. Soft shorts were observed near plated thru holes after approximately 40 hours at 250 C on new builds. It was surmised that the vias were in electrical contact with the surrounding ground plane on the inner layers. As a corrective action, we reduced the number of copper layers from 4 layers to 2 layers. This resulted in reduced board complexity and eliminated the possibility of a via shorting to a copper layer. In addition, the 2 layer polyimide board is readily sourced with short lead time when compared to the previous revision’s 4 layer Rogers 4350 ceramic board. To further prevent the likelihood of two copper nodes shorting together, we increased the minimum copper gap from 0.010” to 0.020”. Other board faults were observed on the surface of the board and are likely attributed to re-work.

Due to the high temperatures required for brazing components and wiring to the PCB, the LPI solder mask had likely decomposed since it has a decomposition temperature of approximately 343 C. The brazing temperature of the soldering iron was set to approximately 454 C. In reworked areas, the solder joint spanned across to the ground plane. The combination of a lack solder mask beneath the solder joint and residual flux left behind likely created the soft short condition. This finding re-emphasizes the need to design the PCB and reflow process to avoid re-work and to minimize human intervention.

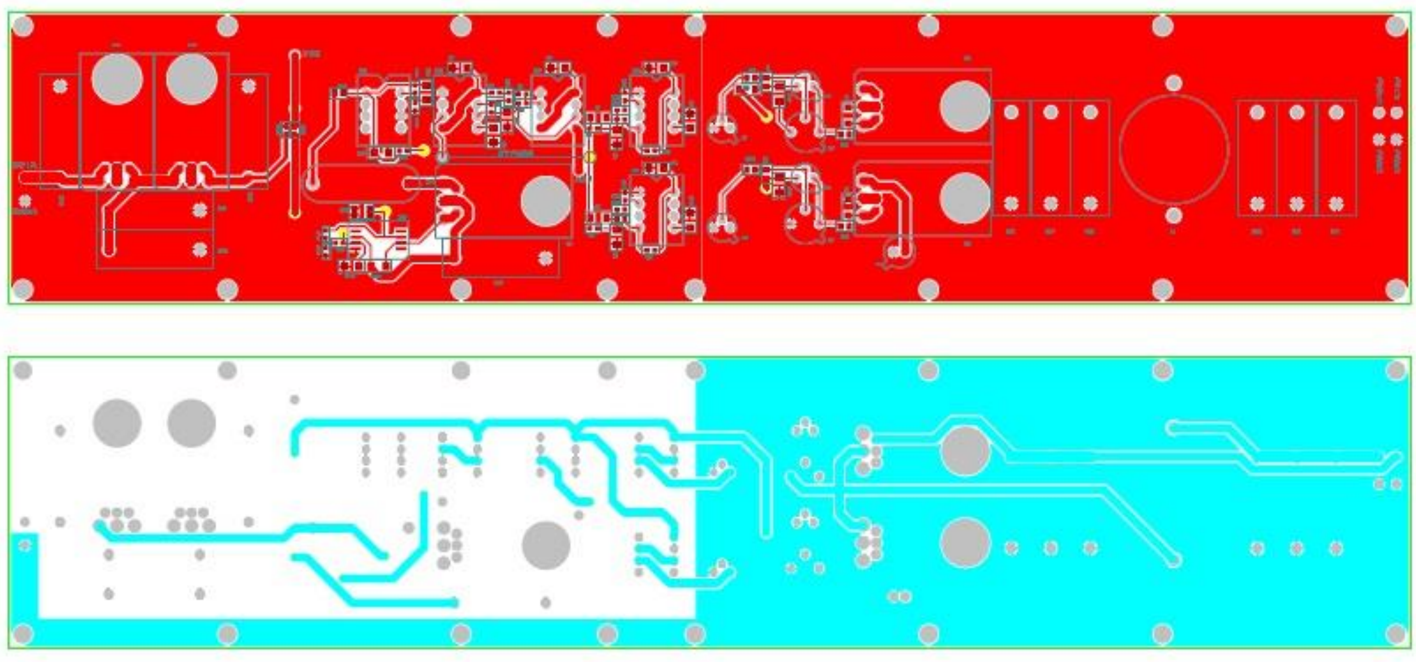
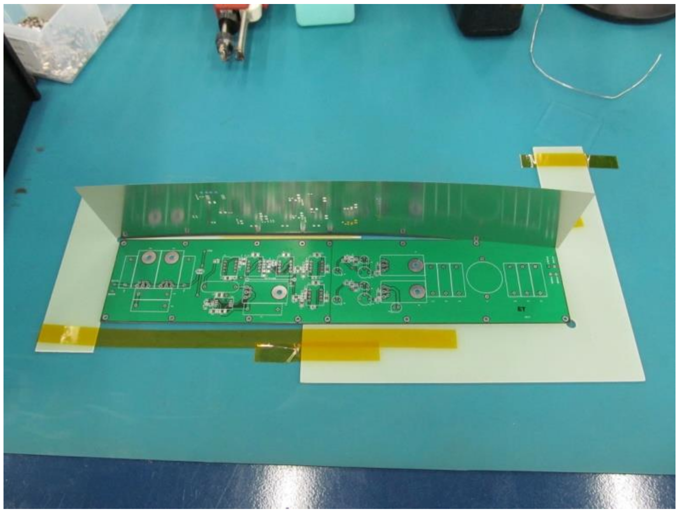
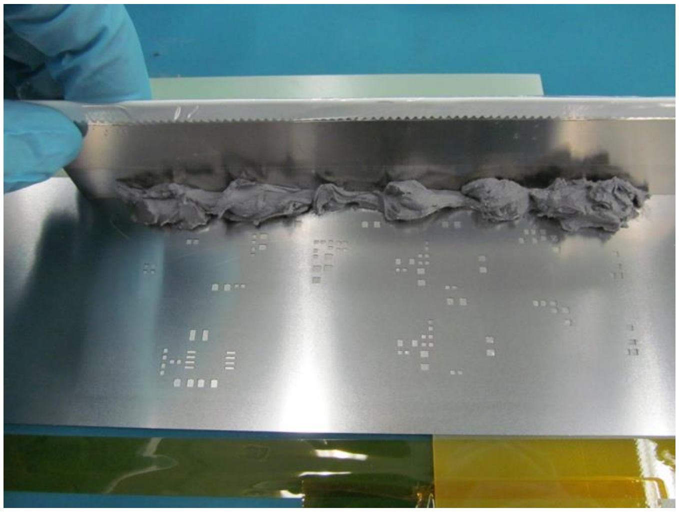
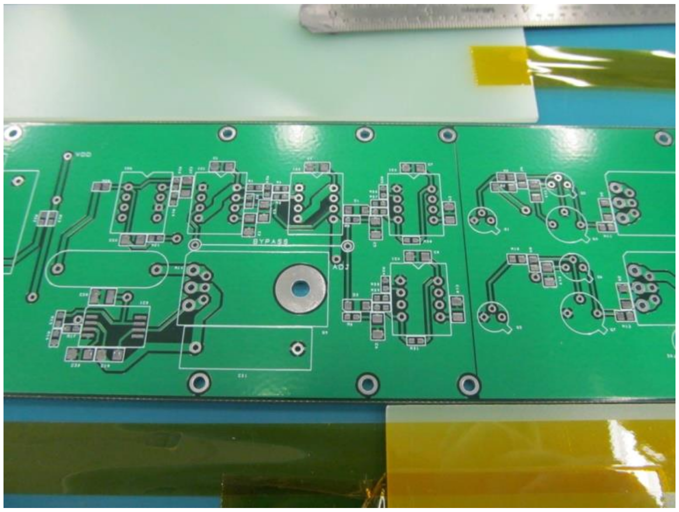
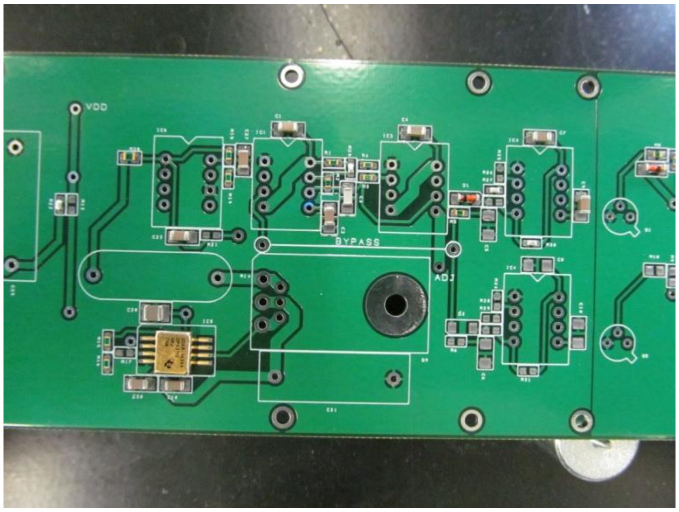


Figure 3: PCB top and bottom copper layers

5.2.2 PCB Assembly

5.2.2.1 Solder

The previous revision used Pb92.5/Sn5/Ag2.5 as the solder paste alloy. This solder alloy was chosen for its high melting point of approximately 290 C. Reflowing this solder required a peak reflow temperature of 340 C. Unfortunately, the reflow oven available to us had a peak reflow temperature of 320 C. This led to the investigation of other solder alloys. Pb88/Sn10/Ag2 was discovered to have a slightly lower liquidus temperature and required a peak reflow of 320 C that was just inside the range of our reflow oven. The lower peak temperature also meant less damage to the circuit components and a lower likelihood of latent failures.

All thru hole parts were soldered with a hand iron set to 800 F. A board preheater and hot air reflow gun were used often in tandem to bring the PCB and components to 200 C prior to application of the iron to facilitate brazing and mitigate the adverse effects of thermal shock.

5.2.2.2 Reflow Profile

The reflow profile developed for this design is shown in the table below.

Mode	Temperature (C)	Time (sec)	Power (%)
Pre-Heat	150	120	-
Step 1	240	120	75
Reflow	320	140	100

5.2.2.3 Thru-hole Assembly
A board pre-heater is used to facilitate through hole by reducing the tip temperature needed to sufficiently inject enough heat to raise the temperature of the both the part and pad. A combination of both top and bottom heat is implemented depending on the part. Simultaneous top and bottom heat is used to attach 8-DIP packages. Only top heat is used to attach larger components such as inductors and bulk capacitors. A thermal imager ensures that the board/part temperature is approximately 200 C.

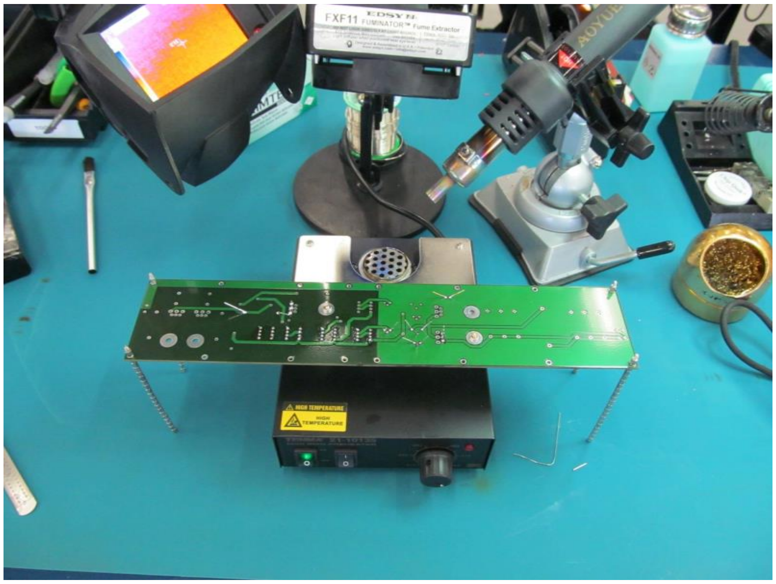


Figure 4: Through hole assembly

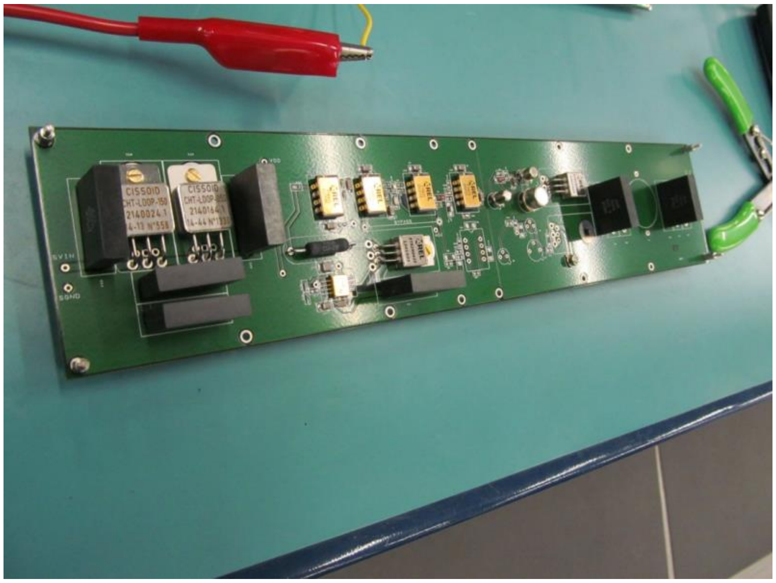
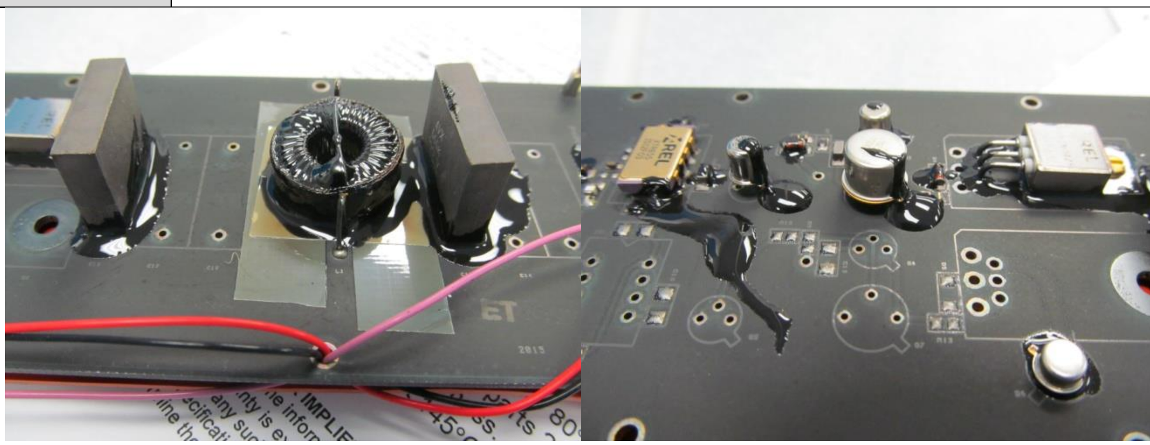


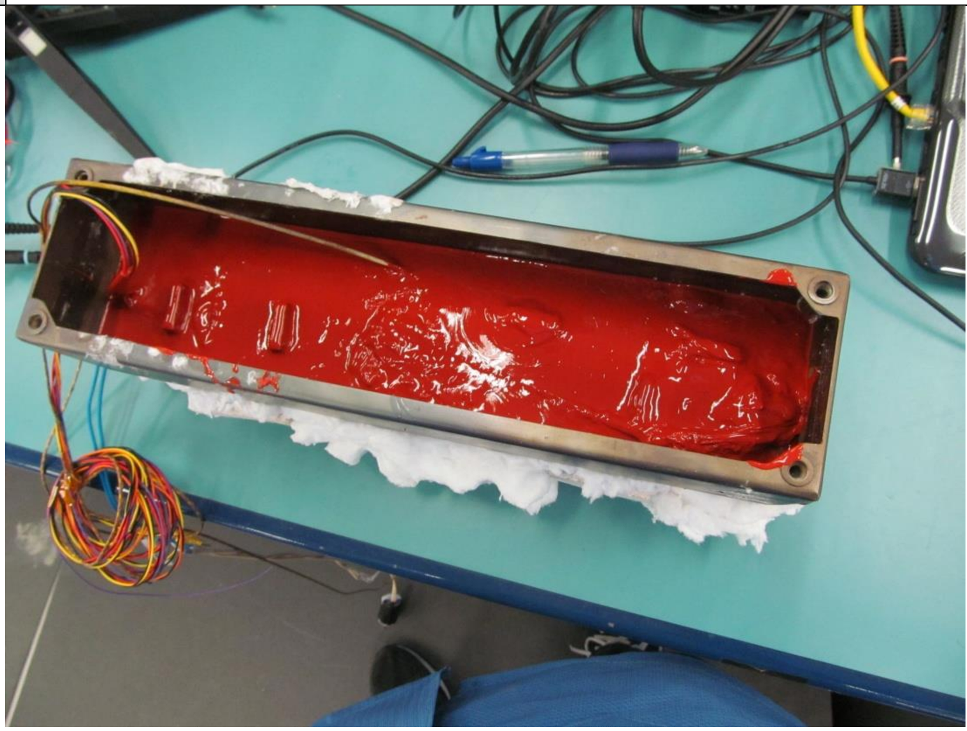
Figure 5: Completed circuit board

5.3 Prototype

The images and data below document the final electronics qualification unit and combined temperature and vibration test.

Sub-Test Title:	**250 C Long Duration Run at 10 W**
Plot Title:	Staking of components



Sub-Test Title:	**250 C Long Duration Run at 10 W**
Plot Title:	300 C rated silicone
	

Sub-test Title:	**250 C Long Duration Run at 10 W**
Photo Title:	DUT Prior to environmental testing at combined temp and vib.

Sub-Test Title:	**250 C Long Duration Run at 10 W**
Plot Title:	Data log for Input / Output, Temperature and Vibration Data (Current and Voltage values are scaled according to the table in the lower right of the plot. Vibration data is shown in a separate plot below).

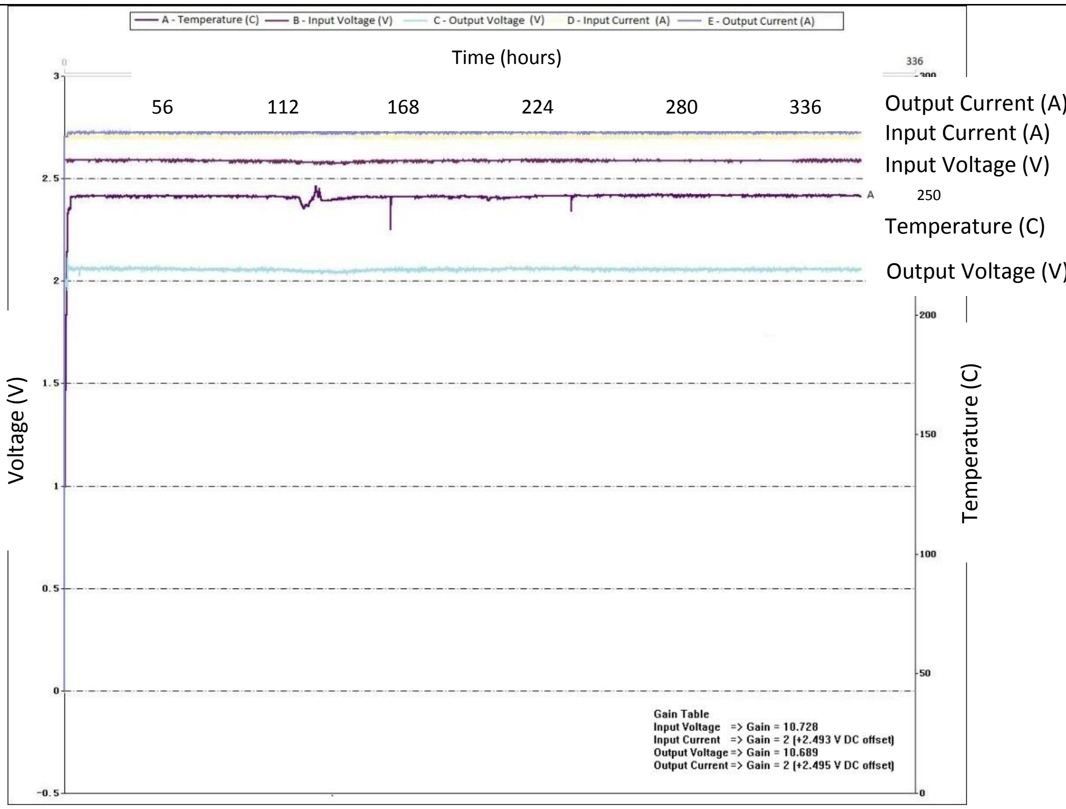


Figure 6: Electrical and Temperature Data (Time: 2304 hours)

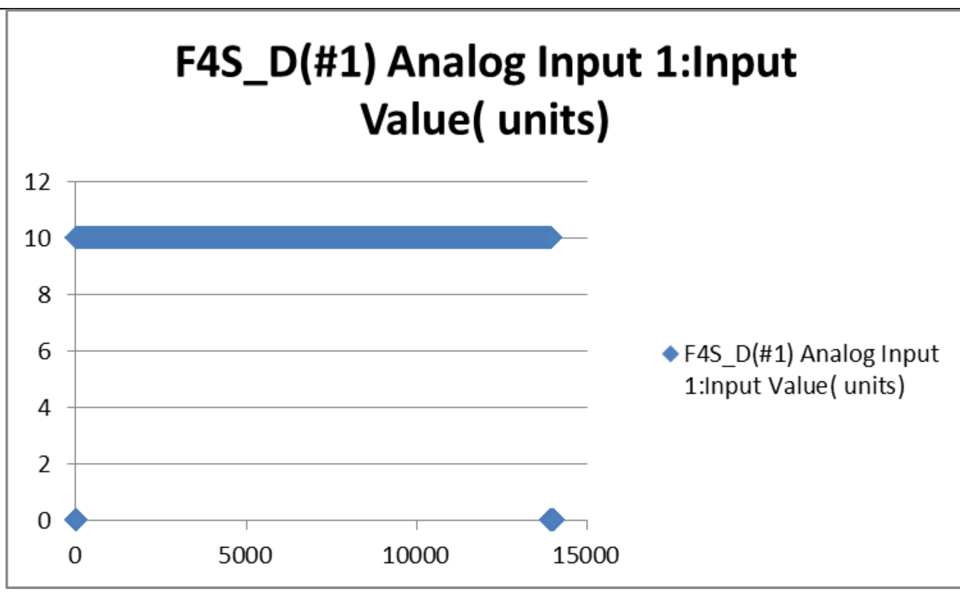


Figure 7: Vibration Data, Vertical Axis is Vibration Table Set point [Grms], horizontal axis is time [minutes]

5.5 Energy Harvester

FastCAP has developed a rotary inertial energy generator (RIEG), to harvest vibration, shock and stick-slip energy. The RIEG can also harvest energy from continuous rotation when it is substantially horizontal. The hottest parts of the well are to be expected in the lateral so we might imagine an operational model having conventional MWD batteries (and tools) in the vertical with this RIEG to power the toolstring in the lower parts of the curve and into the lateral.

FastCAP's principal contribution under this task has been the mechanical and electromechanical design including material selection for an RIEG that can withstand very high temperature and vibration while maintaining generation capabilities. The ratcheting rotational design enables efficient energy generation across a range of excitation frequencies the bandwidth of which is limited only by the ratchet teeth width and radius.

A design narrative and test summary is included below summarizing the more recent activities leading to the final qualification.

5.5.1 Function and Features

- The GEN employs a dual stator design that seeks to increase the voltage generated in a single turn. The stators each contain 8 wound coils. Interspaced with the stators are 3 rotors, each holding 8 samarium cobalt cylindrical magnets as outlined in the BOM. The rotors are coupled to the rotating shaft while the stators remain stationary.
- At either end of the GEN is an endcap that encloses the shaft and generator components. The endcaps each contain a high temperature bearing to constrain shaft rotation.
- A ratchet is coupled to the shaft to allow the storage of the peak vibrational energy. A custom-made pawl was designed and manufactured to fit between the ratchet and outer tubes and is approximately 1/16" wide.
- Rev 3 is 3.25 inches long and a weighs .5238 lbs (.2376kg), resulting in a length reduction of 21% and a weight reduction of 35% from Rev 2

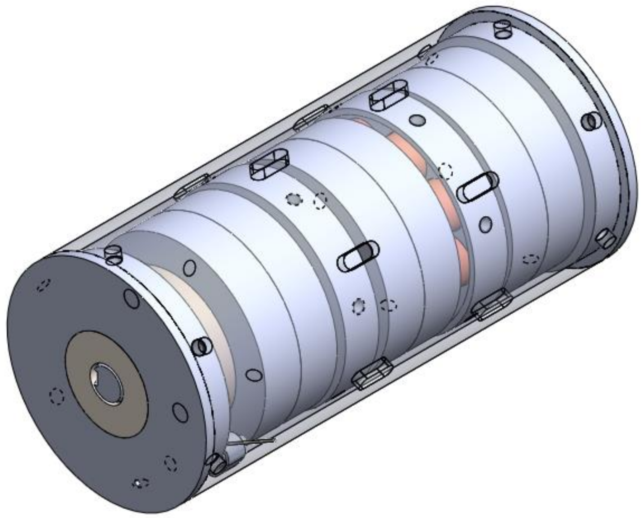


Figure 8: CAD Assembly of the GEN Rev 3 (shown with a transparent outer tube and the radial screws not placed)

5.5.2 Qualification

Qualification of GT Generator (GEN) was determined through a 200 hour heat and vibration spot test. During the test the GEN was subjected to sustained 250°C temperatures and continuous 10Grms vibration.

5.5.2.1 Electrical Testing Set-Up and Goals

The intent of the electrical testing was to characterize the performance of the generator including the power output capability. The results of the spot test will provide the motor constant (k_v) which will be used to determine the power density of the GEN. These results will be compared to the previous Revs of the GEN. The spot test set-up involves coupling the GEN's rotor shaft to a brushless DC motor and measuring the output at a constant RPM.

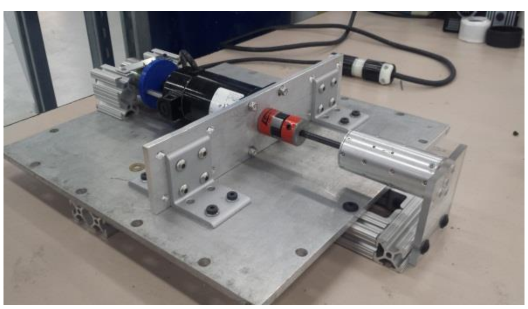


Figure 9: The RIEG prototype test fixtured (left) and on its own (right)

5.5.2.2 Electrical Test Results

Using the scope, the output voltage of the GEN was measured at a constant RPM. For the motor constant calculation the Peak to Peak voltage output was recorded. During the test, peak to peak voltages of **432 m**V and **444 mV** were recorded at approximately **20.90 Hz** and **21.27 Hz** respectively. The results of the test can be found in the table below. When compared to the previous tests the calculated motor constants (K_v) of **14.6 mV/Hz** and **14.75 mV/Hz** for GEN Rev 3 was found to be similar to GEN Rev 2 results. From this result it's clear that improvements to the GEN design and assembly are necessary to improve the mechanical power to electrical power conversion efficiency. One observation that was made from the scope's read out was that the Peak to Peak voltage was not consistent for each cycle. This result suggests either inconsistency in the coil winding or in the position of the Rotor relative to the Stator. Determining the GEN power output required a resistance measurement of the stator coils, which was found to be 4Ω. The reduction in resistance from the GEN Rev 2 can be attributed to the elimination of solder joints between each coil on GEN Rev 3. The 8 stator coils are now wound from one continuous wire.

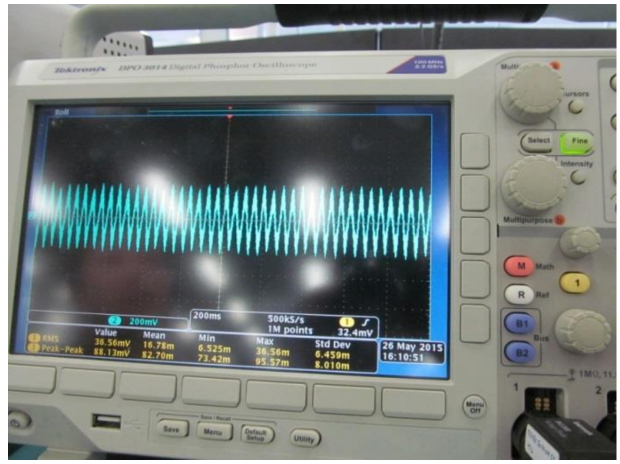


Figure 10: Scope read out during electrical test

Table 1: Generator measured parameters

GEN Rev 3 Test	Angular Freq. (Hz)	Motor Constant K_m [mV/Hz]
1	20.90	14.60
2	21.27	14.75

Figure 11 illustrates the power density of the generator given a 2g amplitude sinusoidal excitation and an impedance matched load as per the contract milestones. According to the plot, the generator will exceed the power density end milestone of 6 W/kg for any excitation frequencies below 1 Hz.

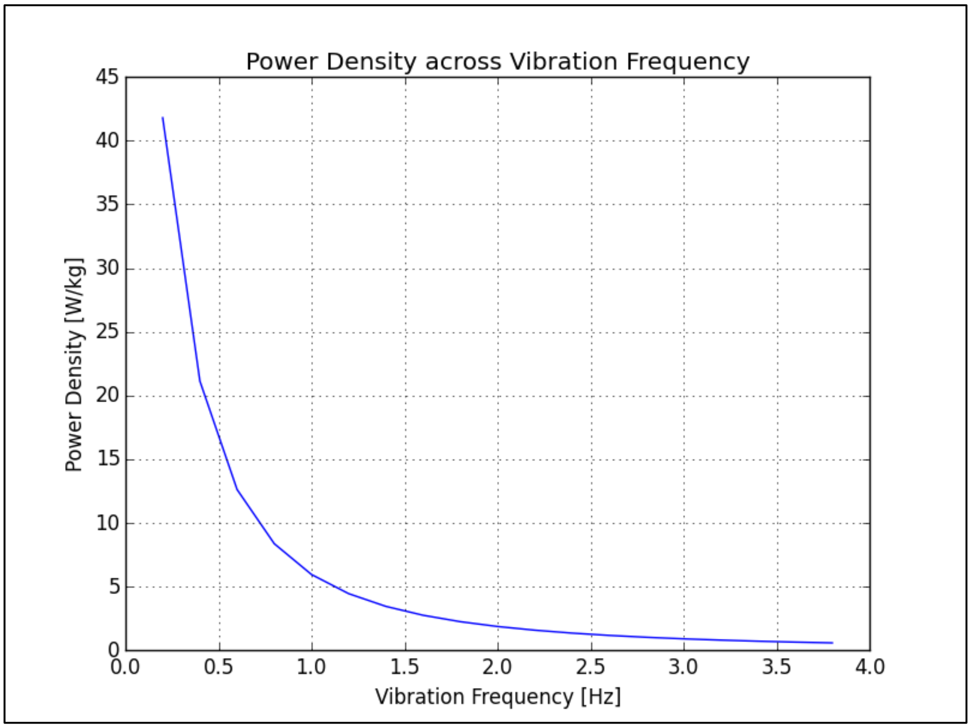


Figure 11: Power Density of the Energy Harvester plotted against rotational frequency.

6 Task 2 - Ultracapacitor Energy Storage System Development

Development of the 250°C ultracapacitor started by redesigning the novel device based on the technology developed for the previous 200°C rated version. In particular each component of the internal architecture of this device has been studied and developed separately by different teams. In the last twelve months, several prototypes have been tested at different temperatures, including 200°C, 225°C and 250°C for a complete characterization and final optimization of the ultra-high temperature device. A target of 200 hours of operation given by the GTO was surpassed by 5 times, reaching 1,000 hours.

All ultracapacitor based final milestones were met. Table 2, below, summarizes the program performance outcomes, compared with program milestones.

Table 2 Performance milestones. No incumbents are available on the current market for comparison.

Parameter	Milestone	Measurement	Milestone Outcome
Max reliable operating temperature:	**250°C**	**≥250°C**	Met

ultracapacitor cell			
Max reliable operating vibration: ultracapacitor cell	**10g$_{rms}$**	**≥10g$_{rms}$**	Met
Max Energy stored in a 70" Length 1.5" OD Pack: ultracapacitor pack	**0.75Wh**	**≥0.75Wh**	Met
Max reliable operating temperature: ultracapacitor pack	**200°C**	**≥200°C**	Met
Max reliable operating vibration: ultracapacitor pack	**5g$_{rms}$**	**≥5g$_{rms}$**	Met
Lifetime @ Max reliable temperature	**200 hours**	**≥1000 hours**	Exceeded
Equivalent Series Resistance increase @ 200 hours	**50%**	**<5%**	Exceeded
Capacitance degradation @ 200 hours	**50%**	**0%**	Exceeded

Several ultra-high temperature prototypes were able to achieve the specification requested by Q10, those tests have been completed and result graphs are shown below. We demonstrated ultracapacitor cells operating at 250°C. Lifetime measurements were carried out both at our facility and at Sandia National Laboratory.

6.1 Prototype GT2014120801-01

The prototype GT2014120801-01 was able to reach **200 hours** of operation at **200°C** and **5G$_{rms}$** failure free while been held at the maximum operating voltage. A series of high temperature ultracapacitors can be assembled in parallel and series to make an ultracapacitor pack. The internal architecture for each ultracapacitor will remain the same providing comparable performance of the single cell (shown below).

6.2 Test Results

Prototype: **GT2014120801-01**

Table 3 GT2014120801-01 Performance:

Parameter	Value	Comment
Temperature	**200°C**	Average temperature over the entire test is 200.1°C
Vibration	**5Grms**	Our ruggedized cell design is able to stand vibration up to

		60Grms
Operating voltage	**1.3V**	Constant voltage
Capacitance	**11.2F**	Considering the highest capacitance reached by the prototype
Volume of the cell	**7cc**	The total volume of the cell has been optimized to achieve higher energy density
ESR increase	**<50%**	It is considered failure when the equivalent series resistance (ESR) is more than 50% respect to the beginning of life
Capacitance (C) loss	**<20%**	It is considered failure when the capacitance (C) is less than 20% compared to the beginning of life
Hours of operation failure free	**200 h**	The test has been stopped at 567 hours of operation

6.2.1 Energy Density

The Max Energy stored in a 70” length 1.5” OD Pack requested is: **0.75 Wh (Q10 milestone requirement).** It is demonstrated that this value has been accomplished by extrapolating the equivalent energy density from a single AA cell. In detail:

Energy stored requested = 0.75 Wh

Total volume available to store this amount of energy = 2.02708 liter

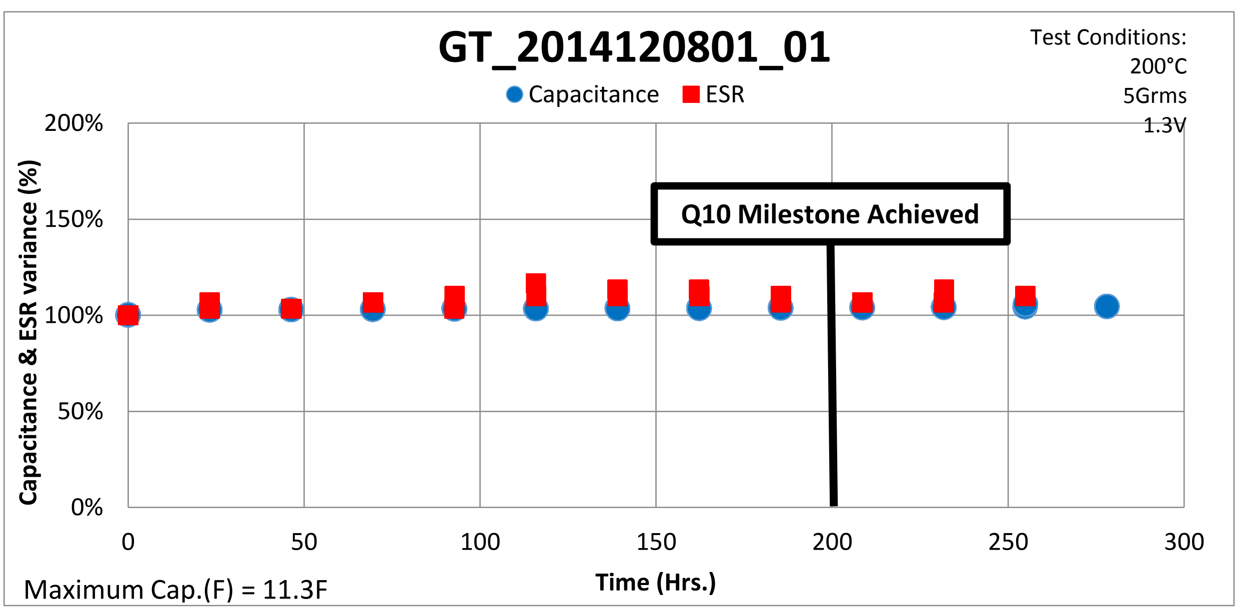


Figure 12: GT_2014120801_01 Lifetime performance – Capacitance and Equivalent Series Resistance variance over time

Energy Density (calculated based on the above data) = **0.36999 Wh/l**

Cell GT2014101801-01 shows:

$$E_v = \frac{\frac{1}{2} * C * V^2}{3600 * Vol_{cell}} = \frac{\frac{1}{2} * 11.2 * 1.30^2}{3600 * 0.007} = \mathbf{0.3755\frac{Wh}{l}} > \ 0.36999\frac{Wh}{l}$$

6.2.2 Lifetime

More than 200 hours lifetime test has been performed evaluating the ultracapacitor performances in terms of equivalent series resistance (ESR) and capacitance (C) variance over time.

6.2.3 Prototype: GT2014121601-01

Parameter	Value	Comment
Temperature	**250°C**	Average temperature over the entire test is 250.6°C
Vibration	**10Grms**	Our ruggedized cell design is able to stand vibration up to 60Grms
Volume of the cell	**7cc**	The total volume of the cell has been optimized to achieve higher energy density
ESR increase	**<50%**	It is considered failure when the equivalent series resistance (ESR) is more than 50% respect to the beginning of life
Capacitance (C) loss	**<20%**	It is considered failure when the capacitance (C) is less than 20% compared to the beginning of life
Hours of operation failure free	**1060 h**	The test has been stopped at 1,300 hours of operation

Table 3. GT2014121601-01 Performance

6.2.4 Lifetime

More than 1000 hours lifetime test has been performed evaluating the ultracapacitor performances in terms of equivalent series resistance (ESR) and capacitance (C) variance over time.

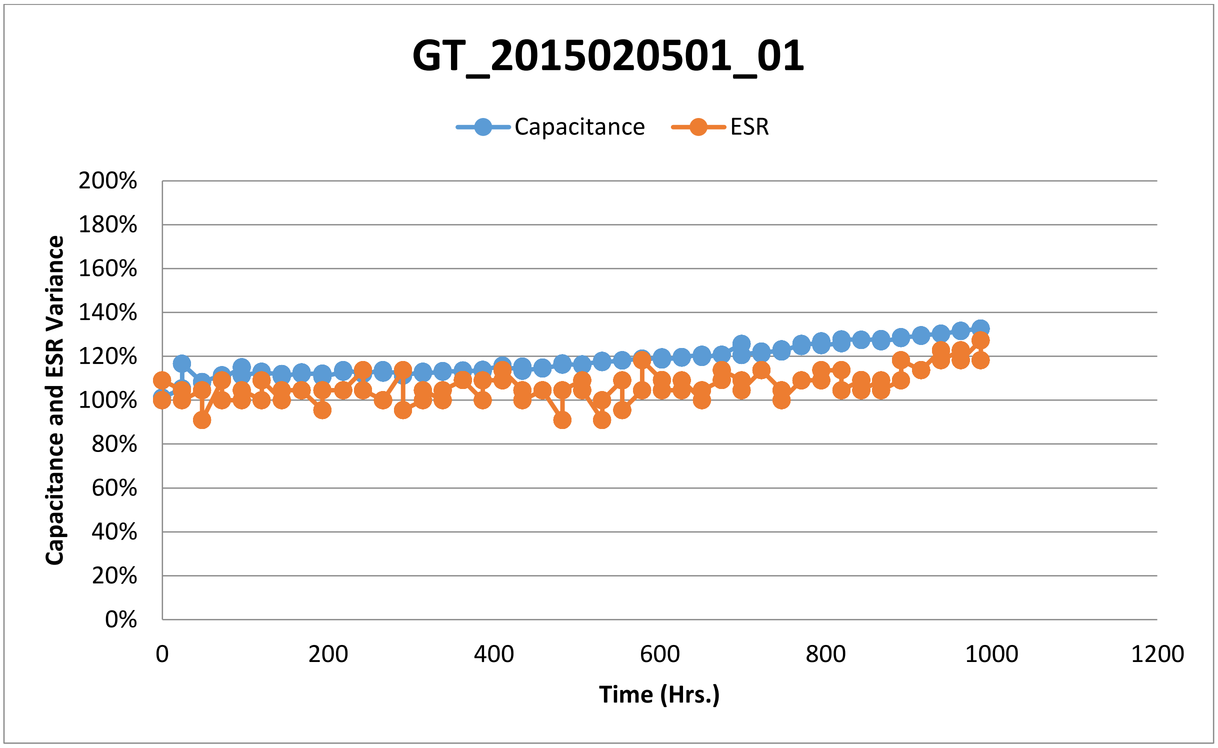


Figure 13: GT_2014121601_01 Lifetime performance – Capacitance and Equivalent Series Resistance variance over time

6.3 Summary of Results

Milestone Metrics by Quarter	Q10	Status	Comment
B. Max reliable operating temperature (°C): ultracapacitor cell	**250**	Met	Failure free operation for at least 200 hours: tested simultaneously at temperature and vibration prescribed by the quarterly milestone while held at max voltage
B. Max reliable operating vibration (g_rms): ultracapacitor cell	**10**	Met	Failure free operation for at least 200 hours: tested simultaneously at temperature and vibration prescribed by the quarterly milestone while held at max voltage
C. Max Energy stored in a 70" Length 1.5" OD Pack (Wh): ultracapacitor pack	**0.75**	Met	Calculated as ½ times the pack capacitance (F) times the square of the max pack voltage (V) divided by 3,600. Max pack voltage is equal to the max. pack voltage used to demonstrate reliability milestone while held at max. voltage

D. Max reliable operating temperature (°C): ultracapacitor pack	**200**	Met	Failure free operation for at least 200 hours: tested simultaneously at temperature and vibration prescribed by the quarterly milestone while held at max voltage
D. Max reliable operating vibration (g_rms): ultracapacitor pack	**5**	Met	Failure free operation for at least 200 hours: tested simultaneously at temperature and vibration prescribed by the quarterly milestone while held at max voltage

Table 4: Final Results showing achieved milestones

Another novelty related to this technology is represented by the fact that these energy storage devices have good cycling capabilities over a wide spectrum of temperatures as well, from -5°C all the way up to 250°C.

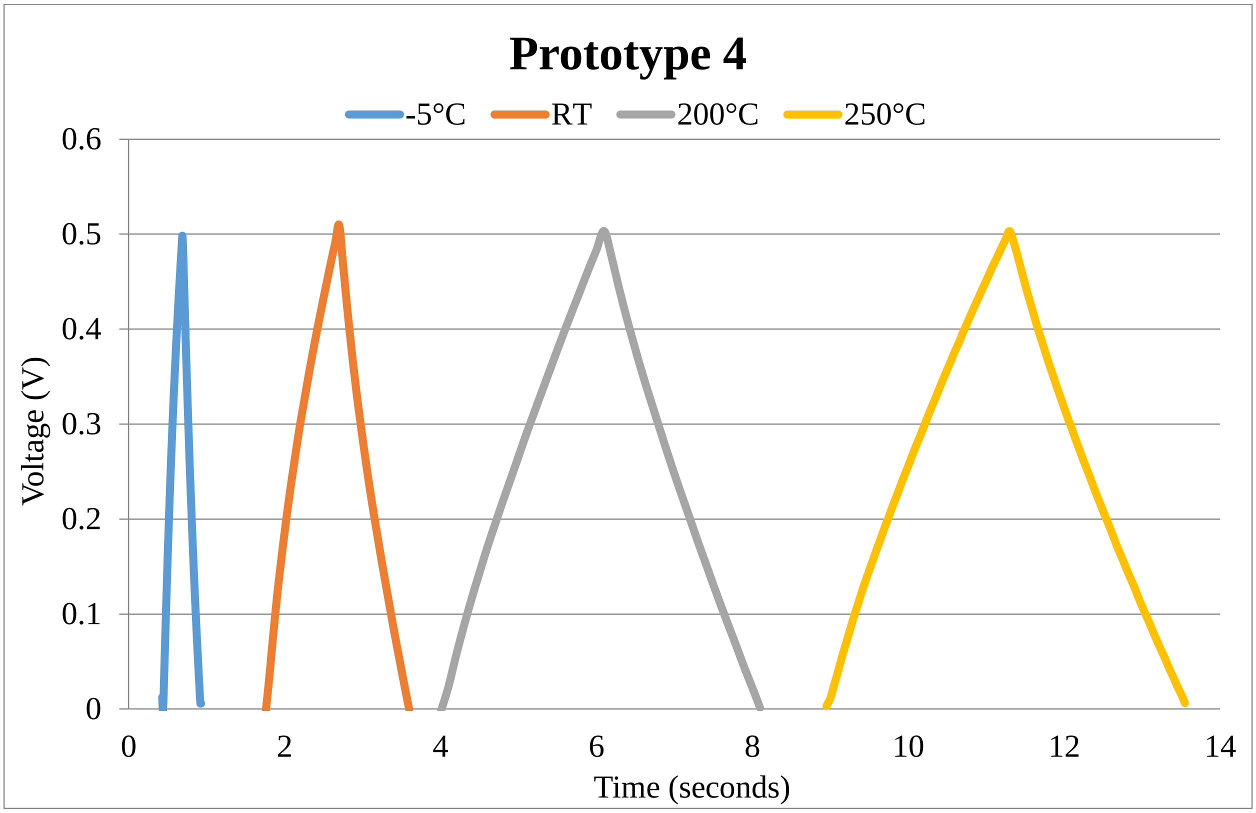


Figure 14 Charge/discharge cycles on the same device at four different temperatures: -5°C, Room Temperature (RT = +25°C), 200°C and 250°C showing cycle ability of the device over a wide operational temperature range

6.4 Validation at Sandia National Laboratory

Similar tests were carried out at Sandia National Labs. The outcome of the tests corroborated the results obtained at our facility. The ultracapacitor cells were showing outstanding stability at 250°C, 225°C and 200°C.

The picture below shows the performance of a prototype held at max voltage while at 250°C: after 500 hours of operation both capacitance and ESR showed negligible degradation. This tests validates the technology developed under this program.

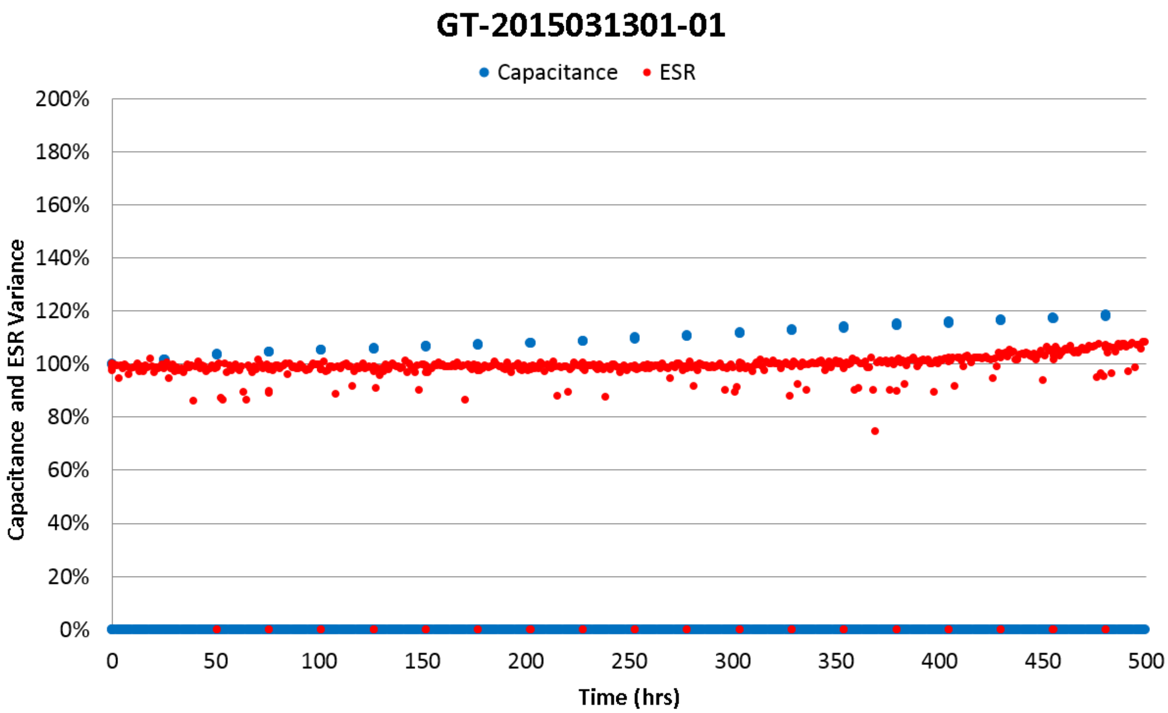


Figure 15: Prototype GT2015031301-01 operated for more than 500 hours at 250°C and max voltage showing minimal degradation

6.5 The Science Behind The High-Temperature Ultracapacitor

6.5.1 High Temperature Electrode

Energy storage devices are typically the most reactive component of any electrical system. Operating at elevated temperatures will accelerate any unwanted chemical reactions, lowering the lifetime of the device. To prolong the system operating time under these conditions, FastCAP's ultracapacitor cells use materials that remain chemically stable at high temperatures. Critical to this is not only selecting the proper materials, but also controlling the purity of each ingredient. Even with the best component selection, the side reactions and products of decomposing impurities can severely impact the performance of a device. Therefore, in addition to selecting the most stable ingredients, FastCAP has developed procedures for purifying the crucial system components. In this way, FastCAP can provide systems that perform in the widest possible range of environments.

The amount of energy a capacitor is able to store is directly related to the surface area of the active material in the capacitor's electrodes. FastCAP uses carbon nanotubes (CNTs) as the active material for its ultracapacitors. The nanostructure of the CNTs allow for a very high surface area compared its volume or mass. Additionally, CNTs are chemically stable well above 400°C in an oxygen atmosphere, and much higher when the environment is oxygen-free. To take full advantage of these properties, the CNTs are processed in order to remove the impurities that not only decompose at the proposed cell operating temperature, but also reduce the surface area density of the active material when they are agglomerated on the structures.

FastCAP produces CNTs on substrates using a high-temperature chemical vapor deposition (CVD) process. The substrates are loaded into a controlled atmosphere vacuum furnace for CNT growth. Hydrocarbon gas is introduced into the furnace chamber, where it decomposes against the catalyst and reforms as nanotubes over the sputtered substrates. This process yields higher purity nanotubes than many of the competing methods

The electrode for this project is made of two high-stability materials. The active material is composed of carbon nanotubes (CNTs). The CNTs have high surface area qualities desirable in a capacitor. The second material used in the electrode is aluminum. Aluminum is used as the current collector (to which the active material is adhered) and also for the tabs and electrical connections within the cell. There are several advantages offered by aluminum for these components. It is a highly conductive material, lowering the internal resistance of the cell and allowing for high efficiency. While there are better conductors available, none of them match aluminum for its low density or chemical stability. The low density enables a lighter cell and superior energy density. More significantly, the chemical stability of aluminum permits the devices to operate in extended voltage and temperature ranges. Aluminum exposed to air quickly oxidizes to form a continuous passivation layer. This metal-oxide layer is particularly inert and more stable than the oxide layer of other metals because it stays as a smooth surface instead of rough scales. Therefore, once formed, there are no gaps for air to get through, and the aluminum surface below the passivation layer remains protected.

While the passivation layer is described as smooth, that smoothness is on a nano-scale. On a micro-scale the aluminum foil used for the current collector has been etched to generate a rough surface. This gives the foil a greater surface area and better gripping capability for attaching the active material. These properties yield a stronger assembly, lower internal resistance, and higher power density. Another feature maintaining low internal resistance is the welding procedure to attach tabs. The tab is used to make the connection between the current collector and the electrical feed-through of the cell. It is ultrasonically welded to the foil at several points. This welding method keeps the material at room temperature and requires no additional filler materials. Without excessive heat there is no opportunity to scorch or melt the thin foil, further reducing the chance of introducing unwanted impurities.

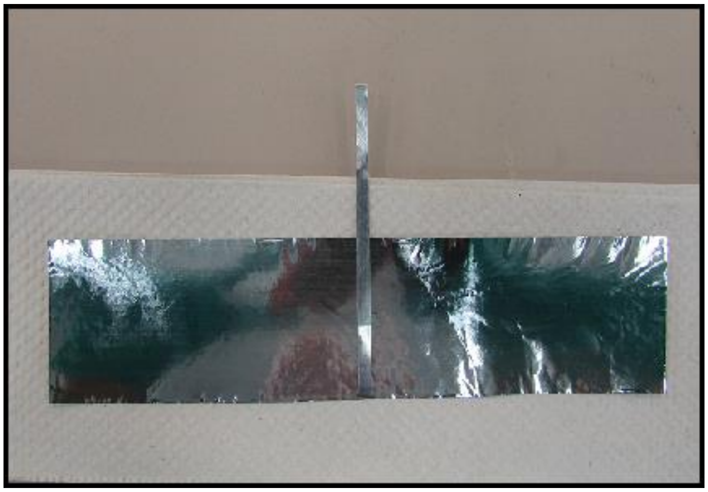


Figure 16: Aluminum foil CC with centered aluminum tab

The foil sheet can be a variety of thicknesses, depending on the need. Thinner foils make a smaller and lighter system with higher power and energy density. Thicker foils are mechanically stronger and offer less internal resistance.

CNTs have a channel-like morphology, which facilitates the movement of ions through the active material. The average pore diameter of the electrode is greater than 10nm and therefore easily accessible by the ions contained in electrolyte, which have average diameter of 0.5 – 2nm. The average pore size is controlled during the CNT synthesis and subsequent electrode fabrication. Pressure, temperature, feedstock gas flow, and growth time during the CVD process are optimized in order to control the CNT spacing and diameter and initial thickness, while the pressure during roll-to-roll transfer controls the final thickness and density of the CNT active material.

The current collector is placed on top of the CNTs on their substrate, and the layers are compressed between two heavy rollers.

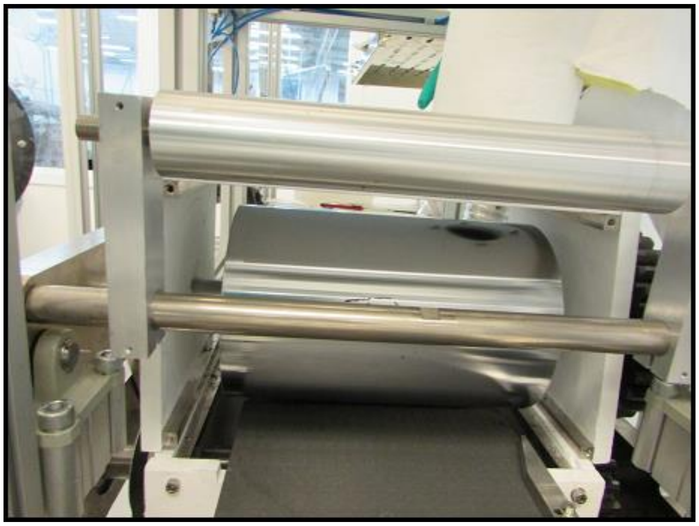


Figure 17: Pressing roller within the roll-to-roll machine

Due to the higher surface area caused by the etching, the CNTs preferentially adhere to the aluminum foil. After compression, the substrate comes away clean and the nanotubes have formed a compact layer on the current collector.

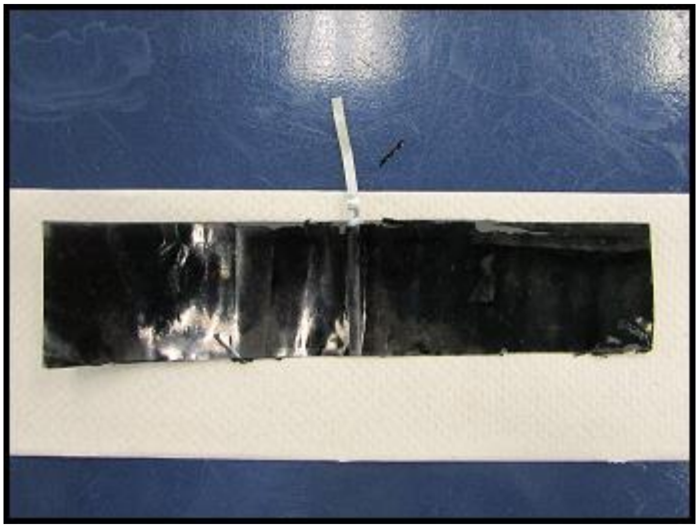


Figure 18: Current collector with CNT layer adhered

6.5.2 High Temperature Electrolyte

A critical component needed to operate an ultracapacitor cell at 250°C is an electrolyte that will remain stable at this temperature. To this end, FastCAP developed a high temperature electrolyte. Significantly, this electrolyte will be functional both at room temperature and at the final operating temperature. This will be accomplished by forming a gel electrolyte, which will consist of an ionic liquid and a gelation material. Both ingredients must remain stable through the whole temperature range.

Ionic liquids are molten salts which are liquid at room temperature, composed entirely of ions, nonflammable, and usually possess no significant vapor pressure. Particularly, some ionic liquids have a decomposition temperature greater than 400°C. The high purity and low moisture level of the ionic liquids achieved after implementing the electrochemical purification methods FastCAP has developed increases the stability of the final device at 250°C.

FastCAP has performed extensive research and characterization of a wide range of high quality ionic liquids.

Three room temperature ionic liquids were selected for high temperature applications, referred to as X Type, Y Type, and Z Type. The reported decomposition temperatures provided by the supplier were obtained through dynamic thermogravimetric analysis (TGA), and are all above 400°C. The electrochemical window was tested in-house for X Type and Y Type at room temperature, 150°C, 200°C, and 250°C. The results, along with the decomposition temperatures, are reported in Table 2.

Ionic Liquid	Reported Decomp. Temp.	Elect.chem. Window at 25°C	Elect.chem. Window at 150°C	Elect.chem. Window at 200°C	Elect.chem. Window at 250°C
X Type	424°C	-1.8V to 2.0V	-0.45V to 1V	-0.20V to 0.75V	-0.10V to 0.40V
Y Type	431°C	-2.3V to 2.7V	-0.6V to 1.2V	-0.45V to 0.80V	-0.05V to 0.40V

Table 5: Properties of selected ionic liquids

In each case only the pure ionic liquid was tested, without any additives or separators. The final application uses the ionic liquids in a hermetically sealed ultracapacitor, with the ionic liquid integrated into a gel form. To simulate the isolated nature of the application, all construction and testing takes place in a glovebox under argon atmosphere.

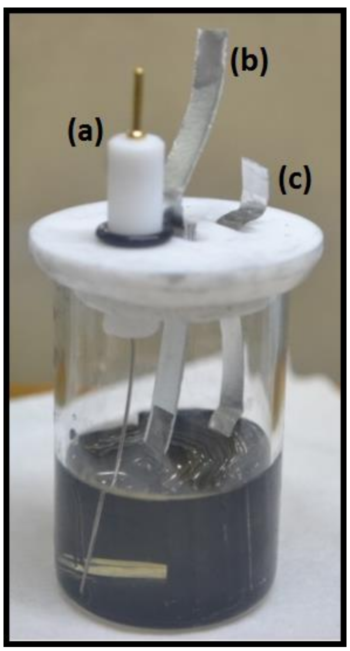


Figure 19: Electrochemical Window Test Cell: (a) Working Platinum Electrode (b) Reference Small AC Electrode (c) Counter Large AC Electrode

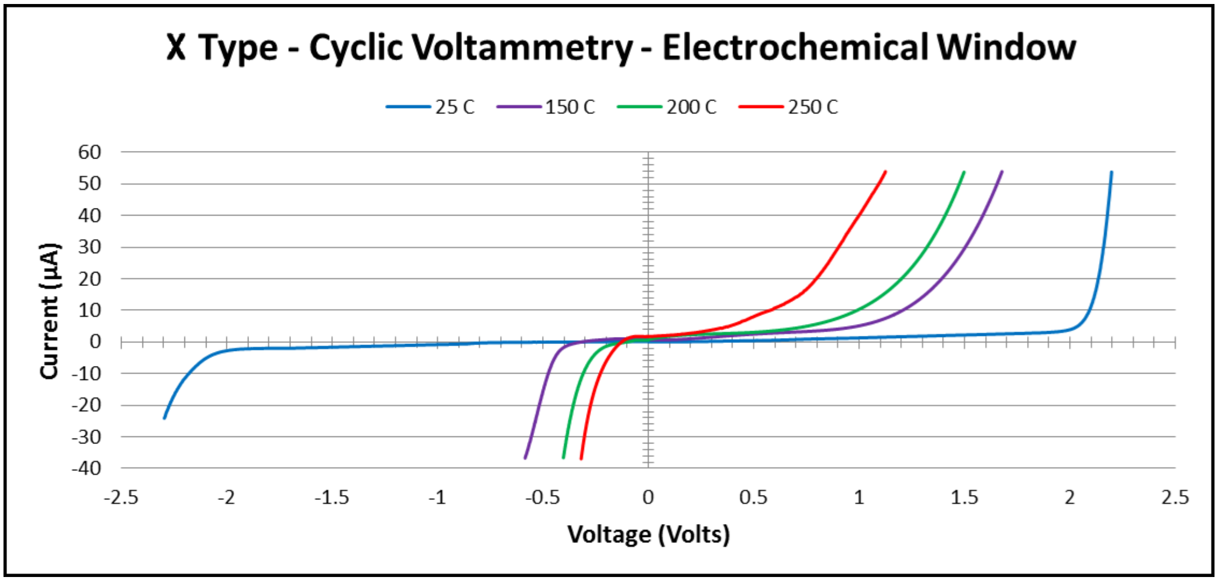


Figure 20: Cyclic Voltammetry Tests - Determination of electrochemical window at selected temperatures - X Type

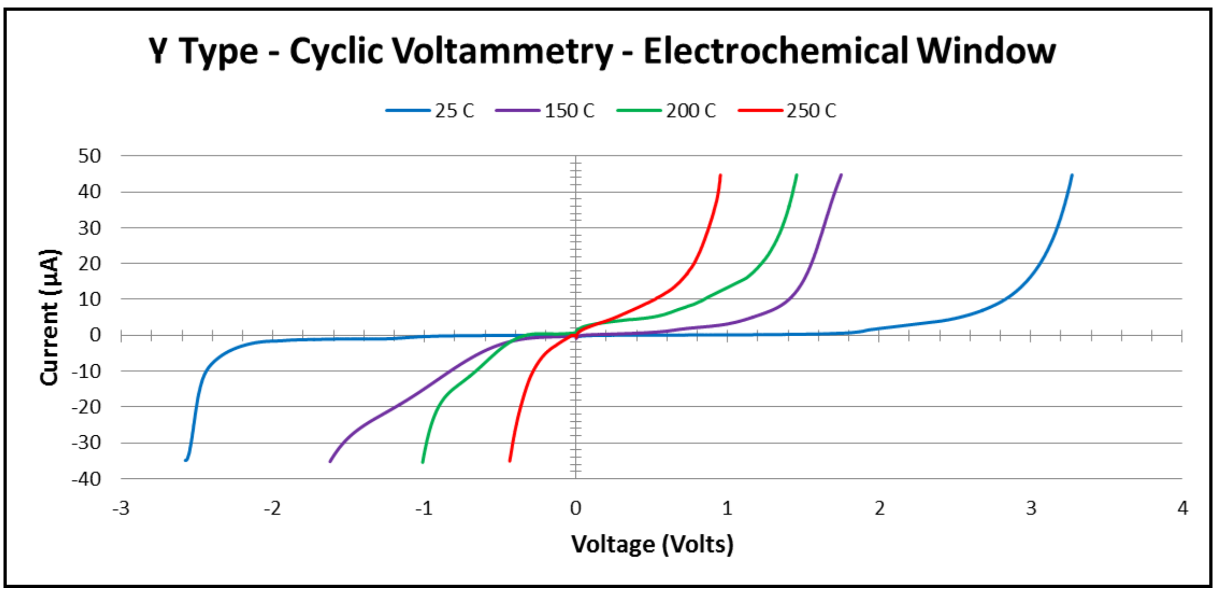


Figure 21: Cyclic Voltammetry Tests - Determination of electrochemical window at selected temperatures - Y Type

Voltammetry tests have be performed with a three-electrode electrochemical cell. All electrochemical tests are carried out in a glovebox refilled with argon and an attached oven is used for the thermal tests.

6.5.3 Ultracapacitor Cell Assembly and Testing

The cell assembly procedure has been fully developed by FastCAP and is currently in use producing cells for large temperature range testing. These prototypes have been assembled in an argon atmosphere glovebox to avoid contamination from either moisture or oxygen, which have the potential to chemically react with and degrade the cell components.

Assembly starts with a pair of CNT electrodes stacked on top of each other with gel electrolyte layered between them. The gel electrolyte is embedded with ions that allow the charges to move back and forth, but prevents the direct contact between electrodes. To further reduce the potential for contamination, all components are vacuum dried before the final assembly to remove residual moisture. After the vacuum step, the components are enclosed in a laser welded package.

After assembly, there are several standard tests used to evaluate the cell performance. Nyquist plots are obtained through frequency response analysis, measuring the equivalent series resistance (ESR) and the specific capacitance of the electrodes. With this data the electrode-electrolyte interactions are evaluated; if the ions have easy access to the channel-like pores of the CNT electrodes, the Nyquist plot will show a 90° line at low frequencies (<0.1Hz). The ESR is an indicator of the cell's power density, but power is also dependent on voltage. Finding the best operating voltage is done using cyclic voltammetry. The cell is charged and discharged at constant scan rate (V/s) and the current is plotted against the voltage. This test will show the stability of the ultracapacitor at different voltages, from which the operating voltage is decided. While the cycling may indicate that a cell can operate at a high voltage, the operating voltage may be lowered to improve the lifetime of the device.

Frequency response analysis and cyclic voltammetry can be used to find the power density, but the energy density is found with galvanostatic discharge. During this test, the cell is kept at maximum voltage and then discharged at constant current.

The few energy storage devices able to operate at temperatures above 250°C are not able to operate at lower temperatures. Our proposed technology is able to store and deliver energy in a very wide temperature range. In the experiment reported below (Figure 9) the 300°C rated prototype UHT_2015072701_01 was able to successfully achieve the official milestone of 100,000 cycles at room temperature, about 25°C. Currently this prototype is still charging and discharging at constant temperature (25°C) showing extremely good results; it has reached 300,000 cycles (on September 17th, 2015) with no significant capacitance and ESR degradation.

Further steps to enhance the cell design include improving and optimizing the current advanced technology and to incorporating the final recipe into large size cells. Current prototypes have a AA cylindrical cell form factor (about 7.9cc in volume for each cell).

Figure 22: Representative AA size cells design

7 References

[1] Watts, M, "High Temperature Circuit Reliability Testing," Quartzdyne Inc., Salt Lake City, UT USA, Feb. 2003