High Temperature Capacitor Development

Final Scientific/Technical Report

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ABSTRACT

The absence of high-temperature electronics is an obstacle to the development of untapped energy resources (deep oil, gas and geothermal). US natural gas consumption is projected to grow from 22 trillion cubic feet per year (tcf) in 1999 to 34 tcf in 2020. Cumulatively this is 607 tcf of consumption by 2020, while recoverable reserves using current technology are 177 tcf. A significant portion of this shortfall may be met by tapping deep gas reservoirs. Tapping these reservoirs represents a significant technical challenge. At these depths, temperatures and pressures are very high and may require penetrating very hard rock. Logistics of supporting 6.1 km (20,000 ft) drill strings and the drilling processes are complex and expensive. At these depths up to 50% of the total drilling cost may be in the last 10% of the well depth. Thus, as wells go deeper it is increasingly important that drillers are able to monitor conditions down-hole such as temperature, pressure, heading, etc.

Commercial off-the-shelf electronics are not specified to meet these operating conditions. This is due to problems associated with all aspects of the electronics including the resistors and capacitors. With respect to capacitors, increasing temperature often significantly changes capacitance because of the strong temperature dependence of the dielectric constant. Higher temperatures also affect the equivalent series resistance (ESR). High-temperature capacitors usually have low capacitance values because of these dielectric effects and because packages are kept small to prevent mechanical breakage caused by thermal stresses. Electrolytic capacitors do not operate at temperatures above 150°C due to dielectric breakdown.

The development of high-temperature capacitors to be used in a high-pressure high-temperature (HPHT) drilling environment was investigated. These capacitors were based on a previously developed high-voltage hybridized capacitor developed at Giner, Inc. in conjunction with a unique high-temperature electrolyte developed during the course of the program.

During this program the feasibility of operating a high voltage hybridized capacitor at 230°C was demonstrated. Capacitor specifications were established in conjunction with potential capacitor users. A method to allow for capacitor operation at both ambient and elevated temperatures was demonstrated. The program was terminated prior to moving into Phase II due to a lack of cost-sharing funds.

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EXECUTIVE SUMMARY

This project was focused on the development of high-temperature capacitors to be used in a high-pressure high-temperature (HPHT) drilling environment. These capacitors were based on a previously developed high-voltage hybridized capacitor developed at Giner, Inc. in conjunction with a unique high-temperature electrolyte developed during the course of the program. A three-phase program was proposed, with only Phases I and II being funded. The program objectives were as follows:

During Phase I, Giner, Inc. proposed the development of a high-temperature, high-voltage all-solid electrochemical-electrolytic capacitor, yielding a low ESR device capable of operation at temperatures up to 232°C and at pressures exceeding 137.9MPa. Specific Phase I objectives included:
- Initial investigations to modify the internal anode structure and porosity of the tantalum anode in order to accommodate high-temperature electrolyte within the pore structure.
- Low-cost, highly conductive high-temperature electrolyte materials will be developed and identified.
- Various innovative techniques will be used to improve the electrode-electrolyte interface contact in order to lower the ESR and utilize the surface of the electrode.
- High-temperature high-voltage all-solid electrochemical-electrolytic capacitor cells will be fabricated and characterized/tested to demonstrate the feasibility of our approach.

The technical objectives for the Phase II development program included:
- Miniaturization of the overall high-temperature capacitor footprint
- Based on the Phase I results and input, further refinement to improve capacitor performance, if necessary, which include materials and procedures
- Packaging options and packaging design specifications for the development of the capacitor
- Fabrication of prototype devices for use in the deep drilling applications.
- Conduct laboratory tests to demonstrate and validate performance including energy storage and discharge, unattended operation, heat buildup and dissipation, and endurance.

Technical objectives for the Phase III program included:
- Fabrication of a sufficient quantity of high-temperature capacitors for field testing
- Field testing of the high-temperature capacitors in a downhole environment

The key findings from this program were as follows:
- The feasibility of operating a high voltage hybridized capacitor at 230°C was demonstrated.
- Capacitor specifications were established in conjunction with potential capacitor users.
- A method to allow for capacitor operation at both ambient and elevated temperatures was demonstrated.

The program was terminated prior to moving into Phase II due to a lack of cost-sharing funds.

1.0   APPROACH

1.1. Introduction

The absence of high-temperature electronics is an obstacle to the development of untapped energy resources (deep oil, gas and geothermal). US natural gas consumption is projected to grow from 22 trillion cubic feet per year (tcf) in 1999 to 34 tcf in 2020. Cumulatively this is 607 tcf of consumption by 2020, while recoverable reserves using current technology are 177 tcf. A significant portion of this shortfall may be met by tapping deep gas reservoirs. Tapping these reservoirs represents a significant technical challenge. At these depths, temperatures and pressures are very high and may require penetrating very hard rock. Logistics of supporting 6.1 km (20,000 ft) drill strings and the drilling processes are complex and expensive. At these depths up to 50% of the total drilling cost may be in the last 10% of the well depth. Thus, as wells go deeper it is increasingly important that drillers are able to monitor conditions down-hole such as temperature, pressure, heading, etc. (Mallison et al., 2005).
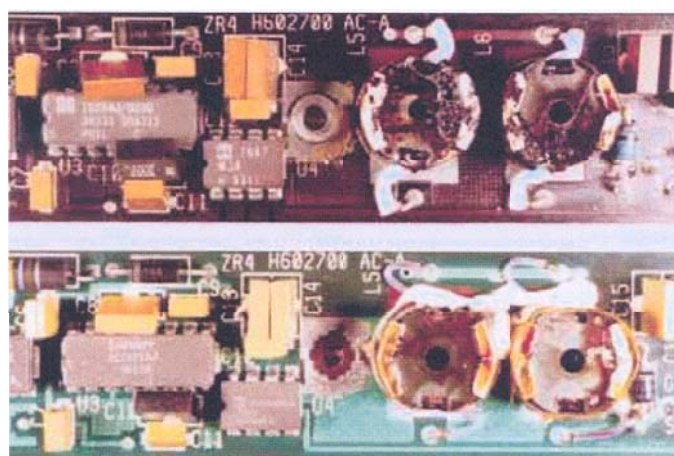

Figure 1. Temperature Effects on Circuit Board

Commercial off-the-shelf electronics are not specified to meet these operating conditions. This is due to problems associated with all aspects of the electronics including the resistors and capacitors. **Figure 1** shows the effect of temperature on logging tool circuits. The top scorched circuit board was mounted on a tool exposed to a 177^oC (350^oF) bottomhole temperature while the bottom circuit board is new (from Baird et al., 1998). With respect to capacitors, increasing temperature often significantly changes capacitance because of the strong temperature dependence of the dielectric constant. Higher temperatures also affect the equivalent series resistance (ESR). High-temperature capacitors usually have low capacitance values because of these dielectric effects and because packages are kept small to prevent mechanical breakage caused by thermal stresses. Electrolytic capacitors do not operate at temperatures above 150^oC due to dielectric breakdown.

Conventional logging tools (rated to 177^oC and 137.9 MPa (20,000 psi)) are upgraded to high-temperature specifications by installing all sensitive electronics in a 137.9 MPa pressure rated Dewar flask housing. The Dewar flask protects the electronic circuits from excessive borehole temperatures. However, weight becomes a concern in high pressure, high temperature (HPHT) wells because the flasks add weight to long combinations of tools. Inside the Dewar, the temperature will increase slowly as there is no way to dissipate the heat generated by the electronics itself. After a sufficiently long time period, the temperatures inside and outside of the Dewar may be comparable.

To overcome some of the problems of the electronics, Giner, Inc. will develop high-temperature capacitors for use on the circuit boards used by the logging equipment. In a Deep Trek Workshop held in March 2001, electronic assemblies that operate at temperatures >177^oC were identified as Priorities 2 and 3. Capacitors with ratings of 100 μF, 100 volts were included in this category. Subsequent studies have identified a specification of 200 μF, 100V. The high-temperature capacitors will be based on a unique electrolyte to be developed by Giner, Inc. This work will be conducted in conjunction with Evans Capacitor Company, a commercial

manufacturer of specialty capacitors. In addition, both Baker-Hughes and Schlumberger have expressed an interest in field testing the final device.

1.2. Experimental Methods

Giner, Inc. has recently developed a high-voltage all-solid electrochemical-electrolytic capacitor. This capacitor is similar in concept to the liquid acid Hybrid® Capacitor (Registered Trademark, Evans Capacitor Corp.) developed by Evans (Evans, 1994) except the Giner, Inc. capacitor uses a solid polymer electrolyte ionomer (i.e. Nafion) within and between the porous positive (anode) and negative (cathode) electrode structures. This capacitor combines an electro-chemical capacitor cathode and an electrolytic capacitor anode. By employing a dielectric anode electrode, the single-cell hybrid capacitor is able to withstand high breakdown voltages. A ten-to-one improvement in energy density compared to state-of-the-art aluminum electrolytic capacitors with comparable electrical performance has been achieved in liquid acid hybrid capacitors using a tantalum anode, sulfuric acid electrolyte, and a RuO_2 cathode (Evans, 1995). Because of their relatively smaller size, hybrid capacitors also have higher power densities than electrolytic capacitors. Liquid acid hybrid tantalum capacitors are manufactured in a variety of configurations. Capacitances of 100 μF-200 mF and voltage ratings of 3-125V are available. A high-voltage all-solid electrochemical-electrolytic capacitor cell is shown in **Figure 2**.
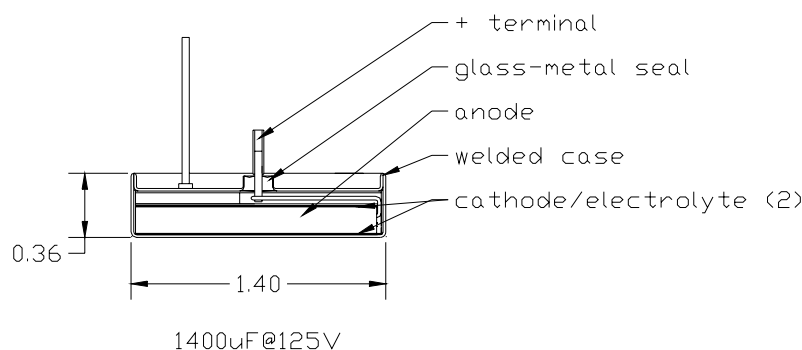

Figure 2. Hybrid Capacitor

The anode in a tantalum high-voltage electrochemical-electrolytic capacitor is comprised of a sintered slug of commercially available capacitor grade tantalum powder which is electrochemically oxidized, coating the surface with Ta_2O_5 dielectric material. The density of the slug is controlled during manufacture to be in the range of 30-35% of theoretical tantalum density (~ 5 g/cm^3). This leads to a highly porous structure with a large surface area. The weight of the slug and the formation voltage determine the capacitance and voltage rating of the anode. The cathode is thermally prepared RuO_2 bonded to a thin metal foil. Because of its high capacitance density, the amount of RuO_2 needed is relatively small, on the order of 2-4 mg/cm^2 of cathode area. The cathode capacitance density is usually about 50 mF/cm^2. The total thickness of the cathode, including the foil substrate is 50-100 μm. As long as the magnitude of the cathode capacitance is sufficiently high, the performance of the capacitor depends exclusively on the performance of the Ta_2O_5 anode.

Giner, Inc. will develop an all solid or immobilized electrolyte high-voltage electrochemical-electrolytic capacitor for high-temperature operation, yielding a low-cost, low ESR device. The negative electrode or cathode will be made from highly conductive stabilized metal oxide (particulate formed RuO_x) while the positive electrode or anode will be made from a pressed tantalum particulate electrode, modified to have enhanced porosity and a Ta_2O_5 barrier oxide. The challenge is to modify the internal structure and porosity of the tantalum anode to

accommodate the high-temperature electrolyte within the anode pore structure. The specific innovative concept is the development of an all-solid high-voltage capacitor in conjunction with a high-temperature electrolyte by combining the modified porous tantalum oxide structure of a high-voltage electrolytic type anode with a low-voltage, high-energy-density electrochemical redox pseudocapacitance cathode. It combines the advantages of the electrochemical capacitor (*i.e. high energy density, high power density)* and the electrolytic capacitor *(i.e. low ESR, high voltage rating*) to provide efficient power transfer for the given application.

Anodes are fabricated using standard methods. A known quantity of Ta powder (H.C. Stark No. NA30KN) is placed in a pressing die. The powder is then compacted under pressure in a Carver Press to form a pellet. The pellet is sintered under high vacuum (<3x10-6 torr) at elevated temperature for 20 minutes. After cooling to room temperature and removing from the vacuum furnace, the pellet is anodically oxidized in an ethylene glycol/H_3PO_4 mixture to form a layer of Ta_2O_5 coating on the Ta surface. Finally the pellet is rinsed several times in distilled water.

Subsequent to anode formation the pellets are imbibed with a solubilized ionomer to impart ionic conductivity to the anode. The solubilized ionomer, in an appropriate solvent, is applied using a pipette, evaporating the solvent between applications. A total of 20 applications are required to form a uniform coating for baseline capacitors.

The capacitor cathode is formed from RuO_x on a Ti foil collector. A known quantity of RuO_x (Aesar, No. 11803) is mixed with a low boiling point organic liquid. The Ti foil is placed on a hotplate and, using a pipette, layers of RuO_x are built up on the Ti foil by applying a layer of RuO_x, allowing the solvent to evaporate, followed by addition of another layer.

Capacitance was measured by charging the capacitors to a set voltage and discharging across a 48 Ω load while recording the discharge potential vs. time. The RC time constant of the capacitor was taken as the time of the voltage decay from 90% of maximum voltage (V_1) to V_1/e. Capacitance is equal to the RC time constant divided by the load resistance, ohms. The capacitors were charged with a XANTREX model XHR600-1 DC power supply and the discharge curves were recorded on a computer using LabTech Notebook data acquisition software.

Electrical impedance measurements were made with an EG&G Model 263 A potentiostat and an EG&G Model 5210 lock-in-amplifier. A 10-mV sine wave was applied at frequencies ranging from 1 Hz to 100 kHz. The real and imaginary impedance components, Z_{RE} and Z_{IM} were used to evaluate resistance.

2.0 RESULTS AND DISCUSSION

2.1 Capacitor Specifications

In order to generate specifications for the capacitors to be developed on this program, requests were made to several drilling companies for specifications of the capacitors that they currently use for drilling applications. Responses were not received. In order to obtain information so that realistic capacitor specifications could be generated, the NETL Program Manager suggested conducting a survey of various users, to determine their needs and wants. A survey was prepared, submitted to NETL, and then distributed by NETL to various users.

A total of 5 responses were received to the survey. Based on feedback to the survey, the following capacitor specifications, summarized in **Table 1**, were generated for both the capacitor electrical characteristics and physical size.

No specification was established for mechanical vibrations. Input for this parameter ranged from "compliant lead frames" to "handle shock of truck transport" to "high impact shock 20,000g, 50µS".

Table 1. Capacitor Specifications

Parameter	Specification
Capacitance (µF)	220
Voltage (V)	100
Operating Temperature (^{o}F (^{o}C))	450 (232)
Outside Diameter (inches (cm))	1 (2.56)
Length, excluding leads (inches (cm))	1 (2.56)

2.2   High Temperature Capacitor Fabrication and Testing
2.2.1   Baseline Capacitors

To verify electrolyte suitability for high temperature operation, conventional capacitors consisting of RuO_x for both the anode and cathode were fabricated. These capacitors had a 1-cm^2 active area. Prior to testing with the high temperature electrolyte (HTE), the capacitors were tested using a sulfuric acid electrolyte by both AC impedance and DC discharge. For the AC impedance testing, measured capacitances were 11.3, 6.0, 0.9 mF/cm^2 at 10, 100, 1 kHz respectively, and an ESR = 0.6 ohms. The capacitor was charged to 1V and discharged through a 48 Ω resistor, yielding a capacitance of 18.0 mF/cm^2. The electrodes were rinsed, filled with the high temperature electrolyte and tested by AC impedance at 200, 250, 300°C. Performance was poor with a very high resistance.

Several additional capacitors were fabricated using RuO_x for both electrodes and the HTE as the capacitor electrolyte. These capacitors were placed in a Ta clip holder and tested by both AC impedance and DC discharge at temperatures ranging from 50 to 350°C in 50°C increments. At the low temperatures the capacitors exhibited high resistance and low capacitance. At 250°C the highest capacitance (measured at 100 kHz by AC impedance) was 168 mF/cm^2, with a resistance of 96 mΩ. When tested by DC discharge across a 48 Ω load (charging to1V) the best capacitance was 633 mF/cm^2.

These tests demonstrated that the HTE was capable of 250°C operation.

2.2.2   Hybridized Capacitors

Hybridized capacitors were fabricated using Ta_2O_5 anodes and RuO_x cathodes. To expedite cathode fabrication, cathodes were procured from Evans Capacitor Corp. This allowed us to utilize a pre-made production cathode in our capacitor. Since this was a production item, it was expected to be more uniform than individual cathodes fabricated at Giner, Inc. The anodes and cathodes were charged with HTE, formed into high-temperature, high-voltage (HTHV) hybridized capacitors, and tested by both AC impedance and DC discharge at temperatures up to 250°C.

Capacitance, measured by AC impedance, on most capacitors was low, on the order of 80 µF at 100 Hz at 250°C. When tested by DC discharge the capacitors would not charge above 70V. As the capacitor voltage goal was 100V, various methods to achieve this voltage were evaluated.

2.2.2.1 Methods to Increase Capacitor Voltage

When the high-temperature capacitors were tested at temperatures above 200^oC, they could only be charged to a maximum of 70V. Efforts were spent evaluating methods to increase the capacitor voltage. A number of capacitor variations were fabricated and tested; these are described in more detail below. Capacitance was measured by both AC impedance and by charging and discharging the capacitors across a 48Ω resistor.

High-Voltage Powders: One method to increase the formation voltage to allow higher operating voltage is to change to a lower surface area powder and/or higher sintering temperature. Capacitors were initially fabricated using NA30KN tantalum powder for the anode. This material was formed into Ta_2O_5 using a 150V formation voltage. At the suggestion of Evans Capacitor, anodes were fabricated using two different high voltage (lower surface area) Ta powders, QR3 and HVTT. These were formed into Ta_2O_5 at 250V. The HVTT disk broke apart. The QR3 disk was filled with HTE and made into a high temperature, high voltage (HTHV) hybridized capacitor with an Evans RuO_x cathode. The capacitor was tested by an AC impedance scan and DC discharge. At 100 Hz capacitance was 35 µF (250^oC). By DC discharge at 20V and 50V, capacitance was ~ 200 µF (~80 $µF/cm^2$) at 250^oC. However, the capacitor would not charge above 75V; it would only pass a constant current.

A Ta_2O_5 anode was held overnight at 125V in 38% H_2SO_4 to try to increase the potential range in a HTHV hybridized capacitor by increasing the oxide thickness. Tested by DC discharge in H_2SO_4 at ambient temperature before and after the overnight procedure, capacitance was 688 µF, (265 $µF/cm^2$), and the anode charged to 125V, although the leakage current at 125V increased from 275 to 320 µA overnight. The anode was used to make a HTHV hybridized capacitor, filled with melted HTE and paired with an Evans cathode. Tested by DC discharge at 130^oC, the capacitor charged to 125V and capacitance decreased to 38 µF (14 $µF/cm^2$). At 200^oC, it only charged to ~85V (3.0 mA), with a capacitance of 108 µF. At 250^oC capacitance was 588 µF but it only charged to ~50V. At 230^oC it only charged to ~69V.

Thermal Oxidation: A useful step when making anodes with high formation voltage is a so-called mid-form-anneal step. This involves a soak either in air or vacuum at about 300°C for up to an hour. It is thought this step helps rearrange the oxide by oxygen diffusion, making the formation more isotropic. Sometimes, it helps to significantly reduce leakage current. Oxygen migration out of the Ta_2O_5 layer into the Ta base electrode has been suggested before, but we know of no published experimental evidence of this. To evaluate the effect of the mid-form-anneal step, or thermal oxide layer, four anodes were fabricated, two with NA30KN Ta powder, and two with HVTT Ta powder. The anodes were kept in a vacuum furnace chamber overnight to cool in argon before removing. For each run, on removal from the vacuum furnace (at 16^oC), one anode was immediately put in a beaker of N_2, resealed and reflushed with N_2. The other was left in open air at room temperature. The Ta_2O_5 formation was begun 2.5 – 3 hours after removal from the furnace. The NA30KN anodes were formed at 150V, the HVTT disks formed at 250V, all were rinsed, boiled and dried. HTHV hybridized capacitors were made with the NA30KN disks, dip-filled with molten HTE, and mated with an Evans cathode.

The HTHV hybridized capacitor that used NA30KN Ta which had been kept in N_2 (at room temp) before Ta_2O_5 formation had good capacitance in AC impedance testing and DC discharge tests at 50V, among the best at lower temperatures, but only charged to 60-80V at 200, 230, and 250^oC in DC discharge testing. The HTHV capacitor that used NA30KN Ta that had been kept in air at room temperature before Ta_2O_5 formation performed similarly. Likewise, the HTHV hybridized capacitor using an anode fabricated with HVTT Ta that had been kept in N_2 at room temperature before Ta_2O_5 formation had lower capacitance than the NA30KN disks (as

expected) but still only went to 60-70V at 200°C. No advantage was observed with the use of a controlled thermal oxide layer.

Separator: An HTHV hybridized capacitor was made with a ceramic felt separator to try to avoid shorting, one possible reason the capacitors could not be charged above 70V. The anode was dip-filled with molten HTE, a 2.54 mm (0.010 inch) thick porous felt disk was placed over the anode, the felt covered with more HTE, and the Evans RuO_x disk put on top. Tested after cooling, capacitance was low and resistance high; HTE may not have adequately wet the ceramic felt. By RC discharge testing, it only charged to 66V, with a 10 mA constant current indicating a partial short.

Mixed Electrolyte: A new HTE variation was tried in an HTHV hybridized capacitor. The anode was filled with molten HTE and a disk of mixed HTE and SiP_2O_7, 1:1 by weight, was put over the anode, an Evans cathode placed on top, and re-melted to bond. By AC impedance scans, capacitance was 55 $\mu F/cm^2$ at 100 Hz. By RC discharge test the capacitor charged to 73V; SiP_2O_7 did not help to increase the voltage.

Alternate Filling Methods: An alternate method was evaluated to fill the anodes with HTE. One Ta_2O_5 anode was pre-filled with an aqueous solution of HTE by repeated applications and drying at 120°C. The other was filled with solution to form the HTE within the disk. Both were dip-filled with molten HTE and placed in a ceramic ring-mold; molten HTE and an Evans cathode disk were added to form the HTHV hybridized capacitor. Both hybridized capacitors were tested by an AC impedance scan and by DC discharge, performance was similar to HTHV hybridized capacitors made by filling with molten HTE; no improvement was observed by pre-filling the anodes.

Modified Formation Procedure: In an effort to increase the HTHV hybridized capacitor operating voltage, testing was focused on modifying the Ta_2O_5 dielectric. A new Ta_2O_5 formation solution was made (Kinard et al, 1999), which reportedly can make Ta_2O_5 layers of unlimited thickness. The solution was 10wt% dibasic potassium phosphate in glycerol. The solution was heated to and held at 175°C. A Ta anode disk was installed and Ta_2O_5 formation initiated at 20V (limit setting). During this process the color of the Ta anode changed from green to deep blue, which may indicate a thicker Ta_2O_5 layer.

After formation the Ta disks were filled with HTE, bonded to an Evans cathode and tested. With DC charging at 20 mA, the capacitors could only be charged to 19V. Capacitance by RC discharge was high: 223 $\mu F/cm^2$ at 230°C and 2931 $\mu F/cm^2$ at 250°C. An AC impedance test showed high capacitance at high temperature also but with a large drop in capacitance at temperatures at or below 200°C. A new solution of dibasic potassium phosphate was prepared and used for Ta_2O_5 formation on an NA30KN disk at 20V and 175°C.

Another disk was Ta_2O_5-formed using a pulse routine, alternating applying 20V, then open circuit (equal time) with a frequency of ~1Hz. This procedure produces a more uniform Ta_2O_5 thickness within the disk.

All disks prepared above were washed with distilled H_2O, and dried overnight at 110°C. A high temperature capacitor was made using an anode disk formed in the alternate formation electrolyte. The anode was filled with HTE, then bonded to an Evans cathode disk. The capacitor, tested from room temperature to 250°C, would only charge to 36V at room temp at 10mA charging current. At 250°C, it would only charge to ~10V. At 250°C capacitance (best)

was only 26 µF at 100Hz with an ESR of 110 ohms; by RC discharge across a 48 ohm resistor capacitance was ~200 µF.

A capacitor pretreatment procedure was evaluated to determine if this would improve capacitor performance. The pretreatment procedure will repair any defects in the Ta_2O_5 by forming a new oxide. This procedure is performed in H_2SO_4 electrolyte and allows the electrodes time to fully wet out with electrolyte. The handling and assembly of tantalum capacitor anodes inevitably causes physical damage to the dielectric, which is repaired in the working electrolyte by forming new oxide. This occurs naturally during the pretreatment procedure. After the process, the leakage current has been reduced by orders of magnitude, the ESR and capacitance have stabilized. Anode disks were prepared and pretreated, but were never tested.

Membrane Electrolytes: Two approaches were evaluated in the development of a high-temperature electrolyte. The first, described above, involved filling both the anode and cathode with HTE. The second approach involved imbibing membranes with phosphoric acid.

A HTHV hybridized capacitor was made with the NA30KN powder, imbibing the anode with solubilized membrane, allowing the solvent to evaporate, and finally soaking in phosphoric acid. The capacitor was tested by AC impedance, with results shown in **Table 2**.

Table 2. Capacitance (mF/cm^2)

	10 Hz	100 Hz	1KHz	R (ohms)
Room temp.	0.223	0.0956	0.0208	3.7
100°C	0.473	0.137	0.0048	6.5
150°C	0.624	0.093	0.0013	8.9
200°C	0.139	0.0041	0.0005	7.8

As the table illustrates, the results were unexpected. The resistance initially increased with temperature and, after 150°C, began to decrease. The resistance was also higher than that observed with the HTHV hybridized capacitors fabricated using HTE. DC charge and discharge testing was conducted at 200°C; the capacitor could only be charged to ~50V.

Another HTHV hybridized capacitor was fabricated, this time using the HVTT Ta powder and the phosphoric acid imbibed membrane. This capacitor could not be charged above 50V.

2.2.2.2 Discussion

Discussions concerning the inability to achieve a high working voltage were held with our partner and consultant, Evans Capacitor Company. According to Evans, as the working temperature increases, the dielectric becomes progressively leakier for reasons related to electron tunneling and not necessarily to imperfections in the dielectric.

At constant voltage, the leakage current increases exponentially with temperature. At some level of current, I^2R heating at electron tunneling sites or imperfections raises the local temperature and can cause more defects in the oxide, for instance, thermal conversion of the amorphous oxide to crystalline form. This kind of defect does not "heal" in sulfuric acid and probably will not heal in the HTE. Defects of this type appear as grey oxide.

Even if permanent defects do not occur, the local heating causes a current run away effect, because of the dual exponential relation between current and temperature. The higher the

temperature goes, the higher the current, and so on. This mechanism leads quickly to breakdown failure.

2.2.3 Finalized Design, HTHV Hybridized Capacitor

As discussed above, when the HTHV hybridized capacitors were tested at temperatures above $200^{\circ}C$, they could only be charged to a maximum of 70V. A decision was made to limit the capacitor voltage to a maximum of 50V and utilize a 2-cell capacitor stack as a means to achieve the 100V goal. Variations of the HTE were re-evaluated to determine which electrolyte variation would provide the highest capacitance and lowest resistance at 50V. Capacitance was measured by both AC impedance and by charging and then discharging the capacitors across a 48 Ω resistor.

HTHV capacitors were fabricated using Ta_2O_5 anodes and RuO_x cathodes. All anode disks were washed with distilled H_2O, and dried overnight at $110^{\circ}C$. The anode was filled with HTE, and bonded to an Evans cathode disk. Three different high temperature electrolytes were tested; one was the conventional HTE used for the bulk of the testing in this program, one was a modified HTE that incorporated SiP_2O_7, and the third was a new HTE, designated HTE-2.

Results of the testing are summarized in **Table 3**. All values listed in the table are the averages of multiple tests. Testing was conducted at $230^{\circ}C$, charging the capacitors to a maximum of 50V. Capacitance values listed in the table are calculated by discharging the capacitor across a 48-ohm resistor.

Table 3. Capacitance Measured with Various Electrolytes

Electrolyte		$25^{\circ}C$	$230^{\circ}C$	
	Voltage (V)	Capacitance (µF)	Capacitance (µF)	Resistance (Ω)
HTE-2	50	54	587	14
HTE	50	43	556	7
HTE-SiP$_2$O$_7$	50	60	794	4
HTE-SiP$_2$O$_7$	100	48	380	7

As can be seen, at elevated temperature, all the single cells had a high capacitance. Resistance, however, was higher than desirable. Room temperature capacitance, however, was quite low, typically only 10% of that seen at elevated temperature. This was because of the nature of the HTE, which does not become readily conductive until the temperature exceeds $100^{\circ}C$.

Of the three HTEs tested at 50V, the HTE-SiP$_2$O$_7$ electrolyte was selected to be used in a 2-cell capacitor stack. It was selected based on providing the highest capacitance and lowest resistance of the 3 electrolytes evaluated. A 2-cell stack is typically implemented by placing the

negative electrode of one capacitor in contact with the positive electrode of the other capacitor. For this testing, however, the capacitor cells were connected in series by means of jumper wires, to allow the capacitance and resistance of the individual cells to be measured.

Capacitance of the 2-cell stack was 380 microfarads, exceeding the Phase 1 goal of 220 microfarads at 100V. This was achieved with a rather high cell resistance. Lowering the capacitor resistance will allow us to obtain an even higher capacitance, which would then allow the capacitor footprint to be made smaller.

The capacitors used in the above testing were circular in shape, with a positive electrode that was 1.78 cm (0.7 inch) in diameter. The capacitors were not enclosed in a final package but, based on the physical size of the capacitors, the final package is expected to be significantly thinner than the 2.54 cm (1 inch) height specified in the goals for this program.

2.2.3.1 Capacitor Electrolyte Modifications

When used in an actual drilling environment, the drilling electronics are tested at ambient temperature prior to insertion of the drill and electronics into the ground. Therefore, the HTHV hybridized capacitor has to operate at ambient temperature. Efforts were directed at improving ambient temperature performance. A literature search was conducted to identify an ambient temperature electrolyte (ATE) that would be compatible with the HTE and would provide adequate conductivity at ambient temperature. Attempts were made to synthesize the electrolyte, which were not successful. A commercial version of the material was purchased and tested.

Apparatus was fabricated to measure the conductivity of the electrolytes as a function of temperature. Duplicates of three different materials were evaluated: the current HTE, a mixture of the ATE and the HTE, and the ATE alone.

Test results were not encouraging. The ambient temperature resistance of all three materials was extremely high. We suspect that the commercial version of the room temperature electrolyte was not in the proper chemical form to allow for ambient temperature conductivity.

A new synthesis route was used to make the ambient temperature electrolyte. Subsequent to synthesis, the material was blended with the current HTE and incorporated into a HTHV hybridized capacitor. Resistance and capacitance were measured at both ambient temperature and elevated temperature. Results summarized in **Table 4** are average values from tests on multiple capacitors; leakage currents were also measured.

Table 4. Comparison of HTE Performance with and without ATE

Electrolyte	23°C			230°C		
	Capacitance (μF)	Resistance (Ω)	Leakage Current (μA)	Capacitance (μF)	Resistance (Ω)	Leakage Current (μA)
HTE Alone	60	156K	25 - 69	794	4	1368 - 3489
HTE + ATE	48	337	38 - 60	673	24	553 - 3145

As can be seen, the presence of the ATE significantly reduced the ambient temperature capacitor resistance; a decrease in ambient temperature capacitance was also noted.

For the capacitors with the original HTE, the average ambient temperature resistance was 156 Kohms while the average measured capacitance was 60 microfarads; leakage currents ranged from 29 to 69 microamps. At elevated temperature the average resistance was 4 ohms while the average capacitance was 794 microfarads. Leakage currents at elevated temperature ranged from 1368 to 3489 microamps.

For the capacitors that contained the ATE combined with the HTE, the average ambient temperature resistance was 337 ohms while the average ambient temperature capacitance was 48 microfarads; leakage currents ranged from 38 to 60 microamps. At elevated temperature the average resistance was 24 ohms while the average capacitance was 673 microfarads; leakage currents ranged from 553 to 3145 microfarads.

Therefore, addition of the ATE to the HTE resulted in the ambient temperature resistance **decreasing** from 156 Kohms to 337 ohms. Further work is required to determine the optimum HTE:ATE ratio to use in the capacitor in order to additionally lower the ambient temperature resistance.

3.0   DISCUSSION

Results described above demonstrated the feasibility of fabricating a HTHV hybridized capacitor that could provide >220 microfarads at 100V, 230°C in a compact package. This capacitor was comprised of a 2-cell stack, in which each cell utilized a Ta_2O_5 anode, a HTE-SiP_2O_7 electrolyte, and a RuO_x cathode. The goals of the Phase I effort of the program were met, and a recommendation to proceed into Phase II was prepared but never submitted due to lack of a Phase II cost-share funding partner.

During the course of the program our cost-share partner informed us they were not interested in continuing on the program past the Phase I effort. Therefore a search was initiated for a new cost share partner. Over a several month period a total of 7 different capacitor companies and 2 drilling companies were contacted. Meetings were held with 3 of the capacitor companies. None of the companies decided to provide cost share, resulting in recommendation by Giner, Inc. for termination of the program at the end of Phase I.

4.0   REFERENCES

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5.0 LIST OF ACRONYMS AND ABBREVIATIONS

ATE	ambient temperature electrolyte
ESR	equivalent series resistance
H_2SO_4	sulfuric acid
HPHT	high-pressure high-temperature
HTE	high temperature electrolyte
HTHV	high-temperature, high-voltage
NETL	National Energy Technology Laboratory
RC	resistor capacitor
RuO_2	ruthenium oxide
SiP_2O_7	silicon pyrophosphate
Ta_2O_5	tantalum pentoxide
tcf	trillion cubic feet
Ti	titanium
Z_{RE}	real impedance component
Z_{IM}	imaginary impedance component