Solid-State BATTERY

2006

R&D 100 NOMINATION

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Solid-State Environmentally Safe Battery for Replacing Lithium Batteries

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Affirmation

I affirm that all information submitted as a part of, or supplemental to, this entry is fair and accurate representation of this product.

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Submitter Signature

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3. Product Name

HTSS10V Fluoride Battery

4. Description

HTSS10V is a solid-state, fluoride-based battery that improves on traditional batteries in consumer and environmental safety aspects and in high-temperature applications such as gas and oil drilling.

5. Product First Marketed/Available for Order

Limited production within Russia's VNIIEF Institute began in May 2005. Under a joint program with Sandia and General Atomics, these batteries will be produced in Sarov, Russia, and in San Diego, CA, for high-end oil and gas drilling customers.

6. Inventor/Principal Developer

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7. Product Price

Batteries built in Russia have sold for ~$2500 per 10-volt battery pack (seven cells), with four 10-volt battery packs in parallel. The commercial target cost is expected to open at $50 per 1.5-volt cell. This price is comparable to existing lithium cells used in high-temperature industrial applications. Once commercial production exceeds the demands of the high-end industrial customers, prices will drop and become commercially comparable to existing consumer products.

Sandia's HTSS10V solid-state fluoride-based batteries are safer than traditional batteries in high-temp activities such as oil, gas, and geothermal drilling.

8. Patents/Patents Pending

The original patent was published in 2002 through the Department of Energy. An exclusive licensing agreement has been negotiated with General Atomics.

9. Primary Function

The unique qualities of the HTSS10V battery make it the best and safest choice for high-temperature arenas such as oil and gas drilling, its primary application at this point. Because all

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three battery components – anode, cathode, and ionic conductor – are solid, the battery is safer than traditional batteries that explode or gasout (leak chemicals) under high-temperature uses.

Solid-state fluoride-based battery technology offers the largest temperature range (room temperature to 500^{o}C) of ANY battery technology. The chemical reaction used to create electrical energy occurs as a solid-state reaction. The ionic conductors use tysonite structure and are characterized by a highly disordered anion sub-lattice and, as a result, by a high-fluoride ion conductivity. Lanthanum fluoride possesses the conductivity of (0.5 – 3.0) 10-6 S·cm-1 at room temperature. Doping of LaF_3 lattice with a small amount of bivalent metal fluoride (BaF_2) leads to the conductivity growth in the LaF_3-BaF_2 solid solution by factor of 5-8 as compared to the initial LaF_3.

At room temperature the internal resistance is ~1800 ohms, while at 250^{o}C (482^{o}F) the internal resistance is 2 ohms. The battery anode, cathode, and fluoride ion conductor are stable up to 500^{o}C. This stability allows this battery to be used, for example, in the geothermal industry.

10A. Product's Competitors

The only competitor to this technology is lithium sulfuryl chloride batteries. There are several manufacturers; however, about 90% of the market comes from Electrochem, a division of Wilson Greatbatch Ltd.

10B. Comparable Products/Technologies Matrix

The easiest means to show the benefits of this technology over the competitors is to review the MSDS of the two products (attached in Appendix).

	Lithium Sulfuryl Chloride	Fluoride
Hazard Label	Extremely Hazardous	NA
Corrosive Disposal	May Explode Hazardous Waste	NA Ok to discard
Transportation	>1.0 gm ship by ground only	Unlimited transportation
Cell Voltage	3.5V	1.5V
Energy Density	1000 mA/l 10,000	up to 800 mA/l
Operating temperature	-25 to 150C	23 to 250C
Shelf life	Months	Years

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10C. How Product Improves on Competitive Products/Technologies

Solid state fluoride ion batteries have near the energy density of lithium sulfuryl batteries while being inherently safe. They can go into any onshore or offshore oil or natural gas well. They can be flown on commercial aircraft, while lithium sulfuryl chloride batteries can only be transported by ground and must be stored in explosive containers when on a drill rig. Any short circuit of a lithium sulfuryl chloride battery can lead to an explosive accident. Battery explosions inside an oil well or on a drill rig cause hundreds of millions of dollars of damage each year, and have even caused deaths of those working on the rigs. Because of the fluoride base and solid-state feature, the HTSS10 V battery is safer to use than traditional lithium batteries.

11A. Principal Applications

The initial application for this product is in deep, high-temperature drilling, normally below 17,000 feet. At these depths, drilling is very expensive and occurs at temperatures above 150ºC. The principal application is any drilling or industrial application requiring battery power. The inherent safety of these batteries reduces hazardous work and environmental waste. Lithium batteries are very toxic and hazardous. Unlike lithium batteries, this battery consists of non-toxic fluoride and because of its solid-state, it will not leak into the environment.

The battery cell on the right looked like the one on the left before being heated to 250°C and crushed under 60 tons, replicating typical down-hole drilling conditions. The battery functioned as expected and didn't explode or outgas; it is completely safe.

11B. Other Applications

Because HT flouride batteries have a longer shelf life and withstand heat better than traditional batteries, they are more reliable in emergency situations and, thus, make a good choice for battery back-up or life support systems during a fire or other emergencies. An expected application, which is currently under development, is a rechargable version for laptop computers. The battery is used as a heat sink for the microprocessor and assists the microprocessor in better performance. It is also enabling the design of new tools within the drilling industry, such as Sandia's diagnosis-while-drilling system, which makes drilling safer and more efficient.

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12. Summary

This battery enables deep drilling exploration for fossil energy. Deep drilling below 20,000 feet often reaches temperatures above 200°C. There is NO battery technology able to operate that temperature except our HT battery. As the need for oil increases, the search for fossil energy continues to reach deeper.

General Atomics believes this battery technology will displace dangerous and environmentally unsafe lithium-based battery cell technology. Because of the safety characteristics of the battery, explosive batteries can be removed from ships and offshore drilling rigs, providing the potential for saving lives, time, and money.

The call for a HT battery for the drilling industry has been ongoing for 20 years. It wasn't until Dr. Alexander Potanin started looking at solid-state chemical reactions that breakthroughs in icon conductors occurred. Until then, researchers had been looking at doping existing lithium cells with retardant chemicals to extend the operating temperature range. These efforts returned extremely poor performance or very limited temperature ranges, resulting in a 70°C to 200°C lithium cell with only half the energy density.

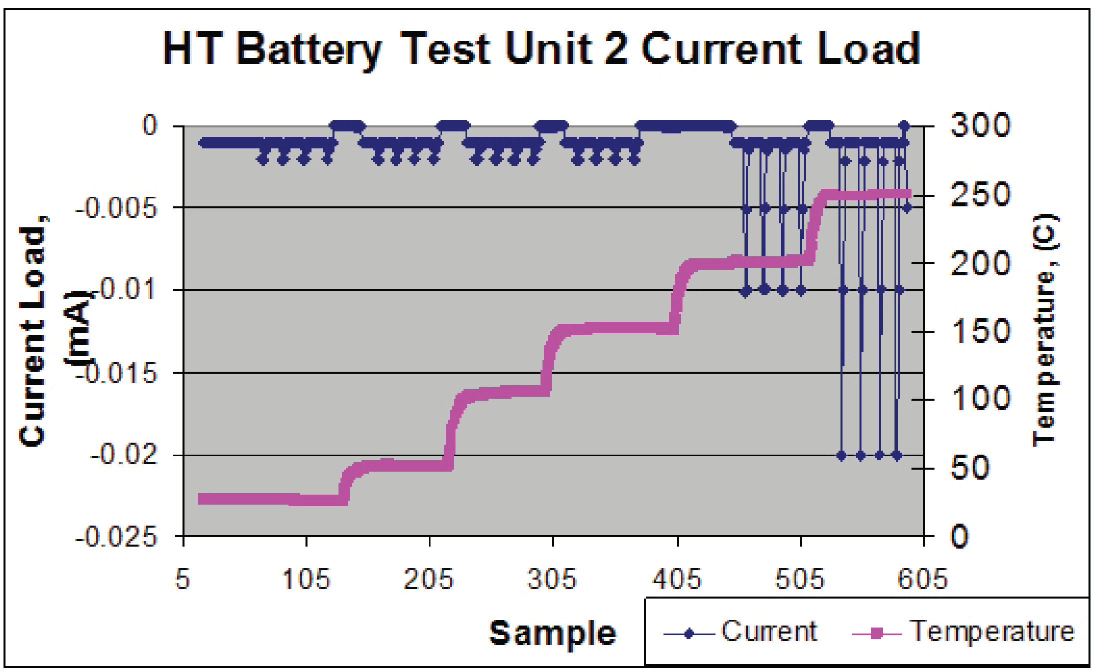
Dr. Alexander Potanin (left) hands over two HT battery prototypes to Lester Begg, General Atomics. The prototypes, designed and built by Dr. Potanin, underwent temperature testing at Sandia's Battery Research Department.

APPENDIX

Battery Test Results
October 5, 2005

The batteries were developed for the target operating temperature range of 25ºC to 250ºC. The open circuit voltage is ~10 volts with a discharged voltage not less than 5 volts. A discharge current is 1 mA with an additional 2 mA recurrent pulses. The battery prototypes are tubular with a 33 mm outer diameter and 52 mm length. The targeted energy capacity is 0.5 A·h (ampere hours) or better. The main task was to prove that the batteries were capable of working at 25ºC to 250ºC.

In total, four prototypes were built. Two were tested at Dr. Potanin's facilities with positive results. Two are at Sandia. For tracking purposes, we are labeling these batteries at Units 1, 2, 3, and 4. Unit 2 was tested in a Sandia laboratory oven. ***The temperature profile and actual current loads are shown in the plot, Figure 1, below.*** Note: The X axis "Sample" refers to a data point taken, done to compress time needed to oven heat the battery.



Unit 2 was held without a current load during oven ramp-ups. A temperature probe was placed on the battery case. Once the case reached the target temperature, a 1 mA load was placed on the battery. This load was held for 2 hours with an additional 10 mS current pulse load every 30 minutes. The 1 mA steady-state load was kept small because of the high internal impedance of the battery at 25ºC. However, the current pulses ranged from 1 mA to 20 mA as the battery was heated.

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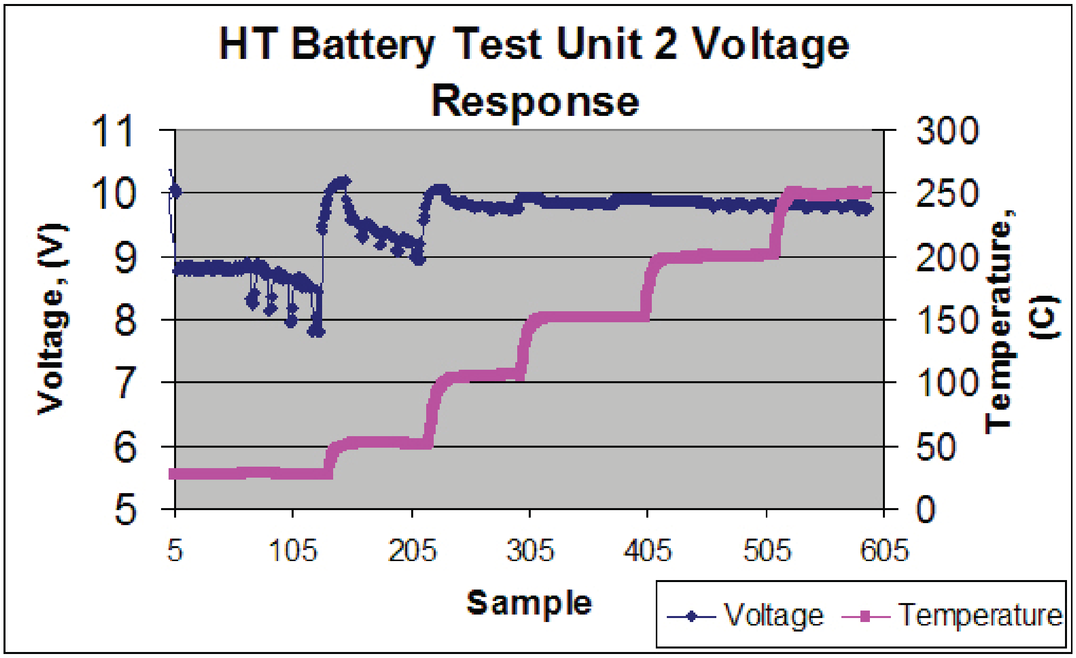
Figure 2, below, is a plot of the battery voltage output in response to the current load and ambient temperature.



The nominal open circuit voltage was 10.4 volts at room temperature. As the temperature increased from 25°C to 250°C, the battery's voltage response improved. At 25°C the 1 mA load reduced the voltage to ~8.8 volts for a steady-state impedance of 1550 ohms. The battery's ability to respond to a transient load was also measured during the test by creating 10 mS current pulse loads. At 25°C the dynamic impedance was measured as 710 ohms. Using this process the table below was filled in. The battery met the 1 mA load requirement for operation between 25° and 250°C.

Table 2. Measurements

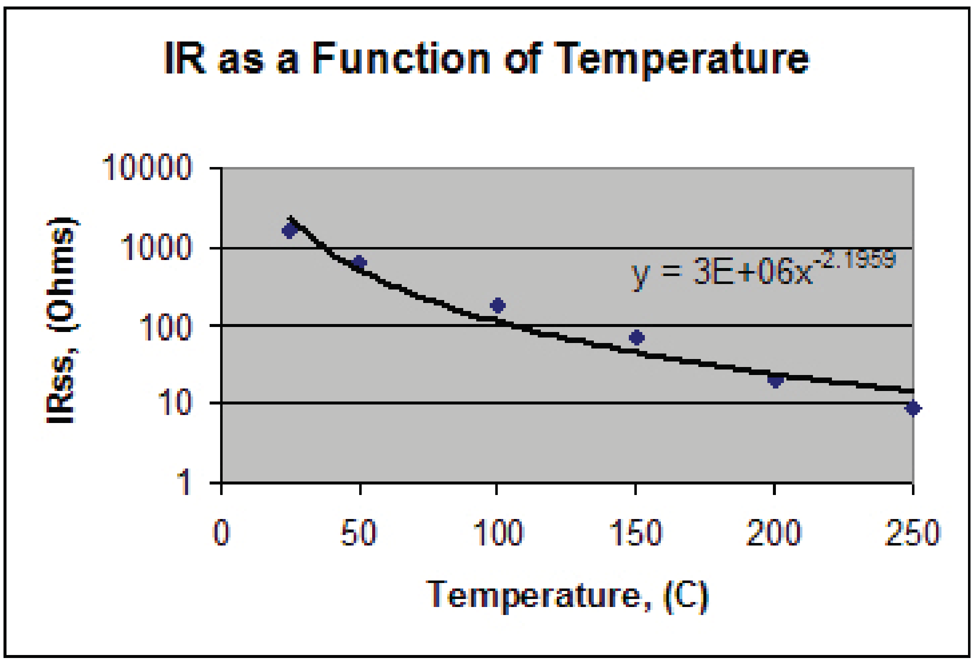
Temperature, C	Voltage Open Circuit (V)	Voltage @ 1mA Load	Internal Resistance (?)	Dynamic Imp., (?)
25	10.42	8.87	1550	710
50	10.17	9.54	630	200
100	10.05	9.87	180	40
150	9.91	9.84	70	20*
200	9.84	9.82	20*	5.4
250	9.806*	9.797*	9*	2.9

* These measurements made with currents or voltages too small for valid resolution by the Sandia tester. This battery tester is normally used to test much larger batteries. Future testing will have higher resolution.

The internal resistance under steady-state load (IR) is important for providing battery power to the electronic components that run most drilling and logging tools.

The tested battery has a distinctive dependence of IR versus temperature. For example, a tool drawing a steady current load of 100 mA would reduce the battery voltage by 7 volts (0.1 mA * 70 ohms) at 100ºC. This is unacceptable in most any application. However, increase the temperature to 200ºC and the voltage drop is now a more agreeable 2 volts. Two batteries in parallel at 100ºC would drop ~4 volts at 100ºC and render a much better result.

These prototype batteries were developed for holding the load of 1 mA at the voltage not less than 5 volts. Future batteries could be modernized for meeting the higher discharge current, i.e., they can have the lower IR and the higher energy density. *Figure 3, below, is a log plot of the IR values under steady state loads.*



These batteries offer several unique advantages over existing technology. Their uniqueness comes from their design in that these are solid-state batteries, so there is no liquid component to boil or quickly outgas at higher temperatures. Below is a short list of benefits.

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Advantages of the HT Battery

1. **Wide operating temperature range.**
   The limitation of 250ºC in these tests is a function of battery packaging not the battery active components. It is expected that this technology could operate much hotter.

2. **Safety.**
   Because of the solid-state nature of this battery, there is no danger of explosion during use or transport. These batteries can be shipped via commercial air without restrictions and do not require explosive handing procedures. Traditional batteries, because of their potentially explosive nature, must be shipped by truck, which adds to the time and cost of using that type of battery.

3. **Green.**
   Fluoride batteries can be disposed of in normal waste streams and, because of their solid state, the chemical will not leak into landfill soil.

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Unfortunately, the battery tester developed an instrumentation issue during the current stabilization in the full discharge of the battery, making the total energy measurement questionable. At the same time, the battery test results obtained in Dr. Potanin's laboratory at 1 mA load and 250^{0}C have shown that the battery has a steady continuous discharge for 425 hours. A third (Unit 3) battery is still being tested.

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batteries testing

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