

Molten salt battery Technologies

Molten salt batteries (including liquid metal batteries) are a class of battery that uses molten salts as an electrolyte and offers both a high energy density and a high power density. Traditional 'use-once' thermal batteries can be stored in their solid state at room-temperature for long periods of time before being activated by heating. Rechargeable liquid metal batteries are used for electric vehicles and potentially also for grid energy storage, to balance out intermittent renewable power sources such as solar panels and wind turbines.



History

Thermal batteries originated during WWII when German scientist Georg Otto Erb developed the first practical cells, using a salt mixture as an electrolyte. Erb developed batteries for several military applications, including the V-1 flying bomb and the V-2 rocket, and artillery fusing systems. None of these batteries entered field use before the end of WWII. After the war, Erb was interrogated by British intelligence and his work was reported in a document titled "The Theory and Practice of Thermal Cells".

This information was subsequently passed on to the United States Ordnance Development Division of the National Bureau of Standards.^[1] When the technology reached the United States in 1946 it was immediately applied to replacing the troublesome liquid-based systems that had previously been used to power artillery proximity fuses. These batteries have been used for ordnance applications (e.g., proximity fuses) since WWII and later in nuclear weapons. The same technology was also studied by Argonne National Laboratories in the 1980s for possible use in electric vehicles, since the technology is rechargeable.

Technologies

Thermal batteries use an electrolyte that is solid and inactive at normal ambient temperatures. They can be stored indefinitely (over 50 years) yet provide full power in an instant when required. Once activated, they provide a burst of high power for a short period (a few tens of seconds) to 60 minutes or more, with output ranging from a few watts to several kilowatts. The high power capability is due to the very high ionic conductivity of the molten salt, which is three orders of magnitude (or more) greater than that of the sulfuric acid in a lead-acid car battery.

There are two types of design. One uses a fuse strip (containing barium chromate and powdered zirconium metal in a ceramic paper) along the edge of the heat pellets to initiate burning. The fuse strip is typically fired by an electrical igniter or squib by application of electric current through it. The second design uses a center hole in the middle of the battery stack into which the high-energy electrical igniter fires a mixture of hot gases and incandescent particles. The center-hole design allows much faster activation times (tens of milliseconds) vs. hundreds of milliseconds for the edge-strip design. Battery activation can also be accomplished by a percussion primer, similar to a shotgun shell. It is desired that the pyrotechnic source be gasless. The standard heat source typically consist of mixtures of iron powder and potassium perchlorate in weight ratios of 88/12, 86/14, or 84/16.^[citation needed] The higher the potassium perchlorate level, the higher the heat output (nominally 200, 259, and 297 calories/gram, respectively). This property of inactivated storage has the double benefit of avoiding deterioration of the active materials during storage, and eliminating capacity loss due to self-discharge until the battery is activated.

Older thermal batteries used calcium or magnesium anodes, with cathodes of calcium chromate, vanadium or tungsten oxides, but lithium-alloy anodes replaced these in the 1980s, with lithium-silicon alloys being favored over the older lithium-aluminum alloys. The corresponding cathode for use with the lithium-alloy anodes is mainly iron disulfide (pyrite) with cobalt disulfide being used for high-power applications. The electrolyte is normally a eutectic mixture of lithium chloride and potassium chloride.

More recently, other lower-melting, eutectic electrolytes based on lithium bromide, potassium bromide, and lithium chloride or lithium fluoride have also been used to provide longer operational lifetimes; they are also better conductors. The so-called "all-lithium" electrolyte based on lithium chloride, lithium bromide, and lithium fluoride (no potassium salts) is also used for high-power applications, because of its high ionic conductivity. A radioisotope thermal generator, such as in the form of pellets of $^{90}\text{SrTiO}_4$, can be used for long-term delivery of heat for the battery after activation, keeping it in molten state.^[2]

Uses

Thermal batteries are used almost exclusively for military applications, notably for guided missiles.^{[3][4]} They are the primary power source for many missiles such as the AIM-9 Sidewinder, MIM-104 Patriot, BGM-71 TOW, BGM-109 Tomahawk and others. In these batteries the electrolyte is immobilized when molten by a special grade of magnesium oxide that holds it in place by capillary action. This powdered mixture is pressed into pellets to form a separator between the anode and cathode of each cell in the battery stack. As long as the electrolyte (salt) is solid, the battery is inert and remains inactive. Each cell also contains a pyrotechnic heat source which is used to heat the cell to the typical operating temperature of 400–550 °C.

Rechargeable Configurations

Since the mid-1960s much development work has been undertaken on rechargeable batteries using sodium (Na) for the negative electrodes. Sodium is attractive because of its high reduction potential of -2.71 volts, low weight, non-toxic nature, relative abundance and ready availability and its low cost. In order to construct practical batteries, the sodium must be used in liquid form. The melting point of sodium is 98 °C (208 °F). This means that sodium based batteries must operate at high temperatures between 400–700 °C (752–1,292 °F), with newer designs running at temperatures between 245–350 °C (473–662 °F).^[5]

Sodium–Sulfur

The Sodium–sulfur battery (or NaS battery), along with the related lithium sulfur battery, is one of the more advanced molten salt battery systems. The NaS battery is attractive since it employs cheap and abundant electrode materials. Thus the first alkali metal commercial battery produced was the sodium–sulfur battery which used liquid sulfur for the positive electrode and a ceramic tube of beta-alumina solid electrolyte (BASE) for the electrolyte. Corrosion of the insulators was found to be a problem in the harsh chemical environment as they gradually became conductive and the self-discharge rate increased. This problem of dendritic-sodium growth in Na-S batteries has been addressed in the development of the ZEBRA battery in 1985, which uses NaAlCl_4 with Na^+ -beta-alumina ceramic electrolyte.^[6]

Because of their high specific power, NaS batteries have been proposed for space applications.^{[7][8]} A test of a NaS battery for space use was successfully demonstrated on the space shuttle mission STS-87 in 1997,^[9] but the batteries have not been used operationally in space. NaS batteries have also been proposed for use in the high temperature environment of Venus.^[9]

The NaS battery has reached a more advanced developmental stage than its lithium counterpart. The possibility of construction of a potassium-ion battery with a molten electrolyte has been recently patented.

Na-NiCl₂

The Na-NiCl₂ battery operates at 245 °C (473 °F) and utilizes molten sodium tetrachloroaluminate (NaAlCl_4), which has a melting point of 157 °C (315 °F), as the electrolyte. The negative electrode is molten sodium. The positive electrode is nickel in the discharged state and nickel chloride in the charged state. Because nickel and nickel chloride are nearly insoluble in neutral and basic melts, intimate contact is allowed, providing little resistance to charge

transfer. Since both NaAlCl_4 and Na are liquid at the operating temperature, a sodium-conducting β -alumina ceramic is used to separate the liquid sodium from the molten NaAlCl_4 . The primary elements used in the manufacture of these batteries have much higher worldwide reserves and annual production than the Li used in Li-ion batteries.^[10]

This battery was invented in 1985 by the Zeolite Battery Research Africa Project (ZEBRA) group led by Dr. Johan Coetzer at the Council for Scientific and Industrial Research (CSIR) in Pretoria, South Africa. In 2009, the battery had been under development for more than 20 years. There are several advantages to the Na-NiCl₂ cell. One is that it can be assembled in the discharged state, using NaCl, Al, nickel and iron powder. Another advantage is that the positive electrode of the ZEBRA cell is composed mostly of materials in the solid state, which reduces the likelihood of corrosion, thus making the cell safer than the Na-S cell.^[11] It has a specific energy of 90 Wh/kg and a specific power of 150 W/kg. The β -alumina solid electrolyte that has been developed for this system is very stable, both to sodium metal and the sodium aluminum chloride. Lifetimes of over 1,500 cycles and five years have been demonstrated with full-sized batteries, and over 3,000 cycles and eight years with 10- and 20-cell modules.

For comparison, LiFePO_4 lithium iron phosphate batteries store 90–110 Wh/kg and the more common LiCoO_2 lithium ion batteries store 150–200 Wh/kg. Nano Lithium-Titanate Batteries store 72 Wh/kg and can provide a power of 760 W/kg.^[12] The ZEBRA's liquid electrolyte freezes at 157 °C (315 °F), and the normal operating temperature range is 270 °C (518 °F) to 350 °C (662 °F). Recent research has shown that the addition of iron to the cell increases its power response.^[11] ZEBRA batteries are currently manufactured by FIAMM Sonick^[13] and are used in the Modec Electric Van^[citation needed], the IVECO daily 3.5 ton delivery vehicle,^[citation needed] and the Th!nk City.^[14] The US Postal Service began testing all-electric delivery vans, one of which uses a ZEBRA battery, in 2011.^[15]

In 2010 General Electric announced a Na-NiCl₂ battery that it called a sodium-metal halide battery, with a 20-year lifetime. The cathode structure of a GE cell consists of a conductive Ni network, molten salt electrolyte, metal current collector, carbon felt electrolyte reservoir, and the active sodium-metal halide salts.^{[16][17]} In 2015, General Electric terminated the development of its Durathon battery and laid off most researchers who worked on that project.^[18]

Sumitomo developed a battery using a salt that is molten at 61 °C (142 °F), far lower than sodium based batteries, and operational at 90 °C (194 °F). It offers energy densities as high as 290 Wh/L and 224 Wh/kg and charge/discharge rates of 1C with a lifetime of 100 - 1000 charge cycles. The battery employs only nonflammable materials and will not ignite on contact with air, nor is there thermal runaway. This eliminates waste-heat storage or fire- and explosion-proof equipment, and allows closer packing of cells. The company expects that the battery requires half the volume of lithium-ion batteries and one quarter that of sodium-sulfur batteries.^{[19] [20]}

In 2014 researchers identified a liquid sodium-cesium alloy that operates at 150 C in this battery type and produced 420 milliampere-hours per gram. The new material was still able to fully coat, or "wet," the electrolyte. After 100 charge/discharge cycles, a test battery maintained about 97% of its initial storage capacity. The lower operating temperature allowed the use of a less-expensive polymer external casing instead of steel, offsetting some of the increased cost associated with using cesium.^[21]

When not in use, Na-NiCl₂ batteries are typically kept molten and ready for use because if allowed to solidify they typically take 12 hours to reheat and charge. This reheating time varies depending on the battery-pack temperature, and power available for reheating. After shutdown a fully charged battery pack loses enough energy to cool and solidify in 3–4 days.

Liquid Metal

Both Magnesium-antimony and more recently lead-antimony have been used in a new experimental arrangement with potential of use for grid energy storage. The electrode and electrolyte layers are heated until they are liquid when the self-segregate due to density and immiscibility. They may have longer lifetimes than conventional batteries, as the electrodes go through a cycle of creation and destruction during the charge-discharge cycle which makes them immune to degradation affecting conventional battery electrodes.^[22] High operating temperatures of 400 °C (752 °F) to 700 °C (1,292 °F), lead to challenges of thermal management and safety, increases corrosion and self-discharge rates, complicates sealing and thermal management and make stringent requirements on the rest of the battery

components.^[23] The three layer nature of the battery also causes issues, making the batteries sensitive to short-circuiting on movement.^[22]

The technology was first proposed by In 2009 by Donald Sadoway and his team at the Massachusetts Institute of Technology as a very low cost molten salt battery originally based on magnesium and antimony separated by a molten salt that could be potentially used in grid energy storage systems.^{[24][25][26]} Magnesium was chosen as the negative electrode for its low cost and low solubility in the molten salt electrolyte. Likewise, antimony was selected as the positive electrode due to its low cost and higher anticipated discharge voltage.

In 2011 the researchers turned their attention to cells with a lithium anode and a lead-antimony cathode, which had high ionic conductivity and lower melting points (350-430 °C).^[23] The likely reason for the switch was the low power/energy efficiency and the high operating temperature of the Mg chemistry. The drawback of the Li chemistry is the higher cost of energy. Ambri's patents disclose a Li/LiF+LiCl+LiI/Pb-Sb cell with ca 0.9 V ocp operating at 450 °C with the electroactive material cost of 100 \$/kWh and 100 \$/kW and projected 25y lifetime. This battery still needs an improvement in discharge power since the energy efficiency on discharge at 1.1 A/cm² is only 44% (and 88% at 0.14A/cm²).

Experimental data showed 69% storage efficiency, with good storage capacity (over 1000mAh/cm²), low leakage (< 1 mA/cm²) and high maximum discharge capacity (over 200mA/cm²).^[27] In 2012 the research received funding from ARPA-E,^[28] Bill Gates, Khosla Ventures and Total S.A.^[29]

In May 2014 Ambri received \$35 million of investment, allowing it to start manufacturing batteries for commercial testing.^[30] By October 2014 the team achieved an operational efficiency of approximately 70% at high charge/discharge rates (275mA/cm²), similar to that of pumped-storage hydroelectricity and higher efficiencies at lower currents. Tests showed that even after 10 years of regular use, the system would retain about 85% of its initial efficiency.^[31]

In September 2014 in a paper in Nature Sadoway described an arrangement using a molten alloy of lead and antimony for the positive electrode, liquid lithium for the negative electrode; and a molten mixture of lithium salts as the electrolyte. Storage costs using this format are estimated at US\$500 per kilowatt-hour of electricity stored, still higher than the \$100 per kilowatt-hour that the US Joint Center for Energy Storage Research says is needed for cost effective adoption but better than current alternatives which also suffer from damage to electrodes on each cycle.^[32]

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