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Reliability of Thermal Batteries

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Thermal batteries are known by different names: molten salt batteries, or liquid sodium batteries. All these refer to the fact that the electrolyte is a mixture of solid sodium or lithium salt that becomes liquid when heated. The batteries are designed for a specific application so that the electrical characteristics, activation time, environmental conditions, and mounting conditions are satisfied. This type of battery is useful in applications that need a long shelf life with no maintenance, high power density, or a ruggedization. [1] It has shown to be useful in guided weapon systems and is gaining popularity in electric vehicles. This technology has been successfully utilized in ground vehicles, launch vehicles, marine applications, oil and gas drilling and satellites. Figure 1 shows some examples of the applications where thermal batteries work reliably. When used, thermal batteries can provide several output voltages from one battery and are compatible with either steady load conditions or pulsed applications. Their versatility permits them to replace several power sources due to their reduced size, weight and improved reliability.

Figure 1 - Ground Vehicle application (left) and HARM Missile (right)

Similarly, thermal batteries are finding application in electric vehicles. For example the Toyota Prius' dashboard energy monitor shows the power moving from the batteries to an electric motor and ultimately to the wheels. Thermal batteries are finding use in hybrid buses, rail vehicles, and a number of hybrid and electric cars (Toyota Highlander, Ford Escape, Honda Insight, Saturn). Figure 2 shows the Toyota Prius Hybrid Battery.

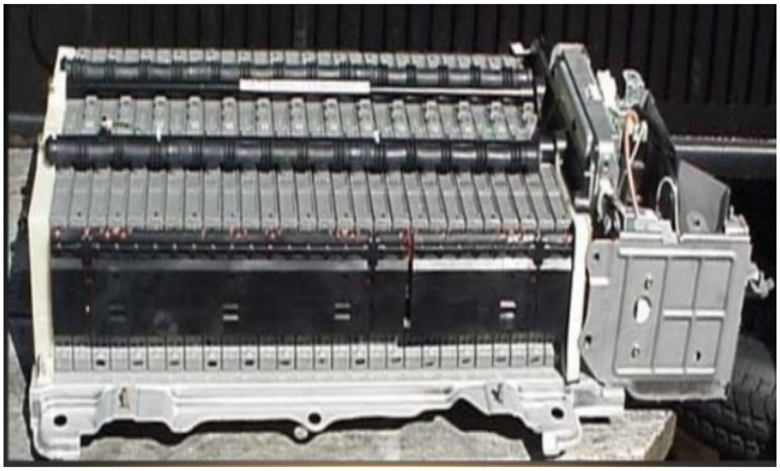

Figure 2 - Toyota Prius Hybrid Battery

Advantages

The main advantages of this battery technology is that it can be stored for over 20 years and brought into operational service immediately because they have virtually no self-discharge. In fact, they can be activated within fractions of a second after the storage period. The batteries remain inert during storage and are typically hermetically sealed so they can withstand environmental stresses. They are designed to handle extreme temperatures (either high or low and have a range of more than 100C), vibration, mechanical shock, vacuum, very high or low pressures, EMI, and acceleration. The batteries are classified as non-explosive with respect to transportation, can be handles without risk to the user and can be destroyed by conventional techniques. Figure 3 illustrates some examples of thermal batteries.

Figure 3 - ASB Thermal Battery (left) and Eagle Picher Batteries (right)

Disadvantages

While offering several distinct advantages, thermal batteries do have some disadvantages as well. They have a relatively short activated life, can develop high surface temperatures, can have non-linear output voltages, and are one time use batteries.

History of Thermal Battery Terminals

The early thermal battery anodes were made of calcium and magnesium which led to many oxidation states and voltage plateaus. This approach was replaced by calcium anodes in direct contact with the calcium chromate cathodes. When the battery would activate, the chemical reaction between the anode, cathode and electrolyte would create a liquid calcium lithium alloy that became the actual anode. The liquid anode would lead to inter-cell shorting.

The anode was then made of magnesium and other magnesium alloys. This led to the possibility of rechargeable batteries with magnesium silicon and magnesium boron anodes. [3] Anodes then shifted to being made from lithium aluminum on one side and lithium silicon (LiSi) on the other side. The other option for anode material is pure lithium in a metallic matrix known as "LAN" technology. [2] Figure 4 shows how the latest anode technology compares at 0.1 A/cm^2 and $1A/cm^2$. There is a greater difference between the LAN and LiSi at the higher current density than the lower current density. The difference is due to the chemical reaction between the anodes and the electrolyte. Pure lithium has a higher electromotive force (emf) than a lithium alloy such as LiSi. The electromotive force allows power to flow through the battery. The difference in the emf is amplified when the current density is change by an order of magnitude as done in Figure 4. It is this difference that is important when a thermal battery is being designed for an application. The difference in the emf of the anode materials allows for the manufacturer's to tailor the output power of the battery to the application.

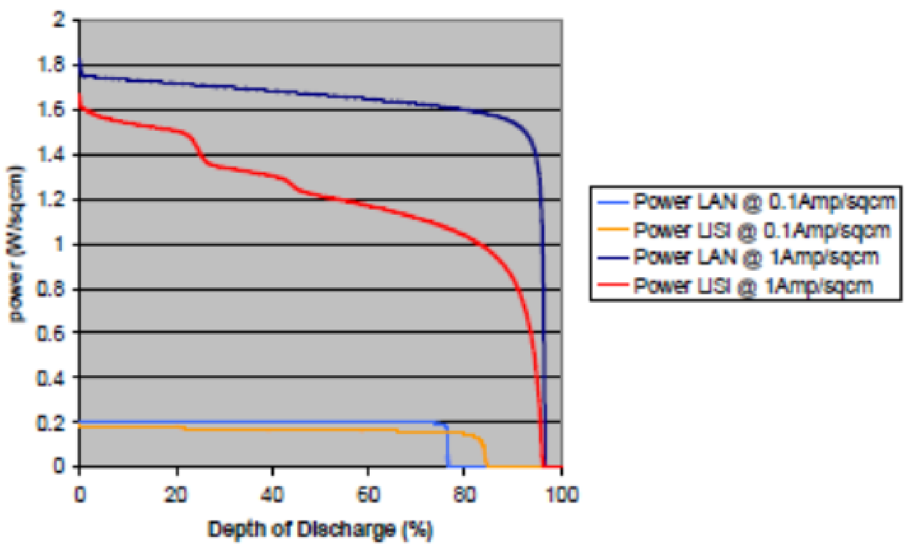

Figure 4 - Comparison of LAN and LiSi discharge rate at different current densities [2]

The cathode is mainly made from iron disulfide. Iron disulfide exists in two forms: pyrite and marcasite. Pyrite is the form most discussed in the construction of thermal batteries because it is stable above 700K. [4] Cobalt sulfide has been developed for rechargeable applications since it has a lower solubility in the molten electrolyte than iron disulfide. For secondary batteries in the automotive industry, iron (II) sulfide can be used. It is only of interest in secondary battery systems due to the lower voltage plateau it creates. Other transition metal sulfides are under study for use as the cathode in thermal batteries. [4] The electrolyte is a proprietary mixture of lithium salts. The type of salt and ratio of the mixture differs based on the manufacturer and the desired battery capacity, voltage and amperage. The salt mixture is formulated so that it is highly conductive and has low polarization. [2] Alkali halide salts have been used for the lower melting temperature so the pyrotechnic igniter can be eliminated from the battery design. [5] The standard igniter of the thermal battery chemical reaction is a hot thin film bridge wire with patterns of heat generating materials. [6] The patterns are designed so that different pyrotechnic powders will be ignited in the correct order. Semiconductor bridges have also been considered for igniters for thermal batteries. [8]

How Do Thermal Batteries Work?

Thermal batteries work through a chemical reaction of the lithium salt mixture. The battery has many cells in series that each has an anode, cathode, electrolyte, and igniter. The igniter sets off pyrotechnic reactions in each cell which increases the temperature to the melting point of the electrolyte. The molten electrolyte is highly conductive which allows current to flow between the anode and cathode of each cell.

Reliability Risks

As with any electronic device, there are some reliability risk associated with the storage and use of thermal batteries. Thermal batteries are designed to be in storage for 20+ years then be used at full capacity. The electrolyte is stored as a solid salt, but still can react with the anode and cathode materials over the expected storage time. The chemical reaction can reduce the power capacity of the battery as well as damage the anode or cathode. Selecting the correct anode, cathode, and electrolyte is important to minimize this chemical degradation over time. This is the least common of the possible failure modes since manufacturer's take great care in selecting the correct materials. The igniter is the primary cause of failure in thermal batteries. The igniter relies on good construction during manufacturing for correct operation. The metal filaments used in the filament bridge can have kinks or other material flaws. These flaws lead to uneven heating of the filament and ultimately ignition failure. [6] The igniter failure can be the igniter not firing correctly such as only igniting some of the cells which causes the voltage to be less than the designed voltage. The igniter can fail by not activating the cells in the correct order or timing which changes the voltage and current of the battery and activation time of the battery. In some applications, the activation time of the battery is critical. Manufacturers have been working on increasing the reliability of the igniter. They have considered two other technologies to replace the current ignition system: semiconductor bridge and laser ignition. They have also changed the manufacturing process such as using directional physical vapor deposition to create the metal filament.

Application

Manufacturers are developing better cathode, anode, and electrolyte chemistries for better stability and better ignition systems for improved safety and reliability. They are also working to increase the operating time of the battery. The ASB-Group has developed a new cathode technology called MS2 which increases the safe operating temperature of the battery. They have also worked to improve the ignition system by changing the hot wire electrical igniter with a laser igniter seen in Figure 5. The laser allows for the battery to not accidentally ignite at temperatures up to 400C. [2]

Figure 5 - Laser igniter from Photonics

Thermal batteries are designed for long term storage which is ideal for smart munitions developed for the military. These batteries are very reliable, but have some room for improvement. The igniter can have manufacturing defects which would cause it to not melt the electrolyte. The long storage time can lead to undesired chemical reactions between the anode, cathode, and electrolyte. Manufacturers of these batteries are developing new technologies to improve the reliability of the batteries and increase the battery capacity.

Future

Future application of thermal batteries will likely depend on technological innovation, flexible design and the development of new materials.

References

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