

Sodium Metal Chloride Battery Safety in Standby Applications

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Abstract

The new high density battery technologies have provided room for new application growth in many industries, such as: telecom, data centers, electric vehicles, aviation, and energy storage systems. Rapid deployments of these new products and recent events have raised industry engineering suspicion where safety is concerned.

This paper will discuss the details of the safety features of the sodium metal chloride battery, including chemistry, product design and construction, and electronic control systems. The Fiamm Telecom series batteries will be used as examples in this discussion. Particular attention will be given to conditions that can lead to events that have been known to cause catastrophic failures in battery systems, such as mechanical damage, temperature events, and mishandling or incorrect installation. Both internal and third party testing data will be referenced in this discussion.

Introduction

Battery safety has always been an engineering concern when it comes to power system design. With the introduction of new chemistries and new high density storage batteries and systems, new undiscovered failure modes have occurred when these products have been applied in real world applications. Safety concerns by Engineering and Management people have been raised for all new technologies as a result.

Several factors can contribute to the failures experienced by new energy storage technologies including improper or poor design, misuse, and misapplication. Most systems designed today are reasonably safe if the application is never subject to conditions outside of the design parameters. Variable environmental conditions and increased demand for performance are challenging power engineers, making new, relatively unproven technologies more and more attractive alternatives. This pressure to apply new products to solve these challenges has presented the industry as a whole with new problems that affect the culture, techniques and methodologies we have always relied on in the industry.

Battery and Energy Storage Systems Design Limitations

Different battery or energy storage systems have very different design limitations, with the chemistry and materials used in their construction being one of the main elements that control that determination. One of the main design considerations for battery or energy storage products is operating temperature; most applications have a wide operating range requirement. This is a challenge for most battery chemistries, as the performance is generally reduced at the extremes of these ranges. Other considerations include mechanical stresses, cycling, storage and design life. All of these limitations must be considered in the engineering and design of these power systems.

Energy Storage System Failures

By design, any energy storage system has the potential to release the energy it has stored. Hopefully in the controlled manner it was designed to do. Accidental or unintentional release of this energy is generally what most engineers fear. This uncontrolled release of energy can be caused by system failures, application outside of the design limits, external environmental incidents causing mechanical damage, and of course human error. If this does occur, chain reactions and cascade events can exaggerate any damage to the surrounding equipment and facilities.

Energy storage system engineering teams make every effort to design systems to operate safely under all reasonable design conditions as the norm; it is the unreasonable conditions that are hard to design around. Engineering for every contingency may produce a design that is too costly or too complicated for the application. The alternative is a design that may not perform at the required level, or in the worst case fail to deliver the required energy at all.

The engineering challenges that concern safety in the above mentioned design limitations and potential failure modes are solved by different technologies in different ways. Presented below is a description of the intrinsic safety that one of the SMC technologies **Sodium Nickel Chloride** offers in its chemistry and system design.

SMC Battery General Description

The Sodium Nickel Chloride battery is a complete battery system designed for applications in multiple markets. The battery is assembled with multiple 2.58 OCV Sodium-Nickel cells in a series configuration. The multi-cell strings are paralleled to increase capacity (Amp Hour ratings). The battery is provided with internal electric heaters to achieve and maintain the internal working temperature of 265°C. The thermal insulation of the battery is such that, with an internal temperature of 265°C, the surface temperature of the enclosure is just a few degrees above the environment. The Sodium-Nickel technology has proven to present relatively low intrinsic risks during normal operation. Additional safety is provided by the integrated Battery Management System (BMS) which issues warning signals when the operating conditions exceed the limits and disconnects the battery if the dangerous condition persists.

Multiple levels of safety

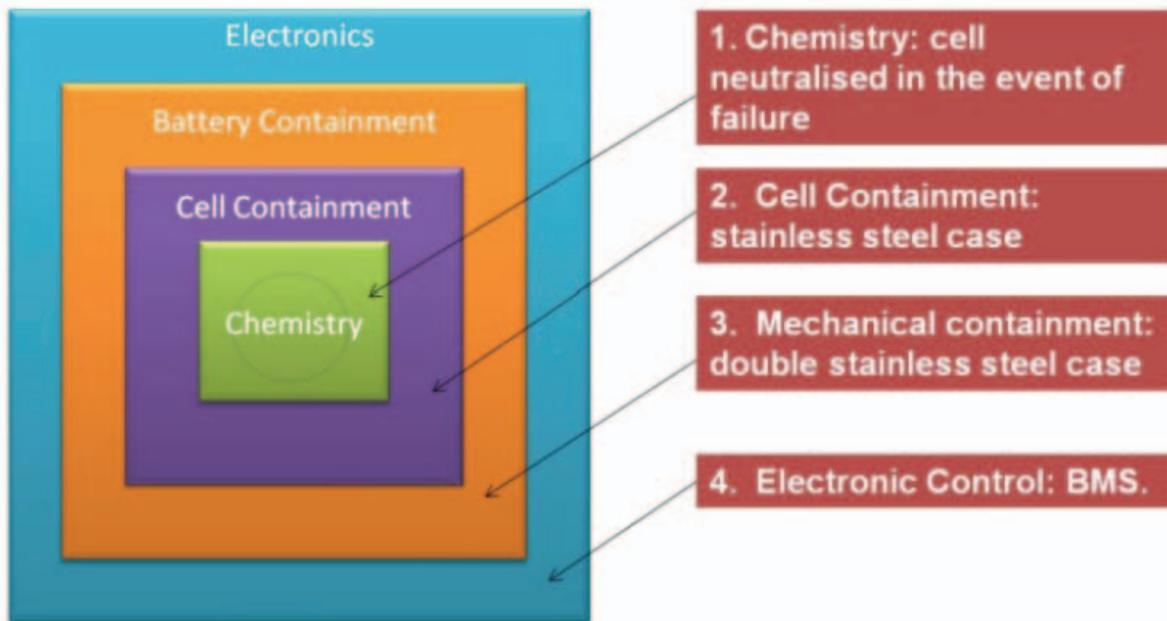


Figure 1 - SMC Multiple Levels of Safety

Figure 1 shows four levels of safety of the SMC's technology design used in field deployments to date. The four levels represented above will be described in detail.

Level 1 Cell Chemistry

The first level is a condition of the cell chemistry, SMC batteries are comprised of Sodium/Nickel chloride (Na/NiCl_2) cells that operate at relatively high temperatures (265°C), and use a **negative electrode composed of liquid metal sodium**, and an **impermeable solid synthesized electrolyte**, that is, a white ceramic β'' **alumina** (produced from oxides and hydroxides of aluminum, sodium, and other trace metals), to separate the negative electrode from the positive electrode.

The **Positive electrode section** is constituted by an insoluble transition metal chloride (a mixture of FeCl_2 and NiCl_2 + minor quantities of other halogenated salts) supported on a sintered nickel metal porous matrix and a **secondary electrolyte of molten sodium tetrachloroaluminate** (NaAlCl_4), which serves to conduct sodium ions between this electrode and the ceramic electrolyte tube. The positive electrode metal chloride phase is fabricated in the discharged state from a mixture of common salt, nickel, iron, and aluminum in an inert (nitrogen) atmosphere. The initial charge oxidizes these metals and decomposes the salt to sodium and chloride ions, with the chloride ions combining with the oxidized metals. Battery discharge results in the reverse reaction.

The tube-like structure ceramic β'' **alumina** serves as a physical separator, preventing direct chemical reactions between the electrode constituents, and as a conductor of sodium ions between the electrodes. This physical separator is several millimeters thick which allows it to be a very sturdy barrier.

The **negative electrode** consists of sodium metal in liquid phase. The material is contained between the cell casing and exterior of the **β'' -alumina** tube. Because the sodium constituting the negative electrode is obtained during the initial charge, metallic sodium need not be handled or used during the manufacture of the SMC cells. The metallic sodium is minimized in the fully discharged state and can be left in this condition indefinitely.

The cells **do not vent gases or other substances during normal operation**, and **do not contain materials characterized by high vapor pressures** at the temperature ranges associated with such operation. Among the different chemicals inside the cell, metal liquid sodium (Na) has the higher vapor pressure, but it boils at 882°C, i.e., at a temperature about 600°C greater than the normal operating temperature of the battery (265°C). This temperature is very unlikely to be reached even during failure conditions.

The **Main hazards related to the chemical components of the battery cells** are reported in the following paragraphs, including some considerations about their relevance in abnormal behavior or failure conditions of the battery that will be better addressed later in this document, discussing each possible accident or failure of interest.

Nickel, nickel chloride, sodium, and some cell additives (iron sulphide and nickel fluoride) are potentially hazardous. The actual severity and nature of risk imposed depend on specific circumstances such as the amount of material, the length and type of exposure, and factors such as the presence of ignition sources or incompatible substances, such as strong acids.

Positive Electrode

Nickel metal and Nickel chloride powders are considered hazardous and should be handled according to appropriate safety guidelines. Fine nickel powder or dust is highly combustible; however during the first charging cycle, these powders present in the cell cathode undergo a thorough sintering process and are transformed into a porous solid body. Therefore, nickel fine powders are not present in the battery during service.

Nickel chloride (NiCl₂) does not support combustion and is not considered to be a fire hazard, nor is it considered to be particularly reactive. Acute and chronic health hazards may include dermal, eye, and respiratory irritation and may cause allergic reactions.

Aluminum (Al) is not considered to be particularly hazardous, either in safety or toxicological terms. Aluminum dusts are considered to be nuisance particulates, with few adverse effects on respiratory tissues when exposures are kept under reasonable control. Powdered aluminum is stable under ordinary conditions of use and storage. Very small quantities of the metal are used in the cell.

Sodium chloride (NaCl), that is the common salt, is not considered to be particularly hazardous, though it may irritate the skin and eyes.

Sodium tetrachloroaluminate (NaAlCl₄) is reactive with water and in the presence of water will corrode steel. Exposure to high enough temperatures, in the presence of moisture, may result in the formation of **hydrochloric acid (HCl)**, followed, possibly but unlikely, by the formation of **Chlorine gas (Cl₂)**.

β'' -Alumina Ceramic Electrolyte

Sodium β'' -alumina is incombustible, nonreactive and is not known to present any health hazards beyond irritation to the eyes and respiratory system upon exposure to high concentrations of dust. Upon exposure to air, it absorbs CO₂ and water without significant heat evolution.

Negative Electrode

Sodium metal (Na) is highly reactive. It presents internal and external health hazards, including the risk of burns and irritation to the mucous membranes and respiratory tract. Safe handling requires a ventilation system, personal respirators, impervious clothing, and eye or face protection. Sodium reacts violently with water and oxygen and virtually anything else that is capable of being reduced. It is flammable in a normal atmosphere, corrosive and exothermically reactive with water or atmospheric moisture, releasing **Hydrogen gas (H₂)** that is ignited by the heat of the reaction. Sodium fires burn violently and may be accompanied by explosions that splatter the molten metal. Absolutely, water cannot be used as a fire extinguishing agent; nor should carbon dioxide or dry chemical extinguishing agents be used. Fires should be suppressed with powdered graphite, dry soda ash, powdered salt, sand, or metal-fire extinguishing powder such as Met-L-X. It should be noted, that SMC product safety is designed around minimizing any metallic sodium available in the event of a failure of one or more of the systems as discussed below.

Additives

Powdered aluminum does not pose health hazards beyond physical dust irritation and is stable under ordinary conditions of use and storage. However, it is moderately flammable and can produce **Hydrogen** when exposed to water, although it is much less hazardous than Sodium is. During the first charge, performed within the manufacturing process, all the aluminum powder is sintered and becomes part of the cathodic porous structure.

Sodium fluoride (NaF) can irritate tissue if inhaled or ingested. It does not present unusual fire or explosive hazards and fires in which it is involved can be extinguished with agents appropriate for the other materials around it. Sodium fluoride is stable and not considered to pose a fire hazard, but it will react with acids to form corrosive **Hydrofluoric acid (HF)**. Inhalation may be harmful or fatal even at low concentrations (30 ppm).

Iron sulphide (FeS) is considered stable under normal temperatures and pressures, but should not be combined with strong acids or oxidants, since sulfur oxides and **Hydrogen sulfide (H₂S)** may be produced as a result. Iron sulfide dust may cause physical irritation to the respiratory and digestive tracts.

Other Cell Materials

Materials such as copper, aluminum, mild steel and the alumina used in the seals do not pose significant intrinsic safety or health hazards.

Level 2 Cell Containment

The SMC cells are contained within a hermetically-sealed, nickel-plated steel case, 100% X-rayed during the manufacturing process. Enclosure within the case makes exposure to nickel, nickel compounds, or sodium unlikely during normal operation. The cells do not vent gases or other substances during normal operation, and do not contain materials characterized by having high vapor pressures at the temperature ranges associated with such operation.

Among the different chemicals inside the operational cell, metallic liquid sodium (Na) has the higher vapor pressure, but it boils at 882°C, i.e., at a temperature about 600°C greater than the normal operating temperature of the battery (265°C), that is very unlikely to be reached, even in failure conditions.

Level 3 Battery Containment

SMC battery cells are housed within a temperature-controlled, stainless steel double-walled, mechanically-insulated battery case that does not include any combustible materials. This battery case or enclosure is intended to both protect the outside environment from the effects of mishaps within, and to protect internal battery components from external hazards (high-low temperature, water, humidity, corrosive agents, fire, impact, mechanical damage, etc.).

The micro porous silica insulated enclosure prevents heat buildup on the outside of the product even in the event of minor mechanical damage to the exterior of the product. Accidents resulting in the penetration of the battery case can be expected to compromise its insulating and containment functions, and, if severe enough, to rupture the cells contained inside, and, most likely the β'' -alumina tube that separate positive and negative electrodes, thus resulting in recombining of Na with molten sodium tetrachloroaluminate (NaAlCl_4) to salt (NaCl) and metal Aluminum (Al), minimizing or excluding the possibility of a liquid Na release outside the battery.

Level 4 Electronic Control (BMS)

The Battery Management System (BMS or BMU) is an electronic control and safety interlock, preventing and protecting cells against unwanted physical/electro-chemical deviations that could lead to hazardous conditions. Redundant safety micro-controllers watchdog all processes to ensure compliance to design intentions. The system utilizes multiple temperature sensors to measure operating parameters at various points in the product, in order to provide proper control in changing environmental conditions. A microprocessor-controlled overcurrent disconnect protects equipment and personnel in the case of external short circuits. Mechanical fusible links provide redundant protection to critical components should a control system fault occur.

In most DC system designs, multiple storage devices are connected to a common bus in parallel for increased capacity or redundancy. This can complicate safety as external energy is available and may contribute to further damage to equipment. The ability to isolate the energy storage portion of a modular system can have advantages in the event a problem develops in the system. This ability can allow remote disconnection capabilities for first responders if required.

Ability to provide state of health reports remotely simplifies maintenance related to the health and safety of the DC energy system.

Battery Failures

Internal battery failures caused by operational or environmental conditions outside of the design limits may cause failures of the internal working of the cell. Much of the challenge of safe Sodium Metal Chloride cells may be summarized as follows: minimize the quantity of sodium immediately available after failure of the ceramic electrolyte.

The fracture of the interposed β'' -alumina ceramic tube-shape electrolyte causes the reaction of sodium with sodium tetrachloroaluminate in the positive electrode side, which produces common salt and metal Aluminum, without any relevant effects, preventing release of any free Na outside the cell containment, as described below.

The β'' -alumina electrolyte serves to physically separate the electrodes, preventing direct chemical reactions between their constituents, but allowing sodium ions to pass.

In the case of failure of the solid ceramic electrolyte the anode material (liquid sodium), being of low viscosity, flows readily through the cracks into the positive electrode chamber and into contact with the molten electrolyte (sodium tetrachloroaluminate).

It is expected that the reaction between the anodic active material (molten metallic sodium) and the cathodic electrolyte (NaAlCl_4) will occur according to the following equation. The sodium reacts primarily with the molten electrolyte, as opposed to the positive electrode material (nickel or chlorinated nickel):



This reaction converts liquids to chemically stable solids (Table salt and Aluminum). No gasses are produced and it delivers only 2/3 of the overall energy as heat. Sodium tetrachloroaluminate vigorously reacts with sodium if agitated with it, but, in practical cells, it resides in the porous structure of the positive electrode. This has the effect of reducing the reaction rate, and hence, reducing heat generation.

Under test, positive electrodes were inserted into liquid sodium at cell operating temperatures. The temperature rose slowly up to a maximum of 400°C in about 10 minutes. In these tests, the cell remained sealed and conducting.

Aluminum, besides being non-hazardous and non-reactive, is electrically conductive and solid at the operating temperature range. As a result, when a β'' -alumina fracture takes place in a Sodium Nickel Chloride cell, the aluminum resulting from the ensuing reaction creates a physical barrier that prevents further reaction. This prevents additional release of the electrochemical energy potentially available (resulting in a lower than potentially possible temperature rise), but allows electrical conductivity between the cathode and the anode.

This effectively shorts the cell. The impedance remains very close to the value of an operating cell. This fault only causes a battery pack to have an overall voltage of approximately 2.58V lower per failed cell.

By design a failed cell should never reach a temperature which could cause adjacent cells in the cell pack to fail in a cascading manner.

Cell seal leakage: Laser welded 100% radiographed (X-Rayed) hermetic seals are used in cell manufacturing. Seal fatigue caused by excessive thermal cycling and/or vibration is considered unlikely. Should the outer seam open, liquid sodium escapes from the cell (the maximum amount of sodium that can escape from a cell is 40g or 1.4oz at 100% SOC) and reacts with atmospheric oxygen in the inner battery containment case to form solid sodium oxide. However, this solid blocks the opening and reseals the cell, preventing the further loss of sodium. If this fails to happen, oxygen diffuses into the negative electrode compartment of the cell, and the remaining sodium is oxidized, resulting in the gradual failure of the cell. Adjacent cells in the cell pack are not affected by this reaction.

If the inner seam fails, liquid sodium tetrachloroaluminate can leak out from the top of the cell and into the battery compartment, resulting in a small amount of "white smoke" (presumably Hydrochloric acid - HCl), with no damage to the battery other than to the immediate area exposed to the molten electrolyte. In good product designs, every battery is provided with an electronic circuit that measures the electric insulation between the cells and the battery box and in this way a leakage can be quickly detected.

Battery case damage: The steel casings are not considered to be subject to internal failure and would probably resist failure longer than the hermetic seals in the case of a buildup of internal pressure. SMC cells do not contain substances (such as polysulfide) that can attack the cell casing and compromise its containment function. Designers knowledgeable about the cells have found that any trauma capable of breaching the cell casing or seals will almost certainly also fracture the β'' -alumina (see above).

Non-combustible materials are interposed within the insulated double case; hence, no combustion can occur or can be sustained.

Events in which cells fail with intact cell casings have relatively straightforward consequences. The β'' -alumina tube fractures and relatively inconsequential amounts of heat are released, but no toxic or otherwise harmful substances are released into either the battery case or outside of it, as described above.

On the contrary, cell rupture or breaching, is potentially much more severe, given the reactive nature of sodium and, to a lesser degree, the chlorinated nickel present in the positive electrode. It has previously been emphasized that trauma capable of damaging a cell's casing or seal will almost certainly also fracture its β'' -alumina tube since that is the more fragile material. Most or all of the sodium is "consumed" in the resulting reaction between it and the molten sodium tetrachloroaluminate electrolyte, leaving little or none to escape outside of the cell.

In most standby applications an additional layer of mechanical protection is designed into the battery enclosure, cabinet, or rack, further preventing accidental mechanical damage to the product while it is in service.

In motive power applications the potential for more severe mechanical damage is of course possible. Should some sodium, however, escape the cell, it quickly reacts with the oxygen inside of the battery casing, given the high operating temperature of the battery. Nevertheless, the failure mode in which a cell case rupture occurs while the β'' -alumina tube remains intact has also been investigated. In this case, although somewhat unlikely, given the configuration of the cell, there could be the exposure of the molten electrolyte to atmospheric moisture and its subsequent decomposition into aluminum hydroxide and hydrochloric acid, in trace amounts. Aluminum hydroxide is not considered to be particularly hazardous, but hydrochloric acid can be dangerous if present in high enough concentrations.

The second possibility is the release or exposure to air of liquid sodium and its subsequent oxidation to sodium oxide and hydrogen. Should this occur via a seal failure, the nascent sodium oxide blocks the opening and prevents further sodium loss; however, assuming it were not, the sodium would either:

- (1) Gradually be converted to sodium oxide as oxygen diffused into the anode compartment through the rupture, resulting in the gradual failure of the cell
- (2) Spill into the battery compartment to react with oxygen there.

Overheating cells by a few hundred degrees above the normal operating temperature of 260°C has negligible effects.

All constituents of SMC cells have low vapor pressures below temperatures of approximately 800°C. Theoretically, the only component that would be expected to vaporize near this temperature vicinity is sodium itself, with a boiling point of 882°C. Therefore, it is unlikely that cells would be overheated to temperatures that approach the boiling points of any constituent; if this does occur, the consequences appear to be limited to a small amount of leakage of sodium outside the external battery case and reaction with air moisture, producing sodium hydroxide (NaOH) and Hydrogen gas.

Operational failures Overcharge and Over discharge conditions.

Recall that for nickel cells, the normal charging reaction is:

Normal Charge: $\text{Ni} + 2\text{NaCl} \rightarrow \text{NiCl}_2 + 2\text{Na}$.

The cell enters the overcharge phase when all its NaCl is consumed. Chlorination of the nickel cathode continues, but according to the following reaction:

1st Phase of Overcharge: $2\text{NaAlCl}_4 + \text{Ni} \rightarrow \text{NiCl}_2 + 2\text{Na} + 2\text{AlCl}_3$

If overcharge continues past the point at which all the cathode metal (nickel) is consumed, the liquid electrolyte decomposes:



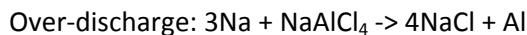
However, the second overcharge phase is unlikely to be reached in practical cells because of the likelihood of cell failure during the 1st Phase. The β'' -alumina tube fracture is likely to result during this phase, before the excess Nickel is depleted, since the space available in the anode is quickly exhausted by the excess sodium produced.

The result is that cells can, by default, be designed to tolerate a certain degree of overcharge, and then to fail safely, before chlorine is released.

The normal discharge reaction consists of de-chlorination of the nickel and iron in the cathode, respectively.



The cell enters the over-discharge phase when all the nickel and iron in the cathode are de-chlorinated; theoretically, discharge continues with the dissolution of the liquid electrolyte:



The over-discharge reaction is reversible, as long as it is not permitted to extend to proceed too far.

Continued over-discharge will result in cell failure via β'' -alumina fracture, because the excess aluminum and sodium chloride produced in the cathode compartment cannot be accommodated, in terms of space, or because they unevenly distribute current, creating localized high flux regions on the electrolyte.

In either case, the over-charge or over-discharge condition is very unlikely due to the functionalities of the Battery Management System (BMS), that is able either to set the charging voltage and to disconnect the battery from the charger when an anomalous high charging voltage is measured or is capable of detecting the different voltages produced during the discharge of iron, nickel and aluminum, and terminate the discharge function before the breakdown of the melt actually transpires.

Handling and Installation safety of SMC batteries is enhanced because of several factors. The number one factor is the product can be handled while there is no energy available on the output terminals. When the battery is in the cold state the reaction is halted and little to no energy is available. The energy storage elements are mechanically isolated by the BMS so even if the batteries are at operating temperature when handled, it can be done safely. This greatly reduces the chance of accidental short circuits during installation or maintenance. Special PPE or highly trained labor is not required to reduce the cases of human error when handling the product. Not all personnel in the supply chain have experience handling energy storage products, such as shipping and storage facility workers, this feature helps protect the product handlers from factory to end user.

Mechanical design of the external enclosure provides for lifting handles or lifting locations, making installation of the product above floor level safer as well.

These features help eliminate human error as a contributing factor to power systems accidents.

Summary

According to available literature and test documentation, a SMC battery system appears to present relatively low intrinsic risks during normal operation and in case of internal or externally-induced accidents:

1. Cell failures have been shown to have non-catastrophic results.
2. Cell failure chain reactions are difficult to start or sustain.
3. Cell constituents have low vapor pressures at operating temperatures and most temperatures to which they are likely to be exposed.
4. Sources of chronic corrosion are absent.
5. Cells are designed to fail safely when overcharged.
6. Cells fail safely when over-discharged.
7. Installation and maintenance safety enhanced by lack of energy on exposed terminals.

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