



# Sodium nickel chloride battery technology for large-scale stationary storage in the high voltage network



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## HIGHLIGHTS

- Sodium Nickel chloride batteries are suitable for large-scale stationary storage.
- Fire risk is negligible because of the intrinsic safety of the cell.
- The 3 h rate discharge makes this technology attractive for network services.
- All the risk indexes related to large-scale installations are quite low.
- All the NaNiCl<sub>2</sub> battery materials are recyclable with recycling efficiency of 50%.

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## ABSTRACT

The extensive application of Sodium–Nickel Chloride (Na–NiCl<sub>2</sub>) secondary batteries in electric and hybrid vehicles, in which the safety requirements are more restrictive than these of stationary storage applications, depicts the Na–NiCl<sub>2</sub> technology as perfectly suitable for the stationary storage applications. The risk of fire is negligible because of the intrinsic safety of the cell chemical reactions, related to the sodium-tetrachloroaluminate (NaAlCl<sub>4</sub>) content into the cell, which acts as a secondary electrolyte (the primary one being the ceramic β"-alumina as common for Na-Beta batteries). The 3 h rate discharge time makes this technology very attractive for load levelling, voltage regulation, time shifting and the power fluctuation mitigation of the renewable energy sources in both HV and EHV networks.

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## 1. Introduction

Batteries using molten sodium as anode and beta-alumina (β"-Al<sub>2</sub>O<sub>3</sub>) as solid ceramic electrolyte are sodium–nickel (Na–NiCl<sub>2</sub>) batteries, also known as ZEBRA batteries, and sodium–sulphur (Na–S) batteries, part of the sodium family [1–15].

The sodium–nickel technology was developed in the 80's in South-Africa and in Great Britain (ZEBRA Project) with the main purpose of development of high-performance batteries for zero-emission electrical vehicles.

The ZEBRA IP technology was purchased in 1999 by MES-DEA,

and then industrialized in Switzerland. In 2011 MES-DEA was sold to Fiamm Group which sets up a new company, Fiamm Sonick.

The beta-alumina ionic conductivity (of sodium ions) increases significantly with the temperature: at 300 °C the conductivity is equal to about 0.25 Ω<sup>-1</sup> cm<sup>-1</sup> and at 350 °C to 0.4 Ω<sup>-1</sup> cm<sup>-1</sup> [5]. The sodium cell operating temperature range is from about 250 °C to about 300 °C. For these characteristics sodium batteries are also called high temperature batteries.

The crystalline structure of the electrolyte allows the flow of sodium ions (fast ionic transport) while acting as good electric insulator. This characteristic, as well as the absence of secondary reactions, implies that there is not self-discharge in this type of cells. The reversible chemical reactions inside the cell at 300 °C provide an open circuit voltage (OCV) of 2.58 V. The anode chemical

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reaction is:



The voltage rises up to 3.05 V. In the overdischarge condition the chemical reaction is:



With regard to the sodium leakage from the cell to the external environment given by a strong external shock, it is worth noting that, in this occurrence, the  $\beta''$ -alumina would also break as well. Therefore the chemical reaction (4) excludes the sodium contact with the external environment that would have a theoretic specific energy equal to 3883 Wh/kg, through the reaction:



Moreover, before the battery initial charge operations, there is no metallic sodium inside the cell because it is present in the form of sodium chloride in the cathode zone, whereas the anode zone is empty. The anode material, that is the metallic sodium, is produced during the first charge operation.

Fig. 1 shows the constitutive elements of a cell.

It is worth noting that differently from Na-S technology, Na–NiCl<sub>2</sub> batteries are not affected by repeated freeze–thaw cycles because of the moderate differences between the thermal expansion coefficients of the ceramic separator, and the other battery components.

### 1.1. Description of the cell structure and of the cell electrical characteristics

From a structural stand point, the cell has a prismatic shape (see Fig. 1). For  $\beta''$ -alumina, as it is shown in Fig. 1, the four-lobe shape is the preferred one because it increases the active surface area minimizing the internal resistance. The positive pole is connected to a current collector which consists in a nickel conductor with the shape of a hairpin. The cathode material, in the form of granules of sodium chloride, nickel and iron, is poured inside the ceramic electrolyte which is externally surrounded by a mild steel profile which has the same shape of the ceramic electrolyte. The cell housing, which represents the negative pole, is made by a continuous welded steel tape with a nickel coating. An  $\alpha$ -alumina (Al<sub>2</sub>O<sub>3</sub>) collar is welded between the  $\beta''$ -alumina tube and the cell covering by means of borosilicate glass welding, so that the cell is hermetically sealed. Moreover there is not any battery emission in the atmosphere. The external terminal sealings are obtained by means of thermocompression bonding (TCB) of two nickel rings to the  $\alpha$ -alumina collar. Table 1 shows the principal electrical data of the cell. As it is well known, the voltage is not related to the cell dimensions, but it depends upon the cell thermodynamics.

Fig. 2 shows the cell voltage as a function of the State of Charge (SoC). The represented voltage behaviour from 100%–0% of SoC derives from experimental measurements. In this SoC range the open circuit voltage (OCV), which is related to the expression (3), is constantly equal to 2.58 V (it is worth comparing this value with the Na–S technology OCV, which is 2.076 V) from 98% to 30% of SoC.

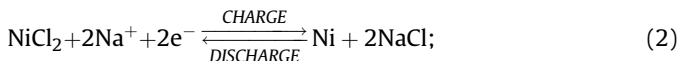
If the state of charge is greater than 105%, the OCV rises up to 3.05 V because of the over-charge reactions (5). Under 30% of SoC the OCV reduces to 2.35 V because of the reaction (6). The OCV behaviour in this SoC range, shown in Fig. 2 (grey zones), comes from the scientific literature.

### 1.2. Module assembly and electrical characteristics

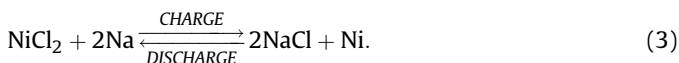
A module made of a series or parallel connection of



the cathode chemical reaction is:



so that the overall chemical reaction is



The theoretical specific energy associated with the expression (3) is equal to 788 Wh/kg. The key element in the intrinsic safety of Na–NiCl<sub>2</sub> technology is the presence of a secondary electrolyte in form of liquid salt, sodium-tetrachloroaluminate (NaAlCl<sub>4</sub>), added to the cathode compartment. This represents one of the major differences with the sodium-sulphur technology. The melting point of NaAlCl<sub>4</sub> is 158 °C, corresponding to the theoretical minimum operating temperature of the cell. The molten NaAlCl<sub>4</sub> dissociation involves the Na<sup>+</sup> ions and AlCl<sub>4</sub><sup>−</sup> ones conduction between the  $\beta''$ -alumina internal surface and the reaction zone of the NiCl<sub>2</sub> porous cathode. In normal working condition, the secondary electrolyte does not participate to the charge/discharge reactions, but it has a key role in the most likely failure mode of sodium cells, which is the  $\beta''$ -alumina breaking. In this situation, if the cell is based on Na–S technology, sulphur gets in contact with sodium (even if the safety tube presence reduces this interaction). On the contrary, in NaNiCl<sub>2</sub> cells, the presence of the secondary electrolyte (NaAlCl<sub>4</sub>) chemical reactions themselves reduces the effects of the exothermic reactions, which could be potentially dangerous. In fact, the secondary electrolyte reacts with the sodium and the products are sodium chloride and metallic aluminium through the following reaction:



The energy released by reaction (4) is just 2/3 than the normal charge/discharge energy released by reaction (3); therefore the reaction (4) is moderately exothermic and generates solid products with low vapour pressure that are not dangerous, or corrosive or reactive. Hence, the heat generated by the reactions does not create high pressures in both the steel cell enclosure and the cell sealing. Moreover, the generated aluminium acts as a short circuit between the anode and the cathode, so that the cell internal resistance becomes negligible. This implies that in fault conditions, a circuit consisting of several cells in series can continue to safely operate, even though with lower performances due to the reduction of the total voltage. In the same situation, a circuit made of Na–S cells in series would determine the opening of the circuit, and the entire string of cells would not be able to continue to operate. Therefore the Na–NiCl<sub>2</sub> batteries are more fault tolerant: it has been determined in Ref. [2] that the batteries can work even if the 5% ÷ 10% of the cells are internally short circuited. This makes possible the connection of several cells in series without employing parallel series connection. This characteristic plays a key role in stationary applications because the single cell failure rate has a very small influence on the availability of the entire module.

The cell overcharge performance depends upon the sodium quantity in the cathode part. If the charge operation continues even if the cell is fully charged, the secondary liquid electrolyte NaAlCl<sub>4</sub> guarantees a sodium reserve through the following reaction:

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