

Salt Batteries: Opportunities and applications of storage systems based on sodium nickel chloride batteries



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Abstract

Sodium-Nickel-Chloride (Na-NiCl₂) batteries have risen as sustainable energy storage systems based on abundant (Na, Ni, Al) and non-critical raw materials. This study offers a general overview of this technology from its initial conceptualization, along with research and development perspectives and areas of use. Applications are for grid storage mainly due to the temperature of operation (275 – 350 °C). There is no critical issue on patent portfolio as the key IP is in the public domain. In addition, Switzerland is active in this technology with FzSoNick being a producer of commercial Na-NiCl₂.

This document was provided by the Policy Department for Economic, Scientific and Quality of Life Policies at the request of the Committee on Industry, Research and Energy (ITRE).

This document was requested by the European Parliament's committee on Industry, Research and Energy (ITRE).

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Original: EN

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Manuscript completed: January 2023
Date of publication: January 2023
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This document is available on the internet at:
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For citation purposes, the publication should be referenced as: Armand M., Ortiz-Vitoriano, N., Olarte, J., Salazar, A., Ferret, R., 2023, *Salt Batteries: Opportunities and applications of storage systems based on sodium nickel chloride batteries*, Publication for the committee on Industry, Research and Energy (ITRE), Policy Department for Economic, Scientific and Quality of Life Policies, European Parliament, Luxembourg. © Cover image used under licence from Adobe Stock.

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LIST OF ABBREVIATIONS

AEG	Anglo Batteries
BASE	Beta-Alumina Solid Electrolyte
CAPEX	Capital Expenditure
C-rate	Unit measuring the full charge/discharge rate of a battery
EV	Electric Vehicle
GW	Gigawatt
H₂	Hydrogen
kWh	Kilowatt-hour
LCOS	Levelized Cost of Storage
LIB	Li-ion Battery
Na[°]	sodium (Na) metal
NaAlX	Sodium Haloaluminate
Na-NiCl₂	Sodium-Nickel-Chloride
Na-S	Sodium-Sulfur Batteries
Ni[°]	Nickel (Ni) metal
NMC811	LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂
PHS	Pumped Hydro Storage
SIBs	Sodium-ion Batteries
TES	Thermal Energy Storage
UPS	Uninterruptible power supply
ZEBRA	Zeolite Battery Research Africa

EXECUTIVE SUMMARY

Background

Within modern society there is an increasing demand for efficient, economical, and sustainable energy storage solutions, driven in part by the integration of the greater shares of renewable energy required to counter the risk of climate change catastrophe. In this scenario, energy shifting and flexibility services are critical to securing system reliability, and are essential to ensuring energy supply in times of low renewable energy generation and maximum utilization in those moments of high renewable energy production. While other technologies¹ like demand-side flexibility that can reduce, increase or shift the demand within a specific duration may provide flexibility within the grid, the use of energy storage systems remains the preferably solution capable of providing the critical energy shifting service required to minimize renewable energy curtailment.

Among the available energy storage technologies², electrochemical energy in the form of batteries is key to the transformation of our society towards reduced and then zero, net greenhouse gas emissions. This is due to the ability of batteries to fulfil a range of important roles, such as increasing the use of solar and wind energy by balancing the supply and use of these intermittent renewable energies, increasing resiliency, providing backup power during power outages, stabilizing the grid and lowering the cost of meeting peak power demand, as well as facilitating the use of battery-powered road vehicles (EVs).

However, frequently different roles have different requirements, and thus may be best fulfilled by different battery technologies. For example, a simple approximation suggests that, assuming an energy density of 120 Wh/kg, 20 million tonnes of batteries would be required to turn 10% of the global car fleet into EVs, while with the same assumption approximately 60 million tonnes of the same type of batteries would be needed to store 10% of daily global renewable electricity production. Consequently, while volumetric and gravimetric energy densities are the most important parameters for EV batteries, there is a bigger market of grid storage that emphasises the sustainability of its material resources - and it is unlikely that a single system will meet all potential applications.

Looking to the future, markets based on lithium-ion battery (LIB) technology will face significant challenges. Being ideally suited to EV applications, LIB demand and production is expected to rise dramatically, and it is probable that Li will be in short supply within 20 years³. Moreover, the deployment of LIBs for stationary electrical energy storage applications and the following stress of Li and Co supply chains makes it critical to develop alternative technologies capable of supporting this other area. A major investment and research effort is, therefore, ongoing to develop new chemistries based on abundant and non-critical raw materials with a low environmental impact.

In this scenario, sodium is one of the elements showing great promise and systems capable of exploiting this metal are attracting considerable interest. Consequently, high-temperature sodium-based batteries, such as sodium-nickel chloride (Na-NiCl₂), are being carefully reconsidered, as they are based on abundant and non-critical raw materials (non-CRMs).

¹ Aggarwal, S., Orvis, R., Grid flexibility; methods for modernizing the power grid, March 2016.

² Pfeifenberger, J., The future of energy storage: An interdisciplinary, MIT study, 17 November 2022.

³ Skidmore, Z., Lithium shortages: threat or opportunity?, Mining Technology, 16 June 2022.

Longo et al.⁴ presents one of the first life-cycle assessment analyses of sodium/nickel chloride batteries in energy and environmental impacts of this technology and provides a set of energy and environmental outcomes identifying the “hot spots” of the selected technology that must be carefully considered to upgrade the current efficiency and sustainability.

The aim of this report is an evaluation of the performances, sustainability and applications of Na-NiCl₂ batteries, which belong to the class of molten salt batteries also called ZEBRA and operate at around 300°C. Na-NiCl₂ batteries may arise as a market opportunity in the integration of renewable energy storage technologies due to the expected large market growth and possible material supply shortage of currently used technologies (e.g., LIB). This scenario would be possible if Na-NiCl₂ safety and cost advantages can be demonstrated.

This technology, like other cell-based chemistries, is made up of modular units that can be scaled up to store energy ranging from a few kilowatt-hours (kWh) to tens of megawatt-hours (MWh). The ZEBRA batteries meet the requirements in terms of performance (~120 Wh/kg), cycle life (~5000 cycles, 10 years operation) and cost (550-750 €/kWh). In terms of material costs (except for Ni), this technology has the potential to compete well with other technologies, despite the disadvantage of the additional cost of thermal control systems. It should be noted that production costs are highly sensitive to production volume, and Na-NiCl₂ technology has yet to reach a high level of production volume (e.g., when compared to lithium), putting it at a disadvantage. In addition, their temperature of operation (300°C) is a handicap, since, as reported by P. Van den Bossche et al.⁵, 7.2% of the battery energy is used for heating. This fact prevents their use for EV applications, making them instead well suited for grid storage and load levelling applications. Their main competitors are sodium-sulphur batteries (Na-S), which work at same temperatures and have similar costs and cycle life.

Regarding environmental concerns, the main raw materials used in the production of Na-NiCl₂ batteries are sodium (Na), chlorine (Cl), and nickel (Ni), which are non-hazardous and globally available elements. In addition, discharged batteries can be easily recycled and their nickel recovered. Na-NiCl₂ cells, if completely discharged, no longer contains dangerous (reactive) materials. Their batteries are shorted before beginning their recycling process. Regarding safety, Na-NiCl₂ batteries are considered reliable and low maintenance. The use of Na metal at high temperature poses a significant risk, which is mitigated by a specific cell design, leading to solid precipitates in case Na metal gets in contact with the liquid electrolyte. The ZEBRA battery system is a mature technology and research efforts are focused on reducing its operating temperature; however, with limited success. Some EU companies are committed to industrially launch a new promising ad-hoc product for stationary electrical energy storage applications with an expected competitive cost and relatively long-life in terms of both years (15) and cycles (~ 5000).

From an application standpoint, the ZEBRA technology can be a substitute of Na-S technology. It can be applied in cases of similar power and energy range and discharge rates of hours, and has thus been primarily used in time-shifting and EVs. Na-NiCl₂ batteries offer high scalability and flexible assembly in many battery and system sizes for a wide variety of applications, being the most developed grid load levelling and energy storage device for renewable energy production. Their main challenge is the implementation of a robust thermal control system keeping the battery temperature at 300°C.

⁴ Longo, S. et al., Life cycle assessment of storage systems: the case study of sodium/nickel chloride battery, *Journal of Cleaner Productions*, Elsevier, January 2013.

⁵ Van den Bossche, P., Vergels, F., Van Mierlo, J., Matheys, J., Van Autenboer, W., SUBAT: An assessment of sustainable battery technology, *Journal of Power Sources*, vol. 162, n.o 2, pp. 913-919, November 2006.

Market requirements, driven by improvements of Levelized Cost of Storage (LCOS), tend to prioritize cells in the segment of higher production volumes. The benefits of using cheap and readily available materials may pique interest in this technology, but its operating temperature and slow charging process (over 8 hours, or C/8) put it at a disadvantage when compared to other technologies, such as Na-ion.

In 2022, the only remaining producer of commercial sodium-nickel-chloride batteries is the Swiss company FzSoNick. Their batteries are primarily used as backup power sources for telecommunication antennas but have a high potential for the large-scale grid storage required for the implementation of renewable energy production.

1. INTRODUCTION

KEY FINDINGS

Energy storage undoubtedly plays a fundamental role in the process of total decarbonisation of the global economy, which is expected to take place in the coming decades. The transition to renewable and sustainable energy generation and electrified transport will contribute to reducing greenhouse gas emissions. Consequently, Europe intends to achieve the goal of becoming the world's first decarbonized economy by 2050.

In this transition scenario, there is a strong reliance on the use of batteries, which must become cleaner, safer, and cheaper while maintaining good performance. Batteries enable increasing use of solar and wind energy, but may also increase resiliency, provide backup power during power outages, stabilize the grid, and lower the cost of meeting peak power demand. In addition, batteries are one key technology in facilitating high levels of EV penetration in the future.

To meet the wide range of needs, high-temperature batteries, such as sodium-nickel-chloride (Na-NiCl₂), arise as a sustainable approach to developing energy storage applications based on abundant and non-critical raw materials.

Because of the expected large market growth and possible material supply shortage of existing technologies, in a scenario of global competition where there will not be a single technology winner there may well be room for Na-NiCl₂ in the renewable integration energy storage market providing its safety and cost advantages can be proven.

Our society is in dire need of efficient, economical, and sustainable ways of store the higher shares of renewable energy needed to counter climate catastrophe.

While flexibility services can be delivered by many technologies, energy storage is the preferably solution able to provide the essential energy shifting service, which is key to minimising renewable energy curtailment. An efficient energy storage will ensure a self-sufficient European energy economy by maximising utilisation of local renewables, reducing reliance on external fossil fuel imports, which in turn will alleviate the high electricity prices seen today⁶.

Analysts at the European Association for Storage Energy (EASE) have modelled a need for ca. 14 GW (Gigawatt) per year of new energy storage deployment in Europe to meet the forecasted requirements of 200 GW by 2030 and 600 GW by 2050⁷. Large amounts of renewable energy will be therefore necessary. Together with battery installations, they represent already a practical alternative in terms of cost and technology to conventional power plants.

However, stationary electrical energy storage is a small proportion of the total battery production capacity, which is led by the EV industry. The demand for batteries is expected to grow by around 30 percent, nearing 4,500 Gigawatt-hours (GWh) a year globally by 2030. The battery value chain is expected to increase by as much as ten times between 2020 and 2030 to up to €379 billion⁸.

⁶ European Commission, REPowerEU Plan, May 2022.

⁷ EASE, Energy Storage Targets 2030 and 2050, Ensuring Europe's Energy Security in a Renewable Energy System, June 2022.

⁸ Campagnol, N. et al., Capturing the battery value-chain opportunity, McKinsey, 7 January 2022.

For EVs batteries and energy storage alone, Europe will need up to 18 times more lithium by 2030 and up to 60 times more by 2050⁹.

Today the sustainability of this booming market is being questioned due to the energy-intensive manufacturing process of the batteries, demand for scarce resources and limited recyclability, among other reasons. In future, energy storage markets based on Li-ion battery (LIB) technology will face significant challenges. Nonetheless, European battery energy storage deployments are expected to plateau over the 2024 - 2027 period due to Li-ion scarcity¹⁰. Moreover, currently the weakest point in the EU battery supply chain is its reliance upon critical raw materials, particularly graphite, cobalt, and lithium. Anode production is another weak point, though in 2020 the EU battery alliance announced certain positive developments, mostly in Finland and Sweden¹¹.

Based on this scenario, a major research and investment effort is underway to develop new chemistries based on more abundant and low environmental impact materials. Sodium is one of the most promising elements and systems based on high temperature salts, which are being re-evaluated. In this scenario, high-temperature sodium-based batteries, such as sodium-nickel chloride (Na-NiCl₂), arise as a sustainable technology based on abundant and non-critical raw materials (non-CRMs). Currently such energy storage systems have only been successfully utilized in a few niche applications (e.g., submarines and missile power supplies), despite their demonstrated reliability and safety¹². Some uses of large-scale stationary battery storage in application areas similar to high-temperature sodium-sulphur batteries have been considered.

1.1. Brief history of technology development

There are several energy-storage approaches such as the mechanical (e.g., PHS power plants), TES (e.g., thermochemical storage), chemical (e.g., hydrogen-electrolyser & combustion cells), electrochemical (e.g., batteries), and superconducting magnetic¹³ (e.g., superconducting magnetic coils). However, currently the widely implemented predominant technologies are PHS power plants and batteries. Batteries cost reduction together with the advantage of providing more power per area unit, better deploying conditions offering a wide range of scales (kilowatts to megawatts) is causing that battery energy storage systems are one of the fastest growing technologies in the sustainable energy industry.

A battery is composed of electrochemical cell(s), which are devices capable of either converting between chemical and electrical energy. There are many ways to classify batteries apart from whether they are primary (single use) or secondary (more than one use, i.e. rechargeable). For example, secondary batteries can be classified considering the main metal involved (e.g., lithium-based, zinc-based, sodium-based, etc.), or considering the state of the electrolyte (e.g., liquid, solid, etc.).

A molten salt battery is a class of batteries, which uses molten salts as the electrolyte and for this reason must operate at a high temperature. At room temperature, the components of molten salt batteries are solid, allowing them to be stored inactive for long periods of time (which is intrinsically safer than the storage of the extensively used lithium-ion batteries). These batteries have a main drawback in the design of a robust thermal system needed to keep their components in the liquid state.

⁹ European Commission, Commission announces actions to make Europe's raw materials supply more secure and sustainable, EU Press Corner, 3 September 2020.

¹⁰ Murray, C., Energy storage news, June 15, 2022.

¹¹ InnoEnergy, Supply of graphite from Europe, European Battery Alliance, 10 November 2020.

¹² Dühnen, S. et al., Toward Green Battery Cells: Perspective on Materials and Technologies, Small Methods, 4, 7, 2000039, 6 April 2020.

¹³ Superconducting Magnetic Energy Storage (SMES) is a novel technology that stores electricity from the grid within the magnetic field of a coil comprised of superconducting wire with near-zero loss of energy.

The idea of using high-temperature battery systems emerged in the 1970s, with the goal of outperforming the state of the art at that time. Sodium-sulphur (Na-S), one of the first molten salt battery concepts, became commercially available in the '90s for stationary electrical energy storage applications and had a normal operating temperature range of 300-350°C.

The sodium-metal chloride electrochemical cell was patented in 1975 by John J. Werth of ESB Incorporated¹⁴. Development of sodium-metal chloride electrochemical cells for use in batteries began in 1978, with the efforts of Johan Coetzer at the Council for Scientific and Industrial Research (CSIR) in Pretoria¹⁵, South Africa. Initially, sodium-metal chloride cells were developed with iron (Na/Fe-FeCl₂) as low-cost active material, exhibiting a theoretical capacity of 310 mAh/g, which was judged as the optimal capacity for stationary electrical energy storage applications. Na/Fe-FeCl₂ cells had already been successfully used in electric cars with kWh (kilowatt-hour)-scale batteries.

In the same institution (CSIR), in 1985 Coetzer developed a sodium-nickel chloride (Na-NiCl₂) battery through the Zeolite Battery Research Africa Project (ZEBRA). This version of the sodium-metal chloride battery, known as the ZEBRA battery, used a solid-state electrolyte (beta-alumina ceramic) and demonstrated a comparable capacity (305 mAh/g) but with a higher voltage and superior cycle life¹⁶. Moreover, cells were assembled in the discharged state, which eliminated the need for handling metal chlorides and metallic sodium.

In 1998, one decade later, Anglo Batteries (AEG) assembled maintenance-free ZEBRA battery systems for electric vehicles in a pilot line, providing higher energy density than NiMH and lead acid batteries¹⁷. One year later, Galloway and Haslam developed a ZEBRA battery with a specific energy of 140 Wh/kg¹⁸, while that same year the MES-DEA company industrialized ZEBRA battery technology in Stabio, Switzerland, focusing on electromotive applications¹⁹. A few years later, in 2011, General Electric commercialised Na-NiCl₂ batteries in the US targeting large-scale grid applications. However, due to the slow market for grid-scale energy storage, General Electric had no option but to scale back, finally stopping production in 2015²⁰.

In 2022, the only remaining producer of commercial sodium-nickel-chloride batteries is the Swiss company FzSoNick. Their batteries are primarily used as backup power sources for telecommunication antennas but have a high potential for the large-scale grid storage required for the implementation of renewable energy production. Currently, Na-NiCl₂ technology is already commercially available at grid-scale, offering a battery-level energy density of 120 Wh/kg and a normal operating temperature range of 270-350°C. A recent initiative impulse by Altech Chemicals Limited has executed a joint venture agreement with the leading German battery institute Fraunhofer IKTS to commercialise the Sodium Alumina Solid State (SAS) Battery²¹. The consortium claims batteries with stable, safe, and cost-competitive performances. Another novel Na-Zn ZEBRA battery replacing its Ni-electrode with cheap and abundant Zn has also been proposed for transfer to the market (SOLSTICE company)²².

¹⁴ U.S. Patent #3877984, April 15, 1975. The patent was filed on April 24, 1974 and references patents #3663295 (May 1972, by Baker) and #3751298 (August 1973, by Senderoff).

¹⁵ Sudworth, J. L., The sodium/nickel chloride (ZEBRA) battery, *J. Power Sources*, 100, 149, 2001.

¹⁶ Coetzer, J. et al., Patent: Cathode for an electrochemical cell and an electrochemical cell, US 4288506, 1978.

¹⁷ Dustmann, C. H., ZEBRA battery meets USABC goals, *J. Power Sources*, 72, 27, 1998.

¹⁸ Galloway, R. C., et al., The ZEBRA electric vehicle battery: power and energy improvements, *J. Power Sources*, 80, 164, 1999.

¹⁹ Sudworth J. L., Zebra Batteries, *J. Power Sources* 51, 105, 1994.

²⁰ John, J. St., GE scales back production of grid-scale Durathon batteries, 2015.

²¹ Altech Chemicals LTD, German Sodium Alumina Solid State (SAS) Battery Project.

²² Solstice, Sodium-Zinc molten salt batteries for low-cost stationary storage company.

1.2. What is a Na-NiCl₂ battery?

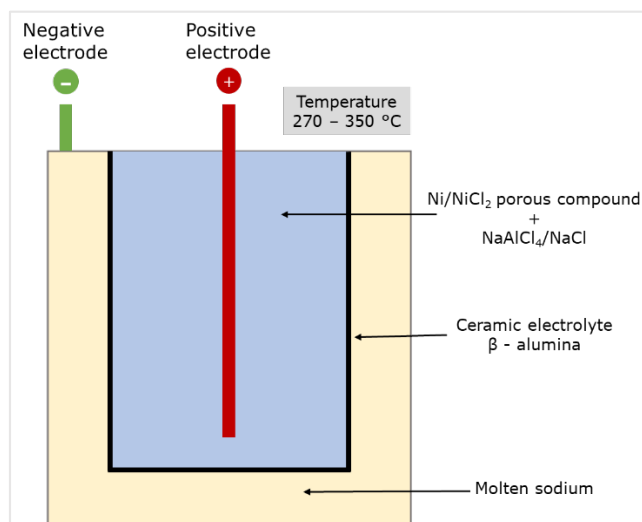
1.2.1. Working principle

As shown in Figure 1, a Na-NiCl₂ battery consists of a ceramic tube with a positive terminal (i.e., cathode) in its centre. The solid ceramic tube, composed of β -alumina material, performs the same function as a liquid electrolyte in a Li-ion battery, allowing for the transfer of sodium ions through it. The ceramic tube is filled with the cathode, which consists mainly of nickel and sodium chloride. The tube is also flooded with a secondary electrolyte consisting of molten tetrachloroaluminate (NaAlCl₄) saturated with sodium chloride (NaCl), which fills the pores in the positive electrode compartment. The ceramic tube is housed in a steel canister acting as negative terminal. The Na-NiCl₂ battery operating mechanism relies on the electrochemical reactions between the positive electrode (cathode) and the negative electrode (anode). The overall chemical reaction of the battery is:



The battery temperature is maintained between 270 °C and 350 °C to keep the electrolytes in a molten state (i.e., independent heaters are included in the battery system).

Figure 1: Configuration of a Na-NiCl₂ battery



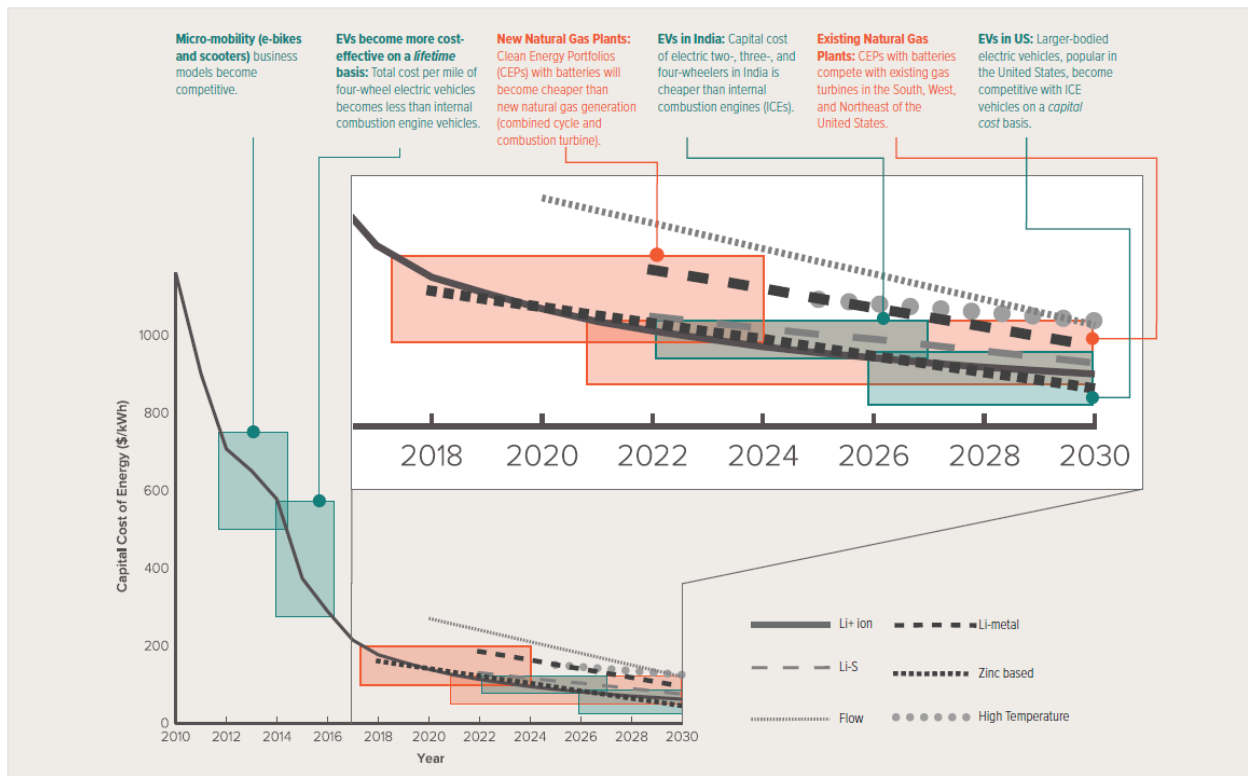
Source: Authors' own elaboration.

1.2.2. Cell, module and unit characteristics

Similar to other cell-based chemistries, this technology consists of modular units that can be scaled-up to store energy from anywhere between a few kilowatt-hours (kWh) to tens of megawatt-hours (MWh). Table 1 shows some typical values for commercially available products.

From the point of view of cost of materials, this technology has the potential to compete with other technologies as shown in figure 2, although having the handicap of the additional thermal control systems cost. It should be noted that production costs are very sensitive to production volume and that the Na-NiCl₂ technology has yet to reach high production levels (e.g., compared to lithium), which does place it at a disadvantage. While there is little available market information on materials and system costs, the following tables provide data on constituent costs for both the ZEBRA case and cell, allowing a certain degree of comparison among different battery designs.

Figure 2: Battery cost learning curve and market opportunities



Source: Rocky Mountain Institute, *Seven Challenges for Energy Transformation*, 2019.

Table 1: Key performance data of Na-NiCl₂ battery

Power range	Several MW
Energy range	4 kWh up to several MWh
Lifetime	4500 cycles
Life duration	< 15 years
Reaction time	A few milliseconds
Operating temperature	270 – 300 °C
Efficiency	85 -95% (*)
Energy (power) density	100 – 120 Wh/kg
CAPEX: energy	550 – 750 €/kWh
CAPEX: power	150 – 1000€/kW

Note: (*) Including auxiliary loads.

Source: Ease, *Sodium-Nickel-Chloride Battery*, European Association for Storage of Energy, July 2016 and DOE *ESHB Chapter 4: Sodium-Based Battery Technologies*, Sandia National Laboratories, US, February 2021.

Table 2: ZEBRA Battery Z5 (21 kWh) Case Material Cost

Material	kg/bat	kg/kWh	€/kg	€/bat	€/kWh
Stainless Steel	18	0.85	2,95	53,18	2,51
Steel (cooling system)	7.5	0.35	1,38	10,39	0,49
Thermal isolation	7.5	0.35	11,54	6,55	4,08
Miscellaneous	4	0.19	8,31	33,23	1,57
Total	37	1.75	4,99	183,35	8,65

Source: Galloway, R.C., et al., *ZEBRA Battery - Material Cost Availability and Recycling*, EVS, Long Beach, California, 2003.

Table 3: ZEBRA Cell Design (ML3P)

Material	kg/cell	kg/kWh	€/kg	€/cell	€/kWh
Ni (powder + sheet)	0.15	1.53	10,71	1,61	16,39
Iron (powder + sheet)	0.14	1.43	3,10	0,43	4,43
Copper	0.03	0.31	1,85	0,055	0,56
Halide salts	0.22	2.24	0,71	0,16	1,60
Beta alumina (boehmite)	0.14	1.43	2,20	0,30	3,14
Total	0.68	6.94	3,77	2,56	26,11

Source: Galloway, R.C., et al., *ZEBRA Battery - Material Cost Availability and Recycling*, EVS, Long Beach, California, 2003.

1.3. Sustainability

Nowadays, sustainability and raw material availability have become major issues when considering batteries. There is a growing number of political initiatives designed to reduce the carbon footprint of batteries in Europe (regulations in other countries tend to focus on competition rather than sustainability).

In December 2020, the European Commission proposed an update to the 2006 Battery Directive²³ that aims to ensure the growth of the battery industry is carried out sustainably. According to the recent interinstitutional agreement of 18/01/2023, any person (natural or legal) that place into the market any product that include portable batteries has to ensure that they will be easily removed or replaced by the user along the product life cycle.²⁴

The growth of the electric vehicle market necessarily requires more raw material resources, particularly cobalt, nickel, and lithium. According to the Sustainable Development Scenario of the IEA (International Energy Agency), by 2040 the demand for cobalt will increase 21-fold, nickel 19-fold, and lithium 42-fold for the manufacture of batteries (especially those used in EVs). The main raw materials used in the production of Na-NiCl₂ batteries, are sodium (Na), chlorine (Cl), and nickel (Ni), which are non-hazardous and globally available²⁵. The dominant element is nickel, which is also available worldwide. Its production amounts to around 2.5 million tons/year extracted in mines²⁶, but currently it is expensive. New ideas to considerably reduce the degree of Ni content are being explored²⁷.

Discharged batteries can easily be recycled and their nickel reclaimed²⁸. The sodium-nickel chloride cell, if completely discharged, no longer contains dangerous (reactive) materials; as a result, the battery is shorted before beginning the recycling process. Soluble components, such as NiCl₂, NaCl, and NaAlCl₄, are leached out after slicing the cells into pieces. These soluble components are further separated by precipitating the nickel as nickel sulfide, and by the subsequent crystallization of NaCl and NaAlCl₄ from the solution. The insoluble case material and ceramics undergo mechanical sieving and magnetic separation, and the valuable components, such as metals, are recovered for metallurgical processing and subsequent reuse. Unfortunately, currently the relatively expensive beta alumina ceramic electrolyte would most probably go to very low-value uses or sent for disposal. The cost of the Na-NiCl₂ battery would likely be strongly influenced by the price of nickel, the most valuable constituent. Recovery of all the nickel is important if the process is to be carried out in locations that regulate nickel for disposal. However, a preliminary evaluation of recycling costs showed that these are just about offset by the value of the recovered materials²⁹. Thus, it is believed that recycling can play an important role in ensuring the sustainability of these systems³⁰.

²³ European Union, Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EE, OJ L 266, 26.9.2006, p. 1–14, 2006.

²⁴ See the proposal for a regulation of the European Parliament and of the Council concerning batteries and waste batteries, repealing Directive 2006/66/EC and amending Regulation (EU) No 2019/1020 (COM(2020)0798 – C9-0400/2020 – 2020/0353(COD)), *Batteries and Waste Batteries* and the latest interinstitutional compromise reached on 18 January 2023.

²⁵ Dustmann, C. -H., et al., Secondary batteries – high temperature systems, safety, Encyclopaedia of Electrochemical Power Sources, 324–333, 2009.

²⁶ Statista, Mine production of nickel worldwide, 2021.

²⁷ Hee-Jung Chang, et al., Advanced Na-NiCl₂ Battery Using Nickel-Coated Graphite with Core-Shell Microarchitecture, ACS Applied Materials & Interfaces 2017 9 (13), 11609–11614.

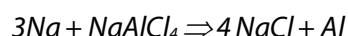
²⁸ Bradbury, K., Energy Storage Technology Review, 1–33. 2010.

²⁹ Climate Policy Watcher, Sodium Nickel Chloride NaNiCl₂, 2022.

³⁰ Solyali, D., et al., A comprehensive state-of-the-art review of electrochemical battery storage systems for power grids, International Journal of Energy Research, 46 (13), 17786.

1.4. Safety

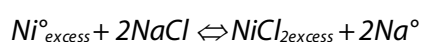
When compared to other batteries, Na-NiCl₂ batteries have been considered reliable and low maintenance³¹. However, the use of alkali metals like sodium or lithium at high temperature has raised the question of safety (which is always a concern for electrochemical cells). The problem is quite evident with sodium-sulphur batteries, as the rupture of the ceramic puts Na metal and the molten sulphur/sulfides in contact, releasing a high amount of energy. To limit the consequences of the loss of the electrolyte (beta alumina solid electrolyte – BASE) integrity in both the Na/S and ZEBRA systems, only a thin film of molten sodium is put in contact with the electrolyte by imbining a steel mesh fed using capillarity. In addition, in case of BASE rupture, the reaction of Na metal with the liquid electrolyte results in the formation of aluminium and sodium chloride, both solids:



These reaction products, well below their melting point (Al: 660°C, NaCl: 801°C), caulk the crack preventing further reaction.

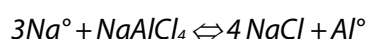
Another safety concern is the resistance to overcharge and over-discharge.

The charge capacity of the ZEBRA cell is determined by the quantity of salt (NaCl) available in the cathode. When overcharging the battery (i.e. charging when it is already fully charged) there is an excess of nickel vs. stoichiometry:



The consequence is that this overcharge reaction requires a higher voltage than the normal charge (~3.05 V vs 2.58 for normal operation)³².

When over discharging, however, the reaction beyond the full reduction of NiCl₂ is the reversible reduction of the NaAlCl₄ in the catholyte (i.e. the portion of an electrolyte near a cathode):



The consequence is that this over discharge reaction requires a lower voltage than the normal charge (~1.58 vs 2.58 for normal operation).

Typical operating conditions of Na-NiCl₂ batteries comprise charging in 6 and 8 hours (i.e. C/6 – C/8 rate, which means that the battery is charged from 0-100% in 6 and 8 hours, respectively) and discharging in 3 hours. Typical time scales are days to solidify during cooling and tens of hours to liquidize during reheating. During operation, Na-NiCl₂ batteries can be repeatedly cooled to ambient temperatures and reheated, i.e., undergo so-called freeze-thaw cycles, without any decrease of battery lifetime.

³¹ Christensen, R., Na-NiCl₂ batteries. In Technology Data for Energy storage, Danish Energy Agency, 2018.

³² Dustmann, C-H., Advances in ZEBRA batteries, Journal of Power Sources 127, 85, 2004.

2. RESEARCH AND DEVELOPMENT PERSPECTIVES

KEY FINDINGS

At present, the ZEBRA battery technology seems to be relatively fixed. Most research in the field focuses on reducing the temperature of operation, with limited success. The main competition arises from Na-S systems and room temperature sodium-ion batteries (SIBs) with no use of critical elements.

However, some EU companies are committed to industrially launch a new promising ad-hoc product for stationary electrical energy storage applications with an expected competitive cost and relatively long-life in terms of both years (15) and cycles (5000).

2.1. Research and development perspectives

In the last years, ZEBRA batteries have reached industrial maturity. All related new development perspectives deal with the reduction of their operating temperature, which is limited by the melting point of the NaAlCl_4 melt of 154°C and the poor wetting characteristics of the molten sodium in contact with the ceramic electrolyte below 200°C . Presently, no system has proven to be able to cycle at the faster C-rates³³, which is needed for viable use at the grid storage level.

On the other hand, there is intense worldwide activity on room temperature sodium-ion batteries (SIBs): since 2010, more than 4,700 priority patent applications have been filed in this area. In contrast to LIBs, SIBs do not need cobalt-containing electrode materials, while in most cases the negative electrode is hard carbon, a widely available material. The company Tiamat in France focusses on vanadium-sodium fluorophosphate, though this raises the problem of the sustainability of vanadium. In China, the start-up HiNa uses a sodium-iron-manganese-copper oxide ($\text{P2-Na}_{7/9}\text{Cu}_{2/9}\text{Fe}_{1/9}\text{Mn}_{2/3}\text{O}_2$) positive electrode. Among them, copper is an element in tension for its availability (having a production of 21 million tons/year) and it is expected that Mn could reach the same situation in the near future. In 2022, a 1 MWh grid storage unit was completed and is currently being tested with encouraging results – its energy density is approximately 150 Wh/kg ³⁴. Its two current collectors made of aluminium (in contrast with LIBs, which use copper at the negative electrode) and the use of the same material for both current collectors enable in principle a lighter bipolar configuration. In a near future, this technology will be compared to its competitors in terms of price and usable lifespan.

2.2. IP Situation

Patents are tools to protect innovation and statistical patent data can be used as an indicator of research and development activity and changes over time. This section provides a snapshot of patent data up to September 2022 obtained from PatSnap³⁵ by using a combination of relevant general keywords and classification codes. The state of patent activity in the area of sodium-nickel chloride batteries (salt batteries) was examined while including aspects such as: time evolution, main territories, major patent filers, key protected technologies, and relevant patent documents.

To assist in quantifying patent activity in this area, we first present data showing overall patent activity for the years 2010 to 2022. Figure 2 shows the total number of worldwide patent applications published

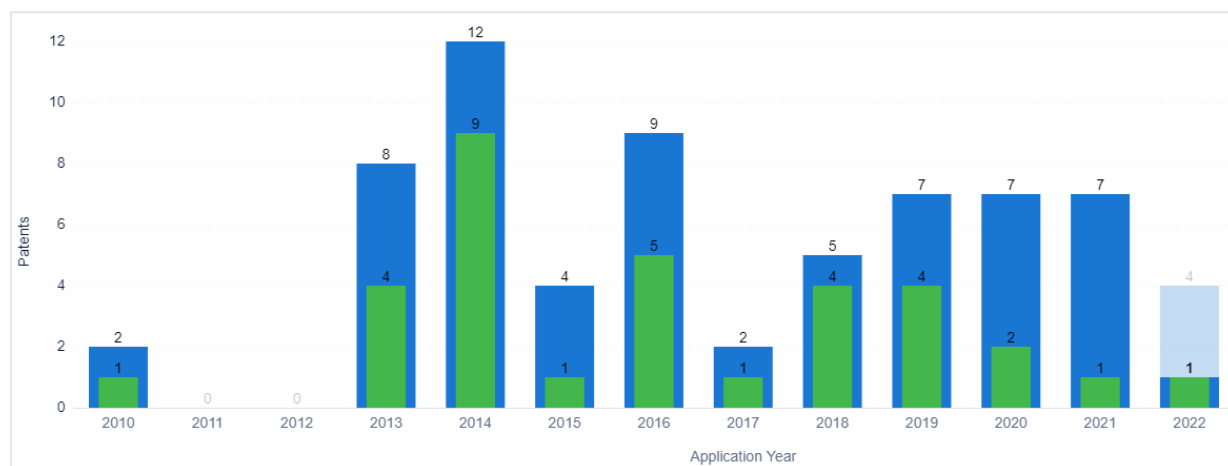
³³ Such as C/3, a 3-hour battery full discharge/charge cycle.

³⁴ Global Times, World's first 1MWh Na-ion battery energy storage system launched in North China, 28 June 2021.

³⁵ Patsnap is an IP Commercial Platform perform highly targeted global searches.

(blue bars) and granted (red bars), year-on-year, between 2010 and 2022. The figure clearly indicates that in the last decade overall patent activity was modest and even declined.

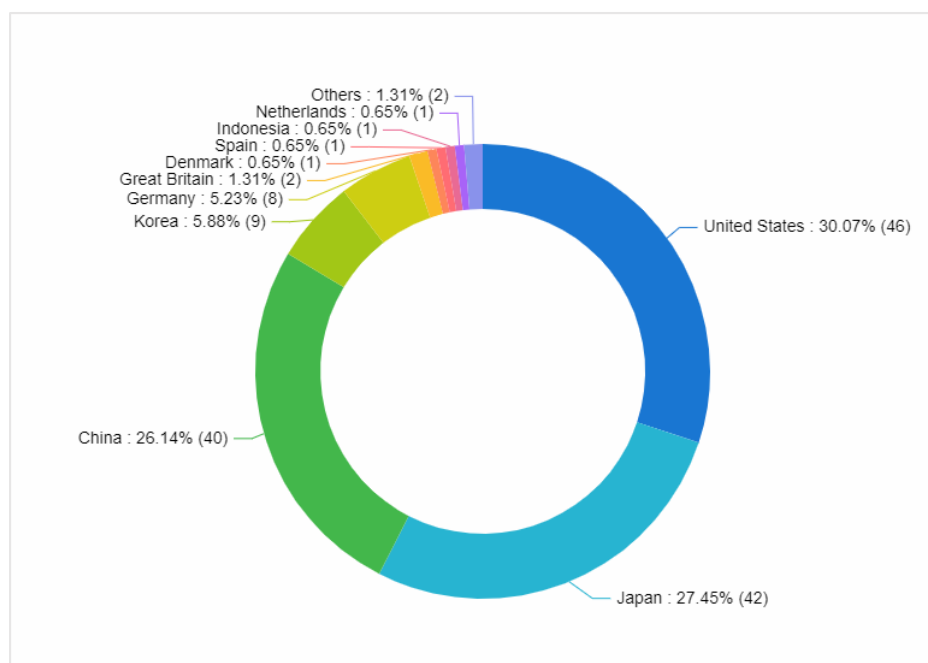
Figure 3: Total published patent (blue) and granted applications (green), 2010-2022



Source: PatSnap, 2022.

The worldwide patent offices considered the most significant and receiving the highest number of patent application filings are the USA, Japan, China, and the Republic of Korea, which account for more than the 75% of patent applications in the area.

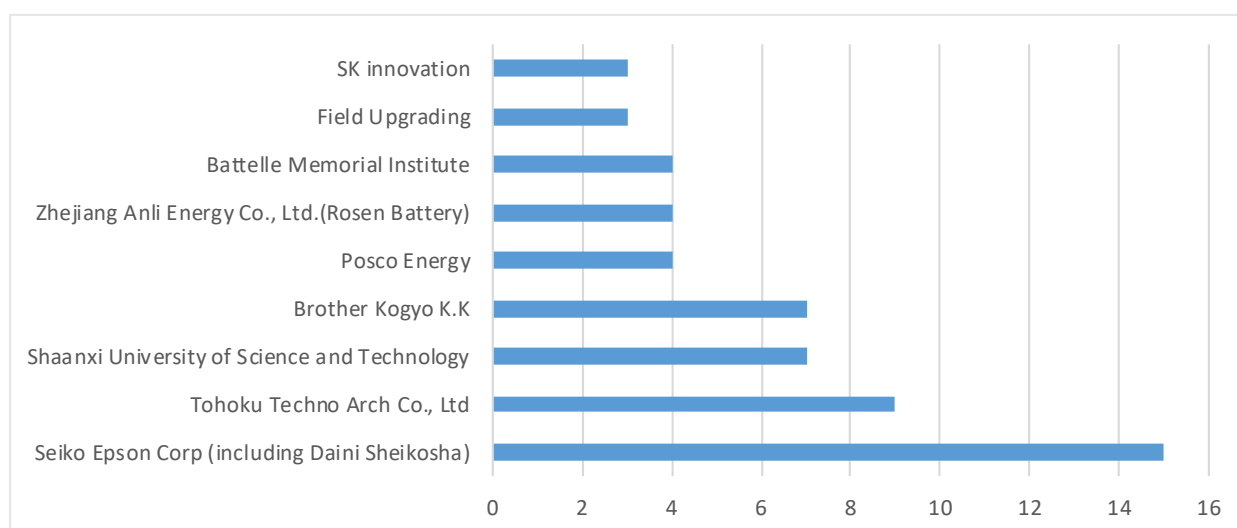
Figure 2: Published patent applications for the top patent offices



Source: PatSnap, 2022.

Although the greatest number of patent applications are registered in the United States, the top 10 applicants are dominated by Japanese corporations, with Seiko Epson Corp. consistently remaining in the leading position. It should be noted that the top applicants include only two research institutes, the rest being manufacturing companies.

Figure 3: Worldwide top applicants, 2010-2022



Source: PatSnap, 2022.

To explain the main classification codes, it should be noted that the key technologies protected by patents in this field are related to the overall cell system (H01M10), the electrodes (H01M4), and the processes of manufacturing and non-active parts (H01M2).

From the search results, it was possible to identify the most frequently cited key documents, allowing to understand which records are the most prolific and have foundational to subsequent developments:

- The most cited patent is a Chinese document (CN101752614A) disclosing a new, low-cost, high-density sodium-nickel chloride single battery and battery pack, manufactured under normal temperature conditions and reaching 120 Wh/kg;
- The second most cited patent is a US document (US3650834A) relating to a secondary electric energy storage battery, which contains a molten salt electrolyte (aluminium halide-containing electrolyte) and has the advantage of being operable in a low temperature range, thus avoiding many of the difficulties associated with high temperature batteries (such as corrosion, sealing problems, and leakage); and
- The third most cited patent is another Chinese document (CN101090168A) describing a saltwater battery which uses a neutral electrolyte (sodium chloride solution, seawater, etc.).

In addition, PatSnap allows the calculation of patent market values using more than 80 indicators (e.g., forward- and backwards-citations, patent family sizes, geographical coverage, patent age, legal status, etc.), including empirical data from historical patent transactions. The highest market-valued patents selected in this search belong to companies such as General Electric, Field Upgrading USA, and Lina Energy. In the first case, the patent document describes an electric battery system installed in an off-road vehicle with a hybrid power system whose battery belongs to the group consisting of sodium nickel chloride or sodium sulphur batteries. The second and third positions correspond to Field Upgrading's patents related to an intermediate temperature, molten sodium-metal halide rechargeable battery and to an additive used in a sodium haloaluminate (NaAlX) electrolyte for a ZEBRA battery, which enables lower temperature operation of the battery, respectively.

2.2.1. IP perspectives

The annual number of relevant global patent applications of salt batteries is lower than twenty; their trends for filed and granted patents are decreasing. The USA and Japan appear to be the dominant countries in terms of patent filings, followed by China and South Korea. Leader businesses in filing salt batteries patent applications are based in Japan, and dominated by electronic component companies. Whilst a few large players mainly represent statistics, patent filings are still relatively diverse, with different businesses actively filing patent applications. In summary, research and development in global salt batteries is restricted and focused on a very specific niche market.

3. FIELD OF APPLICATION

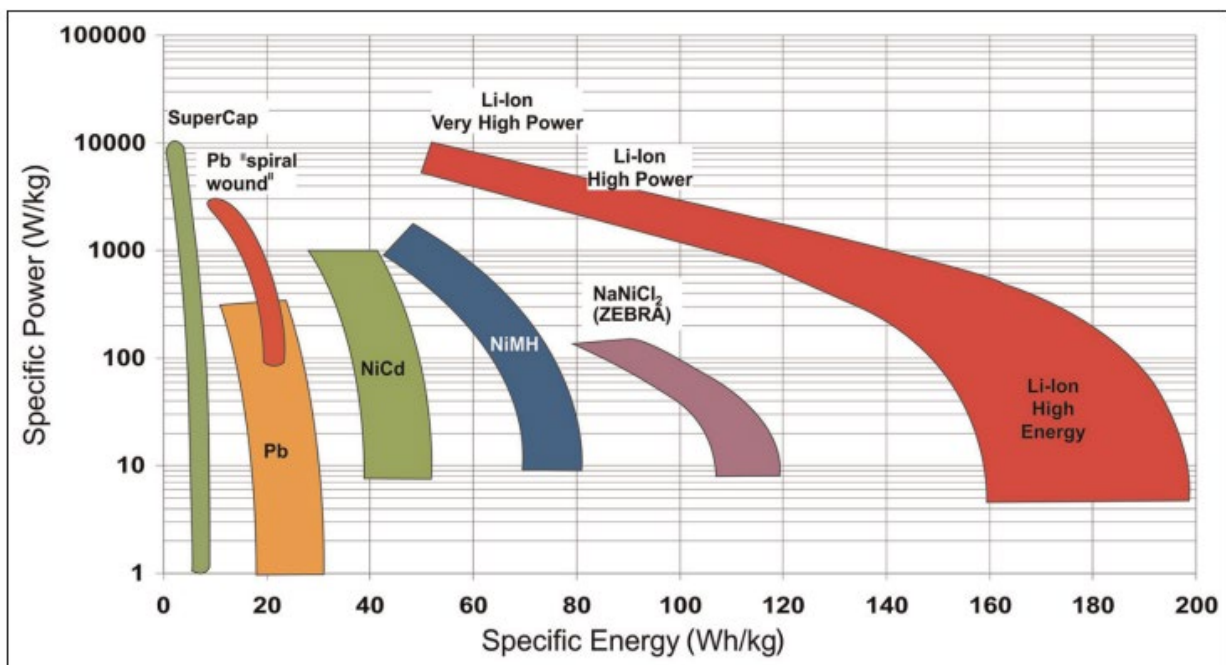
KEY FINDINGS

Evaluation of KPIs (energy density, power, scalability, C-rates and cycling) reveals that the Na/NiCl₂-based technology has a very similar application range to other established technologies in the stationary electrical energy storage market.

Its thermal management and self-discharge specificity is an aspect that may impact some use cases in comparison to other technologies. In the mobility sector, although theoretically feasible, the reported experiences together with the performance advances of other technologies place Na/NiCl₂ chemistry at a disadvantage.

Sodium-metal chloride batteries ZEBRA are considered one of the most important electrochemical devices for stationary electrical energy storage applications due to its advantages with respect to good cycle life, safety, and reliability. From an application point of view, this technology can be used in applications with a power and energy range similar to Na-S technology for hours discharge range, such as time-shifting and electric vehicles. Figure 5 shows the energy density and power density values of NaNiCl batteries compared to other battery technologies.

Figure 6: Ragone plot of various battery technologies with specification at cell level



Source: Budde-Meiwes. H. et al., *A review of current automotive battery technology and future prospects*, Proceedings of the Institution of Mechanical Engineers Part D Journal of Automobile Engineering, May 2013.

Note: SuperCap: supercapacitor; Pb: lead; Li-ion: lithium-ion; NiCd: nickel–cadmium; NiMH: nickel–metal hydride; NaNiCl₂: sodium–nickel chloride; ZEBRA: Zero Emission Battery Research Activities.

Table 4: Features of Energy Storage Technologies

Storage Technology	Energy Density (Wh/kg)	Energy Density (Wh/L)	Power Density (W/L)	Typical Discharge Time	Efficiency	Typical Applications
Pumped hydro	0.2-2	0.2-2	0.1-0.2	Hours	70-80	Time shifting, power quality, emergency supply
Compressed air	-	2-6	0.2-0.6	Hours	41-75	Time shifting
Flywheel	5-30	20-80	5000	Seconds	80-90	Power quality
Lead-acid	30-45	50-80	90-700	Hours	75-90	Off-grid, emergency supply, time shifting, power quality
NiCd vented	15-40	15-80	75-700	Hours	60-80	Off-grid, emergency supply, time shifting, power quality
Sealed	30-45	80-110	(vented)	Hours	60-70	Off-grid, emergency supply, time shifting, power quality
NiMH sealed	40-80	80-200	500-3000	Hours	65-75	Electric vehicle
Li-ion	60-200	200-400	1300-10000	Hours	85-98	Power quality, network efficiency, off-grid, time shifting, electric vehicle
Zinc air	130-200	130-200	50-100	Hours	50-70	Off-grid. Electric vehicle
Sodium-sulfur	100-250	150-300	120-160	Hours	70-85	Time shifting, network efficiency, off-grid
NaNiCl	100-200	150-200	250-270	Hours	80-90	Time shifting, electric vehicles
Vanadium redox Flow battery	15-50	15-50	0.5-2	Hours	60-75	Time shifting, network efficiency, off-grid
Hybrid flow battery	75-85	75-85	1-25	Hours	65-75	Time shifting, network efficiency, off-grid
Hydrogen central	33,330	33,330	0.2-2	Hours to weeks	34-44	Time shifting
Decentral			0.2-20			
Synthetic natural gas	10,000	1800 (200 bar)	0.2-2	Hours to weeks	30-38	Time shifting
Double-layer capacitor	1-15	10-20	40,000-120,000	Seconds	85-98	Power quality, effective connection
Superconducting magnetic energy storage	-	6	2600	Seconds	75-80	Time shifting, power quality

Source: Revankar, S. T., *Chemical Energy Storage in Storage and Hybridization of Nuclear Energy*, Elsevier, 2019.

Due to their high scalability and flexibility in assembling different battery and system sizes, Na-NiCl₂ batteries have been used in a wide variety of applications. The most developed use of ZEBRA batteries is for **load levelling and storage of grid** or **renewable energy production**.

The initial use of ZEBRA batteries was within EVs, whose modules were implanted in Mercedes cars in Germany, Th!nk City microcars in Norway, City Logistics vans in the Netherlands, hybrid buses in Italy, and fully electric city busses in California, with up to 220 km driving range. The tramway in Padua, Italy is powered by a ZEBRA battery and used in the central part of the city with no catenaries. It rapidly appeared that the continuous power required to maintain the operating temperature (15% of the battery charge/day) was too much of an impediment³⁶ compared to the ambient temperature of lithium systems, being incompatible with private car ownership and driving patterns. Moreover, the system is not compatible with the fast charge rates (3C; i.e. charging the battery in 20 minutes – 3 times faster than 1C) that seem to become a requirement for EV adoption. For busses and tramways having a fixed schedule and returning to a docking station at night, the energy drawback of needed to keep operating temperature is eased as their recharge time can also be used to bring the battery to the high-end operating temperature. Moreover, for these applications, C/6 – C/8 recharge rates are acceptable.

Today this technology finds use in stationary electrical energy storage systems, on- and off-grid smart grids, support of renewable energy, uninterruptible power supply (UPS) systems for data centre applications. However, it is not easy to obtain market share data for this technology because the installed base is very small in stationary applications compared to other mainstream technologies.

Although the number of installed systems comparatives to those of other technologies is relatively low and, in some cases, they have subsequently been replaced with lithium technology, it is still possible to identify perspective reports that give recommendations on their use, fields of application, and lines of research to improve costs and performance (which is probably one of the challenges to be overcome in order to achieve greater market presence).

The following table shows the key data of some of the installations carried out between 2010 and 2015.

Table 5: Selected Na-NiCl₂ installations in Europe

Name	Location	Years of commissioning	Storage capacity (kWh)	Rated power output capacity (kW)
FIAMM Green Energy Island	Almisano, Italy	2010	230	180
EDF EN Gabardone Project	Colombiers, France	2013	70	20
Terna Storage Lab 1+2 (3 installations)	Codrongianos (Sardinia)* and Ciminna (Sicily), Italy [#]	2014* 2015 [#]	4150* 2000* 4150 [#]	1200* 1000* 1200 [#]

Note: * Data from Codrongianos (Sardinia) [#]Data from Ciminna (Sicily).

Source: Authors' own elaboration and Christensen, R., *Na-NiCl₂ batteries*, Technology Data for Energy storage, 2018.

³⁶ Wind Energy and Electric Vehicle Magazine (REVE), ZEBRA batteries.

4. CONCLUSIONS

KEY FINDINGS

The ZEBRA battery is a mature technology, which meets the stationary electrical energy storage application requirements for safety, long cycle life (5000 cycles) and calendar life (over 10 years). Its advantage derives from the use of cheap and abundant materials, which could make this technology attractive for some uses.

The implementation of a robust thermal control system to ensure safe operation at 300°C regardless of ambient temperature remains an open challenge. ZEBRA batteries would compete with existing lithium-based LiFePO₄ batteries, as well as with other emerging room-temperature technologies in stationary electrical energy storage applications (some of which are also based on the use of Na, like Na-ion batteries).

However, because of expectations of significant market growth and potential supply shortages for existing technologies, if certain requirements of cost reduction and abundant material use are met, in a scenario of global open competition among energy storage technologies ZEBRA batteries could well find a position in the market. Under these assumptions, supporting existing innovation in ZEBRA batteries would clearly be a wise EU strategy.

The ZEBRA (salt) battery is, after 35 years, a quite mature technology. It meets the requirements for safety, long cycle life (5000 cycles) and calendar life (10 years). Its materials requirement is only for relatively easily sourced elements (Ni, Fe, Al, Na). The main investment required is for nickel, the core element of the cathode, whose share of immobilised metal is only 40% of a comparable Li-ion battery with NMC811 as positive electrode. The materials necessary for a 1 kWh of stored capacity can be estimated to €65 in 2022 (updated from \$30 in 2003)³⁷, considering some analysis made by Fraunhofer IKTS technology, which works in a “redevelopment” of Na/NiCl₂. According to this analysis³⁸ that considers cell and system design, used materials and production, targeted costs are noticeably below 100 €/kWh on cell level. The materials cost for the double-walled stainless-steel casing can be extrapolated to 20 €/kWh (assuming a stainless-steel price of €5.53 per kg). An advantage of this technology is that iron impurities in the nickel, which are inevitable with the more abundant metal coming from laterite ores, do not affect the viability of the battery. Laterite nickel mines are more widespread and less strategic than sulphide-based mines³⁹.

Implementing a robust thermal control system to keep the battery at 300°C is the principal challenge of ZEBRA systems. Heat loss is reported⁴⁰ to be less than 0.6% of total energy storage capacity per hour for a 17.8 kWh battery used at 15% per day, resulting in an 85% round trip efficiency for daily use. When compared with similar Na/S batteries, the lifetime does not seem to be affected by freeze-thaw cycles (i.e. a freeze-thaw cycle (FTC) occurs when air temperature drops low enough to freeze water (32°F), then increases enough for it to thaw again), implying that the battery modules can be serviced more conveniently.

³⁷ Galloway, R.C., et al., ZEBRA Battery - Material Cost Availability and Recycling, EVS, Long Beach, California, 2003.

³⁸ Schulz, M., cerenergy® – the high-temperature battery for stationary energy storage.

³⁹ Ni from sulfide mines is needed to meet the more stringent metal purity requirements of lithium-ion batteries.

⁴⁰ Christensen, R. (2018). Na-NiCl₂ batteries. In Technology Data for Energy storage, (pp. 147-160). [183] Danish Energy Agency, November 2018.

While beyond the scope of this report, it would be very interesting to identify how the carbon footprint of this technology compares with other reference technologies, such as lithium (approximately 200 kg/kWh for LIBs).

In terms of market penetration, other technologies, such as lithium have conquered the mobility market⁴¹. In the stationary energy storage market, there are no relevant references identified. In a first analysis the requirements of this market, which are driven by Levelized Cost of Storage (LCOS) improvements, prioritise development using cells from the higher volume production market. The advantages derived from the use of cheap and highly available materials could attract sufficient interest in this technology, but their operating temperature and sluggish charging process (C/8) puts ZEBRA batteries at a disadvantage when compared to other technologies (such as Na-ion).

⁴¹ Even though ZEBRA batteries have been validated for use in this sector.

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Sodium-Nickel-Chloride (Na-NiCl₂) batteries have risen as sustainable energy storage systems based on abundant (Na, Ni, Al) and non-critical raw materials. This study offers a general overview of this technology from its initial conceptualization, along with research and development perspectives and areas of use. Applications are for grid storage mainly due to the temperature of operation (275–350 °C). There is no critical issue on patent portfolio as the key IP is in the public domain. In addition, Switzerland is active in this technology with FzSoNick being a producer of commercial Na-NiCl₂.

This document was provided by the Policy Department for Economic, Scientific and Quality of Life Policies at the request of the Committee on Industry, Research and Energy (ITRE).
