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Innovative electrolytes and electrodes for a new generation of sodium-based batteries for stationary applications (NABASTAT)

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Plan de Recuperación, Transformación y Resiliencia

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POWER ELECTRONICS

Pla de Carrases B, CV-35, Salida 30,
46160 Llíria, Valencia, España.

(+34) 90 240 20 70
(+34) 96 136 65 57
power-electronics.com

20220120_WP2_ Requirements Collection

Abstract

The world is facing the biggest challenge ever faced, which is the climate change. With a steadily growing population, an increasing standard of living, and an energy model based on a carbon-based origin, we are accelerating climate change and our challenge is to try to slow down the rate of emissions and mitigate our carbon footprint.

As always, every problem has a solution, reducing the use of fossil fuels to generate energy is one of the most important pillars and the shift towards a model based on renewable energy generation is being put in place. However, the intermittency of renewable energy generation makes it necessary to add storage systems to balance demand and production.

In recent years, the most widely used storage technology has been lithium-based batteries, stretching the lithium supply chain, limiting availability and an expected price increase, requiring battery manufacturers to explore new options.
The use of lithium-ion as ion transport can be exchanged for another alkali metal, the sodium-ion (SIB). As all alkali metal, easily them lose the outermost electron to form cations with charge +1. Being sodium the alkali metal most abundant, this material features high abundance and cost-effectiveness, offering the potential to be competitive with lithium-ion batteries and compensating its lower energy density.

As well as the previous advantages, compared with its lithium-ion counterparts, sodium-ion batteries present several benefits, such as lower charging times and wider operating temperature ranges. In addition, they have a safer and stable performance and less demanding dryness conditions during the manufacturing process. Due to the lower energy density and the operating temperatures range, sodium-ion batteries are especially suitable for Battery Energy Storage System.

Furthermore, the possibilities of SIB could be further incremented by finding sustainable materials for the electrodes. Hard carbons are the most successful material of the anode of SIBs. Their production from waste materials could have positive ecological consequences, as well as give the product an important added value. Examples of this option can be frequently found in recent literature, and excellent reviews have been published.

Another interesting point that SIB batteries offer is the possibility to achieve high recycling efficiency. In a world where it is necessary to reduce the raw material mining and attempt to reuse the raw material, the capability of recycling becomes crucial. In some papers, a solid-component 99.7% recycling efficiency have been achieved, making almost circular sodium-ion battery production-recycling process.

Nevertheless, this developing technology presents multiple disadvantages, among which are low energy density, short battery cycle life, and its derived need to consume great quantities of auxiliary materials to have a standard performance. This last fact, although the raw material cost for sodium-ion batteries is low, elevates the total cost per kilowatt-hour and results in more voluminous batteries.

As a result, many research centers, start-ups, and well-established energy sector companies are getting involved in sodium-ion battery technology development.
These joint efforts to master an efficient production of this battery type, pave the way for a much better performing and environmentally respectful way of storing energy.

The objective of this document is to compile detailed studies concerning sodium-ion battery technology state of the art, market trends, and technical requirements of its specific outputs and manufacturing process. These collected requirements are divided into two categories: they refer to the battery (application-level) or to the electrochemical cell level (both functional and non-functional traits).

Although the previous requirement categories are precisely defined, both are merged into a structure consisting of data tables divided by the corporation (with information related to electrochemical cell level), a section of companies that are considered to stand out but don't reveal data, and information about stationary applications' needs.

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Stationary storage technologies comparative

Nowadays, different chemical compositions are being employed for Battery Energy Storage Systems (BESS), such as: LFP, NCA, NMC. Specifically, lithium ferro phosphate battery is one with the more extended use between battery technologies for the BESS.

$LiFePO_4$ is a natural mineral of the olivine family. Firstly, it was identified as a cathode for using in batteries in 1996. Years later, reversible extraction of lithium from $LiFePO_4$ and insertion of lithium into $FePO_4$ was demonstrated, which along the solving of its intrinsically low electrical conductivity, helped its industrialization and distribution. Because of its low cost, non-toxicity, the natural abundance of iron, its excellent thermal stability, safety characteristics, electrochemical performance, and specific capacity (170 mAh/g, or 610 C/g) it has gained considerable market acceptance over the years.

On the other hand, the development of the sodium-ion battery took place side-by-side with that of the lithium-ion battery in the 1970s and early 1980s. However, by the 1990s, it had become clear that lithium-ion batteries had more commercial promise, causing interest in sodium-ion batteries to decline. In the early 2010s, sodium-ion batteries experienced a resurgence in interest, driven largely by the increasing demand for and cost of lithium-ion battery raw materials.

Furthermore, several companies propose battery management systems that will integrate lithium and sodium batteries in the same battery packs. That means manufacturers could create battery packs tailored to meet the needs of customers in various climates and with different energy and power needs. This is not the best case environmentally, but it can help with extending the use of sodium-ion batteries and reducing even more its manufacturing cost.

Some relevant information about the LFP and Sodium-ion technology to compare its pros and cons, based on parameters such as energy density, storage cost, number of cycles and general safety.

	Sodium-ion battery	Lithium-ion battery
Cost (€/kWh)	38-73	≈ 130
Volumetric Energy Density	250-375 Wh/L, based on prototypes	200-683 Wh/L
Gravimetric Energy Density (specific energy)	75-165 Wh/kg, based on prototypes	120-260 Wh/kg
Cycles at 80% depth of discharge	≈ 1.000-10.000	≈ 3.500
Safety	Low risk	High risk
Materials	Earth-abundant	Limited
Cycling Stability	High (negligible self-discharge)	High (negligible self-discharge)
Direct Current Round-Trip Efficiency	Up to 92%	85-95%
Temperature Range	-20°C to 60°C (more suitable for extreme weather)	Acceptable: -20°C to 60°C Optimal: 15°C to 35°C
Self-discharge per month	<10%	<5%
Environmental impact	Raw materials are readily accessible	Produces substantial pollution from fossil fuels consumptions and wastewater
Charging time	Depending on chemistry	Generally lower due to lower internal resistance and higher voltage

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(+34) 96 136 65 57
power-electronics.com

Current sodium ion batteries materials available for investigation

Set of materials that are currently being investigated for sodium ion batteries, including their chemical composition. Also, two options are founds related to the whole prototype cell construction.

Cathodes	Anodes
Laminar oxides $Na_{y-x}Co_zO_2 + xNa^+ + xe^- \leftrightarrow Na_yCo_zO_2$	Hard carbons $C + xNa^+ + xe^- \leftrightarrow Na$
Prussian blue analogues $Mn[Fe(CN)_6] + 2Na^+ + 2e^- \leftrightarrow Na_2Mn[Fe(CN)_6]$	Graphitic carbons $C + xNa^+ + 2diglyme + xe^- \leftrightarrow [Na(diglyme)_2]C$
NASICON phosphates $Na_{3-x}V_2(PO_4)_3 + xNa^+ + xe^- \leftrightarrow Na_3V_2(PO_4)_3$	Pseudocapacitive oxides $TiO_2 + xNa^+ + xe^- \leftrightarrow Na_xTiO_2$
Fluorophosphates $NaFePO_4F + Na^+ + e^- \leftrightarrow Na_2FePO_4F$	Alloys $4Sn + 15Na^+ + 15e^- \leftrightarrow Na_{15}Sn_4$
Organics: quinones $Na_2C_6H_2O_4 + 2Na^+ + 2e^- \leftrightarrow Na_4C_6H_2O_4$	Conversion $NiCo_2O_4 + 8Na^+ + 8e^- \leftrightarrow Ni + 2Co + 4Na_2O$
Ammonia electrolyte	Anodeless

Materials to be reduced in our composites

Whilst some materials feature a great behavior, they come with increasing downsides that encourage companies and universities to look for feasible alternatives to the lithium-ion extended cells.

The main materials to avoid that are used in the lithium-ion battery are cobalt, lithium, and nickel, being the last one, which is difficult not to use, it is possible to reduce its percentage.

Cobalt is toxic and unstable, and when used in lithium-ion batteries provides the risk of thermal runaway. This thermal runaway causes a toxic fire that is not possible to be extinguished by water or flame retardants, so it must be allowed to burn, releasing toxic fumes to the atmosphere. Beyond the previous risks, cobalt puts humans and the environment at risk at every point along the supply chain (from extraction to battery recycling). Furthermore, Democratic Republic of the Congo (DRC) concentrates more than 80% of cobalt presence, making it scarce (only 0.0029% of the Earth's crust) and a possible cause of geopolitical conflicts, without mentioning the extremely inhumane extraction conditions. Lastly, due to the increasing electric vehicle battery demand, cobalt price is volatile and has doubled the last year reaching the 62.500 euros/metric ton.

Lithium-ion batteries are expensive to manufacture, representing material the 60% of the total cell cost. The increase in the consumer demand and the weakness of the raw material supply chain makes the lithium-ion batteries a difficult market (for example, it's 35% more costly than to manufacture a Nickel-cadmium cell). Also, this kind of batteries require protection from being overcharged and discharged with excessive Depth of Discharge (DoD), otherwise they also may enter thermal runway. Lithium is toxic for wildlife and pollutant too. Furthermore, at present, nearly 50% of lithium production is concentrated in Australia and 20% in Chile,

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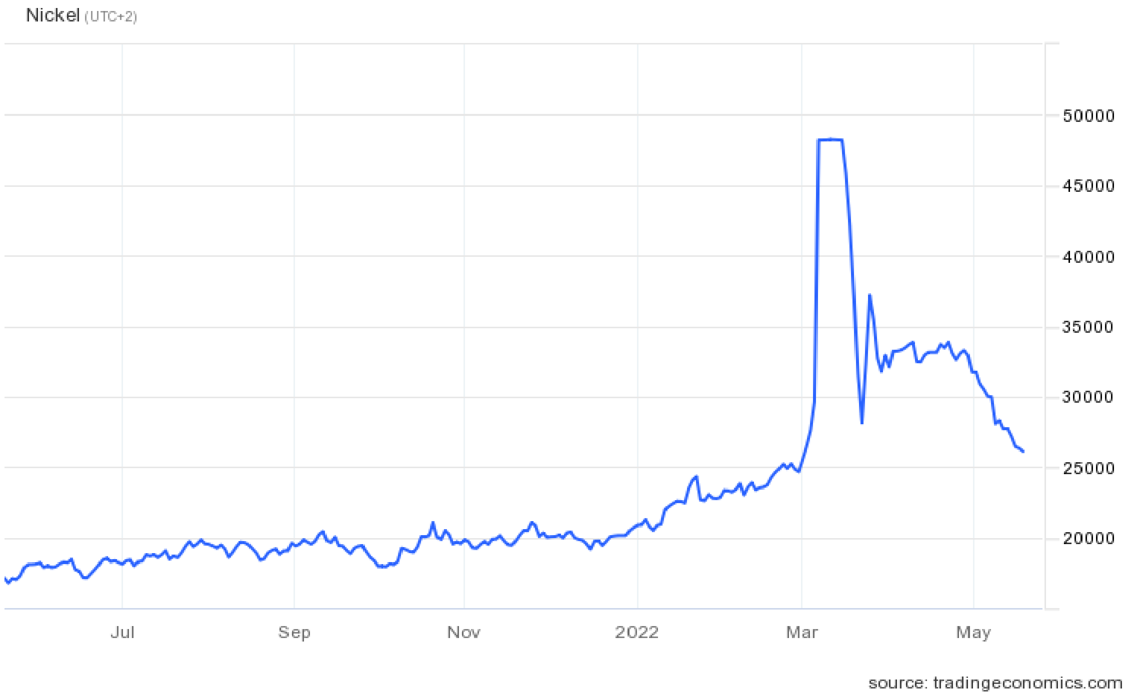
being this last one with Argentina and Bolivia, the lithium triangle with more than 75% of the world's supply beneath and it's as abundant as Cobalt, just 0.002% of Earth's crust.

In nature, Cobalt is frequently associated with Nickel, Cobalt in compound form occurs in Copper and Nickel minerals. It is found in tiny concentrations usually around 1-2% which means that a significant amount of material must be mined to produce any significant quantities of nickel product. The problem with most of the today's nickel production is that most of it is not suited for production of nickel sulphate powder to be used in the batteries that power EVs and energy storage systems due to its purity and iron content. Nickel, as a heavy metal, is also toxic and pollutant. Finally, nickel price is extremely fluctuant, as it shows the graphic (this curve corresponds to the price per metric ton of nickel, from June 2021 to current May 2022).



Summary table of Na-ion batteries producers

	Faradion Limited	Tiamat	HiNa Battery	Altris AB	Natron Energy	CATL	AMTE	ESS	NABASTAT
Country	UK	French	China	Sweden	US	China	UK	USA	Spain
Established	2011	2017	2017	2017		2011	1997		2021
Cathodes	mixed-phase O3/P2-type Na–Mn–Ni–Ti–Mg layered oxide	fluorinated vanadium-based polyanionic Na3V2(PO4)2F3	O3-type Na–Cu–Fe–Mn layered oxide	Prussian blue analogue	Prussian blue	Prussian white y layered oxide materials (160 mAh/g)		Carbon	Co-free layered oxides; organic dyes/polymers, inorganic oxide
Anodes	Hard carbon	Hard carbon	Soft carbon	Hard carbon	Prussian blue	Hard but porous carbon (350 mAh/g)		Plastic spacer	Sn alloys (nanostructures), Hard carbon, TiO2-based materials, Nanostructured metal collectors for anodeless batteries.
Electrolytes	non-aqueous (Mixed carbonate-based solvents; NaPF6 salt)	Non-aqueous	Non-aqueous	Non-aqueous	Non-aqueous			Saltwater and iron solution	NH3 as additives or solvents in electrolytes, ionic liquids as electrolytes and/or additives use of cost-effective Na salts, semi-solid and solid electrolytes based on polymers.
Remark		Raw material availability, necessary to change to Fe and Mn	NaCP08/80/138 soft pack batteries, cylindrical NaCR26650 , NaCR32138	Fennac can be paired against anode materials which do not contain sodium	Aqueous solvents and PBA-based.	No copper current collector needed			Fast charge/recharge of the cell
Energy density (Wh/L)	290						215-280		

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	Faradion Limited	Tiamat	HiNa Battery	Altris AB	Natron Energy	CATL	AMTE	ESS	NABASTAT
Wh/kg	190					≥160	135-140	170	180
Specific Energy (Wh/kg)	200	55	≥145						
Specific Capacity (Ah/kg)	157			160		160	45, 45-46, 154		
Nominal Capacity (mAh)	Up to 5.000								
Specific Power (W/kg)	1.000 2000 (objective)	4.000			350 100				Less than 50% capacity degradation after 5000 cycles
Cycle life (Cycles)	>1000 cycles to 80 % original discharge capacity	> 3.750	≥4.500 @ 83 % (2C/2C)		> 10.000 (~50.000)		> 1.000 (0.5C charge/discharge, 100% DoD)		
Power rating	Peak 16 Wh				Peak 6kW		Peak 0.43-0.56 kW/l Peak power density (10 s pulse)		
Pulse discharge	20C for 10s				Delivers 4kW at 48V DC over a 2-minute discharge				

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	Faradion Limited	Tiamat	HiNa Battery	Altris AB	Natron Energy	CATL	AMTE	ESS	NABASTAT
Temperature range	-20°C to 60°C	-40°C to 80°C							-20°C to 60°C
Safety	Max self-heating rate ~52°C/min		Meets GB/T31845-2015 standard		UL 1973 Approved				
Cell BOM	25%-30% lower than LFP								
Application	ESS		Large-scale energy storage systems, mobile charging piles and low-speed electric vehicles	Electric cars, power tools and grid and home batteries	ESS				ESS
Working voltage	3.2 V		3.2 V	3.25 V		3-3.2 V	3.1 V		
Storage performance	The maximum for no degradation at 0V is 6 months		100% SOC at room temp for 28 days, capacity retention ≥94%, capacity recovery ≥99%						
Rate performance	Round trip energy efficiency > 91 %		Capacity at 5C ≥ 90% of 1C rate capacity						Round trip energy efficiency 90-95 %
Internal resistance									

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	Faradion Limited	Tiamat	HiNa Battery	Altris AB	Natron Energy	CATL	AMTE	ESS	NABASTAT
Target cost						Small-scale (MWh): 65€/kWh Large-scale (GWh): ~30€/kWh			0.05 €/kWh/cycle
Links	Faradion Cell Designs	Tiamat homepage	HiNa Achievements	Altris Technology Fennac (Prussian White analogue)	Natron products	CATL presents sodium-ion battery design (electrive.com) CATL will reveal its first sodium-ion battery tomorrow CATL Releasing Its First Generation of Sodium-ion Batteries	Sodium-ion pouch cell datasheet Productos AMTE AMTE compró derechos de Faradion.	ESS Homepage Bill Gates-backed ESS — which makes giant batteries out of iron, salt and water — starts trading	

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Summary table of Na-ion batteries projects

	NAIADES Design project	Toyota Motor	Wollongong University	Nanode Battery Technologies	Aquion Energy
Country	France	Japan	Australia	USA	USA
Established	2015	1933	1951	2020	2022
Cathodes		Sodium - containing cathode material	Layered Transition Metal Oxides		
Anodes		Lithium - containing anode material			
Electrolytes		Solid electrolyte layer comprising a sulfide - based sodium - containing solid electrolyte material			Saltwater batteries & Organosilicon Electrolyte Batteries
Remark	Long cycle life, compatible with existing Li-ion battery production processes	Has a sulfide - based mixture layer		High performance, free-standing, drop-in anodes that fit directly in your sodium ion battery production line and lab tests.	These batteries use organosilicon electrolyte solvent to help stabilize the elements involved in the electron and ion transfer inside the battery.
Wh/kg	90				
Links	Naiades Home Page	Toyota Motor Na Li Battery Patent	The Cathode Choice for Commercialization of Sodium-Ion Batteries	Nanodetech Protfolio	Aquion Energy Battery Innovations

- Faradion, the world leader in sodium-ion battery technology, announces a collaboration and licensing deal with AMTE Power "Our aim is to further accelerate large-scale industrialization of Faradion's safe, low-cost sodium-ion energy technology" (Faradion and AMTE collaboration and licensing deal).
- Natron Energy Inc. announced during June 2022 that it will manufacturing in a Clarios International Inc. plant in Michigan under a strategic a strategic agreement the Sodium ion cells. The world's first mass-produced sodium-ion batteries (Milwaukee Business Jounal: Clarios plant to mass produce California company's sodium-ion batteries).
- In December 2021, Hina Battery announced that it will cooperate with China Three Gorges Energy, China Three Gorges Capital and the People's Government of Fuyang Municipality, Anhui Province, to build the world's first large-scale production line of sodium ions: the production line is planned to have a production capacity of 5GWh.
- In November 2021, Natrium Energy's cathode material project with an annual output of 80,000 tons of sodium-ion batteries was officially signed, and the construction included sodium ferrite ternary cathode material precursor and cathode material production line.
- In addition, among battery manufacturers, Great Power Energy has entered the pilot stage of sodium-ion batteries; Sunwoda has a number of patents for sodium ion battery sodium supplementation, sodium ion battery and preparation, and cooperates with Nankai University to set up an academician workstation; Among the anode manufacturers, Beiterui has achieved mass production of hard carbon and soft carbon anode, and anode enterprises such as Shanshan Shares, Putailai, Xiangfenghua and other anode companies have successively developed sodium electric anode materials, and have successively entered the pilot stage.
- In addition to the above-mentioned enterprises to lay out sodium-ion battery technology, there are also giants such as Huawei and Country Garden entering the sodium-ion battery project across the track.

Other companies of interest which don't reveal information:

- Reliance Industries, bought Faradion (Reliance Industries - The Reliance Story (ril.com), Reliance New Energy Solar to Acquire Faradion Limited).
- Sodion Energy Pte Ltd (Sodion Energy Pte Ltd - Powering the Future).
- China Greatwall Technology Group publishes sodium-ion batteries production process and pouch resulting product images. Gives no additional data (china great wall technology group co., ltd).
- Blackstone announces bringing 3D-printed sodium-ion batteries to market from 2025 (Elective - Blackstone announces plans for 3D printed sodium-ion batteries).

Information about stationary applications' requirements:

Working voltage → The solar and storage inverters of Power Electronics work with a minimum of +700 Vdc and a maximum of +1500 Vdc → Optimal working range 1100-1500Vdc. Depending on cell voltage we will connect more or fewer cells to reach the optimum working range, if we suppose a nominal 2.8V of each cell, it will be necessary for around 400 cells in series. In that case, individual cells should be able to hold a range of voltage between 2.75 V ($+1100\ \mathrm{Vdc}/400\ n$) and 3.75 V ($+1500\ \mathrm{Vdc}/400\ n$).

High power, energy, or durability → The product should aim to search for a compromise between high energy and durability.

Capacity → The goal is to achieve a DC nominal power at 25°C of 1.2MW, for which it is necessary to integrate the cabinet of x cells in series and integrate the cabinet in parallel to obtain the capacity objective. A cabinet can be defined as between 266 kWh → $\frac{266kW}{2.8\ V} = \frac{95kAh}{400n} = \frac{235Ah/n}{135mAh/g} =$ 1567g/n and 400 kWh → $\frac{400kW}{2.8\ V} = \frac{143kAh}{400n} = \frac{357Ah/n}{135mAh/g} =$ 2645g/n.

Discharge time → 266 kWh → $\frac{266kWh}{1.2MW} =$ 15min, 400 kWh → $\frac{400kWh}{1.2MW} =$ 20min.

Working temperatures → From -35 °C to 50 °C ideally / experimentally from -10°C to 50°C.

DOD (Depth of Discharge) → If the main intended usage is Peak Shaving a deep DOD (60-80% of its nominal capacity) is advised to obtain the maximum profit.

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Number of cycles → Our goal is to achieve less than 50% capacity degradation after 5000 cycles. With the assumption of two cycles per day, it features an almost 7-year cycle life.

Calendar life → Calendar life is a multi-factor process, that depends on operating temperature (by Arrhenius law, the rate at which a chemical reaction continues doubles for every 10 degrees rise in temperature). Also, the usage and DoD utilized takes a toll on capacity fading in the battery. It is expected to last generally from 5 to 10 years (for LFP technologies) until it reaches 80% of its original capacity.

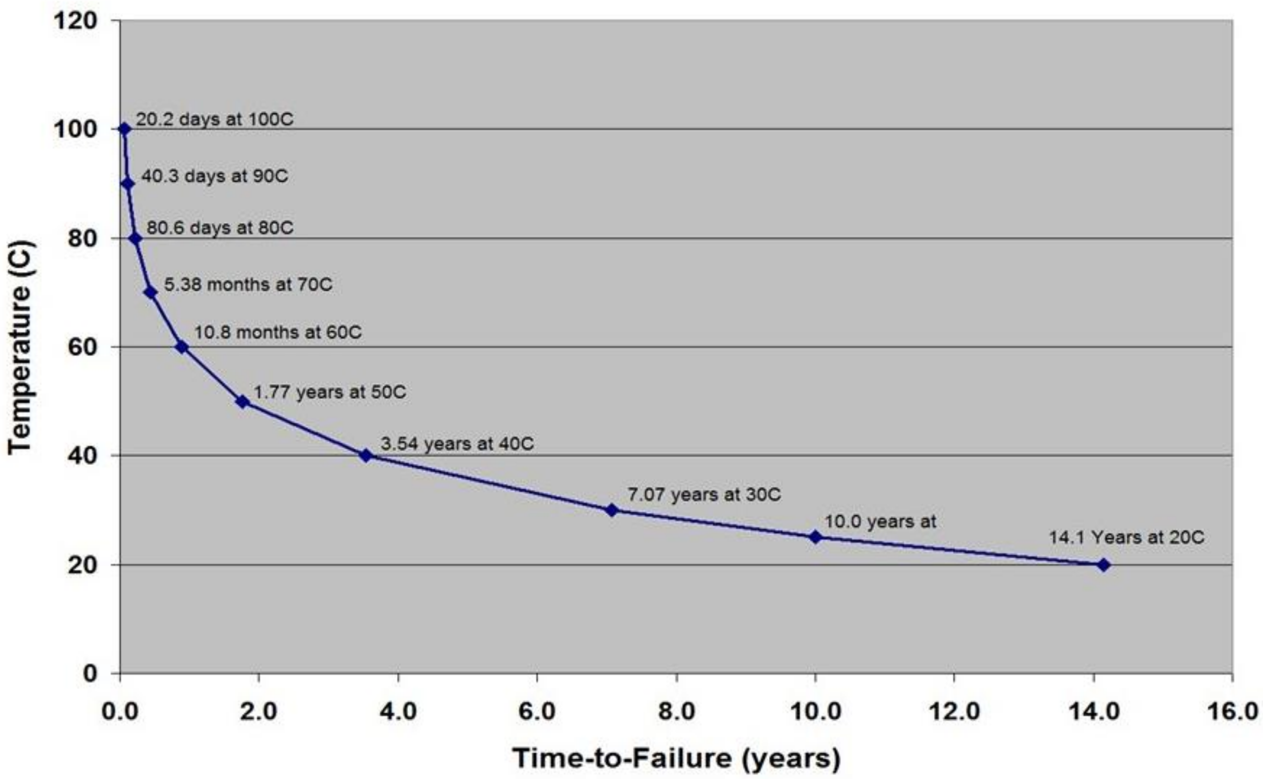

Figure 1: Plot of "Rule of Thumb" temperature behavior where the reaction rate doubles for each 10ºC rise in temperature. In this plot, the reference time-to-failure (TTFt1) has been set to 10 years at 25ºC and shows estimated times-to-failure needed at other temperatures to demonstrate 10 years at 25ºC.

$$\mathrm{TTF}_{\mathrm{T2}} = \mathrm{TTF}_{\mathrm{T1}} * 2^{\frac{T1-T2\ (^{\circ}C)}{10}}$$

Cell price target → 70-80 $/kg

Cell configuration / design → Between cylindrical, pouch and prismatic the chosen configuration is prismatic.

Dimensions and volume → 360 x 55 x 305 mm → 6039 cm^3

Chemistries → LFP/G (Graphite included in the anode)

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Conclusions and requirements

In recent years, the most competitive energy storage technology due to its efficiency, competitiveness has been lithium-based batteries. Although the lithium-ion batteries have advantages, the scarce presence of raw materials, makes think about new solutions. Being Sodium-ion batteries (SIBs) the most credible alternative to LIBs, because of its abundance and cost-effectiveness, offering the potential to be competitive with current lithium-ion batteries. Its positives aspects outweigh the disadvantages which are expected to be reduced in this study and prototype experimentation. Also, its investigation is paving the way to more sustainable battery production, involving non-polluting electrodes, electrolyte, and energy consumption during manufacturing, among others.

This work package is intended to define the operational requirements and to establish the detail of the requirements of all parts of the prototype.
The main tasks dealt with in this work package are:

- Bibliographic analysis of the studies carried out in this technology and analysis of the market trend. This analysis gives a clear idea about what to expect from our SIBs prototypes and how comparable are their characteristics to current technologies (such as LFP). Also, the benchmark of the state of the art of sodium ion batteries will be interesting for defining further work package.
- Specification of the technical requirements that the parts of the prototype must have and for the prototyping process production. For reference, we used a Battery Energy Storage System thought to operate with our arrayed cells, always considering the capabilities of them.

With these determined parameters and better understanding of sodium-ion cells state of the art, the next step is to be able to begin the synthesis, modification, and physico-chemical characterization of the different electrode and electrolyte materials to be developed in this project. Different anodes, cathodes and electrolytes are to be studied in Work Package 3, such as:

- Substrates for Na deposition. Copper-based substrates seem to be promising in this respect. Sodium deposition on nanostructured substrates or foams will be investigated.
- TiO2 anodes. The expected deliverable is a nanostructured TiO2-based anode with anatase or rutile structure and with modifications in the composition by anion doping with fluoride ions.
- Carbon anodes. Hard carbon prepared by pyrolysis of organic precursors and graphitized carbon in which the use of diglyme-base electrolytes would allow sodium countercoalition
- Inorganic oxide cathodes. A conveniently high-voltage and stable cathode will be developed in the field of sodium transition metal layered oxides. The material will avoid cobalt in its composition by selecting Mn and Ni in the TM layer.
- Organic cathodes. Implementation of quinonoid organic compounds for the positive electrode of Na and Na-ion batteries.
- Electrolytes and separators. Both inorganic electrolytes based on liquid ammonia as a solvent, and organic electrolytes with organic/inorganic (including ionic liquids) additives will be developed. Different types of separators will be studied according to the nature of the electrolyte.